

Curvature dependence of the surface tension of liquid and vapor nuclei

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The surface tension and the Tolman length have been presented as series in terms of the interface curvature c . The expansion has been limited by a linear term on c for the Tolman length and a square one for the surface tension. In the framework of the van der Waals capillarity theory the expansion coefficients have been expressed in terms of the planar interface characteristics. The coefficients asymptotic behavior has been derived in the vicinity of the liquid-vapor critical point. For the van der Waals fluid, the results of expansions have been compared with the data of direct numerical calculations. A wide curvature interval of the suitability of derived formulas has been stated. This fact allows the use of them in the homogeneous nucleation theory to calculate the critical nucleus formation work. [S1063-651X(99)02201-1]

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I. INTRODUCTION

The problem of the dependence of droplets and bubble surface tension σ on the dividing surface curvature $c = 1/R$ is the subject of numerous theoretical [1–7] and experimental [8–11] investigations. The variability of the approaches and methods has not yet lead to a consensus even on the qualitative character of this dependence.

It is necessary to take the curvature effect into account to explain the initial stage of a phase transition when the new phase nuclei have a size of the order of several tens to hundreds of angstroms. Experimental data on the nucleation in simple classical liquids [12] indicate that at temperatures $T \approx 0.9T_c$, where T_c is the critical temperature, the surface tension of bubbles having radii 35–45 Å is some 5–7% below the planar surface tension σ_0 . This result is confirmed by investigations of tensile stresses at the capillary condensation of liquid between mica cylinders [8] and conflicts with experiments on the mesopore absorption of organic liquids [9] where the surface tension of a curved surface was found to exceed the planar limit by 5–30%. Computer simulations [13–15] of droplets indicate that the surface tension decreases with a reduction of the curvature radius ($R \approx 8$ –12 Å). However, in these simulations the problem of the asymptotic behavior of the quantity σ at $R \rightarrow \infty$ as well as $R \rightarrow 0$ remains unsolved too.

Tolman [16] defined the curvature dependence $\sigma(R)$ at large R as

$$\sigma = \sigma_0 / (1 + 2\delta_0 c), \quad (1)$$

where the coefficient δ_0 is known as the Tolman length and is the distance between the equimolecular dividing surface and the surface of tension. A statistical calculation by Kirkwood and Buff [2] and the quasithermodynamic approach by Hill [3] gave the quantity $\delta_0 > 0$. This implies that the surface tension decreases monotonically with a reduction of R for droplets and the dependence $\sigma(R)$ has a maximum for bubbles. The axis z of a Cartesian coordinate system is implied to direct normally to the planar interface and aim away from a liquid to a vapor. In the framework of the van der Waals capillarity theory numerical calculations of the droplet

and bubble surface tension [11,17–19] resulted in an inverse value ($\delta_0 < 0$) and demonstrated an extremely small curvature region of suitability of Eq. (1).

In capillarity theory the functional density method [20–24] has recently gained wide interest. This method is based upon rigorously proven theorems that justify the theoretical possibility of describing the properties of systems in thermodynamic equilibrium merely in terms of the one-body density. When irregularities are weak the nonlocal expressions of thermodynamic potentials may be transformed to the local form of the gradient expansion [11]. The last approach is known as the van der Waals capillarity theory.

In this work a different approximation to the curvature dependence of the surface tension has been obtained. This approximation has a wider curvature region of suitability than Eq. (1). Within the van der Waals capillarity theory all the arbitrary parameters of the equation obtained are defined. The approach developed makes it possible to describe the properties of phase nuclei at the borders of spontaneous boiling of a superheated liquid and condensation of a supersaturated vapor, which is where the Tolman formula is unusable.

II. SURFACE TENSION EXPANSION

In the framework of the van der Waals capillarity theory [25] when a spherical irregularity appears within a uniform isotropic system the change of the grand potential is given by the relations

$$\Delta\Omega = 4\pi \int_0^\infty \left[\Delta\omega + \kappa \left(\frac{d\rho}{dr} \right)^2 \right] r^2 dr, \quad (2)$$

$$\Delta\omega = p' - p + \rho(\mu - \mu'). \quad (3)$$

Here $\rho(r)$ is the local density at a distance r away from the nucleus center, p and μ are the pressure and the chemical potential for a fluid constrained to have a uniform density ρ , and κ is the influence parameter, which is assumed to be density independent. Hereinafter, one prime indicates the initial metastable phase and two primes indicate the incipient phase. The density profile $\rho(r)$ corresponding to the saddle

point of the functional (2) determines the critical nucleus one and is deduced from the solution of Euler-Lagrange equation

