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Surface thermodynamics revisited

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Abstract

The last decade has brought a number of new results related to the thermodynamic fundamentals of surface science. Increasing the generality and rigor of known methods and obtaining new relationships make necessary supplementing the previous review of the author [A.I. Rusanov, Surf. Sci. Rep. 23 (1996) 173–247] to provide a fresh insight into the modern higher-level state of surface thermodynamics. A deeper understanding of such basic notions of surface thermodynamics as dividing surface, excess surface stress (surface tension), transversal surface tension, line tension, and mechanical equilibrium is reviewed for curved interfaces. At the same time, the development of the local thermodynamics (including surface layers with a real surface stress) is exhibited with the gateway to mechanochemistry, which is practically a department of surface science for solids. The chemical approach to the thermodynamics of nanoparticles is described and illustrated by examples. Polymorphous transformations in nanoparticles are characterized. New relationships for thin wetting films (on the surface, in slits and pores) are given, and various cases of non-uniform (in thickness) films are analyzed. The modern theory of an equation of state of an adsorbed monolayer is formulated, and the survey of old and new equations of state is given within the hierarchy of approximations.

Keywords: Surface thermodynamics and mechanics; Dividing surface; Surface stress; Surface tension; Transversal surface tension; Line tension; Nanoparticles; Polymorphous transformations; Wetting; Thin films; Monolayers; Two-dimensional equation of state

Contents

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1. Introduction

The previous review by the author devoted to surface thermodynamics [1] was published a time ago long enough to need updating. Remarkably, the last decade has brought a number of new results related to the thermodynamic fundamentals of surface science, and this is the main reason for writing a new review paper. We will try to avoid duplication and concentrate on new achievements. The report will proceed along three lines. The first one is the reformulation of some known basic concepts of surface thermodynamics in the light of new results. This concerns, first of all, the dividing surface and surface tension, the most important concepts of Gibbs' surface thermodynamics, as well as the mechanical equilibrium condition at an interface. We earlier [1] cited Gibbs' saying "*One of the principal objects of theoretical research in any department of knowledge is to find the point of view from which the subject appears in its greatest simplicity*" [2]. Such a point of view seems to be found for the formulation of the mechanical equilibrium condition (including the generalization of the Laplace equation) in a vector form. Surprisingly, transition to a maximum possible generality and rigor is here accompanied by a great simplification. Defining the surface tension tensor as an excess quantity, the excess normal component of the stress tensor is called the transversal surface tension. The third dimension aspect of surface tension is discussed, and the role of transversal surface tension is illustrated by examples.

The second line of consideration is supplementing the topics presented earlier [1] with new results. This concerns wetting phenomena, the line tension, and the Shuttleworth–Herring relation dealing with two different surface tensions (mechanical and thermodynamic) for solid surfaces. As was shown by the author earlier [1], the difference of the two surface tensions is related to the behavior of the chemical potential of a solid in its surface layer. However, the situation with chemical potential seems to need better understanding. In spite of that the tensorial nature of chemical potential in solids was convincingly exhibited many times in the literature (and also in Ref. [1]), the concept of the chemical potential anisotropy seems to become choky for many solid state scientists. It is typical that, artistically operating with the stress and strain tensors, they deal with the chemical potential in a solid as with that related to a fluid. The situation forces the author to represent a new detailed and transparent derivation of the known expression for the chemical potential tensor as a direct consequence of the thermodynamic definition of chemical potential.

The line tension plays a significant role in wetting phenomena. Up to the present time, the information about the line tension has become such numerous and diversified that a systematization is needed in this field. The line tension classification includes two- and three-dimensional systems with rigid or deformable solids. Similarly to surfaces, a distinction is also made between the excess line stress (mechanical line tension) and the excess line free energy (thermodynamic line tension). The latter is used in the generalized Young equation for the three-phase contact line, which is the most important practical case. Using Gibbs method of dividing surfaces, the condition of equilibrium of a sessile drop on a flat non-deformable solid substrate is investigated. The dependence of the line tension on the curvature radius of the dividing three-phase contact line is found and other useful formulas for the line tension and its derivatives are reviewed.

The third line of the review is characterizing the topics and areas of surface science not described or only barely touched upon earlier [1]. This includes mechanochemistry, nanoparticles, and thin films and monolayers on a solid surface. As in all above cases, the description is provided on the basis of newly obtained results. Since every solid typically participates in chemical reactions with it surface, the solid state mechanochemistry actually is a department of surface science. In mechanochemistry, not an excess surface stress introduced in surface thermodynamics, but a real surface stress is important as directly influencing the solid chemical potential and the affinity and, as a consequence, the rate of a chemical reaction. This requires the development of local thermodynamics of anisotropic solid states presented in Section 2. The distinctive of this description is, first, the use of the volume displacement tensor (together with or replacing the strain tensor) and, second, the use of the Cauchy stress tensor that is a real stress tensor in contrast with the Piola tensor (related to the hypothetical initial unstrained state) used, e.g. by Landau and Lifschitz. This approach simplifies understanding the mechanical term in fundamental thermodynamic equations. Affinity, a certain combination of chemical potentials, is known to be a driving force for all processes occurring with matter (diffusion, phase transitions, chemical reactions, etc.). The affinity tensor can be easily incorporated in the fundamental equations for solids, and this makes the thermodynamic basement for mechanochemistry.

The description concerns not only bulk masses, but also small pieces of matter. The thermodynamics of curved interfaces, and, in particular, the dependence of surface energy on the particle size, is of especial importance for nanoparticles. It was experimentally discovered for a long time ago that phase transitions could occur in nanoparticles in the course of their preparation by disintegrating a solid. In spite of a small size of particles, this phenomenon was usually described in the language of the Clapeyron–Clausius equation for macroscopic phases, and rigorous equations for nanoparticles presented in the review were derived only recently. Being of an intermediate position between single atoms and macroscopic phases, nanoparticles are completely described when both their internal and external energies are taken into account. For this reason, the phase approach, accounting only for internal energy and neglecting external energy, seems to be insufficient for nanoparticles. As an alternative to the phase approach, a quasi-chemical approach to thermodynamic description of solid nanoparticles is formulated when nanoparticles are regarded as supramolecules, their set of same nature and increasing size as homologous series, nanoparticles of same composition but different structure as isomers, etc.

Thin wetting films can be located both on the solid surface and inside the pores or/and slits in a solid. The main characteristic of a thin film is that its both surface layers are incompletely developed (say, because of not enough space in a slit). As a result, conditions for equilibrium for thin films do not coincide with those for interfaces. In particular, an additional thermodynamic property, the disjoining pressure, appears in relationships for thin films, defined as a difference between the normal pressure in a film and the pressure in the mother bulk phase having the same values of chemical potentials as in the film. The equilibrium conditions for thin films, non-uniform in thickness, on solids are reviewed, and the disjoining pressure definition for non-uniform films is discussed.

A monolayer is a particular case of a thin film that lowers the surface free energy and the positive surface stress of solids. The problem of an equation of state for an adsorbed or spread surface monolayer is reviewed in the final section. A novel approach to the theory of an equation of state is described based on the notion of excluded area. Surveying the hierarchy of approximations, many old and famous (the Planck, van der Waals, Frumkin, and of the scaled particle theory) equations, as well as recent and precise two-dimensional equations of state, are presented in a systematic manner and verified by comparison with the modern data on computer simulation with hard disks by the methods of molecular dynamics and Monte Carlo. The attempts to formulate an orientation equation of state and the relation between molecular orientation in monolayers and two-dimensional phase transitions are reviewed. When formulating the novel approach to the theory of equation of state, we again meet the strong requirement of simplicity (this principle is often called ‘‘Ockham's razor’’), so that the above Gibbs' saying could serve as an epigraph to this paper.

Surface science develops not uniformly in all its departments. So, if we try to touch upon all achievements of surface thermodynamics, this makes the review to some extent fragmentary by necessity. It is of hope, however, that, taken together with the previous review by the author [1], this paper presents the state of the art of surface thermodynamics in good coverage. Since the historical background of surface thermodynamics as a whole was given in Ref. [1], we do not repeat it here and practically give no references in the introduction. However, when considering new areas of surface thermodynamics, a necessary historical sketch will be given separately in corresponding sections with all references. Before we proceed to surface thermodynamics, it is natural to survey modern local relationships for anisotropic (solid) states that can be equally applied to bulk phases and surface layers.

2. Local thermodynamics of solids

The mechanical part of the local thermodynamics of solids is formulated in the theory of elasticity [3] quite independently of the chemical part including chemical potentials. This is attained by assuming the amount of matter to be constant in all processes, so that the chemical term in fundamental equations disappears automatically. Furthermore, the mechanical part is formulated in such a form (using the Piola stress tensor) that makes it scarcely suitable for serving as a template in formulating the chemical part. To overcome this difficulty, we first have to reformulate the mechanical part of the local thermodynamics of solids. The second step will be the formulation of the chemical part in a similar way. Eventually, we will unite both the parts in fundamental equations making the thermodynamic basement of mechanochemistry [4,5].

2.1. Mechanically anisotropic states in a solid

The anisotropy of a body element can be caused by the nature of the body itself or by external actions transforming the element to an anisotropic state. Mechanically anisotropic states are especially typical for solids where such states easily arise under the action of external forces. If the stress vector $\mathbf{E}_n$ is applied to the unit area of an arbitrary cross-section passing through a given point of a solid and having unit normal **n**, the set of $\mathbf{E}_n$ as a function of **n** completely characterizes the local mechanical state. The physics of the stressed state is such that, for finding this function, it is enough to know three stress vectors $\mathbf{E}_s$ (s = 1–3) on the surfaces perpendicular to the three basic directions. The set of the three vectors yields the stress tensor $\hat{E}$ in the diadic form (the second order tensor)

$$\hat{E} \equiv \sum_{s=1}^{3} \mathbf{i}_s \mathbf{E}_s \tag{2.1}$$

where the diadic (tensorial) product of the basic unit vector $\mathbf{i}_s$ and the corresponding stress vector $\mathbf{E}_s$ stands under the symbol of summation (we set the basic unit vector on the left and shall below carry out the multiplication by vector from the left, bearing in mind that operators can also been taken in the vector form). The vectors $\mathbf{E}_s$ have components E_{st} (t = 1–3; the subscript sequence is here more conventional and different from that used in Ref. [3]). The stress tensor given by the table of E_{st} (s, t = 1–3) is always (even under non-equilibrium conditions) symmetrical (i.e. $E_{st} = E_{ts}$) by physical conditions (the second law of motion by Cauchy [6]). Therefore, the number of components diminishes down to six in the general case. Furthermore, as for any symmetrical tensor, the number of the components of the stress tensor can be reduced to the three principal values E_k (k = 1–3) by the corresponding choice of an orthogonal coordinate system (with the axes along the principal directions), so that one can write

$$\hat{E} = \begin{pmatrix} E_{11} & E_{12} & E_{13} \\ E_{21} & E_{22} & E_{23} \\ E_{31} & E_{32} & E_{33} \end{pmatrix} = \begin{pmatrix} E_1 & 0 & 0 \\ 0 & E_2 & 0 \\ 0 & 0 & E_3 \end{pmatrix}. \tag{2.2}$$

Irrespective of the stress tensor form (diagonal or non-diagonal), the stress tensor always contains diagonal components which are normal stresses. If, however, the stress tensor is taken in the diagonal form, tangential stresses disappear and only normal stresses are maintained, which can be created, for example, by the contact of a solid with a liquid of a given pressure (pressure always acts as a normal force). Therefore, if we imaginary select an elementary rectangular parallelepiped with its faces perpendicular to the principal directions, the mechanical state at this place may be identified with the state of the parallelepiped when it contacts (with its different faces) three different liquids of pressures $p_1 = -E_1$, $p_2 = -E_2$, and $p_3 = -E_3$ (Fig. 1). The stress $\mathbf{E}_n$ on the unit surface of arbitrary orientation **n**, is

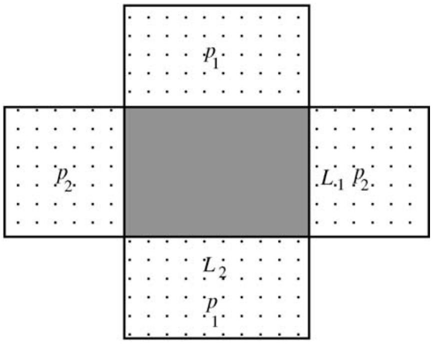

Fig. 1. An elementary parallelepiped in contact with three liquids (the third liquid contacts the parallelepiped in the drawing plane).

found from the condition (a dot symbolizes a scalar product; the scalar product of a tensor and a vector is a vector)

$$\mathbf{E}_n = \mathbf{n} \cdot \hat{E}. \tag{2.3}$$

Putting (2.1) in (2.3), we obtain

$$\mathbf{E}_n = \sum_{s=1}^{3} (\mathbf{n} \cdot \mathbf{i}_s)\mathbf{E}_s. \tag{2.4}$$

Every stress is a force which is capable to do a work if the elementary surface to which the force is applied, is able to moving. Let a displacement of a unit elementary surface of orientation **n** be given by vector $\mathbf{u}_n$ (that can be not collinear with the stress vector $\mathbf{E}_n$ at the same surface). Then the elementary displacement work is $\mathbf{E}_n \cdot \mathrm{d}\mathbf{u}_n$. Applying this expression to the element of the surface of an equilibrium body with the outer normal **n** and integrating over the whole closed surface A of the body, we evidently obtain the elementary work of deformation of the body (if the process is quasi-static, this work yields the change in free energy F under the condition of the constancy of the mole numbers N_i of all components):

$$(\mathrm{d}F)_{N_i} = \oiint (\mathbf{E}_n \cdot \mathrm{d}\mathbf{u}_n)\mathrm{d}A \tag{2.5}$$

We choose, as a body, an elementary rectangular parallelepiped with its faces perpendicular to the Cartesian coordinate axes x_s ($s = 1$–3), with its edges of lengths L_s ($s = 1$–3) along the corresponding axes, and with its volume $V = L_1L_2L_3$. For such a body, Eq. (2.5) takes the form

$$(\mathrm{d}F)_{N_i} = \sum_{s=1}^{3} A_s\mathbf{E}_s \cdot \mathrm{d}\mathbf{u}_s = \sum_{s=1}^{3} \mathbf{E}_s \cdot \mathrm{d}\mathbf{V}_s = V\sum_{s=1}^{3} \mathbf{E}_s \cdot \mathrm{d}\mathbf{e}_s, \tag{2.6}$$

where A_s is the area of the face perpendicular to the direction s, $\mathbf{V}_s$ and $\mathbf{e}_s$ are, respectively, the volume displacement vector (of the volume dimension) and the strain vector (dimensionless) at the s-face, defined through the linear displacement vector as

$$\mathbf{V}_s = A_s\mathbf{u}_s \tag{2.7}$$

$$\mathbf{e}_s = \frac{\mathbf{u}_s}{L_s} \tag{2.8}$$

The terns of these vectors at the elementary surfaces perpendicular to the basis directions, form the volume displacement tensor

$$\hat{V} \equiv \sum_{s=1}^{3} \mathbf{i}_s\mathbf{V}_s = \begin{pmatrix} V_{11} & V_{12} & V_{13} \\ V_{21} & V_{22} & V_{23} \\ V_{31} & V_{32} & V_{33} \end{pmatrix} \tag{2.9}$$

and the strain tensor

$$\hat{e} \equiv \sum_{s=1}^{3} \mathbf{i}_s\mathbf{e}_s = \begin{pmatrix} e_{11} & e_{12} & e_{13} \\ e_{21} & e_{22} & e_{23} \\ e_{31} & e_{32} & e_{33} \end{pmatrix}. \tag{2.10}$$

For small displacements, the diagonal components of tensor $\hat{V}$ yield the absolute volume changes and the diagonal components of tensor $\hat{e}$ yield the relative changes of volume or of linear dimensions along corresponding axes (non-diagonal components describe the deformation of beveling the right angle). The tensor trace (symbol Tr), i.e. the sum of the diagonal components, is known to be an invariant (independent of the coordinate system) and gives the absolute, in the case of $\hat{V}$, or the relative, in the case of $\hat{e}$, change of the volume of the whole body:

$$\mathrm{Tr}\,\hat{V} \equiv \hat{1} : \hat{V} = \sum_{s=1}^{3} V_{ss} = \Delta V, \tag{2.11}$$

$$\mathrm{Tr}\,\hat{e} \equiv \hat{1} : \hat{e} = \sum_{s=1}^{3} e_{ss} = \frac{\Delta V}{V}, \tag{2.12}$$

where two dots denote a biscalar product (as in the (single) scalar product of vectors, this is the sum of the pair products of corresponding components of tensors under multiplication).

Using tensorial symbolism (appropriate for any coordinate system), we now can write Eq. (2.6) in two equivalent forms

$$(\mathrm{d}F)_{N_i} = \hat{E} : \mathrm{d}\hat{V} \equiv \sum_{s,t=1}^{3} E_{st}\mathrm{d}V_{st} \tag{2.13}$$

$$(\mathrm{d}F)_{N_i} = V(\hat{E} : \mathrm{d}\hat{e}) \equiv V\sum_{s,t=1}^{3} E_{st}\mathrm{d}e_{st} \tag{2.14}$$

From (2.13) and (2.14), the important relations follow

$$E_{st} = \frac{\partial F}{\partial V_{st}} = \frac{\partial F}{V\partial e_{st}} \quad (s, t = 1\text{–}3) \tag{2.15}$$

The reader has noticed that we use full free energy in all relationships and do not use the free energy density, as it is generally accepted at the formulation of the thermodynamics of deformation in continuum mechanics. Not referring to the unit volume initial state, we also use the real stress tensor (the Cauchy tensor) that is applicable to every actual anisotropic state (see Ref. [4] for comparing the above equations in terms of Cauchy and Piola tensors).

We considered above the relationships for small uniform regions of a mechanically anisotropic system. However, the system as a whole can be nonuniform and characterized by a given stress tensor field in whose formation also external fields (gravity, an electrical field, etc.) can take part. In such a system, the obvious condition of mechanical equilibrium is the equality to zero for the total force acting on any fragment selected of the system. This force is composed of the contact force given in (2.3), after its integration over the closed surface A of the system fragment selected, and the force $\mathbf{F}$ of an external field:

$$\oint (\hat{E} \cdot \mathbf{n})\mathrm{d}A + \mathbf{F} = 0. \tag{2.16}$$

By dividing (2.16) by the volume V of the fragment selected and letting $V \rightarrow 0$ (then, by definition, the first term yields the divergence of the $\hat{E}$ tensor), we pass to the local formulation of the mechanical equilibrium condition

$$\nabla \cdot \hat{E} = -\mathbf{f} \tag{2.17}$$

where the divergence of the stress tensor is represented as the scalar product of the nabla-operator and the stress tensor, and $\mathbf{f} \equiv \mathbf{F}/V$ is the external field force per unit volume. Depending on the stress tensor definition, this force can be also included into the stress tensor as its component (for example, as the Maxwell stress tensor to speak about an electromagnetic field). This reduces Eq. (2.17) to the form similar to that in the absence of fields

$$\nabla \cdot \hat{E} = 0. \tag{2.18}$$

The advantage of Eq. (2.18) is its simplicity, although the stress tensor itself acquires a more complicated structure.To conclude this section, we touch the relation between the stress and strain tensors. This already refers to the problem of a solid state equation, which is often used as the Hook law. However, we postulate no equation of state, but only introduce the components λ_{lmst} of the elasticity modulus tensor $\hat{\lambda}$ (a tensor of the fourth order)

$$\lambda_{lmst} = \frac{\mathrm{d}E_{lm}}{\mathrm{d}e_{st}} \tag{2.19}$$

not assuming the constancy of these quantities. Since each of the tensors $\hat{E}$ and $\hat{e}$ contains six different components, the number of components in the six-dimensional tensor $\hat{\lambda}$ is 36, but, accounting for that, similarly to $\hat{E}$ and $\hat{e}$, $\hat{\lambda}$ is a symmetrical tensor, the maximum number of modules in one tensor is reduced to 21. As for the total number of modules, it should be estimated from the number of possible derivatives of the form (2.19). The matter is that the derivative in (2.19) is taken not only at the natural constancy of the temperature and the mass of a body, but also at additional conditions imposed on the tensors $\hat{E}$ and $\hat{e}$ and influencing the meaning of a modulus defined. For example, one can define the modulus of stretching λ_{1111} with the following variations (the exclusive disjunction $\oplus$ is of the meaning “either, or”)

$$\lambda_{1111} = \left(\frac{\mathrm{d}E_{11}}{\mathrm{d}e_{11}}\right)_{e_{22}\oplus E_{22}, e_{33}\oplus E_{33}, e_{12}\oplus E_{12}, e_{13}\oplus E_{13}, e_{23}\oplus E_{23}} \tag{2.20}$$

where always, as in every other modulus, five quantities are fixed in addition to temperature and mass. If all the five are strains, λ_{1111} is the one-dimensional stretching modulus. If, however, all the five are stresses, λ_{1111} is Young’s modulus (other combinations still have no their terminology). Each of the five conditions in (2.20) yields two variants, and they all together form $2^5 = 32$ variants for every of the 21 modules. Thus, the theoretically maximum total number of elasticity modules of an anisotropic solid is 672 (the reduction of this number for real crystals is larger, the higher is the crystal symmetry).

Having the relation between the components of the stress and strain tensors, we can choose the variables in thermodynamic equations at discretion. The components of the strain tensors play the role of independent variables in Eq. (2.14). Choosing now the stress tensor components as independent variables, we may write

$$\mathrm{d}e_{st} = \sum_{l,m=1}^{3} \frac{\partial e_{st}}{\partial E_{lm}} \mathrm{d}E_{lm} = \sum_{l,m=1}^{3} \frac{\mathrm{d}E_{lm}}{\lambda_{lmst}} \tag{2.21}$$

where λ_{lmst} is defined by (2.19) at the constancy of all components of the stress tensor E_{st}, except E_{lm}. Putting (2.21) in (2.14) yields the expression for the partial differential of free energy in terms of the stress tensor components:

$$(\mathrm{d}F)_{N_i} = V \sum_{l,m=1}^{3} \sum_{s,t=1}^{3} \frac{E_{st}}{\lambda_{lmst}} \mathrm{d}E_{lm} \tag{2.22}$$

From (2.22), the important relationship follows

$$\frac{\partial F}{\partial E_{lm}} = V \sum_{s,t=1}^{3} \frac{E_{st}}{\lambda_{lmst}} \tag{2.23}$$

The above relationships will be helpful at the formulation of the chemical terms in fundamental equations for anisotropic bodies.

2.2. Chemical potential tensor

It is possible to show that the anisotropy of the stress tensor in a solid leads to the anisotropy of chemical potential, which supplies the chemical potential with a tensorial character. This fundamental statement slowly penetrates into theory (e.g. it has not yet been used in mechanochemistry), so it is worthy to consider it in more detail.

2.2.1. Historical background

Although chemical potential is one of the central quantities of Gibbsean thermodynamics, Gibbs himself scarcely applied this notion to solids. Nevertheless, it was Gibbs who was first to show that a soluble solid can be not only in mechanical, but also in chemical (diffusion) equilibrium simultaneously with three its solutions at different pressures (Fig. 1). Gibbs derived the equilibrium condition [7, pp. 195, 217]

$$\frac{f - E_k - \sum_i \mu'_i c_i}{c_j} = \mu''_{j(k)} \quad (k = 1\text{–}3), \tag{2.24}$$

where f is the free energy density, c concentration (the amount of matter per unit volume); the subscripts refer: i to mobile species of a solid (Gibbs called them “fluids absorbed by a solid”), j to the matter of the solid (the immobile species forming the solid lattice), k to the orientation of the solid surface (when the normal to the surface corresponds to one of the principal directions 1–3). The chemical potentials have been marked with the single prime if they refer to the solid and with the double prime if they refer to the liquid, so that Eq. (2.24) represents the phase equilibrium condition which is traditionally perceived as the equality of chemical potentials in adjacent phases. Of course, this interpretation has to be proven (and will be proven below). If we actually identify the left-hand side of (2.24) with the chemical potential of the immobile species in a solid $\mu'_{j(k)}$:

$$\mu'_{j(k)} = \frac{f - E_k - \sum_i \mu'_i c_i}{c_j}, \tag{2.25}$$

such chemical potential seems to be defined not uniquely since it depends on the choice of direction k. In reality, however, the chemical potential is defined quite uniquely, but as a tensor:

$$\hat{\mu}'_j \equiv \begin{pmatrix} \mu'_{j(1)} & 0 & 0 \\ 0 & \mu'_{j(2)} & 0 \\ 0 & 0 & \mu'_{j(3)} \end{pmatrix}. \tag{2.26}$$

We have here written tensor $\hat{\mu}'_j$ straightway in the diagonal form since, according to Eq. (2.25), it should reproduce the symmetry of the stress tensor. It should be noted, however, that Eq. (2.25) certainly cannot serve as the definition of the chemical potential. Actually, Eq. (2.25) is a thermodynamic relationship and needs a proof (see below). As for the definition of the chemical potential tensor, it should be formulated by using the conventional method accepted in thermodynamics (we will represent it too).

It looks like a historical paradox that Gibbs, who was engaged not only in thermodynamics, but also in the vector and tensor calculus, did not introduce the notion of the chemical potential tensor. However, there was a reason for this since the chemical potentials of immobile species in solids did not play the same role as the chemical potentials of mobile species in fluids. In any case, Gibbs actually substantiated the tensorial nature of chemical potential. Nevertheless, he did not write the word ‘‘tensor’’ for chemical potentials, and this stimulated a number of scientists (see, e.g. [8–14]) to useless attempts to create the thermodynamics of elastic bodies on the ground of combining anisotropic stress with isotropic chemical potential. A survey was given by Kamb [15] who concluded: ‘‘among the outstanding theories, only that of Gibbs has any validity’’.

1960s were marked with a hitch in understanding the tensorial nature of chemical potential. Podstrigach, with respect to solids [16–19] (see also [20]), and Stuke, with respect to irreversible processes [21,22], were first to speak openly about the chemical potential (and Stuke also about temperature) as a tensor. Sooner or later (and often independently of each other), a number of other researchers had come to the same approach [23–31]. However, the theories formulated are not quite consistent. Stuke [22] has come to the denial of possibility of the equilibrium anisotropy of the stress tensor in fluids, although such anisotropy is known to be typical for fluid surface layers or smectic liquid crystals. Also the formulation of the problem of diffusion in elastic bodies [24] seems to be contradictory.

At the same time, the very elementary problem, a rigorous definition of the chemical potential tensor, was not understood completely. Most authors gave no definition at all and postulated thermodynamic relationships for the chemical potential tensor at once. Meanwhile, the problem is not so simple. First, if the chemical potential is a tensor, its conjugate quantity, mass or the number of moles, should also be a tensor, which looks quite improbable (mass is a typical scalar). Second, turning to the known thermodynamic definition of chemical potential

$$\mu_j \equiv \left(\frac{\mathrm{d}F}{\mathrm{d}N_j}\right)_{T,V,N_{i\neq j}}, \tag{2.27}$$

free energy F and the number of moles of the jth component N_j, as well as the temperature T, the volume V, and the number of moles of other components as subscripts, are scalar quantities. A similar situation, however, exists for the known pressure formula

$$p = -\left(\frac{\mathrm{d}F}{\mathrm{d}V}\right)_{T,N_i}, \tag{2.28}$$

where only scalars stand too. We know that, when passing to a mechanically anisotropic system, the constant volume condition is replaced by the more detailed condition of fixed boundaries (configuration) of the system, and the volume change (as a shift of one of the boundaries characterized by the volume displacement vector in (2.7)) is related to a direction, which results in introducing the volume displacement tensor in (2.9) and the strain tensor in (2.10). As a result, (2.28) is replaced by (2.15). Similarly, we should attach a directed character to the mole number variation in Eq. (2.27) when passing to an anisotropic body. In other words, the definition of the chemical potential tensor according to Eq. (2.27) implies the derivative denominator to be converted into a tensorial quantity. However, this can be done in various ways. Operating with the free energy density (as a scalar), Podstrigach introduced a density tensor [19] (or a concentration tensor to speak about a multicomponent system [20]), but this is the same as introducing the mass tensor. Logically, the free energy density should also be understood as a tensor in this formalism, which is nonsense. By contrast, not mass itself but its directed variation was considered as a tensor in the author's approach [1,30,31], whereas density, concentration, and the free energy density remain ordinary scalar quantities. Below, we will show how the chemical potential tensor is derived from a correct definition.

2.2.2. Direct derivation of the chemical potential tensor from its thermodynamic definition

First of all, we have to reformulate the chemical potential definition to make it applicable to anisotropic systems. For a mechanically anisotropic body, the condition of constancy of the volume in (2.27) is replaced by the much more powerful condition of a fixed configuration (the constancy of the volume displacement tensor $\hat{V}$) of the body, as if it were placed in a rigid container. We characterize the local orientation of the body boundary with the unit vector of the outer normal $\mathbf{n}$. The change of the body mass can only result from the matter transfer through the boundaries, which can occur in any direction. Therefore, the local directed change, $\mathbf{N}_j$, of the number of moles of the jth component may be identified with the transfer vector $-\mathbf{N}_j$ taken with the opposite sign (since the mass growth direction is always reverse to the direction of the mass transfer to the body). The transfer vector is defined as the amount of matter N_j transferred in the direction $-\mathbf{N}_j/N_j$ through an elementary (unnecessarily unit) area perpendicular to the direction of transfer. If such an area is oriented arbitrarily with its unit normal $\mathbf{n}$, the matter amount $N_{j(n)}$ transferred through it, is

$$N_{j(n)} = -\mathbf{N}_j \cdot \mathbf{n} = N_j \cos\varphi \tag{2.29}$$

where φ is the angle between the transfer vector and the direction of a normal to the surface (the normal flux transfers the maximum amount of matter through the surface, while the tangential flux transfers no matter at all).

One more simple interpretation of the vector $\mathbf{N}_j$ is possible. We above introduced the volume displacement vector describing a displacement of one of the body boundaries at a fixed mass of the body when any displacement is a strain. Let us now imagine the state of strain to be fixed while the condition of the mass constancy is canceled. Then the same vector will describe the boundary movement due to the mass change, and we may introduce the mass displacement vector of the jth component, $\mathbf{N}_j$, as the product of the concentration of the jth component c_j and the volume displacement vector $\mathbf{V}$:

$$\mathbf{N}_j = c_j\mathbf{V}. \tag{2.30}$$

The volume displacement vector just equals the transfer vector taken with the reverse sign, so that both the definitions of $\mathbf{N}_j$ coincide. However, the boundary is immobile in our process of transfer, and Eq. (2.30) is simply the method of calculation of $\mathbf{N}_j$, such as if the boundary would move. One may always imagine that the boundary first moves, containing a new portion of matter, and then returns to its original position by means of deformation of the system at a given amount of matter. The second stage of the process does not contribute to Eq. (2.30) which, thus, is also quite applicable to the case of transfer with a fixed boundary.

Since the transfer of matter in the system with fixed boundaries under consideration, is determined by the fields of two independent vectors $-\mathbf{N}_j$ and $\mathbf{n}$, it is possible to introduce the transfer tensor $-\hat{N}_j$ and its reversal, the mass displacement tensor $\hat{N}_j$. By analogy with Eq. (2.30), it is the simplest to define the mass displacement tensor via the volume displacement tensor (2.9) as

$$\hat{N}_j = c_j\hat{V}. \tag{2.31}$$

Designating the values of vector $\mathbf{N}_j$ corresponding to the coordinate axes directions as $\mathbf{N}_{j(1)}$, $\mathbf{N}_{j(2)}$, and $\mathbf{N}_{j(3)}$, we write by analogy with (2.9)

$$\hat{N}_j \equiv \sum_{s=1}^{3}\mathbf{i}_s\mathbf{N}_{j(s)} \equiv \begin{pmatrix} N_{j(11)} & N_{j(12)} & N_{j(13)} \\ N_{j(21)} & N_{j(22)} & N_{j(23)} \\ N_{j(31)} & N_{j(32)} & N_{j(33)} \end{pmatrix} \tag{2.32}$$

As the three vectors are chosen arbitrarily, we may choose them in parallel with the coordinate axes, so defining the mass displacement tensor as diagonal in a given (and symmetrical in any other) coordinate system. Its diagonal term $N_{j(ss)}$ (s = 1–3) determines the amount of the jth component added through the boundary perpendicular to the s-direction. The trace of the tensor (2.32) yields the total change of the number of moles of the jth species along all directions (cf. (2.11))

$$\mathrm{Tr}\,\hat{N}_j \equiv \sum_{s=1}^{3} N_{j(ss)} = N_j (= \Delta N_j) \tag{2.33}$$

(the form given in parenthesis refers to the case when N_j is understood as not transferred but the whole amount of component j in the system, the differentials of both the quantities coinciding). As for non-diagonal terms, they refer to the displacement of matter along the boundaries and produce no increase of matter in the system. We now can generalize Eq. (2.27) and define the chemical potential tensor of the jth species, $\hat{\mu}_j$, as

$$\mu_{j(st)} \equiv \left(\frac{\partial F}{\partial N_{j(st)}}\right)_{T,\hat{V},N_{i\neq j}} \qquad (s,t = 1\text{–}3), \tag{2.34}$$

where $\mu_{j(st)}$ are the components of the chemical potential tensor. The corresponding contribution to the free energy differential from the jth species is

$$\mathrm{d}\mu^{\sigma} = v^{\sigma}_{\alpha}\,\mathrm{d}p^{\alpha} + v^{\sigma}_{\beta}\,\mathrm{d}p^{\beta} - a\,\mathrm{d}\sigma. \tag{2.35}$$

By using the definition of the mass displacement tensor, we simply formulate the algorithm of transfer of matter from various sides to the system under consideration. This does not yet mean that the works of transfer of a given amount of matter from different sides are different. The result depends on the behavior of a given species in the system. If the species is mobile and moves freely over the whole volume of the system, all positions of its particles are equivalent, and, therefore, the work of transfer can in no way depend on the direction of transfer. Such situation is typical for fluids, but can be also realized in solids if they contain mobile species (as, for instance, metal's own electron gas or a foreign gas dissolved in a metal) migrating inside the solid lattice. In such cases, the chemical potential tensor is isotropic ($\mu_{j(1)} = \mu_{j(2)} = \mu_{j(3)} \equiv \mu_j$), and, according to Eq. (2.26), we have

$$\hat{\mu}_j = \mu_j \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \equiv \mu_j \hat{1} \tag{2.36}$$

This permits returning to the simple definition, Eq. (2.27), although a mobile species can be subjected to anisotropic stresses in some lattice cavities due to the action of the lattice field. As for an immobile species forming the solid lattice, it is unable to penetrate into the lattice depth and only can throw out the lattice outside. The transfer of an additional portion of matter in a rigid container inevitably leads to the compression of the body present in the container, the work of compression being dependent on direction for the body in the mechanically anisotropic state. Hence, the work of transfer itself and the corresponding change of free energy depend on the direction of transfer, which just cause the tensorial character of the chemical potential.

Possessing now a rigorous definition of the chemical potential tensor, Eq. (2.34), we can proceed to the direct calculation of the chemical potential of an immobile species. Let us select an imaginary elementary cube with its faces perpendicular to the coordinate axes (generally, not coinciding with the principal directions of the stress tensor). Fig. 2 shows the section of the cube by the coordinate plane xy (x_1x_2) and the direction of the mass displacement vector $\mathrm{d}\mathbf{N}_j$ of species j on the selected face 1 perpendicular to the x-axis (other faces of the cube are assumed to be rigid walls). In the course of transfer, a new portion of matter builds an addition to the lattice and simultaneously deforms all the contents of the cube. The change of the free energy F of the cube in this complex process can be estimated as follows.

We divide the process into two stages. In the first stage, the solid lattice simply grows in the direction pointed out (getting out of the cube, Fig. 2) with maintaining its mechanical state. With the transfer vector $-\mathrm{d}\mathbf{N}_{j(1)}$ (and the mass displacement vector $\mathrm{d}\mathbf{N}_{j(1)}$), $\mathrm{d}N_{j(11)}$ moles of component j will attach to the cube

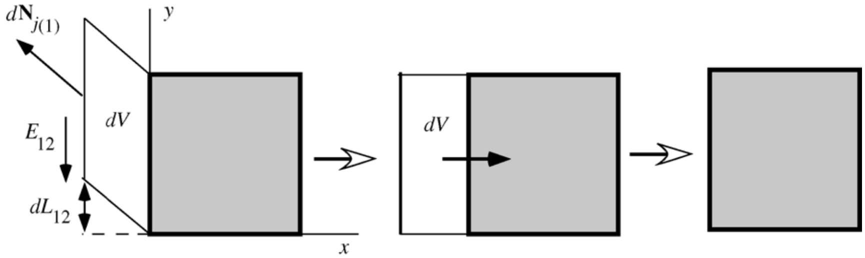

Fig. 2. Illustration of calculating chemical potential according to Eq. (2.34).

face and occupy the volume

$$\mathrm{d}V_{11} = v_j\,\mathrm{d}N_{j(11)}, \tag{2.37}$$

where v_j is the molar volume of the solid in its initial state. Herewith, the configuration of the new portion of the lattice will turn to be skew if the transfer vector is not directed along the normal to the face selected. In the second stage, we so deform the new portion of the lattice as to insert it within the initial cube boundaries. We organize the deformation in two steps: we first rectify the skew configuration of the new portion of the lattice (not yet inserting it in the cube) and then slide the whole portion (already as a rectangular plate) inside the cube (Fig. 2). Pure shear (with no change of the volume $\mathrm{d}V_{11}$) work of rectifying the skew angle in the xy-plane is

$$\mathrm{d}F_{12} = -E_{12}\,\mathrm{d}V_{12} = -E_{12}v_j\,\mathrm{d}N_{j(12)}, \tag{2.38}$$

where E_{12} is the component of the shear stress along the y-axis. The shear work along the z-axis is calculated similarly. Obviously, this type of contribution to free energy only exists provided the vector $\mathrm{d}\mathbf{N}_{j(1)}$ deviates from the normal to the cube face.

It remains to estimate the change in free energy at inserting the already rectangular plate into the cube. This change includes two contributions. The first corresponds to the compression of the matter, being present before in the cube, in the x-direction to make room of the volume $\mathrm{d}V_{11}$ for the new portion of matter. The work done yields the first contribution to the free energy change. The second contribution results from filling the volume $\mathrm{d}V_{11}$ with the immobile species in the form of the same lattice as in the rest volume. Evidently, this contribution can be written as $f\,\mathrm{d}V_{11}$ if the lattice initially did not contain mobile species. If, however, there are mobile species, f has a contribution from them and refers to the initial content of the cube. The free energy density in the volume $\mathrm{d}V_{11}$, where there are no mobile species, will be smaller by the quantity $\sum_i \mu_i c_i$ As a result, the free energy change in the unit cube will be

$$\mathrm{d}F_{11} = -E_{11}\,\mathrm{d}V_{11} + \left(f - \sum_i \mu_i c_i\right)\mathrm{d}V_{11} = v_j\left(f - \sum_i \mu_i c_i - E_{11}\right)\mathrm{d}N_{j(11)}. \tag{2.39}$$

Summing up (2.38), (2.39) and their analogues for other faces, we now can write the expression for the partial differential of free energy at a fixed system configuration and constant amounts of all other species but species j, as

$$(\mathrm{d}F)_{\hat{V},N_{i\neq j}} = v_j\sum_{s,t=1}^{3}\left[\left(f - \sum_i \mu_i c_i\right)\delta_{st} - E_{st}\right]\mathrm{d}N_{j(st)}. \tag{2.40}$$

Dividing now the left-hand and right-hand sides of (2.40) by $\mathrm{d}N_{j(st)}$ and using the definition expressed in (2.34), we arrive at the expression for chemical potential

$$\mu_{j(st)} = v_j\left[\left(f - \sum_i \mu_i c_i\right)\delta_{st} - E_{st}\right] \tag{2.41}$$

or, in a tensorial form,

$$\hat{\mu}_j = v_j\left(f - \sum_i \mu_i c_i\right)\hat{1} - v_j\hat{E}, \tag{2.42}$$

where $\hat{1}$ is the unit tensor shown in (2.36).

Since the unit tensor is maintained in any coordinates, it follows from (2.42) that the chemical potential tensor becomes diagonal in the same coordinate system that diagonalizes the stress tensor. For the principal directions, Eq. (2.41) takes the form

$$\mu_{j(k)} = v_j\left(f - E_k - \sum_i \mu_i c_i\right) \quad (k = 1\text{–}3). \tag{2.43}$$

It is easy to see that (2.43) is the same as (2.25). Hence, we have proved that the left-hand side of Gibbs' Eq. (2.24) may be really understood as the principal values of the chemical potential tensor of an immobile species of a solid. The values of the chemical potential in all directions can be calculated from the principal values of the chemical potential. By the scalar multiplication of $\hat{\mu}_j$ by the unit normal vector **n** at an arbitrary section of a solid (the surface of the solid is a particular and most important practical case of such a section), we obtain the chemical potential vector at the section (cf. (2.3)):

$$\boldsymbol{\mu}_{j(n)} = \mathbf{n}\cdot\hat{\mu}_j. \tag{2.44}$$

This vector points out the direction in which the chemical potential possesses its maximum value and allows the determination of the chemical potential values in all other directions. Sooth to say, for the interior of the solid lattice, these values are of interest only in the pure scientific respect and of no practical value since an immobile species is capable to migration in no direction. If, however, one addresses to the solid surface, the movement of the immobile species along the surface is also impossible, whereas the recession of matter from the surface (at evaporation, dissolution, etc.) is quite real. Thus, the normal component of the chemical potential vector

$$\mu_{j(nn)} = \mathbf{n}\cdot\boldsymbol{\mu}_{j(n)} \tag{2.45}$$

is of the most practical significance. In the isotropic case, putting (2.36) reduces Eq. (2.44) to the form

$$\boldsymbol{\mu}_{j(n)} = \mu_j(\mathbf{n}\cdot\hat{1}) = \mu_j\mathbf{n}, \qquad \mu_{j(nn)} = \mu_j,$$

from where the chemical potential vector is seen to be same by its module in all directions.

To summarize the said above about chemical potential, we now can answer all the questions put above concerning the relation between the anisotropy of stress and that of chemical potential. Generally, chemical potential is a tensorial quantity. To speak about a mobile species, the tensor of its chemical potential is always isotropic irrespective of the presence or absence of the stress (pressure) anisotropy. As for the case of an immobile species, the symmetry of the tensor of its chemical potential always reproduces the stress tensor symmetry, and, together with the stress tensor, the chemical potential tensor can be both isotropic and anisotropic. On the other side, as is seen from (2.43), the fulfillment of the mechanical equilibrium condition (2.18) for the stress tensor ($\partial E_k/\partial x_k = 0$ in the absence of fields) does not secure the uniformity of the principal values of chemical potential, as it happens with mobile species at equilibrium.

The chemical potential tensor is defined similarly for particles of any nature, including ions whose chemical potential (usually called electrochemical potential) contains the electric potential. This means that, in principle, the chemical potential anisotropy in an electrochemical system can be verified by measuring the anisotropy of the electric potential. This idea was realized by Durham and Schmalzried [32]. To explain the scheme of their experiment, let us return to Fig. 1 and imagine a solid depicted to be a metal and an adjacent liquid to be replaced (from all the sides) by a solid electrolyte. The metal ions form a lattice and are immobile inside the metal, but, passing to the solid electrolyte, become mobile and capable of free moving. Their saturation concentration is very small, so that only a negligible part matter passes from the metal to the solid electrolyte. Similarly to a liquid, the solid electrolyte is capable of transmitting pressure, but, in contrast with a liquid, the solid electrolyte has its own lattice that secures mobile ions from a large pressure. If one assumes that stresses applied do not act on the mobile metal ions at all, the difference of the ion electrochemical potentials in the solid electrolyte at different stresses will be determined only by the electric potential difference, which is directly measurable. In this way the anisotropy of the electric potential was registered. Thus, one can say that the tensorial nature of chemical potential has been verified by experiment.

2.3. Fundamental thermodynamic equations

After deriving the mechanical and chemical terms, Eqs. (2.13) and (2.35), we now can compose the fundamental equation for free energy as

$$\mathrm{d}F = -S\,\mathrm{d}T + \hat{E} : \mathrm{d}\hat{V} + \hat{\mu}_j : \mathrm{d}\hat{N}_j + \sum_i \mu_i\,\mathrm{d}N_i, \tag{2.46}$$

where S is entropy and T is temperature, superscripts j and i refer to immobile and mobile species, respectively (the entropic term appears in the standard form according to the Gibbs equilibrium principle). For the sake of simplicity, we assume a single immobile species to form the solid lattice. This, however, is not a great loss in generality since any combination of solid species of a strictly fixed composition (often called *a material*) can be thermodynamically considered as a unique immobile species. Eq. (2.46) describes the thermochemical, thermomechanical, and mechanochemical effects in solids. We begin the discussion with the first term on the right-hand side of Eq. (2.46).

2.3.1. The thermal term: is temperature also a tensor?

We have written the thermal term in its traditional form in Eq. (2.46). However, after we have converted the material term to a tensorial form, the question arises: should the thermal term also been written in a tensorial form? That was Stuke [21] who first declared temperature to be a tensor. Indeed, if we remember that the entropy fluxes are vectors and that several fluxes can attack a system simultaneously, why not to introduce a tensorial temperature like we did with the chemical potential of an immobile species when considering the matter flux vectors? However, we spoke just about an immobile species. Once a species becomes mobile, its chemical potential acquires isotropy even in the case when the anisotropy of stresses is maintained. The surface layer of a liquid can be an example: the normal and transverse pressures are different in the surface layer (because of what surface tension arises), whereas the chemical potentials of species are isotropic. All-pervading heat can scarcely remind an immobile species and can rather be compared with a mobile species. The analogy between heat and a mobile species becomes absolute if one turns to the phonon theory of dielectrics whose thermal properties are determined by the behavior of a gas of quasi-particles, phonons. Phonons move freely over the whole volume of a system, and, no doubt, they form a mobile component. Then considering the temperature as a kind of chemical potential of the phonons, we can conclude that it should be isotropic. When passing from dielectrics to metals, electrons (to be more exact, their part forming the electron gas) join phonons in the process of heat conduction, but the electrons are also typical mobile species. Thus the arguments related to the nature of heat draw us to the following conclusion: even if temperature is really a tensor, it should be a spherical tensor. Then, similarly, to the last chemical term in Eq. (2.46), the thermal term may also be written in a scalar form.

2.3.2. Generalized Gibbs–Duhem equation

Following the standard procedure, we first have to deduce an integral expression for free energy. Let us choose a direction r in space (with one of the axes of Cartesian coordinates along the direction) and move the body boundary in this direction simultaneously with adding matter only along this direction at a fixed physical state. For such process, Eq. (2.46) takes the form

$$\mathrm{d}F = E_{rr}\,\mathrm{d}V_{rr} + \mu_{j(rr)}\,\mathrm{d}N_{j(rr)} + \sum_i \mu_i\,\mathrm{d}N_i, \tag{2.47}$$

where all the rest components of the volume and mass displacement tensors are zero. The integration of Eq. (2.47) yields

$$F = E_{rr}V + \mu_{j(rr)}N_j + \sum_i \mu_i N_i. \tag{2.48}$$

Since the free energy value should be independent of the choice of the integration direction, it follows from (2.48) that the sum $E_{rr}V + \mu_{j(rr)}N_j$ is an invariant with respect to direction.

By differentiating Eq. (2.48), we have

$$\mathrm{d}F = E_{rr}\,\mathrm{d}V + V\,\mathrm{d}E_{rr} + \mu_{j(rr)}\,\mathrm{d}N_j + N_j\,\mathrm{d}\mu_{j(rr)} + \sum_i \mu_i\,\mathrm{d}N_i + \sum_i N_i\,\mathrm{d}\mu_i \tag{2.49}$$

Accounting for that the perfect differentials of volume and the number of moles are composed of their directed variations (see Eqs. (2.89), (2.90), and (2.33)), we can rearrange Eq. (2.49) as

$$\mathrm{d}F = E_{rr}\sum_{l=1}^{3} V\,\mathrm{d}e_{ll} + V\,\mathrm{d}E_{rr} + \mu_{j(rr)}\sum_{s=1}^{3}\mathrm{d}N_{j(ss)} + N_j\,\mathrm{d}\mu_{j(rr)} + \sum_i \mu_i\,\mathrm{d}N_i + \sum_i N_i\,\mathrm{d}\mu_i \tag{2.50}$$

Equating now the right-hand sides of (2.46) and (2.50) and taking into account (2.14) and (2.35), we obtain

$$\begin{aligned}&\sum_{l,m=1}^{3}(E_{lm} - \delta_{lm}E_{rr})V\,\mathrm{d}e_{lm} - V\,\mathrm{d}E_{rr}\\ &\quad = S\,\mathrm{d}T - \sum_{s,t=1}^{3}(\mu_{j(st)} - \delta_{st}\mu_{j(rr)})\mathrm{d}N_{j(st)} + N_j\,\mathrm{d}\mu_{j(rr)} + \sum_i N_i\,\mathrm{d}\mu_i\end{aligned} \tag{2.51}$$

where the Kronecker symbol δ_{lm} represents the components of the unit tensor $\hat{1}$. If the amount of the immobile species does not change from any side ($\mathrm{d}N_{j(st)} = 0$) and only a change occurs in the mechanical state, Eq. (2.51) takes the form

$$\sum_{l,m=1}^{3}(E_{lm}-\delta_{lm}E_{rr})V\,\mathrm{d}e_{lm}-V\,\mathrm{d}E_{rr}=S\,\mathrm{d}T+N_j\,\mathrm{d}\mu_{j(rr)}+\sum_i N_i\,\mathrm{d}\mu_i, \tag{2.52}$$

where, as in (2.51), the summation is actually carried out with respect to five and not six components of the strain tensor since the coefficient of $\mathrm{d}e_{rr}$ is zero (the fundamental Eq. (2.52) has been formed in such manner that the independent variable e_{rr} has been replaced by the independent variable E_{rr}). Dividing Eq. (2.52) by the volume of the system V, we obtain

$$\sum_{l,m=1}^{3}(E_{lm}-\delta_{lm}E_{rr})\mathrm{d}e_{lm}-\mathrm{d}E_{rr}=s_v\,\mathrm{d}T+c_j\,\mathrm{d}\mu_{j(rr)}+\sum_i c_i\,\mathrm{d}\mu_i \tag{2.53}$$

(s_v is the bulk density of entropy) or, using the tensorial notation,

$$(\hat{E}-\hat{1}E_{rr}):\mathrm{d}\hat{e}-\mathrm{d}E_{rr}=s_v\,\mathrm{d}T+c_j\,\mathrm{d}\mu_{j(rr)}+\sum_i c_i\,\mathrm{d}\mu_i. \tag{2.54}$$

When passing to an isotropic fluid system, the conditions are fulfilled $\hat{E}=E_{rr}\hat{1}=-p\hat{1}$ (i.e. $E_{lm}=-p\delta_{lm}$ where p is hydrostatic pressure), $N_j=0$, and Eq. (2.52) changes to the well-known Gibbs–Duhem equation

$$V\,\mathrm{d}p=S\,\mathrm{d}T+\sum_i N_i\,\mathrm{d}\mu_i. \tag{2.55}$$

Thus, the fundamental Eq. (2.52) is a generalization of the Gibbs–Duhem equation for mechanically anisotropic states. If a solid is isotropic, Eq. (2.52) is again reduced to classical Eq. (2.55), but with immobile species included in the summation.

