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Analysis of the Suitability of Mechanics Models for Calculating Interface Surface Tension

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Abstract—The suitability of mechanics models for calculating interface surface tension (ST) is analyzed from the viewpoint of molecular kinetic theory. A theory based on the lattice gas model is shown to consider the intermolecular interactions of comparable components and a change in the average bond lengths between dense phase particles in a quasi-chemical approximation that describes direct correlations. It can be applied to three aggregate states and their interfaces, allowing comparison of mechanics and thermodynamics models if the concept of ST is introduced. It is found that the Laplace equation is incompatible with the conditions of the equilibrium of coexisting phases on distorted vapor—liquid interfaces, but it can be used to describe the mechanical equilibrium in systems with an intermediate film between the neighboring phases (if there is no chemical equilibrium between them). Mechanical and thermodynamic definitions of ST under different conditions are discussed. It is shown that to calculate equilibrium ST, we must use the Gibbs definition as the excess free energy at the interface. A procedure for calculating nonequilibrium analogs of surface characteristics (free Helmholtz energy, chemical potential, ST) of solid solutions is formulated that considers internal deformations of solid boundaries and the effect of external loads.

Keywords: thermodynamics, deformed states, phase, relaxation times, microscopic theory, interface, surface tension

INTRODUCTION

We always deal with continuum mechanics models in thermodynamic approaches to processes in liquid and solid phases. These are primarily models of vapor—liquid systems and their interfaces, which are used in the theory of condensation [1—4] and new phase formation [5—7], and models for solids and their interfaces with mobile vapor—liquid phases and between different solid phases in colloidal chemistry [8—11]. These models play an important role in describing physical adsorption [12—20] and chemisorption [21—25].

Thermodynamics and mechanics models are normally assumed to be fully compatible. This belief is based on Gibbs' fundamental work in which solid mechanics was considered as a part of thermodynamics [26]. This relationship was apparently analyzed for the first time in [27] in describing internal and external deformations of solids, both from the correspondence between the principles of continuum mechanics and thermodynamics [28, 29] and the molecular kinetic theory for defective one- and multicomponent systems [30—35].

Ways of describing deformed solid phases in thermodynamics [27] were analyzed from the viewpoint of the concept of phase separation, which rests on Gibbs's familiar result that the overall equilibrium of a system represents the necessary simultaneous presence of three partial equilibria: mechanical, thermal, and chemical [26]. Each of these equilibria has its own characteristic relaxation times, so to reach overall equilibrium we must consider the relaxation times for attaining all partial equilibria [29]. It was shown in [27] that the main postulates of equilibrium thermodynamics and continuum mechanics are mutually exclusive. The internal deformations of solids are caused by the slow mixing of components over the system's space. It was also shown that the concepts of interface equilibrium and relaxation times allow us to make distinctions in the interpretations of the major ideas for deformed and undeformed bodies by focusing only on the character of the mass distribution without using specific model/microscopic representations of solids.

The main concepts of continuum mechanics are stresses and deformations. For interfaces, the key concept is surface tension (ST), which was first introduced as a boundary condition, ending the description of the properties of bulk phases in mechanics models. Gibbs later introduced it into thermodynamics [26]. This work compares the mechanical and thermodynamic interpretations of the ST concept itself and its

definitions according to these two approaches. In [26, p. 299], Gibbs remarked that in discussing the state of a system with a distorted boundary, the presence of a membrane between different phases is assumed. (This is the model of continuum mechanics, in which there is no concept of chemical potential is absent.) Since Gibbs, all scientists have dealt with the concept of the equality of pressures on both sides of an interface, which he mentioned after Eq. (500) in [26], provided that a membrane was present. At the same time, in discussing the physical picture of a vapor–liquid interface, it has been repeatedly stated [36] that in a two-phase system, vapor and fluid molecules are in direct contact with one another (i.e., are in direct chemical equilibrium) without any membrane or film, so the mechanical Gibbs model does not correspond to a real system.

The idea of a possible transfer of the scheme proposed by Gibbs to the vapor–liquid interface has become popular [1–7, 37–39], though Gibbs's note on the presence of the membrane is omitted everywhere. As a result, different ways of interpreting ST calculations using mechanical and thermodynamic definitions have been formulated. These definitions were reviewed in [40]. The multiplicity of the existing ST definitions for distorted interfaces indicates that their introduction is fundamentally incorrect, due to the active use of the concepts of continuum mechanics, even though the physical situation is different.