$$\frac{d^2\rho}{dr^2} + \frac{2}{r} \frac{d\rho}{dr} = \frac{\mu - \mu'}{2\kappa} \quad (4)$$

with the borderline conditions $\rho \rightarrow \rho'$ at $r \rightarrow \infty$ and $d\rho/dr \rightarrow 0$ at $r \rightarrow 0$ and $r \rightarrow \infty$. In this case, the critical nucleus formation work is

$$W = \min \max \Delta\Omega\{\rho(r)\}. \quad (5)$$

The expression for W as given by the Gibbs dividing surface approach [26] has the form

$$W = 4\pi R^2\sigma + (p' - p'')4\pi R^3/3. \quad (6)$$

The nucleus pressure p'' and hence the density ρ'' are defined by the condition of the metastable and incipient phases chemical potential equality

$$\mu(p'', T) = \mu(p', T). \quad (7)$$

From Eq. (6) and taking Eqs. (2) and (5) into account it follows that the expression for the curved interface surface tension is

$$\begin{aligned} \sigma = & \int_0^R (p'' - p) \frac{r^2}{R^2} dr + \int_R^\infty (p' - p) \frac{r^2}{R^2} dr \\ & + \int_0^\infty \left[\rho(\mu - \mu') + \kappa \left(\frac{d\rho}{dr} \right)^2 \right] \frac{r^2}{R^2} dr. \end{aligned} \quad (8)$$

At a small dividing surface curvature σ can be presented as a series in terms of the quantity c , where the first term is the planar surface tension. Keeping terms up to order c^2 , we have

$$\sigma = \sigma_0 + \sigma_1 c + \sigma_2 c^2. \quad (9)$$

To obtain the coefficients σ_0 , σ_1 , and σ_2 we shall put into use the formula (8). Following Fisher and Wortis [27], let us introduce a variable $z = r - R$ and expand the quantities of the relations (4) and (8) in a Taylor series

$$1/r = c - zc^2 + z^2c^3 + \dots, \quad (10)$$

$$\rho = \rho_0 + \rho_1 c + \rho_2 c^2/2 + \rho_3 c^3/6 + \dots, \quad (11)$$

$$\mu = \mu_0 + \mu_1 c + \mu_2 c^2/2 + \mu_3 c^3/6 + \dots, \quad (12)$$

$$p = p_0 + p_1 c + p_2 c^2/2 + p_3 c^3/6 + \dots. \quad (13)$$

With Eqs. (10)–(12), from Eq. (4) we arrive at a system of equations for the functions $\rho_i(z)$,

$$\frac{d^2\rho_0}{dz^2} = \frac{\mu_0 - \mu'_0}{2\kappa}, \quad (14)$$

$$\frac{d^2\rho_1}{dz^2} + 2 \frac{d\rho_0}{dz} = \frac{\mu_1 - \mu'_1}{2\kappa}, \quad (15)$$

$$\frac{d^2\rho_2}{dz^2} + 4 \frac{d\rho_1}{dz} - 4z \frac{d\rho_0}{dz} = \frac{\mu_2 - \mu'_2}{2\kappa}, \quad (16)$$

$$\frac{d^2\rho_3}{dz^2} + 6 \frac{d\rho_2}{dz} - 12z \frac{d\rho_1}{dz} + 12z^2 \frac{d\rho_0}{dz} = \frac{\mu_3 - \mu'_3}{2\kappa}. \quad (17)$$

Integrating Eq. (14) yields an equation for the calculation of the planar density profile

$$\kappa \left(\frac{d\rho_0}{dz} \right)^2 = \Delta\omega(\rho_0) \equiv \Delta\omega_0. \quad (18)$$

From Eq. (8), taking Eqs. (11)–(13) and (18) into account, we obtain expressions for the coefficients of the expansion (9),

$$\sigma_0 = 2\kappa \int_{-\infty}^{\infty} \left(\frac{d\rho_0}{dz} \right)^2 dz, \quad (19)$$

$$\begin{aligned} \sigma_1 = & 4\kappa \int_{-\infty}^{\infty} \left(\frac{d\rho_0}{dz} \right)^2 z dz + \int_{-\infty}^0 (p''_1 - p_1) dz \\ & + \int_0^{\infty} (p'_1 - p_1) dz + \int_{-\infty}^{\infty} \left[\rho_0(\mu_1 - \mu'_1) + \rho_1(\mu_0 - \mu'_0) \right. \\ & \left. + 2\kappa \frac{d\rho_0}{dz} \frac{d\rho_1}{dz} \right] dz, \end{aligned} \quad (20)$$