2.3.3. Directed partial quantities, a new class of thermodynamic variables

As is known, free energy is a thermodynamic potential at constant strain tensor, i.e. at a constant volume to speak about isotropic systems. Isothermal–isobaric conditions are more practical, and that is why free energy is often replaced by Gibbs energy $G=F+pV$. However, the definition of Gibbs energy becomes not unique for mechanically anisotropic states since pressure (as well as stress) is different along different directions. The quantity $-E_{rr}$ plays the role of pressure in the r-direction, and we may define Gibbs energy G in an anisotropic system as

$$G_r\equiv F-E_{rr}V \tag{2.56}$$

to relate it, in this manner, to the direction choice (this is marked by the subscript at G). It can be emphasized that, herewith, Gibbs energy does not become a directed quantity and remains, like any energy, a typical scalar.

By differentiating Eq. (2.56) with putting (2.47) and accounting for (2.14) and (2.35), we arrive at the differential fundamental equation for the Gibbs energy of a uniform anisotropic system

$$\mathrm{d}G_r=-S\,\mathrm{d}T+V\sum_{l,m=1}^{3}(E_{lm}-\delta_{lm}E_{rr})\mathrm{d}e_{lm}-V\,\mathrm{d}E_{rr}+\sum_{s,t=1}^{3}\mu_{j(st)}\,\mathrm{d}N_{j(st)}+\sum_i\mu_i\,\mathrm{d}N_i \tag{2.57}$$

or, in tensorial notation,

$$\mathrm{d}G_r = -S\,\mathrm{d}T + V(\hat{E} - \hat{1}E_{rr}) : \mathrm{d}\hat{e} - V\,\mathrm{d}E_{rr} + \hat{\mu}_j : \mathrm{d}\hat{N}_j + \sum_i \mu_i\,\mathrm{d}N_i. \tag{2.58}$$

By integrating Eq. (2.57) along the r-direction at constant E_{rr}, we obtain the integral expression for Gibbs energy

$$G_r = \mu_{j(rr)}N_j + \sum_i \mu_i N_i. \tag{2.59}$$

Correspondingly, for Gibbs molar energy, we have

$$g_r = \mu_{j(rr)}x_j + \sum_i \mu_i x_i, \tag{2.60}$$

where x is the mole fraction. After the differentiation of (2.59) and comparison with (2.57), we again arrive, as expected, at Eq. (2.51) from where Eqs. (2.53) and (2.54) follow whose form does not depend on the choice of a thermodynamic potential.

Eq. (2.59) shows that the Gibbs energy for a direction chosen is composed of chemical potentials. This usually leads in thermodynamics to the representation of the chemical potential as a partial molar Gibbs energy, and we see, in our particular case, that $\mu_{j(rr)}$ is a partial molar quantity of G_r. Indeed, from Eq. (2.57) we obtain

$$\mu_{j(rr)} = \left(\frac{\partial G_r}{\partial N_{j(rr)}}\right)_{T,e_{lm\neq rr},E_{rr},N_{j(st\neq rr)},N_i}, \tag{2.61}$$

from where it follows that the normal component of the chemical potential tensor of an immobile species in the r-direction is the increment of the Gibbs energy corresponding to this direction, at adding 1 mole of the immobile species in the same direction to an infinitely large system. The addition is carried out at a constant temperature and stress in the direction chosen, let alone that the variation of the mass of species and of the system dimensions on all sides is forbidden. Changing G_r for an arbitrary extensive quantity, the derivative in Eq. (2.61) provides the general definition of a partial molar quantity for a given direction. Since the matter transfer is always directed, such extension of the notion of a partial molar quantity in thermodynamics is natural and turns to be useful for quantities depending on direction. At the same time, the application of this definition to quantities independent of direction, leads to ordinary partial molar quantities (volume, entropy, the chemical potentials of mobile species, etc.).

For the sake of illustration, let us consider entropy S as a function of the independent variables indicated in Eq. (2.57) and write the exact differential of entropy in the form

$$\mathrm{d}S = \frac{\partial S}{\partial T}\mathrm{d}T + \sum_{\substack{l,m=1\\(lm\neq rr)}}^{3} \frac{\partial S}{\partial e_{lm}}\mathrm{d}e_{lm} + \frac{\partial S}{\partial E_{rr}}\mathrm{d}E_{rr} + \sum_{s,t=1}^{3}\frac{\partial S}{\partial N_{j(st)}}\mathrm{d}N_{j(st)} + \sum_i \frac{\partial S}{\partial N_i}\mathrm{d}N_i. \tag{2.62}$$

Here the r-direction is the only direction along which the variation of the geometrical dimensions of a system is possible. In this sense, the r-direction can be named a free direction, while the others can be named restricted directions. Nevertheless, the addition of matter is possible from all sides, but the matter is not compressed when adding in the free direction and is compressed by necessity when adding in restricted directions (to return the system to the original size in each restricted direction). In a mechanically anisotropic system, compression in different directions leads to different states, including also a difference in entropy, so that the value of the derivative $\partial S/\partial N_{j(st)}$ depends on the choice of a restricted direction. Let us now see whether or not the choice a free direction influences the value of the derivative $\partial S/\partial N_{j(st)}$.

In accordance with the terminology accepted in thermodynamics, we denominate as "open" the directions along which the matter exchange is possible and as "closed" the directions along which the matter exchange is forbidden. Let the matter transfer be possible only along the open direction r and all other directions be closed. For this case, we write Eq. (2.62) as

$$\mathrm{d}S = \frac{\partial S}{\partial T}\mathrm{d}T + \sum_{\substack{l,m=1\\(lm\neq rr)}}^{3} \frac{\partial S}{\partial e_{lm}}\mathrm{d}e_{lm} + \frac{\partial S}{\partial E_{rr}}\mathrm{d}E_{rr} + \bar{s}_{j(rr)}\mathrm{d}N_{j(rr)} + \sum_i \bar{s}_i\,\mathrm{d}N_i, \tag{2.63}$$

where $\bar{s}_{j(rr)}$ and $\bar{s}_i$ are the partial molar entropies of the immobile (in the r-direction) species and of mobile species, respectively, defined, according to (2.61), as

$$\bar{s}_{j(rr)} \equiv \left(\frac{\partial S}{\partial N_{j(rr)}}\right)_{T,e_{lm\neq rr},E_{rr},N_{j(st\neq rr)},N_i}, \tag{2.64}$$

$$\bar{s}_i \equiv \left(\frac{\partial S}{\partial N_i}\right)_{T,e_{lm\neq rr},E_{rr},N_{j(st)},N_{k\neq i}} \tag{2.65}$$

(the subscript k, as well as the subscript i, refers to mobile species). We apply Eq. (2.63) to a parallelepiped slice of infinitesimal thickness in the r-direction and integrate Eq. (2.63) along the r-direction at a given physical state (at constant T, $e_{lm\neq rr}$, E_{rr}, $\bar{s}_{j(rr)}$, and $\bar{s}_i$). The result of integration

$$S = \bar{s}_{j(rr)}N_j + \sum_i \bar{s}_i N_i \tag{2.66}$$

shows that $\bar{s}_{j(rr)}$ and $\bar{s}_i$ are really partial molar quantities. Formally, $\bar{s}_{j(rr)}$ is a partial molar quantity in the r-direction, but, since the result (the quantity S) must be independent of direction, the quantity $\bar{s}_{j(rr)}$ should be the same for all directions. Thus, in contrast with the derivatives of entropy for restricted directions in Eq. (2.62), the derivative shown in Eq. (2.64) for a free and open direction does not depend on the direction choice. Therefore, we may now omit the additional subscript (rr) by setting $\bar{s}_{j(rr)} = \bar{s}_j$.

The same can be said about the partial molar volume

$$\bar{v}_{j(rr)} \equiv \left(\frac{\partial V}{\partial N_{j(rr)}}\right)_{T,V_{lm\neq rr},E_{rr},N_{j(st\neq rr)},N_i}. \tag{2.67}$$

However, it should be added here that the specificity of an immobile species (which forms the solid lattice containing mobile species *inside*) makes the partial molar volume of an immobile species practically undistinguishable from its molar volume. Thus, we may set $\bar{v}_{j(rr)} = v_j$.

2.3.4. Thermomechanical relationships

If the amount of an immobile species is fixed (the system being closed all round for this species, so that $\mathrm{d}\hat{N}_j = 0$) and numbers 1 mole, Eq. (2.46) for free energy and Eq. (2.57) for Gibbs energy can be written as

$$\mathrm{d}f_j = -s_j\,\mathrm{d}T + v_j \sum_{l,m=1}^{3} E_{lm}\,\mathrm{d}e_{lm} + \sum_i \mu_i\,\mathrm{d}N_{i(j)}, \tag{2.68}$$

$$\mathrm{d}g_{r(j)} = -s_j\,\mathrm{d}T + v_j \sum_{l,m=1}^{3} (E_{lm} - \delta_{lm}E_{rr})\mathrm{d}e_{lm} - v_j\,\mathrm{d}E_{rr} + \sum_i \mu_i\,\mathrm{d}N_{i(j)}, \tag{2.69}$$

where $f_j \equiv F/N_j$, $g_{r(j)} \equiv G_r/N_j$, $s_j \equiv S/N_j$, and $N_{i(j)} \equiv N_i/N_j$ are free energy, Gibbs energy G_r, entropy, and the number of moles of the ith mobile species per 1 mole of the immobile species, respectively. By the cross differentiation in (2.68), we obtain the relationship

$$\left(\frac{\partial s_j}{\partial e_{lm}}\right)_{T,e_{st\neq lm},\hat{N}_j,N_i} = -v_j\left(\frac{\partial E_{lm}}{\partial T}\right)_{\hat{v},\hat{N}_j,N_i} \equiv -\,v_j\eta_{lm}, \tag{2.70}$$

where, at fixing quantities, dummy indices run all possible values (the restrictions, if any, are pointed out: for example, the condition of constancy $e_{st\neq lm}$ means that s and t run all possible values except l and m, respectively, i.e. all the components of the strain tensor are fixed except e_{lm}; the constancy of the tensor itself is indicated if all its components are fixed simultaneously). In Eq. (2.70), η_{lm} is the thermal stress coefficient showing what an additional stress, in a direction chosen, arises in a closed system of a fixed configuration (therefore, v_j acts as a constant here) when changing the temperature by one degree. The value of the coefficient is determined by the equation of state of a system. The set of the coefficients η_{lm} (l, m = 1–3) makes the tensor of thermal stress coefficients, $\hat{\eta}$, that may be defined as the temperature derivative of the stress tensor:

$$\hat{\eta} \equiv \left(\frac{\partial \hat{E}}{\partial T}\right)_{\hat{e},\hat{N}_j,N_i}. \tag{2.71}$$

The tensor of thermal strain coefficients $\hat{\theta}$ (an analogue of the thermal dilatation coefficient for isotropic systems) is defined as

$$\hat{\theta} \equiv \left(\frac{\partial \hat{e}}{\partial T}\right)_{\hat{E},\hat{N}_j,N_i}. \tag{2.72}$$

Both the tensors, $\hat{\eta}$ and $\hat{\theta}$, serve as main characteristics of the thermomechanical effect.

From Eq. (2.69) the cross relationships follow

$$\left(\frac{\partial s_j}{\partial e_{lm}}\right)_{\substack{T,e_{st\neq lm},E_{rr},\hat{N}_j,N_i\\ st\neq rr}} = -\left(\frac{\partial[v_j(E_{lm} - \delta_{lm}E_{rr})]}{\partial T}\right)_{e_{st\neq rr},E_{rr},\hat{N}_j,N_i}, \tag{2.73}$$

$$\left(\frac{\partial s_j}{\partial E_{rr}}\right)_{T,e_{lm\neq rr},\hat{N}_j,N_i} = \left(\frac{\partial v_j}{\partial T}\right)_{e_{lm\neq rr},E_{rr},\hat{N}_j,N_i}, \tag{2.74}$$

$$\left(\frac{\partial[v_j(E_{lm}-\delta_{lm}E_{rr})]}{\partial E_{rr}}\right)_{T,e_{st\neq rr},\hat{N}_j,N_i} = -\left(\frac{\partial v_j}{\partial e_{lm}}\right)_{\substack{T,e_{st\neq lm},E_{rr},\hat{N}_j,N_i\\ st\neq rr}}. \tag{2.75}$$

Introducing the thermal coefficient of linear dilatation in the r-direction (all other directions are blockaded by the conditions of fixation of the strain tensor components):

$$\theta_{rr} \equiv \frac{1}{v_j}\left(\frac{\partial v_j}{\partial T}\right)_{e_{lm\neq rr},E_{rr},\hat{N}_j,N_i}. \tag{2.76}$$

the thermal stress coefficient under the condition that the normal stress in the r-direction is kept constant

$$\eta_{lm(rr)} \equiv \left(\frac{\partial E_{lm}}{\partial T}\right)_{e_{st\neq rr},E_{rr},\hat{N}_j,N_i}, \tag{2.77}$$

and the isothermal compressibility in the r-direction

$$\chi_{rr} \equiv \frac{1}{v_j}\left(\frac{\partial v_j}{\partial E_{rr}}\right)_{T,e_{lm\neq rr},\hat{N}_j,N_i}, \tag{2.78}$$

we rewrite Eqs. (2.73)–(2.75) in the form

$$\left(\frac{\partial s_j}{\partial e_{lm}}\right)_{\substack{T,e_{st\neq lm},E_{rr},\hat{N}_j,N_i\\ st\neq rr}} = -\theta_{rr}v_j(E_{lm}-\delta_{lm}E_{rr}) - v_j\eta_{lm(rr)}, \tag{2.79}$$

$$\left(\frac{\partial s_j}{\partial E_{rr}}\right)_{T,e_{lm\neq rr},\hat{N}_j,N_i} = v_j\theta_{rr}, \tag{2.80}$$

$$\left(\frac{\partial E_{lm}}{\partial E_{rr}}\right)_{T,e_{st\neq rr},\hat{N}_j,N_i} = \delta_{lm} - \frac{1}{v_j}\left(\frac{\partial v_j}{\partial e_{lm}}\right)_{\substack{T,e_{st\neq lm},E_{rr},\hat{N}_j,N_i\\ sr\neq rr}} - \chi_{rr}(E_{lm}-\delta_{lm}E_{rr}). \tag{2.81}$$

In accordance with (2.11), only the normal components of the strain tensor contribute to the volume change. Therefore, only a small (because of small compressibility) term $-\chi_{rr}E_{lm}$ remains for the shear components of the stress tensor E_{lm} ($l \neq m$) on the right-hand side of Eq. (2.81). For the normal component E_{ll} ($ll \neq rr$), with the account for the fixation of the strain tensor component in the third direction, we have

$$\frac{1}{v_j}\left(\frac{\partial v_j}{\partial e_{lm}}\right)_{\substack{T,e_{st\neq lm},E_{rr},\hat{N}_j,N_i\\ st\neq rr}} = \frac{\partial(e_{ll}+e_{rr})}{\partial e_{ll}} = 1-\kappa_{rl}, \tag{2.82}$$

where κ_{rl} is two-dimensional Poisson's ratio in the *rl*-plane. In this case, Eq. (2.81) changes to the form

$$\left(\frac{\partial E_{ll}}{\partial E_{rr}}\right)_{T,e_{st\neq rr},\hat{N}_j,N_i} = \kappa_{rl} - \chi_{rr}(E_{ll} - E_{rr}). \tag{2.83}$$

For an incompressible medium ($\kappa_{rl} = 1$, $\chi_{rr} = 0$), Eq. (2.83) yields equal variations of the acting stress and the transverse stress at a one-sided compression (the result is known in the theory of elasticity when using ordinary Poisson's ratio). The same result directly follows from Eq. (2.81) at a constant v.

2.3.5. Expressions for chemical potentials

In the absence of mobile species, Eq. (2.52) yields the differential of the chemical potential of an immobile species in a given direction

$$\mathrm{d}\mu_{j(rr)} = -s_j\,\mathrm{d}T + v_j\left[\sum_{l,m=1}^{3}(E_{lm} - \delta_{lm}E_{rr})\mathrm{d}e_{lm} - \mathrm{d}E_{rr}\right], \tag{2.84}$$

where s_j and v_j are the molar entropy and volume of the immobile species, respectively. The chemical potentials of mobile species are controllable, and, if they are fixed, Eq. (2.52) again changes to (2.84). In this case, however, s_j and v_j should be called not the molar entropy and volume of an immobile species, but the entropy and volume of a system per 1 mole of the immobile species (as in Eqs. (2.68) and (2.69)). Herewith, the quantity v_j maintains its meaning as the molar volume of an immobile species if mobile species do not outstep the boundary of a lattice formed by the immobile species. Eq. (2.84) is evident to be valid not only in the absence of mobile species, but also when the chemical potentials of mobile species are kept constant. It is more typical for practice, however, that not chemical potentials but the amounts of mobile species are constant (say, in a single piece of a solid). So we have to find expressions for the chemical potentials of both immobile and mobile species under such conditions. General expressions for chemical potentials can be derived from fundamental equations.

Turning first to Eq. (2.46), we rewrite it in the form

$$\mathrm{d}F = -S\,\mathrm{d}T + V\sum_{l,m=1}^{3}E_{lm}\,\mathrm{d}e_{lm} + \sum_{s,t=1}^{3}\mu_{j(st)}\,\mathrm{d}N_{j(st)} + \sum_i \mu_i\,\mathrm{d}N_i. \tag{2.85}$$

If the amount of an immobile species is fixed on all sides ($\mathrm{d}\hat{N}_j = 0$), the variables T, e_{lm} and N_i remain in Eq. (2.85). Writing the perfect differentials of $\mu_{j(st)}$ and μ_i in this variables and using the cross relationships following from Eq. (2.85), we arrive at the expressions

$$\mathrm{d}\mu_{j(st)} = -\frac{\partial S}{\partial N_{j(st)}}\mathrm{d}T + \sum_{l,m=1}^{3}\frac{\partial E_{lm}}{\partial N_{j(st)}}V\,\mathrm{d}e_{lm} + \sum_i\frac{\partial\mu_i}{\partial N_{j(st)}}\mathrm{d}N_i, \tag{2.86}$$

$$\mathrm{d}\mu_i = -\frac{\partial S}{\partial N_i}\mathrm{d}T + \sum_{l,m=1}^{3}\frac{\partial E_{lm}}{\partial N_i}V\,\mathrm{d}e_{lm} + \sum_i\frac{\partial\mu_i}{\partial N_i}\mathrm{d}N_i. \tag{2.87}$$

All the derivatives in Eqs. (2.86) and (2.87) are taken under the conditions shown in Eq. (2.34). Due to the constancy of the volume, Eq. (2.87) for the chemical potential of a mobile species can be written as

$$\mathrm{d}\mu_i = -\frac{\partial s_v}{\partial c_i}\mathrm{d}T + \sum_{l,m=1}^{3}\frac{\partial E_{lm}}{\partial c_i}\mathrm{d}e_{lm} + \sum_i \frac{\partial \mu_i}{\partial c_i}\mathrm{d}c_i, \tag{2.88}$$

where $s_v \equiv S/V$ is the entropy density and $c_i \equiv N_i/V$ is the concentration of the ith mobile species.

It is implied in the derivative $\partial E_{lm}/\partial N_{j(st)}$ that the lattice of an immobile species is built up under the condition of the volume constancy, i.e. under compression. The relation of this derivative to the elastic properties of the lattice is [5]

$$\frac{\partial E_{lm}}{\partial N_{j(st)}} = -\frac{v_j}{V}\frac{\partial E_{lm}}{\partial e_{st}} \equiv -\frac{v_j}{V}\lambda_{lmst}, \tag{2.89}$$

where λ_{lmst} is a corresponding elasticity modulus. Putting Eq. (2.89) in Eq. (2.86) yields

$$\mathrm{d}\mu_{j(st)} = -\frac{\partial S}{\partial N_{j(st)}}\mathrm{d}T - v_j \sum_{l,m=1}^{3}\lambda_{lmst}\mathrm{d}e_{lm} + \sum_i \frac{\partial \mu_i}{\partial N_{j(st)}}\mathrm{d}N_i. \tag{2.90}$$

It is of note that the derivatives of entropy in Eqs. (2.88) and (2.90) are not partial molar quantities. Indeed, these derivatives are taken at the constancy of the temperature and of the strain tensor of a system (i.e. at the invariability of the whole boundary of the system). Under such conditions, the injection of an additional amount of the immobile species to the lattice along a certain direction, means the lattice compression and a change in the mechanical state (stress) of the lattice even in this direction, let alone the others.

More convenient expressions can be obtained from Eq. (2.57) for Gibbs energy in the r-direction where, comparably with Eq. (2.85), the independent variable e_{rr} has been replaced by E_{rr}. Considering the chemical potentials as functions of temperature T, the components e_{lm}, except e_{rr}, of the strain tensor, and the amounts (the mole numbers) of mobile components N_i (at $\mathrm{d}\hat{N}_j = 0$) and using the cross relationships following from Eq. (2.57), the differentials of chemical potentials $\mu_{j(st)}$ and μ_i are given, in this case, by the expressions

$$\mathrm{d}\mu_{j(st)} = -\frac{\partial S}{\partial N_{j(st)}}\mathrm{d}T + \sum_{\substack{l,m=1\\ lm\neq rr}}^{3}\frac{\partial[V(E_{lm} - \delta_{lm}E_{rr})]}{\partial N_{j(st)}}\mathrm{d}e_{lm} - \frac{\partial V}{\partial N_{j(st)}}\mathrm{d}E_{rr} + \sum_i \frac{\partial \mu_i}{\partial N_{j(st)}}\mathrm{d}N_i, \tag{2.91}$$

$$\mathrm{d}\mu_i = -\frac{\partial S}{\partial N_i}\mathrm{d}T + \sum_{\substack{l,m=1\\ lm\neq rr}}^{3}\frac{\partial[V(E_{lm} - \delta_{lm}E_{rr})]}{\partial N_i}\mathrm{d}e_{lm} - \frac{\partial V}{\partial N_i}\mathrm{d}E_{rr} + \sum_i \frac{\partial \mu_i}{\partial N_i}\mathrm{d}N_i. \tag{2.92}$$

The volume V in these expressions is not constant any longer and is subjected to differentiation. By contrast, the stress E_{rr} is considered as a constant, so that the term $\delta_{lm}E_{rr}$ disappears at differentiation. As a result, Eqs. (2.91) and (2.92) take the form (for mobile species, the derivatives of entropy and volume may at once be replaced by partial molar quantities):

$$\mathrm{d}\mu_{j(st)} = -\frac{\partial S}{\partial N_{j(st)}}\mathrm{d}T + \sum_{\substack{l,m=1\\ lm\neq rr}}^{3}\left[\frac{\partial V}{\partial N_{j(st)}}(E_{lm}-\delta_{lm}E_{rr}) + V\frac{\partial E_{lm}}{\partial N_{j(st)}}\right]\mathrm{d}e_{lm} - \frac{\partial V}{\partial N_{j(st)}}\mathrm{d}E_{rr} + \sum_{i}\frac{\partial \mu_i}{\partial N_{j(st)}}\mathrm{d}N_i, \tag{2.93}$$

$$\mathrm{d}\mu_i = -\bar{s}_i\,\mathrm{d}T + \sum_{\substack{l,m=1\\ lm\neq rr}}^{3}\left[\bar{v}_i(E_{lm}-\delta_{lm}E_{rr}) + V\frac{\partial E_{lm}}{\partial N_i}\right]\mathrm{d}e_{lm} - \bar{v}_i\,\mathrm{d}E_{rr}. \tag{2.94}$$

Eq. (2.93) can be further transformed by detailing the derivatives $\partial V/\partial N_{j(st)}$ and $\partial E_{lm}/\partial N_{j(st)}$ with accounting for that the r-direction is free. For the first of these derivatives, there is the relationship [5]

$$\frac{\partial V}{\partial N_{j(st)}} = \delta_{st}\kappa_{sr}v_j, \tag{2.95}$$

where $\kappa_{sr} \equiv -\mathrm{d}e_{rr}/\mathrm{d}e_{ss}$ is two-dimensional Poisson's ratio in the sr-plane. As for the derivative $\partial E_{lm}/\partial N_{j(st)}$, we may again use Eq. (2.89) with the specification that the modulus λ_{lmst} is now of another meaning (we mark it with a prime). Indeed, since the r-direction is free, the addition of matter along another (always restricted) direction will mean not only compression of matter in this direction, but also dilatation in the r-direction in the accordance with Poisson's ratio. If, however, the matter is introduced along the free direction, the intensive parameters of a system do not change at all and the derivative $\partial E_{lm}/\partial N_{j(st)}$ becomes zero. Accounting for the said above, we write Eq. (2.93) at $st \neq rr$ as

$$\mathrm{d}\mu_{j(st)} = -\frac{\partial S}{\partial N_{j(st)}}\mathrm{d}T + v_j\sum_{\substack{l,m=1\\ lm\neq rr}}^{3}[\delta_{st}\kappa_{sr}(E_{lm}-\delta_{lm}E_{rr}) - \lambda'_{lmst}]\mathrm{d}e_{lm} - \delta_{st}\kappa_{sr}v_j\,\mathrm{d}E_{rr} + \sum_{i}\frac{\partial \mu_i}{\partial N_{j(st)}}\mathrm{d}N_i \tag{2.96}$$

The simplest expression for the chemical potential of an immobile component results at $st = rr$. Then, according to the definition of partial molar quantities, the derivatives of entropy and volume are replaced by their partial molar values for the immobile component (herewith, the partial molar volume may be replaced by the molar volume, as it was said above), whereas λ'_{lmrr} becomes zero. As a result, we have

$$\mathrm{d}\mu_{j(rr)} = -\bar{s}_j\,\mathrm{d}T + v_j\sum_{\substack{l,m=1\\ lm\neq rr}}^{3}(E_{lm}-\delta_{lm}E_{rr})\mathrm{d}e_{lm} - v_j\,\mathrm{d}E_{rr} + \sum_{i}\frac{\partial \mu_i}{\partial N_{j(rr)}}\mathrm{d}N_i. \tag{2.97}$$

By comparing Eq. (2.97) at fixed amounts of mobile species ($N_i = 0$) with Eq. (2.84), we notice that the only difference is the replacement of molar entropy by partial molar entropy. The conditions of applicability of Eq. (2.97) are of practical significance since the transfer of matter more often than not occurs along the free direction (other conditions can take place, for example, in the presence of rigid semipermeable walls).

2.4. Affinity tensor. Mechanochemistry of solids

The concept of (chemical) affinity was introduced in thermodynamics by De Donder in 1920s and became widely known after ‘‘Chemical Thermodynamics’’ by Prigogine and Defay formulated using Gibbs’ and De Donder’s methods (see, e.g. [33]). Affinity was primarily referred to chemical reactions, but can be understood more generally and also applied to physical processes. For every physicochemical process (or every process stage), there are an initial state and a final state, which can differ not only in time, but also in space. We represent the equation of a physicochemical process in the general form

$$\sum_i \nu_i' B_i' \Rightarrow \sum_i \nu_i'' B_i'', \tag{2.98}$$

where B_i and ν_i are the chemical symbol and the stoichiometrical coefficient of the ith species in a system, respectively, the single prime refers to the initial state and the double prime to the final state (in particular, primes are necessary for distinguishing between states of a given substance in different points of space). The summation in Eq. (2.98) is carried out formally over all species, although some of the stoichiometrical coefficients can be zero. For example, the stoichiometrical coefficients of reaction products are equal to zero on the left-hand side of Eq. (2.98) and the stoichiometrical coefficients of initial species are equal to zero on the right-hand side of Eq. (2.98) in the case of a chemical reaction without transport (when there are no spatial distinctions). For transport processes without chemical reactions (diffusion, evaporation, dissolution, etc.), the stoichiometrical coefficients of a given substance on the left-hand and right-hand sides of Eq. (2.98) are not zeros, but coincide and are eliminated when Eq. (2.98) is written for each substance separately

$$B_i' \Rightarrow B_i''. \tag{2.99}$$

For the process described by Eq. (2.98), affinity $\mathcal{A}$ is defined as

$$\mathcal{A} \equiv \sum_i (\nu_i' \mu_i' - \nu_i'' \mu_i''), \tag{2.100}$$

where μ_i is the chemical potential of the ith species. If the affinity expressed in (2.100) is positive, the process described by Eq. (2.98) is realized and the process rate is proportional to $\mathcal{A}$. If, however, the affinity expressed in (2.100) is negative, the reverse process will take place. The primes in Eq. (2.100) may be omitted for a chemical reaction without transport, which changes Eq. (2.100) to the traditional form

$$A \equiv \sum_i \nu_i \mu_i, \tag{2.101}$$

where, as usual, the stoichiometrical coefficients are taken with the ‘‘plus’’ sign for initial substances and with the ‘‘minus’’ sign for reaction products. In the opposite case when chemical reactions are absent, and there are only transport processes, Eq. (2.100) is written separately for each substance with introducing individual affinities A_i:

$$\mathcal{A}_i \equiv \mu_i' - \mu_i'', \tag{2.102}$$

which corresponds to the transport process Eq. (2.99).

The above expressions imply the affinity to be isotropic, which corresponds to fluid systems. However, chemical reactions and transport processes occur in solids too. Accounting for the tensorial nature of chemical potential, we have to redefine, in accordance with (2.100), affinity as a tensor [4]:

$$\hat{\mathcal{A}} \equiv \sum_k (\nu'_k \hat{\mu}'_k - \nu''_k \hat{\mu}''_k) \equiv \Delta \sum_k \nu_k \hat{\mu}_k, \tag{2.103}$$

where Δ symbolizes a difference between quantities marked with a single and double primes. Since both immobile (j) and mobile (i) species can participate simultaneously in a process, and the chemical potential tensor of a mobile species is of spherical symmetry, we may rewrite Eq. (2.103) as

$$\hat{\mathcal{A}} \equiv \Delta \sum_j \nu_j \hat{\mu}_j + \hat{1} \Delta \sum_i \nu_i \mu_i \tag{2.104}$$

or, for the components of the chemical affinity tensor,

$$\mathcal{A}_{st} \equiv \Delta \sum_j \nu_j \mu_{j(st)} + \delta_{st} \Delta \sum_i \nu_i \mu_i. \tag{2.105}$$

To bring into the picture the influence of temperature and mechanical state on the components of chemical affinity (at given amounts of all substances in the initial and final states of a physicochemical process), one should write Eq. (2.105) in a differential form

$$\mathrm{d}\mathcal{A}_{st} = \Delta \sum_j \nu_j \, \mathrm{d}\mu_{j(st)} + \delta_{st} \Delta \sum_i \nu_i \, \mathrm{d}\mu_i \tag{2.106}$$

and apply any of the above expressions for the chemical potentials of immobile and mobile species, Eqs. (2.88), (2.90) or (2.94), (2.97). If the transport of matter proceeds in the r-direction, the most important for practice turns to be the expression

$$\mathrm{d}\mathcal{A}_{rr} = \Delta \sum_j \nu_j \, \mathrm{d}\mu_{j(rr)} + \Delta \sum_i \nu_i \, \mathrm{d}\mu_i. \tag{2.107}$$

Substituting first Eqs. (2.88) and (2.90), and then Eqs. (2.94) and (2.97) in Eq. (2.107), we obtain two expressions for the chemical affinity differential with different sets of variables:

$$(\mathrm{d}\mathcal{A}_{rr})_{\hat{N}_j, N_i} = -\Delta \sum_j \nu_j \left(\frac{\partial S}{\partial N_{j(rr)}} \mathrm{d}T + v_j \sum_{l,m=1}^{3} \lambda_{lmrr} \, \mathrm{d}e_{lm} \right) - \Delta \sum_i \nu_i \left(\frac{\partial s_v}{\partial c_i} \mathrm{d}T - \sum_{l,m=1}^{3} \frac{\partial E_{lm}}{\partial c_i} \mathrm{d}e_{lm} \right), \tag{2.108}$$

$$\begin{aligned}(\mathrm{d}\mathcal{A}_{rr})_{\hat{N}_j, N_i} = & -\Delta \sum_j \nu_j \bar{s}_j \, \mathrm{d}T - \Delta \sum_i \nu_i \bar{s}_i \, \mathrm{d}T + \Delta \sum_j \nu_j v_j \left[\sum_{l,m=1}^{3} (E_{lm} - \delta_{lm} E_{rr}) \, \mathrm{d}e_{lm} - \mathrm{d}E_{rr} \right] \\ & + \Delta \sum_i \nu_i \left\{ \sum_{l,m=1}^{3} \left[\bar{v}_i (E_{lm} - \delta_{lm} E_{rr}) + V \frac{\partial E_{lm}}{\partial N_i} \right] \mathrm{d}e_{lm} - \bar{v}_i \, \mathrm{d}E_{rr} \right\}. \end{aligned} \tag{2.109}$$

For processes developing without the movement of matter in space (chemical reactions, polymorphous transitions, etc.), the initial and final states are usually compared at same temperature. Then the perfect differential of chemical affinity, Eq. (2.108), can be written in a more compact form as

$$(\mathrm{d}\mathcal{A}_{rr})_{\hat{N}_j,N_i} = -\Delta\left(\sum_j \nu_j \frac{\partial S}{\partial N_{j(rr)}} + \sum_i \nu_i \frac{\partial S}{\partial N_i}\right)\mathrm{d}T - \sum_{l,m=1}^{3}\Delta\left[\left(\sum_j \nu_j v_j \lambda_{lmrr} - \sum_i \nu_i \frac{\partial E_{lm}}{\partial c_i}\right)\mathrm{d}e_{lm}\right]. \tag{2.110}$$

If not only temperature, but also stress E_{rr} is equal for the initial and final states, the representation of the perfect differential of chemical affinity (2.109) is simplified:

$$(\mathrm{d}\mathcal{A}_{rr})_{\hat{N}_j,N_i} = -\Delta\bar{S}\,\mathrm{d}T - \Delta\bar{V}\,\mathrm{d}E_{rr} + \sum_{l,m=1}^{3}\Delta\left\{\left[\bar{V}(E_{lm} - \delta_{lm}E_{rr}) + V\sum_i \nu_i \frac{\partial E_{lm}}{\partial N_i}\right]\mathrm{d}e_{lm}\right\}. \tag{2.111}$$

Here $\bar{S}$ and $\bar{V}$ are the entropy and volume of the stoichiometric mixture of substances:

$$\bar{S} \equiv \sum_j \nu_j \bar{s}_j + \sum_i \nu_i \bar{s}_i, \tag{2.112}$$

$$\bar{V} \equiv \sum_j \nu_j v_j + \sum_i \nu_i \bar{v}_i, \tag{2.113}$$

so that $-\Delta\bar{S}$ and $-\Delta\bar{V}$ are the entropy and volume effects of a physicochemical process under consideration, respectively.

The value of chemical affinity determines the rate of a physicochemical process, while the sign of chemical affinity determines the direction of the process (“plus” corresponds to the direct, a “minus” to the reverse process). When affinity is zero, process ceases and the equilibrium occurs between the substances in the initial and final states. Generally, chemical affinity and the rate of a physicochemical process are related by a coefficient whose value depends on the temperature and mechanical state of a system. Therefore, one cannot ensure that, in the course of the process, the constancy of chemical affinity means the stationarity of the process. This is true only in the case of equilibrium since the process rate will be always zero if the chemical affinity stays equal to zero. For this reason, equations for stationary affinity (which are valid at any its value) turn to be the most important in practice for the states of equilibrium and are chiefly used for studying just equilibrium states.

At given amounts of substances in the initial and final states of a physicochemical process, the differential equation of the stationarity of chemical affinity can be obtained from Eqs. (2.110) and (2.111) by setting $\mathrm{d}\mathcal{A}_{rr} = 0$:

$$\Delta\left(\sum_j \nu_j \frac{\partial S}{\partial N_{j(rr)}} + \sum_i \nu_i \frac{\partial S}{\partial N_i}\right)\mathrm{d}T = -\sum_{l,m=1}^{3}\Delta\left[\left(\sum_j \nu_j v_j \lambda_{lmrr} - \sum_i \nu_i \frac{\partial E_{lm}}{\partial c_i}\right)\mathrm{d}e_{lm}\right], \tag{2.114}$$

$$\Delta\bar{S}\,\mathrm{d}T = -\Delta\bar{V}\,\mathrm{d}E_{rr} + \sum_{l,m=1}^{3}\Delta\left\{\left[\bar{V}(E_{lm} - \delta_{lm}E_{rr}) + V\sum_i \nu_i \frac{\partial E_{lm}}{\partial N_i}\right]\mathrm{d}e_{lm}\right\}. \tag{2.115}$$

Eq. (2.114) gives temperature as a function of the components of the strain tensor in the initial and final states of a process. Eq. (2.115) gives temperature as a function of the normal component of the stress tensor in the r-direction and the complementary components of the strain tensor for the initial and final states. If a process is carried out, as it often occurs, at a constant stress, all the components of the strain tensor can be expressed through (common for the initial and final states) six components of the stress tensor. Using these variables, the dimensionality of the state diagram is 7, and the temperature of stationary affinity makes a six-dimensional hypersurface in a seven-dimensional space. It is of note that the second term on the right-hand side of Eq. (2.115) reflects the specificity of the mechanical anisotropy of a system. This term disappears at passing to a mechanically isotropic state (we remind that the derivative standing there is taken at constant E_{rr} and, therefore, becomes zero at $E_{lm} = E_{rr}$).

The above relationships are of general character and applicable to any processes in time and space. To understand them better, we below consider polymorphous transitions as a representative example in which both directed and not directed processes act and the role of mechanical anisotropy is pronounced.

2.5. Polymorphous transformations

The gist of polymorphism is that, depending on external conditions (thermal and mechanical action, external fields, etc.), spatial structures of various types can arise in a system of a given chemical composition. In other words, the lattice formed by an immobile species can change its type (symmetry) depending on external conditions. The concept of a lattice is applicable not only to crystals, but also to amorphous solids (in the latter case, the lattice is characterized by a random locations of the lattice sites in space). Therefore, the amorphization of solids can also be classified conditionally as a polymorphous transformation. From the thermodynamic standpoint, polymorphous transformations are phase transitions of the first or second order. Let us consider both the cases separately. For the sake of simplicity, a system is implied to contain only a single immobile species, mobile species being absent.

2.5.1. First-order phase transitions

If phase α transforms to phase β through the mechanism of a first-order phase transition, the phases contact each other and have a common interface. The *r*-direction of the matter transfer from phase α to phase β can be then defined as the direction of the external, with respect to phase α, normal to the interface. Correspondingly, the transition will be governed by the chemical affinity

$$\mathcal{A}_{rr} \equiv \mu^{\alpha}_{j(rr)} - \mu^{\beta}_{j(rr)}, \tag{2.116}$$

where $\mu^{\alpha}_{j(rr)}$ and $\mu^{\beta}_{j(rr)}$ are the components in the *r*-direction of the chemical potential tensor for the only immobile component in phases α and β, respectively. At the phase equilibrium, we have

$$\mathcal{A}_{rr} = 0, \qquad \mu^{\alpha}_{j(rr)} = \mu^{\beta}_{j(rr)} \tag{2.117}$$

The range of the state parameters where the maintenance of the phase equilibrium is possible is determined, depending on the choice of variables, by Eqs. (2.114) and (2.115) which, in this case ($\nu_j = 1$, $\nu_i = 0$, $\bar{S} = s_j$, $\bar{V} = v_j$), are of the form

$$\Delta \frac{\partial S}{\partial N_{j(rr)}} \mathrm{d}T = -\sum_{l,m=1}^{3} \Delta(v_j \lambda_{lmrr}\, \mathrm{d}e_{lm}), \tag{2.118}$$

$$\Delta s_j\,\mathrm{d}T = -\Delta v_j\,\mathrm{d}E_{rr} + \sum_{l,m=1}^{3} \Delta[v_j(E_{lm} - \delta_{lm}E_{rr})\mathrm{d}e_{lm}], \tag{2.119}$$

where Δ now symbolizes the difference in a quantity for phases α and β. In particular, Δs_j and Δv_j are the molar entropy and molar volume effects for the reverse phase transition $\beta \to \alpha$:

$$\Delta s_j \equiv s_j^{\alpha} - s_j^{\beta}, \qquad \Delta v_j \equiv v_j^{\alpha} - v_j^{\beta} \tag{2.120}$$

(molar and partial molar quantities coincide for one-component phases). Eq. (2.118) is convenient when polymorphous modifications are compared at the same state of strain. If, however, the comparison of polymorphous modifications is made at given stresses, Eq. (2.119) turns to be more convenient. At the equilibrium state diagram, both the equations specify a hypersurface separating the regions of existence of phases α and β (the coexistence of the two phases is possible on the hypersurface itself).

Eq. (2.119) can be obtained directly from Gibbs' equilibrium condition, Eq. (2.25), for a stressed solid driven in contact with a liquid along a certain direction [29]. At an isotropic strain due to hydrostatic pressure p ($E_{lm} = \delta_{lm}E_{rr} = -\delta_{lm}p$), Eq. (2.119) is reduced to the known Clapeyron–Clausius equation

$$\frac{\mathrm{d}T}{\mathrm{d}p} = \frac{\Delta v_j}{\Delta s_j}. \tag{2.121}$$

The equation of the same simple form is obtained from (2.119) in the case of one-sided compression (in the theory of elasticity, this term designates longitudinal compression of a column under the condition that its transverse dimensions cannot change):

$$\left(\frac{\partial T}{\partial E_{rr}}\right)_{e_{lm\neq rr}} = -\frac{\Delta v_j}{\Delta s_j}. \tag{2.122}$$

As it was correctly noted in Ref. [29], the same equation is also obtained for any small strain if the initial state of a solid is isotropic, i.e. $E_{lm} = \delta_{lm}E_{rr}$ (Kumazava has derived a similar equation for the one-sided compression of a specimen under the condition of uniform hydrostatic pressure [34,35]). As for Eq. (2.122), it is not related to the vicinity of an isotropic state.

It is seen from comparison of (2.121) and (2.122) that the dependence of the temperature of polymorphous transformation on stress is the same for all-sided and one-sided compression. The sign of the entropy effect Δs_j is the same for all substances since the molar entropy of the high temperature phase is always larger than the molar entropy of the low temperature phase. However, the sign of the volume effect Δv_j can be any. Most typically, the molar volume of the high temperature phase is also larger than the molar volume of the low temperature phase. Then the signs of the volume and entropy effects of the phase transformation coincide, and the temperature of polymorphous transformation decreases with increasing stress, as is shown in Fig. 3 (the character of the dependence will be opposite when stress is replaced by pressure). However, there exist also abnormal cases of polymorphous transformations (we can point out red and yellow modifications of PbO or monoclinic and tetragonal forms of ZrO_2 as an example) when the high temperature phase turns to be denser than the low temperature phase, so that the derivative $\mathrm{d}T/\mathrm{d}E_{rr}$ becomes positive (and the pressure derivative negative).

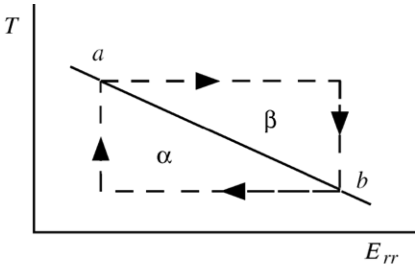

Fig. 3. The fragment of the phase boundary *ab* in the E_{rr}–T coordinate plane.

Eq. (2.119) can also describe the case of simple stretching (or compression) of a column when the lateral stresses (but not strain) are constant, as it happens, for example, at stretching a column in the open air. The matter is that any diagonal summand of the sum standing in (2.119) disappears not only at constant strain, but also at constant stress if it is equal to E_{rr}. We first consider the case when stretching is carried out along a certain direction (direction 1) parallel to the interface whereas the stress on the interface E_{rr} is kept constant. If the column consists of two phases, for the phases will be subjected to the action of the variable stress E_{11} and of the constant stresses $E_{22} = E_{33} \equiv E_{rr}$ (herewith $E_{l\neq m} = 0$). Then Eq. (2.119) takes the form

$$\Delta s_j\,\mathrm{d}T = (E_{11} - E_{rr})\Delta(v_j\,\mathrm{d}e_{11}) \tag{2.123}$$

and describes the behavior of the temperature of a phase transition in a mechanically anisotropic system. Note that passing to an isotropic system is impossible in Eq. (2.123) which then simply loses its sense. Passing to the independent variable E_{11} and dividing both the parts of Eq. (2.123) by $\mathrm{d}E_{11}$, we arrive at the relationship

$$\left(\frac{\mathrm{d}T}{\mathrm{d}E_{11}}\right)_{E_{lm\neq 11}} = \frac{E_{11} - E_{rr}}{\Delta s_j}\Delta\left(v_j\frac{\mathrm{d}e_{11}}{\mathrm{d}E_{11}}\right). \tag{2.124}$$

The derivative $\mathrm{d}e_{11}/\mathrm{d}E_{11}$ may be represented as

$$\frac{\mathrm{d}e_{11}}{\mathrm{d}E_{11}} = \left(\frac{\partial e_{11}}{\partial E_{11}}\right)_{T,E_{lm}\neq E_{11}} + \left(\frac{\partial e_{11}}{\partial T}\right)_{\hat{E}}\frac{\mathrm{d}T}{\mathrm{d}E_{11}} \equiv \frac{1}{\lambda_{1111}} + \theta_{11}\frac{\mathrm{d}T}{\mathrm{d}E_{11}}, \tag{2.125}$$

where λ_{1111} and θ_{11} are Young's modulus and the thermal strain coefficient (the component of tensor (2.72) in direction 1), respectively. Putting Eq. (2.125) in Eq. (2.124) yields

$$\left(\frac{\mathrm{d}T}{\mathrm{d}E_{11}}\right)_{E_{lm\neq 11}} = \frac{(E_{11} - E_{rr})}{\Delta s_j}\Delta\left(\frac{v_j}{\lambda_{1111}}\right)\Big/\left[1 - \frac{E_{11} - E_{rr}}{\Delta s_j}\Delta(v_j\theta_{11})\right]. \tag{2.126}$$

Eq. (2.126) describes the dependence of the phase transition temperature on the excess stress $E_{11} - E_{rr}$ applied in parallel to the interface. In the initial isotropic state, the derivative $\mathrm{d}T/\mathrm{d}E_{11}$ is zero, but becomes more and more appreciable as the excess stress increases. Until the excess stress is small, the denominator of (2.126) is scarcely different from unity. So one may set

$$\left(\frac{\mathrm{d}T}{\mathrm{d}E_{11}}\right)_{E_{lm\neq 11}} \approx \frac{(E_{11} - E_{rr})}{\Delta s_j}\Delta\left(\frac{v_j}{\lambda_{1111}}\right), \tag{2.127}$$

from where it is seen that the phase transition temperature increases or decreases proportionally the square of the stress applied. If, however, the stress is so large that, inversely, one may neglect unity in the denominator of (2.126), Eq. (2.126) changes to

$$\left(\frac{\mathrm{d}T}{\mathrm{d}E_{11}}\right)_{E_{lm\neq 11}} \approx -\frac{\Delta(v_j/\lambda_{1111})}{\Delta(v_j\theta_{11})}. \tag{2.128}$$

The dependence of T on E_{11} given by Eq. (2.128) is practically rectilinear. Especially demonstrative is the case when the difference in the molar volume of polymorphous modifications is negligible. Then Eq. (2.128) becomes

$$\left(\frac{\mathrm{d}T}{\mathrm{d}E_{11}}\right)_{E_{lm\neq 11}} \approx -\frac{\Delta(1/\lambda_{1111})}{\Delta\theta_{11}}. \tag{2.129}$$

Such a case should be scarcely considered as rare since polymorphous transformation is a structural one with a more important change in the body shape than in its volume (which is usually rather small). To speak about anisotropic solids, we can easily imagine the case of the first-order phase transition when the molar volumes are strictly the same, whereas some components of the strain tensor have a break, let alone such structural characteristics as Young's modulus and the thermal strain coefficient.

