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CHEMICAL THERMODYNAMICS AND THERMOCHEMISTRY

Analisys of Methods for Calculating the Equilibrium Surface Tension of Vapor–Liquid Systems in the Lattice Gas Model

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Abstract—Definitions of the equilibrium surface tension (ST) existing in thermodynamics are analyzed along with reasons for their ambiguity. A molecular statistical analysis of the concept of equilibrium ST at the vapor–liquid interface is given and a procedure for calculating it within the simplest microscopic model of statistical physics (the lattice gas model) is formulated. Equilibrium ST is shown to be a mechanical characteristic calculated under the condition of a rigorous phase equilibrium over three partial equilibria (mechanical, energy, and chemical). Violation of the chemical equilibrium results in non-equilibrium ST. The emergence of metastable STs is due to the artificial introduction of a foreign film boundary into the model through the Laplace equation, which distorts the real properties of the system. Means of statistical physics for obtaining existing definitions of equilibrium ST in the theory of integral equations for fluids and molecular dynamics are discussed along with a criterion for distinguishing between equilibrium and non-equilibrium STs, metastable and otherwise. Analysis shows that none of the current means of statistical physics ensures correct calculations of equilibrium STs with regard to all molecular features of the considered systems.

Keywords: surface tension, interfaces, mechanical approach, thermodynamics, statistical physics, lattice gas model, periods of relaxation, non-equilibrium processes, dynamic surface tension

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INTRODUCTION

Surface tension (ST) is one of the main characteristics of multiphase systems, and its role grows as phases shrink [1–9]. The question of interpreting it during experimental measurements and calculations for evaluating predictions remains relevant. Existing representations of the key term in the theory of surface phenomena are reflected most by the statement that ST (interface tension) is a *mechanical and thermodynamic* characteristic of the interface [10]. This definition is of a dual nature that reflects the simultaneous use of concepts of continuum mechanics [11] and thermodynamics [1–8]. It should be noted that mechanics and thermodynamics deal with different numbers of variables of a system's state. Variables such as temperature and chemical potential are missing from mechanics while they are key in considering the thermodynamic functions of two- and multiphase systems. This is imperative when discussing the meaning of equilibrium ST.

The concept of ST (σ) was first introduced by J. Segner (1752), who explained the spherical shape of a droplet on a non-wetting surface and the cylindrical shape of a moving jet [10]. In these systems, the vapor–liquid boundary is free, with no mechanical stresses on it. The mechanical (or mathematical) theory of capillary phenomena was developed on the basis of this concept in [5, 7], where only the effect of potential interactions between molecules was considered.

The thermodynamic concept of ST was given by Gibbs [1] through an excess of free energy for two-phase equilibrium systems forming a given interface. The qualitative distinction between the thermodynamic and mechanical definitions of ST is that it requires the chemical equilibrium of two-phase systems, which is missing from the mechanical definition. Recall that the condition of a two-phase equilibrium contains three types of partial equilibria [1]: pressure (mechanical equilibrium), temperature, and the chemical potential of components. The last is responsible for there being no material flows between phases [12]. The introduction of ST in thermodynamics is closely associated with the concept of Gibbs phase approximation when describing the equilibrium properties of heterogeneous systems [1], in which a real heterogeneous system us replaced by a set of homogeneous regions that have identical internal properties. Each region is limited by its surface, and its contribution to the thermodynamic functions of the full system grows as phases shrink.

If there is a curved interface of coexisting phases α and β in a two-phase system, elementary work dW

performed by the system when its volume (*dV*) and interface area (*dA*) are changed, is written as

$$dW = P_\beta dV_\beta + P_\alpha dV_\alpha - \sigma dA - \left[\frac{\partial\sigma}{\partial R}\right] A dR, \qquad \left[\frac{\partial\sigma}{\partial R}\right] = P_\alpha - P_\beta - 2\sigma/R, \tag{1}$$

where R is the radius of the separating surface. It was considered in (1) that the position of the separating surface affects the area of the interface, and thus the ST [3]. This derivation is based on the inequality of pressures in the neighboring phases generating metastable droplets that is postulated in classical thermodynamics. Expression $[\partial\sigma/\partial R]$ determines distinctions between different ways of describing a thermodynamically spherical interface. A so-called tension surface is introduced using this expression for metastable droplets: $[\partial\sigma/\partial R]_{R=\rho_r} = 0$ (where ρ_r is the radius of a reference separating surface). On this tension surface, pressure jump $P_\alpha - P_\beta = 2\sigma/R$ (the Laplace equation), $P_\alpha > P_\beta$, and the pressure at the boundary inside the fluid differs from the vapor pressure outside. For a flat boundary, the ST does not depend on the position of the separating surface, and changes in the latter do not affect the area of the interface. There is thus no summand $[\partial\sigma/\partial R]AdR$ in (1), since $[\partial\sigma/\partial R] = 0$ for large droplets.

The free Helmholtz energy of an open system with a curved boundary is therefore expressed as

$$\begin{aligned} dF &= -P_\alpha dV_\alpha - P_\beta dV_\beta - SdT \\ &+ \sigma dA + \left[\frac{\partial\sigma}{\partial R}\right] A dR + \sum_{i=1}^{s_c} \mu_i dN_i, \end{aligned} \tag{2}$$

where s_c is the number of system components; μ_i is the chemical potential calculated for a molecule of the *i*th component, which must be constant over the entire system if it is in chemical equilibrium; and N_i is the number of molecules of the *i*th component.

