

Thermodynamic Analysis of Adsorption and Line-Tension Contributions to Contact Angles of Small Sessile Droplets

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Abstract—Relations for the contact angles of sessile liquid droplets with axially symmetric or cylindrical shapes and different equilibrium sizes have been considered using a general thermodynamic approach. For a multicomponent system comprising a liquid droplet, a vapor–gas medium, and a solid substrate, influence of dependence of the surface tension on the chemical potentials related to equilibrium droplet size (i.e., the effect of adsorption) and the effect of size-dependent line tension on the contact angles have been discussed. It has been shown that, for an axially symmetric sessile droplet, the effects of adsorption and line tension are, in the general case, comparable and manifest themselves already at the first order with respect to the droplet curvature. For a cylindrical droplet, the effect of adsorption is observed already in the first order with respect to the droplet curvature, while the influence of the line tension manifests itself only in the second order and is governed by the droplet-size dependence of the line tension.

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INTRODUCTION

When considering macroscopic sessile droplets on partially wettable surfaces, the cosine of the contact angle can be found from the classical Young equation [1]

$$\sigma^{\alpha\beta} \cos \theta = \sigma^{\beta\gamma} - \sigma^{\alpha\gamma}, \quad (1)$$

where $\sigma^{\alpha\beta}$, $\sigma^{\beta\gamma}$, and $\sigma^{\alpha\gamma}$ are the thermodynamic surface tensions of the three interfaces, which come across at the contact line of phases α , β , and γ . The measurements of contact angles θ of rather small (sub-micron) droplets have shown a dependence of $\cos \theta$ on droplet size. Commonly, this dependence is described using a modified (generalized, extended) Young equation/relation that takes into account the thermodynamic tension of the three-phase contact line [2–7]. Under the assumption of constant line tension κ , this yields correction κ/r , where r is the base radius of a sessile droplet (i.e., the curvature radius of the three-phase contact line). Therefore, the object for study is, as a rule, the dependence of $\cos \theta$ on $1/r$, which must, in this case, have a linear pattern, while the determination of the slope of this dependence is widely used to find the line tension [8, 9]. Some measurements of the contact angles for nanosized droplets have also shown nonlinear dependences of $\cos \theta$ on $1/r$ [10].

It has recently become possible to study partial wetting and nanosized sessile droplets numerically by molecular simulation methods, such as the molecular

dynamics and Monte Carlo methods. These studies involve both axially symmetric [11–16] and cylindrical droplets [13–20], with the latter having a translational symmetry along a single direction. The latter droplets are also referred to as liquid channels, bridges, etc., in the literature. In spite of the possible existence of the Rayleigh–Plateau instability [21–24], thermodynamic consideration of cylindrical droplets is of practical interest. It is believed that the contact angle of such a droplet should only weakly depend on its size (width), thereby enabling one to accelerate the calculations by diminishing the size of a model system and using periodic boundary conditions along the longitudinal axis of a cylindrical droplet. In contrast to experiments, for which rather large droplets (with base radii of several hundred nanometers and larger) are primarily available, the molecular dynamics and some other calculations involve namely nanosized sessile droplets, while the study of larger droplets substantially increases the required computational resources. As a whole, molecular simulation makes it possible to essentially refine the influence of size effects on the contact angle of a sessile droplet on both planar and curved substrates and relate these effects to the parameters of the substrate–condensate and condensate–condensate intermolecular interactions. However, these methods require a rigorous thermodynamic substantiation of equilibrium equations for the contact line.

The goal of this work is to perform a rigorous thermodynamic analysis of the contact angle versus drop-

let size dependence with account of the relation between this size and the thermodynamic state of a system (the chemical potentials of the components), with this relation affecting the values of the surface and line tensions. Previously, we considered a similar problem for an axially symmetric droplet of a one-component fluid [25, 26]. The inferred conclusions were supported by calculations [25] performed in terms of a model, in which a sessile droplet was considered as a film of varying thickness with the use of a disjoining pressure isotherm for describing wetting properties of the film [27, 28]. In this work, we extend the thermodynamic approach to systems comprising multicomponent fluid phases and cylindrical droplets.

In Section 1, we shall consider the cases of equilibrium axially symmetric and cylindrical droplets on a planar partially wettable substrate and show the form, in which the Laplace and generalized Young equations must be written as the conditions of equilibrium in these cases. A variational derivation performed using a transversality condition at the three-phase contact line [3, 6, 29, 30] will be considered. This will enable us to discuss in greater detail the terms of the generalized Young equation and, in particular, consider the question of which variable characterizing the droplet size must the line tension explicitly depend on. In Section 2, we shall discuss the equations that determine the dependence of the surface and line tensions on the thermodynamic state of the system (the chemical potentials of the components), as well as the relation between this state and the equilibrium curvature radius of a free droplet surface. Taking into account these results and the results of Section 1, we shall consider the dependences of the contact angle on droplet base radius/half-width r and obtain asymptotic expressions for the slopes of the $\cos\theta-1/r$ dependences for axially symmetric and cylindrical droplets. The results obtained will be discussed in Section 3.

1. THERMODYNAMIC DESCRIPTION OF A DROPLET WITH A CONTACT ANGLE

Let us consider a system in thermodynamic equilibrium in which a sessile liquid droplet is located on a planar partially wettable solid surface and brought in contact with an ambient vapor.¹ We shall study both an axially symmetric sessile droplet (such a macroscopic droplet will be shown below to have the shape of a spherical cap) and a droplet having the shape of a (curvilinear) cylinder with the zero surface curvature at any point along one of directions (such a macroscopic droplet will be shown below to have the shape of a horizontal cylindrical segment).

In the general case, we shall consider a multicomponent fluid; i.e., the liquid droplet and the ambient

vapor–gas medium will consist of some set of mobile components $\{i\}$ that, in the general case, may also be present in the solid phase. The solid phase necessarily contains at least one immobile component j . The liquid phase, vapor–gas phase, and solid phase of the substrate material will be denoted as α , β , and γ , respectively. These denotations will be used as superscripts at physical parameters: single and double superscripts will mark the phases and interfaces, respectively. Let the pressures in the droplet and the vapor be equal to p^α and p^β , respectively, while the thermodynamic surface tensions (the specific surface excesses of the grand thermodynamic potential) of corresponding interfaces be equal to $\sigma^{\alpha\beta}$, $\sigma^{\alpha\gamma}$, and $\sigma^{\beta\gamma}$, whereas the thermodynamic line tension (the specific line excess of the grand thermodynamic potential) of the three-phase contact line be equal to κ . Thus, the expression for the grand thermodynamic potential of the system decomposes into volume, surface, and line contributions:

$$\Omega = -p^\alpha V^\alpha - p^\beta V^\beta + \omega^\gamma V^\gamma + \sigma^{\alpha\beta} A^{\alpha\beta} + \sigma^{\alpha\gamma} A^{\alpha\gamma} + \sigma^{\beta\gamma} A^{\beta\gamma} + \kappa L, \quad (2)$$

where V , A , and L are the volume corresponding to a phase, the area of an interface, and the length of the three-phase contact line, respectively. Here, it has been taken into account that the pressure in the fluid phase corresponds, up to a sign, to the density of the grand thermodynamic potential: $\omega^{\alpha\beta} = -p^{\alpha\beta}$. The grand thermodynamic potential in the solid phase and its surface excesses may be understood in the sense defined in [31, 32].

The shape of the droplet surface and the relations for the droplet sizes can be obtained by determining the stationary profile for the functional of the grand thermodynamic potential.

1.1. An Axially Symmetric Droplet

Cylindrical coordinates are convenient to use for an axially symmetric droplet. Denoting the droplet surface profile as $m_a(x)$, where x is the radial coordinate in the substrate plane, and assuming, in the general case, the thermodynamic line tension to depend on the droplet base radius r (the curvature radius of the three-phase contact line), we may write the functional Ω_a of the grand thermodynamic potential of the system as

$$\Omega_a [m_a(x)] = \Omega^\gamma - p^\beta (V^\alpha + V^\beta) + \sigma^{\beta\gamma} A^{\beta\gamma} + 2\pi \int_0^r dx [x(-(p^\alpha - p^\beta)m_a(x) + \sigma^{\alpha\gamma} - \sigma^{\beta\gamma}) + \sigma^{\alpha\beta} \sqrt{1 + (m'_a)^2} + \kappa(r)], \quad (3)$$

where Ω^γ is the grand thermodynamic potential of the bulk solid substrate and $A^{\beta\gamma}$ is the area of $\beta\gamma$ interface.

¹ Critical droplets in nucleation that are in unstable material equilibrium with an ambient supersaturated vapor are also involved.