$$\begin{aligned} \sigma_2 = & 2\kappa \int_{-\infty}^{\infty} \left(\frac{d\rho_0}{dz} \right)^2 z^2 dz + 2 \int_{-\infty}^0 (p''_1 - p_1) z dz \\ & + 2 \int_0^{\infty} (p'_1 - p_1) z dz + \frac{1}{2} \int_{-\infty}^0 (p''_2 - p_2) dz \\ & + \frac{1}{2} \int_0^{\infty} (p'_2 - p_2) dz + 2 \int_{-\infty}^{\infty} \left[\rho_0(\mu_1 - \mu'_1) \right. \\ & \left. + \rho_1(\mu_0 - \mu'_0) + 2\kappa \frac{d\rho_0}{dz} \frac{d\rho_1}{dz} \right] z dz \\ & + \frac{1}{2} \int_{-\infty}^{\infty} \left[\rho_0(\mu_2 - \mu'_2) + 2\rho_1(\mu_1 - \mu'_1) \right. \\ & \left. + \rho_2(\mu_0 - \mu'_0) + 2\kappa \frac{d\rho_0}{dz} \frac{d\rho_2}{dz} \right. \\ & \left. + 2\kappa \left(\frac{d\rho_1}{dz} \right)^2 \right] dz. \end{aligned} \quad (21)$$

Hereinafter, the limits of integration have been expanded to $\pm\infty$. The validity of this results from the functions $\rho_i(z)$ tending quickly to a constant far from the interface.

From the thermodynamic expression $dp = \rho d\mu$, the coefficients p_i in Eq. (13) and μ_i, ρ_i of the expansions (11) and (12) have been connected by the relations

$$\begin{aligned} p_1 &= \rho_0 \mu_1, & p_2 &= \rho_0 \mu_2 + \rho_1 \mu_1, \\ p_3 &= \rho_0 \mu_3 + 2\rho_1 \mu_2 + \rho_2 \mu_1. \end{aligned} \quad (22)$$

An interconnection of the coefficients μ_i and ρ_i can be found by expanding the function $\mu(\rho)$ in a Taylor series in terms of quantity $\rho - \rho_0$ about $\rho = \rho_0$. Making use of Eq. (11) and comparing the result of expansion with Eq. (12) yield

$$\begin{aligned}\mu_1 &= \rho_1 \frac{d\mu_0}{d\rho_0}, & \mu_2 &= \rho_2 \frac{d\mu_0}{d\rho_0} + \rho_1^2 \frac{d^2\mu_0}{d\rho_0^2}, \\ \mu_3 &= \rho_3 \frac{d\mu_0}{d\rho_0} + 3\rho_1\rho_2 \frac{d^2\mu_0}{d\rho_0^2} + \rho_1^3 \frac{d^3\mu_0}{d\rho_0^3}.\end{aligned}\quad (23)$$

The expressions (20) and (21) involve the bulk phase values of μ_i and ρ_i . Multiplying Eq. (15) by $d\rho_0/dz$, integrating the relation derived, and taking Eq. (23) into account gives

$$\mu'_1 = \mu''_1 = 2\sigma_0 / (\rho''_0 - \rho'_0). \quad (24)$$

In a similar manner, multiplying Eq. (15) by $z d\rho_0/dz$ and Eq. (16) by $d\rho_0/dz$ and taking the relations (14), (23), and (24) into account, we find, on integration of the expressions derived,

$$\begin{aligned}-2\kappa \int_{-\infty}^{\infty} \frac{d\rho_0}{dz} \frac{d\rho_1}{dz} dz &= \frac{\sigma_0}{\rho'_0 - \rho''_0} \int_{-\infty}^{\infty} \frac{d\rho_0}{dz} z dz \\ &\quad - 2\kappa \int_{-\infty}^{\infty} \left(\frac{d\rho_0}{dz} \right)^2 z dz,\end{aligned}\quad (25)$$

$$\begin{aligned}(\rho'_0 - \rho''_0)\mu'_2 &= 8\kappa \int_{-\infty}^{\infty} \left(\frac{d\rho_0}{dz} \right)^2 z dz - (\rho'_1 - \rho''_1)\mu'_1 \\ &\quad - 16\kappa \int_{-\infty}^{\infty} \frac{d\rho_0}{dz} \frac{d\rho_1}{dz} dz.\end{aligned}\quad (26)$$

From Eqs. (25) and (26), introducing designations

$$z_e = \frac{1}{\rho'_0 - \rho''_0} \int_{-\infty}^{\infty} \frac{d\rho_0}{dz} z dz, \quad (27)$$

$$z_* = \frac{2\kappa}{\sigma_0} \int_{-\infty}^{\infty} \left(\frac{d\rho_0}{dz} \right)^2 z dz \quad (28)$$

for the coefficient $\mu'_2 = \mu''_2$, we obtain

$$\mu'_2(\rho'_0 - \rho''_0) + \mu'_1(\rho'_1 - \rho''_1) = 8\sigma_0(z_e - z_*) + \sigma_0 z_*. \quad (29)$$