In this work, we first compare the mechanics and thermodynamics models when introducing the ST concept itself, and then present the results from calculating ST in equilibria and with regard to deformations (internal and external) at an interface. In the first part, we consider in detail problems for a vapor–liquid interface, where the surface is presented as a membrane/film separating two phases (conditions for applying the Laplace equation at distorted interfaces of the coexisting vapor–liquid phases). In the second part, distinctions in the mechanical and thermodynamic definitions of ST and ways of considering two types of deformations (internal and external) in calculating ST are discussed.

CONDITIONS OF PHASE SEPARATION AND RELAXATION TIMES

A traditional way of determining conditions of phase equilibrium in thermodynamics is to search for the free energy minimum of a separating system in the isothermal process ($T = $ const) [26, 41, 42]. A model of an interface with an infinite homogeneous elastic thin film ($\alpha\beta$) between phases α and β is considered. Let the ST coefficient σ not depend on the curvature of a droplet's surface. Variation of the system's Helmholtz energy is written as

$$\delta F = \delta F^{\alpha} + \delta F^{\beta} + \delta F^{\alpha\beta}. \quad (1)$$

At total system volume $V = $ const we have the expressions for the three summands:

$$\delta F^{\alpha} = -P_{\alpha}\delta V_{\alpha} + \mu_{\alpha}\delta N_{\alpha},$$

$$\delta F^{\beta} = -P_{\beta}\delta V_{\beta} + \mu_{\beta}\delta N_{\beta},$$

$$\delta F^{\alpha\beta} = \sigma\delta A,$$

where surface A, as an area without volume, does not have mass either. Since the total volume and mass are constant ($V_{\alpha} + V_{\beta} = V$, $N_{\alpha} + N_{\beta} = N$, $\delta N_{\alpha} + \delta N_{\beta} = \delta N = 0$, $\delta V_{\alpha} + \delta V_{\beta} = \delta V = 0$), and excluding the characteristic of phase β, we have

$$\delta F = (\mu_{\alpha} - \mu_{\beta})\delta N_{\alpha} - (P_{\alpha} - P_{\beta})dV_{\alpha} + \sigma dA. \quad (2)$$

If the geometric parameters of a spherical droplet with radius r are substituted into this relation, $V_{\alpha} = 4\pi r^{3}/3$, $dV_{\alpha} = 4\pi r^{2}dr$, $A = 4\pi r^{2}$, $\delta A = 4\pi r\delta r$, we obtain the standard thermodynamic equation for free energy variation,

$$\delta F = (\mu_{\alpha} - \mu_{\beta})\delta N_{\alpha} - (P_{\alpha} - P_{\beta} - 2\sigma/r)4\pi r^{2}\delta r. \quad (3)$$

For two independent variations of δN_{α} and dV_{α} there must be the equalities reflecting the conditions of the chemical and mechanical equilibria: $\mu_{\alpha} = \mu_{\beta}$ and $P_{\alpha} - P_{\beta} = 2\sigma/r$ (the Laplace equation). This result is a consequence of using the usual quasistatic (hypothetical) conditions of moving to equilibrium. It implies the comparability of relaxation times of momentum and mass transfer processes. In [29, 43], it was proposed that experimental data on the relaxation times of momentum and mass transfer processes be used instead. It is known that $\tau_{mom} \ll \tau_{mass}$ [36, 44]; i.e., quasi-static consideration contradicts the experimental data.

Let us consider the conditions for establishing a two-phase equilibrium from the viewpoint of a system's evolution to its equilibrium state in considering the above-mentioned relaxation time ratio during the isothermal process. The time evolution of free energy (2) near the equilibrium point is written as

$$\frac{d\delta F(t)}{dt} = \frac{d}{dt}\big[\{\mu_{\alpha}(t) - \mu_{\beta}(t)\}\delta N_{\alpha}(t) \\ - \{P_{\alpha}(t) - P_{\beta}(t)\}\delta V_{\alpha}(t) + \sigma(t)\delta A(t)\big]. \quad (4)$$

By introducing differences in the forms $\Delta\mu(t) = \mu_{\alpha}(t) - \mu_{\beta}(t)$ and $\Delta P(t) = P_{\alpha}(t) - P_{\beta}(t)$, we rewrite (4) as

$$\frac{d\delta F(t)}{dt} = \frac{d}{dt}[\Delta\mu(t)\delta N_{\alpha}(t) - \Delta P(t)\delta V_{\alpha}(t) + \sigma(t)\delta A(t)].$$