Equation (2) is the fundamental Gibbs equation for a two-phase system, which can be considered to define ST σ on the tension surface in an open system [3]. If free energy F is the function of volume, temperature, interface area, and the number of molecules, σ can easily be calculated using the relation

$$\sigma = \left(\frac{\partial F}{\partial A}\right)_{T, V_\alpha, V_\beta, \mathbf{N}}, \tag{3}$$

where $\mathbf{N}$ represents the set of numbers $N_1, N_2, \ldots, N_s$. Separating contribution F_b from the transitional region of the system defined as $F_b = F - F_\alpha - F_\beta$, we have

$$F_b = \sum_{i=1}^{s_c} \mu_i N_b^i + \sigma A, \tag{4}$$

where $N_b^i = N_i - N_\alpha^i - N_\beta^i$ is the excess number of molecules of the *i*th component in the transitional region with respect to N_α^i and N_β^i in the coexisting phases.

Unlike σ, such excess values as F_b and N_b^i, depend on the position of the separating surface. By selecting a separating surface on which

$$\sum_{i=1}^{s_c} \mu_i N_b^i = 0, \tag{5}$$

expression (4) is simplified:

$$F_b = \sigma A. \tag{6}$$

With a one-component system, this special separating surface plays an important role in the theory of ST and is known as an *equimolecular* separating surface.

The literature describes four ways of defining ST in vapor–liquid systems for metastable droplets [3, 4, 9]. Two mechanical ways of introducing ST were proposed in [3, 13]: (1) through the work performed by the system in creating the surface and (2) through the definition of ST on a separating surface determined by the equilibrium with respect to the *resultant force moment*. There are also two thermodynamic definitions of ST: (1) according to Gibbs, this derivative implies displacement of the position of the separating surface at all fixed *external* parameters of the system [1, 4]. (2) According to Kondo [3, 14], this derivative corresponds to mental displacement of the separating surface at a *fixed density concentration profile*.

A detailed list of features of each definition of ST within the theory of LGM was given in [15], in addition to the results in [9] that confirm the numerical distinctions in different definitions of ST.

Formally, these definitions can be duplicated upon moving from a vapor–liquid system to solid–vapor and solid–liquid systems, since Gibbs separated the processes of creating a new interface for a solid due to a mechanical perturbation/impact and those of chemical crystallization and dissolution (γ and σ respectively) [1]. Concepts of a dynamic ST have used this as well [3, 16, 17]. This indicators there is no consensus on the subject, meaning it cannot be used as long as there are no direct ST measurements.

We refer here to the equilibrium and dynamic distributions of mobile components in polydisperse materials (e.g., adsorbents, absorbents, catalysts, membranes, and composites) with high degrees of heterogeneity caused by porous, grain, and mixed porous-grain structures of existing materials [18–24]. ST in this case determines the spatial distribution of mobile phases inside solid cores of polydisperse matrices. With a macroscopic vapor–liquid system, ST is always assumed to be based on experimental values regardless of how it is defined, so the way in which it is done is not of fundamental importance. Since it is impossible to directly measure ST, however, the way in which it is calculated is very important. This applies to problems of the behavior of small droplets in different phases [1–8, 25–28] and that of an adsorbate in porous materials [4, 5, 18–24].

The discovery of equilibrium droplets [9, 29, 30] changed the situation qualitatively. The concept of equilibrium droplets assumes a rigorous equilibrium between a liquid droplet and the surrounding vapor, provided there are three partial equilibria: mechanical, thermal, and chemical. Gibbs obtained these conditions of phase equilibrium for macroscopic phases [1]: Under isothermal conditions ($T = \text{const}$), the internal vapor and liquid pressures are equal in equilibrium droplets ($P_\alpha = P_\beta$) as are their chemical potentials ($\mu_\alpha = \mu_\beta$). The concept of a tension surface as one on which there is a pressure jump according to the Laplace equation does not apply to equilibrium droplets.

Equilibrium droplets are forbidden in classical thermodynamics. The discovery of equilibrium droplets exposed a fundamental error in classical thermodynamics and statistical theories of curved surfaces based on it for surface phenomena and small systems. It was later found [9] that this error was due to incorrect use of experimental data on the periods of relaxation of momentum and mass transfer processes, τ_P and τ_μ. The general relationship between these periods is always valid: $\tau_P \ll \tau_T \ll \tau_\mu$. In both classical and statistical thermodynamics, the assumption that $\tau_P \gg \tau_\mu$ is now universally used for curved interfaces, while under real conditions the relationship between periods of relaxation times is the reverse: $\tau_P \ll \tau_\mu$.

The only definition of ST suitable for all three types of interfaces in a three-aggregate system was given in [31, 32] on the basis of equilibrium droplets. The only correct way of calculating the ST of equilibrium systems according to Gibbs' thermodynamic definition using excess free energy has several requirements that are the same for any interface curvature.

(1) Bulk states of coexisting phases must satisfy the strict equality of chemical potentials (the Yang–Lee theory [33–35] of a vapor–liquid system and Landau relationships of symmetry with the participation of solid phases [36]), which excludes the concept of metastability.

(2) The phase equilibrium must satisfy three partial equilibria: mechanical, thermal/energy, and chemical, along with additional requirements for the boundary.