Eq. (2.124) can be represented in one more very compact form. Since Eq. (2.124) actually describes the dependence of the phase transitions temperature on the excess stress $E_{11} - E_{rr}$, the isotropic state at $E_{11} = E_{22} = E_{33}$ may be conditionally taken for the initial state of zero strain. Although the derivative $\mathrm{d}e_{11}/\mathrm{d}E_{11}$ is here not isothermal, one may assume (because of the smallness of strain) a linear dependence between e_{11} and $E_{11} - E_{rr}$. Then, by putting the difference $E_{11} - E_{rr}$ under the symbol Δ, we can write Eq. (2.124) as

$$\left(\frac{\mathrm{d}T}{\mathrm{d}E_{11}}\right)_{E_{lm\neq 11}} = \frac{\Delta(v_j e_{11})}{\Delta s_j}. \tag{2.130}$$

We now consider the case when the interface is perpendicular to the direction of uniaxial dilatation. Then $E_{33} \equiv E_{rr}$ is the variable stress applied to both the phases simultaneously at the constancy of all other stresses ($E_{11} = E_{22} \equiv E_{ll}$, $E_{l\neq m} = 0$). From Eq. (2.119) we have

$$\left(\frac{\mathrm{d}T}{\mathrm{d}E_{rr}}\right)_{E_{lm\neq rr}} = -\frac{\Delta v_j}{\Delta s_j} - \frac{E_{rr} - E_{ll}}{\Delta s_j}\sum_{l=1}^{2}\Delta\left(v_j\frac{\mathrm{d}e_{ll}}{\mathrm{d}E_{rr}}\right). \tag{2.131}$$

By analogy with Eq. (2.125), one may use the representation

$$\frac{\mathrm{d}e_{ll}}{\mathrm{d}E_{rr}} = \left(\frac{\partial e_{ll}}{\partial E_{rr}}\right)_{T,E_{lm}\neq E_{rr}} + \left(\frac{\partial e_{ll}}{\partial T}\right)_{\hat{E}}\frac{\mathrm{d}T}{\mathrm{d}E_{rr}} \equiv -\frac{\kappa_{lr}}{\lambda_{rrrr}} + \theta_{ll}\frac{\mathrm{d}T}{\mathrm{d}E_{rr}}, \tag{2.132}$$

where κ_{lr} is usual (three-dimensional) Poisson's ratio, λ_{rrrr} is Young's modulus for the r-direction, θ_{ll} is the thermal strain coefficient (the component of the tensor shown in Eq. (2.72)) in the l-direction. Putting

Eq. (2.132) in Eq. (2.131) leads to the relationship

$$\left(\frac{\mathrm{d}T}{\mathrm{d}E_{rr}}\right)_{E_{lm\neq rr}} = \left[-\frac{\Delta v_j}{\Delta s_j} + \frac{E_{rr}-E_{ll}}{\Delta s_j}\Delta\left(\frac{v_j}{\lambda_{rrrr}}\sum_{l=1}^{2}\kappa_{lr}\right)\right] \Big/ \left[1+\frac{E_{rr}-E_{ll}}{\Delta s_j}\Delta\left(v_j\sum_{l=1}^{2}\theta_{ll}\right)\right] \tag{2.133}$$

exhibiting how the excess uniaxial dilatation in the direction perpendicular to the interface, influences the phase transitions temperature. In the initial isotropic state, the value of the derivative $\mathrm{d}T/\mathrm{d}E_{rr}$ exactly corresponds to the Clapeyron–Clausius equation (and can be small if the molar volumes of polymorphous modifications are close). In the region of small excess stresses, Eq. (2.133) can be written as

$$\left(\frac{\mathrm{d}T}{\mathrm{d}E_{rr}}\right)_{E_{lm\neq rr}} \approx -\frac{\Delta v_j}{\Delta s_j} + \frac{E_{rr}-E_{ll}}{\Delta s_j}\Delta\left(\frac{v_j}{\lambda_{rrrr}}\sum_{l=1}^{2}\kappa_{lr}\right), \tag{2.134}$$

from where it is seen that the dependence is still practically linear (unless the volume effect of the polymorphous transformation is too small). In the limit of large excess stresses, Eq. (2.133) is reduced to

$$\left(\frac{\mathrm{d}T}{\mathrm{d}E_{rr}}\right)_{E_{lm\neq rr}} \approx \Delta\left(\frac{v_j}{\lambda_{rrrr}}\sum_{l=1}^{2}\kappa_{lr}\right) \Big/ \Delta\left(v_j\sum_{l=1}^{2}\theta_{ll}\right) \tag{2.135}$$

and becomes still simpler when the molar volumes of the polymorphous modifications are close to each other:

$$\left(\frac{\mathrm{d}T}{\mathrm{d}E_{rr}}\right)_{E_{lm\neq rr}} \approx \Delta\left(\frac{1}{\lambda_{rrrr}}\sum_{l=1}^{2}\kappa_{lr}\right) \Big/ \Delta\left(\sum_{l=1}^{2}\theta_{ll}\right). \tag{2.136}$$

Aside from the detailed representation of Eq. (2.131) in the form of Eq. (2.133), we can (using the same arguments as at passing from (2.124) to (2.130)) reduce Eq. (2.131) to the compact form

$$\left(\frac{\mathrm{d}T}{\mathrm{d}E_{rr}}\right)_{E_{lm\neq rr}} = -\frac{\Delta v_j}{\Delta s_j} - \frac{1}{\Delta s_j}\Delta\left(v_j\sum_{l=1}^{2}e_{ll}\right), \tag{2.137}$$

where the strain tensor components e_{ll} includes not only the (negative) deformations of transverse compression reckoned from a mechanically isotropic state, but also thermal effects. The first term on the right-hand side of Eq. (2.137) corresponds to the Clapeyron–Clausius equation. The second term plays the role of a correction whose value depends on the elastic and thermal properties of coexisting phases, as well as on the degree of deviation from the mechanically isotropic state (for the isotropic state itself, $e_{ll} = 0$, and Eq. (2.137) strictly changes to the Clapeyron–Clausius equation).

From Eq. (2.119), the relationship also follows

$$\left(\frac{\partial T}{\partial e_{lm}}\right)_{\substack{E_{rr}, e_{st\neq rr} \\ st\neq lm}} = -\frac{2v_j\,\Delta E_{lm}}{\Delta s_j} \tag{2.138}$$

describing the influence of the shear strain on the phase transitions temperature. Here the coefficient 2 appears because of the symmetry of the strain and stress tensors ($e_{lm} = e_{ml}$, $E_{lm} = E_{ml}$). In addition, the shear strain does not influence the molar volume v_j so that v_j may be factored outside the difference sign.

We have shown above how phase transitions in non-isotropically stressed solids should be considered on the basis of the chemical potential tensor and accounting for the interface orientation [5]. In the old literature the notion of chemical potential was not used at all, and the problem was solved within the frames of the truncated thermodynamics of deformation (see, e.g. [3]). Instead of the equality of the normal-to-interface components of chemical potential, it was postulated the equality of molar Gibbs energy or the function $\Phi \equiv F - V_0 \sum_{l,m} E_{lm} e_{lm}$ where V_0 is a certain constant volume in the strainless state usually introduced when using the Piola stress tensor. In this way, Coe and Paterson [36] derived the equation (in our notation)

$$\left(\frac{\mathrm{d}T}{\mathrm{d}E_{lm}}\right)_{E_{st \neq lm}} = -\frac{v_{j0}\,\Delta e_{lm}}{\Delta s_j}, \tag{2.139}$$

where v_{j0} is the molar volume value for a standard state (from which strain is reckoned) assumed to be the same for both polymorphous modifications. This means that, at least for one of the phases, the standard state possesses appreciable stresses which, in addition, are not given uniquely (same volume can results from various combinations of stresses). Therefore, the final strains present in Eq. (2.139) are, at $l = m$, of another (and less clear) meaning than strains given in Eqs. (2.130) and (2.137). Coe and Paterson [36] passed from their Eq. (2.139) to the Clapeyron–Clausius equation by setting $l = m$ and summing up the right-hand side over all directions. Herewith the use of Eq. (2.11) is needed, but this standard relationship of theory of elasticity evidently implies all e_{ll} to refer to the same state of strain, i.e. all e_{ll} are simultaneously obtained from the same (one) experiment. However, the right-hand sides of Eq. (2.139) refer to simple dilatations in different directions (i.e. to different experiments), so the strains standing there do not coincide generally with their values at the all-sided tension of the same specimen.

2.5.2. Second-order phase transitions

Polymorphous modifications cannot coexist if the polymorphous transformation $\alpha \rightarrow \beta$ is a second-order phase transition. There is no interface in this case and no direction selected in space. However, the boundary between the regions of phases α and β in the above mentioned state diagram, does still exist as a hypersurface of six dimensions. The difference is that the hypersurface corresponded to the phase equilibrium α–β in the case of the first-order phase transition, but now simply separates two one-phase regions. In the case of a first-order phase transition, thermodynamic potentials and their first derivatives do not change at the transition point and belong to both the phases simultaneously. Therefore, one can say that Eq. (2.117) (for an arbitrary direction) are still valid, but now as identities.

To derive the phase boundary equation, let us use the following procedure. We select points a and b infinitesimally close to each other on the phase-boundary hypersurface in the state diagram (as an example, the points are depicted in Fig. 3 as their projections on the $E_{rr} - T$ coordinate plane) and consider a change in a certain property when moving from one point to the other. As such a property, we first choose the component, for an arbitrary direction, $\mu_{j(rr)}$ of the chemical potential tensor. Its change, $\mathrm{d}\mu_{j(rr)}$, at passing from point a to point b can be calculated in various ways by subsequent changing the state parameters. As it is seen from Fig. 3, the path from a to b goes through the region of phase α if we first reduce temperature and then increase stress E_{rr}, or, the reverse, through the region of phase β if we first increase stress and then reduce temperature. Involving also the rest variables, we may say that there are always two routes from point a to point b: one through the region of phase α and the other through the region of phase β. We designate the quantity $\mathrm{d}\mu_{j(rr)}$ calculated by using the first route and the second route as $\mathrm{d}\mu^{\alpha}_{j(rr)}$ and $\mathrm{d}\mu^{\beta}_{j(rr)}$, respectively. Since the result of calculation must be independent of the route, we have

$$\mathrm{d}\mu^{\alpha}_{j(rr)} = \mathrm{d}\mu^{\beta}_{j(rr)}. \tag{2.140}$$

If we now put the expression for the chemical potential of an immobile species given by Eq. (2.90) or (2.97) into Eq. (2.140), we formally obtain again Eq. (2.118) or (2.119), respectively (to speak about a one-component system). However, the first derivatives of the molar Gibbs energy (chemical potentials belong to that category in this case) exhibit no jump at passing from one phase to the other in the case of a second-order phase transition ($\Delta S = 0$, $\Delta V = 0$, etc.). Therefore, the resultant equations degenerate into identities, and nothing can be calculated with the aid of these equations.

Phase transitions of second-order differ from phase transitions of first-order in that not the first, but the second derivatives of thermodynamic potentials undergo a jump at changing from one phase to another. Therefore, if we wish to derive the equation of the boundary between the phase regions α and β in the state diagram for a second-order phase transition, we have, turning to Fig. 3, to consider the variation, along the phase boundary, of such a property which itself is the first derivative of a thermodynamic potential (of free energy or Gibbs energy in the case under consideration). The standard procedure for isotropic systems is the use of entropy and volume. Let us see what this give for anisotropic bodies.

Taking the molar entropy of an immobile species s_j for the property required and repeating all the above reasoning related to Fig. 3, we arrive at the condition

$$\mathrm{d}s^{\alpha}_{j} = \mathrm{d}s^{\beta}_{j}, \tag{2.141}$$

which is evident to be true at any choice of variables. Choosing first temperature and the strain tensor components as variables, we have the expression for the perfect differential of molar entropy in a closed system

$$\mathrm{d}s_j = \frac{\partial s_j}{\partial T}\mathrm{d}T + \sum_{l,m=1}^{3} \frac{\partial s_j}{\partial e_{lm}}\mathrm{d}e_{lm} = \frac{c_{\hat{e}}}{T}\mathrm{d}T - v_j \sum_{l,m=1}^{3} \eta_{lm}\,\mathrm{d}e_{lm}. \tag{2.142}$$

In the second form of Eq. (2.142), Eq. (2.70) has been used and two quantities have been introduced: heat capacity at constant configuration of the system $c_{\hat{e}}$ (an analogue of specific heat at constant volume in isotropic systems) and the thermal stress coefficient η_{lm} (showing what additional stress in a direction chosen arises at changing temperature by one degree in a closed system of a fixed configuration). Putting (2.142) in (2.141) leads to the equation

$$\Delta \frac{c_{\hat{e}}}{T}\mathrm{d}T = \sum_{l,m=1}^{3} \Delta(v_j \eta_{lm})\mathrm{d}e_{lm}, \tag{2.143}$$

where Δ symbolizes the difference of values of a quantity in phases α and β. Eq. (2.143) in other terms describes the same hypersurface as that described by Eq. (2.118), but now for the case of a second-order phase transition.

Choosing now temperature, the normal stress in the r-direction and the strain tensor components in the rest directions as variables, we write the expression for the perfect differential of molar entropy in a closed system as

$$\begin{aligned} \mathrm{d}s_j &= \frac{\partial s_j}{\partial T}\mathrm{d}T + \frac{\partial s_j}{\partial E_{rr}}\mathrm{d}E_{rr} + \sum_{\substack{l,m=1 \\ (lm \neq rr)}}^{3} \frac{\partial s_j}{\partial e_{lm}}\mathrm{d}e_{lm} \\ &= \frac{c_{E_{rr},e_{lm\neq rr}}}{T}\mathrm{d}T + v_j\theta_{rr}\,\mathrm{d}E_{rr} - v_j \sum_{\substack{l,m=1 \\ (lm \neq rr)}}^{3} [\theta_{rr}(E_{lm} - \delta_{lm}E_{rr}) + \eta_{lm(rr)}]\mathrm{d}e_{lm}. \end{aligned} \tag{2.144}$$

In the second form of Eq. (2.144), Eqs. (2.79) and (2.80) have been used containing the quantities $\eta_{lm(rr)}$ (the thermal stress coefficient under the condition that the normal stress in the r-direction is kept constant) and θ_{rr} (the thermal linear dilatation coefficient in the r-direction under the condition that all other direction are blocked). Besides, it has been introduced the specific heat $c_{E_{rr},e_{lm\neq rr}}$ at constant pressure in one direction and constant system boundaries in all other directions. The substitution of (2.144) in (2.141) leads to the equation

$$\Delta\frac{c_{E_{rr},e_{lm\neq rr}}}{T}\mathrm{d}T = -\Delta(v_j\theta_{rr})\mathrm{d}E_{rr} + \sum_{\substack{l,m=1 \\ (lm \neq rr)}}^{3} \Delta[v_j\theta_{rr}(E_{lm} - \delta_{lm}E_{rr}) + v_j\eta_{lm(rr)}]\mathrm{d}e_{lm} \tag{2.145}$$

that describes the phase boundary as a hypersurface in the state diagram in the case of a second-order phase transition.

An interesting result is obtained when molar entropy is replaced by molar volume. Then, instead of Eq. (2.141), we have the initial equality

$$\mathrm{d}v_j^{\alpha} = \mathrm{d}v_j^{\beta}. \tag{2.146}$$

The choice of temperature and the strain tensor components as the variables of the phase state, as in Eq. (2.142), is of no interest in this case. The matter is that the variation of molar volume with temperature becomes impossible at the constancy of the configuration of a closed system ($e_{lm} = 0$), so that the expression for the perfect differential of molar volume in the closed system will not contain the temperature differential needed. Therefore, we use the set of variables standing in Eq. (2.144) and implying the presence of a free direction. We write the expression for the perfect differential of molar volume in a closed system as

$$\mathrm{d}v_j = \frac{\partial v_j}{\partial T}\mathrm{d}T + \frac{\partial v_j}{\partial E_{rr}}\mathrm{d}E_{rr} + \sum_{\substack{l,m=1 \\ (lm \neq rr)}}^{3} \frac{\partial v_j}{\partial e_{lm}}\mathrm{d}e_{lm}. \tag{2.147}$$

Using Eq. (2.76), we express the first derivative on the right-hand side of (2.147) through the thermal linear dilatation coefficient in the r-direction θ_{rr}. We express the next derivative through the one-sided isothermal compressibility χ_{rr} in the same direction given by Eq. (2.78). The last term in Eq. (2.147) is transformed with the account of Eq. (2.82) introducing two-dimensional Poisson's ratio κ_{rl} in the rl-plane (dilatation in the r-direction is accompanied by lateral compression in the l-direction at the constancy of all other components of the strain tensor). The resultant form of Eq. (2.147) is

$$\mathrm{d}v_j = v_j\theta_{rr}\,\mathrm{d}T + v_j\chi_{rr}\,\mathrm{d}E_{rr} + v_j\sum_{l\neq r}(1-\kappa_{rl})\mathrm{d}e_{ll} \tag{2.148}$$

or

$$\mathrm{d}\ln v_j = \theta_{rr}\,\mathrm{d}T + \chi_{rr}\,\mathrm{d}E_{rr} + \sum_{l\neq r}(1-\kappa_{rl})\mathrm{d}e_{ll}. \tag{2.149}$$

We now may substitute (2.148) in (2.146). However, it will be simpler if, instead of considering the variation of molar volume, we now consider the variation of the logarithm of molar volume along the phase boundary in the state diagram. Instead of (2.146), we write

$$\mathrm{d}\ln v_j^{\alpha} = \mathrm{d}\ln v_j^{\beta}. \tag{2.150}$$

and substitute (2.149) in (2.150). This yields the phase boundary equation at a second-order phase transition

$$\Delta\theta_{rr}\,\mathrm{d}T = -\Delta\chi_{rr}\,\mathrm{d}E_{rr} - \sum_{l\neq r}\Delta\kappa_{rl}\,\mathrm{d}e_{ll}. \tag{2.151}$$

Eq. (2.151) is essentially simpler and, simultaneously, poorer than Eq. (2.144) since Eq. (2.151) contains only the diagonal components of the strain tensor and only for two directions (different from *r*).

As was already noted in the preceding section for the case of anisotropic bodies, the volume change can be continuous even for a first-order phase transition. More generally, the observation of only volume behavior in phase transitions is quite insufficient for anisotropic bodies: it is necessary to control the whole strain tensor. In the case of a second-order phase transition, the strain tensor $\hat{e}$ itself is continuous at intersecting the phase boundary in the state diagram (this means that all its components e_{lm} are continuous), but some of its derivatives undergo discontinuity. In place of Eq. (2.146), we now write

$$\mathrm{d}e_{lm}^{\alpha} = \mathrm{d}e_{lm}^{\beta} \quad (l,m=1\text{–}3) \tag{2.152}$$

and choose temperature T and the stress tensor components E_{st} as independent variables:

$$\mathrm{d}e_{lm} = \left(\frac{\partial e_{lm}}{\partial T}\right)_{\hat{E}}\mathrm{d}T + \sum_{l,m=1}^{3}\left(\frac{\partial e_{lm}}{\partial E_{st}}\right)_{T,E_{lm\neq st}}\mathrm{d}E_{st} \equiv \theta_{lm}\,\mathrm{d}T + \sum_{l,m=1}^{3}\frac{\mathrm{d}E_{st}}{\lambda_{stlm}} \tag{2.153}$$

(here θ_{lm} is the thermal strain coefficient and λ_{stlm} is the elasticity modulus at given stresses). The substitution of (2.153) in (2.152) leads to the relationship

$$\Delta\theta_{lm}\,\mathrm{d}T + \sum_{l,m=1}^{3}\Delta\left(\frac{1}{\lambda_{stlm}}\right)\mathrm{d}E_{st} = 0 \quad (l,m=1\text{–}3) \tag{2.154}$$

which describes the influence of stresses on the phase transition temperature.

We now apply the above equations to the examples considered in the preceding section for first-order phase transitions. In the case of one-sided stretching (in the *r*-direction), according to Eqs. (2.145) and

(2.151), the variation of the polymorphous transformation temperature is given by the relationship

$$\left(\frac{\partial T}{\partial E_{rr}}\right)_{e_{lm\neq rr}} = -\frac{\Delta(v_j\theta_{rr})}{\Delta(c_{E_{rr},e_{lm\neq rr}}/T)} = -\frac{\Delta\chi_{rr}}{\Delta\theta_{rr}}. \tag{2.155}$$

If, however, the matter has been placed inside a tube with open ends at constant external pressure (E_{rr} = constant), the equations obtained yield

$$\left(\frac{\partial T}{\partial e_{ll}}\right)_{E_{rr},e_{st\neq rr}} = \frac{\Delta[v_j\theta_{rr}(E_{ll}-E_{rr})+v_j\eta_{ll(rr)}]}{\Delta(c_{E_{rr},e_{lm\neq rr}}/T)} = -\frac{\Delta\kappa_{rl}}{\Delta\theta_{rr}} \tag{2.156}$$

for the one-sided transverse compression. If a specimen is subjected to shear strain, the corresponding equation can be obtained from Eq. (2.145):

$$\left(\frac{\partial T}{\partial e_{lm}}\right)_{\substack{E_{rr},e_{st\neq rr}\\ st\neq lm}} = \frac{\Delta[v_j\theta_{rr}(E_{lm}-\delta_{lm}E_{rr})+v_j\eta_{lm(rr)}]}{\Delta(c_{E_{rr},e_{lm\neq rr}}/T)}. \tag{2.157}$$

We now turn to the case of simple stretching. Eq. (2.151) originating from the continuity of the volume logarithm yields

$$\left(\frac{\mathrm{d}T}{\mathrm{d}E_{rr}}\right)_{E_{lm\neq rr}} = -\frac{\Delta\chi_{rr}}{\Delta\theta_{rr}} - \frac{1}{\Delta\theta_{rr}}\sum_{l\neq r}\Delta\kappa_{rl}\frac{\mathrm{d}e_{ll}}{\mathrm{d}E_{rr}}. \tag{2.158}$$

Eq. (2.154) produces a still simpler result. Writing Eq. (2.154) for the condition of the continuity of the strain tensor component e_{rr} at fixing all the stress tensor components but E_{rr}, we have

$$\left(\frac{\mathrm{d}T}{\mathrm{d}E_{rr}}\right)_{E_{lm\neq rr}} = -\frac{\Delta(1/\lambda_{rrrr})}{\Delta\theta_{rr}}, \tag{2.159}$$

where λ_{rrrr} is Young's modulus in the r-direction. Eq. (2.159) gives evidence, first, of the linear character of the dependence of the phase transitions temperature on the one-sided stress value and, second, of that the slope of the line depicting this dependence can be different for different directions for an anisotropic body. In the case of a second-order phase transition, it is canceled the problem of mutual orientation of the physical phase boundary and the direction of a stress applied. Therefore, the phase transitions temperature may be assumed to be a function of the principal stresses E_1, E_2, and E_3 only:

$$\mathrm{d}T = \frac{\partial T}{\partial E_1}\mathrm{d}E_1 + \frac{\partial T}{\partial E_2}\mathrm{d}E_2 + \frac{\partial T}{\partial E_3}\mathrm{d}E_3. \tag{2.160}$$

Passing in (2.160) to the isotropic case $\mathrm{d}E_1 = \mathrm{d}E_2 = \mathrm{d}E_3 \equiv \mathrm{d}E$, we obtain the relationship

$$\frac{\mathrm{d}T}{\mathrm{d}E} = \frac{\partial T}{\partial E_1} + \frac{\partial T}{\partial E_2} + \frac{\partial T}{\partial E_3} \tag{2.161}$$

that was confirmed experimentally by Coe and Paterson [36] who studied the influence of the one-sided stress on the temperature of transformation of α-quartz to β-quartz (all the four derivatives in (2.161) were determined independently). They obtained a pure linear dependence of the transition temperature on stress. One can say more. Since, according to their data, α-quartz possesses a higher linear compressibility and a higher linear thermal dilatation coefficient as compared with β-quartz, Eq. (2.159) also correctly predicts the sign of the linear dependence (the phase transition temperature increased when applying one-sided compression in experiment). The above facts incline to the known interpretation of the α–β-transformation as a second-order phase transition, although Coe and Paterson eventually adopted the variant of a coherent first-order phase transition.

2.6. Surface mechanochemistry

An interface is always subjected to the field of adjacent phases. Therefore, the regularities typical for systems in external fields, nonuniformity and anisotropy, are manifested in interfacial layers. The interfacial nonuniformity develops at a distance of order of molecular dimensions, which gives evidence of huge gradients of density or concentration. At the same time, the effective thickness of interfacial layers is small and seldom exceeds molecular dimensions by the order of magnitude (far from the critical point). The appearance of the strong nonuniformity in one direction itself leads to the anisotropy of physicochemical properties of an interface. Even for liquids, the surface layer is distinct from the bulk phase by the presence of anisotropy of the pressure tensor (this means that the Pascal law fails for the surface layer of a liquid). In solids, the anisotropy of chemical potential is complicated by its nonuniformity (even at equilibrium), which makes especially important the use of the above local thermodynamic equations. Of course, the application of the thermodynamic relationships derived in this section to the interfacial region is an approximation since the behavior of a strongly nonuniform matter is determined not only by local properties, but also by their gradients of all orders. Selecting a certain layer of an interface (like a surface monolayer) and averaging properties along the gradient direction (for the other directions, an interface is locally uniform in reality), we create the basis for the application of the local thermodynamic equations.

The role of surface phenomena in the processes of deformation is small and is usually neglected in continuum mechanics. However, the situation is quite opposite in the mechanochemistry of solids. As we already noted, a solid typically reacts with its surface. Therefore, just the state of matter at the surface is determinant for solid reactions including heterogeneous catalysis, and mainly the solid surface monolayer is chemically active. Correspondingly, not the whole surface tension (which is an excess surface stress integrated over the interface thickness), but the real surface stress in the monolayer region is the main mechanical parameter in mechanochemistry. The origin of surface stress is the same as that of surface tension. The difference between the local surface stress in a monolayer and the corresponding bulk stress multiplied by the monolayer thickness can be called the monolayer tension and is a part of the whole surface tension. Since a surface monolayer yields the main contribution to surface tension, the monolayer tension can be close to surface tension and, if measured experimentally, can be used for finding an approximate value of surface tension. This was described earlier [1] and is especially important in view of the opinion that excess surface stress (surface tension) cannot be determined experimentally [37]. For this reason it is worthy to return to this problem in the light of the above thermodynamic theory.

The fact itself of the natural existence of surface stress is not provided in the theory of elasticity [3] that banks upon the fact that there are no internal stresses in the initial state when external forces do not act on a solid. This is not the case in reality. Stress is always present in the surface layer and changes (in any way) in the course of mechanical treatment. In the above equations, this circumstance has already been taken into account in that respect that we never used the prehistory of a body and never used the strain itself in the equations, but used only the differential of strain. In other words, all the relationships have been formulated in terms of a given strain and can be used regardless of the absence or presence of an initial stress. Meanwhile, the presence of an initial surface stress results in the mechanical effect of the strain sign, which was unknown in the classical theory of elasticity and surface thermodynamics. The theory of this phenomenon can easily be formulated on the ground of the above thermodynamic relationships [4].

2.6.1. Theory of the mechanochemical effect of the strain sign

Let the solid surface monolayer participate in an isothermal physicochemical process (e.g. it can be a chemical reaction) with a monomolecular mechanism, so that its chemical potential enters the process affinity with the unit coefficient (otherwise we should simply multiply the chemical potential by the corresponding stoichiometric coefficient). We consider the typical situation when the process develops along the normal to the surface. Then only normal components of affinity and chemical potentials are in action. For the sake of simplicity, we assume all other participants of the process to be in a fluid state and have their chemical potentials kept constant (e.g. with the aid of a large fluid mass). According to Eq. (2.107), we have, in this particular situation,

$$\mathrm{d}\mathcal{A}_{nn} = \mathrm{d}\mu'_{j(nn)}. \tag{2.162}$$

To establish the strain sign effect, we have to compare the affinities of the stretched and compressed states with exactly same absolute values of strain. To speak about experiment, a too great force is needed to produce an appreciable effect by direct stretching or compressing a solid [38]. However, even slight bending a solid plate creates big stresses, opposite in sign, on the plate sides. It is also important in this experimental scheme that the additional stresses and strains arise just in the direction where surface stress acts. For this reason, it is convenient to apply the consideration to an elastically bent plate. Denoting $\Delta\mathcal{A}_{nn}$ the affinity difference between the convex and concave sides of the plate and accounting for Eq. (2.162), we have

$$\Delta\mathcal{A}_{nn} = \Delta\mu'_{j(nn)}. \tag{2.163}$$

According to Eq. (2.41), the quantity $\mu'_{j(nn)}$ itself is given by the expression (in the absence of mobile species in the solid phase)

$$\mu'_{j(nn)} = v_j(f - E_{nn}). \tag{2.164}$$

Because of the constancy of temperature and chemical potentials, the pressure in the adjacent fluid phase and, therefore, E_{nn} are constant too. A change in the molar volume v_j is negligible due to low compressibility of a solid, and, hence, the behavior of $\mu'_{j(nn)}$ is practically determined only by the free energy density f.

The problem of a bent plate was thoroughly analyzed in the classical theory of elasticity (see, e.g. [3,p. 60]), and we begin with reviewing the corresponding results. At a small bend of an originally flat plate, its convex side undergoes one-direction stretching and its concave side undergoes axial compression. We assume this to occur along the $x(x_1)$-axis, while the $z(x_3)$-axis is directed along the normal to the surface (the origin of coordinates is positioned at the plate center, Fig. 4). In the case of an isotropic material, the theory of elasticity yields the following expression for the increment of the local density of free energy of

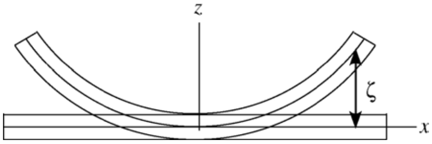

Fig. 4. A bent solid plate in contact with a fluid medium.

the bent plate (referred to the not distorted state):

$$f(x,z) - f_0 = \frac{(\partial^2\zeta/\partial x^2)^2 Y z^2}{2(1-\kappa^2)} > 0, \tag{2.165}$$

where f_0 is the free energy density for the plate in the not distorted state, ζ the displacement of the points of the middle plane of the plate along the z-axis at bending the plate (Fig. 4), Y the Young's modulus, and κ is the Poisson's ratio. According to (2.165), the free energy density increases with the plate bend. This means, in accordance with (2.164), that the chemical potential of the plate matter increases and, hence, the chemical affinity of the process under consideration increases too. The opposite sides of the plate differ in the sign of the z-coordinate. However, z stands only in the second power in Eq. (2.165). Then it follows at once from Eq. (2.165) that the free energy density is the same on the two sides of the bent plate, i.e. $\Delta f = 0$. Turning now to Eq. (2.163), we obtain $\Delta\mu'_{j(nn)} = \Delta\mathcal{A}_{nn} = 0$ in the same approximation (accounting for the local density change in the process of deformation of the plate leads only to a small correction, sometimes by two orders of magnitude smaller than the effect observed in experiment [39], so it makes no sense to discuss it here).

Thus, one can say that the classical theory of elasticity predicts the mechanochemical effect of bending (the process rate increases as the plate is bent), but denies the influence of the strain sign on the effect. This result for incompressible Hookean bodies is a consequence of the fact that the free energy change at axial stretching and compression (to the same extent) is the same not only in sign (free energy increases in both the cases) but also in value. As we already noted above, this is true only under condition with no stresses in the initial state of a body. The existence of surface stress changes the entire picture and requires another approach, which can be based on the relationships of Section 2.3.5.

We start with Eq. (2.97) that, at constant T, E_{nn}, and with $N_i = 0$ and the diagonal form of the stress tensor, becomes

$$\mathrm{d}\mu'_{j(nn)} = v_j[(E_{11} - E_{nn})\mathrm{d}e_{11} + (E_{22} - E_{nn})\mathrm{d}e_{22}] \tag{2.166}$$

for each of the plate sides. Using Poisson's ratio $\kappa_{21} = -\mathrm{d}e_{22}/\mathrm{d}e_{11}$, we can rewrite (2.166) as

$$\frac{\mathrm{d}\mu'_{j(nn)}}{\mathrm{d}e_{11}} = v_j[(E_{11} - E_{nn}) - \kappa_{21}(E_{22} - E_{nn})]. \tag{2.167}$$

We shall consider the initial configuration of a not yet bent plate (but with surface stress) in contact with an adjacent fluid phase as a not distorted configuration with respect to which the strain is measured. Then each of stresses E_{11} and E_{22} can be decomposed into the initial stress and the acquired stress according to the equation

$$E_{ll} = E_{ll0} + \lambda_{ll11}e_{11} \qquad (l = 1, 2), \tag{2.168}$$

where the quantity related to the initial state is marked with zero and the acquired stress is expressed through the elasticity modulus and strain (which, naturally, is assumed to be small). Putting (2.168) in (2.167) leads to the expression

$$\frac{\mathrm{d}\mu'_{j(33)}}{\mathrm{d}e_{11}} = v_j(E_0 + \lambda e_{11}), \tag{2.169}$$

where $E_0 \equiv E_{110} - E_{nn} - \kappa_{21}(E_{220} - E_{nn})$ and $\lambda \equiv \lambda_{1111} + \kappa_{21}\lambda_{2211}$. The integration of Eq. (2.169) yields

$$\mu'_{j(nn)} = \mu'_{j(nn)0} + v_j E_0 e_{11} + v_j \lambda e_{11}^2. \tag{2.170}$$

Stress E_0 is assumed to be zero in the classical theory of elasticity. So, if we followed the theory, we would investigate only the quadratic term in the expansion of the chemical potential, whereas there is a more important (at small deformation) linear term in reality. Thus, it may be said that not we are finding a correction to the classical theory of elasticity, but rather the classical theory of elasticity gives a correction to the effect under investigation.

Let us consider the linear term in (2.170) in detail. Not to complicate the problem with the additional factor of anisotropy, we assume the plate material to be isotropic ($E_{110} = E_{220}$, $\kappa_{21} = \kappa$) and write Eq. (2.170) as

$$\mu'_{j(nn)} = \mu'_{j(nn)0} + v_j(1-\kappa)(E_{110} - E_{nn})e_{11} + v_j \lambda e_{11}^2. \tag{2.171}$$

Since the liquid, with pressure $p = -E_{nn}$, surrounds the plate all round, the stress tensor in the plate bulk can be considered to be isotropic and to have only one component E_{nn}. In other words, $E_{110} = E_{nn}$ in the bulk. This means that the difference $E_{110} - E_{nn}$ is the local excess stress in the surface zone (typically a monolayer) participating in the process under consideration. Let us refer Eq. (2.171) to the convex (stretched) side of the plate. Then, as is seen from the contribution of the linear term in Eq. (2.171), the chemical potential increases or decreases as the plate is bent if the excess surface stress is positive or negative, respectively. According to (2.162), the affinity behaves similarly. The concave side of the plate differs from the convex one by the strain sign. Therefore, if the strain value e_{11} for the convex side is also used for the concave side, we have

$$\mu'_{j(nn)} = \mu'_{j(nn)0} - v_j(1-\kappa)(E_{110} - E_{nn})e_{11} + v_j \lambda e_{11}^2 \tag{2.172}$$

for the concave side in place of Eq. (2.171). As is seen from Eq. (2.172), the effect produced by the linear term for the concave side, is of the opposite sign: as the plate is bent, the chemical potential (and, therefore, the chemical affinity of dissolution) increases at a negative value and decreases at a positive value of the excess surface stress. Subtracting (2.172) from (2.171) and accounting for (2.163), we obtain

$$\Delta\mu'_{j(33)} = 2v_j E_0 e_{11} = 2v_j(1-\kappa)(E_{110} - E_{33})e_{11}. \tag{2.173}$$

In the classical theory of elasticity $E_0 = 0$, and the effect described by Eq. (2.173) is absent. In reality, as we see, the mechanochemical effect of the strain sign does exist and depends on the sign of excess surface stress. The chemical potential (and affinity) on the convex side is higher than on the concave side at a positive value of excess surface stress. The reverse, the chemical potential (and affinity) on the convex side is lower than on the concave side at a negative value of excess surface stress.

2.6.2. *Experimental discovery of the mechanochemical effect of the strain sign and measuring absolute surface stress*

The above mechanochemical effects have already been discovered in experiment. The first observation of the strain sign effect was related to the rate of dissolution of a bent monocrystalline (cleaved along the (1 0 0) crystalline plane) plate of KCl in a water stream [39]. The dissolution rate was determined by the visual microscopic examination of the movement of the crystal boundary surface. Both the convex and concave sides increased their dissolution rates with the additional surface stress applied. However, the concave side dissolved somewhat faster, and this gave evidence of the negative sign of the excess surface stress. It was also possible to find the equilibrium (when the boundary surface was at rest) solubility separately for the opposite plate sides, and the solubility was again larger for the concave side. With such data, the chemical potential difference $\Delta\mu'_{j(nn)}$ in Eq. (2.173) can be determined as

$$\Delta\mu'_{j(nn)} = RT\,\Delta\ln(c''_j f''_j), \tag{2.174}$$

where c''_j and f''_j are the equilibrium concentration (solubility) and the activity coefficient (the mean activity coefficient to mention electrolytes) of the matter of the solid in solution, Δ symbolizes the difference between quantities related to the convex and concave sides of the plate. Putting (2.174) in (2.173) leads to the estimate

$$E_{110} - E_{nn} = \frac{RT\,\Delta\ln(c''_j f''_j)}{2v_j(1-\kappa)e_{11}} \tag{2.175}$$

to yield the excess surface stress $E_{110} - E_{nn} \approx -4 \times 10^5$ Pa and the monolayer tension about -0.12 mN/m, as was reported earlier [1].

Another confirmation of the strain sign effect was obtained from experiments on corrosion under stress. It has been known for a long time that strain promotes corrosion (see the literature in Ref. [40]). It was discovered recently that the corrosion rate is different for the convex and concave sides of a polycrystalline carbon steel plate when it is bent and drawn in contact with hydrochloric or sulfuric acid [41]. Since corrosion destroys a specimen and cracking occurs on the convex side, the mechanochemical effect can scarcely be noticed in the case of a positive excess surface stress (when the convex side is to be mechanochemically active). In many cases, however, the corrosion rate turned to be greater on the concave side at the early stage of the process (the convex side will inevitably prevail sooner or later). This indicates the strain sign effect and the existence of a negative value for the excess surface stress. Although the possibility of the existence of negative surface tension was predicted long ago (see, for example, Refs. [42,43]), the experimental confirmation of that fact failed for a long time. This is explained, in the first turn, by the lack of direct methods for measuring the surface tension of solids. In the above examples, we exhibited a reliable method for determining surface stress and negative values for the local tension at the surface. However, we dealt with a solid/liquid interface and, moreover, with a solid electrolyte/electrolyte solution interface with a powerful electrical double layer. If one imagines the surface monolayer of a solid as a capacitor plate chiefly consisting of ions of one sign, a negative value for the monolayer tension is seen rather expectable than surprising.

3. Development of principal notions of surface thermodynamics

Surface tension is the central quantity of Gibbs' theory of capillarity. Promoting the simplification of the apparatus of surface thermodynamics, surface tension itself meets difficulties in interpretation, especially for curved interfaces. In this connection, Guggenheim wrote: "The more I read it, the less I understood" [44]. The procedure of introducing surface tension as an excess quantity becomes ambiguous for curved interfaces and leads to several definitions. Additional terminological problems arise for solid surfaces. Even the trivial difference between surface tension and surface free energy forced some authors (see, e.g. [37,45]) to avoid the term "surface tension". The use of "surface stress" instead seems scarcely to be the way out. First, it is not quite exact. We considered above the local surface stress in a given direction (1) along the surface as E_{11}, the local excess surface stress as $E_{11} - E_{11}^{\alpha}$, the tension of an interface element of thickness δ as $(E_{11} - E_{11}^{\alpha})\delta$, and surface tension as the sum of all the element tensions across the interface. Second, even if we understand surface tension in the sense of surface stress (which is correct in principle), the ambiguity of the surface tension definition remains for curved interfaces. Surface tension is closely related to the dividing surface and to the condition of mechanical equilibrium at an interface. We reviewed all these topics earlier [1], but we now have to say more. We will show that surface thermodynamics developments become more understandable and still more elegant. In this section, we follow the logic sequence: the introduction of a surface, the introduction of a surface tension for the surface, the introduction of the equilibrium condition for the surface tension, and, finally, fundamental equations.

3.1. Dividing surface

The concept of a dividing surface is a quintessence of Gibbs' approach in surface thermodynamics. He defined it in the following words: "*... let us take some point in or very near to the physical surface of discontinuity, and imagine a geometrical surface to pass through this point and all other points which are similarly situated with respect to the condition of the adjacent matter. Let this geometrical surface be called the dividing surface ...*" The ambiguity of this definition is obvious. To be more exact, this is not a definition, but an intuitive conceptualization of a certain image. To make it a definition, it is necessary to show how "the condition of the adjacent matter" should be formulated. Since only interfaces of simple symmetry (flat, spherical, etc.) were under consideration for a long time, the dividing surface shape was reasonably postulated, and only the choice of the dividing surface location was discussed. The common practice rooted in Gibbs' approach was reduced to shifting a dividing surface along its normal by a certain distance. Mathematically, this means the conformal transformation of a dividing surface. The case of a non-uniformly curved interface is much more complex. Although the above procedure is also applied to non-uniformly curved interfaces, this operation looks proofless. Both the questions, how to find the dividing surface shape and how to change its position, are raised again when passing to an interface of arbitrary shape. The theory has been formulated recently [46–49] and is presented below.

"The condition of the adjacent matter" is the ability of creating an external field influencing the interface. External fields of another nature can also contribute to this field to make it more complex. As a result, an interface becomes non-uniform and is characterized by the gradient lines of local properties, first of all, density (concentration), which makes the interface shape visible. We take gradient lines for the coordinate lines (let it be coordinate u_3 corresponding to Cartesian $z \equiv x_3$) of a certain curvilinear coordinate system including also coordinates u_1 and u_2 whose lines are perpendicular to the gradient lines at each point. Such a coordinate system forms the interface metrics (mathematically, the Riemann space with curvature) characterized by the metric tensor g_{ik} relating coordinates u_i to Cartesian coordinates x_i as

$$g_{ik} \equiv \frac{\partial \mathbf{r}}{\partial u_i} \cdot \frac{\partial \mathbf{r}}{\partial u_k} = \sum_{j=1}^{3} \frac{\partial x_j}{\partial u_i} \frac{\partial x_j}{\partial u_k} \quad (i, k = 1\text{–}3), \tag{3.1}$$

where $\mathbf{r}$ is the radius vector of a point inside the interfacial region (vector $\partial \mathbf{r}/\partial u_i$ is directed along the coordinate line u_i) and the dot designates the scalar product of vectors. As is seen from Eq. (3.1), the metric tensor takes the diagonal form if the coordinate system u_1, u_2, u_3 is orthogonal. Then only the diagonal components g_{ii} are retained. Their square roots are also known as the Lame coefficients

$$h_i = \frac{\partial r}{\partial u_i} = \sqrt{g_{ii}} \tag{3.2}$$

relating the coordinate line length l_i to the corresponding coordinate u_i as

$$\mathrm{d}l_i = h_i \, \mathrm{d}u_i. \tag{3.3}$$

We now can define a dividing surface as any coordinate surface u_1, u_2 of the above coordinate system. In other words, we define a dividing surface as a coordinate surface, normal to the gradient lines, of an orthogonal curvilinear coordinate system that diagonalizes the metric tensor of an interface. The dividing surface equation is

$$u_3 = u_{30}, \tag{3.4}$$

where u_{30} is a constant whose value is arbitrary to some extent. A dividing surface itself possesses a metrics formed by its coordinate lines, and obeys regularities of orthogonal curvilinear coordinates. First of all, the coordinate lines coincide with the curvature lines according to Dupin's theorem of differential geometry. This means that the curvatures $c_1 \equiv 1/R_1$ and $c_2 \equiv 1/R_2$ of the dividing surface along the coordinate lines 1 and 2 are the principal curvatures (correspondingly, R_1 and R_2 are the principal curvature radii). As a consequence, the Rodrigues formula is valid

$$\frac{\partial \mathbf{n}}{\partial u_i} = c_i \frac{\partial \mathbf{r}}{\partial u_i} \quad (i = 1, 2), \tag{3.5}$$

where $\mathbf{n}$ is the unit normal to the dividing surface. Eq. (3.5) shows that the variation of the dividing surface orientation at moving along its coordinate line is determined only by the curvature in a given direction. Finally, the important geometrical relationship

$$\frac{\partial \ln l_i}{\partial l_3} = \frac{\partial \ln h_i}{h_3 \partial u_3} = c_i \quad (i = 1, 2) \tag{3.6}$$

describes shifting a dividing surface element along the coordinate line 3.

The dividing surface definition given in Eq. (3.4) is not only strict as compared with Gibbs' definition, but also more general since it permits geometrical inconformity of different positions of a dividing surface. Gibbs' conformal approach is a particular case of the general definition and can be commented as follows. Let the Lame coefficient have a value h_{i0} for a certain point of the dividing surface with $u_3 = u_{30}$. After shifting the dividing surface by a small value Δu_3, the point chosen is displaced to a new position with the Lame coefficient h_i. Expanding h_i in a power series of Δu_3 in the vicinity of h_{i0} with using

Eq. (3.6), we have

$$\frac{h_i}{h_{i0}} = 1 + \frac{h_{30}\Delta u_3}{R_{i0}} + \frac{1}{2}\left[1 + \frac{R_{i0}}{h_{30}}\frac{\partial \ln h_3}{\partial u_3}\bigg|_0 - \frac{1}{h_{30}}\frac{\partial R_i}{\partial u_3}\bigg|_0\right]\left(\frac{h_{30}\Delta u_3}{R_{i0}}\right)^2 + \cdots. \tag{3.7}$$

It is seen from Eq. (3.7) that the expansion is actually carried out with respect to the dimensionless parameter λ/R_{i0} where $\lambda \equiv h_{30}\Delta u_3$. If the coordinate line of u_3 is straight ($h_3 = h_{30} = 1$, $\lambda = \Delta u_3$, $R_i = R_{i0} + \lambda$, $\partial R_i/\partial\lambda = 1$), the third and all subsequent terms on the right-hand side of (3.7) become zeros. Then Eq. (3.7) changes to

$$\frac{h_i}{h_{i0}} = \frac{R_i}{R_{i0}} = 1 + \frac{\lambda}{R_{i0}}, \tag{3.8}$$

where λ means a shift of the dividing surface along the normal, i.e. the conformal mapping of the dividing surface. As a strict relationship, Eq. (3.8) corresponds to a certain model of an interface. On the other side, passing to a slightly curved interface, we may simply neglect the third and all subsequent terms on the right-hand side of (3.7) since the expansion is carried out with respect to λ/R_{i0}. Then we again arrive at Eq. (3.8), but now as an approximation for a slightly curved interface of an arbitrary metrics. Fig. 5 illustrates the difference between Gibbs' approach and the above general definition of a dividing surface. Only for infinitesimal displacements, both the methods coincide: since we deal with an orthogonal coordinate system, every shift along the coordinate line 3 primarily means the movement along the normal to the dividing surface.

3.2. Excess surface stress (surface tension) for curved interfaces

In Section 2, we met the situation when only the excess surface stress in the surface monolayer was important for solid state surface chemical reactions. In many other cases, however, the excess stress of the whole interface resulting in surface tension is of practical importance. The surface tension definitions by force and the force moment were reviewed earlier [1], but we now have to reformulate them in view of the above general definition of a dividing surface.

We will also discuss the third-dimension aspect of surface tension as a reply to the most intriguing question of the theory: is it always that surface tension is directed along the surface?

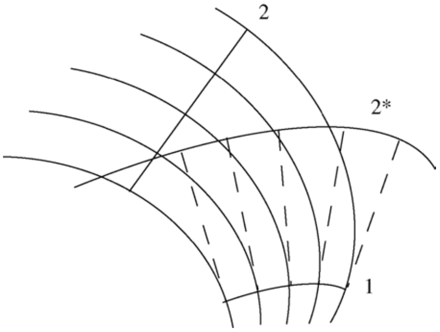

Fig. 5. Gradient lines (the family of lines 3) and shifting the dividing surface in the correct (1→2) and traditional (1→2*) way.

3.2.1. Definition by moment

Let us consider the interface occupying the space between the coordinates u_3^α and u_3^β in phases α and β, respectively, and introduce a dividing surface defined by Eq. (3.4). Following the general rule of composing Gibbs' surface excess quantities, we have to integrate a local excess quantity over the non-uniform interfacial region, the excess being estimated with respect to the reference system with imaginarily uniform bulk phases up to the dividing surface. We choose the local stress tensor differences $\hat{E}-\hat{E}^\alpha$ and $\hat{E}-\hat{E}^\beta$ as excess quantities for the regions on the sides of phases α and β of the dividing surface, respectively. With a closed move of the normal coordinate line, we select a narrow "flux tube" of the normal coordinate lines within Δu_1 and Δu_2, which intersects every u_1, u_2 coordinate surface over the area $A = h_1h_2\Delta u_1\Delta u_2$ and intersects the dividing surface over the area $A_0 = h_{10}h_{20}\Delta u_1\Delta u_2$. Referring the integral to the dividing surface unit area, we obtain the expression for the surface excess stress tensor $\hat{\gamma}$ as

$$\hat{\gamma}=\frac{1}{A_0}\left[\int_{u_3^\alpha}^{u_{30}}(\hat{E}-\hat{E}^\alpha)Ah_3\,\mathrm{d}u_3+\int_{u_{30}}^{u_3^\beta}(\hat{E}-\hat{E}^\beta)Ah_3\,\mathrm{d}u_3\right]. \tag{3.9}$$

Using now the above expressions for A and A_0 and letting Δu_1 and Δu_2 tend to zero, Eq. (3.9) acquires the local form (for a given point on the dividing surface) [46]

$$\hat{\gamma}=\frac{1}{h_{10}h_{20}}\left[\int_{u_3^\alpha}^{u_{30}}(\hat{E}-\hat{E}^\alpha)h_1h_2h_3\,\mathrm{d}u_3+\int_{u_{30}}^{u_3^\beta}(\hat{E}-\hat{E}^\beta)h_1h_2h_3\,\mathrm{d}u_3\right]. \tag{3.10}$$

Similarly to the bulk stress tensor (see Section 2), the surface excess stress tensor has three vector components

$$\boldsymbol{\gamma}_1\equiv\mathbf{i}_1\cdot\hat{\gamma},\qquad \boldsymbol{\gamma}_2\equiv\mathbf{i}_2\cdot\hat{\gamma},\qquad \boldsymbol{\gamma}_3\equiv\mathbf{i}_3\cdot\hat{\gamma}, \tag{3.11}$$

which are the scalar products of tensor $\hat{\gamma}$ and unit vectors $\mathbf{i}_1$ (along the coordinate line of u_1), $\mathbf{i}_2$ (along the coordinate line of u_2), and $\mathbf{i}_3$ (normal to the dividing surface). The three vectors contain nine scalar components of which the diagonal components

$$\gamma_{ii}=\frac{1}{h_{10}h_{20}}\left[\int_{u_3^\alpha}^{u_{30}}(E_{ii}-E_{ii}^\alpha)h_1h_2h_3\,\mathrm{d}u_3+\int_{u_{30}}^{u_3^\beta}(E_{ii}-E_{ii}^\beta)h_1h_2h_3\,\mathrm{d}u_3\right]\quad(i=1\text{–}3) \tag{3.12}$$

are the most important. The components γ_{11} and γ_{22} make the scalar surface tension γ as

$$\gamma=\frac{\gamma_{11}+\gamma_{22}}{2}, \tag{3.13}$$

whereas $\gamma_{33}\equiv\gamma_N$ is a specific quantity termed "transversal surface tension" and mirroring the third-dimension aspect of surface tension.