We then divide the change in F caused by the evolution of extensive and intensive parameters of the system's state:

$$d\delta F(t)/dt = d\delta F_{int}(t)/dt + d\delta F_{ext}(t)/dt,$$

where

$$\frac{d\delta F_{\text{ext}}(t)}{dt} = \Delta\mu(t)\frac{d\delta N_\alpha(t)}{dt} \\ - \Delta P(t)\frac{d\delta V_\alpha(t)}{dt} + \sigma(t)\frac{d\delta A(t)}{dt}, \quad (5)$$

$$\frac{d\delta F_{\text{int}}(t)}{dt} = \frac{d\Delta\mu(t)}{dt}\delta N_\alpha(t) \\ - \frac{d\Delta P(t)}{dt}\delta V_\alpha(t) + \frac{d\sigma(t)}{dt}\delta A(t). \quad (6)$$

The evolution of extensive parameters (5) does not alter the values of the intensive parameters of the state. We therefore limit ourselves to expression (6) and rewrite it, moving phase volume α (of a droplet) $\delta V_\alpha(t)$ to the right, and consider that by definition of extensive variables $\delta V_\alpha(t)$, $\delta N_\alpha(t)$, and $\delta A(t)$, there are coefficients of the proportionality of contributions of these values to the thermodynamic functions: $\delta N_\alpha/\delta V_\alpha = v_\alpha^{-1}$, v_α is the specific volume of molecules in phase α, $\delta A/\delta V = 2/r$. Then

$$\frac{1}{\delta V_\alpha(t)}\frac{d\delta F_{\text{int}}(t)}{dt} = \frac{1}{v_\alpha}\frac{d\Delta\mu(t)}{dt} - \frac{d\Delta P(t)}{dt} + \frac{2}{r}\frac{d\sigma(t)}{dt}. \quad (7)$$

This equation is similar to Eq. (45.7) from [29] (though they differ in sign). All values in Eq. (7) are described by different kinetic equations in partial derivatives (hyperbolic for momentum (pressure) transfer and parabolic for mass (chemical potential) transfer). Nonetheless, general relations are preserved between pressure τ_P associated with time dependence $d\Delta P(t)/dt$, chemical potential τ_μ associated with $d\Delta\mu(t)/dt$, and relaxation times with respect to that of the surface's contribution τ_σ associated with $d\sigma(t)/dt$, allowing us to discuss the limiting cases of establishing the equilibrium of a heterogeneous system.

1. Coexisting Equilibrium Phases in Contact with Each Other

Since an interface is not an autonomous phase and does not affect the internal properties of phases, the properties of an interface cannot be parameters of a system's state. ST relaxation time τ_σ is thus shorter than relaxation time τ_P of pressure in the coexisting phases ($\tau_P \gg \tau_\sigma$), and the third summand equal to the derivative with respect to $\sigma(t) \to \sigma_e$ can be ignored in (7). The the relaxation time of the system is then completely governed by the relaxation time of mass transfer, and the evolution of pressure is written as $\Delta P(t) = \Delta P(\Delta\mu(t))$, i.e., in the form of a functional dependence on the evolution of chemical potential. In terms of construction, $\Delta\mu(t \to \infty) = 0$ in the limit, which leads to $\Delta P(t \to \infty) = 0$ at any size of the coexisting phases or $P_\alpha = P_\beta$. This is the case of an equilibrium droplet, which was described in [29, 43, 45, 46]. This droplet

corresponds to the vapor–liquid phase equilibrium over three partial equilibria of the inner states of coexisting phases, which is entirely consistent with the Yang–Lee theory of condensation [47] (see also [48]), according to which the thermodynamic parameters corresponding to a strict equilibrium must agree with the parameters of the coexistence curve.

2. A Foreign Film Separates Two Phases

If a foreign film excludes molecular exchange between phases in internal equilibrium states, the time of the full relaxation of the film itself is much longer than that of the mobile phases. This is a typical case of a dense material film (e.g., latex or rubber) [3] confining the mobile vapor and liquid phases. The time of the film's relaxation is determined by its internal properties and has nothing in common with the state of matter in either phase. We denote the mechanical ST of the material as σ_m. Like any dense phase, the film itself is also characterized by relaxation times in accordance with the relations in the introduction: $\tau_{\text{mom}}(\text{film}) \ll \tau_{\text{mass}}(\text{film})$. Pressure $\tau_{\text{mom}}(\text{film})$ and mass $\tau_{\text{mass}}(\text{film})$ relaxation times can be distinguished in it. The pressure relaxes almost instantly and the relaxation of mass is governed by internal processes in the material (a description of these relaxation processes was the subject of [49, 50]).