The relations (22)–(29) make it possible to simplify the expressions (20) and (21). From Eq. (20), taking Eqs. (14), (22), and (24) into account, we arrive at

$$\sigma_1 = 2\sigma_0(z_* - z_e). \quad (30)$$

In a similar manner, the expression (21) in combination with Eqs. (14), (15), and (22) gives

$$\begin{aligned}\sigma_2 &= J_1 + 2J_2 + J_3 - J_4 + \sigma_0 \frac{\rho'_1 - \rho''_1}{\rho'_0 - \rho''_0} (z_e - z_*) \\ &\quad + 3\sigma_0(z_e - z_*)^2 + \sigma_0 z_e^2.\end{aligned}\quad (31)$$

Here the following designations have been introduced:

$$J_1 = 2\kappa \int_{-\infty}^{\infty} \left(\frac{d\rho_0}{dz} \right)^2 (z - z_*)^2 dz, \quad (32)$$

$$J_2 = \frac{\mu'_1}{2} \int_{-\infty}^{\infty} \frac{d\rho_0}{dz} (z - z_*)^2 dz, \quad (33)$$

$$J_3 = \frac{\mu'_1}{2} \int_{-\infty}^{\infty} \frac{d\rho_1}{dz} (z - z_*) dz, \quad (34)$$

$$J_4 = 2\kappa \int_{\rho'_0}^{\rho''_0} \rho_1 d\rho_0. \quad (35)$$

As is evident from Eqs. (31)–(35), to calculate σ_2 it is necessary to have, apart from $\rho_0(z)$, the function $\rho_1(z)$ (integrals J_3 and J_4). Integrating the Eq. (15) yields

$$\frac{d\rho_1}{d\rho_0} = \frac{1}{2} \frac{\mu_0 - \mu'_0}{\Delta\omega_0} \rho_1 + \frac{\psi(\rho_0)}{\Delta\omega_0}, \quad (36)$$

where

$$\psi(\rho_0) = -2h\sqrt{\kappa} \int_{\rho'_0}^{\rho_0} \sqrt{\Delta\omega_0} d\rho_0 + \sigma_0 \frac{\rho_0 - \rho''_0}{\rho'_0 - \rho''_0}. \quad (37)$$

Hereinafter, $h = +1$ for a bubble ($\rho''_0 < \rho'_0$) and $h = -1$ for a drop ($\rho''_0 > \rho'_0$). The solution of the inhomogeneous differential equation (36) can be represented as

$$\rho_1 = \rho_{1,pa} + C\sqrt{\Delta\omega_0}, \quad (38)$$

where $\rho_{1,pa}$ is a particular solution of Eq. (36) and C is a constant of integration whose value depends on choosing the dividing surface position R . When substituting the solution (38) into Eqs. (31)–(35) the constant C is eliminated. Thus, to calculate the coefficient σ_2 , it is reasonable to use the particular solution $\rho_{1,pa}$ rather than the general solution ρ_1 .

III. THE CHOICE OF A DIVIDING SURFACE

As is evident from Eqs. (19) and (30), the values of σ_0 and σ_1 are independent of the location of R and hence the Tolman equation (1) holds at all choices of a dividing surface. A different situation arises with the coefficient σ_2 . An increase of R by some constant causes a variation in the value of the last term on the right-hand side of the expression (31). Differentiating Eq. (31) with respect to R , we obtain

$$\left[\frac{d\sigma_2}{dR} \right] = -2\sigma_0 z_e, \quad \left[\frac{d^2\sigma_2}{dR^2} \right] = 2\sigma_0. \quad (39)$$

Here the square brackets denote that the surface tension variation is caused by a mathematical displacement of the dividing surface if the external conditions are constant. Differentiating the relation (9) and taking Eq. (39) into account yields

$$\left[\frac{d\sigma}{dR} \right] = \frac{2\sigma_0 z_*}{R^2}, \quad \left[\frac{d^2\sigma}{dR^2} \right] = \frac{2\sigma_0}{R^2}. \quad (40)$$