In the particular case when either the normal coordinate is rectilinear ($h_3 = 1$, $u_3 = l_3$) or the interface thickness is small as compared with the principal curvature radii of the dividing surface, Eq. (3.8) holds and permits writing Eq. (3.12) in the form (we now supply γ_{11} and γ_{22} with the moment superscript "m" not to confuse them with similar quantities in the next section)

$$\gamma_{11}^{\mathrm{m}} R_{10} R_{20} = \int_{\lambda^{\alpha}}^{0} (E_{11} - E_{11}^{\alpha}) R_1 R_2 \, \mathrm{d}\lambda + \int_{0}^{\lambda^{\beta}} (E_{11} - E_{11}^{\beta}) R_1 R_2 \, \mathrm{d}\lambda, \tag{3.14}$$

$$\gamma_{22}^{\mathrm{m}} R_{10} R_{20} = \int_{\lambda^{\alpha}}^{0} (E_{22} - E_{22}^{\alpha}) R_1 R_2 \, \mathrm{d}\lambda + \int_{0}^{\lambda^{\beta}} (E_{22} - E_{22}^{\beta}) R_1 R_2 \, \mathrm{d}\lambda, \tag{3.15}$$

$$\gamma_{\mathrm{N}} R_{10} R_{20} = \int_{\lambda^{\alpha}}^{0} (E_{33} - E_{33}^{\alpha}) R_1 R_2 \, \mathrm{d}\lambda + \int_{0}^{\lambda^{\beta}} (E_{33} - E_{33}^{\beta}) R_1 R_2 \, \mathrm{d}\lambda, \tag{3.16}$$

where $\lambda \equiv u_3 - u_{30} = l_3 - l_{30}$ is the distance reckoned from the dividing surface and varying between λ^{α} and λ^{β} within the interfacial zone. Multiplying Eq. (3.14) by the elementary angle $\delta\theta_2 = \delta l_2/R_2 = \delta l_{20}/R_{20}$, we obtain

$$\gamma_{11}^{\mathrm{m}} R_{10} R_{20} \delta\theta_2 = \int_{\lambda^{\alpha}}^{0} R_1 (E_{11} - E_{11}^{\alpha}) R_2 \delta\theta_2 \, \mathrm{d}\lambda + \int_{0}^{\lambda^{\beta}} R_1 (E_{11} - E_{11}^{\beta}) R_2 \delta\theta_2 \, \mathrm{d}\lambda. \tag{3.17}$$

Obviously, $\gamma_{11}^{\mathrm{m}} R_{20} \delta\theta_2 = \gamma_{11} \delta l_{20}$ is the excess force applied to the arc δl_{20} on the dividing surface and directed along the unit vector $\mathbf{i}_1$. Since this direction is perpendicular to the radius vector $\mathbf{R}_{10}$ and unit vector $\mathbf{i}_3$, the product $\gamma_{11}^{\mathrm{m}} R_{10} R_{20} \delta\theta_2$ is the absolute value of the moment of the above force $\gamma_{11}^{\mathrm{m}} R_{20} \delta\theta_2$ with respect to the first curvature center. The integrand $(E_{11} - E_{11}^{\alpha}) R_2 \delta\theta_2 \, \mathrm{d}\lambda = (E_{11} - E_{11}^{\alpha}) \delta l_2 \, \mathrm{d}\lambda$ is the excess force acting on the area element $\delta l_2 \mathrm{d}\lambda$ and directed perpendicularly to the radius vector $\mathbf{R}_1$. The product of this force and R_1 is the absolute value of the moment of this local force with respect to the first curvature center. The integration yields the force moment for the whole interface. Hence, Eq. (3.14) establishes the equivalence between the dividing surface and the real interface with respect to the force moment of surface tension with respect to the first curvature center. Similarly, the equivalence with respect to the second curvature center is established by Eq. (3.15). As for the transversal surface tension γ_{N}, it is directed along the normal $\mathbf{i}_3$, so that its moment with respect to both the curvature centers is zero. Therefore, Eq. (3.16) for γ_{N} has not such meaning as Eqs. (3.14) and (3.15) for γ_{11}^{m} and γ_{22}^{m}. Concerning Eqs. (3.14) and (3.15), it should be noted that, as a result of miswriting in the author's monograph [50], related Eqs. (4.23)–(4.26) reviewed earlier [1] were written with squared principal curvature radii instead of their product, which can be true only for a spherical surface.

Returning to Eq. (3.10), let us see the dependence of $\hat{\gamma}$ on the dividing surface location at a given physical state. Differentiating Eq. (3.10) with respect to u_{30} yields

$$\frac{\partial\hat{\gamma}}{h_{30}\partial u_{30}} + \frac{\hat{\gamma}\partial \ln(h_{10}h_{20})}{h_{30}\partial u_{30}} = \hat{E}^{\beta}(u_{30}) - \hat{E}^{\alpha}(u_{30}) \tag{3.18}$$

or, accounting for (3.6),

$$\frac{\partial\hat{\gamma}}{\partial l_{30}} + \hat{\gamma}(c_{10} + c_{20}) = \hat{E}^{\beta}(u_{30}) - \hat{E}^{\alpha}(u_{30}) \tag{3.19}$$

(if superscript α corresponds to the phase with larger pressure and smaller stress, the right-hand side of Eqs. (3.18) and (3.19) is positive). It is seen from Eq. (3.19) that the surface excess stress tensor is dependent on the dividing surface location. This is true for every component of the surface excess stress tensor. In particular, we can write, using (3.12), for the scalar surface tension defined by Eq. (3.13)

$$\frac{\partial\gamma^{\mathrm{m}}}{\partial l_{30}}+\gamma^{\mathrm{m}}(c_{10}+c_{20})=\frac{E_{11}^{\beta}(u_{30})+E_{22}^{\beta}(u_{30})-E_{11}^{\alpha}(u_{30})-E_{22}^{\alpha}(u_{30})}{2}. \tag{3.20}$$

In the case of a spherical interface and isotropic bulk phases ($c_{10}=c_{20}\equiv 1/R_0$, $E_{11}=E_{22}=E_{33}\equiv E=-p$), Eq. (3.20) is reduced to the Kondo equation for a liquid drop [51]

$$\frac{\partial\gamma^{\mathrm{m}}}{\partial R_0}+\frac{2\gamma^{\mathrm{m}}}{R_0}=E^{\beta}-E^{\alpha}=p^{\alpha}-p^{\beta}, \tag{3.21}$$

which describes a curve with a unique minimum. The position of the dividing surface corresponding to the minimum is Gibbs' "surface of tension" that is equivalent to the real interface both by moment and force.

A similar equation follows from Eq. (3.12) for the transversal surface tension

$$\frac{\partial\gamma_{\mathrm{N}}}{\partial l_{30}}+\gamma_{\mathrm{N}}(c_{10}+c_{20})=E_{33}^{\beta}(u_{30})-E_{33}^{\alpha}(u_{30}). \tag{3.22}$$

The analysis and solution of differential Eqs. (3.20) and (3.22) [49] show that, in spite of their formal similarity, they describe very different behaviors. For liquids, the surface tension γ^{m} itself cannot be zero, but can have a zero derivative (leading to the existence of a minimum as was mentioned above). By contrast, γ_{N} can become zero itself (as composed of two integrals of opposite signs according to Eq. (3.16)), but cannot have a zero derivative (there is a monotonic change of the normal stress when passing from phase α to phase β). This behavior of the transversal surface tension will be important for the analysis of the third-dimension aspect of surface tension in Section 3.2.3.

3.2.2. *Definition by force*

We now again calculate the excess surface stress replacing the integration over the interfacial volume by the integration over the interface cross-section. Let us first consider the vector component $\mathbf{E}_1=\mathbf{i}_1\cdot\hat{E}$ of the stress tensor $\hat{E}$, corresponding to the coordinate line 1. We choose the cross-section as a narrow strip of the coordinate surface u_2, u_3 within the intervals u_2, $u_2+\Delta u_2$ and u_3^{α}, u_3^{β} (Fig. 6). As Δu_2 tends to

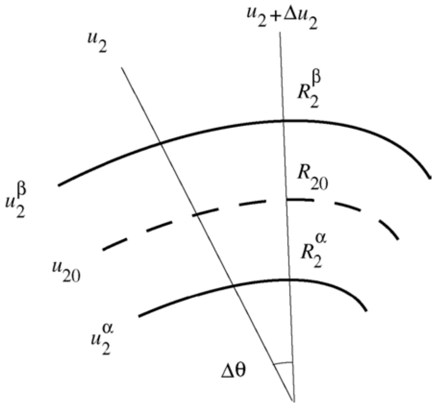

Fig. 6. The interface cross-section.

zero, we obtain, similarly to (3.10),

$$\boldsymbol{\gamma}_1^{\mathrm{f}} = \frac{1}{h_{20}}\left[\int_{u_3^\alpha}^{u_{30}} (\mathbf{E}_1 - \mathbf{E}_1^\alpha) h_2 h_3 \, \mathrm{d}u_3 + \int_{u_{30}}^{u_3^\beta} (\mathbf{E}_1 - \mathbf{E}_1^\beta) h_2 h_3 \, \mathrm{d}u_3\right], \tag{3.23}$$

where $\boldsymbol{\gamma}_1^{\mathrm{f}}$ is the excess surface stress vector on the cross-section perpendicular to the coordinate line 1 (superscript "f" has been introduced to distinguish the definition by force from the definition by moment in the preceding section). By analogy, we can write for the other principal cross-section (perpendicular to the coordinate line 2)

$$\boldsymbol{\gamma}_2^{\mathrm{f}} = \frac{1}{h_{10}}\left[\int_{u_3^\alpha}^{u_{30}} (\mathbf{E}_2 - \mathbf{E}_2^\alpha) h_1 h_3 \, \mathrm{d}u_3 + \int_{u_{30}}^{u_3^\beta} (\mathbf{E}_2 - \mathbf{E}_2^\beta) h_1 h_3 \, \mathrm{d}u_3\right]. \tag{3.24}$$

In the particular case when the coordinate u_3 is rectilinear, Eq. (3.23), accounting for (3.8), can be written in the form

$$\boldsymbol{\gamma}_1^{\mathrm{f}} R_{20} = \int_{\lambda^\alpha}^{0} (\mathbf{E}_1 - \mathbf{E}_1^\alpha) R_2 \, \mathrm{d}\lambda + \int_{0}^{\lambda^\beta} (\mathbf{E}_1 - \mathbf{E}_1^\beta) R_2 \, \mathrm{d}\lambda. \tag{3.25}$$

Multiplying both the sides of Eq. (3.25) by the elementary angle $\mathrm{d}\theta_2$ (Fig. 6), we obtain, on the left-hand side, the excess force applied to the arc $R_{20}\,\mathrm{d}\theta_2$ of the dividing surface cutting line. The integrand on the right-hand side is the excess force applied to the elementary area $R_2\,\mathrm{d}\theta_2\,\mathrm{d}\lambda$, and the integrals yield the total excess force applied to the interface cross-section within the elementary angle $\mathrm{d}\theta_2$. Thus, Eq. (3.25) determines the excess force $\boldsymbol{\gamma}_1$ per unit length of the cutting line on the dividing surface, exactly equal to the real excess force on the corresponding cross-section of the interface. The same can be said about every component of vectors $\boldsymbol{\gamma}_1^{\mathrm{f}}$ and $\boldsymbol{\gamma}_2^{\mathrm{f}}$. We now see that Eqs. (3.23) and (3.24) correspond to the force definition of surface tension.

Among the components of vectors $\boldsymbol{\gamma}_1^{\mathrm{f}}$ and $\boldsymbol{\gamma}_2^{\mathrm{f}}$, γ_{11}^{f} and γ_{22}^{f} are of the most importance. From Eqs. (3.23) and (3.24), we have

$$\gamma_{11}^{\mathrm{f}} = \frac{1}{h_{20}}\left[\int_{u_3^\alpha}^{u_{30}} (E_{11} - E_{11}^\alpha) h_2 h_3 \, \mathrm{d}u_3 + \int_{u_{30}}^{u_3^\beta} (E_{11} - E_{11}^\beta) h_2 h_3 \, \mathrm{d}u_3\right], \tag{3.26}$$

$$\gamma_{22}^{\mathrm{f}} = \frac{1}{h_{10}}\left[\int_{u_3^\alpha}^{u_{30}} (E_{22} - E_{22}^\alpha) h_1 h_3 \, \mathrm{d}u_3 + \int_{u_{30}}^{u_3^\beta} (E_{22} - E_{22}^\beta) h_1 h_3 \, \mathrm{d}u_3\right]. \tag{3.27}$$

According to Eq. (3.13), γ_{11}^{f} and γ_{22}^{f} compose the scalar surface tension γ^{f}.

By direct differentiating Eqs. (3.23), (3.24), (3.26), and (3.27) with respect to u_{30}, it is easy to establish that $\boldsymbol{\gamma}_1^{\mathrm{f}}$ and $\boldsymbol{\gamma}_2^{\mathrm{f}}$ and all their components are dependent on the dividing surface location. The resulting equations for γ_{11}^{f}, γ_{22}^{f}, and γ^{f} (written with accounting for Eq. (3.6)) are

$$\frac{\partial \gamma_{11}^{\mathrm{f}}}{\partial l_{30}} + \gamma_{11}^{\mathrm{f}} c_{20} = E_{11}^\beta(u_{30}) - E_{11}^\alpha(u_{30}), \qquad \frac{\partial \gamma_{22}^{\mathrm{f}}}{\partial l_{30}} + \gamma_{22}^{\mathrm{f}} c_{10} = E_{22}^\beta(u_{30}) - E_{22}^\alpha(u_{30}), \tag{3.28}$$

$$\frac{\partial\gamma^{\mathrm{f}}}{\partial l_{30}}+\frac{\gamma_{11}^{\mathrm{f}}c_{20}+\gamma_{22}^{\mathrm{f}}c_{10}}{2}=\frac{E_{11}^{\beta}(u_{30})+E_{22}^{\beta}(u_{30})-E_{11}^{\alpha}(u_{30})-E_{22}^{\alpha}(u_{30})}{2}. \tag{3.29}$$

The analysis and solution of differential Eq. (3.28) [49] show that they describe the dependence with a unique minimum of the surface tension, similarly to Eq. (3.21) leading to the existence of the surface of tension. In the general case, however, the existence of a minimum cannot serve as a universal evidence of the surface of tension. The necessary requirement is that the surface tension defined by moment should coincide with the surface tension defined by force for a certain location of a dividing surface. Evidently, the simultaneous validity of the conditions $\gamma_{11}^{\mathrm{f}}=\gamma_{11}^{\mathrm{m}}$ and $\gamma_{22}^{\mathrm{f}}=\gamma_{22}^{\mathrm{m}}$ is scarcely attainable by moving the dividing surface. However, the requirement (subscript s refers to the surface of tension)

$$\gamma^{\mathrm{m}}=\gamma^{\mathrm{f}}\quad(l_{30}=l_{3s}) \tag{3.30}$$

is quite realizable and can be taken for the general and rigorous definition of the surface of tension. Indeed, comparing Eqs. (3.20) and (3.29), we obtain the relationship

$$\frac{\partial\gamma^{\mathrm{m}}}{\partial l_{30}}+\gamma^{\mathrm{m}}(c_{10}+c_{20})=\frac{\partial\gamma^{\mathrm{f}}}{\partial l_{30}}+\frac{\gamma_{11}^{\mathrm{f}}c_{20}+\gamma_{22}^{\mathrm{f}}c_{10}}{2} \tag{3.31}$$

that exhibits a difference between the derivatives $\partial\gamma^{\mathrm{m}}/\partial l_{30}$ and $\partial\gamma^{\mathrm{f}}/\partial l_{30}$. This means that the curves depicting the dependencies of the two surface tensions on the dividing surface location have different slopes and, therefore, are capable of intersecting to satisfy Eq. (3.30).

Using (3.30), we obtain from Eq. (3.31) for the surface of tension

$$\left(\frac{\partial\gamma^{\mathrm{m}}}{\partial l_{30}}\right)_s=\left(\frac{\partial\gamma^{\mathrm{f}}}{\partial l_{30}}\right)_s-\frac{\gamma_{11}^{\mathrm{f}}c_{10}+\gamma_{22}^{\mathrm{f}}c_{20}}{2}. \tag{3.32}$$

Turning, for the sake of simplicity, to the diagonal form of the stress tensor and using the simple equilibrium condition [1] (the general case will be considered in Section 3.3)

$$\gamma_{11}^{\mathrm{f}}c_{10}+\gamma_{22}^{\mathrm{f}}c_{20}=E_{33}^{\beta}(l_{30})-E_{33}^{\alpha}(l_{30}), \tag{3.33}$$

we can write Eq. (3.32) as

$$\left(\frac{\partial\gamma^{\mathrm{m}}}{\partial l_{30}}\right)_s=\left(\frac{\partial\gamma^{\mathrm{f}}}{\partial l_{30}}\right)_s-\frac{E_{33}^{\beta}(l_{30})-E_{33}^{\alpha}(l_{30})}{2}, \tag{3.34}$$

whereas Eq. (3.20) takes the form

$$\left(\frac{\mathrm{d}\gamma^{\mathrm{m}}}{\mathrm{d}l_3}\right)_s=\frac{1}{2}(\gamma_{11}^{\mathrm{f}}-\gamma_{22}^{\mathrm{f}})(c_1-c_2)+\left[E_{33}^{\alpha}-\frac{E_{11}^{\alpha}+E_{22}^{\alpha}}{2}\right]-\left[E_{33}^{\beta}-\frac{E_{11}^{\beta}+E_{22}^{\beta}}{2}\right]. \tag{3.35}$$

If both the bulk phases, α and β, are mechanically isotropic, Eq. (3.35) is reduced to

$$\left(\frac{\mathrm{d}\gamma^{\mathrm{m}}}{\mathrm{d}l_{30}}\right)_s=\frac{(\gamma_{11}^{\mathrm{f}}-\gamma_{22}^{\mathrm{f}})(c_1-c_2)}{2}. \tag{3.36}$$

Eq. (3.36) shows that, even in the simple case under consideration, the surface tension minimum can correspond to the surface of tension only for an isotropic interface. The direct calculation shows that the coincidence of locations of the surface of tension and the surface tension minimum already fails for a circular cylindrical interface [49].

General equations relating surface tensions γ^{m} and γ^{f} to each other can be easily found for the cases when either the coordinate line 3 is straight or the curvature radii are much larger than the effective interface thickness. In both the cases, Eq. (3.8) holds and causes Eqs. (3.14) and (3.15), which we now rewrite in the common form

$$\gamma_{ii}^{\mathrm{m}} = \int_{\lambda^{\alpha}}^{\lambda^{\beta}} (E_{ii} - E_{ii}^{\alpha,\beta})(1 + c_{10}\lambda)(1 + c_{20}\lambda)\,\mathrm{d}\lambda \quad (i = 1, 2), \tag{3.37}$$

where $E_{ii}^{\alpha,\beta}$ is E_{ii}^{α} at $\lambda < 0$ and E_{ii}^{β} at $\lambda > 0$. Using Eq. (3.8), we also can rearrange Eqs. (3.26) and (3.27) to the form

$$\gamma_{11}^{\mathrm{f}} = \int_{\lambda^{\alpha}}^{\lambda^{\beta}} (E_{11} - E_{11}^{\alpha,\beta})(1 + c_{20}\lambda)\,\mathrm{d}\lambda, \qquad \gamma_{22}^{\mathrm{f}} = \int_{\lambda^{\alpha}}^{\lambda^{\beta}} (E_{22} - E_{22}^{\alpha,\beta})(1 + c_{10}\lambda)\,\mathrm{d}\lambda. \tag{3.38}$$

Differentiating now Eq. (3.37) with respect to c_{10} and c_{20} and accounting for Eq. (3.38), we arrive at the relationships sought for:

$$\gamma_{11}^{\mathrm{f}} = \gamma_{11}^{\mathrm{m}} - \frac{\partial \gamma_{11}^{\mathrm{m}}}{\partial \ln c_{10}}, \qquad \gamma_{22}^{\mathrm{f}} = \gamma_{22}^{\mathrm{m}} - \frac{\partial \gamma_{22}^{\mathrm{m}}}{\partial \ln c_{20}}, \tag{3.39}$$

$$\gamma^{\mathrm{f}} = \gamma^{\mathrm{m}} - \frac{1}{2}\left(\frac{\partial \gamma_{11}^{\mathrm{m}}}{\partial \ln c_{10}} + \frac{\partial \gamma_{22}^{\mathrm{m}}}{\partial \ln c_{20}}\right). \tag{3.40}$$

3.2.3. Transversal surface tension

The existence of the transversal surface tension γ_{N} imparts a three-dimensional character to the surface excess stress tensor $\hat{\gamma}$ defined by Eq. (3.10). Therefore, it is important for surface thermodynamics to select cases when $\gamma_{\mathrm{N}} = 0$. A general formula for γ_{N} is given by Eq. (3.12) at $i = 3$, and the dependence of γ_{N} on the dividing surface location is given by Eq. (3.22). In the simplest case of a flat interface, these relationships are reduced to

$$\gamma_{\mathrm{N}} = \int_{z^{\alpha}}^{z_0} (E_{33} - E_{33}^{\alpha})\mathrm{d}z + \int_{z_0}^{z^{\beta}} (E_{33} - E_{33}^{\beta})\mathrm{d}z, \tag{3.41}$$

$$\frac{\mathrm{d}\gamma_{\mathrm{N}}}{\mathrm{d}z_0} = E_{33}^{\beta}(z_0) - E_{33}^{\alpha}(z_0), \tag{3.42}$$

where z is the Cartesian coordinate replacing u_3, z_0 correspondingly marking the dividing surface location (the partial derivative in (3.22) has been replaced by the total derivative since all the quantities are now dependent on z only). The mechanical equilibrium condition expressed in Eq. (2.17) now reads

$$\frac{\mathrm{d}E_{33}}{\partial z} = -f_3, \tag{3.43}$$

where f_3 is the third component of an external force. If $f_3 = 0$, the value of E_{33} should be the same along the z-axis. Eq. (3.41) then yields $\gamma_N = 0$, and we may conclude that the surface excess stress tensor is pure two-dimensional for a flat interface in the absence of external fields.

The presence of an external field reverses the situation. We illustrate this by the direct calculation of the transversal surface tension via Eq. (3.41) in the presence of gravity. Let phase α be located below phase β, and the z-axis is directed upwards from phase α to phase β. Using Eq. (3.43) as a barometric formula (with $f_3 = -\rho g$ where ρ is density and g is acceleration due to gravity), we have

$$E_{33}(z) - E_{33}^{\alpha}(z) = g\int_{z^{\alpha}}^{z}(\rho - \rho^{\alpha})\mathrm{d}z \equiv g\Gamma^{\alpha}(z), \tag{3.44}$$

where $\Gamma^{\alpha}(z)$ is the current value of adsorption (mass per unit area) on the side of phase α (the boundary condition $\rho = \rho^{\alpha}$ at $z = z^{\alpha}$ has been taken into account). Similarly,

$$p_N^{\beta}(z) - p_N(z) = g\int_{z^{\beta}}^{z}(\rho - \rho^{\beta})\mathrm{d}z \equiv -g\Gamma^{\beta}(z), \tag{3.45}$$

where $\Gamma^{\beta}(z)$ is the current value of adsorption on the side of phase β. Putting (3.44) and (3.45) in (3.41) yields

$$\gamma_N = g\left[\int_{z^{\alpha}}^{z_0}\Gamma^{\alpha}(z)\,\mathrm{d}z - \int_{z_0}^{z^{\beta}}\Gamma^{\beta}(z)\,\mathrm{d}z\right]. \tag{3.46}$$

Assuming the local density to decrease monotonously when ascending from phase α to phase β, we have $\Gamma^{\alpha}(z) < 0$, $\Gamma^{\beta}(z) > 0$, and, therefore, $\gamma_N < 0$. The transversal surface tension is negative in this case, i.e. changes to a transversal pressure created by gravity.

Differentiating Eq. (3.46) with respect to z_0, we obtain

$$\frac{\mathrm{d}\gamma_N}{\mathrm{d}z_0} = g[\Gamma^{\alpha}(z_0) + \Gamma^{\beta}(z_0)] \equiv g\Gamma(z_0), \tag{3.47}$$

where $\Gamma(z_0)$ is the total adsorption related to the dividing surface with the coordinate z_0. Comparing now Eqs. (3.42) and (3.47), we arrive at the known condition of equilibrium [52]

$$E_{33}^{\beta}(z_0) - E_{33}^{\alpha}(z_0) = g\Gamma(z_0). \tag{3.48}$$

Considering the dividing surface as a two-dimensional strained membrane, Eq. (3.48) expresses the trivial fact that, under gravity, a flat membrane can influence the phase stress difference only with its weight. Since the total adsorption is dependent on the dividing surface location and the above Γ^{α} and Γ^{β} have different signs, it is always possible to find such position of the dividing surface within the limits of the interface that the total adsorption becomes zero. Then Eq. (3.48) becomes of the same form as in the absence of an external field (the equality of stresses in adjacent phases). However, the transversal surface tension itself remains different from zero and negative, as a certain indicator of an external field.

Turning to the case of a spherical interface, Eq. (3.12) at $i = 3$ and Eq. (3.22) become

$$\gamma_N = \frac{1}{R_0^2}\left[\int_0^{R_0}(E_{33} - E_{33}^{\alpha})r^2\,\mathrm{d}r + \int_{R_0}^{R^{\beta}}(E_{33} - E_{33}^{\beta})r^2\,\mathrm{d}r\right], \tag{3.49}$$

$$\frac{d\gamma_N}{dR_0} + \frac{2\gamma_N}{R_0} = E^{\beta}_{33}(R_0) - E^{\alpha}_{33}(R_0), \tag{3.50}$$

where r is the radial coordinate replacing u_3, and $r = R_0$ corresponds to the dividing surface location. The conspicuous identity of Eqs. (3.21) and (3.50) for the ordinary and transversal surface tensions raises the question of validity of the above statement about different behavior of functions $\gamma^m(R_0)$ and $\gamma_N(R_0)$. If two differential equations are identical, their solutions should also be identical. Indeed, the solution of Eq. (3.50)

$$\gamma_N = \frac{R_0[E^{\beta}_{33}(R_0) - E^{\alpha}_{33}(R_0)]}{3} + \frac{C}{R_0^2} \tag{3.51}$$

is also suitable for Eq. (3.21) if replacing γ_N by γ^m. However, the integration constant C is quite different in the two cases. The integration constant of the Kondo equation is known to be positive, whereas the constant C in Eq. (3.51) is negative. According to Eq. (3.49), γ_N should become negative as $R_0 \to 0$ since E_{33} decreases with R_0. On the other side, γ_N should be positive as $R_0 \to R^{\beta}$. Hence, there always exists such a dividing surface location inside the interface that corresponds to the condition $\gamma_N = 0$.

Naturally, the question arises: if we consider the dividing surface where $\gamma_N = 0$, does it coincide with the surface of tension? The reply is easily shown to be positive. It is enough to use the equation determining the location R_s of a spherical surface of tension [53]

$$\int_0^{R_s} (E_{11} - E^{\alpha}_{33})(r - R_s)r\,dr + \int_{R_s}^{R^{\beta}} (E_{11} - E^{\beta}_{33})(r - R_s)r\,dr = 0 \tag{3.52}$$

and the equilibrium condition (Eq. (2.18) written in spherical coordinates)

$$\frac{d(E_{33}r^2)}{dr^2} = E_{11}. \tag{3.53}$$

Combining (3.52) and (3.53) leads to the relationship

$$\int_0^{R_s} (E_{33} - E^{\alpha}_{33})r^2\,dr + \int_{R_s}^{R^{\beta}} (E_{33} - E^{\beta}_{33})r^2\,dr = 0. \tag{3.54}$$

Comparing Eqs. (3.49) and (3.54), it follows that replacing R_0 by R_s in Eq. (3.49) immediately coverts γ_N to zero. Thus, the surface of tension does coincide with the surface of zero transversal surface tension and secures the pure two-dimensional character of the surface excess stress tensor for a spherical interface.

The plane or spherical shape of an interface is typically realized in the absence of external fields or in the special case when a field is directed along the normal coordinate. The general case is more complex, but, to simplify the formulation, we can pass to the total stress tensor obeying Eq. (2.18) even in the presence of external fields. The inconveniency arising is the necessity of considering off-diagonal components of the surface excess stress tensor. For a slightly curved interface of an arbitrary shape or for the case of the rectilinear normal coordinate, a remarkable relationship has been derived [49]

$$\gamma_N = (\gamma^f_{11} - \gamma^m_{11}) + (\gamma^f_{22} - \gamma^m_{22}) - \frac{\partial}{\partial l_{10}}[R_{10}(\gamma^f_{13} - \gamma^m_{13})] - \frac{\partial}{\partial l_{20}}[R_{20}(\gamma^f_{23} - \gamma^m_{23})]. \tag{3.55}$$

Passing to the surface of tension according to Eq. (3.30) eliminates only first two terms on the right-hand side of Eq. (3.55). Other terms are absent only if the surface excess stress tensor is of diagonal form. It is known from the tensorial analysis that every tensor can be converted to a diagonal form by turning the coordinate axes. However, the directions of the coordinate axes, which we have chosen above, correspond to the interface metrics and cannot be changed arbitrarily. In the absence of fields, the metric tensor and the stress tensor are typically of the diagonal form simultaneously since the stress tensor is formed under the influence of the interface metrics. In the presence of external fields of arbitrary directions, the stress tensor is typically non-diagonal, so that the terms with off-diagonal components in Eq. (3.55) are retained even for the surface of tension. Correspondingly, the transversal surface tension is not zero for the surface of tension in the general case.

3.3. General condition of mechanical equilibrium at a curved interface

The most popular relationship in this field is the classical Laplace equation for a spherical interface

$$\frac{2\gamma}{R_s} = E^{\beta} - E^{\alpha} = p^{\alpha} - p^{\beta} \tag{3.56}$$

that follows from Eq. (3.21) for the surface of tension ($\gamma^{\mathrm{m}} = \gamma^{\mathrm{f}} \equiv \gamma$, $R_0 = R_s$). Many attempts of generalizing the Laplace equation were reviewed in a number of surveys in the modern literature [1,54–58]. However, the results obtained referred to the traditional variant of the theory with the rectilinear normal coordinate, which correspond to a relatively simple interfacial metrics. A more general approach was suggested later on [47,48] and is presented below.

Let us consider an element of an interface between phases α and β within the coordinates $u_1, u_1 + \Delta u_1$; $u_2, u_2 + \Delta u_2$; and $u_3^{\alpha}, u_3^{\beta}$, the last two being located already in the bulk phases (Fig. 7). Using the total stress tensor (including the contribution of external fields), we write the mechanical equilibrium condition, Eq. (2.16), for the element as

$$\oint \mathbf{E}\,\mathrm{d}A = 0, \tag{3.57}$$

where **E** is the stress vector and the integration is carried out over the whole element surface. This surface consists of six faces, so that the integral in Eq. (3.57) splits into six parts. The integrals for the lower and upper faces can be written as $(\mathbf{E}_3 \Delta l_1 \Delta l_2)^{\alpha}$ and $(\mathbf{E}_3 \Delta l_1 \Delta l_2)^{\beta}$ where $\Delta l_1 = h_1 \Delta u_1$ and $\Delta l_2 = h_2 \Delta u_2$. We also have $\mathrm{d}A_1 = \Delta l_2\,\mathrm{d}l_3 = \Delta l_2 h_3\,\mathrm{d}u_3$ and $\mathrm{d}A_2 = \Delta l_1\,\mathrm{d}l_3 = \Delta l_1 h_3\,\mathrm{d}u_3$ for the element faces perpendicular to directions 1 and 2, respectively. We also should take into account that forces applied to the opposite faces act oppositely. Thus, Eq. (3.57) becomes

$$(\mathbf{E}_3 \Delta l_1 \Delta l_2)^{\alpha} - (\mathbf{E}_3 \Delta l_1 \Delta l_2)^{\beta} - \Delta \int_{u_3^{\alpha}}^{u_3^{\beta}} \mathbf{E}_1 \Delta l_2 h_3\,\mathrm{d}u_3 - \Delta \int_{u_3^{\alpha}}^{u_3^{\beta}} \mathbf{E}_2 \Delta l_1 h_3\,\mathrm{d}u_3 = 0, \tag{3.58}$$

where symbol Δ at the integrals denotes their increment when moving along the coordinate lines 1 and 2.

Introducing a dividing surface with coordinate u_{30} and area $\Delta l_{10} \Delta l_{20}$ divides the element into parts α and β (Fig. 7) adjacent to the corresponding phases. Filling up imaginarily the parts α and β with the matter of phases α and β, respectively, and assuming them to be at mechanical equilibrium, we can write,

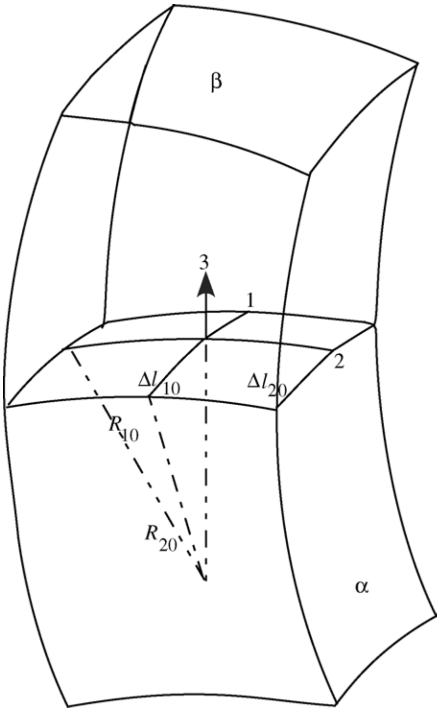

Fig. 7. The element of a curved interface.

for each part separately, a condition similar to Eq. (3.58):

$$(\mathbf{E}_3\Delta l_1\Delta l_2)^{\alpha} - \mathbf{E}_3^{\alpha}(u_{30})\Delta l_{10}\Delta l_{20} - \Delta\int_{u_3^{\alpha}}^{u_{30}} \mathbf{E}_1^{\alpha}\Delta l_2 h_3\,\mathrm{d}u_3 - \Delta\int_{u_3^{\alpha}}^{u_{30}} \mathbf{E}_2^{\alpha}\Delta l_1 h_3\,\mathrm{d}u_3 = 0, \tag{3.59}$$

$$\mathbf{E}_3^{\beta}(u_{30})\Delta l_{10}\Delta l_{20} - (\mathbf{E}_3\Delta l_1\Delta l_2)^{\beta} - \Delta\int_{u_{30}}^{u_3^{\beta}} \mathbf{E}_1^{\beta}\Delta l_2 h_3\,\mathrm{d}u_3 - \Delta\int_{u_{30}}^{u_3^{\beta}} \mathbf{E}_2^{\beta}\Delta l_1 h_3\,\mathrm{d}u_3 = 0. \tag{3.60}$$

Subtracting Eqs. (3.59) and (3.60) from Eq. (3.58) leads to the condition

$$[\mathbf{E}_3^{\alpha}(u_{30}) - \mathbf{E}_3^{\beta}(u_{30})]\Delta l_{10}\Delta l_{20} - \Delta\boldsymbol{\gamma}_1^{\mathrm{f}}\Delta l_{20} - \Delta\boldsymbol{\gamma}_2^{\mathrm{f}}\Delta l_{10} = 0, \tag{3.61}$$

where $\boldsymbol{\gamma}_1^{\mathrm{f}}$ and $\boldsymbol{\gamma}_2^{\mathrm{f}}$ are given by Eqs. (3.23) and (3.24), respectively. Dividing now Eq. (3.61) by the area $\Delta l_{10}\Delta l_{20}$ and letting Δu_1 and Δu_2, as well Δl_{10} and Δl_{20}, tend to zero, we obtain the local mechanical equilibrium condition at an interface in the form

$$\mathbf{E}_3^{\alpha}(u_{30}) - \mathbf{E}_3^{\beta}(u_{30}) = \frac{\partial\boldsymbol{\gamma}_1^{\mathrm{f}}}{\partial l_{10}} + \frac{\partial\boldsymbol{\gamma}_2^{\mathrm{f}}}{\partial l_{20}}. \tag{3.62}$$

Eq. (3.62) is applicable to an interface of any shape and curvature. Remarkably, being the most general among the mechanical equilibrium conditions, Eq. (3.62) is also very simple in form (a reader can compare Eq. (3.62) with other formulations reviewed earlier, see, e.g. Eq. (4.43) in Ref. [1]). Because of its vector form, Eq. (3.62) can scarcely be qualified as a generalized Laplace equation, which, however, can be deduced from Eq. (3.62) as a consequence.

Expressing the vectors through their components and unit vectors $\mathbf{i}_1$, $\mathbf{i}_2$, and $\mathbf{i}_3$, we rewrite Eq. (3.62) as

$$\sum_{k=1}^{3}(E_{k3}^{\alpha}-E_{k3}^{\beta})\mathbf{i}_k=\sum_{k=1}^{3}\frac{\partial\gamma_{k1}^{\mathrm{f}}}{\partial l_{10}}\mathbf{i}_k+\sum_{k=1}^{3}\gamma_{k1}^{f}\frac{\partial\mathbf{i}_k}{\partial l_{10}}+\sum_{k=1}^{3}\frac{\partial\gamma_{k2}^{\mathrm{f}}}{\partial l_{20}}\mathbf{i}_k+\sum_{k=1}^{3}\gamma_{k2}^{\mathrm{f}}\frac{\partial\mathbf{i}_k}{\partial l_{20}}. \tag{3.63}$$

In order to evaluate Eq. (3.63) in terms of local curvatures, we have to reformulate the coordinate system u_1, u_2, u_3 in terms of the local tangent $\mathbf{t}$, normal $\mathbf{n}$, and bi-normal $\mathbf{b}$ of the coordinate lines on the surface. For a spatial line, the standard Serret–Frenet formulas of differential geometry read

$$\frac{\mathrm{d}\mathbf{t}}{\mathrm{d}L}=c\mathbf{n},\qquad\frac{\mathrm{d}\mathbf{n}}{\mathrm{d}L}=-c\mathbf{t}+T\mathbf{b},\qquad\frac{\mathrm{d}\mathbf{b}}{\mathrm{d}L}=-T\mathbf{n}, \tag{3.64}$$

where c and T are the line curvature and torsion, respectively. The torsion is zero for our choice of the coordinate system. Eq. (3.64) may be used to write the derivative factors involving $\mathbf{i}_k$ ($k = 1$–3) in Eq. (3.63) in terms of the local curvature radii. Two cases of interest exist: when $\mathbf{t} = \mathbf{i}_1$ with $L = l_{10}$ and when $\mathbf{t} = \mathbf{i}_2$ with $L = l_{20}$. In the first case, the related normal and bi-normal vectors are, $\mathbf{n} = -\mathbf{i}_3$ and $\mathbf{b} = \mathbf{i}_2$ and the corresponding derivatives are

$$\frac{\partial\mathbf{i}_1}{\partial l_{10}}=-\frac{\mathbf{i}_3}{R_{10}},\quad\frac{\partial\mathbf{i}_2}{\partial l_{10}}=0,\quad\frac{\partial\mathbf{i}_3}{\partial l_{10}}=\frac{\mathbf{i}_1}{R_{10}}. \tag{3.65}$$

In the second case, for $\mathbf{t} = \mathbf{i}_2$ the related normal and bi-normal vectors are $\mathbf{n} = -\mathbf{i}_3$ and $\mathbf{b} = -\mathbf{i}_1$, and the derivatives are

$$\frac{\partial\mathbf{i}_2}{\partial l_{20}}=-\frac{\mathbf{i}_3}{R_{20}},\qquad\frac{\partial\mathbf{i}_1}{\partial l_{20}}=0,\qquad\frac{\partial\mathbf{i}_3}{\partial l_{20}}=\frac{\mathbf{i}_2}{R_{20}}. \tag{3.66}$$

After putting (3.65) and (3.66) in Eq. (3.63), we multiply it separately by $\mathbf{i}_1$, $\mathbf{i}_2$, and $\mathbf{i}_3$ to obtain three scalar equations equivalent to the vector Eq. (3.62):

$$E_{31}^{\alpha}-E_{31}^{\beta}=\frac{\gamma_{13}^{\mathrm{f}}}{R_{10}}+\frac{\partial\gamma_{11}^{\mathrm{f}}}{\partial l_{10}}+\frac{\partial\gamma_{21}^{\mathrm{f}}}{\partial l_{20}}, \tag{3.67}$$

$$E_{32}^{\alpha}-E_{32}^{\beta}=\frac{\gamma_{23}^{\mathrm{f}}}{R_{20}}+\frac{\partial\gamma_{12}^{\mathrm{f}}}{\partial l_{10}}+\frac{\partial\gamma_{22}^{\mathrm{f}}}{\partial l_{20}}, \tag{3.68}$$

$$E_{33}^{\alpha}-E_{33}^{\beta}=-\frac{\gamma_{11}^{\mathrm{f}}}{R_{10}}-\frac{\gamma_{22}^{\mathrm{f}}}{R_{20}}+\frac{\partial\gamma_{13}^{\mathrm{f}}}{\partial l_{10}}+\frac{\partial\gamma_{23}^{\mathrm{f}}}{\partial l_{20}}. \tag{3.69}$$

Eq. (3.69) is a generalization of the Laplace equation. Remarkably, both Eq. (3.69) and, generally, Eq. (3.62) correspond to the results of the theory of shells [20,59]. In the absence of the shear components of vectors $\boldsymbol{\gamma}_1^{\mathrm{f}}$ and $\boldsymbol{\gamma}_2^{\mathrm{f}}$, Eq. (3.69) takes the form derived first by Buff [52] for the anisotropic case and changes to the classical form, Eq. (3.56), for the isotropic spherical case. Some other approaches [60,61], with $\gamma_{13} = \gamma_{23} = 0$ as a requirement of the momentum moment conservation [62] (in the absence of external fields), lead to similar results. However, the surface stress components (γ_{ik}^{m} or γ_{ik}^{f}) were not introduced as excess tensions and operated rather as real quantities, which complicates the comparison. (In some cases, the procedure itself determines the type of tension: it should be γ^{m}_{ik}, for example, when the mechanical equilibrium condition is deduced [63] as corresponding to the free energy minimum).

The three-dimensional aspect of surface tension is illustrated by the presence of quantities γ^{f}_{31} and γ^{f}_{32} in Eqs. (3.67)–(3.69). These quantities would be absent if surface tension were a pure two-dimensional quantity as in the classical Laplace equation. However, passing of Eq. (3.69) to the classical form is also possible when γ^{f}_{31} and γ^{f}_{32} are present but are constant along their coordinate lines, so that their derivatives become equal to zero. Also Eqs. (3.67) and (3.68) are maintained in this case. In the simple case when the coordinate system chosen diagonalizes the stress tensor, γ^{f}_{31} and γ^{f}_{32} become zeros automatically. Then Eq. (3.69) again takes the classical form, whereas Eqs. (3.67) and (3.68) yield the condition of constancy of γ^{f}_{11} and γ^{f}_{22} along their coordinate lines:

$$\frac{\partial \gamma^{\mathrm{f}}_{11}}{\partial l_{10}} = \frac{\partial \gamma^{\mathrm{f}}_{22}}{\partial l_{20}} = 0. \tag{3.70}$$

It should be emphasized a non-trivial character of the condition expressed in Eq. (3.70) since the surface tension is always considered as dependent on the surface curvature that can vary along the coordinate lines.

3.4. Fundamental equations and the Shuttleworth–Herring relation

Constructing thermodynamics is deriving fundamental equations. A detailed derivation of interfacial fundamental equations for excess quantities was presented earlier [1]. However, not all aspects were touched upon, and their interpretation in modern reviews [45,64] requires additional comments.

3.4.1. How many dividing surfaces are needed?

The most general way of introducing interfacial excess quantities implies the use of two dividing surfaces on both the sides of an interface. A rigorous formulation of the procedure for a flat interface was given by Eriksson [65,66]. For example, locating the dividing surfaces at the normal coordinates z^{α} and z^{β}, we can write the expression for the excess amount n_i of the ith species per unit area of the interface between phases α and β as

$$n_i = \Gamma^{\alpha}_i + \int_{z^{\alpha}}^{z^{\beta}} c_i \, \mathrm{d}z + \Gamma^{\beta}_i, \qquad \Gamma^{\alpha}_i \equiv \int_{-\infty}^{z^{\alpha}} (c_i - c^{\alpha}_i)\mathrm{d}z, \qquad \Gamma^{\beta}_i \equiv \int_{z^{\beta}}^{\infty} (c_i - c^{\beta}_i)\mathrm{d}z, \tag{3.71}$$

where c_i, c^{α}_i, and c^{β}_i are the local concentration of the ith species and its values in phases α and β, respectively; Γ^{α}_i and Γ^{β}_i are the adsorptions of the ith species at the above dividing surfaces only on the side of phase α and only on the side of phase β, respectively, the z-axis being directed from phase α to phase β. We see that n_i is combined of two excess quantities, the one-sided adsorptions Γ^{α}_i and Γ^{β}_i, and the integral that represents a real amount of the ith species in between the two dividing surfaces. Such a mixed character of n_i complicates its understanding and use (it is used by necessity in the theory of films, see Section 5.3).

However, there are two simple limiting cases of n_i. When z^{α} and z^{β} tend to each other, the first integral in (3.71) vanishes to yield

$$n_i = \Gamma^{\alpha}_i + \Gamma^{\beta}_i = \Gamma_i. \tag{3.72}$$

In this case the two dividing surfaces merge in a single surface, n_i becomes a pure excess quantity equal to the ordinary (two-sided) adsorption, and we pass to Gibbs' thermodynamics. Since Γ_i^α and Γ_i^β are typically of different signs, it is possible to shift the dividing surface to the location where $\Gamma_i = 0$. Such a location is called an equimolecular surface.

The opposite limiting case corresponds to $z^\alpha \to -\infty$ and $z^\beta \to \infty$. Then Γ_i^α and Γ_i^β vanish, and n_i becomes a pure real quantity. In fact, Γ_i^α and Γ_i^β become negligible already at sufficiently small displacements of the dividing surfaces along the z-axis, so that one can say about an interface of a finite thickness considered as a real physical body. The idea of this approach was forwarded by van der Waals [67–69] and developed by Bakker [70], Verschaffelt [71], Guggenheim [72], and the author whose monograph [50] presents the most detailed description of this method and is the counterpart of the book by Defay and Prigogine [73] describing Gibbs' method. Regarding an interface as a real physical body has an advantage that not only equilibrium, but also stability conditions, as well as the powerful apparatus of the modern thermodynamics of solutions, can be applied to a multicomponent interface. At the same time, Gibbs' concept of surface tension as an excess quantity is maintained. The concept of the interface thickness appears in thermodynamics in a conditional meaning since, naturally, the absolute interface thickness does not exist. For example, one can define the interface thickness as the difference $z^\beta - z^\alpha$ for such positions of z^α and z^β on the z-axis where Γ_i^α and Γ_i^β amount to 1% (or 0.1%, etc.) of the integral value in Eq. (3.71). This uncertainty in the interface thickness does not impede the derivation of main thermodynamic regularities. Moreover, stability conditions establish the lowest limit for the interface thickness in some cases, which can be verified in experiments with fluid interfaces [50].

Nozieres and Wolf [74] exploited the idea of two dividing surfaces for a solid/solid interface. In this case (as in the case of two quite immiscible different liquids), there is a natural boundary surface between the adjacent phases (with no mass transport through the surface). So it is quite reasonable to choose the boundary surface as a dividing surface. At the same time, one may introduce the equimolecular surfaces for both the solids, which cannot coincide and should be separated by a certain distance l. However, this procedure is principally different from the above method of two dividing surfaces, and the distance l has nothing to do with the interface thickness (width). The difference is that Γ_i vanishes for the equimolecular surface as a result of mutual compensations of Γ_i^α and Γ_i^β in Eq. (3.72), but not due to vanishing each of Γ_i^α and Γ_i^β. The adsorption is two-sided in this case, and, hence, we deal with ordinary Gibbs' thermodynamics and with a single dividing surface. We simply compare two positions of the single dividing surface: the first where $\Gamma_1 = 0$ and the second where $\Gamma_2 = 0$ (numbers 1 and 2 refer to the species of phases α and β, respectively). Distances between various positions of a dividing surface are often used as parameters in surface thermodynamics (e.g. the Tolman parameter in the dependence of surface tension on surface curvature, see Eq. (4.15) below), but it would be too inexact to identify them with the interface thickness. By contrast, the distance between the two equimolecular surfaces of a film can be a good approximation for the film thickness provided the latter is much larger than the interface thickness.

Accounting for the said above, it is reasonable to stick to the Gibbs method with using a single dividing surface as we did earlier [1].

3.4.2. Excess surface strain

Nozieres and Wolf [74] also introduced an excess surface strain as a new concept of surface thermodynamics that previous theories "were missing" [75]. In their beautiful derivation for a flat interface [45], Mueller and Saul showed that, after proceeding to excess quantities, the mechanical work (2.14) takes the form

$$\mathrm{d}W = A\sum_{s,t}(\gamma_{st}\,\mathrm{d}e^{\parallel}_{st} + E^{\perp}_{st}\,\mathrm{d}\bar{e}_{st}), \tag{3.73}$$

where the parallel and perpendicular (to the dividing surface) components of the tensors are taken in the bulk, A is the surface area, γ_{st} is the surface tension tensor and $\bar{e}_{st}$ is the excess surface strain tensor (whose parallel components are zeros due to the non-gliding conditions). Because of its artificial symmetry, the strain tensor is easily converted to a diagonal form, so that the only component $\bar{e}_{zz}$ is maintained. Multiplied by A, $\bar{e}_{zz}$ yields a relative excess volume, and this is a physical meaning of surface strain. Since such kind of strain is also proper to fluids, the concept of surface strain is equally applicable to solid and fluid interfaces. Therefore, a general question arises: after the centenary of development of the thermodynamics of fluid interfaces, should it be reformulated in terms of surface strain?

To answer the question, let us consider the general definition of excess quantities. Taking an extensive property M of a system with volume V, we define the density of M as $m = M/V$ or, locally, as $\mathrm{d}M/\mathrm{d}V$. According to Gibbs' method, we use a single dividing surface and take an excess by integrating over the volume as in the definition (by moment) of the surface tension tensor (3.10). Quite similarly, we can write as a general definition

$$\bar{m} \equiv \frac{1}{h_{10}h_{20}}\left[\int_{u_3^{\alpha}}^{u_{30}}(m - m^{\alpha})h_1h_2h_3\,\mathrm{d}u_3 + \int_{u_{30}}^{u_3^{\beta}}(m - m^{\beta})h_1h_2h_3\,\mathrm{d}u_3\right], \tag{3.74}$$

where $\bar{m}$ is the excess value of M per unit area. This formula is valid for adsorption, surface energy, surface entropy, etc. Setting now $M = V$, we have $m = m^{\alpha} = m^{\beta} = 1$ to yield $\bar{m} \equiv 0$. To say in words, *the excess volume always and identically equals zero* according to Gibbs' definition of excess quantities. This statement is well known in surface thermodynamics. We only comment the word "always". The matter is that, according to Gibbs' approach and as it is generally accepted in thermodynamics, all thermodynamic quantities and equations always refer to *a current state* of a system. Finding an excess quantity for an unstrained state, the integration is carried out over the volume of the unstrained system, but, proceeding to a strained state, we already have to integrate over the volume of the strained system. As a result, we obtain $\bar{e}_{zz} = 0$.