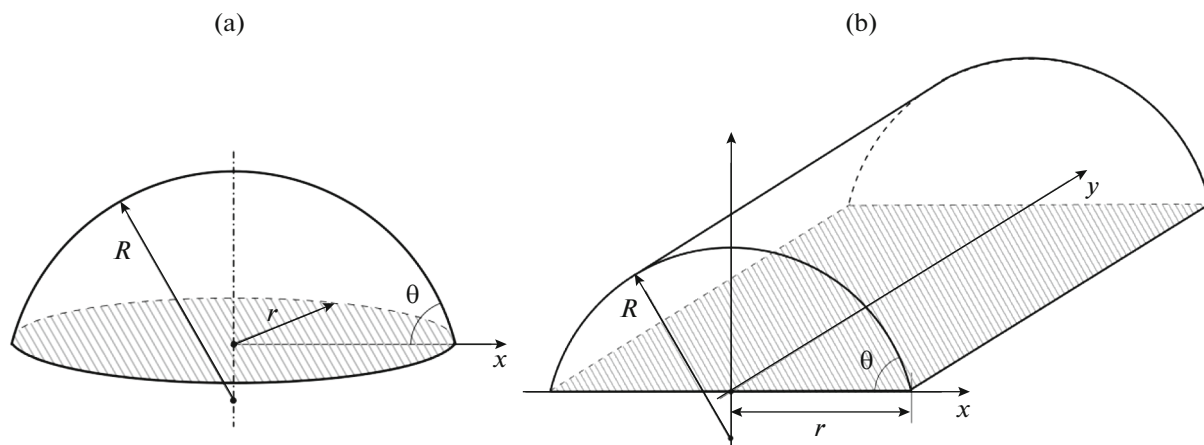


Fig. 1. Sessile liquid droplets on a solid substrate: (a) axially symmetric droplet and (b) cylindrical droplet.

The introduction of $\kappa(r)$ into the integrand makes it possible to formally include the contribution of line excess $2\pi r\kappa(r)$ associated with the existence of the three-phase contact line into the integral functional. For convenience, non-variable contributions to the functional are isolated in separate non-integral terms.

The equilibrium profile of a sessile droplet may be found by equating the first variation of the functional (3) to zero, while fulfilling the transversality condition at the three-phase contact line *and* the following condition:

$$m'_a(0) = 0. \quad (4)$$

The latter condition follows from the smoothness of the axially symmetric profile. This yields the Euler–Lagrange equation for the functional (3),

$$\left(\frac{d}{dx} + \frac{1}{x}\right) \frac{m'_a}{(1 + (m'_a)^2)^{1/2}} = -\frac{p^\alpha - p^\beta}{\sigma^{\alpha\beta}} \equiv -\tilde{\mu}, \quad (5)$$

with the condition (4) and the transversality condition $m_a(r) = 0$ imposed on the three-phase contact line as boundary conditions. The latter condition implies free motion of this line along the substrate surface [33, 34] and takes form

$$r \left(\sigma^{\alpha\gamma} - \sigma^{\beta\gamma} + \sigma^{\alpha\beta} \sqrt{1 + (m'_a(r))^2} \right) + \kappa + r \frac{\partial \kappa}{\partial r} = \frac{r \sigma^{\alpha\beta} (m'_a(r))^2}{\sqrt{1 + (m'_a(r))^2}}. \quad (6)$$

The left-hand side of Eq. (5) comprises the local mean curvature of the droplet surface multiplied by $\sigma^{\alpha\beta}$. This curvature is negative at $p^\alpha > p^\beta$, thereby corresponding to a surface convex upward, and, as can be seen, must be constant. This is nothing but the Laplace equation for curvature radius R of a droplet

having the shape of a spherical cap with its vertex located at $x = 0$ (see Fig. 1a):

$$\frac{2}{R} = \frac{p^\alpha - p^\beta}{\sigma^{\alpha\beta}} \equiv \tilde{\mu}. \quad (7)$$

Condition (6) yields the *generalized Young relation*

$$\sigma^{\alpha\beta} \cos \theta = \sigma^{\beta\gamma} - \sigma^{\alpha\gamma} - \kappa/r - \partial \kappa / \partial r, \quad (8)$$

where θ is the contact angle ($\tan \theta \equiv -m'_a(r)$), while the derivative $\partial \kappa / \partial r$ should be understood as that taken at constant values of the temperature T and the chemical potentials $\{\mu_i\}$ of the molecules of the components composing the fluid phases α and β (it corresponds to conditions under which the functional (3) was varied). For more detailed information, see [7], where Eqs. (7) and (8) were also derived primordially assuming the sphericity of the sessile droplet surface. The above-described derivation using the functional (3) is based on the scheme employed in [3, 6]. This may appear to be more convenient for subsequent comparison with a model system (e.g., within the framework of the model, in which a droplet is represented by a film of varying thickness [25]) and will enable us to discuss which variable characterizing the droplet size must the line tension explicitly depend on.²

1.2. A Cylindrical Droplet

The Cartesian coordinate system is convenient to use for a cylindrical droplet. Let the y axis be directed along the droplet axis, while the x axis be oriented transversely to it and in parallel to the substrate surface. Denoting the droplet surface profile as $m_c(x)$ and, also, assuming that the thermodynamic line ten-

² We assume that the line tension κ depends on the radius r of the three-phase contact line. However, explicit dependences of κ on the contact angle θ [13, 37, 38] and even on both these variables [6, 39] are also considered in the literature.

sion depends on the half-width r of the droplet base (here, r does not play the role of the curvature radius of the three-phase contact line, the latter is always straight in this system), we may write the functional Ω_c of the grand thermodynamic potential of the system per unit length along the y axis in the following form analogous to Eq. (3):

$$\begin{aligned} \Omega_c [m_c(x)] = & \Omega^\gamma - p^\beta (V^\alpha + V^\beta) + \sigma^{\beta\gamma} A^{\beta\gamma} \\ & + 2 \int_0^r dx \left[- (p^\alpha - p^\beta) m_c(x) + \sigma^{\alpha\gamma} - \sigma^{\beta\gamma} \right. \\ & \left. + \sigma^{\alpha\beta} \sqrt{1 + (m'_c)^2} \right] + 2\kappa(r). \end{aligned} \quad (9)$$

Since the three-phase contact line length in this system is independent of r , the term comprising the line tension is left non-integral.

The Euler–Lagrange equation for the functional (9) has the form of

$$\frac{m_c''}{(1 + (m'_c)^2)^{3/2}} = - \frac{p^\alpha - p^\beta}{\sigma^{\alpha\beta}} \equiv -\tilde{\mu}, \quad (10)$$

with condition (4) and the transversality condition $m_c(r) = 0$ imposed on the three-phase contact line as boundary conditions. In this system, the latter condition acquires the following form:

$$\sigma^{\alpha\gamma} - \sigma^{\beta\gamma} + \sigma^{\alpha\beta} \sqrt{1 + (m'_c(r))^2} + \frac{\partial\kappa}{\partial r} = \frac{\sigma^{\alpha\beta} (m'_c(r))^2}{\sqrt{1 + (m'_c(r))^2}}. \quad (11)$$

The left-hand side of Eq. (10) comprises the local mean curvature of the droplet surface multiplied by $\sigma^{\alpha\beta}$. This curvature is negative at $p^\alpha > p^\beta$, thereby corresponding to a surface convex upward, and, in this case, it is equal to the main curvature along the x axis; according to the equation, it is constant. This is nothing but the Laplace equation for the curvature radius R of a droplet having the shape of a circular cylinder (hereafter, a cylinder segment for short) with a vertex at $x = 0$ (see Fig. 1b):

$$\frac{1}{R} = \frac{p^\alpha - p^\beta}{\sigma^{\alpha\beta}} \equiv \tilde{\mu}. \quad (12)$$

With allowance for $\tan\theta \equiv -m'_c(r)$, condition (11) leads to the generalized Young relation, the form of which is, in this geometry, different from Eq. (8):

$$\sigma^{\alpha\beta} \cos\theta = \sigma^{\beta\gamma} - \sigma^{\alpha\gamma} - \partial\kappa/\partial r. \quad (13)$$

The term $-\kappa/r$ is absent in the right-hand side of Eq. (13), because variations in cylindrical droplet profile $m_c(x)$ lead to variations in the base half-width r ; however, the length of the three-phase contact line remains unchanged and independent of r . At the same time, the term $-\partial\kappa/\partial r$ has remained preserved,

because the line tension does change upon such variations.