(3) The same three types of partial equilibria must be inside each point of the transitional region. This is impossible in thermodynamics, since it does not deal with boundary states. This point is also missing from all other definitions of ST in microscopic theory.

(4) There must be no excess adsorption of molecules in the transitional region. With a mixture, this means using the standard Gibbs condition that the sum over components for the product of the chemical potential of a component on its excess concentration must be zero.

I proposed [31, 32] a way of determining how necessary and sufficient the thermodynamic Gibbs definition was for calculating ST (i.e., without considering the specific mechanical properties of vacancies) or whether ST could be an clear thermodynamic function of the thermodynamic parameters of phase states and the transition regional. This approach differed qualitatively from the classical thermodynamic definition of ST [1–10] in that the requirement of observing the relationship between the periods of relaxation of momentum and mass transfer processes, which are missing from both classical thermodynamics (dealing with the Laplace equation for curved boundaries) and statistical thermodynamics (see details below), was transferred to the transitional region [3, 7, 9]. This specificity of the LGM leads to the use of average local chemical potentials and pressures inside local regions of the boundary rather than their tensor components in calculating ST. However, results from analyzing the thermodynamic definition of ST [37] showed that the way of calculating ST was as unclear for equilibrium droplets as it was for metastable droplets.

In this work, we discuss the ambiguity of ST definitions in the approach in [31, 32] and give the general definition of ST for arbitrarily shaped interfaces. Molecular statistical theory based on the LGM was used in [9, 18, 34, 35, 38] to solve this problem. It is the only theory of statistical physics that provides equally accurate descriptions of the three aggregate states of a compound [39], including their three types of interfaces. LGM is used most widely to study the phase states of compounds, and the most important results on the theory of phase transitions, including critical regions of a vapor-liquid system, were obtained with it [40–45]. This model has long been used to study flat interfaces [38, 46–51]. Approaches were later developed within the LGM to describe curved surfaces (spherical and cylindrical droplets) [9, 29, 30, 52, 53] and curved vapor–liquid interfaces with complex geometry in three-aggregate systems [18, 54, 55].

The central problem of this analysis is thus the reason for the ambiguity of defining the ST as a thermodynamic function in [31, 32] and the possibilities of statistical physics to correctly calculate equilibrium ST. The LGM and expressions for the concentration profile and excess free energy are briefly described below along with the relationship between ST and individual contributions from particles to the free energy of a heterogeneous system and the features of the LGM explaining the unclarity of the ST definition and its true nature. We also discuss the possibilities of other means of statistical physics to calculate equilibrium ST and the correctness of calculations made with current models of statistical physics. For simplicity, we consider a pure fluid (the generalization of the considered approaches to mixtures has been demonstrated in many works [1–9, 18]).

PRINCIPLES OF THE LGM

In [37], the simplest variant of the LGM [34, 35, 38] was used in calculations with allowance for the interaction between nearest neighbors in the quasi-chemical approximation (QCA) on a rigid lattice structure with number of neighbors z. A two-phase system consisting of a droplet with radius R and a vapor–liquid interface (limit case $R \to \infty$ corresponds to a flat interface) was considered at fixed temperature T [9]. The transitional region of the interface was divided into monomolecular layers with width λ (the average distance between molecules in the liquid phase) and homogeneous properties. These layers are denoted as q, which is the number of the site corresponding to the considered monolayer, $1 \le q \le \kappa$, where κ is the width of the transitional region plus one monolayer from bulk phases ($q = 1$ corresponds to the liquid and $q = \kappa$ corresponds to vapor).

The structure of the fluid in the bulk phase is characterized by values z^*_{qp} denoting the number of the nearest neighboring sites of layer p around sites of layer q: $\sum_{p=q-1}^{q+1} z^*_{qp} = z$. The total balance of bond sites between the neighboring molecules is written as $\sum_{p=q-1}^{q+1} z_{qp}(R) = z$. For spherical droplets in the thermodynamic version of the model, the structural numbers of curved lattice $z_{qp}(R)$ are expressed through similar numbers for flat lattice z^*_{qp} as corrections that depend on the radius of the monolayer in the transitional region [9, 29]:

$$\begin{aligned} z_{q<p}(R) &= z^*_{qp}, \quad (1 - 1/R_q), \\ z_{q>p}(R) &= z^*_{qp}[1 + 1/(R + q - 1)], \\ z_{q=p}(R) &= z - z_{q<p}(R) - z_{q>p}(R). \end{aligned} \tag{7}$$

In the asymptotic limit of large drops, all $z_{qp}(R)$ values tend to their limits z^*_{qp} for a flat interface.

To analyze the thermodynamic definition of ST, it is enough to limit ourselves to a binary mixture of the lattice system in which the components are molecules A and vacancies V corresponding to a pure fluid. Molecular distributions of particles A (and thus vacancies V, $\theta^V_q = 1 - \theta^A_q$) are determined by densities θ^A_q of particles A in layer q, $1 \le q \le \kappa$, which are described in the QCA by the equations

$$\beta v_0 P = \theta^A_q/(1 - \theta^A_q) \prod_{p=q-1}^{q+1} [1 + t^{AA}_{qp} x_{AA}]^{z_{qp}(R)}, \tag{8}$$