The situation would change if we defined an excess quantity as referring to a certain reference state. This resembles the theory-of-elasticity method adopted in the popular textbook by Landau and Lifschitz [3] (which we do not follow as was commented in Section 1 regarding the Cauchy and Piola stress tensors). Not only a hypothetical unstrained state typically assumed in the theory of elasticity, but also an arbitrarily strained state (including a state with unstrained bulk phases and a strained interface) may be taken for the reference state. If the system volume in a reference state is V_0, we now have $V/V_0 \neq 1$, and an excess volume appears. Setting $m = e_{zz}$ in Eq. (3.74), we can write the definition of excess surface strain for an interface of arbitrary shape as

$$\bar{e}_{zz} \equiv \frac{1}{h_{10}h_{20}}\left[\int_{u_3^{\alpha}}^{u_{30}}(e_{zz} - e^{\alpha}_{zz})h_1h_2h_3\,\mathrm{d}u_3 + \int_{u_{30}}^{u_3^{\beta}}(e_{zz} - e^{\beta}_{zz})h_1h_2h_3\,\mathrm{d}u_3\right]. \tag{3.75}$$

By differentiating (3.75) by u_{30}, we disclose the dependence of the excess surface strain on the dividing surface location:

$$\frac{\mathrm{d}\bar{e}_{zz}}{\mathrm{d}u_{30}} = e^{\beta}_{zz} - e^{\alpha}_{zz}. \tag{3.76}$$

If e_{zz} is in between e^{α}_{zz} and e^{β}_{zz} (which is a typical situation in the absence of adsorbed layers of foreign substances), it is possible to find such dividing surface location that $\bar{e}_{zz} = 0$. The use of this dividing surface is easily realizable for flat interfaces. In the case of a curved interface, however, the problem arises of compatibility of this surface with the surface of tension since only the latter is equivalent to a real interface both by moment and force.

The existence of excess surface strain can be interpreted as a change of the local spacing of a crystalline lattice at the interface as compared with a bulk phase. This can be easily detected experimentally by LEED. However, the Gibbs approach explains the same effect in another language, considering the above change as an excess of matter at the interface (adsorption or, for a single species, self-adsorption). To derive interfacial fundamental equations, we have to put the items of Eq. (2.85) in (3.74) to calculate all excess quantities in a similar way. If, in addition, we address a reference state, excess entropy and other thermodynamic functions become less understandable and operable, and the whole theory becomes less transparent. On the other side, remaining within the frames of the Gibbs approach, we can naturally join classical surface thermodynamics and the theory of elasticity based on the Cauchy stress tensor with no use of a reference state (to be more exact, a current state plays the role of a reference state in this approach). We now can answer the above general question as follows: one may but should not reformulate classical surface thermodynamics in terms of surface strain since surface thermodynamics is self-consistent without this concept. At the same time, surface strain can be used in particular tasks of the interfacial theory of elasticity when the method chosen corresponds to this concept. We also can conclude that surface strain was not missed in the classical theory of capillarity; this concept simply does not exist in the Gibbs approach.

3.4.3. Excess surface chemical potential

What modern theories are really missing is the excess surface chemical potential. We wrote above about the chemical potential anisotropy. However, the inhomogeneity of the chemical potential of an immobile species is still more important factor for a solid, and this factor is directly related to elasticity. As an immobile species (forming the crystal lattice) is not capable of migration (diffusion), there is no mechanism of leveling its chemical potential in an ideally elastic solid. They usually ascribe the common value of the chemical potential to the whole bulk phase of a solid, but this can only means that all parts of the phase are identical by their origin. As for the interface, the inhomogeneity of chemical potential is here evident, and the excess surface chemical potential inevitably exists.

To illustrate the importance of this concept, let us consider excess relationships following from Eq. (2.43). As a preliminary, we represent Eq. (2.43) in terms of the hybrid thermodynamic potential $\Omega \equiv F - \sum_i \mu_i N_i$ playing the role of free energy with respect to an immobile species and grand thermodynamic potential with respect to mobile species [1]. As earlier [1], we denote the local density of Ω as ω to rewrite Eq. (2.43) as

$$\omega = \mu_{j(k)} c_j + E_k \quad (k = 1\text{–}3). \tag{3.77}$$

Eq. (3.77) represents three equivalent but different relationships for three uniform directions in a bulk phase. Applying (3.77) to an interface, we have only two uniform directions $k = 1, 2$ along the dividing surface, so that the relationship for $k = 3$ should be omitted. The surface excess of ω is known to be Gibbs' quantity σ (the work of formation of a new unit surface area by cutting), which we termed *thermodynamic surface tension* [1,76] since it was a scalar and coincided with surface tension in case of liquids. Setting now $m = \omega$ and putting (3.77) in Eq. (3.74) and accounting for Eq. (3.10), we obtain two relationships for excess quantities

$$\sigma = \langle \mu_{j(k)} c_j \rangle + \gamma_k \quad (k = 1, 2), \tag{3.78}$$

where the angle brackets symbolize excess. Using the definition of isotropic surface tension (3.13), we also can write (3.78) as a difference between the thermodynamic and mechanical surface tensions

$$\sigma - \gamma = \frac{\langle \mu_{j(1)} c_j + \mu_{j(2)} c_j \rangle}{2}. \tag{3.79}$$

If the chemical potential were uniform across the interface, the right-hand side of Eq. (3.79) would be $\mu_j \Gamma_j$ where Γ_j is the adsorption of species j. Then $\sigma = \gamma$ for the equimolecular surface ($\Gamma_j = 0$), which is the well known result for liquids. Thus, Eq. (3.79) clearly shows that the difference between σ and γ for solid surfaces is caused by the non-uniformity of the chemical potential of an immobile species across a solid interface, i.e. by the existence of excess surface chemical potential.

In a similar way, an excess fundamental equation is obtained from Eq. (2.85) which we, for the sake of convenience, can write as

$$\mathrm{d}\Omega = -S\,\mathrm{d}T + V \sum_{l,m=1}^{3} E_{lm}\,\mathrm{d}e_{lm} + \sum_{k=1}^{3} \mu_{j(k)}\,\mathrm{d}N_{j(k)} - \sum_i N_i\,\mathrm{d}\mu_i. \tag{3.80}$$

The procedure was described in detail in [1], and only a small correction should be made. The normal component of chemical potential μ_j does not contribute to the excess equation not because of the uniformity of $\mu_{j(3)}$ (of course, $\mu_{j(3)}$ should be non-uniform across the interface similarly to $\mu_{j(1)}$ and $\mu_{j(2)}$), but due to the obvious condition $\mathrm{d}N_{j(3)} = 0$ with respect to the interface (adding matter in the normal direction can enlarge only the bulk phases and produces no excess). The resulting equation is [1,77]

$$\mathrm{d}\sigma = -\bar{s}\,\mathrm{d}T + (\hat{\gamma} - \sigma\hat{1}) : \left(\mathrm{d}\hat{e}^{\sigma} - \frac{\mathrm{d}\hat{N}_j}{N_j}\right) - \sum_i \Gamma_i\,\mathrm{d}\mu_i, \tag{3.81}$$

where $\bar{s}$ is the excess surface entropy per unit area and two dots denote a biscalar product of tensors (cf. (2.13)). The two-dimensional tensor $\hat{e}^{\sigma}$ becomes identical to the strain tensor $e^{\|}_{st}$ in Eq. (3.73) provided $\mathrm{d}\hat{N}_j = 0$. Otherwise tensor $\hat{e}^{\sigma}$ is of more general meaning, and the difference $\mathrm{d}\hat{e}^{\sigma} - \mathrm{d}\hat{N}_j/N_j$ is written to avoid translational motion of a two-phase system as a whole with no change in state. Eq. (3.81) seems to contain no contribution from the excess surface chemical potential, but this is not true: this contribution is masked in the difference $\hat{\gamma} - \sigma\hat{1}$.

Eq. (3.81) has two consequences of paramount importance. First, for liquids (when $\hat{\gamma} = \gamma\hat{1}$ and $\sigma = \gamma$) and for non-deformable solids of a given mass (when $\mathrm{d}\hat{e}^{\sigma} = 0$ and $\mathrm{d}\hat{N}_j = 0$), Eq. (3.81) yields the Gibbs adsorption equation, a central relationship of the theory of capillarity

$$\mathrm{d}\sigma = -\bar{s}\,\mathrm{d}T - \sum_i \Gamma_i\,\mathrm{d}\mu_i. \tag{3.82}$$

Remarkably, the Gibbs adsorption equation turns to be valid not only for fluid systems (for which Gibbs derived it), but also for rigid solids, which justifies numerous “illegal” applications of the Gibbs adsorption equation to the case of adsorption on solid adsorbents. The presence of σ in the Gibbs adsorption equation for solids also explains why σ can be termed the thermodynamic surface tension.

Second, at constant temperature, chemical potentials of mobile species, and the amount of an immobile species, Eq. (3.81) yields the Shuttleworth–Herring relation [78–80]

$$\hat{\gamma} = \sigma\hat{1} + \frac{\mathrm{d}\sigma}{\mathrm{d}\hat{e}^{\sigma}}, \quad \gamma_{st} = \sigma + \frac{\partial\sigma}{\partial e^{\sigma}_{st}}, \tag{3.83}$$

which seems to be the most popular relationship of the theory of solid surfaces. Eq. (3.83) was many times derived in the literature in different ways. Recently, Mueller and Saul [45] showed that the derivation of the Shuttleworth–Herring relation at ignoring the non-uniformity of chemical potential requires double introducing the surface area: the first time as corresponding to the creation of a new surface and the second time as corresponding to the stretching of an existing surface. The duality of such simple notion as surface area enlarges the shortcomings of such theories. We should also mention some alternative formulations of the Shuttleworth–Herring relation [81,82], which seem to be misunderstandings and were correctly criticized [45].

Eq. (3.82) shows that positively adsorbed substances lower the thermodynamic surface tension σ. As for the (mechanical) surface tension γ, direct experiments with bending thin plates after one-sided adsorption clearly manifest a similar influence of adsorbed foreign species on surface stress, which was lively discussed in the literature (see reviews [37,45,64]). A generalization of the Gibbs adsorption equation in terms of γ was given in due time [76], but was not included in our previous review [1] because of its relative complexity. In a parallel publication by Halsey [83], a simple method of passing from σ to γ was suggested based on the Eriksson equation [84] (a particular case of Eq. (3.81) for an isotropic state)

$$\mathrm{d}\sigma = (\gamma - \sigma)\mathrm{d}\ln A - \Gamma_2\,\mathrm{d}\mu_2 \tag{3.84}$$

where A is surface area and subscript 2 refers to an adsorbate. From Eq. (3.84), the relationship follows

$$\left(\frac{\partial\gamma}{\partial\mu_2}\right)_A = -\left(\frac{\partial(\Gamma_2 A)}{\partial A}\right)_{\mu_2}, \tag{3.85}$$

which predicts a decrease of surface tension with increasing the adsorbate chemical potential with an accompanying increase of adsorption. Indeed, the total excess amount of a positively adsorbed substance $\Gamma_2 A$ can only increase when the surface is enlarged by stretching, so that $\partial(\Gamma_2 A)/\partial A > 0$ and $\partial\gamma/\partial\mu_2 < 0$ (the plate side with adsorbate should become convex in experiments with thin plates). A more detailed description of this case can be found in review [45]. The modern data on the numerical values of σ and γ are summarized in reviews [37,45,64,85,86]. Methods of measuring σ and γ are described in monograph [87].

4. Nanothermodynamics

We can define nanothermodynamics as the thermodynamics of nanoparticles, nanostructures, and nanosystems (i.e. systems consisting of a large number of nanoparticles). It follows from this definition that a nanoparticle is a principal object of nanothermodynamics. As for a nanostructure, it can be understood not only as the structure of a single nanoparticle, but also as a structure formed by a conglomerate of nanoparticles of any size. A distinctive feature of a small particle is the dependence of its properties on the particle size, which was recognized still in the classical theory of capillary due to the Laplace Eq. (3.56). Speaking about the internal mechanical state of a small particle, not only the surface stress of the first monolayer, but the whole surface tension γ is important. A nanoparticle differs from a small particle at all in that respect that the surface tension itself manifests its size dependence, though this only play the role of a "fine structure" in the whole effect. Although thermodynamics never deals with the process mechanism or acting forces, it is appropriate to mention the influence of the quantum-size effects of surface energy and on the dependence of surface tension on the particle size (to make it sharper).

An excess stress created by surface tension in a solid particle causes its strain. In the simplest case of an elastic isotropic spherical particle, the pressure p^α inside the particle is related to the radial strain $\Delta R/R$ as

$$p^\alpha = \frac{3K\Delta R}{R} \tag{4.1}$$

where K is the dilatation modulus. Reckoning the pressure and strain from the standard state corresponding to the external pressure p^β and applying Eq. (3.56), we can rearrange Eq. (4.1) to the form

$$\Delta R = \frac{2\gamma}{3K}, \tag{4.2}$$

from where it follows that the absolute radial deformation ΔR is independent of the particle size at still constant γ and K (i.e. for large particles). Since ΔR is composed of the increments of interatomic distances in the course of strain, the latter should increase with decreasing the particle size and can be measured by LEED (the particles are assumed to be sufficiently small, but considerably exceeding the interface thickness). If ΔR is determined from experiment, Eq. (4.2) estimates surface tension. In this way the values of γ 1.4, 1.2, and 2.6 $\mathrm{N\,m^{-1}}$ were obtained for small particles of silver, gold and platinum, respectively [88–90].

The surface tension of small particles also influences their chemical potential, which is of importance for the processes of particle nucleation and growth. They now pay attention to the synthesis and growth of nanoparticles in closed or quasi-closed systems, such as polymeric matrices, (see reviews [91,92]). Since Gibbs created only the thermodynamics of open systems, this problem requires a special consideration [93].

4.1. Influence of surface tension on chemical potential of a nanoparticle

To make our derivation quite transparent, we first consider the case of a liquid particle when nucleation is condensation. For a spherical drop (α) with surface tension σ and radius R, a trivial relation holds

$$\mu^\alpha = \mu^\alpha_\infty + \frac{2\sigma v^\alpha}{R}, \tag{4.3}$$

where μ_{∞}^{α} is the limiting value of the molecular chemical potential μ^{α} at $R \to \infty$ and v^{α} is molecular volume (that is assumed to be constant). Although Eq. (4.3) implies the mechanical surface tension γ (because of the Laplace equation), we use the symbol of the thermodynamic surface tension σ (which is numerically equal to γ for liquids) for the reason that will be clear below when passing to the case of a solid particle. From (4.3) we have

$$\frac{\mathrm{d}\mu^{\alpha}}{\mathrm{d}R} = -\frac{2\sigma v^{\alpha}}{R^2} + \frac{2v^{\alpha}}{R}\frac{\mathrm{d}\sigma}{\mathrm{d}R}. \tag{4.4}$$

Outside of the nano-scaled range of R, when surface tension is still constant, Eq. (4.4) predicts a decrease of chemical potential with increasing the drop size. The situation can change for a nanodrop whit a size-dependent surface tension. In particular, chemical potential will grow if

$$\frac{\mathrm{d}\sigma}{\mathrm{d}R} > \frac{\sigma}{R}. \tag{4.5}$$

Differentiating (4.4) yields

$$\frac{\mathrm{d}^2\mu^{\alpha}}{\mathrm{d}R^2} = \frac{4\sigma}{\rho R^3} - \frac{4}{\rho R^2}\frac{\mathrm{d}\sigma}{\mathrm{d}R} + \frac{2}{\rho R}\frac{\mathrm{d}^2\sigma}{\mathrm{d}R^2} \tag{4.6}$$

that shows the $\mu^{\alpha}(R)$ curve to be concave at least for large R.

Eq. (4.3) implies the existence of a bulk phase (α) inside a drop. It may happen, however, that a small cluster (symbol σ) consists of a monolayer of sized molecules (as for solid particles, only the surface monolayer is typically capable of exchange with the surrounding medium irrespective of the particle size). In such a cluster, a dividing surface passes through surface molecules as if cutting their volume v^{σ} into two parts. A part of a molecule with volume v_{α}^{σ} will be in phase α under the pressure p^{α}, and the other part of volume v_{β}^{σ} will refer to outer phase β with pressure p^{β}. Herewith, the evident relationship holds

$$v^{\sigma} = v_{\alpha}^{\sigma} + v_{\beta}^{\sigma}. \tag{4.7}$$

In addition, surface molecules are subjected to the action of surface tension. Then, in place of the standard relationship $\mathrm{d}\mu = v\,\mathrm{d}p$ at fixed temperature and composition, we now have

$$\mathrm{d}\mu^{\sigma} = v_{\alpha}^{\sigma}\,\mathrm{d}p^{\alpha} + v_{\beta}^{\sigma}\,\mathrm{d}p^{\beta} - a\,\mathrm{d}\sigma. \tag{4.8}$$

where a is the dividing surface area per a molecule (the term $-a\,\mathrm{d}\sigma$ is substantiated in the surface thermodynamics [50]). Using Eqs. (4.7) and (3.56), Eq. (4.8) can be written as

$$\frac{\mathrm{d}\mu^{\sigma}}{\mathrm{d}r} = v^{\sigma}\frac{\mathrm{d}p^{\beta}}{\mathrm{d}R} - \frac{2\sigma v_{\alpha}^{\sigma}}{R^2} + \left(\frac{2v_{\alpha}^{\sigma}}{R} - a\right)\frac{\mathrm{d}\sigma}{\mathrm{d}R} \tag{4.9}$$

Let us see what conclusions follow from Eq. (4.9).

We first consider the case when the outer pressure p^{β} is maintained constant. This is typical for open systems, but can be realized in closed systems with a soft capsule. If surface tension is still constant, we have from (4.9)

$$\left(\frac{\mathrm{d}\mu^{\sigma}}{\mathrm{d}R}\right)_{T,p^{\beta},\sigma} = -\frac{2\sigma v_{\alpha}^{\sigma}}{R^2}, \tag{4.10}$$

which differs from the standard relationship of the nucleation theory only by replacing v^{α} by v^{σ}_{α}. Qualitatively, the result is traditional: chemical potential decreases with increasing the drop size. The size dependence of surface tension is involved in the range of sufficiently small (1–100 nm) radii. It plays a certain role the sign of the coefficient of $\mathrm{d}\sigma/\mathrm{d}R$ in Eq. (4.9), which, in its turn, depends on the drop size. For surface molecules, a is usually larger than $2v^{\sigma}_{\alpha}/R$ at radii exceeding the molecular size. Then, for passing to a symbate dependence of μ^{σ} on R, surface tension should decrease with the particle growth and obey the condition

$$-\frac{\mathrm{d}\sigma}{\mathrm{d}R} > \frac{\sigma}{R(aR/v^{\sigma}_{\alpha} - 1)} \tag{4.11}$$

This condition is realized, for example, in surfactant micelles. Thus, the symbate type of dependence of μ^{σ} on R is possible on the nano-scaled size range, and, therefore, a maximum of chemical potential is possible in the range between macro- and nano-scaled radii.

Turning now to limitedly small radii, we have to consider the opposite condition $a < 2v^{\sigma}_{\alpha}/R$. The case when a is initially small as compared with $2v^{\sigma}_{\alpha}/R$ is of no interest (this means that a molecule is situated inside the drop and is subjected to the analysis given at the beginning of this section). But, even if the dividing surface bisects a molecule at its widest dimension, this condition turns to be real for a limitedly small R. For example, $a = \pi R^2 < (4/3)\pi R^2 = 2v^{\sigma}_{\alpha}/R$ for spherical molecules. We then again arrive at the condition expressed in (4.5) for the symbate dependence, which is scarcely fulfilled [50]. If, nevertheless, one accepts the symbate dependence for limitedly small radii, one should permit the existence of one more extreme of the chemical potential (a minimum, this time) at a radius smaller than for a maximum.

We now discuss the cancel of the pressure constancy in the surrounding medium. Let a phase transition proceed in a closed system of a given volume. If the molecular volume is smaller in phase α than in phase β, the particle growth is accompanied by decreasing p^{β} (the gas condensation is a typical case). The first derivative on the right-hand side of Eq. (4.9) is negative in this case, and nothing changes in the above consideration. If, the reverse, the molecular volume is larger in phase α than in phase β (which is evident to be a condensed phase), the derivative $\mathrm{d}p^{\beta}/\mathrm{d}R$ is positive. Its value increases with R, so that, sooner or later, this derivative will prevail in the whole Eq. (4.9) (it is known what enormous pressures develop, for example, in the process of ice crystallization in a closed vessel). Then the derivative $\mathrm{d}\mu^{\sigma}/\mathrm{d}r$ becomes positive at a sufficiently large R, and we come to the conclusion of inevitable arising one more minimum of chemical potential when passing from a nano- to a macro-size of phase α. Thus, our arguments detect the possible existence of three extremes in the dependence of chemical potential μ^{σ} on the drop radius, two minima and one maximum. As for the chemical potential μ^{β}, its behavior is considerably simpler. μ^{β} is usually constant in open systems. In closed systems, the surrounding medium is depleted with the drop matter in the course of the drop growth, and, hence, μ^{β} monotonically decreases with increasing R. The decrease rate is accrescent and acquires its maximum value ($\mathrm{d}\mu^{\beta}/\mathrm{d}R = -\infty$) at attaining a maximum possible value of R (when the whole matter has overpassed to phase α).

Considering the dependence of the drop formation work W on the drop size, minima correspond to stable and maxima to unstable states of equilibrium. It was established that the derivative of W with respect to the drop molecular number n equals the difference between chemical potentials inside and outside the drop [50]:

$$\frac{\mathrm{d}W}{\mathrm{d}n} = \mu^{\sigma} - \mu^{\beta}. \tag{4.12}$$

It follows from (4.12)

$$\frac{d^2W}{dn^2} = \frac{d\mu^\sigma}{dn} - \frac{d\mu^\beta}{dn}, \tag{4.13}$$

and we may write the stable equilibrium condition as

$$\mu^\sigma = \mu^\beta, \quad \frac{d\mu^\sigma}{dn} > \frac{d\mu^\beta}{dn} \quad \text{or} \quad \frac{d\mu^\sigma}{dR} > \frac{d\mu^\beta}{dR} \tag{4.14}$$

According to Eq. (4.14), the equilibrium states are easily found as intersection points of the curves of dependence of chemical potentials μ^σ and μ^β on the particle size, while the comparison of their slopes (accounting for the sign) at an intersection point determines the state stability. Fig. 8 illustrates the case of an open system when the state of the surrounding medium is fixed. The $\mu^\beta(n)$ plot is a horizontal line whose level characterizes the degree of saturation of the surrounding medium with the particle matter. At $\mu^\beta = \mu_1^\beta$ the surrounding medium is undersaturated with respect to formation of a stable particle, but supersaturated with respect to formation of a macroscopic phase. The case corresponds to the classical nucleation theory of Gibbs and Volmer with a unique unstable particle of the critical size. Increasing μ^β to μ_2^β leads to arising a second equilibrium particle size where the particle is stable with respect to growth, but unstable with respect to the size decrease. Above this value (say, at μ_3^β), the surrounding medium turns to be supersaturated with respect to both a macroscopic phase and stable particles. In this situation, already three equilibrium particle sizes occur, of which two correspond to unstable particles, the largest particle as the above critical nucleus of a macroscopic phase and the smallest one as a critical nucleus of a stable particle. At $\mu^\beta = \mu_4^\beta$ is attained the limiting supersaturation with respect to formation of a stable particle. Above this value (say, at μ_5^β), the stable particle formation proceeds with the barrierless mechanism; there are only two equilibrium particle sizes and no critical nucleus. Eventually, at μ_6^β, the limiting supersaturation is attained with respect to formation of a macroscopic phase. This state itself still admits the existence of a unique equilibrium particle (stable to decreasing, but unstable to growth), which, however, becomes impossible at larger values of μ^β (when the spinodal decay occurs).

Passing to a closed system, the dependence $\mu^\beta(n)$ arises (Fig. 9). Its curves can also be positioned on various levels, respectively to the matter amount in the system. This case differs from the previous one in

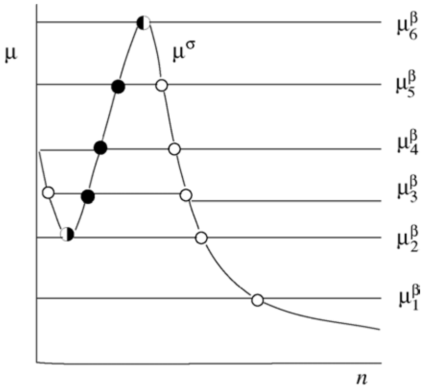

Fig. 8. Stable (filled circles) and unstable (empty circles) states in the curve of the dependence of the molecular chemical potential of a particle μ^σ on the particle molecular number n at six given values of chemical potential μ^β in an open system.

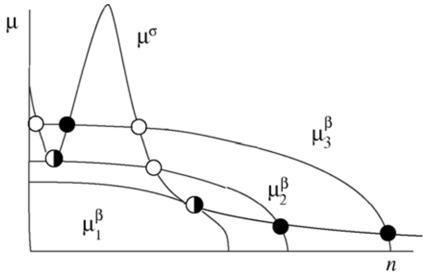

Fig. 9. Stable (filled circles) and unstable (empty circles) states in the curve of dependence of the surface chemical potential μ^σ of a particle on the particle molecular number n at three initial values of chemical potential μ^β in a closed system for the case when the matter concentration inside the particle is larger than in the mother phase.

two respects. First, there are no equilibrium states at all if the initial chemical potential value $\mu^\beta(1)$ is smaller than a certain value $\mu_1^\beta(1)$ (the counting of n begins with unity). In other words, the phase process does not proceed if the initial supersaturation does not exceed a certain value. Second, when $\mu^\beta(1) > \mu_1^\beta(1)$, all the curves $\mu^\beta(n)$ intersect the curve $\mu^\sigma(n)$ by necessity, creating one more stable equilibrium state (Fig. 9). This state corresponds to the largest (up to macroscopic) particle size and is realized at unlimitedly large supersaturation. As for the other intersection points for the curves $\mu^\sigma(n)$ and $\mu^\beta(n)$, they have the same meaning as in the above case of an open system.

Fig. 9 refers to the case when the matter concentration (density) in a particle is larger than in the mother phase. To make the picture complete, Fig. 10 exhibits the opposite case when growing particles in a closed system possess lower density in comparison with the matter concentration in the surrounding medium (as, for example, at the formation of an ice particle in water). Fig. 10 differs from Fig. 9 in the location of the points of additional stable particles. In both the figures, it is conspicuous the existence of even four equilibrium particle sizes at the position of the curves $\mu^\beta(n)$ within the interval between $\mu_1^\beta(n)$ and the curve corresponding to the limiting supersaturation with respect to formation of the smallest stable particle ($\mu_3^\beta(n)$ falls in this interval). The latter arises not always and not in any system (for example, it is typical for micellar systems). So the form of the dependence of μ^σ on n can be simpler that in the above case that we analyzed as the most interesting for nanothermodynamics.

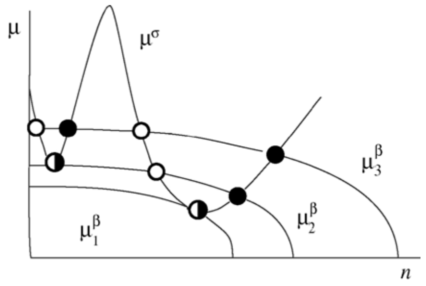

Fig. 10. Stable (filled circles) and unstable (empty circles) states in the curve of dependence of the surface chemical potential μ^σ of a particle on the particle molecular number n at three initial values of chemical potential μ^β in a closed system for the case when the matter concentration inside the particle is lower than in the mother phase.

The application of the above analysis to isotropic solid particles requires some comments. According to Eq. (2.42), the chemical potential of an immobile species is directly dependent on the stress tensor. Therefore, not σ but γ (now different from σ) should stand in Eq. (4.3) to determine the chemical potential of a solid. On the other side, as was first shown by Gibbs and confirmed by the subsequent analysis (see, e.g. [94–98]), the equality of the chemical potential values in a solid and fluid phases at equilibrium is realized only for a flat interface (see Eqs. (2.24), (2.25), and (2.41)). If the solid surface is curved, its true chemical potential (not speaking about the chemical potential in the solid bulk) differs from the chemical potential of the same substance in an adjacent fluid phase even at material equilibrium. However, there is a quantity, just defined by Eq. (4.3), that should be approximately equal to the chemical potential in the fluid phase (to be more exact, the term $2\sigma/R$ should be taken in combination with the derivative $\mathrm{d}\sigma/\mathrm{d}R$). This quantity would be equal to the chemical potential within a nanoparticle if its surface tension coincided with σ. Since just this quantity governs the matter transfer, it can be called the effective chemical potential of an immobile species in a nanoparticle. The effective chemical potential is evident to be used when constructing the affinity of a process with participation of nanoparticles. Thus, to conclude this section, we may say that the above analysis is quite applicable to isotropic solid particles.

4.2. Dependence of surface tension and surface energy on the nanoparticle size

The surface curvature dependence of surface tension is one of the central problems of the theory of capillarity and has been under discussion for a long time. The classical Gibbs–Tolman isotherm for fluid interfaces reads

$$\frac{\mathrm{d}\ln\sigma}{\mathrm{d}\ln R_s}=\frac{(2\delta/R_s)[1+\delta/R_s+(\delta/R_s)^2/3]}{1+(2\delta/R_s)[1+\delta/R_s+(\delta/R_s)^2/3]},\tag{4.15}$$

where R_s is attributed to the surface of tension and $\delta\equiv R-R_s$ (R is the radius of the equimolecular surface) is the Tolman parameter. Expanding Eq. (4.15) in the vicinity of a flat interface ($R_s=R=\infty$) yields

$$\frac{\sigma}{\sigma_\infty}=1-\frac{2\delta}{R}+\cdots\tag{4.16}$$

that predicts qualitatively opposite effects (increasing or decreasing surface tension) when curving a flat interface in different directions. The opposite limit ($R_s\to 0$) requires a monotonic linear decrease of surface tension irrespective of the curvature sign [50]. This means that increasing surface tension at curving a flat interface should be followed by a maximum of surface tension. The first statistical mechanical calculation of δ [99] yielded a positive value for a flat surface of argon, so that it was adopted for a long time that the surface tension monotonically decreases with the drop radius for a drop and passes through a maximum for a bubble. However, the modern data are not always in agreement with this concept [100–102]. Moreover, returning to our molecular dynamics data on argon clusters [103] (which was the first computer simulation on the mechanical surface tension), we could now provide another interpretation. The computer experiment was carried out at a reduced temperature of 0.75 (90 K) when argon clusters can be regarded as liquid with $\gamma=\sigma$. Fig. 11 shows the results. The γ versus R plot scarcely looks as an asymptotic curve and rather conveys the suggestion that the curve intersects the horizontal

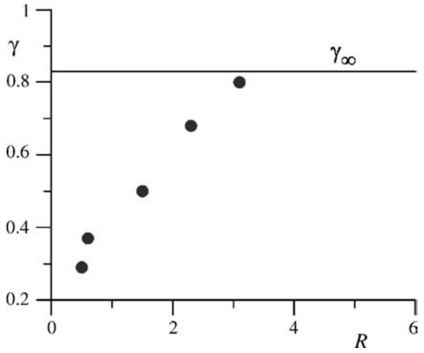

Fig. 11. The molecular dynamics simulation of the dependence of the surface tension of argon clusters on the cluster radius [100]; γ and R are represented in units ε'/σ'^2 and σ', respectively, where ε' and σ' are the parameters of the Lennard–Jones potential.

line depicting the surface tension macroscopic value and, only after passing through a possible maximum, acquires its asymptotic behavior (which would correspond to $\delta < 0$). The general opinion now is that δ is small and rather negative, than positive for argon.

The size dependence of surface tension is especially important for nanoparticles. When relating this problem to the kind of pair interaction [104], one also touches the problem of surface energy [105]. As was stated above, Gibbs defined σ as the work of formation of unit area of a new surface by cutting. Applying this definition to the formation of a curve interface, we can imagine a ball of matter transferred from the interior of a bulk phase to a vacuum. At zero temperature, the work of transfer of the ball from a fixed position in the bulk of a condensed phase to a fixed position in a vacuum is evident to equal the energy of cohesion of the ball with its surroundings in the bulk phase. Using the molecular pair potential $\emptyset(r_{12})$ (which inserts, naturally, a certain error as compared with a multi-body potential) the above cohesive energy, U_{12}, is given by the expression [106]

$$U_{12} = 4\pi^2\rho^2 \int_{r+d}^{\infty} y\,\mathrm{d}y \int_{y-r}^{y+r} \emptyset(r_{12}) r_{12}[r^2 - (y - r_{12})^2]\,\mathrm{d}r_{12}, \tag{4.17}$$

where ρ is the molecular number density in the bulk phase, r the ball radius as the distance from the ball center to the centers of its surface molecules and d is the minimum intermolecular distance (the molecule size) in the bulk phase (Fig. 12). For the particular case of dispersion forces ($\emptyset(r_{12}) = -\lambda r_{12}^{-6}$) and choosing d as unit length, Eq. (1) yields

$$U_{12} = -\frac{\pi^2\rho^2\lambda}{12}\left[4R^2 - 4\ln(2R) - \frac{1}{4R^2}\right], \tag{4.18}$$

where λ is the London constant and $R \equiv r/d + 1/2$ is the dimensionless radius of the equimolecular surface (Fig. 12). By dividing (4.18) by the surface area $4\pi R^2$, we obtain the expression for the cohesive energy u_{12} of a curved interface per unit area

$$u_{12}(R) = -\frac{\pi\rho^2\lambda}{12}\left[1 - \frac{\ln(2R)}{R^2} - \frac{1}{16R^4}\right]. \tag{4.19}$$

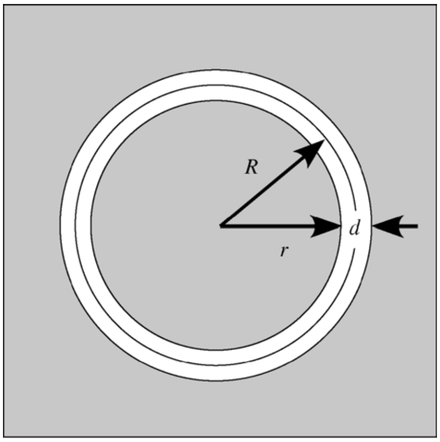

Fig. 12. The interaction of a ball of matter inside a condensed phase with its surroundings.

Passing to the limit $R \to \infty$, Eq. (4.19) changes to the well-known expression for the dispersion-forces cohesive energy of two half-spaces separated by a flat slit of width d ($d = 1$ this time) [107]:

$$u_{12}(\infty) = -\frac{\pi\rho^2\lambda}{12}. \tag{4.20}$$

Since we integrated from a smallest distance, the question arises about the role of repulsion energy. Using the Lennard–Jones potential $\emptyset(r_{12}) = -\lambda r_{12}^{-6} + \lambda r_{12}^{-12}$, we can calculate the contribution of repulsion energy just in the above way. This contribution depends on R, but is small at large R. In particular, when taking the repulsion energy into account, (4.20) is replaced by

$$u_{12}(\infty) = -\frac{29\pi\rho^2\lambda}{360} \tag{4.21}$$

which shows the repulsion energy to amount only about 3% in the limit $R \to \infty$.The opposite limit $R \to 1/2$ (when the ball includes only one molecule) requires a separate calculation in the point-force approach since Eq. (4.19) based on the integration over the ball volume, yields $u_{12} = 0$ when the ball degenerates into a point. The result is

$$U_{12}\left(\frac{1}{2}\right) = 4\pi\rho \int_1^\infty \emptyset(r_{12}) r_{12}^2 \, \mathrm{d}r_{12} \tag{4.22}$$

or, using the Lennard–Jones potential,

$$U_{12}\left(\frac{1}{2}\right) = 4\pi\rho\lambda\left(\frac{1}{9} - \frac{1}{3}\right) = -\frac{8}{9}\pi\rho\lambda, \tag{4.23}$$

where the contribution of repulsion amounts 1/3 of that of attraction. In the dimensionless units used, the volume of a spherical molecule is $\pi/6$ and its surface is π, so that the cohesive energy per unit surface area for a single molecule is

$$u_{12}\left(\frac{1}{2}\right) = \frac{U_{12}(1/2)}{\pi} = -\frac{8}{9}\rho\lambda. \tag{4.24}$$

Assuming the structure of matter unchanged (as a consequence, e.g. of incompressibility and zero temperature), the work of disjoining of the ball and its surroundings is just equal to the reverse cohesive energy. Then surface energy ε (coinciding with the thermodynamic surface tension σ at zero-temperature) is defined as half of reverse cohesive energy per unit surface area. So we have from (4.19) (neglecting the contribution of repulsion)

$$\varepsilon(R) = \frac{\pi\rho^2\lambda}{24}\left[1 - \frac{\ln(2R)}{R^2} - \frac{1}{16R^4}\right], \tag{4.25}$$

which exhibits monotonic increase of surface energy of a nanoparticle with its size. Expanding (4.25) in a power series of $1/R$ ($b = \ln 2 + 1/2 \approx 1.193$)

$$\varepsilon(R) = \left(\frac{\pi\rho^2\lambda}{24}\right)\left(1 - \frac{b}{R^2} + \cdots\right), \tag{4.26}$$

we discover the absence of a linear term in contrast with Eq. (4.16). This effect is predictable. Cohesion energy equally belongs to the convex and concave surfaces in touch with each other if they possess identical structures (coinciding with the structure of the bulk phase). As a result, the surface energies of both of the surfaces are the same and, therefore, are independent of the curvature sign, which is possible only in the absence of a linear term in (4.26). So we can conclude that a linear term can appear due to effects of entropy (at temperatures above zero) and of specific surface structure (different for the convex and concave surfaces) as a consequence of non-zero compressibility.

In two opposite limiting cases $R = \infty$ and $R = 1/2$, we have from (4.21) and (4.24) (an exact results accounting for repulsion)

$$\varepsilon_\infty = -\frac{29\pi\rho^2\lambda}{720}, \tag{4.27}$$

$$\varepsilon_1 = -\frac{4}{9}\rho\lambda \tag{4.28}$$

for a macroscopic body and a single molecule in a vacuum, respectively. From (4.27) and (4.28) we obtain

$$\frac{\varepsilon_1}{\varepsilon_\infty} = \frac{4 \times 720}{29 \times 9 \times \pi\rho} \approx \frac{3.5}{\rho}. \tag{4.29}$$

The result is not surprising: it is much more difficult to extract a molecule from the bulk than to transfer the molecule to the surface. The particular value of $\varepsilon_1/\varepsilon_\infty$ depends on the ρ value ($1 \leq \rho < 2$) that, in its turn, depends on the type of packing. $\rho = 1$ and $\varepsilon_1/\varepsilon_\infty \approx 3.5$ for the cubic packing. The most compact packing of hard spheres requires $\rho = 1.4$ and $\varepsilon_1/\varepsilon_\infty \approx 2.5$.

4.3. Phase transitions in nanoparticles

At studying the process of comminution of solids, it was discovered that one more polymorphous modification could be found in nanoparticles. Formation of a polymorphous modification is a phase transition (of the first or second order), so that one may conclude that phase transitions can occur in the process of dispergation. Already 16 cases of such transformations had been known by 1979 [108]. The mechanism of phase transition in a nanoparticle can be modeled in various ways [108–110]. However, due to its small size, a nanoparticle changes its phase state practically instantaneously so that it is hard to imagine the state of equilibrium between two phases inside the particle. In this case, it is more reasonable to compare the Gibbs energy values for the nanoparticle as a whole before and after the phase transformation. Since the amount of matter in the particle does not change herewith, it is enough, for such consideration, the truncated variant of thermodynamics (without chemical potentials) usually used in the mechanics of continuum media [3]. We only complement this variant with the account for surface phenomena [111].

We begin with the fundamental equation for the free energy, F, of a nanoparticle represented as a combination of a uniform bulk phase α and a piecewise-smooth (faceted) surface:

$$\mathrm{d}F = -S\,\mathrm{d}T + V_0 \sum_{s,t} E^{\alpha}_{st}\,\mathrm{d}e^{\alpha}_{st} + \sum_j A_{j0} \sum_{s,t} (\gamma_{j(st)}\,\mathrm{d}e^{\|}_{j(st)} + E^{\perp}_{j(st)}\,\mathrm{d}\bar{e}_{j(st)}), \tag{4.30}$$

where V_0 is the particle volume in a strainless state (a constant quantity in the strain process) and A_{j0} is the area of the jth surface part in the strainless state, the last term corresponding to Eq. (3.73). If a nanoparticle is subjected to external mechanical actions characterized by the stress tensor E^{β}_{st} (considered to be uniform along the nanoparticle surface for the sake of simplicity), the stable state of the nanoparticle is a state with a minimum value of thermodynamic potential Φ (an analogue of Gibbs energy) defined via free energy F as

$$\Phi \equiv F - V_0 \sum_{s,t} E^{\beta}_{st} e^{\alpha}_{st}. \tag{4.31}$$

Differentiating Eq. (4.31) and expressing dF according to Eq. (4.30), we obtain

$$\mathrm{d}\Phi = -S\,\mathrm{d}T + V_0 \sum_{s,t} (E^{\alpha}_{st} - E^{\beta}_{st})\,\mathrm{d}e^{\alpha}_{st} - V_0 \sum_{s,t} e^{\alpha}_{st}\,\mathrm{d}E^{\beta}_{st} + \sum_j A_{j0} \sum_{s,t} (\gamma_{j(st)}\,\mathrm{d}e^{\|}_{j(st)} + E^{\perp}_{j(st)}\,\mathrm{d}\bar{e}_{j(st)}). \tag{4.32}$$

By the equilibrium conditions, the function Φ must have a minimum at given T and E^{β}_{st}. Therefore, the second and fourth terms on the right-hand side of Eq. (4.32) should cancel each other (which forms the mechanical equilibrium condition) to yield

$$\mathrm{d}\Phi = -S\,\mathrm{d}T + V_0 \sum_{s,t} e^{\alpha}_{st}\,\mathrm{d}E^{\beta}_{st}. \tag{4.33}$$

Note that Eq. (4.33) would be an ordinary fundamental equation for a mechanically anisotropic phase (α) provided quantity E^{α}_{st} stood in place of E^{β}_{st}. However, Eq. (4.33) refers to a particle of any complex structure including its surface layer (according to Gibbs' method, the action of the strain tensor e^{α}_{st} is extended, as well as volume V_0, to include the whole particle).

Let phase α to have a polymorphous modification α′. We may write the same Eq. (4.33) for phase α′. Then subtracting one equation from the other, we obtain

$$\mathrm{d}\Delta\Phi = -\Delta S\,\mathrm{d}T - \Delta\Big(V_0 \sum_{s,t} e^{\alpha}_{st}\,\mathrm{d}E^{\beta}_{st}\Big), \tag{4.34}$$

where Δ symbolizes the difference of a quantity for the two modifications ($\Delta\Phi \equiv \Phi - \Phi'$, etc.). Phase α is more stable at $\Phi < \Phi'$ and phase α′ is more stable at $\Phi > \Phi'$. If, however, $\Delta\Phi = 0$, both the phases are equally stable, and, therefore, the particles of both the modifications can exist with equal probability. For such states Eq. (4.34) changes to the equation

$$\Delta S\,\mathrm{d}T = -\Delta\Big(V_0 \sum_{s,t} e^{\alpha}_{st}\,\mathrm{d}E^{\beta}_{st}\Big) \tag{4.35}$$

showing how the temperature of the polymorphous transformation of a particle depends on external mechanical actions. Since Eq. (4.34) acts at a constant amount of matter, all extensive quantities in Eq. (4.35) may be treated as molar quantities.

Proceeding to the analysis of Eq. (4.35), we first turn to the simplest case when the external action is isotropic: $E^{\beta}_{st} = -p^{\beta}\delta_{st}$ where δ_{st} is Kronecker's delta. Such situation is realized, for example, when a particle is in a medium (liquid or air) with uniform pressure (the influence of gravity is negligible because of a small particle size). Because of the complexity of the interface shape, the condition of isotropy of external action is not yet enough to make the particle internal phase α also mechanically isotropic. So the particle interior and, all the more, the surface layer of the particle can stay mechanically anisotropic. Putting the above isotropic value of E^{β}_{st} in Eq. (4.35) at using Eq. (2.12) reduces Eq. (4.35) to the form

$$\Delta S\,\mathrm{d}T = \Delta(V - V_0)\,\mathrm{d}p^{\beta}, \tag{4.36}$$

where V is the current particle volume. If the initial volume of a particle in the strainless state V_0 is chosen the same for both the modifications (as did Coe and Paterson [36] in their analysis of the polymorphous transformation of quartz), Eq. (4.36) is exactly reduced to the Clapeyron–Clausius equation

$$\frac{\mathrm{d}T}{\mathrm{d}p^{\beta}} = \frac{\Delta V}{\Delta S}. \tag{4.37}$$

This is a truly amazing fact since we consider not the two-phase equilibrium at a flat interface (when the Clapeyron–Clausius equation acts), but a polymorphous transformation in a non-uniform particle with a closed surface. The only condition of applicability of the Clapeyron–Clausius equation to this case turns to be the use of external pressure p^{β} instead of real pressure p^{α} whose action causes phase transition. However, external pressure is just that tool that is used by an experimentalist to influence the phase transition process in a particle (in more general Eq. (4.35), the stress tensor E^{β}_{st} includes kicks, impacts, shear stresses, and all that happens with particles in the comminution process).

As initial Eq. (4.30), Eq. (4.35) is confined with the condition of the constancy of the number of molecules in a particle. Eq. (4.35) shows how external pressure influences the phase transitions temperature in a particle with a given number of molecules, but says nothing about the dependence of the particle structure on the molecule number. Regarding the question how the structure of matter changes in the process of its comminution, we should be guided by the reasoning of Sections 4.1 and 4.2. In addition, we can similarly derive, for the separately-taken phase transformation α → α′, the equation analogous to (4.35) (E_{st}^{β} is replaced by E_{st}^{α}):

$$\Delta S\,\mathrm{d}T = -\Delta\Big(V_0 \sum_{s,t} e_{st}^{\alpha}\,\mathrm{d}E_{st}^{\alpha}\Big). \tag{4.38}$$

For a mechanically isotropic state, Eq. (4.38), with the account for (2.12), is reduced to the relationship

$$\Delta S\,\mathrm{d}T = \Delta(V - V_0)\,\mathrm{d}p^{\alpha} \tag{4.39}$$

or, at the same choice of the initial volume V_0 for phases α and α', to the ordinary Clapeyron–Clausius equation

$$\frac{\mathrm{d}T}{\mathrm{d}p^{\alpha}} = \frac{\Delta V}{\Delta S} \tag{4.40}$$

If bulk phase α exists inside a nanoparticle (due to its sufficiently large size), the application of Eq. (4.40) to the particle does not yet form a direct criterion of phase transformation of the particle. This occurs since surface properties are also important for the particle (for example, a transition predicted by Eq. (4.40) can be unrealizable because another modification has too high surface tension). Although the reasoning of necessity of taking into account the anisotropy and surface properties of a particle was formulated in the literature long ago, the use of the Clapeyron–Clausius equation was the main element of the analysis of phase transformations in the comminution process [108]. Actually, the Clapeyron–Clausius equation only indicates the tendency of the process (which, of course, is also useful). We explain this with an example. If surface tension is positive and the derivative $\mathrm{d}T/\mathrm{d}p^{\alpha}$ negative, we know that pressure inside particles increases and the phase transition temperature decreases with decreasing the particle size in the comminution process. When the phase transition temperature becomes equal to the real temperature of the system, there can be no phase transition because of surface phenomena. However, we may think that phase transition will occur, sooner or later, in the process of further comminution.

It is known that the derivative $\mathrm{d}T/\mathrm{d}p^{\alpha}$ in the Clapeyron–Clausius equation can be of any sign, although molar volume always decreases with increasing pressure under isothermal conditions and molar entropy always increases with temperature under isobaric conditions. The case of positive slope of the line of a polymorphous transformation in the state diagram $T - p^{\alpha}$ is accounted to be normal, and the case of negative slope is accounted to be abnormal. It was claimed by Lin and Nadiv [108] that belonging to this two cases also determines the character of phase transition in the comminution process: matter changes to more dense modification in the normal case and to less dense modification in the abnormal case. However, the connection between these phenomena seems to be problematic. It seems as if the transition to a more dense modification at comminution is still more probable in the abnormal case than in the normal one since inevitable heating (in the process of comminution) works in the same direction as increasing pressure in particles. That fact that, at comminution, $CaCO_3$ subsequently passes the stages of vaterite (density 2.64 kg/l), calcite (density 2.72 kg/l), and aragonite (density 2.95 kg/l) [108], can be explained by a positive value of surface tension and by compression of particles in the comminution process, but not by belonging the phase transitions of $CaCO_3$ to the normal case. As for the transformation of massicot (density 9.64 kg/l) into litharge (density 9.35 kg/l) at the comminution of PbO, this transition, although abnormal indeed for bulk phases, can be explained either by negative surface tension (unless this will be controverted experimentally by independent measuring surface tension) or by the role of shear stresses and strains not taken into account in the Clapeyron–Clausius equation.

It is of interest the case of zirconia. Its synthetic tetragonal modification (density 5.86 kg/l) with the particle size 15 nm completely changes to the monoclinic modification (density 5.74 kg/l) at mechanical treatment. However, at decreasing the particle size to 10 nm, the monoclinic modification is again consolidated to the tetragonal one [112], although this polymorphous transformation in the bulk refers to the abnormal case (the monoclinic modification of ZrO_2 transforms into the tetragonal one at heating up to 1100 °C). Such behavior of zirconia can be explained as follows. The tetragonal modification is metastable at a room temperature and should spontaneously transform into the monoclinic modification. Mechanical treatment activates this process. However, the pressure inside particles increases and the polymorphous transformation temperature decreases as the particle size diminishes, unless (as it turns, at the particle size about 10 nm) the reverse process occurs, the transformation of the monoclinic modification into the more dense tetragonal modification.