The considered system with the cylindrical droplet actually coincides with a two-dimensional system “extended” along the y axis. Therefore, Eqs. (12) and (13) reproduce expressions for two-dimensional systems with the pressures replaced by two-dimensional pressures in corresponding two-dimensional phases, the surface tensions replaced by line tensions of interfacial lines, and the line tension of the three-phase contact line replaced by the point excess of the grand thermodynamic potential at the three-phase contact point [35, 36].

1.3. On Derivation of Equilibrium Conditions for Droplets of Non-Volatile Liquids

The Laplace equation and the generalized Young relation obtained as equilibrium conditions may also be derived when considering the system in a canonical ensemble with fixed numbers of particles of each component in the system rather than the values of the chemical potentials of the particles (molecules and atoms). The need to fix the numbers of particles arises, in particular, when considering droplets of non-volatile liquids or performing molecular dynamics simulation. Therewith, the Helmholtz free energy functional $F[m(\mathbf{x})]$ should be minimized under additional conditions of constant numbers of particles of such “non-volatile” components (as well as immobile components of the solid substrate).

Let us initially discuss derivation of equilibrium conditions in the canonical ensemble, when the numbers of the particles of all system components are fixed. Then, let us indicate the manner in which this may be extended to the case in which only the numbers of particles of some “non-volatile” components are fixed in a multicomponent fluid, while the conditions for other components are set by specifying the values of their chemical potentials.

The structure of the expression for the free energy is analogous to that for the grand thermodynamic potential (2) with replacement of the densities (specific values) of the grand thermodynamic potential by corresponding densities (specific values) of the free energy:

$$\begin{aligned} F = & f^\alpha V^\alpha + f^\beta V^\beta + f^\gamma V^\gamma + \bar{f}^{\alpha\beta} A^{\alpha\beta} \\ & + \bar{f}^{\alpha\gamma} A^{\alpha\gamma} + \bar{f}^{\beta\gamma} A^{\beta\gamma} + \bar{f}L, \end{aligned} \quad (14)$$

where f , \bar{f} , and \bar{f} denote the bulk density and the specific surface and line excesses of the Helmholtz free energy, respectively. The number of particles of an i th component in the system may be written as

$$\begin{aligned} N_i = & n_i^\alpha V^\alpha + n_i^\beta V^\beta + n_i^\gamma V^\gamma + \Gamma_i^{\alpha\beta} A^{\alpha\beta} \\ & + \Gamma_i^{\alpha\gamma} A^{\alpha\gamma} + \Gamma_i^{\beta\gamma} A^{\beta\gamma} + \Lambda_i L, \end{aligned} \quad (15)$$

where n is the number density of particles in the bulk phase and Γ and Λ are the surface and line adsorptions (specific surface and line excess numbers of particles), respectively. The subscript marks a component. Note that expression (15) may also be formally used for immobile component/components j in solid phase γ ; if such a component is absent in adjacent phase α or β , corresponding bulk density n_j and adsorption $\Gamma_j^{\alpha\beta}$ will be equal to zero. Analogously, for components absent in the phase Γ , corresponding densities n_i^γ will be equal to zero.

In this case, minimization of the Helmholtz free energy under conditions (15) of a constant number of particles of each component is reduced, with use of the Lagrange multiplier method [33], to minimization of the functional

$$\Omega[m(\mathbf{x})] \equiv F[m(\mathbf{x})] - \sum_{k \in \{i,j\}} \mu_k N_k[m(\mathbf{x})], \quad (16)$$

while undetermined multipliers μ_k can be found from set of conditions (15) specifying the numbers of particles of each component in the system. It is obvious that, for mobile components i , these multipliers are exactly equal to the chemical potentials of their particles, while the potential (16), whose functional is being minimized, equals the grand thermodynamic potential. When using the definition [31] of the grand thermodynamic potential of a solid, the multiplier μ_j for the component j immobile in the solid phase is equal to the normal component of the chemical potential tensor $\mu_{j(z)}^\gamma$ in the solid phase (see [31, 32] for details). It is also obvious that minimization of the functional (16) will, in this case, yield the same equilibrium conditions as those previously obtained with allowance for the relations between the densities (specific excesses) of the Helmholtz free energy and the grand thermodynamic potential:

$$\begin{aligned} \omega &= f - \sum_{k \in \{i,j\}} \mu_k n_k, \quad \sigma = \bar{f} - \sum_{k \in \{i,j\}} \mu_k \Gamma_k, \\ \kappa &= \bar{\bar{f}} - \sum_{k \in \{i,j\}} \mu_k \Lambda_k. \end{aligned} \quad (17)$$

When both volatile and non-volatile components are present in the system, the equilibrium conditions may be derived analogously starting from the hybrid potential where the Legendre transformation of the Helmholtz free energy F with respect to variables (μ_i, N_i) is performed only for “volatile” components:

$$\tilde{\Omega} \equiv F - \sum_i \mu_i N_i. \quad (18)$$

This potential will, in addition to the temperature and the volume of the system, depend on the chemical potentials $\{\mu_i\}$ of “volatile” components and the particle numbers $\{N_j\}$ of “non-volatile” components (it is convenient to include the immobile components of the solid phase into this list). Minimization of its func-

tional (to be more correct, finding the stationary profile, with the same boundary conditions, for which the first variation equals zero) will give the desired equilibrium conditions. However, the constraint (15) of a constant number of particles must, in this case, be taken into account. In such a condition, the number densities n_j of the particles of “non-volatile” components will be nonzero in an only phase (phase α , if “non-volatile” components in the liquid droplet brought in contact with a vapor–gas medium are concerned). Moreover, adsorption $\Gamma_j^{\beta\gamma}$ of some of these components will possibly (but not necessarily) be equal to zero.

Now, by determining, analogously to the functional (16), a new functional

$$\begin{aligned} \Omega[m(\mathbf{x})] &\equiv \tilde{\Omega}[m(\mathbf{x})] - \sum_j \mu_j N_j \\ &= F[m(\mathbf{x})] - \sum_{k \in \{i,j\}} \mu_k N_k \end{aligned} \quad (19)$$

using the Lagrange multiplier method as applied only to “non-volatile” components $\{j\}$, we again arrive at minimization of the same functional of the grand thermodynamic potential.

When considering non-volatile liquids and performing the variational derivation of the equilibrium conditions, the surface and line excesses are often omitted, and only the bulk contribution proportional to $\int m(\mathbf{x}) d^2\mathbf{x}$ is preserved in expressions similar to Eq. (15) for the number of particles in a system (see, e.g., [29, 30, 37]), thereby ignoring the contributions of adsorptions Γ and Λ to the thermodynamic surface and line tensions. As is seen from expressions (17), the thermodynamic surface tensions σ and the line tension κ are, in this case, actually identified with corresponding excesses \bar{f} and $\bar{\bar{f}}$ of the Helmholtz free energy. As will be shown in section 2, consistent disregard of adsorptions Γ leads to omitting substantial part of the dependence of contact angle θ on radius/half-width r of a droplet base.

In further derivatives, we shall again use the grand thermodynamic potential implying consideration in the grand canonical ensemble. At fixed numbers $\{N_j\}$ of particles of some components in the system, we shall be able to consider these numbers to be independent variables and find the values of the chemical potentials $\{\mu_j\}$ from relations similar to Eq. (15).

1.4. Which Geometric Variable Does Line Tension Depend on?

When performing the variational derivation of the generalized Young relation for axially symmetric (8) and cylindrical (13) droplets, we assumed existence of a size dependence of the thermodynamic line tension specifically on the radius/half-width r of the droplet

base. As a result, the $\partial\kappa/\partial r$ derivative has entered into this equation in both cases.

Some authors involve in the consideration a possible dependence of the line tension on the contact angle [13, 37, 38] or on the radius/half-width of the droplet base and the contact angle simultaneously [6, 39].

When deriving the conditions of equilibrium, we may confine ourselves to a droplet profile with the shape of a spherical cap/horizontal cylindrical segment (as is most often done). In this case, to obtain equations for the parameters of an equilibrium droplet, it is sufficient to determine the conditions under which the partial derivatives of the grand thermodynamic potential over two independent geometric variables (r and θ , r and R , or R and θ) are equal to zero. This leads to two equations. When a possible dependence of the line tension on r alone is considered, these equations, together with the geometrical relation

$$r = R \sin \theta, \quad (20)$$

yield the Laplace equation and the generalized Young relation. When considering a possible dependence of the line tension on both r and θ , an additional term arises in the generalized Young relation containing the $\partial\kappa/\partial\theta$ derivative. However, detailed analysis [39] has shown that this derivative appears to be related to the $\partial\sigma^{\alpha\beta}/\partial R$ derivative. Thus, when choosing the surface of tension as the $\alpha\beta$ dividing surface, both derivatives appear to be equal to zero.