where t^{AA}_{qp} is the conventional probability of particle A being in a cell of layer p near another particle A in a cell of layer q: $t^{AA}_{qp} = \theta^{AA}_{qp}/\theta^A_q = 2\theta^A_p/[\delta^{AA}_{qp} + b^{AA}_{qp}]$, $\delta^{AA}_{qp} = 1 + x_{AA}(1 - \theta^A_q - \theta^A_p)$, $b^{AA}_{qp} = \{[\delta^{AA}_{qp}]^2 + 4x_{AA}\theta^A_q\theta^A_p\}^{1/2}$, where θ^{AA}_{qp} is the probability of particle pair AA being in neighboring cells of monolayers q and p, respectively; P is the pressure in the system; $x_{AA} = \exp\{-\beta\varepsilon_{AA}\} - 1$, $\beta = (R_BT)^{-1}$, where R_B is the universal gas constant and ε_{AA} is the energy of interaction for particle pair AA, described by the Lennard–Jones potential function. There is no interaction with vacancies, so $\varepsilon_{AV} = \varepsilon_{VA} = 0$. Normalizing relations for pairs are written $\sum_{j=A}^{V} \theta^{ij}_{qp} = \theta^i_q$.

Equations (8) on local densities θ^A_q are a concentration profile of the vapor–liquid interface. It is based on the condition of the equality of chemical potential μ_A of particles A in all layers $1 \le q \le \kappa$. Equations (8) with z identical sites are states of the bulk phase that serve as their boundary conditions. In the LGM, one-particle contributions ν^i_q are introduced into free energy F of component i at sites q of a heterogeneous system with an interface. The difference between these contributions $\nu^A_q - \nu^V_q = \beta^{-1}\ln(\beta\nu_0 P)$ contains statistical sums of internal motions of components i and chemical potentials [38] for vacancies, $\nu^V_q = 0$. Or $\nu_0 P$ in Eqs. (8) determines the chemical potential of a compound in different strata of q.

In the bulk phase, the free energy of a lattice system is written in the normalized form per system site as $F/N = \sum_{i=1}^{s} \mu_i\theta_i$, where θ_i is the molar fraction of particles of component i in a homogeneous phase, $N = \sum_{i=1}^{s} N_i$. In the lattice system, $s = s_c + 1$ components, since vacancies that are particles of type $i = s$ are included. Chemical potential μ_s of vacancies ($\mu_s = -P\nu_0$, where ν_0 is the cell volume) corresponds to vacancies.

The dimensionality of the Eqs. (8) with respect to local densities θ^i_q equals the number of layers ($\kappa - 2$) in the transitional region between the vapor and the fluid. It is solved via Newton iteration at fixed densities $q = 1$ for the vapor and $q = \kappa$ for the fluid. The accuracy of the solution for this system is no less than 0.1%. Densities of coexisting vapor and liquid phases in the bulk and equilibrium pressure P in the system were found using Maxwell derivatives [34, 35, 38].

Knowing the solution to equations for the concentration profile, we can calculate ST. In [56, 57], it was found that the free energy of the transitional region can be written in normalized form as

$$F/N = \sum_{q=1}^{\kappa} \sum_{i=1}^{s} M^i_q(k)\theta^i_q, \tag{9}$$

where number N of sites corresponds to those in the transitional region consisting of κ monolayers, $1 \le q \le \kappa$. The $M_i(k)$ values in (9) characterize contributions from components i to the free energy of the bulk phase ($q = 1$ and κ) and the same components to locally heterogeneous regions q of the boundary through which STs are calculated. For spherical droplets, $z_{qp}(R)$ (7) in each monolayer q depends on droplet radius R (below, R in $z_{qp}(R)$ is omitted for the sake of simplicity). Letter k corresponds to the way of obtaining function $M^i_q(k)$, where $k = 1$ means the regrouping of summands in the expression for F with the pair potential; $k = 2$ means differentiation with respect to the molar fraction of particles i at fixed number q of sites; and $k = 3$ means the variable number of sites q [57]. All types of function $M_q^i(k)$ in (9) are associated with the chemical potentials of system components in (2), (3), and (5). Analysis of these equations reveals the relationship between functions $M_q^i(k)$ with ST based on the thermodynamic definition of ST [31, 32].

Based on definitions [15, 31, 32], the expression for the excess free energy F_b (5) related directly to ST by formula (6) was obtained in the LGM [37]:

$$A\sigma = \frac{1}{F_{\rho^*}}\sum_{i=1}^{s}\left(\sum_{q\le q^*} F_q\left(M_q^i(k|R) - M_1^i(k|R)\right)\theta_q^i \right.$$
$$\left. + \sum_{q>q^*} F_q\left(M_q^i(k|R) - M_\kappa^i(k|R)\right)\theta_q^i\right), \tag{10}$$

where F_q denotes the normalized weights of sites q in the transitional region, and q^* corresponds to the reference separating surface:

$$1)\quad M_q^i(1) = \nu_q^i + kT\ln\theta_q^i$$
$$+\frac{kT}{2}\sum_{p=q-1}^{q+1} z_{qp}(R)\ln\frac{\hat{\theta}_{qp}^{ii}\hat{\theta}_{qp}^{ik}}{(\theta_q^i)^2\theta_{qp}^{ki}}, \tag{11}$$
$$\hat{\theta}_{qp}^{ij} = \theta_{qp}^{ij}\exp(-\beta\varepsilon_{AA}),$$

$$2)\quad M_q^i(2) = \nu_q^i + kT\ln\theta_q^i$$
$$+ kT\sum_{p=q-1}^{q+1} z_{qp}(R)\ln\frac{\hat{\theta}_{qp}^{iV}}{\theta_q^i}, \tag{12}$$

$$3)\quad M_q^i(3) = \nu_q^i + kT\ln\theta_q^i$$
$$+\frac{kT}{2}\sum_{p=q-1}^{q+1} z_{qp}(R)\ln\frac{\hat{\theta}_{qp}^{ii}}{\theta_q^i\theta_p^i}. \tag{13}$$

Also possible is $k = 2^*$ with the logarithmic factor in (12) written as $\ln\hat{\theta}_{qp}^{iV}/(\theta_q^i\theta_p^V)$ [37].