If there is no exchange of matter, there is no chemical equilibrium; i.e., $d\Delta\mu(t)/dt = 0$, and only the mechanical equilibrium is considered when the right part of equation (7) is written as

$$\frac{T}{\delta V_\alpha(t)}\frac{d\delta S_{\text{int}}(t)}{dt} = -\frac{d}{dt}(\Delta P(t) - 2\sigma(t)/r). \quad (8)$$

The process of establishing equilibrium is determined by relationships between the pressure and film ST relaxation times. As above, when $t \to \infty$ we have $\Delta P(t \to \infty) = 0$, while $\sigma(t \to \infty) = \sigma_m$. This value obviously does not coincide with equilibrium σ_e discussed in Subsection 1. In the limit, we have another state of the system that differs from the strictly equilibrium state for planar vapor–liquid interface $P_\alpha = P_\beta$ by the value $2\sigma_m/r$; i.e., $P_\alpha = P_\beta + 2\sigma_m/r$ is the Laplace equation for mechanical equilibrium when there is no chemical equilibrium.

3. A Foreign Film Does Not Hinder Molecular Transfer, but Molecular Exchange (Chemical Potential τ_μ) Relaxation Time Is Shorter Than Pressure Relaxation Time τ_P

Relationship $\tau_P \gg \tau_\mu$ contradicts all existing experimental data [36, 44]. This case is discussed from a methodological point of view. We once again obtain Eq. (8), where $\sigma_m \neq \sigma_e$. This corresponds to the accepted sequence of first establishing mechanical

and then chemical equilibria in deriving the Calvin equation [2–5]. There is functional relationship $\Delta\mu(t) = \Delta\mu(\Delta P(t))$ when the chemical potential is adjusted to the pressure at this moment in time. Finally, we again have $P_\alpha = P_\beta + 2\sigma_m/r$, where σ_m cannot be determined experimentally because $\tau_P \gg \tau_\mu$. In practice, σ_m is assumed to be equal to σ_e, but this is meaningless because of contradictions between the conditions of deriving this expression and those of an experiment. Or, the third case contradicts the experimental data on relaxation times and cannot be considered as an area for application of the Laplace equation. The theory [47, 48] states that so-called metastable droplets contradict the existence of equilibrium in the considered system, since we do not even determine the statistical sum or equation of state for them.

Our analysis of relaxation times in establishing overall equilibrium thus demonstrates the incorrectness of the mechanics model for a vapor–liquid interface.

DEFINITION OF ST FOR COEXISTING PHASES

A detailed analysis of the existing mechanical and thermodynamic definitions of equilibrium ST value σ_e was presented in [40]. It was shown that the thermodynamic definition introduced by Gibbs as the excess free energy of interfaces with respect to the free energies in bulk phases exists only formally. Most of the current thermodynamic approaches to calculating ST focus on using the Laplace equation even if there is no intermediate film between the vapor and the fluid [1–7, 37, 38]; i.e., they use representations of metastable states for which not even the concept of the statistical sum and the equation of state are defined [47, 48]. Due to the incorrectness of using mechanical representations, these models do not yield sufficiently grounded results.

There is a similar situation for more accurate molecular theories based on integral equations of the liquid state. The problem is that the virial theorem, which is equivalent to the thermodynamic definition of pressure [37, 38, 51], is used in deriving expressions for ST values. There is also a similar situation when the Irving–Kirkwood equation is used [52]; i.e., all approaches require the mechanical definition of ST instead of calculating it through the free energy or the chemical potential (which is much more labor intensive). The same situation is observed when stochastic means of calculation (molecular dynamics and Monte Carlo) are used.

The only exception seems to be the theory based on the lattice gas model (LGM), which allows us to obtain solutions for the chemical potential relatively simply. This example shows the mechanical and thermodynamic definitions of ST yield different solutions, so a general calculation procedure was proposed in

[53, 54] that allowed a combination of both requirements for the chemical and mechanical equilibria at each point of the transitional region of an interface. This way coincides with the requirements of the overall equilibrium of a system through three partial equilibria (mechanical, thermal, and chemical), the local pressure according to the experimental data, and adjustment to the local chemical potential value.

For calculations we need to determine the concentration profile of mixture components θ_q^i, which characterizes the probability of an i component being in the q layer of the transitional region, and their pair distribution functions (DFs) θ_{qp}^{ij}, characterizing the probability of ij particle pairs being at qp-type sites: $1 \leq i \leq s_c$, $s = s_c + 1$, where s_c is the number of components and s is the number of occupancy states, including a vacancy, of any site of the system. This question has been discussed repeatedly [29, 45, 46, 53, 54].