The Laplace equations (7) or (12), which we obtained when considering the equilibrium conditions in terms of the variational problem, does not comprise the $\partial\sigma^{\alpha\beta}/\partial R$ derivative, which must arise in it at an arbitrary choice of the dividing surface [7, 39]. This indicates that, in the considered variational problem, we are dealing with the surface of tension, and, as follows from the derivations in [39], this must correspond to $\partial\kappa/\partial\theta \equiv 0$. Here, we use the identity sign, because this is not an additional equilibrium condition, it must be fulfilled “automatically.” Thus, the $\kappa(\{\mu_i\}, r, \theta)$ dependence cannot be an arbitrary function of r and θ .

Another argument may be presented. If we confine ourselves only to the droplet profiles with the shapes of spherical cap/horizontal cylindrical segment, variables r and θ cannot be independent at radius R preset by the Laplace equation. However, the variational problem under consideration is free of this confinement. At first sight, this must make it possible to consider arbitrary $\kappa(\{\mu_i\}, r, \theta)$ dependences on variables r and θ and result in the appearance of equation $\partial\kappa/\partial\theta = 0$ as *one more* equilibrium condition in addition to the aforementioned Laplace equation and generalized Young relation [6]. However, it is obvious that, for an arbitrary $\kappa(\{\mu_i\}, r, \theta)$ dependence on variables r and θ , this leads to, generally speaking, an

inconsistent set of four equations with three unknowns, because geometrical relation (20) must also be fulfilled. In the general case, it will have a solution only at $\partial\kappa/\partial\theta \equiv 0$.

If this equality is not fulfilled as an *identity*, the variational problem itself appears to be ill-posed, i.e., having no solution within the class of functions (having the physical meaning of $m(x)$ droplet profiles), for which it has been formulated. Indeed, it is clearly seen that the previously found profile, which satisfies the Laplace equation and the generalized Young relation, will not correspond to a zero first variation of the functional, if, therewith, the contact angle $\theta = \arctan(-m'(r))$ does not satisfy (due to some coincidence) condition $\partial\kappa/\partial\theta = 0$. In the general case, when $\partial\kappa/\partial\theta \neq 0$, the $m(x)$ profile may be somewhat varied in a small vicinity to the left of point r to meet the condition $\partial\kappa/\partial\theta = 0$ at the edge of the segment. In such a way, by varying the value of line tension κ , we can formally cause *substantial* variations in the value of term $2\pi\kappa r$ in the functional $\Omega[m(x)]$ with no or almost no changes in the values of other (integral) contributions to it. Making this small vicinity increasingly smaller, we may approach the first variation of the functional to zero. This procedure will lead to a profile that has a specific singularity at $x = r$, and the regular part of the profile will, this case, coincide with the previously found one. Of course, such a “solution” of the variational problem has no physical meaning.

Thus, the aforementioned arguments support our initial decision to consider the line tension as a function of only $\kappa(\{\mu_i\}, r)$.

2. THERMODYNAMIC EQUATIONS FOR SURFACE AND LINE TENSIONS AND THE DEPENDENCE OF THE CONTACT ANGLE ON DROPLET SIZE

Pressures and thermodynamic surface and line tensions, which enter into Eq. (2) and expressions (3) and (9) for the functionals, also depend on T and $\{\mu_i\}$, so that all the terms in the Laplace Eqs. (7) and (12), as well as in the generalized Young relations (8) and (13), are, strictly speaking, dependent on droplet size. Indeed, at given values of T and $\{\mu_i\}$, the pressures p^α and p^β are determined by the equations of state for the fluid phases, while equilibrium droplet curvature radius R is described by the Laplace equation (7) or (12), and the equilibrium contact angle is expressed by the generalized Young relation (8) or (13), in which the thermodynamic surface and line tensions are, in the general case, also dependent on T and $\{\mu_i\}$. Confining ourselves to the isothermal case, we may ignore the dependence of the parameters on temperature T . However, the chemical potentials $\{\mu_i\}$ for a droplet occurring at equilibrium with a vapor will be deter-

mined by the vapor state, i.e., the set of $\{\mu_i\}$ values. Moreover, we shall be interested in the limiting case of an infinitely large droplet, $R \rightarrow \infty$, $r \rightarrow \infty$, corresponding to a certain point on the binodal and, hence, to the equilibrium between macroscopic liquid and vapor phases (which corresponds to $p^\alpha = p^\beta$). We shall also consider this preset point ($\{\mu_{i0}\}, T$) (on the binodal), which corresponds to a passage to the limiting case of the infinitely large droplet, under the studied conditions (such as fixation of the droplet composition, insolubility of a passive gas, etc.). It is convenient to introduce deviations of the chemical potentials from their limiting values

$$\delta\mu_i \equiv \mu_i - \mu_{i0}. \quad (21)$$

Here and below, subscript "0" at a physical parameter marks its value on the binodal, i.e., at the equilibrium between the bulk liquid and vapor phases (which corresponds to $p^\alpha = p^\beta$ and, hence, to the limiting case of an infinitely large droplet, $R \rightarrow \infty$, $r \rightarrow \infty$).

Using the Gibbs–Duhem relations $dp = \sum_i n_i d\mu_i$ for phases α and β , it is easy to relate difference $p^\alpha - p^\beta$ with the values of $\{\delta\mu_i\}$. When considering the system far from the critical liquid–vapor points/curves, we believe the liquid (phase α) to be incompressible or weakly compressible and much denser than the vapor. Then, taking into account the condition of equilibrium on the binodal, $p_0^\beta = p_0^\alpha$, we easily obtain

$$p^\alpha - p^\beta \approx \sum_i n_{i0}^\alpha \delta\mu_i. \quad (22)$$

From here, it also follows for the value of $\tilde{\mu}$, which has been introduced into the right-hand side of Eq. (5) and is used in Eq. (10), that

$$\tilde{\mu} \approx \sum_i n_{i0}^\alpha \delta\mu_i / \sigma_0^{\alpha\beta}. \quad (23)$$

Taking different values of the chemical potentials, we obtain different values of the thermodynamic surface and line tensions in the generalized Young relations (8) and (13). In the limiting case $\{\delta\mu_i \rightarrow +0\}$, we have $R \rightarrow \infty$, $r \rightarrow \infty$; the contact angle has its limiting value θ_0 , to which a straight three-phase contact line corresponds, while the generalized Young relations (8) and (13) acquire the form of the classical Young equation for a macroscopic contact angle:

$$\sigma_0^{\alpha\beta} \cos \theta_0 = \sigma_0^{\beta\gamma} - \sigma_0^{\alpha\gamma}. \quad (24)$$

As before, subscript "0" here marks a value of a quantity at the point preset on the binodal, i.e., at $\{\mu_i = \mu_{i0}\}$.

Subtracting the generalized Young relation (8) from the classical Young equation (24), we, for the **axially symmetric droplet**, obtain

$$\sigma_0^{\alpha\beta} \cos \theta_0 - \sigma^{\alpha\beta} \cos \theta = \delta\Delta\sigma^\gamma + \kappa/r + \partial\kappa/\partial r, \quad (25)$$

where we have used the quantity

$$\begin{aligned} \delta\Delta\sigma^\gamma &\equiv \Delta\sigma^\gamma - \Delta\sigma_0^\gamma, \quad \Delta\sigma^\gamma \equiv \sigma^{\alpha\gamma} - \sigma^{\beta\gamma}, \\ \Delta\sigma_0^\gamma &\equiv \sigma_0^{\alpha\gamma} - \sigma_0^{\beta\gamma}. \end{aligned} \quad (26)$$

Here and below, the symbol δ denotes the difference between the values of a parameter in the current state and in the considered limiting state on the binodal (at $\{\mu_i = \mu_{i0}\}$).

The difference between the surface tensions at different $\{\mu_i\}$ values is, as a rule, ignored in the literature, the line tension is believed to be constant and equal to its limiting value κ_0 for a straight three-phase contact line, and the generalized Young relation (8) is written in a simplified form

$$\sigma_0^{\alpha\beta} \cos \theta = \sigma_0^{\beta\gamma} - \sigma_0^{\alpha\gamma} - \kappa_0/r, \quad (27)$$

which is called by different authors the *modified* or, sometimes, *extended* Young equation. The values of the surface and line tensions, which enter into this equation, refer to the binodal; hence, they are independent of droplet size. Subtracting this relation from the "classical" Young equation (24), we derive the relation

$$\cos \theta_0 - \cos \theta = \frac{\kappa_0}{\sigma_0^{\alpha\beta} r}, \quad (28)$$

which is widely used to determine the line tension from the slope of the $\cos \theta - 1/r$ dependence [9, 8]. It is clearly seen that expression (28) can also be obtained from relation (25), if we take $\delta\Delta\sigma^\gamma = 0$, $\sigma^{\alpha\beta} = \sigma_0^{\alpha\beta} = \text{const}$, and $\kappa \equiv \kappa_0 = \text{const}$.