The equimolecular surface in monolayer q^*, defined as

$$\sum_{q\le q^*} F_q(\theta_q^A - \theta_1^A) + \sum_{q>q^*} F_q(\theta_q^A - \theta_\kappa^A) = 0, \tag{14}$$

q^* is used as the reference separating surface in the equilibrium system for a flat or curved boundary. There are layers with increased density when $q \le q^*$, and layers with reduced density when $q > q^*$. The contribution from each monolayer is expressed through weight functions $F_q = N_q/N$, $N = \sum_{q=2}^{k-1} N_q$, $2 \le q \le \kappa - 1$.

AMBIGUITY OF THE THERMODYNAMIC DEFINITIONS OF ST

ST values were compared in [37] using calculations at the same state of coexisting phases and the same density concentration profile. The calculations in [37] showed that all functions $M_q^i(k)$, $k = 1, 2, 2^*, 3$ lead to different temperature dependences of ST for a flat boundary and different isothermal dimensional dependences for spherical droplets of different radii.

The obtained ST values depend on the form of functions $M_q^i(k)$, so let us discuss how these functions appear in formula (10) for ST defined thermodynamically. $M_q^i(k)$ are themselves local partial contributions to the free energy. They are formally presented in (9) as analogs of chemical potentials in the lattice system. Let us rewrite formula (10) in the form of its summands over components A and V and introduce the concept of local chemical potential $\mu_q^A(k) = M_q^A(k) - M_q^V(k)$:

$$A\sigma = \frac{1}{F_\rho}\left(\sum_{q\le q^*} F_q\left(\mu_q^A(k) - \mu_1^A(k)\right)\theta_q^A\right.$$
$$+ \sum_{q>q^*} F_q\left(\mu_q^A(k) - \mu_\kappa^A(k)\right)\theta_q^A + \sum_{q\le q^*} F_q\left(M_q^V(k) - \mu_1^V\right) \tag{15}$$
$$\left. + \sum_{q>q^*} F_q\left(M_q^V(k) - \mu_\kappa^V\right)\right).$$

In bulk phases, $\mu_1^A(k) = \mu_\kappa^A(k) = M_A(k) - M_V(k) = \mu_A$ (where μ_A is the chemical potential of component A) and $\mu_1^V(k) = \mu_\kappa^V(k) = \mu_V$ (where μ_V is the chemical potential of vacancies). Note that in the bulk phase, the differences of the function $M_A(k) - M_V(k)$, $k = 1$, 2, 2*, 3 have the same value regardless of how these functions were derived (based on index k)

$$\mu_A = \nu_A + kT\ln(\theta_A/\theta_V) + \frac{zkT}{2}\ln\left[\frac{\hat{\theta}_{AA}(\theta_V)^2}{\hat{\theta}_{VV}(\theta_i)^2}\right] \tag{16}$$
$$= \nu_A + kT\ln(\theta_A/\theta_V) + zkT\ln\left[t_{AV}/t_{VV}\right].$$

First equality (16) corresponds to variants of derivations $k = 1$ and 3; second equality (16) corresponds to $k = 2$, and it can be presented in the equivalent form for variant $k = 2^*$ through the ratio $\ln(t_{qp}^{AV}\theta_p^V)/(t_{qp}^{VV}\theta_p^V)$.

However, functions $M_q^i(k)$ behave differently for the transitional region of the boundary. For functions with $k = 1, 2, 2^*$ we have

$$\mu_q^A(1) = \nu_q^A + kT\ln(\theta_q^A/\theta_q^V)$$
$$+ kT\sum_{p=q-1}^{q+1} z_{qp}\ln(t_{qp}^{iV}/t_{qp}^{VV}) = \mu_q^A(2) = \mu_q^A(2^*) = \mu_A,$$

while $\mu_q^A(3) \neq \mu_A$. This automatically creates corresponding distinctions in calculated STs in variants $k = 3$ and $k = 1, 2, 2^*$. However, variants $k = 1, 2, 2^*$ differ from one another.

We can see from formula (15) that since $\mu_q^A(1) = \mu_q^A(2) = \mu_q^A(2^*) = \mu_A$, the first two summands with local densities become zero, and different expressions are obtained for ST that are associated only with the contributions from vacancies through functions $M_q^V(1)$, $M_q^V(2)$, and $M_q^V(2^*)$. In other words, expression (15) shows that different ST values are obtained for a pure fluid with an equimolecular separating surface. These values depend on the form of functions $M_q^V(k)$ for vacancies.