All the said above referred to first-order phase transitions. For second-order phase transitions, $\Delta S = 0$ and $\Delta V = 0$, so that the Clapeyron–Clausius equation becomes indeterminate. Phases α и α′ become identical at the point of a second-order phase transition. Therefore, not only thermodynamic potentials of phases, but also any other quantities (the first derivatives of thermodynamic potentials are advisable to obtain non-zero values for the difference of the second derivatives of thermodynamic potentials) may be equated. Regarding the number of molecules in a particle to be fixed, we choose the particle volume Vas such quantity and as a function of temperature and the external stress tensorE_{ik}^{β}:

$$\mathrm{d}V = \left(\frac{\partial V}{\partial T}\right)_{E_{st}^{\beta}} \mathrm{d}T + \sum_{s,t} \left(\frac{\partial V}{\partial E_{st}^{\beta}}\right)_{T, E_{lm \neq st}^{\beta}} \mathrm{d}E_{st}^{\beta} \equiv V\,\theta\,\mathrm{d}T + V \sum_{s,t} \chi_{st}\,\mathrm{d}E_{st}^{\beta} \tag{4.41}$$

Here the following designations have been introduced for the sake of brevity: θ is the thermal dilatation coefficient, χ_{st} the isothermal compressibilities corresponding to the components of the stress tensor (in bulk phases, molar volume is not sensitive to the non-diagonal components of the stress tensor; in the case under consideration, however, any change in the particle shape means a change in its surface area accompanied by adsorption and the volume change).

Applying now Eq. (4.32) to phases α and α′ and equating the resultant expressions, we obtain the equation of the hypersurface of a second-order phase transition in the state diagram

$$\Delta\theta\,\mathrm{d}T = -\sum_{s,t} \Delta\chi_{st}\,\mathrm{d}E_{st}^{\beta}. \tag{4.42}$$

Similarly to Eq. (4.35), Eq. (4.42) describes the influence of external pressure on the phase transition temperature, but now for a second-order phase transition. As for the description of a second-order phase transition in an anisotropic bulk phase α in terms of its own stress tensor E_{st}^{α}, corresponding equations were considered in Section 2.5 to which we refer a reader, but with a certain limitation. Such equations with no account for surface phenomena are only able for approximate pointing and do not yield a rigorous description as that given by Eq. (4.42).

4.4. Quasi-chemical description of solid nanoparticles

The dictum "a crystal is a big molecule" is known to a scientist since the student time. At down-the-line holding this point of view (see, e.g. [113,114], not only crystalline, but also amorphous solid nanoparticles should be regarded as "supramolecules", their set of same nature and increasing size as homologous series, and nanoparticles of same composition but different structure as isomers. For a long time, such ideas were not embodied in a corresponding rigorous thermodynamic theory (in fact, they used traditional phase approach when the matter concerns thermodynamics). The corresponding formulation was given only recently [111], and we reproduce it below.

Thus, let us forget that a nanoparticle is a piece of a phase. Now, it is a single large and complex molecule or an ion of multiple charge. Both are below called a supramolecule. Let a supramolecule include n_1 structural units of the first sort, n_2 structural units of the second sort, and so on. We denote the whole set of the numbers n_i as $\{n\}$. The set $\{n\}$ gives the composition of the supramolecule, as if being a supramolecule certificate. The symbol $\{n\}$ will be used below as a subscript to indicate that a quantity belongs to a supramolecule of a certain type. We designate the supramolecule chemical potential $\mu_{\{n\}}$ and write, using known results of statistical mechanics for ordinary molecules, its detailed expression as

$$\mu_{\{n\}} = G^0_{\{n\}} + k_B T \ln(c_{\{n\}} \Lambda^3_{\{n\}} f_{\{n\}}), \tag{4.43}$$

where $G^0_{\{n\}}$ is the Gibbs energy of a supramolecule of sort $\{n\}$ with resting center of mass in a given medium in the absence of other supramolecules, k_B is the Boltzmann constant, $\Lambda_{\{n\}}$ and $f_{\{n\}}$ are the de Broglie wavelength and the activity coefficient of supramolecules, respectively. The de Broglie wavelength of a supramolecule is given by the expression

$$\Lambda_{\{n\}} \equiv h(2\pi m_{\{n\}} k_B T)^{-1/2}, \tag{4.44}$$

where h is the Planck constant and $m_{\{n\}}$ is the supramolecule mass compiled of the masses of supramolecule structural units m_i as

$$m_{\{n\}} = \sum_i m_i n_i. \tag{4.45}$$

The interaction of a supramolecule with a medium is taken into account in $G^0_{\{n\}}$. As for the activity coefficient $f_{\{n\}}$, it reflects the interaction of supramolecule with each other. It is possible to include the quantity $k_B T \ln f_{\{n\}}$ into $G^0_{\{n\}}$ and write Eq. (4.43) in the form

$$\mu_{\{n\}} = G^0_{\{n\}} + k_B T \ln(c_{\{n\}} \Lambda^3_{\{n\}}), \tag{4.46}$$

where $G^0_{\{n\}}$ is already understood as the Gibbs energy of a supramolecule of sort $\{n\}$ with resting center of mass in a dispersion medium containing other supramolecules ($G^0_{\{n\}}$ now accounts for the interaction of the supramolecule not only with the medium, but also with other supramolecules present in the system).

Calculating the Gibbs energy $G^0_{\{n\}}$ may be detailed as follows. First of all, one should take into account the difference in the energetic state of structural units on the surface of a supramolecule and inside the supramolecule. Let there be $b_i n_i^{2/3}$ structural units of the ith sort on the surface where b_i is a numerical coefficient determined by the chemical structure and geometrical shape of a supramolecule. We now imagine that, in the initial state, the structural units of the supramolecule were separated and placed in a vacuum with the resting state of their centers of mass. The Gibbs energy of such a state is $\sum_i g_i^0 n_i$ where g_i^0 is the Gibbs energy of a separate structural unit of the ith sort with resting center of mass in a vacuum. The transfer of this structural unit into the interior of the supramolecule (we mark the supramolecule interior with the symbol α) will require the work w_i^α. Obviously, $w_i^\alpha < 0$ since binding energy in a solid exceeds, in its absolute value, the positive kinetic energy of oscillatory motion acquired by the structural units as a result of such transfer. The subsequent transfer of a structural unit to the supramolecule surface requires an additional work $w_i^{\alpha\sigma}$ (σ symbolizes the surface region of a supramolecule, the sequence of the subscripts indicating the transfer direction). Since such transfer is accompanied by the rupture of bonds, it is evident that $w_i^{\alpha\sigma} > 0$. We now may write the expression

$$G^0_{\{n\}} = \sum_i g_i^0 n_i + \sum_i w_i^\alpha n_i + \sum_i w_i^{\alpha\sigma} b_i n_i^{2/3}, \tag{4.47}$$

and Eq. (4.46), after the substitution of (4.47) in (4.46), takes the form

$$\mu_{\{n\}} = \sum_i g_i^0 n_i + \sum_i w_i^\alpha n_i + \sum_i w_i^{\alpha\sigma} b_i n_i^{2/3} + k_B T \ln(c_{\{n\}} \Lambda^3_{\{n\}}). \tag{4.48}$$

In principle, the quantities w_i^α and $w_i^{\alpha\sigma}$, even in dilute systems, depend on $\{n\}$ and, in particular, on the supramolecule size. However, accounting for this dependence becomes necessary, first, only for very small (one can say small in the limit) particles and, second, only for weak chemical bonds (approaching ordinary molecular forces).

The further algorithm of constructing the theory suggests itself. Any physicochemical process, including chemical reactions, is governed by chemical affinity. If a process is symbolically depicted by the equation

$$\sum_{\{n\}} \nu_{\{n\}} B_{\{n\}} \Rightarrow \sum_{\{n\}} \nu'_{\{n\}} B\nu'_{\{n\}}, \tag{4.49}$$

where the initial substances stand on the left and the process products (marked with a prime) on the right, $\nu_{\{n\}}$ are stoichiometric coefficients, the chemical affinity $\mathcal{A}$ of the process is given by the expression (cf. Eq. (2.100))

$$\mathcal{A} \equiv \sum_{\{n\}} (\nu_{\{n\}} \mu_{\{n\}} - \nu'_{\{n\}} \mu'_{\{n\}}), \tag{4.50}$$

where $\mu_{\{n\}}$ are the chemical potentials of substances $B_{\{n\}}$ that feature in Eq. (4.49). If supramolecules (nanoparticles) participate in the process, their chemical potentials will enter Eq. (4.50). The subsequent analysis is carried out as it is generally accepted in the thermodynamics (both equilibrium and non-equilibrium) of chemical reactions. For the sake of illustration, we consider two examples of physicochemical processes. As a first example, we take a polymorphous transformation considered above within the frames of the phase approach.

4.4.1. Phase transitions

A polymorphous transformation is now meant as a monomolecular isomerization chemical reaction of type

$$B_{\{n\}} \Rightarrow B'_{\{n\}} \tag{4.51}$$

proceeding under the influence of external factors. We assume that factors act simultaneously on all particles of the system, so that the polymorphous transformation simultaneously occurs in all particles of a given composition. The chemical affinity of the reaction expressed in Eq. (4.51) is

$$\mathcal{A} = \mu_{\{n\}} - \mu'_{\{n\}}. \tag{4.52}$$

Substituting (4.46) in (4.52) and accounting for that the concentration and the de Broglie wavelength are the same for both the isomers, we arrive at the expression

$$\mathcal{A} = G^0_{\{n\}} - G'^0_{\{n\}} \equiv \Delta G^0_{\{n\}} (= \Delta G_{\{n\}}). \tag{4.53}$$

It is shown in Eq. (4.53) that the chemical affinity can also be represented as the difference of the total Gibbs energy $G_{\{n\}}$ for the two isomers of a supramolecule (the quantities $G^0_{\{n\}}$ and $G_{\{n\}}$ differ by $3k_BT/2$). If a supramolecule is so large as to obey the mechanics of continuous media, we can define $G^0_{\{n\}}$ as the function Φ by Eq. (4.31) and repeat all the derivations of Section 4.3. In particular, by setting the affinity expressed in (4.53), equal to zero, we will obtain the equations for the equilibrium of the two isomers and again come to the Clapeyron–Clausius equation. It is of note that the problem is now solved to a larger extent since $G^0_{\{n\}}$ also includes the interaction between a given supramolecule and other supramolecules (which can influence polymorphous transformations). Herewith, general thermodynamic equations maintain their form, but the values of the quantities standing there, are implied to be more exact.

4.4.2. Dissolution or evaporation of nanoparticles

As the second example of a physicochemical process, we consider the dissolution (evaporation) of a nanoparticle. Chemically, this is the reaction of dissociation of a supramolecule into its components. For the sake of simplicity, we assume the supramolecule to consist of structural units of only one type (for example, we meet such situation at the dissolution of a molecular crystal). Then Eq. (4.48) is reduced to the form

$$\mu_n = g^0 n + w^\alpha n + w^{\alpha\sigma} b n^{2/3} + k_B T \ln(c_n \Lambda_n^3), \tag{4.54}$$

where n is the number of the structural units in the supramolecule. As a result of dissociation, the structural units take on independence and acquire the chemical potential

$$\mu = g^0 + w^\beta + k_B T \ln(c \Lambda^3), \tag{4.55}$$

where β symbolizes the solution phase and w^β is the work of transfer of a single structural unit with resting center of mass from a vacuum to a fixed point of the real solution (the sign of the work w^β is determined by the character of interaction of the structural unit with a solvent). Turning to Eqs. (4.44) and (4.45), we conclude that, in the case of a one-component supramolecule under consideration, the de Broglie wavelength of the supramolecule Λ_n and the de Broglie wavelength of a single structural unit Λ are related by the simple equation

$$\Lambda_n = \Lambda n^{-1/2}. \tag{4.56}$$

From the chemical point of view, the dissolution process is a sequence of dissociation reactions of the form

$$B_n \Rightarrow B_{n-1} + B, \quad B_{n-1} \Rightarrow B_{n-2} + B, \ldots \tag{4.57}$$

The corresponding chemical affinity (by the first reaction example) is

$$\mathcal{A}_n = \mu_n - \mu_{n-1} - \mu. \tag{4.58}$$

When substituting Eqs. (4.54) and (4.55) in Eq. (4.58), we consider the quantities w_i^{α}, $w_i^{\alpha\sigma}$, and b to be independent of n for the sake of simplicity. As a result, also accounting for Eq. (4.56), we obtain

$$\mathcal{A}_n = w^{\alpha} - w^{\beta} + w^{\alpha\sigma} b[n^{2/3} - (n-1)^{2/3}] - k_B T \ln(c\Lambda^3) + k_B T \ln \frac{c_n n^{-3/2}}{c_{n-1}(n-1)^{-3/2}}. \tag{4.59}$$

Evidently, the work difference $w^{\alpha} - w^{\beta}$ is the work of transfer of a structural unit from solution to the interior of the supramolecule, $w^{\beta\alpha}$ (we remind that the subscript sequence indicates the direction of transfer). The quantity $w^{\beta\alpha}$ is negative, but the reverse quantity $w^{\alpha\beta}$ is positive (the transfer is accompanied by the rupture of bonds in the supramolecule):

$$w^{\alpha} - w^{\beta} \equiv w^{\beta\alpha} = -w^{\alpha\beta}. \tag{4.60}$$

Using the binomial expansion, we come to the relationship

$$n^{2/3} - (n-1)^{2/3} \approx \frac{2}{3} n^{-1/3} \tag{4.61}$$

that turns to be an acceptable approximation practically for all n. We now turn to the last term in Eq. (4.59). Let us assume that supramolecules of sort $n-1$ were absent in the initial state and they all have been formed by the removal of a structural unit from supramolecules of sort n. Then we may set $c_n = c_{n-1}$ if neglecting the system volume change at dissolution. As a result, the last term in (4.59) will differ from zero only at the expense of the difference of the numbers n and $n-1$, so that the last term will amount fractions of $k_B T$. Under such conditions, the last term in (4.59) becomes negligible and may be omitted. We now rewrite Eq. (4.59), accounting for (4.60) and (4.61), in the form

$$A_n \approx -w^{\alpha\beta} + \frac{2}{3} w^{\alpha\sigma} b n^{-1/3} - k_B T \ln(c\Lambda^3). \tag{4.62}$$

The augend on the right-hand side of Eq. (4.62) is negative and constant, whereas the addend is positive and n-dependent. The product $c\Lambda^3$ is of the meaning of a volume fraction (and is close to the real volume fraction for structural units of atomic dimensions) and, therefore, is always smaller than unity. Hence, the last term on the right-hand side of (4.62) is also positive. At a fixed temperature, it depends only on concentration and increases with decreasing concentration. Evidently, irrespective of the supramolecule size, the last term will secure a positive value for the whole right-hand side of (4.62). So we arrive at the condition $\mathcal{A}_n > 0$ that means that the dissolution process develops. We have $\mathcal{A}_n = 0$ at equilibrium. Then Eq. (4.62) immediately yields the detailed expression for the solubility of a particle of size n:

$$c \approx \frac{1}{\Lambda^3} \exp\left\{ \frac{-w^{\alpha\beta} + (2/3) w^{\alpha\sigma} b n^{-1/3}}{k_B T} \right\}. \tag{4.63}$$

It is seen form (4.63) that the particle solubility increases with decreasing the particle size. At passing to a macroscopic solid ($n \to \infty$), the solubility acquires a constant value determined by the work on escaping a structural unit from the solid bulk to the solution:

$$c \approx \frac{1}{\Lambda^3} \exp\left(-\frac{w^{\alpha\beta}}{k_B T}\right). \tag{4.64}$$

Thus, we see that Eq. (4.62) well describes all known regularities of dissolution.

Summing up all Eqs. (4.58), we can write the affinity of complete dissolution of a particle consisting of n structural units as

$$\mathcal{A} = \mu_n - n\mu. \tag{4.65}$$

By substituting Eqs. (4.54) and (4.55) in Eq. (4.65) and accounting for (4.56), we obtain

$$\mathcal{A} = -w^{\alpha\beta}n + w^{\alpha\sigma}bn^{2/3} - nk_B T \ln(c\Lambda^3) + k_B T \ln(c_n \Lambda^3 n^{-3/2}). \tag{4.66}$$

Neglecting a change in the system volume at dissolution, we can write the mass balance condition as $c = c_n n$. Then we may neglect the last term in (4.66) at a sufficiently large n to obtain

$$\mathcal{A} \approx -w^{\alpha\beta}n + w^{\alpha\sigma}bn^{2/3} - nk_B T \ln(c_n n \Lambda^3). \tag{4.67}$$

The process will develop at $\mathcal{A} > 0$. Therefore, we can write the condition of complete dissolution of nanoparticles at a given concentration c_n as

$$-w^{\alpha\beta}n + w^{\alpha\sigma}bn^{2/3} - nk_B T \ln(c_n n \Lambda^3) > 0, \tag{4.68}$$

where c_n plays the role of a constant. The exact analytical solution of this inequality is problematic. However, in the case when the logarithmic term is negligible, the approximate solution is found at once

$$n^{1/3} < \frac{bw^{\alpha\sigma}}{w^{\alpha\beta}}. \tag{4.69}$$

The particular final result depends on the value of the right-hand side of Eq. (4.69). However, the principal significance of this formula is that it shows the possibility of the particle size boundary below which the stable existence of the particles becomes impossible (they dissolve spontaneously). In the size region below the boundary, particles can arise only by fluctuations, and this statement is known to be the cornerstone of the whole physical theory of phase nucleation. Thus, we see that the chemical approach leads to the same conclusions as the phase approach.

In Eq. (4.59) we assumed the concentration of supramolecules of different size to be equal since they change to each other in the simultaneous dissolution process. We now consider the case of equilibrium between supramolecules of different sizes but then, evidently, of different concentrations. Returning to Eq. (4.66), we should now set $\mathcal{A} = 0$ and write the equilibrium condition as

$$c_n = c^n \Lambda^{3n-1} n^{3/2} \exp\left[\frac{-w^{\alpha\beta}n + w^{\alpha\sigma}bn^{2/3}}{k_B T}\right]. \tag{4.70}$$

Now already the concentration c plays the role of a constant, and Eq. (4.70) shows that supramolecular homologues of various mass, each homologue being with its individual concentration c_n, can be in equilibrium with free structural units of a given concentration. We remind that the quantities $w^{\alpha\beta}$ and $w^{\alpha\sigma}$ include the interaction between supramolecules, and, therefore, $w^{\alpha\beta}$ and $w^{\alpha\sigma}$ themselves are dependent on n and c_n. Only in the case of a dilute system when such interaction is negligible (this means that the activity coefficient $f_{\{n\}}$ in Eq. (4.43) is unity), the right-hand side of Eq. (4.70) is an explicit function of n and yields explicitly the equilibrium distribution of supramolecular homologues. Of course, a reader has noticed that Eq. (4.70) contains the mass action law. Actually, our derivation was reduced to finding an expression for the mass-action-law constant in terms of the parameters of the system under consideration.

5. Line tension and wetting

The line tension as a concept of surface thermodynamics seems to be introduced by Gibbs who wrote about "a certain linear tension" in his theory of capillarity [7]. Nevertheless, the wide investigation of this quantity was undertaken a century later and is in full play now. At first sight, linear phenomena should be simpler than surface ones for the reason that the number of dimensions for a line is smaller by one than that for a surface. This would be true if we actually dealt with a one-dimensional system when considering a linear boundary in surface thermodynamics. In reality, however, we deal with a three-dimensional system when considering both surface and linear phenomena. The difference is that we refer excess thermodynamic quantities of a three-dimensional system to a surface in the first case and to a line in the second case. As a result, linear phenomena turn to be more complex than surface ones both experimentally and theoretically. Experimentally, line tension is typically small and is much more difficult for measuring than surface tension. Theoretically, line tension is more complicated than surface tension because only two bulk phases can meet at a surface, whereas several bulk and also surface phases can meet simultaneously at a line.

A review on linear phenomena was given earlier [1], and we only complement it here in some aspects. Importantly, the material collected gives evidence that linear phenomena can occur in a variety of systems with line tensions of different behavior. Practically, we have several line tensions which should be distinguished and classified. So it is useful to begin this section with a modern classification of line tension [115].

5.1. Classification of line tension

5.1.1. Mechanical and thermodynamic line tension

Gibbs [7] was first to distinguish between two definitions of surface tension for solids, the first defining surface tension γ (see Section 3.2) as a mechanical force along the surface per unit perimeter length (an excess mechanical stress) and the second defining surface tension σ (see Section 3.4) thermodynamically as the work (a change in a corresponding thermodynamic potential) of formation of a new surface per unit area. The mechanical surface tension can be different for different directions on the surface, so that the mechanical surface tension γ_k along the direction k is related to the surface excess stress tensor $\hat{\gamma}$ as

$$\boldsymbol{\gamma}_k = \hat{\gamma} \cdot \mathbf{n}_k \tag{5.1}$$

where $\mathbf{n}_k$ is the unit vector along the direction k and γ_k should also be understood as a vector (as a scalar product of a tensor and a vector). The scalar surface tension γ is defined as half of the trace of tensor $\hat{\gamma}$ (see Eq. (3.13)). Comparing γ and σ, the thermodynamic theory shows these quantities to be different at the existence of the chemical potential gradients near the surface (see Eq. (3.79)). For this reason, the difference between γ and σ can be also realized for non-equilibrium fluid interfaces. As was discussed first by Shuttleworth [78], the mechanical surface tension γ and the thermodynamic surface tension σ are also different in their use in the fundamental relationships of the theory of capillarity. For example, γ is used in the Laplace equation and σ is used in the Young equation for wetting. It is important to mention that, according to the stability conditions, σ is always positive (a body with negative σ would disintegrate spontaneously), whereas γ can be of any sign except for the case of an equilibrium fluid interface when $\gamma = \sigma > 0$.

Similarly, the mechanical line tension τ and the thermodynamic line tension κ are defined. Approaching a linear interface, the excess surface stress tensor $\hat{\gamma}$ becomes a function of the coordinate N normal to the dividing line and takes an increment $\Delta\hat{\gamma}(N)$ as compared with its value far from the line. Then τ is defined as [1]

$$\tau \equiv \sum_i \int_0^\infty \Delta\hat{\gamma}_i \, \mathrm{d}N_i \tag{5.2}$$

where the summation is carried out over all surfaces meeting at the line. As is seen from (5.2), τ is of a tensorial origin, although τ often consists of a single component directed along the line. The thermodynamic line tension κ is defined as the work of formation (per unit length) of a new line. κ is a thermodynamic counterpart of τ and a one-dimensional analogue of σ. For a one-component system, σ and κ are surface and line free energy, respectively. Concerning the use of τ and κ in various relationships of the theory of capillarity, one can follow a general rule that τ should be used in combination with (or instead of) γ and κ should be used in combination with (or instead of) σ. As for the sing of τ and κ, it depends on the line tension type to be considered in the subsequent sections.

5.1.2. Line tension in two-dimensional systems

In two-dimensional systems, phases are separated not by surfaces but by lines, and interfacial tension becomes linear. In this case, the line tension is a natural analogue of surface tension at lowering the space dimensionality by one, so that the basic properties of interfacial tension derived in a general way remain valid. In particular, κ is positive by the stability conditions, whereas τ can be of any sign except for the case of a fluid two-dimensional system when $\tau = \kappa > 0$. The last condition, however, can change when a two-dimensional system is on a solid substrate.

The thermodynamics of line tension in fluid two-dimensional systems has been described in detail in Ref. [50]. In particular, there is an analogue of the generalized Laplace equation

$$\pi^{\alpha} - \pi^{\beta} = \frac{\tau}{r} + \frac{\partial \tau}{\partial r}, \tag{5.3}$$

where π is the two-dimensional pressure, r the curvature radius of a dividing line, α and β are the symbols of adjacent two-dimensional phases. For the line of tension (an analogue of Gibbs' surface of tension) $\partial\tau/\partial r = 0$ and Eq. (5.3) takes a traditional form of the Laplace equation.

In reality, a two-dimensional system (e.g. an insoluble surfactant monolayer) is situated between two bulk phases, so it is possible to introduce the notion of surface tension for the two-dimensional system. Then Eq. (5.3) is written

$$\gamma^{\beta} - \gamma^{\alpha} = \frac{\tau}{r} + \frac{\partial \tau}{\partial r}. \tag{5.4}$$

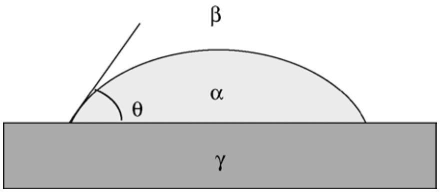

Fig. 13. The equilibrium contact angle of a two-dimensional drop.

In an equilibrium fluid system, Eq. (5.4) can be also written in terms of σ and κ since $\gamma = \sigma$ and $\tau = \kappa$. If, however, one of the phases is solid, $\gamma \neq \sigma$ and $\tau \neq \kappa$, but Eq. (5.4) including force quantities remains valid.

Another basic equation of the theory of capillarity, the Young equation, originally includes energetic quantities. It is easy to derive a two-dimensional analogue of the Young equation [115]. Let us consider a two-dimensional wetting drop (phase α) at the boundary of two-dimensional phases β (a liquid or a gas) and γ (a solid, the symbol γ used below as a superscript not to be confused with surface tension). To find an equilibrium contact angle θ (Fig. 13), we apply the two-dimensional Gibbs–Curie principle as the condition of a minimum of line free energy at a constant area of phase α:

$$\kappa^{\alpha\beta}L^{\alpha\beta} + \kappa^{\alpha\gamma}L^{\alpha\gamma} + \kappa^{\beta\gamma}L^{\beta\gamma} + 2\eta = \text{a minimum}, \tag{5.5}$$

where L is the line length (the double superscripts indicate the phases between which a line is located) and η is the work of formation of the point of the triple contact αβγ. By differentiating (5.5) with the relationships $\mathrm{d}L^{\beta\gamma} = -\mathrm{d}L^{\alpha\gamma}$ and $\mathrm{d}L^{\alpha\beta}/\mathrm{d}L^{\alpha\gamma} = \cos\theta$ in mind, we obtain

$$\kappa^{\beta\gamma} = \kappa^{\alpha\gamma} + \kappa^{\alpha\beta}\cos\theta + L^{\alpha\beta}\frac{\partial\kappa^{\alpha\beta}}{\partial L^{\alpha\gamma}} + L^{\alpha\gamma}\frac{\partial\kappa^{\alpha\gamma}}{\partial L^{\alpha\gamma}} + 2\frac{\partial\eta}{\partial L^{\alpha\gamma}}. \tag{5.6}$$

If the width of the two-dimensional drop is larger than the total effective thickness of the linear interfaces αβ and αγ, the line tensions $\kappa^{\alpha\beta}$ and $\kappa^{\alpha\gamma}$ can be taken as constants. Then, for a not very small drop, Eq. (5.6) becomes

$$\kappa^{\beta\gamma} = \kappa^{\alpha\gamma} + \kappa^{\alpha\beta}\cos\theta + 2\frac{\partial\eta}{\partial L^{\alpha\gamma}}. \tag{5.7}$$

In fact, the point work η depends only on the contact angle θ which is uniquely determined by the length of the linear interface αγ at the constancy of the drop area. For example, in the case of a rectilinear boundary of a solid phase γ when the shape of the two-dimensional drop is a circular segment as is shown in Fig. 13 (two-dimensional phases are usually horizontal and are not influenced by gravity),

$$\frac{\mathrm{d}\theta}{\mathrm{d}L^{\alpha\gamma}} = -\frac{\theta - \sin\theta\cos\theta}{(1-\theta\cot\theta)L^{\alpha\gamma}} < 0, \tag{5.8}$$

and, therefore,

$$\frac{\mathrm{d}\eta}{\mathrm{d}L^{\alpha\gamma}} = -\frac{1}{L^{\alpha\gamma}}\frac{\partial\eta}{\partial\theta}\frac{\theta - \sin\theta\cos\theta}{1-\theta\cot\theta}. \tag{5.9}$$

It is seen from Eq. (5.9) that the last term in (5.7) is negligible for a two-dimensional drop of a sufficiently large length. Then Eq. (5.7) becomes

$$\kappa^{\beta\gamma} = \kappa^{\alpha\gamma} + \kappa^{\alpha\beta}\cos\theta, \tag{5.10}$$

which is a direct analogue of the Young equation.

5.1.3. Line tension of multiphase contact line

For the boundary of contact of three or more three-dimensional phases, it is also necessary to distinguish between the mechanical line tension τ and its thermodynamic analogue κ. These quantities coincide for fluid boundaries, and the general condition of equilibrium can be written

$$\frac{\tau}{r} + \frac{\partial\tau}{\partial r} = -\sum_i \gamma_i \cos\varphi_i, \tag{5.11}$$

where r is the curvature radius of the dividing line (where the dividing surfaces of the phases meet), φ the angle between a dividing surface and the osculating plane of the dividing line, and i is the ordinal number of a surface. For a lens of phase α at the boundary of phases β and γ (Fig. 14), we have $\gamma_1 = \gamma^{\beta\gamma}$, $\varphi_1 = \pi$, $\varphi_2 = \theta_2$, and $\varphi_3 = \theta_3$ (θ_i are the lens contact angles), and Eq. (5.11) takes the form [116]

$$\frac{\tau}{r} + \frac{\partial\tau}{\partial r} = \gamma^{\beta\gamma} - \gamma_2\cos\theta_2 - \gamma_3\cos\theta_3 \tag{5.12}$$

The quantities τ and γ in Eq. (5.12) can be replaced by κ and σ, respectively. The derivative $\partial\tau/\partial r$ can be interpreted doubly as corresponding either to a real variation of the line and the angles or to an imaginary displacement of the location of the dividing line. In the analysis of the dependence of line tension on the dividing line location [116], the problem is that, in reality, there are no surfaces and line but a complex spatial distribution of stresses, which we try to describe with the aid of simple geometrical images. The image of a stretched surface is Gibbs' surface of tension, a particular location of the dividing surface. Similarly, there exists a line of tension for the three-phase contact for which $\partial\tau/\partial r = 0$, and the problem is whether the line of tension coincides or not with the line of intersection of the surfaces of tension. If yes, then a mechanical problem is formulated for a heterogeneous medium with surface and line stresses, which can be described under static or dynamic conditions at an arbitrary configuration [20].

For the line of tension, Eq. (5.12) is written as

$$\frac{\tau}{r} = \gamma^{\beta\gamma} - \gamma_2\cos\theta_2 - \gamma_3\cos\theta_3. \tag{5.13}$$

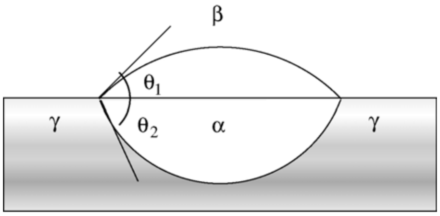

Fig. 14. The contact angles of a liquid lens.

Neglecting line tension, Eqs. (5.12) and (5.13) and, in the general case, Eq. (5.11) express the Davydov equation [117] more widely known as Neumann's triangle [118].

We now turn to analogues of the Young equation. Concerning the case of wetting the flat surface of a rigid solid ($\gamma_2 = \gamma^{\alpha\gamma}$, $\theta_2 = 0$, $\gamma_3 = \gamma^{\alpha\beta}$), the lens of phase α possesses a single contact angle θ, and it seems to be enough to rewrite Eq. (5.13) in the form [119]

$$\frac{\tau}{r} = \gamma^{\beta\gamma} - \gamma^{\alpha\gamma} - \gamma^{\alpha\beta}\cos\theta \tag{5.14}$$

However, Eq. (5.14) has two disadvantages. First, Eq. (5.14) does not include the force of reaction of a solid to the applied force of the surface tension of a wetting liquid. The stress distribution in the solid near the three-phase contact line is such as not to be imitated by a stretched line, so that the formal including this stress (or only its tangential component) in τ changes the meaning of the line tension. Second, if even we accept such a procedure, mechanical Eq. (5.14) does not produce a thermodynamically equilibrium contact angle since any value of θ is mechanically equilibrium (a force applied to a solid in any direction is equilibrated by internal stresses in the solid).

Only the energetic approach yields a correct formulation of the problem of a thermodynamically equilibrium contact angle. The energetic analogue of Eq. (5.14) is [120–124]

$$\frac{\kappa}{r} = \sigma^{\beta\gamma} - \sigma^{\alpha\gamma} - \sigma^{\alpha\beta}\cos\theta. \tag{5.15}$$

In contrast with Eq. (5.14), Eq. (5.15) determines a unique possible equilibrium contact angle. More general relationships were obtained by Toshev [125] (see also [126])

$$\sigma^{\beta\gamma} = \sigma^{\alpha\gamma} + \sigma^{\alpha\beta}\cos\theta + \frac{\kappa}{r}\cos\varphi \tag{5.16}$$

and by the author [1,127]

$$\sigma^{\beta\gamma} = \sigma^{\alpha\gamma} + \sigma^{\alpha\beta}\cos\theta + \left(\frac{\kappa}{r} + \frac{\partial\kappa}{\partial r}\right)\cos\varphi, \tag{5.17}$$

where φ is the angle between the wetted solid surface and the local osculating plane of the three-phase contact line. As compared with Eq. (5.16), Eq. (5.17) includes a correction related to the dependence of κ on the line curvature radius. The larger the line curvature radius (or the smaller line tension), the smaller is the influence of line tension according to Eqs. (5.15)–(5.17) which change to the classical Young equation as $r \to \infty$.

Concerning the sign of the line tension of the three-phase contact line, the rigorous thermodynamic analysis of the stability conditions for heterogeneous systems with taking into account surface and linear phenomena [1,128] does not lead to a certain sign for the line tension of the three-phase contact line (both τ and κ) even in the case of a fluid system. Moreover, the stability conditions are better satisfied with a negative (but restricted in value) line tension in some cases. Both positive and negative values of κ for the three-phase contact line are met in the literature as a result of experimental and theoretical estimations. We will return to the analysis of Eq. (5.17) in Section 5.2.

5.1.4. Effective line tension on deformable solids

As was already noted, the force of surface tension of a liquid ($\gamma^{\alpha\beta}$) acts on a solid at wetting. Because of a very small thickness of a surface layer, such a force is very concentrated and can cause an appreciable surface strain if the elasticity modulus of the solid is sufficiently low. Such effects are observed for gels, rubbers, and other bodies with a low elasticity modulus, the deformation mainly occurring along the three-phase contact line. The work of deformation W per unit length of the three-phase contact line can be included into line tension. In this way, the effective line tension κ' can be defined [127]

$$\kappa' \equiv \kappa + W \tag{5.18}$$

The work W contains contributions from the volume and surface deformation of a solid and also from the change of the solid configuration in a gravitational field. $W \to 0$ and $\kappa' \to \kappa$ in the limit of large values of the elasticity modulus. In the limit of small values of the elasticity modulus, $\kappa' \to W$ and the line tension changes its physical meaning. Herewith, Eq. (5.17) maintains its validity [127,128] and exhibits a direct influence of deformation on the contact angle value. This effect is well illustrated by the experimental dependence of the contact angle on the size of a drop placed on an easily deformable substrate [129].If a solid is not only easily deformable but also anisotropic, the deformation becomes dependent on the direction on the surface. Then the effective line tension changes when moving along the three-phase contact line. According to Eq. (5.17), the contact angle will be a function of a direction on the surface in this case even if the surface is smooth and quite uniform (the anisotropy of wetting at an ordered surface roughness is well known as caused by capillary forces). The anisotropy of wetting of this kind was discovered [130] at studying the wetting of stretched elastomeric substrates whose internal anisotropy appears due to the orientation of molecular chains along the direction of stretching. The new phenomenon related to effective line tension shows how great can be the role of line tension in surface science.

5.1.5. Line tension of a Plateau border in foams

The line tension of a Plateau border in foams is a direct analogue of the line tension of a three-phase contact line. The difference is that interfaces are replaced with foam films meeting at a Plateau border. The Plateau border profile and the scheme of passing to the line tension are shown in Fig. 15. Neglecting the contact angle at meeting a film and a rectilinear Plateau border, the latter can be considered as phase β filling the space between three touching columns, of radius r, of phase α. The Plateau-border cross-section area A_b is

$$A_b = r^2\left(3^{1/2} - \frac{\pi}{2}\right) \approx 0.1613r^2. \tag{5.19}$$

Depicting each film with a single dividing surface (marked with the symbol γ^F of the film tension in Fig. 15), the films should meet at a line (point O in Fig. 15) to which we may ascribe a certain line tension.

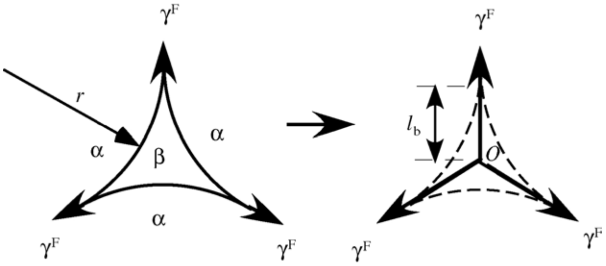

Fig. 15. The Plateau border cross-section and the scheme of passing to the line tension.

We first find the total force f_b acting through the Plateau border cross-section and composed of surface and bulk contributions. The surface contribution is evident to be $\pi r\gamma$ where γ is the ordinary surface tension. According to the Laplace equation, the stress inside the Plateau border is $-p^\beta = -p^\alpha + \gamma/r$. Then the force acting through the bulk cross-section area is $(-p^\alpha + \gamma/r)A_\mathrm{b}$, and the total force is given by the expression

$$f_\mathrm{b} = \pi r\gamma + \left(-p^\alpha + \frac{\gamma}{r}\right)A_\mathrm{b} = -p^\alpha A_\mathrm{b} + \left(3^{1/2} + \frac{\pi}{2}\right)\gamma r, \tag{5.20}$$

where Eq. (5.19) has been used. This force acts through the cross-section shown on the left side of Fig. 15. Introducing now the Plateau border line tension as an excess quantity, we have to compare the force given by Eq. (5.20) with the force

$$-p^\alpha A_\mathrm{b} + 3\gamma^\mathrm{F} l_\mathrm{b} \tag{5.21}$$

corresponding to the right side of Fig. 15, where $l_\mathrm{b} = r/\sqrt{3}$ is the triangle bisectrix length (up to the triangle center). Subtracting (5.21) from (5.20), we arrive at the Plateau border line tension [131,132]

$$\tau = \left(\frac{\pi}{4} - \frac{\sqrt{3}}{2}\right)\gamma^\mathrm{F} r \cong -0.0806\gamma^\mathrm{F} r. \tag{5.22}$$

Similarly to the ordinary surface tension γ, the film tension γ^F is always positive, which yields a negative value for the Plateau border line tension according to Eq. (5.22). Interestingly, still Gibbs predicted a negative value for the Plateau border line tension [7, p. 293]. By its absolute value, the Plateau border line tension is larger than ordinary line tension by several orders of magnitude. For example, setting $\gamma^\mathrm{F} \approx 2\gamma$, $\gamma = 50$ mN m^{-1}, and $r = 0.1$ mm yields $\kappa = -8 \times 10^{-7}$ N against 10^{-10} N as a typical absolute value for the ordinary line tension.

The above model corresponds to a smooth transition from a Plateau border to a film with a zero contact angle. In principle, the contact angle θ is not zero for thin films, although is usually small [133]. For this case, $\gamma^\mathrm{F} = 2\gamma\cos\theta$ and a more exact formula for the Plateau border line tension is [132]

$$\tau = \gamma r\left[\frac{\pi}{2} - \sqrt{3} - 3\theta + \frac{3}{2}\sin 2\theta + \sqrt{3}\sin^2\theta\right]. \tag{5.23}$$

A detailed analysis of the Plateau border line tension and its behavior in a gravitational field was carried out in [131,132].

5.1.6. Line tension of a filament

The line tension as a mechanical quantity can be introduced practically for any capillary body by combining the force of capillary pressure (the product of the capillary pressure p_c and the body cross-section area A) and the force of surface tension (the product of surface tension γ and the cross-section perimeter P). In the vector form, a general formula for the line tension is

$$\boldsymbol{\tau} = -\mathbf{p}_\mathrm{c} A + \oint \boldsymbol{\gamma}\,\mathrm{d}P. \tag{5.24}$$

Herewith, if a body is axial-symmetrical, the line tension is directed along the symmetry axis. The simplest example is a uniform cylindrical filament of radius r. In this case, $p_\mathrm{c} = \gamma/r$, $A = \pi r^2$, $P = 2\pi r$, and

Eq. (5.24) yields

$$\tau = \pi\gamma r. \tag{5.25}$$

An equilibrium shape of a filament or a liquid cylinder of oscillating thickness is an unduloid, which is a figure of revolution whose radius smoothly changes between a minimum and a maximum values, R_1 and R_2. For example, the unduloid shape is typical for liquid bridges connecting solid particles. In cylindrical coordinates r and z, the unduloid surface profile is [134]

$$z = \pm[r_1 F(k,\varphi) + r_2 E(k,\varphi)], \tag{5.26}$$

where F and E are the elliptic integrals of the first and second kind, respectively:

$$F(k,\varphi) = \int \frac{\mathrm{d}\varphi}{(1-k^2\sin^2\varphi)^{1/2}}, \quad E(k,\varphi) = \int (1-k^2\sin^2\varphi)^{1/2}\,\mathrm{d}\varphi, \quad k^2 \equiv \frac{R_2^2 - R_1^2}{R_2^2},$$
$$\sin^2\varphi \equiv \frac{R_2^2 - r^2}{R_2^2 - R_1^2}.$$

The capillary pressure of the unduloid is $2\gamma/(R_1 + R_2)$. Correspondingly, the contribution to the line tension from capillary pressure is

$$-p_c A = -\frac{2\pi r^2\gamma}{R_1 + R_2} \tag{5.27}$$

and changes with r. The contribution from surface tension is

$$2\pi r\gamma\sin\phi = \frac{2\pi\gamma(r^2 + R_1R_2)}{R_1 + R_2} \tag{5.28}$$

and also changes along the axis since the unduloid profile slope ϕ is variable. However, the sum of (5.27) and (5.28) is strictly constant along the axis and makes the unduloid line tension

$$\tau = \frac{2\pi\gamma R_1 R_2}{R_1 + R_2} \tag{5.29}$$

As is seen from Eq. (5.29), the unduloid line tension is positive. This secures the adhesive action of a liquid bridge between solid particles.

5.1.7. Point tension

The further decrease of dimensionality by one leads from line tension to point tension which can also be mechanical (an excess stress at a point) or thermodynamic (the work of formation of a point). Is it possible a classification for point tension? The existence of point tension in a pure two-dimensional system depends on the possibility of realization of one-dimensional phase transitions: if there are no one-dimensional phase transitions, there cannot be a point tension of this type. Point tension is evident to exist in three-phase contact phenomena, as was shown at the derivation of Eqs. (5.6) and (5.7) where the thermodynamic point tension η stands. It should be added that point tension of this type (corresponding to meeting not less than three lines) can be realized also in the three-dimensional space. If a solid is deformable, the introduction of an effective point tension including the deformation work, is possible both in two- and three-dimensional systems, the form of thermodynamic relationships, e.g. of Eq. (5.7), being maintained.

5.2. Line tension and the generalized Young equation

We now return to the generalized Young Eq. (5.17) and the line tension of the three-phase contact line. The Young equation, one of the central relationships of the classical theory of capillarity, was multiply discussed in the literature, and the corresponding survey was presented earlier [1]. We now pay attention to some new results that were obtained recently [135].

5.2.1. Thermodynamic potential of a solid with a sessile drop

Let us consider the system including a substrate, a one-component sessile drop and its vapor. As was explained earlier [1] (see also text before Eq. (3.77)), systems including both solid and fluid phases are better described by a hybrid thermodynamic potential Ω playing the role of free energy with respect to an immobile species and grand thermodynamic potential with respect to mobile species. Neglecting gravity, the expression for Ω of the system under consideration is

$$\Omega = -p^{\alpha}V^{\alpha} - p^{\beta}V^{\beta} + \sigma^{\alpha\beta}A^{\alpha\beta} + \sigma^{\alpha\gamma}A^{\alpha\gamma} + \sigma^{\beta\gamma}A^{\beta\gamma} + \kappa L \tag{5.30}$$

where p is the pressure, V the volume, A the surface area, L the length of the three-phase contact line; the single and double superscripts mark corresponding phases and interfaces, respectively.

If there is no overlapping of the liquid/substrate and liquid/vapour interfaces in the central part of the drop, the drop profile will be spherical far from the three-phase contact line according to the condition of mechanical equilibrium between the liquid and the vapour in the absence of gravity. Overlapping of the surface layers is responsible for the formation of an underlying (precursor) film modifying the solid surface and leading to a difference between $\sigma^{\beta\gamma}$ and the surface tension of a "bare" solid surface. The possible presence of the precursor film on the substrate is taken into account in Eq. (5.30) by the term $\sigma^{\beta\gamma}A^{\beta\gamma}$. Neglecting the precursor film thickness, one can assume the entire sessile drop to have the shape of a spherical segment. Its radius and contact angle can be found from the condition of a minimum of the potential Ω.

We define the excess quantities standing in Eq. (5.30) by choosing the Gibbs dividing surfaces as the segment spherical surface with radius R and contact angle θ and flat surfaces $\alpha\gamma$ and $\beta\gamma$ in the framework of the Gibbs method. Using the spherical segment geometry yields an expression for Ω in terms of R and θ:

$$\Omega = \frac{-(p^{\alpha} - p^{\beta})\pi R^3(2+\cos\theta)(1-\cos\theta)^2}{3} + 2\pi\sigma^{\alpha\beta}R^2(1-\cos\theta) - (\sigma^{\beta\gamma} - \sigma^{\alpha\gamma})\pi R^2\sin^2\theta + 2\pi\kappa R\sin\theta - p^{\beta}V_t - \sigma^{\beta\gamma}A_t, \tag{5.31}$$

where $V_t \equiv V^{\alpha} + V^{\beta}$ is the total volume of the fluid phases and $A_t \equiv A^{\alpha\gamma} + A^{\beta\gamma}$ is the total area of the solid substrate. Evidently, potential Ω also depends on the chemical potential μ of molecules in the system and on the temperature T of the system.

5.2.2. The dependence of the line tension on the dividing surface location

Let us see what condition follows from the variation of the location of the drop dividing surface at maintaining the physical state of the system, i.e. from the choice of various radii R for the drop spherical segment at fixing all physical characteristics within the interface. Naturally, thermodynamic potential Ω (as well as the state parameters for the bulk phases) cannot depend on the pure imaginary variation of radius R. Marking such variations with square brackets, we write this condition as

$$\left[\frac{\mathrm{d}\Omega}{\mathrm{d}R}\right] = 0. \tag{5.32}$$

When applied to a free drop ($\theta = \pi, A_t = 0$) Eqs. (5.31) and (5.32) lead to the Kondo equation (cf. Eq. (3.21))

$$p^{\alpha} - p^{\beta} = \frac{2\sigma^{\alpha\beta}}{R} + \left[\frac{\mathrm{d}\sigma^{\alpha\beta}}{\mathrm{d}R}\right] \tag{5.33}$$

where the pressure difference plays the role of a constant. The solution of differential Eq. (5.33) is

$$\sigma^{\alpha\beta} = \frac{K}{R^2} + cR, \tag{5.34}$$

where the constant K is the work of the drop formation and $c \equiv (p^{\alpha} - p^{\beta})/3$. The plot of the function (5.34) is characterized by a unique minimum of $\sigma^{\alpha\beta}$. The location of the dividing surface at the minimum is called surface of tension, for which Eq. (5.33) changes to the Laplace equation. In terms of the minimum coordinates R_{st} and $\sigma_{st}^{\alpha\beta}$, the constants K and c are

$$K = \frac{\sigma_{st}^{\alpha\beta} R_{st}^2}{3}, \quad c = \frac{2\sigma_{st}^{\alpha\beta}}{3R_{st}}. \tag{5.35}$$

In our case, similar to the case of a free drop, all dividing surface positions are concentric. However, they are segmental but not sectorial in the case of a sessile drop (Fig. 16), so that the relationships hold

$$R\sin\theta = r, \quad R\cos\theta = h = \text{a constant}, \tag{5.36}$$

where r is the three-phase contact line radius and h is the distance from the curvature center to the solid surface. Putting now Eq. (5.31) into Eq. (5.32) and taking into account Eq. (5.36), we obtain

$$\begin{aligned} &-2\pi R^2(p^{\alpha} - p^{\beta})(1-\cos\theta) + 2\pi R\sigma^{\alpha\beta}(2-\cos\theta) + 2\pi R^2(1-\cos\theta)\left[\frac{\mathrm{d}\sigma^{\alpha\beta}}{\mathrm{d}R}\right] \\ &-2\pi R(\sigma^{\beta\gamma} - \sigma^{\alpha\gamma}) + \frac{2\pi\kappa}{\sin\theta} + 2\pi R\sin\theta\left[\frac{\mathrm{d}\kappa}{\mathrm{d}R}\right] = 0. \end{aligned} \tag{5.37}$$

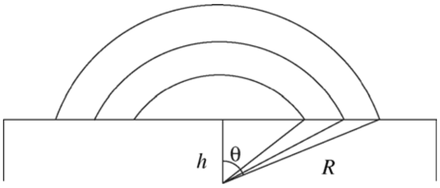

Fig. 16. The dividing surfaces and dividing lines for a spherical segment on a solid substrate.