Let us estimate the $\delta\Delta\sigma^\gamma$ value using the generalized Gibbs adsorption equation for the $\beta\gamma$ and $\alpha\gamma$ interfaces, which is a version of the "classical" Gibbs adsorption equation for solid surfaces [36, 40, 41]:

$$\begin{aligned} d\sigma = -\bar{s}dT + (\hat{\gamma} - \hat{\sigma}^1) : (d\hat{e} - d\hat{N}_j/N_j) \\ - \sum_i \Gamma_i d\mu_i, \end{aligned} \quad (29)$$

where \bar{s} is the specific surface excess entropy, $\hat{\gamma}$ is the tensor of the mechanical surface tension (specific surface excess stress tensor), \hat{e} is the tensor of the surface strain, $\hat{1}$ is the unit tensor, \hat{N}_j is the mass displacement tensor indicating changes in the amount of immobile component j of the solid phase in different directions (see [41] for details), $N_j \equiv \text{Tr } \hat{N}_j$ is the amount of the substance (the number of molecules/atoms) of the immobile component j in the solid phase; subscript i enumerates only mobile components, and the colon denotes the biscalar product of the tensors. For an undeformable solid (or a solid with a constant strain) having a constant mass (within the boundaries speci-

fied by the dividing surfaces), $d\hat{e} = 0$, $d\hat{N}_j = 0$, and Eq. (29) acquires the form of the “classical” Gibbs adsorption equation, as it is written for a dividing surface between fluid phases:

$$d\sigma = -\bar{s}dT - \sum_i \Gamma_i d\mu_i. \quad (30)$$

Let us assume that the solid phase of the substrate contains no mobile components and neglect the dependence of the substrate strain tensor on the sessile droplet size and the chemical potentials of fluid molecules. Choosing the $\beta\gamma$ and $\alpha\gamma$ dividing surfaces to be equimolecular with respect to the immobile component j of the solid (and assuming that they are coplanar), the following may be written for our system under isothermal conditions:

$$d\Delta\sigma^\gamma = \sum_i (\Gamma_i^{\beta\gamma} - \Gamma_i^{\alpha\gamma}) d\mu_i. \quad (31)$$

Integrating this equation from the μ_{i0} value on the binodal to current μ_i values, we derive

$$\begin{aligned} \delta\Delta\sigma^\gamma &= \sum_i \int_{\mu_{i0}}^{\mu_i} (\Gamma_i^{\beta\gamma} - \Gamma_i^{\alpha\gamma}) d\mu_i' \\ &\approx \sum_i (\Gamma_{i0}^{\beta\gamma} - \Gamma_{i0}^{\alpha\gamma}) \delta\mu_i = O(\bar{\mu}). \end{aligned} \quad (32)$$

The approximate equality corresponds to the asymptotic expression for rather low $\delta\mu_i$ values, and subscript “0” refers, as usual, to the values of parameters at $\{\mu_i = \mu_{i0}\}$, corresponding to the limiting state on the binodal.

Let us use the Gibbs adsorption equation for the $\alpha\beta$ interface between the liquid and vapor phases to estimate the correction to the surface tension $\sigma^{\alpha\beta}$ due to changes in μ_i . Since the initial functionals and equilibrium conditions were obtained for the surface of tension³ used as the $\alpha\beta$ dividing surface, i.e., $\partial\sigma^{\alpha\beta}/\partial R = 0$, and the Gibbs adsorption equation in the isothermal case has the form of

$$d\sigma^{\alpha\beta} = -\sum_i \Gamma_i^{\alpha\beta} d\mu_i, \quad (33)$$

similarly to the case of Eq. (32), the integration yields

$$\delta\sigma^{\alpha\beta} \equiv \sigma^{\alpha\beta} - \sigma_0^{\alpha\beta} \approx -\sum_i \Gamma_{i0}^{\alpha\beta} \delta\mu_i = O(\bar{\mu}). \quad (34)$$

Let us rewrite relation (25) as

$$\begin{aligned} \sigma_0^{\alpha\beta} (\cos\theta_0 - \cos\theta) &= \delta\Delta\sigma^\gamma + \delta\sigma^{\alpha\beta} \cos\theta \\ + \kappa/r + \partial\kappa/\partial r &\approx \delta\Delta\sigma^\gamma + \delta\sigma^{\alpha\beta} \cos\theta_0 + \kappa/r + \partial\kappa/\partial r. \end{aligned} \quad (35)$$

³ See [7, 39] and review [36] for detailed discussion of the equilibrium conditions for an arbitrary choice of the $\alpha\beta$ dividing surface.

The latter approximate expression has been obtained under the assumption that correction $\delta\sigma^{\alpha\beta} \cos\theta$ is small due to the smallness of $\delta\sigma^{\alpha\beta}$ or/and the difference between $\cos\theta$ and $\cos\theta_0$ (this is, in particular, true in the limiting case of rather large droplets). The error in this approximation may be estimated as $O(\bar{\mu}^2)$.

To estimate the term κ/r in the right-hand side of the generalized Young relation (8) and relations (25), (27), and (35) for an axially symmetric sessile droplet, we compare the Laplace equation (7), geometric relation (20), and Eq. (23). This will yield the following asymptotic expression for rather large droplets:

$$\frac{\kappa}{r} = \frac{\kappa\bar{\mu}}{2\sin\theta} \approx \frac{\kappa_0}{2\sigma_0^{\alpha\beta} \sin\theta_0} \sum_i n_{i0}^\alpha \delta\mu_i = O(\bar{\mu}). \quad (36)$$

Thus, it can be seen that the terms $\delta\Delta\sigma^\gamma$, $\delta\sigma^{\alpha\beta} \cos\theta$, and κ/r in the right-hand side of relation (35) have the first order with respect to $\bar{\mu}$ or $1/r$. For not too small droplets, the correction $\delta\sigma^{\alpha\beta} \cos\theta$ must be small due to the very small Tolman length as compared with the characteristic values of curvature radius R of the droplet meniscus. It may also be expected that it is small as compared with $\delta\Delta\sigma^\gamma$, e.g., for a free $\beta\gamma$ surface covered with a polymolecular adsorption film or a wetting one (which yields large values of $\sum_i (\Gamma_{i0}^{\beta\gamma} - \Gamma_{i0}^{\alpha\gamma})$ comparing to $\sum_i \Gamma_{i0}^{\alpha\beta}$), as it takes place upon, e.g., nucleation of sessile droplets on a glass surface in supersaturated vapors of water and alcohols, and in a number of other cases [42, 43].

For a **cylindrical droplet**, the generalized Young relation (13) is also transformed into the “classical” Young equation (24) for the macroscopic contact angle in the limiting case of $\{\delta\mu_i \rightarrow +0\}$, i.e., $r \rightarrow \infty$, in which $\partial\kappa/\partial r \rightarrow 0$ [35, 36]. The counterparts of relations (25) and (35), in this case, have no term κ/r in the right-hand side:

$$\sigma_0^{\alpha\beta} \cos\theta_0 - \sigma^{\alpha\beta} \cos\theta = \delta\Delta\sigma^\gamma + \partial\kappa/\partial r, \quad (37)$$

$$\begin{aligned} \sigma_0^{\alpha\beta} (\cos\theta_0 - \cos\theta) &= \delta\Delta\sigma^\gamma + \delta\sigma^{\alpha\beta} \cos\theta + \partial\kappa/\partial r \\ &\approx \delta\Delta\sigma^\gamma + \delta\sigma^{\alpha\beta} \cos\theta_0 + \partial\kappa/\partial r. \end{aligned} \quad (38)$$

To estimate the term $\partial\kappa/\partial r$ in the right-hand side of generalized Young relation (8) and Eqs. (25) and (35) for an axially symmetric sessile droplet, as well as the generalized Young equation (13) and relations (37) and (38) for a cylindrical droplet, we use the line adsorption equation, an analog of the Gibbs–Duhem relation and the Gibbs adsorption equation for the three-phase contact line [41, 44]. We suppose that, taking into account the assumptions used above in Eq. (31) for the strain of the solid substrate and the

choice of the dividing surfaces, this equation for our system will have a form similar to that for a system composed of only fluid phases [7]:

$$d\kappa = -\bar{s}dT - \sum_i \Lambda_i d\mu_i + \frac{\partial\kappa}{\partial r} dr, \quad (39)$$

where \bar{s} is the specific (per unit length of the three-phase contact line) line excess of entropy (the term containing this parameter will be absent in the isothermal case under consideration). The term $(\partial\sigma/\partial R)dR$, which is analogous to $(\partial\kappa/\partial r)dr$, is absent in the Gibbs adsorption equations; namely, it is absent in Eqs. (29) and (30) for a planar interface, because $\partial\sigma/\partial R \rightarrow 0$ in the limiting case $\{\delta\mu_i \rightarrow +0\}$ (i.e., $R \rightarrow \infty$), and in Eq. (33) for a curved $\alpha\beta$ surface, because, for the chosen surface of tension, $\partial\sigma/\partial R = 0$. The choice of three dividing surfaces $\alpha\beta$, $\alpha\gamma$, and $\beta\gamma$ fixes the position of the three-phase contact line, and, in the general case, $\partial\kappa/\partial r \neq 0$ for it [7, 36].