The expression for the free Helmholtz energy in the layered spherical LGM, normalized to one site of the system, is written as

$$
\begin{aligned}
F_{\text{lat}}(R) = \sum_q F_q(R)\sum_i \{\theta_q^i(\nu_q^i + kT\ln\theta_q^i) \\
+ \frac{kT}{2}\sum_{p=q-1}^{q+1} z_{qp}(R)\sum_{j=1}^s [\hat{\theta}_{qp}^{ij}\ln\theta_{qp}^{ij} - \theta_q^i\theta_p^j\ln(\theta_q^i\theta_p^j)]\},
\end{aligned} \tag{9}
$$

where $2 \leq q \leq \kappa(R) - 1$ denotes the numbers of layers in the transitional region of the interface (the κ value also depends on radius R); $z_{qp}(R)$ is the number of neighbors between qp-type sites; $\hat{\theta}_{qp}^{ii} = \theta_{qp}^{ii}\exp(-\varepsilon_{qp}^{ii}/k_BT)$; and ν_q^i are the one-particle contributions to the free energy of q-type sites [53, 54]. Here, $F_q(R) = N_q(R)/\sum_{q=2}^{k-1} N_q(R)$ is the fraction of q-type sites for a droplet with radius R; $\sum_{q=2}^{k-1} F_q(R) = 1$; and $N_q(R) = 4\pi R_q^2$ is the number of sites in a monolayer with number q. For a planar lattice, all $N_q(R)$ numbers are identical: $F_q(R) = 1/(\kappa - 2)$ and

$$
\begin{aligned}
\mu_q^i(\text{con}|R) = \nu_q^i + kT\ln\theta_q^i \\
+ \frac{kT}{2}\sum_{p=q-1}^{q+1} z_{qp}(R)\ln[\hat{\theta}_{qp}^{ii}/(\theta_q^i\theta_p^i)].
\end{aligned} \tag{10}
$$

Equations (9), (10) correspond to allowing for the interaction between nearest neighbors. In the solution volume, in the absence of the interface effect (when all DFs do not depend on site numbers), formula (11) transforms into the expression for the chemical potential of the i component: $\mu_i = \nu_i + kT\ln\theta_i + zkT\ln(\hat{\theta}_{ii}/\theta_i^2)/2$.

According to Gibbs, interface tension σ is determined by the difference between the free energies of the near-surface region in the solution volume [26],

and is written in a similar manner for both planar and distorted interfaces with radius R (as in Subsection 1 in the previous section) [53, 54]:

$$\sigma(R)A = \sum_{q=2}^{\kappa-1} \sum_{i=1}^{s_c} [\mu_q^i(\mathrm{con}) - \mu_i]\theta_q^i,$$

$$B(R) = \sum_{i=1}^{s_c} \mu_i \Gamma_i = 0, \qquad (11)$$

$$\Gamma_i = \sum_{q=2}^{\kappa-1} [\theta_q^i - \theta_\alpha^i|_{q=1}^{q=\rho_e} - \theta_\beta^i|_{q=\rho_e+1}^{q=\kappa}],$$

where A is the surface area, Γ_i is the normalized value of the excess amount of the i component in the transitional region of the interface; $q = \rho_e$ corresponds to the position of the analog of an equimolar separating surface for a multicomponent mixture of any density when $B(R) = 0$. The condition of the local mechanical equilibrium is ensured by using the local Gibbs–Duhem equation (see [55] for details). This approach can be applied to any type of interface that can be described within the LGM.

INTERNAL AND EXTERNAL DEFORMATIONS OF SOLIDS

In [27], it was shown that internally and externally deformed bulk states correspond to nonequilibrium states. Local atomic densities θ_q^i and their pair FDs θ_{qp}^{ij} then become functions of time. The q and p types of the sites belong to local heterogeneities (sublattices for complex crystallographic cells in the bulk phase for the sites of the transitional region at the interface). In [29, 56], it was shown that nonequilibrium thermodynamic potentials are similarly expressed through functions θ_q^i of the i-type and θ_{qp}^{ij} in both equilibrium and nonequilibrium states. This allows us to operate with concepts of the nonequilibrium thermodynamic potentials as analogs of equilibrium thermodynamic potentials F, G, S, U and move from equilibrium to kinetic theory, bypassing the concept of nonequilibrium thermodynamics, where a local equilibrium is postulated. When there is no local equilibrium, the evolution of the system is described by diffusion equations, due to the redistribution of components.

On the other hand, it was shown in [27] that the nonequilibrium states of solid solutions reflect their internal deformations. The elastic free energy of internal deformations of a solid is written as

$$\Delta F_{\mathrm{elast}} = F_{ne} - F_e. \qquad (12)$$

Both summands in (12) are expressed identically (by formulas of type (9)) through unary and pair DFs calculated for current moment in time F_{ne} and equilibrium state F_e. Equations for the nonequilibrium concentration profile at the two-phase boundary were considered in detail in [55].