The dependence of the surface tension on the location of the dividing surface has a minimum $\sigma = \sigma_*$ when $z_* = 0$. That is, the quantity z_* introduced in Eq. (28) determines the tension surface location at the planar interface [28]. Equation (27) determines the surface of zero self-adsorption, namely, the total amount of matter placed along the dividing surface z_e will not vary by replacing the transition region with the corresponding volumes of homogeneous phases. This surface is known as the equimolecular dividing surface. In other words, the difference $z_e - z_*$ is the Tolman length of the planar interface δ_0 . Considering the preceding, from Eq. (31) we have for σ_{*2}

$$\sigma_{*2} = J_1 + 2J_2 + J_3 - J_4 + \sigma_0 \frac{\rho'_1 - \rho''_1}{\rho'_0 - \rho''_0} \delta_0 + 4\sigma_0 \delta_0^2. \quad (41)$$

Gibbs [26] obtained a differential relation that connects σ_* to the tension surface curvature $c_* = 1/R_*$. This relation, as applied to a one-component system, was represented by Tolman [16] as

$$\frac{d\sigma_*}{\sigma_*} = \frac{-2\delta(1 + \delta c_* + \delta^2 c_*^2/3)dc_*}{1 + 2\delta(1 + \delta c_* + \delta^2 c_*^2/3)c_*}, \quad \delta = R_e - R_*, \quad (42)$$

where δ is the Tolman length at a curved interface and R_e is the radius of the equimolecular dividing surface. Expanding δ in a Taylor series in terms of the value c_* ,

$$\delta = \delta_0 + \delta_{*1}c_* + \dots, \quad (43)$$

on substituting Eq. (43) in Eq. (42) and integrating we arrive at the expression (9), where $c = c_*$ and

$$\sigma_{*2} = \sigma_0(3\delta_0^2 - \delta_{*1}). \quad (44)$$

The parameter δ_{*1} can be calculated independently of σ_{*2} . To do this we take advantage of the definition of an equimolecular dividing surface at a curved surface

$$R_e = \left[\frac{3}{\rho' - \rho''} \int_0^\infty (\rho' - \rho) r^2 dr \right]^{1/3}. \quad (45)$$

Introducing the variable $z = r - R_*$ and taking the expansion (11) written in terms of the tension surface curvature c_* into account, from Eq. (45) we obtain

$$R_e = R_* + z_e - c_* \left(\frac{J_2 + J_3}{\sigma_0} + \delta_0^2 + \frac{\rho'_1 - \rho''_1}{\rho'_0 - \rho''_0} \delta_0 \right) + \dots. \quad (46)$$

Comparing the result derived and Eq. (43) yields

$$\delta_{*1} = -\frac{J_2 + J_3}{\sigma_0} - \delta_0^2 - \frac{\rho'_1 - \rho''_1}{\rho'_0 - \rho''_0} \delta_0. \quad (47)$$

The calculation of the value of δ_{*1} as distinct from that of σ_{*2} requires a knowledge of the constant C_* . Substituting Eqs. (47) and (41) into Eq. (44) results in a gauge condition for the function $\rho_{*1}(z)$:

$$J_1 + J_2 - J_4 = 0. \quad (48)$$

The relation (48) can be written in a more compact form. Multiplying Eq. (15) by $z^2 d\rho_0/dz$ and integrating gives

$$4\kappa \int_{-\infty}^{\infty} \frac{d\rho_1}{dz} \frac{d\rho_0}{dz} (z - z_*) dz = 0. \quad (49)$$

Substituting the expression (38) in Eq. (49), we obtain

$$C_* = \frac{4}{\sigma_0} \int_{-\infty}^{\infty} \sqrt{\Delta \omega_0} \frac{d\rho_{1,pa}}{dz} (z - z_*) dz. \quad (50)$$

A knowledge of the constant C_* makes it possible not only to calculate the curvature dependence of the Tolman length δ at a loosely curved interface but also to find the coefficient σ_{*2} from formulas (44) and (47) when the general expression (41) is not in use.

IV. THE VICINITY OF A CRITICAL POINT

To calculate the curvature dependence of the surface tension by the Tolman equation (1) as well as the extended expansion (9), it is necessary to know the planar density profile $\rho_0(z)$. Given the equation of state, the solution of this problem requires integration of the differential equation (18), which usually should be done numerically. However, in the vicinity of a critical point one can obtain an analytical solution of Eq. (18) and hence connect the coefficients σ_i to the thermodynamic state conditions.