Note that use of the generalized Young relation (8) containing total derivative $d\kappa/dr$ along the equilibrium states of droplets instead of partial derivative $\partial\kappa/\partial r$ may be found in the literature [45]. It can be seen from Eq. (39) that disregard of the line adsorptions Λ_i (as in the case of, e.g., minimization of the Helmholtz free energy (14) under the condition of constant particle numbers with allowance for only bulk contributions in (15)) corresponds, in the isothermal case, namely to identification of the $d\kappa/dr$ and $\partial\kappa/\partial r$ derivatives.

Assuming that, for the line tension κ and the line adsorptions Λ_i expressed as functions of the equilibrium radius⁴ (base half-width) r , the following asymptotic (at $\{\delta\mu_i \rightarrow +0\}$) estimates

$$\begin{aligned} \kappa &= \kappa_0 + O(\tilde{\mu}) = \kappa_0 + O(r^{-1}), \\ \Lambda_i &= \Lambda_{i0} + O(\tilde{\mu}) = \Lambda_{i0} + O(r^{-1}) \end{aligned} \quad (40)$$

may be written with finite limiting values of κ_0 and Λ_{i0} , we, from Eq. (39) with allowance for the Laplace equations (7) or (12), geometrical relation (20) and expression (23), obtain the following:

$$\frac{\partial\kappa}{\partial r} = \frac{d\kappa}{dr} - \sum_i \Lambda_i \left(\frac{dr}{d\mu_i} \right)^{-1} = O(\tilde{\mu}^2) = O(r^{-2}). \quad (41)$$

Indeed, it follows from estimates (40) that, along the states of equilibrium, $d\kappa/dr = O(r^{-2}) = O(\tilde{\mu}^2)$. The Laplace equations (7) or (12), geometrical relation (20) and Eq. (23) yield

⁴ That is, along the line ("trajectory") of equilibrium states of the system under preset (e.g., by an experiment) conditions $r(\{\mu_i\})$.

$$\begin{aligned} \frac{\partial r}{\partial \mu_i} &\approx -\frac{k \sin \theta_0}{\tilde{\mu}^2} \frac{d\tilde{\mu}}{d\mu_i} \\ &\approx -\frac{k \sin \theta_0}{\tilde{\mu}^2} \sum_j n_{j0}^\alpha \frac{d\mu_j}{d\mu_i} = O(\tilde{\mu}^{-2}), \end{aligned} \quad (42)$$

where $k = 2$ and 1 for axially symmetric and cylindrical droplets, respectively, and, in the general case, this value is nonzero. The subscript j here and further runs over the same values as the subscript i . Then, $\sum_i \Lambda_i (dr/d\mu_i)^{-1} = O(r^{-2}) = O(\tilde{\mu}^2)$.

Thus, neglecting the term $\partial\kappa/\partial r$ is justified in the asymptotic limit of relatively large droplets [7], while neglecting adsorption effects (nonzero values of corrections $\delta\Delta\sigma^\gamma$ and $\delta\sigma^{\alpha\beta} \cos \theta$) cannot be considered to be justified without certain estimates.

Relation (28) is often used to determine the line tension κ_0 from the slope of the $\cos \theta$ versus the three-phase contact line curvature $1/r$ dependence for axially symmetric sessile droplets. In the majority of experiments, this dependence for micron and submicron sessile droplets is, within the measurement errors, linear. At the same time, the unjustified neglecting adsorption effects does not give grounds to believe that the value measured in such a way is really equal to the line tension κ_0 . Differentiating the right-hand side of expression (35) over $1/r = \tilde{\mu}/(2 \sin \theta)$, we may, similarly to the case of the derivation of Eqs. (41) and (42), show that the real slope of the $\cos \theta - 1/r$ dependence in asymptotic limit $\{\mu_i\} \rightarrow \{\mu_{i0}\}$ (or, equivalently, $r \rightarrow \infty$) will be equal to

$$\begin{aligned} -\frac{\kappa_0}{\sigma_0^{\alpha\beta}} - 2 \sin \theta_0 \sum_i (\Gamma_{i0}^{\beta\gamma} - \Gamma_{i0}^{\alpha\gamma} - \Gamma_{i0}^{\alpha\beta} \cos \theta_0) \\ \times \left(\sum_j n_{j0}^\alpha \frac{d\mu_j}{d\mu_i} \right)^{-1}. \end{aligned} \quad (43)$$

Here, the first term results from the effect of the line tension, while the second term is due to the effect of adsorptions at the interfaces. In [46], it has been rightly pointed out that even the adsorption effect alone may, in principle, be sufficient to explain the existence of the dependence of $\cos \theta$ on $1/r$. In reality, these effects are inseparable and take place simultaneously.

For **cylindrical droplets**, the line tension yields no correction (linear with respect to $1/r$) to the cosine of the contact angle, so that the slope of the $\cos \theta - 1/r$ dependence is governed only by the effect of adsorptions at the interfaces, and, in asymptotic limit $\{\mu_i\} \rightarrow \{\mu_{i0}\}$ (or, equivalently, $r \rightarrow \infty$), it is equal to

$$-\sin \theta_0 \sum_i (\Gamma_{i0}^{\beta\gamma} - \Gamma_{i0}^{\alpha\gamma} - \Gamma_{i0}^{\alpha\beta} \cos \theta_0) \left(\sum_j n_{j0}^\alpha \frac{d\mu_j}{d\mu_i} \right)^{-1}. \quad (44)$$

Note that, in the multicomponent case, the terms that enter into expressions (43) and (44) and are determined by the adsorption effects, depend not only on temperature T and the values of the chemical potentials $\{\mu_{j0}\}$ at the “limiting” point $\{\mu_{j0}\}$ on the binodal, but also, strictly speaking, on the “trajectory” in the space of the chemical potentials $\{\mu_j\}$, over which the droplets “approach” $\{\mu_{j0}\}$. This is evident from the presence of the $d\mu_j/d\mu_i$ derivatives along the “trajectory” in expressions (43) and (44).

It should be noted that the simplified description of axially symmetric sessile droplets by Eqs. (7) and (28) is rather widely used. When it is required to describe the contact angles of not too small droplets, Eq. 28 may be considered as an asymptotic form of the exact relations (25) and (35) with the coefficient in the right-hand side equal to the expression (43) taken with the reverse sign rather than $\kappa_0/\sigma_0^{\alpha\beta}$. For smaller droplets and description of the thermodynamic quantities as the work of droplet formation, it is necessary to take into account the dependences of the surface tensions on the chemical potentials and, generally speaking, the nonlinear character of the $\cos\theta-1/r$ dependence.

The absence of the line tension in the asymptotic expression (44) for the slope of the $\cos\theta-1/r$ dependence for cylindrical droplets partly justifies the assumption used in a number of works [18, 19] that the simulation of namely cylindrical droplets makes it possible to exclude the effect of the line tension on the contact angles of sessile droplets. At the same time, it can be seen that the effect of adsorption at the interfaces remains preserved, and it is this effect that pre-determines the existence of the size dependence of $\cos\theta$ already at the first order with respect to $1/r$. At higher orders with respect to $1/r$, the line tension will also affect the contact angle due to the presence of the term $\partial\kappa/\partial r$ in Eq. (37).