Using λ_{qp}^{ne}, we denote the average distance between q and p sites in the nonequilibrium state at a given moment in time t. For heterogeneous systems, allowing for the deformability of a lattice structure means its constants become dependent on the type of heterogeneity (denoted as $\lambda_{qp} \neq \mathrm{const}$). Partial contributions to local lattice constant λ_{qp}^{ij} from neighboring molecular pairs ij become dependent on the type of sites on which the interacting pairs of molecules are located; $\lambda_{qp} = \sum_{ij} \lambda_{qp}^{ij} \theta_{qp}^{ij}$. Or, the λ_{qp} values are the means over the lattice ensemble. Here, function θ_{qp}^{ij} is the average fraction of pairs of the nearest neighboring ij molecules on a pair of the nearest neighboring sites in qp monolayers.

Let us characterize the correspondence between the local equilibrium and nonequilibrium states of the solution through changes in the average bond lengths [27]. Difference $\Delta\lambda_{qp}^{ne}(t) = \lambda_{qp}^{ne}(t) - \lambda_{qp}^e$ characterizes the degree of internal deformation. Average parameters $\lambda_{qp}^{ne}(t)$ of a nonequilibrium body correspond to the current distribution values $\theta_q^i(t)$ and $\theta_{qp}^{ij}(t)$. Or, a deviation from equilibrium is composed of nonequilibrium mass distribution $\theta_q^i(t)$ over the system volume and nonequilibrium pair distribution $\theta_{qp}^{ij}(t)$ with respect to the local density at any point of the system. Because of the rapid relaxation of momentum, the λ_{qp}^{ne} values are found using an algebraic relationship rather than a kinetic one. This relationship can be described according to the form of the problem. It either must correspond to the F_{ne} minimum over $\lambda_{qp}^{ne}(t)$ at constant current $\theta_q^i(t)$ and $\theta_{qp}^{ij}(t)$ values, or it must be found from the condition of determining the equivalence of the local pressure from the thermodynamic definition and the local Gibbs–Duhem equation (both types of definitions generally correspond to nonequilibrium analogs of thermodynamic relationships).

To describe external deformations, we must introduce relative changes in bond lengths due to applied external load U_{ext} [27]: $\lambda_{qp}^e(d) = \lambda_{qp}^e + \delta\lambda_{qp}^e$ ($\delta\lambda_{qp}^e$ are deformations of the equilibrium state) and $\lambda_{qp}^{ne}(d) = \lambda_{qp}^{ne} + \delta\lambda_{qp}^{ne}$ ($\delta\lambda_{qp}^{ne}$ are deformations of the nonequilibrium state) or $\lambda_{qp}^{ne}(d) = \lambda_{qp}^e + \Delta\lambda_{qp}^{ne} + \delta\lambda_{qp}^{ne}$, where δ corresponds to deformations and Δ corresponds to nonequilibrium ($\Delta\lambda_{qp}^{ne}$ and $\delta\lambda_{qp}^{ne}$ can be either positive or negative). Limiting ourselves to light loads E or $F \gg U_{\mathrm{ext}}$, we have relationships between deformations in the form λ_{qp}^e, $\Delta\lambda_{qp}^{ne}$, and $\delta\lambda_{qp}$: $\lambda_{qp}^e \gg |\Delta\lambda_{qp}^{ne}| \geq |\delta\lambda_{qp}|$. If $|\delta\lambda_{qp}| > |\Delta\lambda_{qp}^{ne}|$, mechani-

cal loads can alter the phase state of an alloy/compound.

In [27], it was shown that the introduced values of bond deformations correspond to

$\delta\lambda_{qp}^e = 0$ for local isotropic pressure at $\lambda_{qq} = $ const or when $\lambda qp \neq$ const for a local heterogeneous structure (e.g., at an interface);

when $\delta\lambda_{qq}^e \neq 0$, there are homogeneous deformations with no shear (e.g., in rods; here, $\lambda_{qq} \neq$ const means there is an anisotropic structure in the system);

and $\delta\lambda_{qp}^e \neq 0$ corresponds to heterogeneous shear deformation for both homogeneous and heterogeneous structures.

STATES OF DEFORMATION FOR MACROSCOPIC INTERFACES

The relaxation process of a non-equilibrium solid outside a chemically active medium is mainly associated with the diffusion redistribution of components. This concept was unknown in Gibbs's times. He therefore described two main ways of creating a new surface: via mechanical perturbations and equilibrium crystallization. (Note that there was no equation of continuity in the initial Lame equations for displacements in solids [57] because constant density was assumed. This contradicts all mechanochemical processes in which density changes due to diffusion and reactions.)