The difference of functions $M_q^A(3) - M_q^V(3)$ in $\mu_q^A(3)$ do not turn the summands in (15) to zero before local densities θ_q^A: $\mu_q^A(3) = \nu_q^A + kT\ln(\theta_q^A/\theta_q^V) + \frac{kT}{2}\sum_{p=q-1}^{q+1} z_{qp}\ln\frac{\hat{\theta}_{qp}^{AA}\theta_q^V\theta_p^V}{\hat{\theta}_{qp}^{VV}\theta_q^A\theta_p^A} \neq \mu_A$, so ST depends on both functions $M_q^V(3)$ and $M_q^A(3)$.

Different functions $M_q^i(k)$ are associated with different types of derivatives in distinguishing effective one-particle contributions in free energy (9). The ΔF value is clearly determined by T and density values, so the ambiguity depends on the relationship between functions $M_q^i(k)$ and chemical potential μ_A, which underlies the derivation of Eqs. (8) for the concentration profile. It was shown above that functions $M_q^i(k)$ in (15) agree with μ_A through difference $M_q^A(k) - M_q^V(k) = \mu_A$ for $k = 1, 2, 2^*$.

For $k = 3$, however, the same difference $M_q^A(3) - M_q^V(3) \neq \mu_A$ does not agree with μ_A, so condition $\mu_A N_b^A = 0$ (5) is not met for $k = 3$. The procedure for deriving functions $M_q^i(k = 3)$ was introduced in analogy with bulk chemical potential μ_i, and it yields the dependence of ST on contributions $M_q^A(k = 3)$ from real particles A, and functions $M_q^V(k = 3)$ from vacancies. This situation results from number of sites N_q being varied when determining derivatives $M_q^i(k = 3)$ [57] while numbers N_p of other types of sites remain fixed. In the macro phase, this dependence on neighboring sites of other types is automatically removed as the number of phase sites increases.

Different ST values obtained in [37] from thermodynamic Gibbs definition (6) or (10) testify to the ambiguity of the concept of ST as a strictly thermodynamic function (TF) at identical external parameters of a system that characterize stratification as a function of temperature. This means ST is not a purely thermodynamic characteristic of the system.

SPECIFICITY OF THE LGM AND THE NATURE OF ST

The plurality of ST values at the same phase states and transitional regions is due to the use of different functions $M_q^i(k)$ employed in different ways of deriving them [56, 57]. The LGM is based on a formal representation of the free element of cell volume in the form of vacancies as a discrete component of the lattice structure. The total number of components is $s = s_c + 1$ (where s_c is the number of real components in a given system). The specificity of the LGM for different components of the system results from different derivatives having different physical meanings [56, 57].

For real components, derivatives of ΔF with respect to partial densities give the corresponding local chemical potentials of components i for different types of sites, and the derivatives correspond to mechanical characteristics for vacancies. In the bulk of a material, $\partial F/\partial N_s = -P$ corresponds to what is often called expansion pressure. For a transitional region, it corresponds to average local pressure $\partial\Delta F/\partial N_q^s = -P_q$.

This distinction means derivative $\partial\Delta F/\partial\theta_q^i = M_q^i(k) - M_q^s(k)$ is expressed as the difference between two functions: $M_q^i(k)$ for $k = 1, 2, 2^*$, $1 \leq i \leq s_c$. From the viewpoint of changes in the occupancy of LGM sites, it follows that the ΔF derivative with respect to particles A at $k = 1, 2, 2^*$ corresponds to variation in the number of particles A at fixed number N_q of sites due to exchanges with vacancies. This scheme corresponds to the condition of a self-consistent description of the kinetics and equilibrium in kinetic processes [38].

For the derivative of ΔF with respect to vacancy densities θ_q^V (for component $i = s = \mathrm{V}$), we must use another derivative related to a simultaneous change in the number of V particles and the total number N_q of sites q [57]. This generates functions $M_q^i(k = 3)$, meaning this type of derivatives is defined only for vacancies for which it determines the average local pressure inside the transitional region in monolayer q.

If the same type of derivatives is used for real particles A and even for their differences with vacancies, they are also not related in any way to the particles' chemical potential μ_A. Finally, functions $M_q^i(k = 3)$ are not related in any way to the kinetics of the redistribution of particles in a fixed volume, though $M_A(3) - M_V(3) = \mu_A$ for macro phases. The formal transfer of the definition of the chemical potential μ_A to the local chemical potential $\mu_q^A(3)$ is consequently not correct, due to fixed number $N_{p\neq q}$ of p-type neighbors (not involved in taking a derivative with respect to N_q^s and N_q). The derivative of ΔF with respect to vacancy densities ($k = 3$) is therefore an analog of deformation changes.

The equilibrium ST value thus has a complex character, and the real nature of ST is not purely thermodynamic. Introducing (1) and (2) into thermodynamics, the ST value becomes a mechanical characteristic. This was initially assumed before the emergence of thermodynamics, but could not be realized under the conditions of a rigorous phase equilibrium of coexisting vapor and liquid phases. These conditions are directly related to the thermodynamics of phase transitions formulated later by Gibbs, and their three partial equilibria.

To obtain the equilibrium ST value it we must satisfy the ratio between momentum and periods of mass relaxation $\tau_P \ll \tau_\mu$, which is consistent with the experimental data; i.e., this is the inverse ratio of the periods of relaxation of momentum and mass transfer processes, which was introduced for metastable droplets in Gibbs thermodynamics. With regard to requirements (1)–(4) and ST being a mechanical characteristic, these two statements together allow us to obtain the equilibrium ST value.