If we now express the surface tension derivative with the aid of Eq. (5.33), Eq. (5.37) immediately leads to the generalized Young equation (cf. Eq. (5.17))

$$\sigma^{\beta\gamma} - \sigma^{\alpha\gamma} = \sigma^{\alpha\beta}\cos\theta + \frac{\kappa}{r} + \left[\frac{\mathrm{d}\kappa}{\mathrm{d}r}\right]. \tag{5.38}$$

The left-hand side of Eq. (5.38) is a constant at a fixed physical state. This allows rewriting Eq. (5.38) as a differential equation

$$\left[\frac{\mathrm{d}\kappa}{\mathrm{d}r}\right] + \frac{\kappa}{r} + \frac{a}{(r^2 + h^2)^{3/2}} = b, \tag{5.39}$$

where

$$a \equiv Kh, \quad b \equiv \sigma^{\beta\gamma} - \sigma^{\alpha\gamma} - ch. \tag{5.40}$$

Thus, three constants h, a, and b are present in Eq. (5.39). The solution of Eq. (5.39) is

$$\kappa = \frac{br}{2} + \frac{a}{r(r^2 + h^2)^{1/2}} + \frac{d}{r}, \tag{5.41}$$

where the integration constant d can be expressed through the radius $r = r_{lt}$ of the dividing surface on the substrate plane at the extreme point (a minimum) for the line tension κ as a function of r:

$$d = \frac{br_{lt}^2}{2} + \frac{a(2r_{lt}^2 + h^2)}{(r_{lt}^2 + h^2)^{3/2}}. \tag{5.42}$$

By analogy with the surface of tension, the dividing line characterized by $r = r_{lt}$ where $[\mathrm{d}\kappa/\mathrm{d}r] = 0$ can be called the line of tension [116]. With this choice of a dividing surface, the generalized Young Eq. (5.38) takes the simplest form

$$\sigma^{\beta\gamma} - \sigma^{\alpha\gamma} = \sigma^{\alpha\beta}\cos\theta + \frac{\kappa_{lt}}{r_{lt}}, \tag{5.43}$$

where κ_{lt} is the value of κ at $r = r_{lt}$. The line tension for the line of tension κ_{lt} can also be expressed as

$$\kappa_{lt} = br_{lt} - \frac{ar_{lt}}{(r_{lt}^2 + h^2)^{3/2}}. \tag{5.44}$$

According to Eqs. (5.35) and (5.40), the constant a is positive, whereas the constant b can be either positive or negative depending on the substrate wettability. Since, obviously, $r_{lt} > 0$, the value of κ_{lt} can be either positive (at $b > a/(r_{lt}^2 + h^2)^{3/2}$) or negative (at $b < a/(r_{lt}^2 + h^2)^{3/2}$).

We designate as r_{st} the radius of the dividing line, on the substrate, corresponding to the choice of the surface of tension as a dividing surface between the liquid and the vapor. From the above phenomenological analysis, it is hard to deduce how the quantities r_{st} and r_{lt} are related to each other. One can only expect that their coincidence can be completely random and rare. In particular, this means that there is no reason for neglecting the last term in Eq. (5.38) when using the surface of tension (as well as the equimolecular surface) as a dividing surface between the liquid and the vapor.

5.2.3. The equilibrium condition at the three-phase contact line

In terms of thermodynamic potential Ω, the equilibrium principle can be formulated as

$$\left(\frac{\partial \Omega}{\partial \theta}\right)_{T,\mu,R} = 0. \tag{5.45}$$

The location of a dividing surface is now considered as given at fixed conditions (and is arbitrary since the conditions themselves are arbitrary). Fixing the temperature and chemical potential means the constancy of all state parameters of the system including the curvature radius R of the drop surface. By contrast, the distance h (see Fig. 16) becomes variable. Herewith the relationship is fulfilled

$$\left(\frac{\partial r}{\partial \theta}\right)_{T,\mu,R} = R\cos\theta. \tag{5.46}$$

Putting Eq. (5.31) in Eq. (5.45) with accounting (5.46) yields

$$\begin{aligned} &-(p^{\alpha}-p^{\beta})\pi R^{3}\sin^{3}\theta + 2\pi\sigma^{\alpha\beta}R^{2}\sin\theta + 2\pi\kappa R\cos\theta - 2\pi(\sigma^{\beta\gamma}-\sigma^{\alpha\gamma})R^{2}\sin\theta\cos\theta \\ &\quad + 2\pi R^{2}\sin\theta\cos\theta\left(\frac{\partial \kappa}{\partial r}\right)_{T,\mu} = 0. \end{aligned} \tag{5.47}$$

It is implied here that the line tension $\kappa = \kappa(T, \mu, r)$ does not explicitly depend on the contact angle θ. If we now replace the difference $p^{\alpha} - p^{\beta}$ by the expression following from the Kondo Eq. (5.33), Eq. (5.47) changes to the generalized Young equation at a certain given (by external conditions) location of the dividing surface and at a dividing line corresponding to this dividing surface:

$$\sigma^{\beta\gamma} - \sigma^{\alpha\gamma} = \sigma^{\alpha\beta}\cos\theta + \frac{\kappa}{r} + \left(\frac{\partial \kappa}{\partial r}\right)_{T,\mu} - \frac{r\tan\theta}{2}\left[\frac{\mathrm{d}\sigma^{\alpha\beta}}{\mathrm{d}R}\right]. \tag{5.48}$$

Taking the surface of tension as the dividing surface, Eq. (5.48) becomes

$$\sigma^{\beta\gamma} - \sigma^{\alpha\gamma} = \sigma^{\alpha\beta}\cos\theta + \frac{\kappa}{r} + \left(\frac{\partial \kappa}{\partial r}\right)_{T,\mu}, \tag{5.49}$$

which coincides with Eq. (5.17) at $\varphi = 0$. Comparing the right-hand sides of Eqs. (5.38) and (5.49), we arrive at the relationship

$$\left(\frac{\partial \kappa}{\partial r}\right)_{T,\mu} = \left[\frac{\mathrm{d}\kappa}{\mathrm{d}r}\right] + \frac{r\tan\theta}{2}\left[\frac{\mathrm{d}\sigma^{\alpha\beta}}{\mathrm{d}R}\right]. \tag{5.50}$$

Eq. (5.50) relates the physical dependence of the line tension on the radius of the three-phase contact line at given temperature and chemical potential to the imaginary dependence of the line and surface tensions on the dividing surface location. If the surface of tension is chosen as a dividing surface, the surface tension derivative in Eq. (5.50) becomes zero, and we arrive at a remarkable relationship

$$\left(\frac{\partial \kappa}{\partial r}\right)_{T,\mu} = \left[\frac{\mathrm{d}\kappa}{\mathrm{d}r}\right]. \tag{5.51}$$

Eq. (5.51) means that, with this choice of a dividing surface, the derivative of the line tension with respect to radius of the three-phase contact line at constant temperature and chemical potential coincides with the line tension derivative at an imaginary shift of the dividing surface at fixed physical state of the system.

5.2.4. *The role of linear adsorption*

As it was shown above, there remains a possibility for the line tension variation together with the radius of the three-phase contact line even when a certain choice is made for the location of the dividing surface between the liquid and the vapor and all the state parameters of the bulk phases and surfaces, like the temperature and the chemical potential, are fixed. The corresponding derivative stands in the equilibrium condition expressed by Eq. (5.48). To write the expression for the total differential of the line tension, it is sufficient to supplement the partial differential corresponding to this derivative with the terms with differentials of temperature and chemical potential:

$$\mathrm{d}\kappa = \left(\frac{\partial\kappa}{\partial r}\right)_{T,\mu}\mathrm{d}r - s_l\,\mathrm{d}T - \Lambda\,\mathrm{d}\mu. \tag{5.52}$$

Coefficients s_l and Λ are known as the linear excesses of entropy and matter, respectively, related to the unit length of the three-phase contact line. Eq. (5.52) is the linear adsorption equation [136,137] called by analogy with the Gibbs adsorption equation for surfaces (the excess Λ plays the role of a linear adsorption). At a constant temperature, Eq. (5.52) yields an important relationship

$$\left(\frac{\partial\kappa}{\partial r}\right)_{T,\mu} = \frac{\mathrm{d}\kappa}{\mathrm{d}r} + \Lambda\frac{\mathrm{d}\mu}{\mathrm{d}r}. \tag{5.53}$$

In particular, Eq. (5.53) permits us finding the partial derivative $(\partial\kappa/\partial r)_{T,\mu}$ from the linear adsorption value Λ and the derivatives $\mathrm{d}\kappa/\mathrm{d}r$ and $\mathrm{d}\mu/\mathrm{d}r$ along equilibrium states. For example, such calculations are possible by applying the density functional method based on the models for intermolecular potentials [138–140] and by applying the method of the functional of the local thickness of a liquid film based on the approximations for the isotherm of the disjoining pressure as a function of the film thickness [140–142]. Both these methods are capable of independent calculating the contact angle, the chemical potential of molecules in a system and the linear adsorption as functions of the dividing line radius.

Some assertions can be made without using any specific model. Let us assume that the line tension κ and the linear adsorption Λ expressed as functions of the equilibrium contact line radius r have the following asymptotic behavior:

$$\kappa = \kappa_0 + O(r^{-1}), \quad \Lambda = \Lambda_0 + O(r^{-1}) \tag{5.54}$$

with the finite limits κ_0 and Λ_0 corresponding to the bulk coexistence at $\mu \to \mu_0$ (where $r \to \infty$, i.e. the contact line becomes straight). Under assumption of incompressible liquid, we have for the pressure difference

$$p^{\alpha} - p^{\beta} \approx \frac{\mu - \mu_0}{v^{\alpha}}, \tag{5.55}$$

where v^{α} is the molecular volume in phase α. Using the Laplace equation and Eq. (5.54) yields $\mathrm{d}\mu/\mathrm{d}r = -2\sigma^{\alpha\beta}v^{\alpha}r^{-2}\sin\theta$, which leads to the following estimation:

$$\Lambda\frac{\mathrm{d}\mu}{\mathrm{d}r} = -2\Lambda_0\sigma_0^{\alpha\beta}v^{\alpha}r^{-2}\sin\theta_0 + O(r^{-3}), \tag{5.56}$$

where $\sigma_0^{\alpha\beta}$ is the value of the surface tension $\sigma^{\alpha\beta}$ at $\mu = \mu_0$ and θ_0 is the limiting macroscopic value of the contact angle. According to Eq. (5.54), there is an estimation $\mathrm{d}\kappa/\mathrm{d}r = O(r^{-2})$. It means that under the assumptions expressed in (5.54), the partial derivative $(\partial\kappa/\partial r)_{T,\mu} = O(r^{-2})$, while for the term κ/r on the right-hand side of the generalized Young Eq. (5.49), the estimation $\kappa/r = \kappa_0/r + O(r^{-2})$ can be made. Therefore, if the linear adsorption Λ has a finite limit at the bulk phase coexistence, the term $(\partial\kappa/\partial r)_{T,\mu}$ can be neglected for sufficiently large drops and the term κ/r can be approximated with its asymptotic form κ_0/r.

5.3. Thin wetting films on/in solids

We begin with some remarks on terminology. Concerning films, the words “thick” and “thin” are not common epithets but rigorous scientific notions. A film is called thick if it contains a bulk phase (α) in the interior. In other words, the film interfaces do not overlap in a thick film, and, as a consequence, the film tension γ^{F} is composed of the interfacial tensions on the film sides. For a thick film between phases β and γ, the film tension is

$$\gamma_{\infty}^{\mathrm{F}} = \gamma_{\infty}^{\alpha\beta} + \gamma_{\infty}^{\alpha\gamma}, \tag{5.57}$$

where subscript ∞ implies the condition for the film thickness $H \to \infty$ (in fact, this means that the film thickness considerably exceeds the interface thickness and atomic dimensions).

Due to overlapping its interfaces, a thin film does not contain a bulk phase inside. A thin film is completely non-uniform along its thickness and may be treated in the same way as we dealt above with interfaces, i.e. a single dividing surface can be introduced and the film tension can be defined by analogy with interfacial tension (see Section 3.2). However, unlike an interface, a thin film always has its mother phase α (of which the film was formed), which is suggestive to introducing two dividing surfaces and using phase α as a reference phase. In this variant of the thermodynamics of thin films [50], Eq. (5.57) is replaced by a more general relationship

$$\gamma^{\mathrm{F}} = \gamma^{\alpha\beta} + \gamma^{\alpha\gamma} + \Pi H, \tag{5.58}$$

where Π is disjoining pressure. All quantities in Eq. (5.58) are dependent on the film thickness, and the additional relationship holds [50]

$$\frac{\partial(\gamma^{\alpha\beta} + \gamma^{\alpha\gamma})}{\partial H} = -\Pi(H). \tag{5.59}$$

Derjaguin [143,144] introduced the disjoining pressure of a film as a difference between the external pressure P^{β} and the pressure P^{α} in the film mother phase taken at the same temperature and chemical potentials as in the film:

$$\Pi \equiv P^{\beta} - P^{\alpha}. \tag{5.60}$$

A modified definition is [145]

$$\Pi \equiv P_{\mathrm{N}} - P^{\alpha} \tag{5.61}$$

where P_{N} is the normal component of the pressure tensor inside a film. Since $P^{\beta} = P_{\mathrm{N}}$ by the mechanical equilibrium condition for a flat film, Eqs. (5.60) and (5.61) express the same definition in the case of flat films. However (Eq. (5.61) is of the local character, which allows to extend the definition to films of arbitrary shape. The behavior of the function $\Pi(H)$ is a result of the play of molecular forces, which was the object of numerous theoretical and experimental studies [144]. Generally not only $\Pi \to 0$, but also $\Pi H \to 0$ as $H \to \infty$ to reduce Eq. (5.59) to Eq. (5.58).

For a long time, the theory was formulated mainly for plane-parallel films. Considering thick films, the attention was paid to the Gibbs elasticity (see review [146]), whereas the problems of thin films were concentrated round the disjoining pressure. Meanwhile, both mechanisms of elasticity, the Gibbs elasticity and the disjoining pressure, can work simultaneously in a thin film provided it consists of more than one species. The thermodynamic theory of this phenomenon was formulated recently [147]. If, however, a film consists of a single species, Gibbs' mechanism of elasticity does not act, and the disjoining pressure remains the only source of the film elasticity and stability.

Some results obtained for flat films were also applied to films with variable thickness when the disjoining pressure is combined with the capillary pressure. For the transitional zone between a meniscus and a wetting liquid film on a solid, Derjaguin proposed the mechanical equilibrium condition [143,144]

$$\gamma(c_1 + c_2) + \Pi(H) = P_{\mathrm{c}}, \tag{5.62}$$

where γ is the ordinary surface tension (usually taken as γ_{∞}), c_1 and c_2 are the principal curvatures of the film surface, and P_{c} is the capillary pressure (i.e. $P^{\alpha} - P^{\beta}$ or $P^{\beta} - P^{\alpha}$) of an equilibrium drop or a meniscus. Because of its simplicity, Derjaguin's method was widely used (see review [148]). A modification of Eq. (5.62) was also suggested including the additional factor $\cos\varphi$ where φ is the local slope angle at the film/fluid interface [142,149]. However, the local disjoining pressure of a non-uniform film was taken from the data for flat films, so that the results were applicable only to slightly non-uniform (in thickness) films. Only recently, there was elaborated a general and rigorous approach to characterize the mechanical equilibrium condition for a non-uniform and anisotropic thin film with arbitrary slopes of its surfaces and an arbitrary gradient of its thickness [150–152]. The results are presented below.

5.3.1. Mechanical equilibrium condition at the surface of a thin film

We now have to return to Section 3.3 and to repeat the derivation of the mechanical equilibrium condition for an interfacial element with the only difference that the lower and upper faces of the element marked with symbols α and β (Fig. 7) are not located inside the corresponding bulk phases which both or one of them can be absent in the system. In comparison with Eq. (3.62), the result now looks more cumbersome:

$$\begin{aligned}\mathbf{E}_3^{\alpha}(u_{30}) - \mathbf{E}_3^{\beta}(u_{30}) = {} & \frac{\partial \boldsymbol{\gamma}_1^{\mathrm{f}}}{\partial l_{10}} + \frac{\partial \boldsymbol{\gamma}_2^{\mathrm{f}}}{\partial l_{20}} - [\mathbf{E}_3(u_3^{\alpha}) - \mathbf{E}_3^{\alpha}(u_3^{\alpha})]\frac{h_1(u_3^{\alpha})h_2(u_3^{\alpha})}{h_{10}h_{20}} \\ & + [\mathbf{E}_3(u_3^{\beta}) - \mathbf{E}_3^{\beta}(u_3^{\beta})]\frac{h_1(u_3^{\beta})h_2(u_3^{\beta})}{h_{10}h_{20}},\end{aligned} \tag{5.63}$$

where force-defined $\boldsymbol{\gamma}_1^{\mathrm{f}}$ and $\boldsymbol{\gamma}_2^{\mathrm{f}}$ are the element tension vectors (we omit superscript αβ for the sake of brevity). The quantities $\mathbf{E}_3(u_3^\alpha)$ and $\mathbf{E}_3(u_3^\beta)$ are the real stress vectors applied to the lower and upper faces of the element, respectively, while $\mathbf{E}_3^\alpha(u_3^\alpha)$ and $\mathbf{E}_3^\beta(u_3^\beta)$ are the stress vectors in the corresponding bulk phases (extrapolated to the coordinates u_3^α and u_3^β if the bulk phases are non-uniform). If the coordinates u_3^α and u_3^β turn to be inside the bulk phases (the case of a thick film), $\mathbf{E}_3(u_3^\alpha)$ and $\mathbf{E}_3^\alpha(u_3^\alpha)$, as well as $\mathbf{E}_3(u_3^\beta)$ and $\mathbf{E}_3^\beta(u_3^\beta)$, become identical, and Eq. (5.63) is reduced to Eq. (3.62) where we should now understand $\boldsymbol{\gamma}_1^{\mathrm{f}}$ and $\boldsymbol{\gamma}_2^{\mathrm{f}}$ as $\boldsymbol{\gamma}_{1\infty}^{\mathrm{f}}$ and $\boldsymbol{\gamma}_{2\infty}^{\mathrm{f}}$.

Applying Eq. (5.63) to the surface of a thin film, we have the situation when the outer phase β is a real bulk phase. Therefore, we always can choose the coordinate u_3^β inside phase β to annul the last term in Eq. (5.63). Then a general formulation of the mechanical equilibrium condition for the surface of a thin film is

$$\mathbf{E}_3^\alpha(u_{30}) - \mathbf{E}_3^\beta(u_{30}) = \frac{\partial \boldsymbol{\gamma}_1^{\mathrm{f}}}{\partial l_{10}} + \frac{\partial \boldsymbol{\gamma}_2^{\mathrm{f}}}{\partial l_{20}} - [\mathbf{E}_3(u_3^\alpha) - \mathbf{E}_3^\alpha(u_3^\alpha)]\frac{h_1(u_3^\alpha)h_2(u_3^\alpha)}{h_{10}h_{20}}. \tag{5.64}$$

The vector Eq. (5.64) corresponds to three scalar equations (cf. (3.67)–(3.69))

$$E_{13}^\alpha(u_{30}) - E_{13}^\beta(u_{30}) = \frac{\gamma_{31}^{\mathrm{f}}}{R_{10}} + \frac{\partial \gamma_{11}^{\mathrm{f}}}{\partial l_{10}} + \frac{\partial \gamma_{12}^{\mathrm{f}}}{\partial l_{20}} - [E_{13}(u_3^\alpha) - E_{13}^\alpha(u_3^\alpha)]\frac{h_1(u_3^\alpha)h_2(u_3^\alpha)}{h_{10}h_{20}}, \tag{5.65}$$

$$E_{23}^\alpha(u_{30}) - E_{23}^\beta(u_{30}) = \frac{\gamma_{32}^{\mathrm{f}}}{R_{20}} + \frac{\partial \gamma_{21}^{\mathrm{f}}}{\partial l_{10}} + \frac{\partial \gamma_{22}^{\mathrm{f}}}{\partial l_{20}} - [E_{23}(u_3^\alpha) - E_{23}^\alpha(u_3^\alpha)]\frac{h_1(u_3^\alpha)h_2(u_3^\alpha)}{h_{10}h_{20}}, \tag{5.66}$$

$$E_{33}^\alpha(u_{30}) - E_{33}^\beta(u_{30}) = -\frac{\gamma_{11}^{\mathrm{f}}}{R_{10}} - \frac{\gamma_{22}^{\mathrm{f}}}{R_{20}} + \frac{\partial \gamma_{31}^{\mathrm{f}}}{\partial l_{10}} + \frac{\partial \gamma_{32}^{\mathrm{f}}}{\partial l_{20}} - [E_{33}(u_3^\alpha) - E_{33}^\alpha(u_3^\alpha)]\frac{h_1(u_3^\alpha)h_2(u_3^\alpha)}{h_{10}h_{20}}, \tag{5.67}$$

where the coordinate u_3^α conditionally demarcates two film parts related to the opposite sides of the film. If bulk phases α and β are uniform and isotropic, all the off-diagonal elements of the bulk pressure tensors, as well as the corresponding components of vectors $\mathbf{E}_3^\alpha$ and $\mathbf{E}_3^\beta$, vanish. The diagonal components can be written as $E_{11} = E_{22} = E_{33} = -P$. In this case, Eqs. (5.65)–(5.67) become

$$\frac{\gamma_{31}^{\mathrm{f}}}{R_{10}} + \frac{\partial \gamma_{11}^{\mathrm{f}}}{\partial l_{10}} + \frac{\partial \gamma_{12}^{\mathrm{f}}}{\partial l_{20}} - E_{13}(u_3^\alpha)\frac{h_1(u_3^\alpha)h_2(u_3^\alpha)}{h_{10}h_{20}} = 0, \tag{5.68}$$

$$\frac{\gamma_{32}^{\mathrm{f}}}{R_{20}} + \frac{\partial \gamma_{21}^{\mathrm{f}}}{\partial l_{10}} + \frac{\partial \gamma_{22}^{\mathrm{f}}}{\partial l_{20}} - E_{23}(u_3^\alpha)\frac{h_1(u_3^\alpha)h_2(u_3^\alpha)}{h_{10}h_{20}} = 0. \tag{5.69}$$

$$P^\alpha - P^\beta = \frac{\gamma_{11}^{\mathrm{f}}}{R_{10}} + \frac{\gamma_{22}^{\mathrm{f}}}{R_{20}} - \frac{\partial \gamma_{31}^{\mathrm{f}}}{\partial l_{10}} - \frac{\partial \gamma_{32}^{\mathrm{f}}}{\partial l_{20}} + [E_{33}(u_3^\alpha) + P^\alpha]\frac{h_1(u_3^\alpha)h_2(u_3^\alpha)}{h_{10}h_{20}}. \tag{5.70}$$

In the absence of external fields, the stress tensor is formed under the influence of the space metrics. Since the metric tensor of a film has the diagonal form in the curvilinear orthogonal coordinate system chosen (see Section 3.1), the stress tensor can also be considered as diagonal in all parts of the film. As a consequence, the surface tension vectors will contain only normal components. In this simple case, Eqs. (5.68)–(5.70) are reduced to the conditions

$$\frac{\partial \gamma_{11}^{f}}{\partial l_{10}} = \frac{\partial \gamma_{22}^{f}}{\partial l_{20}} = 0, \tag{5.71}$$

$$P^{\alpha} - P^{\beta} = \frac{\gamma_{11}^{f}}{R_{10}} + \frac{\gamma_{22}^{f}}{R_{20}} + [E_{33}(u_3^{\alpha}) + P^{\alpha}]\frac{h_1(u_3^{\alpha})h_2(u_3^{\alpha})}{h_{10}h_{20}}. \tag{5.72}$$

In the particular case of a flat film, we use Cartesian coordinates x, y, z, and the Lame coefficient ratio in Eq. (5.72) is unity, whereas the terms related to curvature vanish. Denoting now $E_{33}(u_3^{\alpha})$as the normal pressure $-P_N(z^{\alpha})$, we obtain

$$P^{\alpha} - P^{\beta} = P^{\alpha} - P_N(z^{\alpha}). \tag{5.73}$$

Eq. (5.73), on one side, yields the known equilibrium condition $P_N = P^{\beta}$ and, on the other side, shows the equivalency of the disjoining pressure definitions given in (5.60) and (5.61). Since the coordinate z^{α} is chosen arbitrarily, Eq. (5.73) shows P_N to be independent of z as well as of spatial coordinates at all.

Thin films can be located not only on the solid surface, but also in narrow slits inside a solid. As an example, we consider a film of variable thickness in a wedge-shaped slit with plane sides. If the wedge sides are identical, it is natural to introduce the middle plane as a basement for the interfacial element (Fig. 17). The dividing surface is plane in this case. The coordinates are cylindrical with $u_1 = r$, $u_2 = z$, $u_3 = \varphi$ and with the Lame coefficients $h_1 = 1$, $h_2 = 1$, $h_3 = r$. Eq. (5.72) now becomes

$$P^{\alpha} - P^{\beta} = P^{\alpha} + E_{33}(\varphi^{\alpha}), \tag{5.74}$$

from where E_{33} is seen to be again a constant (with respect to the coordinate φ this time). Denoting $E_{33} = -P_N$, we can again define the disjoining pressure as was shown in Eq. (5.61). We see that introducing the disjoining pressure for a film of variable thickness bears no difficulties in this case. If phase β is a fluid phase of uniform pressure, Eq. (5.74) leads to the absurd conclusion of the independence of the disjoining pressure on the film thickness. This only means that the wedge shape is impossible for a free film. However, the wedge-shaped film is quite realizable inside a rigid solid (Fig. 17), when P^{β} in Eq. (5.74) should be interpreted as the surface local pressure created by internal stresses in the solid (not included into the element tensions). At every surface point, these internal stresses

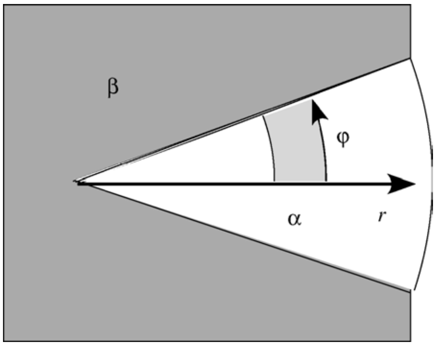

Fig. 17. The element of a thin wedge-shaped film.

counterbalance the disjoining pressure and, of course, are dependent on the location on the surface (on the coordinate r).

The cylindrical coordinates are also natural for a simple case when a film itself is of the shape of a circular cylindrical surface. The dividing surfaces are also cylindrical in this case (with the radii $0 < R_{10} < \infty$, $R_{20} = \infty$). The coordinates are chosen as $u_1 = \varphi$, $u_2 = z$, $u_3 = r$, and the Lame coefficients are $h_1 = r$, $h_2 = 1$, $h_3 = 1$. Correspondingly, Eq. (5.72) takes the form

$$P^\alpha - P^\beta = \frac{\gamma_{11}^{\mathrm{f}}}{R_{10}} + [E_{33}(r^\alpha) + P^\alpha]\frac{r^\alpha}{R_{10}}, \tag{5.75}$$

By choosing r^α in the middle of the film ($r^\alpha = R_{10} - H/2$), Eq. (5.75) can be written as

$$P^\alpha - P^\beta = \frac{\gamma_{11}^0}{R_{10}} - [P_{\mathrm{N}}^0 - P^\alpha]\left(1 - \frac{H}{2R_{10}}\right), \tag{5.76}$$

where H is the distance between the dividing surfaces of the film (the film thickness), $P_N^0 \equiv -E_{33}(r^\alpha = R_{10} - H/2)$, and $\gamma_{11}^0 \equiv \gamma_{11}^{\mathrm{f}}(r^\alpha = R_{10} - H/2)$.A similar formulation can be given for a spherical film when $R_{10} = R_{20} = R_0$ and $\gamma_{11}^{\mathrm{f}} = \gamma_{22}^{\mathrm{f}} = \gamma^{\mathrm{f}}$. The spherical coordinates are $u_1 = \theta$, $u_2 = \varphi$, and $u_3 = r$. Correspondingly, $h_1 = r$, $h_2 = r \sin\theta$, and $h_3 = 1$. Then from Eq. (5.72) we have

$$P^\alpha - P^\beta = \frac{2\gamma^{\mathrm{f}}}{R_0} + [E_{33}(r^\alpha) + P^\alpha]\frac{r^{\alpha 2}}{R_0^2} \tag{5.77}$$

or

$$P^\alpha - P^\beta = \frac{2\gamma^0}{R_0} - [P_{\mathrm{N}}^0 - P^\alpha]\left(1 - \frac{H}{2R_0}\right)^2 \tag{5.78}$$

where $P_{\mathrm{N}}^0 \equiv -E_{33}(r^\alpha = R_0 - H/2)$ and $\gamma^0 \equiv \gamma^{\mathrm{f}}(r^\alpha = R_{10} - H/2)$, the superscript "0" referring to the middle spherical surface inside the film.

For a wetting film of uniform thickness on a cylindrical or spherical solid body of radius R_n, we can choose coordinate u_3^α at the solid surface by setting $r^\alpha = R_n$. As a result, we obtain from Eqs. (5.75) and (5.77)

$$P^\alpha - P^\beta = \frac{\gamma_{11}^{\mathrm{f}}}{R_{10}} - [P_{\mathrm{N}}^{\mathrm{s}} - P^\alpha]\frac{R_n}{R_{10}}, \tag{5.79}$$

$$P^\alpha - P^\beta = \frac{2\gamma^{\mathrm{f}}}{R_0} - [P_{\mathrm{N}}^{\mathrm{s}} - P^\alpha]\frac{R_n^2}{R_0^2}, \tag{5.80}$$

where $P_{\mathrm{N}}^{\mathrm{s}} \equiv -E_{33}(R_n)$ is the normal pressure on the solid surface. According to Eq. (5.61), the difference $P_{\mathrm{N}}^{\mathrm{s}} - P^\alpha$ in Eqs. (5.79) and (5.80) has a meaning of the film disjoining pressure. Eqs. (5.79) and (5.80) are important in the thermodynamics of heterogeneous nucleation on cylindrical or spherical wettable solid particles [153].

The above formulas are of general character and applicable to arbitrary capillary objects. Indeed, the interfacial layers can overlap not only in thin films, but also in thin threads and filaments, small drops and solid particles, etc. In other words, the interfacial layers attain the middle of an object, and, therefore, the interfacial element under consideration should be reckoned from an axial or central point. This means

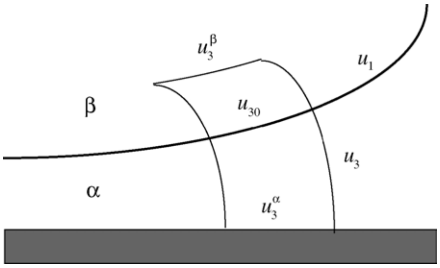

Fig. 18. The element of the transitional zone of a wetting film.

that, when applying Eqs. (5.75) and (5.77) to compact continuous bodies, we have to set $r^\alpha = 0$. Then the term with disjoining pressure disappears from the mechanical equilibrium condition to return to the classical Laplace equation even for very small capillary objects (with no bulk phase inside). Thus, we come to the conclusion that the significance of disjoining pressure is a distinctive feature of thin films.

5.3.2. *Transitional zone of a wetting film*

Fig. 18 shows a fragment of the transitional zone between a meniscus and a thin wetting film on a rigid flat solid surface. The subject discussed is the mechanical equilibrium condition for the upper surface (αβ) of the transitional zone. Choosing an element to which Eq. (5.72) refers, it is convenient to take the coordinate u_3^α on the solid surface (αγ) to refer the whole film interior to the film surface layer αβ. Then $-E_{33}(u_3^\alpha)$ acquires the meaning of the normal pressure P_N^s on the solid surface. In accordance with Eq. (5.72), we have

$$P^\alpha - P^\beta = \frac{\gamma_{11}^\mathrm{f}}{R_{10}} + \frac{\gamma_{22}^\mathrm{f}}{R_{20}} - [P_\mathrm{N}^\mathrm{s} - P^\alpha]\frac{h_1(u_3^\alpha)h_2(u_3^\alpha)}{h_{10}h_{20}}. \tag{5.81}$$

Since the solid surface is flat, the contribution of capillary pressure vanishes, so that the only cause of a difference between P_N^s and P^α is the overlapping of the opposite interfacial layers of the film. Hence we may term the difference $P_\mathrm{N}^\mathrm{s} - P^\alpha$ as a local disjoining pressure

$$\Pi(u_1^\alpha, u_2^\alpha) \equiv P_\mathrm{N}^\mathrm{s} - P^\alpha. \tag{5.82}$$

In this definition, it is shown that the local disjoining pressure depends on the longitudinal coordinates, similarly to all other quantities on the right-hand side of Eq. (5.72). Using (5.82), Eq. (5.72) becomes

$$P^\alpha - P^\beta = \frac{\gamma_{11}^\mathrm{f}}{R_{10}} + \frac{\gamma_{22}^\mathrm{f}}{R_{20}} - \Pi\frac{h_1(u_3^\alpha)h_2(u_3^\alpha)}{h_{10}h_{20}}. \tag{5.83}$$

In the particular case of a cylindrical dividing surface ($R_{20} = \infty$, $h_2 = 1$), the condition expressed in Eq. (5.83) is reduced to

$$P^\alpha - P^\beta = \frac{\gamma_{11}^\mathrm{f}}{R_{10}} - \Pi\frac{h_1(u_3^\alpha)}{h_{10}} \tag{5.84}$$

Comparing Figs. 7 and 18, it is seen that the film surface curvature in Fig. 18 is negative. For this reason, it is convenient to write Eqs. (5.83) and (5.84) in a general form as

$$P^\beta - P^\alpha = P_\mathrm{c} + \Pi L \tag{5.85}$$

where P_c is the capillary pressure and L is the Lame coefficient ratio

$$L \equiv \frac{h_1(u_3^\alpha)h_2(u_3^\alpha)}{h_{10}h_{20}}. \tag{5.86}$$

The explicit expressions for L exist only for simple coordinate systems as we used above. In the general case, the Lame coefficient ratio can be evaluated with the aid of Eq. (3.6). Subsequently applying Eq. (3.6) to h_1 and h_2 with the integration from u_{30} to u_3^α and putting the results in Eq. (5.86), we obtain

$$L = \exp\left[2\int_{u_{30}}^{u_3^\alpha} \mathrm{d}u_3 h_3(u_3)c(u_3)\right], \tag{5.87}$$

where $c(u_3) \equiv [c_1(u_3) + c_2(u_3)]/2$ is the local mean curvature of the coordinate surface $u_1 - u_2$. Applying the mean-value theorem and putting $h_3\mathrm{d}u_3 = \mathrm{d}l_3$, we rewrite Eq. (5.87) as

$$L = \exp(2\bar{c}\Delta l_3), \tag{5.88}$$

where $\bar{c}$ is the averaged value of $c(u_3)$ and Δl_3 is the length of the segment of the coordinate line 3 between u_{30} and u_3^α (the curvilinear "thickness" of the film, Fig. 18). For a thin film whose real local thickness H is considerably smaller than any of the principal curvature radii of a dividing surface, we have $\bar{c}\Delta l_3 \ll 1$, $\bar{c} \approx c$, and, naturally, $\Delta l_3 \approx H$. As a consequence, Eq. (5.88) is represented in an approximate form

$$L \approx 1 + 2cH. \tag{5.89}$$

It is valid $L \leq 1$ at the negative mean curvature of a film (as a reminder, we have $c < 0$ since the curvature centre is located on the side of phase α).

Assuming isotropy of surface tension, Eq. (5.85) can be written as

$$P^\beta - P^\alpha = -2\gamma^{\mathrm{f}}c + \Pi L. \tag{5.90}$$

With $L = 1$ Eq. (5.90) corresponds to Derjaguin's Eq. (5.62), except that Derjaguin treated Π as the disjoining pressure of a flat film of an appropriate thickness. As was already mentioned above, the cosine of the local slope angle was introduced, instead of L, in some versions of Eq. (5.62) [142,149] for the case when the disjoining pressure was defined with respect to the normal to the horizontal plane, but not to the inclined film surface. Such inconsistency was avoided in [150–152] by using curvilinear coordinates. As a result, the disjoining pressure acts along the normal to both the above film surfaces, so that equating the Lame coefficient ratio L to the above cosine looks problematic. It is also of note that using the Cartesian coordinates (as a unique case related to the use of the cosine) has one more undesirable consequence: the capillary part of Eq. (5.90) becomes inexact. This is related to the fact that the pressure tensor of the transitional zone becomes non-diagonal in the Cartesian coordinates, which requires returning to the more general case, Eq. (5.70). As was shown above, $L = 1$ not only for a flat film, but also for a wedge-shaped film. Therefore, the condition $L \approx 1$ can happen to be not bad approximation for calculations according to Eq. (5.90) if the film profile is slightly different from the wedge shape and the profile curvature is sufficiently small.

6. Equation of state for an adsorbed monolayer

The notion of a monolayer is widely used in modern science. By its origin, a monolayer can be adsorbed or spread at an interface of any nature between two bulk phases (if one of the phases is a gas, the other is called a substrate). What is an adsorbed monolayer was beautifully explained by de Boer [154]. When adsorption is localized (including chemisorption), a registered (immobile) monolayer forms. The non-localized adsorption results in an mobile monolayer. The transition between these states was analyzed by Halsey [83]. He also raised the question about the influence of an adsorbed monolayer on γ (the mechanical surface tension) and σ (the thermodynamic surface tension in our terminology) for a solid surface when $\gamma \neq \sigma$. The molecules of a mobile monolayer move freely along the surface and create the two-dimensional pressure π_m, which Halsey defined as $\sigma_0 - \sigma$, the subscript 0 referring to the bare surface (still not covered with a monolayer). With this definition, we can rewrite the Gibbs adsorption Eq. (3.82) as

$$\mathrm{d}\pi_m = \bar{s}\,\mathrm{d}T + \sum_i \Gamma_i\,\mathrm{d}\mu_i. \tag{6.1}$$

Similarly to Eq. (3.82), Eq. (6.1) is valid both for liquid and rigid solid substrates.

The relation of the two-dimensional pressure to other parameters of a mobile monolayer (the area, the number of molecules of each species, and temperature) is established by an equation of state that is often called a two-dimensional equation of state. We understand it as an equation relating only interfacial quantities to each other. The adsorption isotherm equations relating interfacial and bulk quantities make another class of thermodynamic relationships, which we here exclude from consideration with a note that any such relationship can be easily derived from the Gibbs adsorption equation if the equation of state is known. The latter itself cannot be obtained from thermodynamics: either statistical mechanics or an empirical approach is needed.

The history of a two-dimensional equation of state is considerably shorter than that of a three-dimensional one. Nevertheless, the list of equations proposed is long enough, which mirrors the variety of attractive and repulsive forces combined in monolayers of various nature. In addition, the degree of rigor and accuracy divides equations and also increases their number. We here present a novel thermodynamic approach to the equation-of-state theory [155–160] that concentrates on the short-range repulsive part of an equation of state and, therefore, is applicable to any sort of the monolayer particles (molecules, ions, or even nanoparticles) and their mixtures. Constructing the hierarchy of approximations, we will not only derive new equations of state, but also reproduce most important earlier equations (including classical ones). For this reason, we do not give a survey of the state of the art in the field; some previous results will be obtained in the course of derivation.

6.1. Novel approach to the equation-of-state theory

Some distinctive features of the novel approach can be formulated as follows. (a) Three-dimensional aspects of a monolayer (such as orientation of anisometric particles) are taken into account. The theory is generally based on three-dimensional thermodynamic equations. (b) Ockham's razor (the principle of maximum simplicity) is in action to avoid plurality. This means that, when having multiple solutions, we choose the simplest of them. It is possible to meet ten or more fitting parameters in modern equations of state. We use a single fitting parameter if any. (c) The approach novelty is attributed to the new definition and use of the excluded area and the exclusion factor that is a main parameter of the theory. To understand these quantities, a preliminary survey of other geometrical characteristics of monolayer particles is needed.

6.1.1. Geometrical characteristics of monolayer particles

The simplest geometrical characteristic of a monolayer particle is its parking area. Accounting for the Brownian rotation, we can consider monolayer particles as having a disk shape (in the case of the absence of rotation, one can speak about an effective disk shape of a particle) to write

$$a_{i0} = \pi r_i^2, \tag{6.2}$$

where a_{i0} is the parking area of a particle of the ith species and r_i is the particle radius. Let Γ_i be the surface particle density (the monolayer particle number per unit area coinciding with adsorption for a non-soluble and non-volatile monolayer), Γ the total surface particle density for all species, and x_i the mole fraction of particles of the ith species:

$$x_i \equiv \frac{\Gamma_i}{\Gamma}, \quad \Gamma \equiv \sum_i \Gamma_i. \tag{6.3}$$

Using Eq. (6.3), we can define the average parking area a_0 in case of a mixture as

$$a_0 \equiv \sum_i x_i a_{i0}. \tag{6.4}$$

A minimal area per a particle of the ith sort in a densest monolayer (under infinitely large two-dimensional pressure) is designated as $a_{i\infty}$. Generally, a_{i0} and $a_{i\infty}$ are different. They can coincide only in the model of soft disks when particles are capable of two-dimensional straining at maintaining their area. However, $a_{i\infty}$ is always larger than a_{i0} in the model of hard disks, the ratio $a_{i\infty}/a_{i0}$ depending on the packing type. For a single-species monolayer, $a_{i\infty}/a_{i0} = 4/\pi$ for the square packing and $a_{i\infty}/a_{i0} = 3^{1/2}(2/\pi)$ for the hexagonal packing. However, the models of soft and hard disks are insufficient for monolayers with anisometric particles where both the areas are dependent of the particle orientation. For a multicomponent monolayer, we can, by analogy with Eq. (6.4), also introduce the average minimal area per a particle as

$$a_\infty \equiv \sum_i x_i a_{i\infty}. \tag{6.5}$$

Interestingly, the average quantities a_0 and a_∞ are closer to each other than the corresponding areas for individual species. The wider the size distribution, the closer are a_0 and a_∞ because smaller particles fill cavities between large particles. We illustrate this by the example of the square packing of hard disks (Fig. 19). For disks of one size, $a_0/a_\infty = \pi/4 \approx 0.7854$. If we now add disks of smaller size (component 2), the geometrical relationships hold

$$\frac{a_0}{a_\infty} = \frac{\pi(1+\lambda^2)}{4} \quad (0 \le \lambda \le 2^{1/2}-1), \quad \frac{a_0}{a_\infty} = \frac{\pi(1+\lambda^2)}{2(1+\lambda)^2} \quad (2^{1/2}-1 \le \lambda \le 1),$$

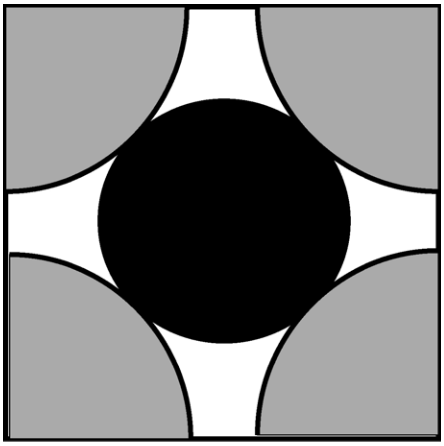

Fig. 19. An elementary cell of a square lattice of disks of two dimensions.

where $\lambda \equiv r_2/r_1$. The value $\lambda = 2^{1/2} - 1$ corresponds to the case when the second disks exactly fit the cavities in the square lattice of the first disks. In this case, the ratio $a_0/a_\infty = 0.92$ attains its maximum, but also remains larger than 0.7854 at all other values of λ.

The above two areas are related to the manner of giving the amount of matter in a surface monolayer. Area a_{i0} participates in formulating the surface packing fraction of the *i*th species φ_i and the total packing fraction of all species φ as

$$\varphi_i \equiv \Gamma_i a_{i0}, \quad \varphi \equiv \sum_i \Gamma_i a_{i0} = \Gamma a_0. \tag{6.6}$$

Area $a_{i\infty}$ stands in the definition of the degree of surface coverage for the *i*th species θ_i and for all species together θ:

$$\theta_i \equiv \Gamma_i a_{i\infty}, \quad \theta \equiv \sum_i \Gamma_i a_{i\infty} = \Gamma a_\infty. \tag{6.7}$$

In view of the said above, a difference between φ and θ can be not significant for a mixture.

The parking area characterizes the particle dimensions in the monolayer plane. However, every particle has also a linear dimension in the third direction (normal to the monolayer plane). Since liquid substrates are always horizontal, this linear dimension is often termed as the particle height. Accepting this terminology (although a solid substrate can be not horizontal) and designating the particle height for the *i*th species as h_i, we can introduce the average monolayer height (thickness) as

$$h \equiv \sum_i x_i h_i. \tag{6.8}$$

We now pass to the definition of the partial particle area a_i in a mixed monolayer. Introducing partial quantities is a standard operation in thermodynamics. We can imagine that we add an additional particle to a monolayer at given two-dimensional pressure and area. This leads to a change of pressure, and, to return pressure to its original value, we have to change the monolayer area. The resulting area increment is just the partial particle area and is defined mathematically as

$$a_i \equiv \left(\frac{\partial A}{\partial N_i}\right)_{T,\pi_m,N_{j\neq i}}, \tag{6.9}$$

where N_i is the number of particles of sort i in the monolayer. Quantity a_i is always larger (for a gaseous monolayer, incomparably larger) than a_{i0} or $a_{i\infty}$. The average partial particle area in a multicomponent monolayer is defined as

$$a \equiv \sum_i x_i a_i. \tag{6.10}$$

Defining the partial particle area, we implied that a particle added is identical with the monolayer particles. In particular, the particle added is involved in thermal motion and contributes both to the kinetic and force parts of the pressure. Let us now assume that a particle is inserted to a certain position on the surface, and the particle center of mass is at rest. Such a particle do not contribute to the kinetic part of pressure, but influences the two-dimensional pressure in two different ways. First, the particle occupies a certain place on the surface to create an excluded area. Second, the particle interacts with other (moving) particles of the monolayer: the attraction decreases the pressure, while the repulsion increases it. Thermodynamically, we may regard particles with resting center of mass as a separate component. By analogy with Eq. (6.9), we can define the partial particle area for resting particles of sort i as

$$a_i^0 \equiv \left(\frac{\partial A}{\partial N_i^0}\right)_{T,\pi_m,N_i,N_{j\neq i}^0}, \tag{6.11}$$

where the superscript 0 denotes that the center of mass of a particle is at rest. We also introduce the average value of a_i^0 in a mixed monolayer

$$a^0 \equiv \sum_i x_i a_i^0. \tag{6.12}$$

Of course, a^0 differs from a, but both the quantities can be of any sign depending on the counterbalance of attractive and repulsive forces. To simplify the situation, we introduce one more quantity, the excluded area a_i^{ex} for particles of sort i, that is a_i^0 in the absence of long-range forces with accounting for only short-range repulsive forces specifying the particle size. In other words, the excluded area is defined as the partial area of a resting particle in the absence of long-range forces:

$$a_i^{\mathrm{ex}} \equiv a_i^0 \ (\text{no long-range forces}). \tag{6.13}$$

The excluded area is evident to be always positive. As usual, we also define the average excluded area a^{ex} in a mixed monolayer

$$a^{\mathrm{ex}} = \sum_i x_i a_i^{\mathrm{ex}}. \tag{6.14}$$

The excluded area is a central quantity of the approach to be presented below. So we now proceed to the analysis of its properties.

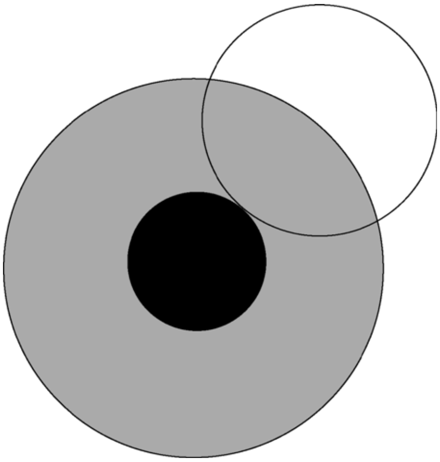

Fig. 20. The excluded area (shaded) created by a resting particle (black) with respect to another particle of different size.

6.1.2. Excluded area and exclusion factor

We begin with the consideration of a rarified gaseous monolayer consisting of discrete particles and not containing clusters. If the particle number is given, the two-dimensional pressure is determined by the surface area where the particle mass centers move. The excluded area created by a resting particle is evident to be an area inaccessible for the centers of mass of moving particles. Then a resting particle of radius r_i creates, for a moving particle of radius r_k, the excluded area $\pi(r_i + r_k)^2$ (Fig. 20). Denoting it a_{ik}^{ex}, we have

$$a_{ik}^{\text{ex}} = (a_{i0}^{1/2} + a_{k0}^{1/2})^2, \tag{6.15}$$

where a_{i0} and a_{k0} are the parking areas of particles of sorts i and k, respectively, defined according to Eq. (6.2). As is seen from Eq. (6.15), the excluded area depends on the sizes of both the particles. The frequency of appearance of particles of various species near the given particle of sort i is determined by the particle mole fractions x_k (see Eq. (6.3)). On average, a particle of sort i creates the excluded area

$$a_i^{\text{ex}} = \sum_k x_k a_{ik}^{\text{ex}} = \sum_k x_k (a_{i0}^{1/2} + a_{k0}^{1/2})^2. \tag{6.16}$$

By averaging this value over all species according to Eq. (6.14), we obtain the average excluded area created by a particle of a multicomponent gaseous mixture

$$a^{\text{ex}} = \sum_i x_i a_i^{\text{ex}} = \sum_{i,k} x_i x_k (a_{i0}^{1/2} + a_{k0}^{1/2})^2. \tag{6.17}$$

For the sake of simplicity, it is convenient to formulate equations in a dimensionless form. The exclusion factor is a dimensionless representation of the excluded area as its ratio to the parking area for a given sort of particles

$$f_i \equiv \frac{a_i^{\text{ex}}}{a_{i0}} \tag{6.18}$$

and, on average,

$$f \equiv \frac{a^{\mathrm{ex}}}{a_0}. \tag{6.19}$$

From Eqs. (6.3), (6.6), (6.14), (6.18), and (6.19), it follows that averaging f_i proceeds with respect to the packing fraction:

$$f = \sum_i \frac{\varphi_i f_i}{\varphi}. \tag{6.20}$$

Eqs. (6.4), (6.17), and (6.19) yield the exclusion factor for a rarified gaseous monolayer f_0 (subscript 0 means the low concentration limit)

$$f_0 = \frac{\sum_{i,k} x_i x_k (a_{i0}^{1/2} + a_{k0}^{1/2})^2}{\sum_i x_i a_{i0}}. \tag{6.21}$$

If the particles of all species possess equal parking areas ($a_{i0} = a_0$ for all i), Eq. (6.21) yields $f_0 = 4$. In the general case, the exclusion factor, even in a gaseous limit, is a function of the parking area ratios and composition. We consider a binary gaseous monolayer for the sake of illustration. Setting $x_1 = x$, $x_2 = 1 - x$, and $\lambda^2 \equiv a_{20}/a_{10}$ (λ is the ratio of linear dimensions) reduces Eq. (6.21) to the form

$$f_0 = \frac{4x^2 + 2x(1-x)(1+\lambda)^2 + 4(1-x)^2\lambda^2}{x + (1-x)\lambda^2}. \tag{6.22}$$

Fig. 21 shows the plot $f_0(x)$ for possible size ratios within the range $0 \leq \lambda \leq 1$ (the particles of the first species are assumed to be larger). The exclusion factor is seen to be smaller for a mixture than for the individual species, which leads to a minimum whose depth and location depend on the particle size ratio. As the size ratio becomes more different from unity, the minimum increases its depth and shifts to the side of the species with larger particles. In any case, however, the exclusion factor remains within the narrow range $4 \geq f_0 \geq 2$.