An interface is a heterogeneous part of a system with variable bond lengths normal to the interface and along it in accordance with the current density value $\{\theta_q^i(e), \ \theta_{qp}^{ij}(e)\}$ inside the transitional region. Under these conditions, the equilibrium chemical potential is of a tensor nature associated with the occurrence of different bond lengths $\{\lambda_{qp}^e\}$ in the transitional region, As noted above, however, this situation does not correspond to the deformed states of particles in the transitional region. In calculating ST, the free energy of the transitional region is measured from bulk free energy value F_e.

Analysis of the conditions in the previous sections shows that different ST values are possible: σ_{ik}^e, σ_{ik}^{ne} and $\sigma_{ik}^e(d)$, $\sigma_{ik}^{ne}(d)$. They correspond, respectively, to equilibrium, internally (deformed) nonequilibrium, and externally deformed states of equilibrium and nonequilibrium alloys.

The structure of Eqs. (9)−(11) is preserved for complex crystal cells when the denotation for the q-type site includes the sublattice number. Instead of the respective A, z_{qp}, ν_q^i values for the vapor−liquid interface, the A_{jk}, $z_{qp}(jk)$, $\nu_q^i(jk)$ values, which correspond to a certain macroscopic crystal face (jk), are used in

formulas (9)−(11). It is considered that the properties of the (jk) face do not depend on other faces occurring in the crystal. In accordance with the general definition of ST, the σ_{ik}^e value is calculated through the equilibrium chemical potential [54], and the other values are calculated through its non-equilibrium analogs [55, 56].

The occurrence of internal deformations due to the bulk phase being nonequilibrium results in nonequilibrium ST. A range of states is possible, from bulk component distributions frozen at the interface $\{\theta_q^i(t), \theta_{qp}^{ij}(t), \lambda_{qp}^{ne}(t)\}$ to the partial or full relaxation of particle distributions inside the transitional region because the mobility is higher at the interface than inside the bulk phase. In both cases, bulk free energy F_{ne} is used in calculating a nonequilibrium ST analog, for which formulas (9)−(11) correspond to nonequilibrium values $\theta_q^i(t)$, $\theta_{qp}^{ij}(t)$. For each moment in time, the $\lambda_{qp}^{ne}(t)$ values are found by employing an additional nonequilibrium analog of the Gibbs−Duhem equation [55].

An external mechanical load complicates the situation because there is then an additional factor affecting the component distributions both inside a solid and on its surface, and thus the mobile phase distributions relative to a mechanically perturbed adsorbent. Note that the boundaries can be coherent, partially coherent, or incoherent [58]. The conjugation of phases with different crystal lattices must ensure the mutual accommodation of these lattices because of elastic displacements of atoms from their equilibrium positions (coherent boundaries) and inelastic displacements caused by discontinuities in the material due to mismatch dislocations and vacancies condensed at the interfaces (partially coherent boundaries). The existence of a completely incoherent conjugation is defined as the absence of tangential shear stresses when a new phase particle is placed into the respective cavity in a matrix where there is no friction between the surface of this particle and the internal surface of the cavity.

Under external actions, the states of solids must be classified according to the way in which they form, since they are all nonequilibrium processes. Essential concepts in this classification are the mechanical perturbation mode and its duration. This can mean the $\sigma(t)$ value corresponding to the surface after removing the applied load or during the action of an external load.

Each nonequilibrium process is characterized by its own kinetic scheme and specific dynamics, which should reflect microscopic models. Otherwise, the process under the effect of mechanical perturbations is not defined [29]. As follows from the situations described in this work, ST $\gamma(\neq\sigma_e)$ introduced by Gibbs, which is generated as a result of mechanical

processes [26], is not an unambiguous value and depends on the course of the external action. Its definition γ is often interpreted as an analog of a situation corresponding to the much later introduction of dynamic ST for liquid systems [59].

Boundary conditions have often been introduced for macroscopic models of external deformations. At the microlevel, only models involving external stresses are going to develop. Many factors of different solids are important here.

LAPLACE EQUATION

The Laplace equation is based on a real elastic film separating two regions with different pressures [3], but the introduction of this film for a vapor–liquid interface is only a mechanical model. As noted above, this model differs qualitatively from the real properties of a interface between coexisting phases whose molecules are in direct contact with no interlayer of another material. The mechanical model and a physical object therefore have nothing in common with each other.