Let us represent the Helmholtz free energy density $f(\rho_0)$ as a series in terms of the reduced temperature $\tilde{T} = T/T_c - 1$ and density $\tilde{\rho}_0 = \rho_0/\rho_{0,c} - 1$:

$$f = \sum_{i,j=0}^{\infty} u_{ij} \tilde{\rho}_0^i \tilde{T}^j, \quad (51)$$

where the expansion coefficients $u_{20} = u_{30} = 0$, $u_{21} > 0$, and $u_{40} > 0$. Equal conditions of the pressures and the chemical potentials give for the densities of coexisting phases $\tilde{\rho}'_0$ and $\tilde{\rho}''_0$

$$\begin{aligned} \left. \begin{aligned} \tilde{\rho}'_0 \\ \tilde{\rho}''_0 \end{aligned} \right\} &= \pm h \sqrt{\frac{u_{21}}{2u_{40}}} \varphi + \left(\frac{u_{31}}{4u_{40}} - \frac{u_{21}u_{50}}{4u_{40}^2} \right) \varphi^2 \\ &\pm h\lambda_1 \left(-\frac{a_1}{2} + \frac{7a_2}{16} - \frac{3a_3}{8} + \frac{3a_4}{16} \right. \\ &\left. + \frac{a_5}{2} - \frac{5a_6}{8} \right) \varphi^3, \end{aligned} \quad (52)$$

with

$$\varphi = \sqrt{-\tilde{T}}, \quad (53)$$

$$a_1 = \frac{u_{22}}{u_{21}}, \quad a_2 = \frac{u_{21}u_{50}^2}{u_{40}^3}, \quad a_3 = \frac{u_{21}u_{60}}{u_{40}^2}, \quad (54)$$

$$a_4 = \frac{u_{31}}{u_{21}u_{40}}, \quad a_5 = \frac{u_{41}}{u_{40}}, \quad a_6 = \frac{u_{31}u_{50}}{u_{40}^2}.$$

Introducing the variable

$$\Phi = h(2\bar{\rho}_0 - \bar{\rho}'_0 - \bar{\rho}''_0)/(\bar{\rho}'_0 - \bar{\rho}''_0), \quad (55)$$

from the expression (3) we have

$$\frac{8\Delta\omega_0 u_{40}}{u_{21}^2(1-\Phi^2)^2} = 2\varphi^4 + \varphi^5 \sqrt{\frac{u_{21}a_2}{2u_{40}}} \Phi + \varphi^6 \left[\frac{3a_4}{8\lambda_1^4} - \frac{5a_7}{2} a_2 - a_3(1-\Phi^2) + 2a_6 - 4a_1 \right]. \quad (56)$$

Formulas (19) and (52)–(56) make it possible to calculate the planar surface tension

$$\sigma_0 = \frac{2\rho_{0,c}u_{21}}{3u_{40}} \sqrt{2\kappa u_{21}} \varphi^3. \quad (57)$$

On substituting in Eq. (18) the nondimensional variables Φ and x ,

$$x = z/\varepsilon, \quad \varepsilon = \varphi^{-1} \rho_{0,c} \sqrt{2\kappa/u_{21}}, \quad (58)$$

one seeks a solution

$$\Phi = \Phi_0 + \Phi_1 \varphi + \Phi_2 \varphi^2. \quad (59)$$

Then

$$\Phi_0 = h \tanh(x), \quad (60)$$

$$\Phi_1 = -\sqrt{a_2}(1-\Phi_0^2)[g_1 + \ln(1-\Phi_0^2)]/8, \quad (61)$$

$$\begin{aligned} \frac{\Phi_2}{1-\Phi_0^2} = & -\frac{3hx}{8} \left(\frac{4a_1}{3} + a_2 - a_3 - \frac{a_4}{8} \right) - \frac{a_3}{4} \Phi_0 \\ & - \frac{a_2}{32} \Phi_0 \ln^2(1-\Phi_0^2) - \frac{a_2}{32} \Phi_0 (g_1^2 + 2g_1 - 6) \\ & - \frac{a_2}{16} \Phi_0 (1+g_1) \ln(1-\Phi_0^2) + g_2, \end{aligned} \quad (62)$$

where g_1 and g_2 are the constants of integration. Taking advantage of the deduced solution and definitions (27) and (28) makes it possible to calculate the locations of the equimolecular dividing surface and the tension surface

$$z_e = h\varepsilon\varphi\sqrt{a_2}[g_1 + 2\ln(2) - 2]/8 - h\varepsilon\varphi^2 g_2, \quad (63)$$

$$z_* = h\varepsilon\varphi\sqrt{a_2}[g_1 + 2\ln(2) - 7/6]/8 - h\varepsilon\varphi^2 g_2. \quad (64)$$

Setting z_* equal to zero gives the constants of integration

$$g_1 = 7/6 - 2\ln(2), \quad g_2 = 0. \quad (65)$$

From Eqs. (63) and (64), for the Tolman length δ_0 we have

$$\delta_0 = -h \frac{5}{24} \sqrt{\frac{\kappa}{u_{40}}} \frac{u_{50}}{u_{40}} \rho_{0,c}. \quad (66)$$