They correspond to the definition of ST given in the first works on equilibrium droplets [9, 29, 30] (based on the vacancies reflecting the mechanical properties of a system), but without clear formulation of requirements (1)–(4) for describing the state of a transitional region. We finally obtain the expression for the equilibrium ST value:

$$4)\quad A\sigma = \frac{1}{F_{\rho*}}\left(\sum_{q\leq q*} F_q(\mu_q^V - \mu_1^V) + \sum_{q>q*} F_q(\mu_q^V - \mu_\kappa^V)\right), \quad (17)$$

where functions $\mu_q^V = M_q^V$ in (3) are defined in (13) with $\nu_q^V = 0$ for any q.

Any deviation of the system from the equilibrium state results in non-equilibrium STs, since the pressure and/or ST values are clearly determined by the current values of correlators calculated using equilibrium or non-equilibrium models [58].

CALCULATING ST

Requirements (1)–(4) for obtaining correct equilibrium ST values are valid for all means of statistical physics. Development of the molecular theory of the vapor–liquid interface began in [59, 60], where the final width of the transitional region of an interface was used in comparison to the mathematical surface in Gibbs thermodynamics. Works on statistical physics began in the middle of the last century [3, 7]. Attempts were made to interpret ST with capillarity theory [7, 61, 62]; integral equations (IEs) [3, 7, 63–67] and simplified versions of them with no correlation effects—i.e., density functional theory (DFT) [68–71]; and molecular dynamics (MD) [72, 73], both Monte Carlo (MC) [63] and the LGM [9, 29–32, 74, 75] (see above).

The Van der Waals theory of capillarity and DFT have become very popular because of great problems in calculating when IEs are used. A growing number of works now use MD. Difficulties in applying it to calculate the characteristics of droplets were noted in [73]. The above molecular means yield strongly differing results, so the thermodynamic approach remains the main one for practical estimates of the energy of nucleus formation in the kinetics of first order phase transitions [1–10].

The key problem in calculating ST is how to determine free energy F. This characteristic is one of the most cumbersome for practical applications because of the difficulty of calculating it along with the chemical potential [76–81], both of which are needed to calculate ST with thermodynamic relations (4)–(6). Technically, this is due to the current theory of the liquid state being based on correlation functions (CFs) [76–83]. The correspondence between IE theory and items (1)–(4) is reflected in analyzing the approaches to calculating ST in [15]. Direct use of thermodynamic definition of ST (6) has never been discussed in IE theory [7, 77], due to great problems in calculating the chemical potential even in the bulk phase. The calculations must be made according to Kirkwood with a parameter of interaction [76, 77] or considerable efforts are required to move directly to calculating the free energy [78, 79]. The hierarchy of Bogolyubov–Born–Green–Kirkwood–Ivon equations [76, 77, 82, 83] contains no chemical potential in explicit form. In order to employ definition (6), we must also satisfy the requirement for a constant chemical potential inside the transition region. Note that different technical approaches are used in IE theory through the virial theorem and the Bogolyubov hierarchy [7, 77, 82, 84–86] when the mechanical definition of ST is used give equivalent results [7]. This means there is no correspondence between the numerical procedures of IE theory and requirements (1)–(4) because molecular statistical theories [3, 7, 9] are based on available thermodynamic approaches, and they all result in metastable states of droplets even today. Another problem of the IE theory is the difficulty of solving the equations themselves, resulting in the need to simplify numerical procedures. DFT is now used to calculate heterogeneous interfaces [68–71], in which there are no correlation effects from interacting molecules.

There is a similar situation with calculation procedures in MD and MC, which are the most popular means of statistical physics for calculating TFs of many systems. Both essentially operate with spatial distributions of molecules rather than deal directly with statistical sums. To some extent, they are similar to the CF model and differ from it by how the spatial distributions of molecules are generated and their subsequent averaging procedures. Existing manuals on MD calculations are based on information about averaging procedures developed in the last century [87] that do not consider the fundamental results of thermodynamics on considering the periods of relaxation of momentum and mass transfer processes [9]. This obviously makes them unsuitable for calculating ST values. There is the same incorrect attitude toward calculating free energy, and no procedures at all for determining the average chemical potential [87].

When discussing how requirements (1)–(4) are met in other means, we should distinguish between the potential abilities of each way and the practical versions of them in the literature. From a formal standpoint, each means of statistical physics can be fundamentally consistent with the above requirements, since all models of statistical physics deal with the full phase space of coordinates and momenta (or energies), while individual variants of calculations are reduced to postulated rules of averaging in phase space. At this stage, information is mainly approximated in deriving average values, expressed first through CFs and then in subsequent averaging through TFs.

In practice, all models of calculation are developed by comparing them to earlier theories (and are oriented toward classical thermodynamics) and other techniques (particularly the theory of non-ideal gases and fluids in a superpositioning approximation [76, 77, 88]). For MC algorithms, approaches have been proposed in literature [89, 90] in which energy distributions through which we can calculate free energy were constructed directly. However, these were never very popular because of the time they took (the latest MC versions are in [91, 92]). When calculating ST and properties of small droplets, thermodynamic representations (usually the Laplace equation) are introduced into stochastic models [92] and IEs [7, 66], distorting the essence of small droplet calculations.