The physical picture of a real vapor–liquid interface can be illustrated by the above correspondence between free energy F and lattice parameter λ. The total pressure is written as the sum of contributions from equilibrium pressure P_e, internal stresses ΔP_{ne}, and deformations caused by external loads δP_{ne}. Each contribution results the respective summands in the expression for the local parameter of a heterogeneous lattice inside the transitional region of the interface: $\lambda_{qp} = \lambda_{qp}^e + \Delta\lambda_{qp}^{ne} + \delta\lambda_{qp}^{ne}$ with a variable profile θ_q. If we hypothetically (in contrast to the experimental data) assume there is some pressure corresponding to excess pressure according to the Laplace equation, it would act only in maintaining the primary distribution of local concentrations and pair DFs in the droplet–vapor system at the initial moment in time. When there is no external load, the contribution from external loads (or $\delta\lambda_{qp}^{ne} \to 0$) disappears first because of the rapid relaxation of momentum, in accordance with the scale of relaxation times. In the beginning of the thermal motion that ensures the relaxation of local concentrations and pair DFs, this pressure would adjust to the mass relaxation process and follow it until chemical equilibrium is established in the system. During mass transfer relaxation in the system, $\Delta\lambda_{qp}^{ne} \to 0$ (tends to zero). Finally, the relaxation of the system results in full equilibrium state $\lambda_{qp} \to \lambda_{qp}^e$, to which pressure P_e corresponds.

The Laplace equation and the condition for the complete equilibrium of the system with the condition of partial chemical equilibrium are thus incompatible, as are the main principles of thermodynamics and continuum mechanics [27]. Here, of course, relatively small systems are considered and the effects of any external fields are eliminated. In any nonequilibrium, local pressures are determined by local densities in the nonequilibrium distribution mode, but they will not correspond to the Laplace equation only if a foreign film of other molecules does not form at the boundary between two phases (in this work, we do not consider questions of practical importance about surfactants being at the interface and processes between the surfactant molecules at the boundary of coexisting phases [3]).

CONCLUSIONS

1. The formal generalization of the conditions of mechanical equilibrium to complete thermodynamic equilibrium requires additional verification over the relaxation times of partial equilibria so that they correspond to the experimental data. The effect relaxation times of the transfer of separate properties have on its limiting state illustrates the existing mix of mechanical and thermodynamic variables in equilibrium thermodynamics.

2. The Laplace equation can be applied to any neighboring phases separated by a thin film of a foreign material with which the components of both phases have no chemical equilibrium. It describes the mechanical equilibrium of the interface but does not reflect the complete phase equilibrium of molecules on either side of the boundary, so it corresponds to any boundaries in the absence of the chemical equilibrium, or at those times when the effect of the mass redistribution can be ignored.

3. In the absence of the effect of external forces on coexisting equilibrium phases, the Laplace equation is not compatible with the condition of chemical equilibrium, or that of complete phase equilibrium. The thermodynamic description corresponds equally to any interfaces, so our conclusions correspond to solid–vapor or liquid interfaces.

4. None of the equations of equilibrium thermodynamics for distorted boundaries of coexisting phases that are based on the Laplace equation correspond to the experimentally measured ratios between the relaxation times of momentum and mass transfer processes, and are therefore incorrect. This is important in the numerous interpretations of experiments with the small systems actively studied in recent years [1−7].

Our discussion of using mechanics models to describe interfaces demonstrates their unsuitability for both defining ST and choosing a definition in calculating ST using molecular statistical approaches. All derivations of classical continuum mechanics were developed before the emergence of thermodynamics. Even after Gibbs introduced the thermodynamic definition of ST, all approaches to the ST interpretation and calculation were based on the mechanical definition of ST, which led to the widespread interpretation

of ST through metastable states that replaced diffusion hindrances by quasi-equilibrium states. The models of classical mechanics cannot reflect the dependences of properties on the partial composition of a solution or its structure, which are very important for thermodynamics. To consider them, we must deal with chemical potentials. Great distinctions between the relaxation times of momentum and mass transfer processes make these characteristics strongly inequivalent, making it difficult to establish a full equilibrium state because of diffusion hindrances in mass redistribution, and local pressures adjust to the current mass distribution in any situation.

The molecular kinetic theory allows us to move to analyzing deformed states of defective one- and multicomponent systems. This is essential for a great many processes involving inclusion and substitution solid solutions, nonstoichiometric compounds and absorption problems, and many more complicated surface processes. The proposed approach to deriving the principles of mechanochemical and physicochemical mechanical models allows evaluation of the properties of deformed bodies from the data for the equilibrium state and the degree of nonequilibrium (of pair DFs) and deformation of states in a system. These bulk properties serve as reference points in calculating and analyzing ST, which also depends on the evolution of the system and the degree of sample deformation.

Moving to a strictly self-consistent description of the equilibrium and nonequilibrium states of solids allows us to associate thermodynamic derivations with other characteristics (e.g., structural, kinetic, mechanochemical).

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