2.1. Results for a One-Component Fluid

When fluid phases α and β consist of particles of a single component, the obtained results look clear and may be interpreted in the simplest way [25]. Under the considered conditions of a preset value of the chemical potential of vapor/liquid particles, the system itself is represented by a critical droplet in nucleation of a supersaturated vapor on a partially wettable solid substrate. The value of the chemical potential μ is related to vapor supersaturation $\zeta \equiv n^\beta/n_0^\beta - 1$ as follows:

$$\mu = \mu_0 + k_B T \ln(1 + \zeta), \quad (45)$$

where k_B is the Boltzmann constant and μ_0 is the value of the chemical potential on the binodal at the considered temperature. In the case of a one-component fluid having a preset temperature, the state of the sys-

tem is governed by single variable μ , deviation $\delta\mu$ of which from μ_0 (cf. Eq. (21)) will, in the asymptotic limiting case of large droplets, be proportional to small parameter $\tilde{\mu}$ determined by Eq. (5) (cf. Eq. (23)):

$$\tilde{\mu} \approx n_0^\alpha \delta\mu / \sigma_0^{\alpha\beta}. \quad (46)$$

The asymptotic estimate (32) of $\delta\Delta\sigma^\gamma$ will acquire the form of

$$\delta\Delta\sigma^\gamma = \int_{\mu_0}^{\mu} (\Gamma^{\beta\gamma} - \Gamma^{\alpha\gamma}) d\mu_i' \approx (\Gamma_0^{\beta\gamma} - \Gamma_0^{\alpha\gamma}) \delta\mu = O(\tilde{\mu}), \quad (47)$$

while the estimate (36) of the κ/r value is as follows:

$$\frac{\kappa}{r} = \frac{\kappa\tilde{\mu}}{2 \sin\theta} \approx \frac{\kappa_0 n_0^\alpha \delta\mu}{2\sigma_0^{\alpha\beta} \sin\theta} = O(\tilde{\mu}). \quad (48)$$

Expression (47) for $\delta\Delta\sigma^\gamma \equiv (\sigma^{\alpha\gamma} - \sigma_0^{\alpha\gamma}) - (\sigma^{\beta\gamma} - \sigma_0^{\beta\gamma})$ is easier to interpret in the one-component case. Variations in each solid–fluid thermodynamic surface tension are governed by fluid adsorption on the surface. In the case of a one-component “volatile” fluid, the equilibrium surface of a solid brought in contact with the vapor (the $\beta\gamma$ surface) is represented by a spontaneously formed metastable condensate film. Of course, the value of the adsorption (or the film thickness), which is unambiguously determined by $\delta\mu$, affects the equilibrium surface tension⁵ (see also our work [25], which contains the results of model calculations performed for an axially symmetric droplet via the interface potential/disjoining pressure isotherms in liquid films on a solid substrate).

In the one-component case, estimate (34) for the quantity $\delta\sigma^{\alpha\beta} \equiv \sigma^{\alpha\beta} - \sigma_0^{\alpha\beta}$ acquires the form of

$$\delta\sigma^{\alpha\beta} \equiv \sigma^{\alpha\beta} - \sigma_0^{\alpha\beta} \approx -\Gamma_0^{\alpha\beta} \delta\mu = O(\tilde{\mu}). \quad (49)$$

The slope of the $\cos\theta-1/r$, dependence given by Eqs. (43) and (44) for axially symmetric and cylindrical droplets, respectively, will, in the one-component case, be equal to

$$-\kappa_0/\sigma_0^{\alpha\beta} - 2 \sin\theta_0 (\Gamma_0^{\beta\gamma} - \Gamma_0^{\alpha\gamma} - \Gamma_0^{\alpha\beta} \cos\theta_0) / n_0^\alpha \quad (50)$$

for the axially symmetric droplet and

$$-\sin\theta_0 (\Gamma_0^{\beta\gamma} - \Gamma_0^{\alpha\gamma} - \Gamma_0^{\alpha\beta} \cos\theta_0) / n_0^\alpha \quad (51)$$

for the cylindrical one.

As a rule, in works where the dependence of the surface tension $\sigma^{\alpha\beta}$ on the droplet size is taken into account in the classical or generalized Young relation

⁵ Change $\sigma^{\beta\gamma} - \sigma_0^{\beta\gamma}$ in the equilibrium solid–vapor surface tension for a condensing vapor may be found from the interface potential/disjoining pressure isotherm [25, 26]. The difference between the surface tensions/spreading coefficients for “bare” and equilibrium solid surfaces may be estimated from the initial region of a model adsorption isotherm [51, 52].

[13, 18, 39, 47], the following asymptotic form of this dependence [48, 49] is used:

$$\sigma^{\alpha\beta} \approx \sigma_0^{\alpha\beta} \left(1 - \frac{k\delta_T^{\alpha\beta}}{R} \right), \quad (52)$$

where $k = 2$ and 1 for axially symmetric and cylindrical droplets, respectively, and $\delta_T^{\alpha\beta}$ is the Tolman length, which is related to the adsorption and number densities of particles in phases α and β on the binodal as follows [48]:

$$\delta_T^{\alpha\beta} = \frac{\Gamma_0^{\alpha\beta}}{n_0^\alpha - n_0^\beta} \approx \frac{\Gamma_0^{\alpha\beta}}{n_0^\alpha}. \quad (53)$$

Taking into account this relation, the correction (obtained for an axially symmetric droplet in [39]) for the size dependence of surface tension $\sigma^{\alpha\beta}$ coincides with the correction that we obtained in Eq. (50). It should, however, be noted that, for rather small droplets, asymptotic equation (52) is an inadequate approximation and must be replaced by an expression comprising a contribution quadratic with respect to the curvature [49, 53–55].

3. DISCUSSION

Let us summarize the results of the above-described thermodynamic analysis of equilibrium conditions for a sessile droplet and the $\cos\theta$ versus $1/r$ dependence, where r denotes the radius of the droplet base and its half-width for axially symmetric and cylindrical droplets, respectively. The equilibrium conditions for sessile droplets are the Laplace equations (Eqs. (7) and (12) for the axially symmetric and cylindrical droplets, respectively) and the generalized Young relations (Eqs. (8) and (13) for the axially symmetric and cylindrical droplets, respectively). The latter relations indicate dependence of $\cos\theta$ on r (more often, the dependence on the curvature $1/r$ is considered). This dependence may be explicit (due to the presence of the term κ/r in Eq. (8) and the term $\partial\kappa/\partial r$ in Eqs. (8) and (13)), and implicit, i.e., expressed via the dependences of all the surface tensions and line tensions on the chemical potentials $\{\mu_i\}$ of the components, with the equilibrium droplet size (and, hence, r) being also governed by $\{\mu_i\}$. As the thermodynamic analysis has shown, in the principal order with respect to $1/r$, the main corrections to the macroscopic value of $\cos\theta_0$ are governed by dependences of the surface tensions on $\{\mu_i\}$ (physically determined by the effect of adsorption at interfaces), as well as (but only for the axially symmetric droplet) by existence of a nonzero line tension κ_0 in the limiting case of a macroscopic droplet, i.e., of a straight three-phase contact line. In the case of a cylindrical droplet, there is no correction

provided by term κ/r of the generalized Young relation.

In the multicomponent case, we should also note the presence of $d\mu_j/d\mu_i$ derivatives along the “trajectory” of droplets in the space of chemical potentials $\{\mu_i\}$ in Eqs. (43) and (44) for the slope of the $\cos\theta$ versus $1/r$ plot in the asymptotic limiting case $\{\mu_i\} \rightarrow \{\mu_{i0}\}$ of infinitely large droplets. These relative variations in the chemical potentials may, in particular, reflect the influence of variations in the droplet composition on its contact angle. This should be taken into account when interpreting $\cos\theta$ versus $1/r$ dependences resulting from the measurements or simulations performed in a multicomponent case. A more detailed analysis requires instantiation of expressions for the dependences of the chemical potentials in mixtures on the number density of molecules/atoms, which is beyond the scope of this study.

For smaller sessile droplets, the size dependence of actually all the terms of the generalized Young relation becomes important (here we are, in fact, dealing with nanosized droplets, which are, at present, accessible for simulation rather than for direct measurements). Presence of an *explicit* size dependence of the line tension gives rise to the separate term $\partial\kappa/\partial r$, which should be discussed in greater detail.