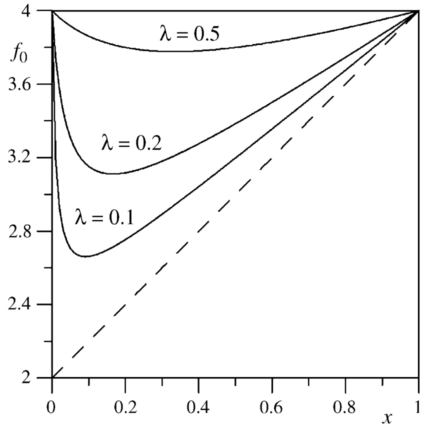

Fig. 21. The composition dependence of the exclusion factor in a binary system at various particle size ratios λ. The dashed line corresponds to the limit λ → 0.

We now turn to a denser state of a monolayer with developing clustering. Let us imagine that not a single particle but a cluster containing n particles of various species is inserted in a monolayer to a certain localized position. If a_c is the average area per particle in the cluster, the cluster will occupy the area na_c to have the radius $R = (na_c/\pi)^{1/2}$. In accordance with Fig. 20, the cluster will create, with respect to a mobile particle of the kth species, the excluded area (cf. Eq. (6.15))

$$A_k^{\mathrm{ex}} = \pi(R + r_k)^2 = [(na_{\mathrm{c}})^{1/2} + a_{k0}^{1/2}]^2. \tag{6.23}$$

The average excluded area created by the cluster is

$$A^{\mathrm{ex}} = \sum_k x_k[(na_{\mathrm{c}})^{1/2} + a_{k0}^{1/2}]^2 \tag{6.24}$$

or, when reckoning per one cluster particle,

$$a^{\mathrm{ex}} = \frac{A^{\mathrm{ex}}}{n} = \sum_k x_k \left[a_{\mathrm{c}}^{1/2} + \left(\frac{a_{k0}}{n}\right)^{1/2}\right]^2. \tag{6.25}$$

Correspondingly, the exclusion factor is determined as

$$f = \frac{a^{\mathrm{ex}}}{a_0} = \sum_k x_k \left[\left(\frac{a_{\mathrm{c}}}{a_0}\right)^{1/2} + \left(\frac{a_{k0}}{na_0}\right)^{1/2}\right]^2, \tag{6.26}$$

The analysis of Eq. (6.26) is complicated by the fact that the area a_c is itself dependent on n (i.e. on the cluster size) due to the boundary effects. For a discrete particle $a_c = a_0$. In a cluster, a_c is always larger than a_0, but diminishes with the cluster growth unless attains its minimal (for a given cluster structure) value a_∞ at $n \to \infty$. The limiting value for the exclusion factor is

$$f_\infty = \frac{a_\infty}{a_0}. \tag{6.27}$$

For a monolayer of a single species, the condition $f_\infty = 1$ is possible only in the model of soft particles (disks). As for a mixed monolayer, approaching the exclusion factor to unity can result from the favor size ratios when smaller particles fill in interspaces between larger particles.

Area a_∞ can also be used for introducing the alternative exclusion factor

$$g \equiv \frac{a^{\mathrm{ex}}}{a_\infty} = \frac{fa_0}{a_\infty}, \tag{6.28}$$

which tends exactly to unity in the densest limit. Using the definitions of φ and θ, Eqs. (6.6) and (6.7), we also can write

$$\varphi f = \theta g = \Gamma a^{\mathrm{ex}}. \tag{6.29}$$

The couple φ and f is convenient for description beginning from a gaseous state, while the couple θ and g is more appropriate for dense states. However, both the variants of description are completely equivalent. Since the value of a_∞ depends on the packing type, the restrictions for f and g should be written separately for every type of packing. As an example, we have for the system of hard disks of one size

$$4 \geq f \geq \frac{4}{\pi} \approx 1.273, \quad \pi \geq g \geq 1 \quad \text{(square packing)}, \tag{6.30}$$

$$4 \geq f \geq 3^{1/2}\left(\frac{2}{\pi}\right) \approx 1.103, \quad \frac{2\pi}{3^{1/2}} \approx 3.628 \geq g \geq 1 \text{ (hexagonal packing)}. \tag{6.31}$$

Although some information on the functions $f(\varphi)$ and $g(\theta)$ can be obtained from the known virial expansions, the problem of finding a general explicit form for these functions has not been solved up to the present. However, we established both the functions to be capable of changing only within a narrow interval as the two-dimensional pressure changes over the whole unlimited range. This allows us to hope that even simple but reasonable approximations for these functions can produce acceptable results. We will see below that, indeed, the exclusion factor turns to be an effective tool for constructing an equation of state.

6.1.3. Master equation

Since an equation of state can always be represented as a set of isotherms, we will deal, for the sake of simplicity, with the isothermal variant of the Gibbs adsorption Eq. (6.1)

$$\mathrm{d}\pi_m = \sum_i \Gamma_i \, \mathrm{d}\mu_i. \tag{6.32}$$

Deviating from the common practice, we refer chemical potentials in Eq. (6.32) to an interface, which immediately allows us to treat Eq. (6.32) as an implicit differential form of an equation of state. Since the adsorption of a substrate is zero in the Gibbs adsorption equation, Eq. (6.32) contains only the adsorptions of the monolayer species. Assuming them to be non-soluble and non-volatile secures the coincidence of the adsorptions and real amounts of the species per unit monolayer area.

Considering a monolayer as a three-dimensional object, we use the standard expression of statistical mechanics for the chemical potential of the ith species (cf. (4.46))

$$\mu_i = \mu_i^0 + k_\mathrm{B} T \ln(c_i \Lambda_i), \tag{6.33}$$

where μ_i^0 is the chemical potential of a particle with resting center of mass (taken with account of all interactions in the system) and c_i is the local concentration (the particle number per unit volume). The resting particles to which chemical potential μ_i^0 refers, can be formally treated as a separate species.

At given temperature and composition, chemical potentials are dependent on pressure. We assume the outer pressure to be constant, so that only the dependence on the two-dimensional pressure remains. The standard thermodynamic relationship is

$$\mathrm{d}\mu_i = a_i \, \mathrm{d}\pi_m, \tag{6.34}$$

where a_i is the partial area of a particle of sort i given by Eq. (6.9). Applying Eq. (6.34) to a resting particle, we have

$$\mathrm{d}\mu_i^0 = a_i^0 \, \mathrm{d}\pi_m, \tag{6.35}$$

where a_i^0 is the partial area of a resting particle given by Eq. (6.11). The three-dimensional local concentration c_i can be expressed as

$$c_i = \frac{\Gamma_i}{h_i}, \tag{6.36}$$

where h_i is the monolayer thickness corresponding to the height of particles of sort i (evidently, particles of different sorts can possess different heights).

Differentiating now Eq. (6.33) and accounting for Eqs. (6.35) and (6.36), we obtain

$$\mathrm{d}\mu_i = a_i^0\,\mathrm{d}\pi_m + k_\mathrm{B}T\,\mathrm{d}\ln\Gamma_i - k_\mathrm{B}T\mathrm{d}\ln h_i. \tag{6.37}$$

Putting now (6.37) in (6.32), we arrive at the equation

$$(1 - \Gamma a^0)\mathrm{d}\pi_m = k_\mathrm{B}T\,\mathrm{d}\Gamma - k_\mathrm{B}Tc\,\mathrm{d}h, \tag{6.38}$$

where Γ, h, and a^0 are defined in Eqs. (6.3), (6.8), and (6.12), respectively, and $c \equiv \sum_i c_i$ is the total concentration of all species. The last term in Eq. (6.38) accounts for the effect of orientation that appears only for anisometric particles and in sufficiently dense monolayers. Apparently, the average monolayer thickness h is itself dependent on π_m and Γ. For this reason, Eq. (6.38) can be written as

$$\frac{\mathrm{d}\pi_m}{\mathrm{d}\Gamma} = \frac{k_\mathrm{B}T(1 - c\mathrm{d}h/\mathrm{d}\Gamma)}{1 - \Gamma a^0}. \tag{6.39}$$

The integration of Eq. (6.39) is possible when the behavior of the partial particle area a^0 is known. However, as was already stated above, even the sign of a^0 is uncertain. At the same time, the direct contribution of long-range forces to pressure has already been estimated and known in many cases. This suggests integrating Eq. (6.39) in the absence of long-range forces and adding the contribution of long-range forces (as π_l where subscript l symbolizes long-range forces) to the final result of integration. In the course of such integration, area a^0 automatically changes to the excluded area a^ex, and the resulting equation is

$$\pi_m = \int_0^\Gamma \frac{k_\mathrm{B}T(1 - c\mathrm{d}h/\mathrm{d}\Gamma)}{1 - \Gamma a^\mathrm{ex}}\,\mathrm{d}\Gamma + \pi_l \tag{6.40}$$

The integration in (6.40) is carried out at constant temperature and composition. A particular expression for π_l depends on the kind of interparticle interaction. For example, for van der Waals forces

$$\pi_l = -\sum_{i,k} \alpha_{ik}\Gamma_i\Gamma_k, \tag{6.41}$$

where α_{ik} is the constant of interaction of particles of sorts i and k. Eq. (6.40) is valid for a monolayer of any nature and can be termed as a master equation for its significance and capability of generating various equations of state.

The master Eq. (6.40) can be rearranged to two equivalent dimensionless forms. Using the average parking area a_0 and the exclusion factor f according to (6.19), the first dimensionless form of Eq. (6.40) is

$$\tilde{\pi} = \int_0^\varphi \frac{1 - ca_0\,\mathrm{d}h/\mathrm{d}\varphi}{1 - f\varphi}\,\mathrm{d}\varphi + \tilde{\pi}_l, \tag{6.42}$$

where $\tilde{\pi} \equiv \pi_m a_0/k_B T$ is the dimensionless two-dimensional pressure and $\tilde{\pi}_l$ its long-range part. Correspondingly, Eq. (6.41) changes to the form

$$\tilde{\pi}_l = -\sum_{i,k} \tilde{\alpha}_{ik}\varphi_i\varphi_k, \tag{6.43}$$

where $\tilde{\alpha}_{ik} \equiv \alpha_{ik}a_0/k_B T a_{i0}a_{k0}$ is the dimensionless interaction constant. Using now the average minimal area a_∞ and the exclusion factor g, we obtain the second dimensionless form of Eq. (6.40) as

$$\tilde{\pi}' = \int_0^\theta \frac{1 - \mathrm{d}\ln h/\mathrm{d}\ln\theta}{1 - g\theta}\,\mathrm{d}\theta + \tilde{\pi}'_l, \tag{6.44}$$

where $\tilde{\pi}' \equiv \pi_m a_\infty/k_B T$ is the alternative dimensionless form for the two-dimensional pressure and $\tilde{\pi}'_l$ its long-range part. Eq. (6.41) is now transformed to

$$\tilde{\pi}'_l = -\sum_{i,k} \tilde{\alpha}'_{ik}\,\theta_i\,\theta_k, \tag{6.45}$$

where $\tilde{\alpha}'_{ik} \equiv \alpha_{ik}a_\infty/k_B T a_{i\infty}a_{k\infty}$ is the other dimensionless form for the interaction constant.

As was already stated above, the derivative $\mathrm{d}h/\mathrm{d}\varphi$ is related to a change in the particle orientation. For the case of symmetrical particles, $\mathrm{d}h/\mathrm{d}\varphi = 0$, and Eqs. (6.42) and (6.44) are reduced to their simplest forms

$$\tilde{\pi} = \int_0^\varphi \frac{\mathrm{d}\varphi}{1 - f\varphi} + \tilde{\pi}_l, \tag{6.46}$$

$$\tilde{\pi}' = \int_0^\theta \frac{\mathrm{d}\theta}{1 - g\theta} + \tilde{\pi}'_l. \tag{6.47}$$

Eqs. (6.46) and (6.47) already do not contain a three-dimensional aspect and can be termed as two-dimensional master equations.

6.1.4. Exclusion factor from the virial equation of state

As is seen from Eqs. (6.46) and (6.47), only the dependence of the exclusion factor on surface concentration is needed to obtain an equation of state in an explicit form. If, the reverse, an equation of state is known, Eqs. (6.46) and (6.47) allows finding the dependence of the exclusion factor on surface concentration. For this purpose, we can use the known virial form of the fluid equation of state, which, although being incomplete, can give us a general idea of the exclusion factor behavior.

A general form of the virial equation of state is

$$\pi_m = k_B T(\Gamma + B_2\Gamma^2 + B_3\Gamma^3 + \cdots), \tag{6.48}$$

where B_i are the virial coefficients ($B_1 = 1$). In the case of a mixed monolayer, the virial coefficients are composed of the partial virial coefficients of individual species B_{ik}, B_{ijk}, etc. The additivity rule reads

$$B_2 = \sum_{i,k} B_{ik}x_i x_k, \quad B_3 = \sum_{i,j,k} B_{ijk}x_i x_j x_k, \text{ etc.} \tag{6.49}$$

Table 1
Eight first virial coefficients for a system of identical hard disks

i	b_i [162]	b'_i (square)	b'_i (hexagonal)
1	1	1	1
2	2	$\pi/2 \approx 1.57079633$	$\pi/3^{1/2} \approx 1.81379936$
3	3.12801775	1.92951861	2.57269148
4	4.25785446	2.062815835	3.17591274
5	5.336897	2.030712	3.610155
6	6.3626	1.90145	3.90329
7	7.351	1.725	4.090
8	8.338	1.537	4.207

Proceeding to the dimensionless variables φ and θ, we can rewrite, alternatively, Eq. (6.48) in two forms

$$\tilde{\pi} = \varphi + b_2\varphi^2 + b_3\varphi^3 + \cdots, \tag{6.50}$$

$$\tilde{\pi}' = \theta + b'_2\theta^2 + b'_3\theta^3 + \cdots, \tag{6.51}$$

where the dimensionless virial coefficients are defined, respectively, as

$$b_i = \frac{B_i}{a_0^{i-1}}, \quad b'_i = \frac{B_i}{a_\infty^{i-1}}. \tag{6.52}$$

Methods of computing the virial coefficients are intensively elaborated in statistical mechanics. The simplest results refer to a system of hard disks of one size, for which eighth first virial coefficients have been computed [161,162]. The corresponding values of b_i are presented in Table 1 together with the values of b'_i calculated for the square and hexagonal packing. These values can be used for estimating $f(\varphi)$ and $g(\theta)$. Let us illustrate this procedure by example of function $f(\varphi)$. Applying Eq. (6.46) to the system of identical hard disks (i.e. setting $\tilde{\pi}'_l = 0$) and equating the right-hand sides of Eqs. (6.46) and (6.50), we obtain

$$f = \frac{\mathrm{d}\tilde{\pi}/\mathrm{d}\varphi - 1}{\varphi\,\mathrm{d}\tilde{\pi}/\mathrm{d}\varphi} = \frac{\sum_{i\geq 2} i b_i \varphi^{i-2}}{1 + \sum_{i\geq 2} i b_i \varphi^{i-1}} = \frac{2b_2 + 3b_3\varphi + \cdots}{1 + 2b_2\varphi + \cdots}. \tag{6.53}$$

Important relationships follow from Eq. (6.53) in the limit $\varphi \to 0$:

$$f_0 = 2b_2, \tag{6.54}$$

$$\left(\frac{\mathrm{d}f}{\mathrm{d}\varphi}\right)_0 \equiv -k_0 = 3b_3 - 4b_2^2, \tag{6.55}$$

where k_0 is the absolute value of the initial negative slope of the exclusion factor isotherm.

Comparing Eqs. (6.21) and (6.54), we obtain a formula for calculating the dimensionless second virial coefficient for the system of hard disks of various dimensions

$$b_2 = \frac{\sum\limits_{i,k} x_i x_k (a_{i0}^{1/2} + a_{k0}^{1/2})^2}{2\sum\limits_i x_i a_{i0}}. \tag{6.56}$$

Naturally, this formula is known in statistical mechanics, which confirms the validity of Eq. (6.21). The algorithm of calculating the partial third virial coefficients for a multicomponent system of hard disks was elaborated by Rowlinson and McQuarrie [163]. Their formula reads

$$B_{ijk} = \frac{4}{3}\pi^2 \sigma_{ij}\sigma_{ik}\sigma_{jk} I(\sigma_{ij}, \sigma_{ik}, \sigma_{jk}) \tag{6.57}$$

where $\sigma_{ij} \equiv r_i + r_j$, and $I(a, b, c)$ is the following function. If each of quantities a, b, c does not exceed the sum of the two others, $I(a, b, c)$ is

$$I = \frac{Abc}{4\pi a} + \frac{Bac}{4\pi b} + \frac{Cab}{4\pi c} - \frac{\Delta(a^2+b^2+c^2)}{4\pi abc}, \tag{6.58}$$

where a, b, c can be interpreted geometrically as the sides of a triangle, Δ being the triangle area and A, B, C angles opposite to corresponding sides. In other cases, the function $I(a,\ b,\ c)$ is defined as

$$I = \frac{ab}{4c} \quad (c \geq a + b), \text{ etc.} \tag{6.59}$$

Proceeding to a dimensionless form of the third virial coefficient is accomplished as

$$b_3 = \frac{\sum_{i,j,k} B_{ijk} x_i x_j x_k}{\left(\sum_i x_i a_{i0}\right)^2}. \tag{6.60}$$

For a system of identical disks, Eqs. (6.56) and (6.60) yield the values $b_2 = 2$ and $b_3 = 4(4/3 - 3^{1/2}/\pi) \approx 3.128$ shown in Table 1. According to Eqs. (6.54) and (6.55), we then obtain $f_0 = 4$ and $k_0 \approx 6.616$. Putting now all eight values of b_i from Table 1 in Eq. (6.53) with truncated (at $i > 8$) sums, we can calculate the initial behavior of the exclusion factor f in more detail. The result is exhibited in Fig. 22 that shows function $f(\varphi)$ to be decreasing and slightly concave. The above formulas for f can be easily reformulated for g by replacing $a_{i0} \to a_{i\infty}$, $b_i \to b_i'$, and $\varphi \to \theta$. Qualitatively, the behavior of $g(\theta)$ (with $g_0 = 2\pi/3^{1/2}$ for hexagonal packing) is similar to that of $f(\varphi)$ shown in Fig. 22.

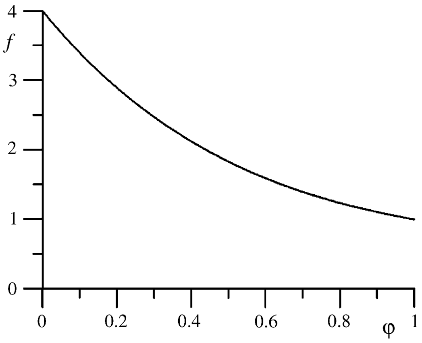

Fig. 22. The plot of $f(\varphi)$ for a system of hard disks according Eq. (6.53) truncated at $i = 8$ and the virial coefficients values taken from Table 1.

6.2. Two-dimensional equations of state

The above part of the equation-of-state theory was thermodynamically rigorous and resulted in the master equation capable of generating equations of state. The particular forms of the master equation, Eqs. (6.46) and (6.47), are destined for deriving two-dimensional equations of state, to which we now proceed. Further development will depend on the rational choice of approximations for the exclusion factor.

6.2.1. Low-density approximations

Looking at Fig. 22, we could omit at once unrealistic assumptions. This, however, would mean missing some famous and classical equations of state. Therefore, we will begin with simplest assumptions for historical reason. The zero approximation is evident to be the constancy of the exclusion factor. Integrating of Eqs. (6.46) and (6.47) at constant f and g yields

$$\tilde{\pi} = -\frac{\ln(1 - f\varphi)}{f} + \tilde{\pi}_l, \tag{6.61}$$

$$\tilde{\pi}' = -\frac{\ln(1 - g\theta)}{g} + \tilde{\pi}'_l. \tag{6.62}$$

Applying Eq. (6.61) to the gaseous region and setting $f = f_0$, we obtain

$$\tilde{\pi} = -\frac{\ln(1 - f_0\varphi)}{f_0} + \tilde{\pi}_l. \tag{6.63}$$

For a one-component monolayer ($f_0 = 4$) and for the van der Waals forces (see Eq. (6.43)), Eq. (6.63) becomes

$$\tilde{\pi} = -\frac{\ln(1 - 4\varphi)}{4} - \alpha\varphi^2, \tag{6.64}$$

which is a two-dimensional analog of the Planck equation of state for a monatomic non-ideal gas [164]. Taking a Taylor series expansion for the logarithm, we see that Eq. (6.64) yields correct values for the first and second virial coefficients (the third one deviates significantly from the known values).

The plot in Fig. 22 suggests that the constancy of the exclusion factor could be a better approximation for denser states. Turning to Eq. (6.62) and setting $g = 1$, we have

$$\tilde{\pi}' = -\ln(1 - \theta) + \tilde{\pi}'_l \tag{6.65}$$

For a one-component monolayer, Eq. (6.65) is known as the van Laar equation at $\tilde{\pi}'_l = 0$ and as the Frumkin equation at $\tilde{\pi}'_l = -\alpha\theta^2$. The van Laar equation was generalized by Krotov [165] for a mixture of particles of equal parking areas, while the Frumkin equation was generalized by Fainerman et al. [166] for a mixed monolayer with van der Waals forces when $\tilde{\pi}'_l$ is given by Eq. (6.45).

For the sake of brevity, we conduct further investigation with Eq. (6.46) only. According to Fig. 22, it is suggestive that the first approximation should be a linearly decreasing function

$$f = f_0 - k_1\varphi, \tag{6.66}$$

where k_1 is a positive constant. Putting (6.66) in Eq. (6.46) yields

$$\tilde{\pi} = \int_0^{\varphi} \frac{\mathrm{d}\varphi}{1 - f_0\varphi + k_1\varphi^2} + \tilde{\pi}_l. \tag{6.67}$$

Not only the numerical value, but also the mathematical form of a result of integration in (6.67) is dependent on the choice of constant k_1. It is time to switch on Ockham's razor: we choose the constant as $k_1 = f_0^2/4$, for which the result is the simplest:

$$\tilde{\pi} = \frac{\varphi}{1 - (f_0/2)\varphi} + \tilde{\pi}_l. \tag{6.68}$$

Passing to a one-component monolayer $f_0 = 4$ with van der Waals forces, Eq. (6.43), and restoring the dimensionality, Eq. (6.68) is represented as

$$\pi_m = \frac{kT\Gamma}{1 - 2a_0\Gamma} - \alpha\Gamma^2 \tag{6.69}$$

that can be easily recognize as the two-dimensional van der Waals equation (the wrong interpretation of coefficient $2a_0$ as an excluded area is also evident). Thus, Eq. (6.68) can be termed the dimensionless generalized two-dimensional van der Waals equation of state.

Proceeding to the second approximation, we try to account for the concavity of the dependence $f(\varphi)$. This can be attained in many ways, and the traditional method is using polynomial representation. The use of a polynomial ratio is a still more general and sensitive method. Starting from Eq. (6.66), the simplest formula of this method is

$$f = \frac{f_0 - k_1\varphi}{1 + k_2\varphi}, \tag{6.70}$$

where k_2 is a second positive constant. Obviously, constants k_1 and k_2 should be so chosen as to satisfy the boundary conditions $f = f_0$ and $(\mathrm{d}f/\mathrm{d}\varphi)_0 = -k_0$ at $\varphi \to 0$. This yields the relationship $k_1 = k_0 - f_0k_2$, so that only one of the coefficients (let it be k_2) can be chosen independently but inside the range $k_2 \leq 27/7$ (this requirement appears because f cannot be smaller than unity, whereas φ cannot be larger than unity). Putting (6.70) in Eq. (6.46) results in

$$\tilde{\pi} = \int_0^{\varphi} \frac{(1 + k_2\varphi)\,\mathrm{d}\varphi}{1 + (k_2 - f_0)\varphi + (k_0 - f_0k_2)\varphi^2} + \tilde{\pi}_l. \tag{6.71}$$

This time Ockham's razor dictates $k_2 = 2k_0^{1/2} - f_0$ (this value changes the denominator of the integrand to the square of a sum). After performing the integration in (6.71), we arrive at the equation of state

$$\tilde{\pi} = \frac{2\beta + f_0}{\beta^2} \ln(1 + \beta\varphi) - \frac{\beta + f_0}{\beta} \frac{\varphi}{1 + \beta\varphi} + \tilde{\pi}_l, \tag{6.72}$$

where a constant $\beta \equiv k_0^{1/2} - f_0$ has been introduced for the sake of convenience.

Eq. (6.72) resembles a combination of the dimensionless two-dimensional Planck and van der Waals equations of state and, naturally, is as simple as both these classical equations. However, Eq. (6.72) is more accurate and exactly reproduces three first virial coefficients. For a monolayer containing a single species, we have $f_0 = 4$ and $\beta \approx -1.428$, which imparts to Eq. (6.72) a numerical form

$$\tilde{\pi} = 0.561\ln(1 - 1.428\varphi) + 1.801\varphi/(1 - 1.428\varphi) + \tilde{\pi}_l. \tag{6.73}$$

For the case of van der Waals forces, Eq. (6.73) becomes

$$\tilde{\pi} = 0.561\ln(1 - 1.428\varphi) + 1.801\varphi/(1 - 1.428\varphi) - \tilde{\alpha}\varphi^2 \tag{6.74}$$

and permits us the direct comparison with the two-dimensional Planck and van der Waals equations. The last attractive term in (6.74) contributes only to the second virial coefficient. The other virial coefficients should be the same as in a system of hard disks, which makes possible to estimate the accuracy of Eq. (6.74) using Table 1. The result follows: three first virial coefficients are reproduced exactly, the fourth is overestimated only by 9% and the fifth by 28%. Thus, Eq. (6.74) is much more accurate than the van der Waals equation. In addition, Eq. (6.74) comprises a wider range of validity ($0 < \varphi < 0.7$) as compared with the van der Waals equation ($0 < \varphi < 0.5$).

For a long time, just the van der Waals equation was used for describing two-dimensional condensation and critical phenomena (see, e.g. [154]). For comparison, it is of interest to determine the critical constants of Eq. (6.74). Equating the first and second derivatives of the right-hand side of Eq. (6.74) with respect to φ to zero, we obtain $\varphi_c = 0.202$, $\tilde{\alpha}_c = 6.019$, and $\tilde{\pi}_c = 0.075$, where subscript “c” indicates the critical state. Other important parameters are the critical compressibility factor $Z_c = \tilde{\pi}_c/\varphi_c$ and the Boyle point as a temperature where the second virial coefficient becomes zero. Since the second virial coefficient (identical for all the three above approximations) is $2 - \tilde{\alpha}$, we obtain $\tilde{\alpha}_B = 2$ for the Boyle point. Table 2 well exhibits how the equation of state is improved when ascending in the hierarchy of approximations.

When Eq. (6.72) is applied to a mixed monolayer, its coefficients are not constant any more. They depend on the size ratios of particles and should be calculated separately for every particular mixed monolayer. Using Eqs. (6.54) and (6.55), we can express the parameter β in Eq. (6.72) via the second and third virial coefficients:

$$\beta = k_0^{1/2} - f_0 = (4b_2^2 - 3b_3)^{1/2} - 2b_2. \tag{6.75}$$

In their turn, the virial coefficients for a mixed monolayer are calculated from their partial virial coefficients as was shown in the preceding section. The computational scheme including virial coefficients seems to be most reliable since the method of calculating partial virial coefficients of mixtures are widely spread and permanently improved. Concluding this section, it should be noted that the above gaseous equations of state were deduced without a fitting procedure and can be calculated pure theoretically. To consider more general equations, we have to proceed to methods including a fitting procedure, although to a minimum extent.

Table 2
Comparison of the zero (Planck equation), first (van der Waals equation), and second (Eq. (6.74)) approximations for the equation of state (m is the number of exact virial coefficients)

Equation	Range	m	$\tilde{\pi}_c$	φ_c	$\tilde{\alpha}_c$	Z_c
Planck	$0 < \varphi < 0.25$	2	0.0483	0.1250	8	0.3864
van der Waals	$0 < \varphi < 0.5$	2	0.0625	0.1667	6.750	0.3749
(6.74)	$0 < \varphi < 0.7$	3	0.0748	0.2022	6.019	0.3699

6.2.2. Equations for the entire density range

Using a set of virial coefficients as a reference system is evident to be suitable only for gaseous equations. Proceeding to dense monolayers, we need another reference system, which can be a database created by numerical computer experiment (Monte Carlo and molecular dynamics). The most appropriate and reliable is the high-precision (with accuracy 0.01%) database (consisting of 10 points) by Erpenbeck and Luban [167] for the system of hard disks (we reproduce it below). Therefore, we will use this database as a reference system in subsequent consideration. That fact that not only accuracy, but also the accessible range rapidly increase in the approximation hierarchy (see Table 2), suggests an idea that the analysis of still higher approximations can lead to an equation of state for the entire density (concentration) range. So we continue constructing the approximation hierarchy by subsequent adding the higher terms ($k_3\varphi^2$, $k_4\varphi^3$, $k_5\varphi^4$, etc.) to the numerator of Eq. (6.70), the denominator being maintained. At each step, after putting the resulting expression for f in Eq. (6.46), all the constants k_i are so chosen as to reduce the integral to its simplest form (again Ockham's razor) with a single parameter k. In this way, a general formula for the equation of state in the nth approximation ($n \geq 3$) was deduced [159,160]

$$\tilde{\pi}^{(n)} = \frac{1}{(1-k\varphi)^{n-1}}\left\{\varphi + \frac{f_0 - 2k(n-1)}{(n-1)(n-2)k^2}\left[(1-k\varphi)^{n-1} - 1 + (n-1)k\varphi\right]\right\} + \tilde{\pi}_l. \tag{6.76}$$

Eq. (6.76) is valid for an arbitrary number of species in a monolayer and is simplified only by setting $f_0 = 4$ in the case of a single species. It is easy to verify at $\tilde{\pi}_l = 0$ that Eq. (6.76) yields a correct value for the second virial coefficient irrespective of a particular value of parameter k. This secures the applicability of Eq. (6.76) to a two-dimensional gas at any choice of k that can be converted into a fitting parameter for the entire density range. Below, we illustrate such a procedure for the system of hard disks of one size.

Let us begin with applying the computer simulation database for estimating the accuracy of the above gaseous equations. For the system of identical hard disks ($f_0 = 4$, $\tilde{\pi}_l = 0$), Eqs. (6.63), (6.68), and (6.73) becomes

$$\tilde{\pi}^{(0)} = -\frac{\ln(1-4\varphi)}{4}, \tag{6.77}$$

$$\tilde{\pi}^{(1)} = \frac{\varphi}{1-2\varphi}, \tag{6.78}$$

$$\tilde{\pi}^{(2)} = 0.561\ln(1-1.428\varphi) + \frac{1.801\varphi}{1-1.428\varphi}. \tag{6.79}$$

We join to them the van Laar equation (Eq. (6.65) at $\tilde{\pi}_l = 0$) that is not gaseous but belongs to the zero approximation (denoted as 0′). In terms of φ and for the densest (hexagonal) packing, it reads

$$\tilde{\pi}^{(0')} = -\frac{\ln(1-1.103\varphi)}{1.103}. \tag{6.80}$$

We also try to apply the fitting procedure to Eq. (6.72). The matter is that, similarly to Eq. (6.76), Eq. (6.72) at $\tilde{\pi}_l = 0$ yields a correct value for the second virial coefficient irrespective of a particular value of parameter β that, therefore, can be replaced by the fitting parameter k to give

$$\tilde{\pi}^{(2)} = \frac{4-2k}{k^2}\ln(1-k\varphi) + \frac{4-k}{k}\cdot\frac{\varphi}{1-k\varphi}. \tag{6.81}$$

Eq. (6.81) fits the standard database [167] with $k \approx 1.2258$ and the coefficient of determination $R^2 = 0.998154$ (the nearness of R^2 to unity determines the fitting quality). With this value of k, Eq. (6.81) takes a numerical form (we denote this approximation as 2′).

$$\tilde{\pi}^{(2')} = 1.0305\ln(1-1.2258\varphi) + \frac{2.2632\varphi}{1-1.2258\varphi}. \tag{6.82}$$

Since the coefficient of the logarithm turns to be very close to unity, we may drop it in Eq. (6.81) and repeat the fitting procedure, which yields

$$\tilde{\pi}^{(2')} = \ln(1-1.214\varphi) + \frac{2.295\varphi}{1-1.214\varphi} \tag{6.83}$$

with $k = 1.21397344 \approx 1.214$ and $R^2 = 0.999047$. The last number shows that Eq. (6.83) is even more accurate than Eq. (6.82). Fig. 23 exhibits the isotherms of the dimensionless two-dimensional pressure according to Eqs. (6.77)–(6.80) and (6.83) (approximations 0, 0′, 1, 2, and 2′) as compared with the standard database. Naturally, Eq. (6.83) is the best for dense states (with deviations not more than 3.5%) but deviates by 7.7% in the point with the lowest density. This stimulates us to consider approximations of higher orders.

Proceeding to Eq. (6.76), we set $\tilde{\pi}_l = 0$ to apply Eq. (6.76) to the system of hard disks. For the sake of comparison with known equations of state, we also introduce the compressibility factor (whose critical value was already used above)

$$Z \equiv \frac{\Pi a}{k_B T} = \frac{\tilde{\Pi}}{\varphi}. \tag{6.84}$$

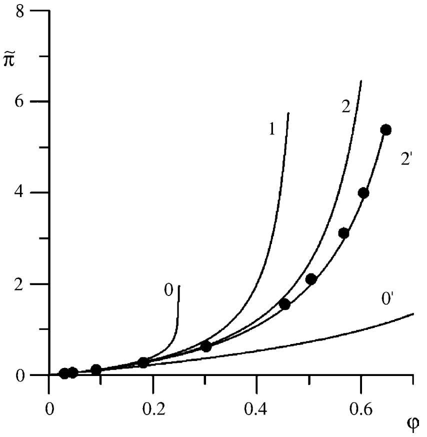

Fig. 23. The isotherms of the dimensionless two-dimensional pressure of the system of hard disks in the zero [0 is Eq. (6.77) and 0′ is Eq. (6.80)], first [Eq. (6.78)], and second [2 is Eq. (6.79) and 2′ is Eq. (6.83)] approximations. Points are the data of computer simulation [168].

Table 3
The values of the fitting parameter k and the coefficient of determination R^2 for various approximations of Eq. (6.85) ($n \geq 3$) and some other equations

n	k	R^2
2 [Eq. (6.82)]	1.225800	0.998154
3	1.014493	0.999908
$3'$ [Eq. (6.88)]	1.009229	0.99995
4	0.876677	0.99999
5	0.787681	0.99993

Then Eq. (6.76) is replaced by the equation

$$Z^{(n)} = \frac{1}{(1-k\varphi)^{n-1}}\left\{1 + \frac{4-2k(n-1)}{(n-1)(n-2)k^2\varphi}\left[(1-k\varphi)^{n-1} - 1 + (n-1)k\varphi\right]\right\} \quad (n \geq 3) \tag{6.85}$$

Taking particular values for n, we find corresponding k-values by the computer fitting procedure. Table 3 shows that the maximum accuracy (with deviations not more than 0.46% from the standard database) is attained in the fourth approximation). Passing to higher approximations, the accuracy becomes worse as a result of using only a single fitting parameter.

Let us have a look at the equations themselves in the third and fourth approximations. At $n = 3$ Eq. (6.85) becomes

$$Z^{(3)} = \frac{1 + 2(1-k)\varphi}{(1-k\varphi)^2}. \tag{6.86}$$

If $k = 1$, Eq. (6.86) reproduces the known equation of the scaled particle theory [168–170]

$$Z = (1-\varphi)^{-2}, \tag{6.87}$$

which simultaneously is a two-dimensional analog of the Carnahan–Starling equation of state for hard spheres [171]. As it follows from Table 3, the coefficient k is indeed close to unity, which gives evidence of a high accuracy of Eq. (6.87). Therefore, one can say that the scaled-particle-theory equation of state corresponds to the third approximation of the excluded area theory. We can simplify the form of Eq. (6.86) by neglecting the second term in the numerator and, for compensation, by repeated finding a k-value form the fitting procedure. The resulting equation (we denote this approximation as $3'$)

$$Z^{(3')} = (1-k\varphi)^{-2} \tag{6.88}$$

turns to be even more accurate than Eq. (6.86) and the new value of k still closer to unity (cf. approximations 3 and $3'$ in Table 3).

Eq. (6.85) in the fourth approximation is

$$Z^{(4)} = \frac{1 - (3k-2)\varphi + k(k-2/3)\varphi^2}{(1-k\varphi)^3}. \tag{6.89}$$

Table 4
The compressibility factor Z for the system of hard disks from the computer simulation data [168] in comparison with the estimates according to Eq. (6.91) [163] and Eq. (6.90) [160]

φ	Z [168]	Z [163]	$Z^{(4)}$
0.030230	1.06337	1.06333	1.06345
0.045345	1.09743	1.0973	1.09757
0.090690	1.21068	1.2095	1.21083
0.181380	1.4983	1.493	1.49930
0.302301	2.0771	2.058	2.08135
0.453451	3.4243	3.372	3.43960
0.503834	4.1715	4.107	4.19089
0.566814	5.4963	5.427	5.51355
0.604601	6.6074	6.558	6.61278
0.647787	8.306	8.359	8.29391

Using the k-value shown in Table 3, Eq. (6.89) acquires a numerical form

$$Z^{(4)} \approx \frac{1 - 0.63\varphi + 0.184\varphi^2}{(1 - 0.876677\varphi)^3}, \tag{6.90}$$

which, according to Table 3, is the most accurate in the family of Eq. (6.85). It remains to ascertain to what extent Eq. (6.90) is competitive with the best equations of state presented in the literature for hard disks.

Santos et al. [162,172] suggested a simple equation of state (written here in our notations)

$$Z = \left(1 - 2\varphi + \frac{2\varphi_\infty - 1}{\varphi_\infty^2}\varphi^2\right)^{-1}, \tag{6.91}$$

where $\varphi_\infty = 1/f_\infty = 3^{1/2}\pi/6$ is the upper limit for the parking area φ at the hexagonal packing. By comparison with the most known equations of state for hard disks [167,173–178], the authors showed Eq. (6.91) to be of the highest precision among simple equations. Thus, apart from complex equations of type of the approximants of Pade [178] and Levin [167], it is enough to compare Eq. (6.90) with Eq. (6.91) and the standard database. Table 4 gives preference to Eq. (6.90) that becomes the most precise among simple equations. It is also competitive with respect to complex equations, being only a little less accurate than the Levin approximant [159].

As the short-range part has been precised, we can return to the general form of Eq. (6.76). For the case of van der Waals forces (see Eq. (6.43)), Eq. (6.76) becomes

$$\tilde{\pi}^{(n)} = \frac{1}{(1 - k\varphi)^{n-1}}\left\{\varphi + \frac{f_0 - 2k(n-1)}{(n-1)(n-2)k^2}\left[(1 - k\varphi)^{n-1} - 1 + (n-1)k\varphi\right]\right\} - \sum_{i,k}\tilde{\alpha}_{ik}\varphi_i\varphi_k. \tag{6.92}$$

In the case of a single species, Eq. (6.92) is reduced to

$$\tilde{\pi}^{(n)} = \frac{1}{(1 - k\varphi)^{n-1}}\left\{\varphi + \frac{4 - 2k(n-1)}{(n-1)(n-2)k^2}\left[(1 - k\varphi)^{n-1} - 1 + (n-1)k\varphi\right]\right\} - \tilde{\alpha}\varphi^2, \tag{6.93}$$

where the values of $n \geq 3$ and k can be taken from Table 3. Since Eq. (6.93) predicts phase transitions and the critical state, the quality of a particular approximation can be estimated by calculating the critical constants, especially the critical compressibility factor Z_c, as we did in Table 2. Such analysis [159,160] shows that, although the equation applicability widens to the entire density range, the compressibility factor only slightly decreases (from 0.3699 in Table 2 to 0.3661 in the fourth approximation) and remains overestimated. The main source of this inaccuracy is the attractive term. Indeed, Eq. (6.93) includes a highly developed and strict repulsive part and a very primitive attractive part taken from the van der Waals equation. This part should be also improved, but not within the theory of excluded area to which we devoted this section.

6.3. Orientation equation of state

Passing to a monolayer with anisometric particles, the role of the geometrical particle individuality increases, which is displayed in the presence of the derivative $\mathrm{d}h/\mathrm{d}\varphi$ in Eq. (6.42) (a similar effect produces the derivative $\mathrm{d}h/\mathrm{d}\theta$ in Eq. (6.44)). An explicit relation between the monolayer thickness, two-dimensional pressure, and surface concentration can be called an orientation equation of state. Finding this equation can be formulated as a separate problem of thermodynamics and statistical mechanics. For a long time, there was no idea of the form of such an equation, and only first steps in formulating theory were undertaken recently [159].

To understand the significance of the orientation equation of state, let us first discuss the role of the derivative $\mathrm{d}h/\mathrm{d}\varphi$ in Eq. (6.42). The thermodynamic stability condition requires that $\mathrm{d}\tilde{\pi}/\mathrm{d}\varphi > 0$. Traditionally imagining that particles pass from "lying" to "standing" positions at increasing φ, we also have $\mathrm{d}h/\mathrm{d}\varphi > 0$. However, this derivative enters Eq. (6.42) with a negative sign, so that the presence of the derivative $\mathrm{d}h/\mathrm{d}\varphi$ in Eq. (6.42) always lowers the derivative $\mathrm{d}\tilde{\pi}/\mathrm{d}\varphi$ and the monolayer stability. One can imagine the case when the derivative $\mathrm{d}h/\mathrm{d}\varphi$ is such large as to reverse the sign of $\mathrm{d}\tilde{\pi}/\mathrm{d}\varphi$, which means instability and phase transition. Thus, we conclude that, in principle, surface orientation can be the cause of a two-dimensional phase transition in a monolayer. This idea was trivially manifested in experiments with surfactant monolayers, but not formulated thermodynamically. Remarkably, this conclusion is valid irrespective of the term $\tilde{\pi}_l$ in Eq. (6.42), i.e. even for hard particles.

The existence of an orientation equation of state is evident even for a rarified gaseous monolayer. The orientation effect is inevitable since collisions of particles occur only in one plane. The condition $\mathrm{d}h/\mathrm{d}\varphi = 0$ is fulfilled in the limit $\varphi \to 0$ when there are no collisions. If h_0 is a minimal initial monolayer thickness at the flat orientation of particles, one can assume the thickness increment $h - h_0$ to be proportional to the collision intensity. The latter is proportional to the square of particle concentration and to the effective cross-section of collisions, which is determined by the longitudinal (along the surface) linear dimension of particles. The particle parking area is proportional to the square of this linear dimension, and the product of the parking area and h is the particle volume that can be assumed constant. Then the particle linear dimension turns to be inversely proportional to the square root of the thickness, and we arrive at the orientation equation of state for a gaseous monolayer

$$h - h_0 = \frac{k_3 \varphi^2}{h^{1/2}}, \tag{6.94}$$

where k_3 is a constant. Eq. (6.94) becomes especially simple if h_0 is negligible as compared with h (e.g. at the orientation of long chains):

$$h^{3/2} \approx k_3 \varphi^2. \tag{6.95}$$

In this case $\mathrm{d}\ln h/\mathrm{d}\ln\varphi = 4/3$, and the contribution of the orientation effect to Eq. (6.42) is reduced to the numerical coefficient.

Proceeding to condensed monolayers (and replacing φ with θ), one can start from the theory of elasticity. This idea was already used in the theory of membranes [179] by introducing a tilt modulus. It is reasonable to assume that a monolayer acquires elastic properties not at once, but after attaining a certain threshold degree of coverage θ_t. In accordance with the theory of elasticity, the cause of the monolayer thickening is the tangential stress π_m/h. The corresponding transversal elasticity modulus is

$$\lambda = \frac{\mathrm{d}(\pi_m/h)}{\mathrm{d}\ln h}. \tag{6.96}$$

The integration of Eq. (6.96) yields the orientation equation of state in the form

$$\pi_m = \frac{\pi_t h}{h_t} + \lambda h \ln\left(\frac{h}{h_t}\right), \tag{6.97}$$

where the values π_t and h_t correspond to θ_t, i.e. to the beginning of orientation within the elasticity mechanism. The transition to such orientation is typically marked with a kink in the pressure isotherm, so that the value π_t is easily measurable. Besides the minimum monolayer thickness h_0 (corresponding to zero pressure), it is convenient to introduce the maximum thickness h_∞ corresponding to the densest packing at infinite pressure. Then we can represent the orientation equation of state (6.97) in a dimensionless form

$$\tilde{\pi}' = \frac{\tilde{\pi}_t' \tilde{h}}{\tilde{h}_t} + \tilde{\lambda}\tilde{h}\ln\left(\frac{\tilde{h}}{\tilde{h}_t}\right), \tag{6.98}$$

where $\tilde{\pi}'$ is of the same sense as in Eq. (6.44), $\tilde{\lambda} \equiv \lambda a_\infty h_\infty / k_\mathrm{B} T$, and $\tilde{h} \equiv h/h_\infty \leq 1$ is the reduced monolayer thickness.

For a dense state under consideration, we may set $a^\mathrm{ex} = a$ and, correspondingly,

$$g^\mathrm{ex} = \frac{a}{a_\infty} = \frac{h_\infty}{h} = \frac{1}{\tilde{h}}. \tag{6.99}$$

Putting Eq. (6.99) in Eq. (6.44) and using (6.45) for the one-component case, we obtain the equation of state for a monolayer with van der Waals forces

$$\tilde{\Pi}' = \int_0^\theta \frac{1 - \mathrm{d}\ln\tilde{h}/\mathrm{d}\ln\theta}{1 - \theta/\tilde{h}}\,\mathrm{d}\theta - \tilde{\alpha}'\theta^2, \tag{6.100}$$

which, together with Eq. (6.98), completely describes the state of a monolayer with variable particle orientation. The joint general solution of Eqs. (6.98) and (6.100) is problematic. However, considering the differential form of the equation of state, we can obtain some qualitative results concerning the kink points of second-order phase transitions related to the particle orientation. After differentiating, Eq. (6.100) becomes

$$\frac{\mathrm{d}\tilde{\Pi}'}{\mathrm{d}\theta} = \frac{1 - \mathrm{d}\ln\tilde{h}/\mathrm{d}\ln\theta}{1 - \theta/\tilde{h}} - 2\tilde{\alpha}'\theta - \theta^2\frac{\mathrm{d}\tilde{\alpha}'}{\mathrm{d}\theta}, \tag{6.101}$$

where, for the sake of generality, the attraction constant $\tilde{\alpha}'$ is assumed to be also variable due to orientation. Since both the derivatives on the right-hand side of Eq. (6.101) are positive, the orientation leads to decreasing the derivative $\mathrm{d}\tilde{\pi}'/\mathrm{d}\theta$. Obviously, there will be a similar behavior of the derivative $\mathrm{d}\pi_m/\mathrm{d}\Gamma = k_\mathrm{B}T\,\mathrm{d}\tilde{\pi}'/\mathrm{d}\theta$. So we conclude that, if a kink point is caused by an orientation phase transition, the positive slop of the pressure isotherm should be smaller on the side of larger coverage degrees θ.

7. Summary and horizons

Although this paper is a review, it contains a lot of material only recently published in the literature and still not familiar to the wide audience of surface scientists. It is of hope, the review promotes accepting this material with better understanding. Using an overall tensorial treatment in the mechanical and chemical parts of the review yields a number of new notions, such as the volume and mass displacement tensors and the chemical affinity tensor, and even a new class of thermodynamic variables, directed partial molar quantities. The chemical potential tensor and the affinity tensor should be formally incorporated in the chemical kinetics of solids. It is although of note that it is more important to understand that to use the tensorial nature of these quantities in practice. The matter is that only a single direction is typically used in a particular practical task, and, correspondingly, a single tensorial component is taken whose tensorial origin can be unnecessarily mentioned (it may be simply called ‘‘chemical potential’’). However, there are special cases when just the tensorial behavior of the chemical potential determines an effect observed. An example considered is the mechanochemical effect of dissolution when applying stress in one direction induces a change in solubility in another direction. No doubt, the discovery of the mechanochemical effect of the strain sign will have further development, both in the theoretical and experimental aspects.

The fast development of nanothermodynamics is expected. First of all, the equilibrium condition should be reformulated. As was reported above, Gibbs established the equilibrium condition for a dissolving solid particle with a special restriction that the solid state is maintained when changing the particle size. This means that Gibbs considered particles large enough as compared with molecular dimensions. For nanoparticles, the size dependence of particle properties cannot be ignored, and, as was mentioned in Section 4.1, the derivative $\mathrm{d}\sigma/\mathrm{d}R$ should be taken into account. Among other important problems, there is accounting for the quantum-size effects. These effects have been investigated in many aspects, but the study of their influence on surface energy, chemisorption, and the size dependence of surface tension, only starts, to speak not only about nanoparticles, but also about thin films.

The excluded-area theory of an equation of state has been placed in this review because it has a thermodynamic basement. This is an exceptional case since, generally, the equation of state is not a consequence of thermodynamics and is something that should complement thermodynamics. The theory results in finding the repulsive term of an equation of state with great precision, but says nothing about the attractive term, which is to be found by quantum and statistical mechanical (not thermodynamic) methods. Using these methods and modeling will secure further progress in the calculation of the attractive part of an equation of state, and the exact knowledge of the repulsive part will promote this progress. It is also important for finding the equation-of-state constant by fitting to experimental results. Having two or more fitting parameters, a god fit for the attractive constant was often attained earlier at the expense of the repulsive constant. With the above theory, this will be excluded in the future when the repulsive constant can be determined irrespective of the attractive one.

However, finding the repulsive constant from the excluded area requires the knowledge of the geometrical shape of a particle. This is of no importance in two cases: if a particle is soft and if a monolayer is of low density. In the first case, a particle (consisting, for example, of flexible fragments) is capable of changing its configuration at various packing. In the second case, a particle (if not at zero temperature) is in a state of thermal Brownian rotation and seems to be round irrespective of its real shape. Thus, above considering the excluded area as the area of a circle is of general significance. The knowledge of the real particle shape and dimensions becomes important for rigid particle in a high-density monolayer. When the theory of excluded area for such particles will be formulated, it will make the basement for the equation of state of anisotropic two-dimensional phases. The classification of such phases will correspond to the classification of the particle types. Further progress is expected in formulating the theory of an orientation equation of state.

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