These distortions were introduced into the theory of capillarity, DFT, and stochastic MC and MD models for the entire range of droplet radii. They manifest in the dependences of ST $\sigma(R)$ on droplet size R in all available works. The criterion $\sigma(R)/\sigma(\text{bulk}) = 1$ was therefore formulated [93] to separate the class of solutions for the profile of densities (8) corresponding to equilibrium droplets from metastable droplets. If the calculated ST $\sigma(R)$ relative to the above line surpasses the accuracy of calculating $\sigma(R)$, it indicates the model can be used to calculate metastable droplets rather than equilibrium characteristics. This property applies to all ways of calculating equilibrium and metastable droplets.

Note that the LGM also has the potential to improve the accuracy of TF calculations and consider specific features of molecules in modified versions of the fluid. Upon moving from the considered simplest variant of the LGM to more accurate models of two-phase systems and their STs that reflect allowance for, e.g., the internal motions of molecules, anharmonism of vibrations, and lattice softness, there are problems in calculating free energy [80, 81] that require the development of new numerical algorithms. Analysis of discrete molecular distributions based on CFs is much simpler in the LGM, and it is easier to study the problem of the ambiguity of calculating TF (these questions were considered in [80, 81].) This means there are currently no ready ways of calculating equilibrium ST that meet requirements (1)–(4) and provide a correct microscopic description of a fluid.

RESULTS AND DISCUSSION

The problem of the ambiguity of the definition of equilibrium ST has existed ever since the thermodynamics of curved boundaries was created. Gibbs's introduction of the Laplace equation for describing the mechanical equilibrium between coexisting phases with its pervasive influence relative to chemical equilibrium resulted in metastable droplets and the multiplicity of determinations of the position of a separating surface on which there is a pressure jump in the Laplace equation. Primary interpretations of ST as a mechanical characteristic were erroneous because they were based on the use of the Laplace equation, which distorts the nature of a transitional region by introducing a hypothetic foreign film [9, 58].

This problem was not solved until the discovery of equilibrium droplets that correspond to the rigorous phase equilibrium. The existence of strictly equilibrium droplets allowed formulation of the question about using the purely thermodynamic Gibbs definition of ST as the excess of the free energy due to the occurrence of the boundary [31, 32]. However, analysis of this approach has shown [37] that ST is not a pure TF of the state parameters of coexisting phases and a transitional region. It follows that the ambiguity of the thermodynamic definition of ST is determined by (1) the types of contributions (functions $M_q^i(k)$) of components i to the free energy of system (9) due to different ways k of introducing them while preserving the identity of system states with chemical potential μ_A and a transitional region profile with excess N_b^A (4) for

$k = 1, 2, 2^*$ and (2) using an analog of local chemical potential $\mu_q^A(3)$ in analogy with macro phases containing contributions $M_q^A(3)$ from real particles and $M_q^V(3)$ from vacancies to the ST value.

Analysis of the concept of equilibrium ST at a vapor–liquid interface has shown that equilibrium ST is a mechanical characteristic that can be calculated if there is a rigorous phase equilibrium over three partial equilibria (mechanical, energy, and chemical). The thermodynamic definition of ST as an excess of free energy is a necessary but not sufficient condition. In addition, we must remember that ST is a mechanical characteristic and must be calculated with regard to the relationship of the periods of relaxation of momentum and mass transfer processes, which correspond to experimental data ($\tau_P \ll \tau_\mu$). Violation of this relationship ($\tau_P \gg \tau_\mu$) gives rise to metastable droplets associated with the artificial introduction of a foreign film boundary into the model through the Laplace equation, which distorts the real properties of the system. Instead of a monotonic change in the properties of molecules inside the transitional region clearly related to a monotonic change in their density from vapor to fluid, the introduction of the Laplace equation means a pressure jump that breaks the relationships between local pressures in a real system and its chemical potential. Finally, when it is simultaneously considered that equilibrium ST corresponds to the condition of a rigorous phase equilibrium over all three partial equilibria and the ratio of respective relaxation times is observed, we obtain a description of the system with no artificial distortion of its properties.

Elementary work dW performed by the system when its volume (dV) and boundary area (dA) change should in this case be formally written instead of Eq. (1) for a two-phase system with a flat boundary (i.e., without indicating two different pressures in the coexisting phases, since $P_\alpha = P_\beta$ and there is no tension surface), allowing for the curvature of the separating equimolecular surface characterized by radius R

$$dW = PdV - \sigma(R)dA(R). \qquad (18)$$

Expression (18) explicitly reflects that both the ST and surface element area dA depend on the curvature of the boundary. To find the equilibrium ST, we must reject formula (10) and use Eq. (17), which follows from considering a vacancy as a mechanical characteristic that is an analogue of pressure (expansion) in the bulk phase.

Violation of the chemical equilibrium at the interface results in non-equilibrium STs.

The problem of calculating ST is closely related to the problem of calculating the free energy, which remains a complex procedure in any means of statistical physics. Our results on the nature of ST follow from the simplest model of statistical physics—the LGM, which provides the best description of phase states and interfaces. Other models (IE theory, MD, and MC) do not ensure correct calculations of equilibrium ST with regard to requirements (1)–(4). So far, these techniques have dealt only with metastable droplets. Versions of the LGM modified with regard to lattice structure softness, internal motions, and the anharmonism of vibrations require the development of new algorithms to allow for these molecular features [81].

The formulated criterion for the size dependence of droplet ST [93] separates equilibrium and non-equilibrium STs, metastable and otherwise. The criterion allows control of the development of calculation procedures for equilibrium ST by different means of statistical physics.

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