Integrating Eq. (36) and taking Eq. (56) into account yields

$$\begin{aligned} -3h \frac{\rho_{1,pa}}{\rho_{0,c}^2} \sqrt{\frac{u_{40}}{\kappa}} = & 1 - \varphi \frac{\sqrt{a_2}}{16} \left[8\Phi + 3(1-\Phi^2) \ln\left(\frac{1-\Phi}{1+\Phi}\right) \right] \\ & + \varphi^2 \left[\left(\frac{99a_2}{160} - \frac{3a_3}{5} \right) (1-\Phi^2) \ln(1-\Phi^2) \right. \\ & - \frac{3a_2}{32} \Phi(1-\Phi^2) \ln\left(\frac{1-\Phi}{1+\Phi}\right) + \frac{89a_2}{80} \\ & \left. - \frac{19a_3}{20} + \frac{a_6}{2} - \frac{5a_7}{8} \right]. \end{aligned} \quad (67)$$

Now, from Eq. (50) we obtain for the constant C_*

$$\begin{aligned} C_* = & h\varphi^2 \{ a_2 [198 \ln(2) - 561 + \pi^2] / 160 \\ & - a_3 [12 \ln(2) - 19] / 10 \}. \end{aligned} \quad (68)$$

The relations (47), (55), and (59)–(68) make it possible to calculate the value of the coefficient δ_{*1} of the Tolman length expansion

$$\begin{aligned} \frac{\delta_{*1}}{\varepsilon^2} = & \frac{\pi^2}{12} + \frac{\varphi^2}{4} \left[\frac{a_1 \pi^2}{3} + \frac{a_2}{5} \left(\pi^2 - \frac{49}{16} \right) \right. \\ & \left. + a_3 \left(\frac{5}{3} - \frac{\pi^2}{4} \right) - \frac{a_4 \pi^2}{8} \right] \end{aligned} \quad (69)$$

and hence the value of the coefficient σ_{*2} of Eq. (9).

V. NUMERICAL CALCULATIONS

Numerical calculations have been performed for the van der Waals fluid, the Helmholtz free energy density of which is

$$\frac{f}{\rho_{0,c} k_B T_c} = \tau \varrho \ln\left(\frac{\varrho}{3-\varrho}\right) - \frac{9}{8} \varrho^2 + \varrho \Theta(\tau). \quad (70)$$

Here $\tau = T/T_c$, $\varrho = \rho_0/\rho_{0,c}$, and $\Theta(\tau)$ is the density-independent quantity. From Eqs. (57), (58), (66), and (69), making use of Eq. (70), we obtain

$$\sigma_0 = 8\rho_{0,c} \sqrt{\kappa \rho_{0,c} k_B T_c} \varphi^3, \quad (71)$$

$$\delta_0 = \frac{h}{9} \sqrt{\frac{\kappa \rho_{0,c}}{k_B T_c}}, \quad (72)$$

$$\frac{\delta_{*1}}{\varepsilon^2} = \frac{\pi^2}{12} + \frac{\varphi^2}{500} \left(\frac{951}{2} - 67\pi^2 \right), \quad \varepsilon = \frac{4}{3\varphi} \sqrt{\frac{\kappa \rho_{0,c}}{k_B T_c}}. \quad (73)$$

Figure 1 demonstrates the comparison of the droplet and bubble dependences $\delta(R)$ obtained when directly integrating

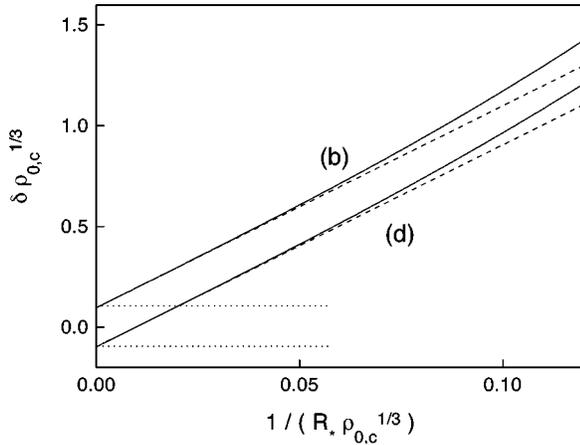


FIG. 1. Tolman length vs the curvature of the tension surface obtained via numerical integration of Eq. (4) with a calculation by Eqs. (27) and (28) (solid line), prediction of the formulas (43), (72), and (73) (dashed line), and the planar value $\delta = \delta_0$ (dotted line): $T = 0.9T_c$ for (b) bubbles and (d) droplets.