The choice of a geometrical variable, which may/must the line tension of a sessile droplet depend on, seems to be a rather formal question, when the consideration is confined to spherical or cylindrical segments (as was the case in our work [7] dealing with an axially symmetric droplet). Therewith, the selection of, in some sense, more “local” variable θ seems to be even more logical especially in the case of a cylindrical droplet, the three-phase contact line of which remains straight at any values of r . However, we have seen that, at a more general variational statement of the problem, when the equilibrium shape of a droplet is not assumed to be known in advance, the choice of variable θ appears to be very inconvenient and leads to an ill-posed variational problem. This is not just a technical problem, but, on the contrary, indicates that an explicit $\kappa(\theta)$ dependence cannot be realized in a physical system. Indeed, the $\kappa(\theta)$ dependence must, at an arbitrary value of the angle θ , induce some force that tends to change this angle, thereby distorting the droplet profile as *locally* as possible (because the profile with the shape of spherical/cylindrical segment is determined by a corresponding Euler–Lagrange equation, and a change in droplet base radius/half-width r also affects the value of the functional and, therewith, may be realized *independently* of a change in θ). This force disappears only at θ values for which $\partial\kappa/\partial\theta = 0$. In the general case, this gives rise to a non-physical singularity of the profile shape in the vicinity of the three-phase contact line or implies the existence

of *separate* equilibrium condition $\partial\kappa/\partial\theta = 0$. The latter leads, generally speaking, to an inconsistent set of equations, because the number of the equations exceeds the number of unknowns.

In connection with the conclusion on the incorrect consideration of the $\kappa(\theta)$ dependence, a question arises how to interpret results, where such a dependence has been obtained in the explicit form for the line tension (see, e.g., [38]) or the effective line tension [6]. Possibly, this dependence should, in such cases, be interpreted as $\kappa(\arcsin(r/R))$ and considered as an explicit dependence of κ on r .

The existence of nonzero term $\partial\kappa/\partial r$ may be verified by independent calculations of the surface tensions (as well as the line tension and the base radius of a sessile axially symmetric droplet) in terms of any model. For example, we have performed such calculations in [25] for axially symmetric droplets within the framework of a model describing a sessile droplet as a liquid film of varying thickness, while the specific properties of thin liquid films were taken into account using a model short-range interface potential related to disjoining pressure isotherm. The data obtained have confirmed both the existence of an additional correction to the contact angle cosine (we have related this correction to the $\partial\kappa/\partial r$ derivative) and the second order of smallness of this correction with respect to $1/r$. The results of calculating $\partial\kappa/\partial r$, $d\kappa/dr$, and the line adsorption Λ have also appeared to be in agreement with the line adsorption equation (39), with this fact, however, being omitted in the text of the article.

In some works (see, e.g., [47]), the authors have, in accordance with the previous analysis [39], used the generalized Young relation containing the $\partial\kappa/\partial\theta$ derivative, and, in the general case, the $\partial\kappa/\partial r$ derivative as well. When comparing the relations obtained in [39] with the results of this work, we should, first of all, make two preliminary comments.

(1) Among two definitions of the line tension for a sessile droplet considered in [39], our definition coincides with the quantity denoted as τ_w and corresponds to allowance for surface contribution $\sigma^{\alpha\gamma} A^{\alpha\gamma}$ (in our notations) to the grand thermodynamic potential of the system with thermodynamic surface tension $\sigma^{\alpha\gamma}$ calculated at the current value of the droplet pressure p^α , which differs from the pressure p^β in the vapor–gas medium.

(2) In [39], relations were obtained for arbitrary dividing surfaces, while we have made a certain choice. For example, we have chosen the *surface of tension*, for which $\partial\sigma^{\alpha\beta}/\partial R = 0$, as the $\alpha\beta$ dividing surface. The quantity $\partial\kappa/\partial\theta$ (denoted in this work as $d\tau_w/d\theta$) is not independent, but is rather related to

the $\partial\sigma^{\alpha\beta}/\partial R$ derivative (denoted in this work as $d\sigma_{\alpha\beta}/dR$) via relation (6.44)

$$\sin^2 \theta \frac{\partial\kappa}{\partial\theta} = \frac{r^2}{2} \frac{\partial\sigma^{\alpha\beta}}{\partial R},$$

so both these quantities vanish at the surface of tension.

Thus, the use of a nonzero $\partial\kappa/\partial\theta$ derivative is justified only when the $\alpha\beta$ dividing surface different from the surface of tension is chosen. This also implies appearance of an additional nonzero term $\partial\sigma^{\alpha\beta}/\partial R$ in the Laplace equation. Therewith, the quantity $\partial\kappa/\partial r$ must, as before, be taken into account in the exact form of the generalized Young relation.

In this work, we discuss the adsorption-related correction to $\cos \theta$ that was also discussed in [46] as a correction sufficient, in principle, for describing the size dependence of the contact angle of an axially symmetric sessile droplet even without including the line tension. This correction is of the first order with respect to $1/r$ and associated with existence of adsorption at interfaces (specifically, at solid–fluid interfaces). It is clear that, in practice, the line tension cannot be excluded from a real system; therefore, both effects will take place (in the case of a cylindrical droplet, only the effects of adsorption manifest themselves and yield the correction to $\cos \theta$, with the correction having the first order with respect to $1/r$, while the line tension must affect $\cos \theta$ only in the second order of smallness with respect to $1/r$). The results of model calculations performed in our work [25] have confirmed the existence of *two* corrections having the first order of smallness with respect to $1/r$. A feature of the model gives rise to only one correction related to adsorption $\Gamma^{\beta\gamma}$ (adsorption values $\Gamma^{\alpha\beta}$ and $\Gamma^{\alpha\gamma}$ are equal to zero in the used model). The authors of recent work [50], who studied sessile droplets by the Monte Carlo method within the framework of the lattice gas model, have also come to the conclusion that there are comparable effects of the adsorption ($\Gamma^{\alpha\gamma}$ and $\Gamma^{\beta\gamma}$) and the line tension.

In this work, we have involved in the consideration the influence of adsorption at all three interfaces on the of the contact angle cosine. In our previous works [25, 26], we ignored the dependence of surface tension $\sigma^{\alpha\beta}$ on the curvature of free surface $\alpha\beta$ of the considered droplets keeping in mind, primarily, sessile droplets formed on top of a precursor adsorbed/wetting film. For polar liquids, the thickness of such a film (and corresponding adsorption $\Gamma^{\beta\gamma}$) will be rather large (for water on the surfaces of quartz, glass, etc., the thickness of such a film may be as large as 1 nm [42, 43], thereby exceeding the Tolman length by sev-

eral orders of magnitude). However, in works devoted to molecular simulation of sessile droplets, there is often no adsorbed film on the solid surface, while the droplets under investigation are very small, and the curvature radii of their free $\alpha\beta$ surfaces may be of the same order with the Tolman length. This gives sense to the including of corresponding correction $\delta\sigma^{\alpha\beta} \cos\theta$ into the exact form of relations (35) and (38). The replacement of this correction by approximate correction $\delta\sigma^{\alpha\beta} \cos\theta_0$ formally yields an error of the same order $O(\tilde{\mu}^2) = O(r^{-2})$ as the term $\partial\kappa/\partial r$ does, as well as corrections of the same order to other terms in right-hand side of Eqs. (35) and (38). However, the use of this less accurate expression for the correction $\delta\sigma^{\alpha\beta} \cos\theta$ may make sense even in higher orders with respect to $\tilde{\mu}$ (or $1/r$), when this correction is small as compared with others. In any case, expressions (43) and (44) for the slope of the $\cos\theta$ versus $1/r$ plot, as well as their forms (50) and (51) for a one-component fluid, have been obtained within the framework of a linear approximation with respect to $\tilde{\mu}$ (or $1/r$) and are exact in this order. Obtaining expressions with higher orders with respect to $\tilde{\mu}$ (or $1/r$) requires to control derivations of all the used equations, because many of them are valid only in the first order with respect to $\tilde{\mu}$ (or $1/r$).

It should be separately noted that, when analyzing the results of a measurement or simulation of small droplets, an important question arises regarding to the choice of the plane in which dividing surfaces $\alpha\gamma$ (substrate–liquid) and $\beta\gamma$ (substrate–gas) are located [47]. Adsorption-related corrections to $\cos\theta_0$ in Eqs. (43) and (44) will be of the same order as a change in $\cos\theta$ upon a shift of the plane of the $\alpha\gamma$ and $\beta\gamma$ dividing surfaces by a value comparable with the thickness of the adsorbed layers. This may explain why, in [18], even in the presence of adsorption on the substrate surface, the simulated system did not demonstrate noticeable corrections to the contact angles of rather large cylindrical droplets. These corrections would be unexplainable by only the effect of adsorption at the liquid–vapor interface with the Tolman length calculated for the model fluid.

Remember that, in this work, we fixed the position of the plane of the $\alpha\gamma$ and $\beta\gamma$ dividing surfaces by imposing the equimolecular condition with respect to the immobile component of the solid substrate, thereby substantially simplifying the choice of generalized Gibbs adsorption equation (29) for the solid substrate. Another position of the plain of these dividing surfaces may be chosen for convenience [25]. However, in view of the complex structure of Eq. (29), such a different choice would, in our opinion, require separate consideration similar to [31, 32], i.e., more detailed than that performed in [39].

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