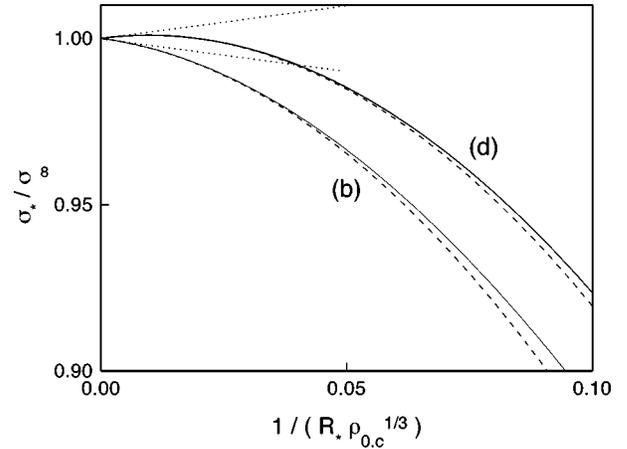


FIG. 2. Surface tension vs the curvature of the tension surface obtained via numerical integration of Eq. (4) with a calculation by Eq. (8) (solid line), prediction of the formula (9) (dashed line), and prediction of the Tolman equation (dotted line): $T = 0.9T_c$ for (b) bubbles and (d) droplets.

Eq. (4) and calculating by formula (43) and the expressions (72) and (73). Figure 2 demonstrates a similar comparison of the surface tension. At a surface tension deviation of 7% from the planar limit the value of σ given by the expression (9) is less than 0.2% in error. An accuracy as high as this becomes possible due to the presence of an extended rectilinear portion of the dependence $\delta(R)$ (see Fig. 1).

The van der Waals equation of state is that of the mean field theory. Thus moving away from the critical point does not result in any perceptible loss in accuracy. So at $T = 0.5T_c$ the values of δ_{*1} given by Eq. (47) when directly integrating Eq. (4) and from Eq. (73) differ by less than 5%.

VI. CONCLUSIONS

A thermodynamic treatment leads to the differential equation (42), which defines the curvature dependence of the surface tension. This equation can be integrated if the value of δ is a known function of R . In the framework of the van der Waals capillarity theory numerical calculations indicate [18,19] that the dependence $\delta(R)$ is nearly linear over a wide range of dividing surface curvatures. When the expansion $\delta(R)$ is limited by a linear term the surface tension dependence has the form of Eq. (9). The coefficients of expansions (9) and (43) are defined in terms of planar interface characteristics. In this work, these coefficients are calculated within the van der Waals capillarity theory. Keeping terms up to order c^2 , the expression for σ at an arbitrary dividing surface is obtained [Eqs. (9), (19), (30), and (31)] and the linear term of the Tolman length expansion with respect to the tension surface curvature is calculated. The latter makes it possible to simplify the expression (9) when writing it for a special dividing surface, the surface of tension [Eqs. (9), (19), (30), (44), and (47)].

The values of δ_0 , σ_0 , and the asymptotic dependence of coefficient $\delta_{*1}(T)$ have been calculated with the use of the classical expansion of the Helmholtz free energy in the vicinity of the liquid-vapor critical point. For the van der

Waals fluid numerical calculations indicate a wide region of suitability of Eq. (9) with respect to the interface curvature. In particular, the expansion (9) may be recommended for application when calculating the nucleus formation work at the borders of spontaneous boiling of a superheated liquid and condensation of a supersaturated vapor at a nucleation rate up to $10^{20} \text{ cm}^{-3} \text{ s}^{-1}$. Here, as illustrated in [10] and [12], the critical bubble surface tension is less by 5–7% than its planar limit. A deviation of the results of Eq. (9) and a rigorous solution would be in the region of 0.2%.

An approach analogous to that used by us when obtaining the coefficient σ_2 of the formula (9) was applied by Blokhuis and Bedeaux [29]. However, as distinct from us, the expanded value was not the excess grand potential $\Delta\Omega$ but the excess Helmholtz free energy for a unit interface, which is the surface tension at an equimolecular dividing surface. The doubtless advantage of Ref. [29] is the introduction of a squared Laplacian term in the expansion of the free energy. However, as distinct from the formula (31), the expression obtained by Blokhuis and Bedeaux [29] makes it impossible to calculate the value σ at an arbitrary dividing surface.

It must be noted that the gradient approach presented in the paper is rigorous only at weak gradients, which is in the vicinity of the critical point. At low temperatures the application of the functional density model [20–23] is more correct. However, as can be seen from the comparison of the gradient expansion with the functional density model on the Tolman length δ_0 [24], the results of both approaches are qualitatively similar. The quantitative difference of δ_0 is under 10%. This causes the curvature dependence of the surface tension to be only in negligible errors.

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