Surface Tension, Tolman Length, and Effective Rigidity Constant in the Surface Layer of a Drop with a Large Radius of Curvature

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Abstract—A system of integral equations defining the density profile for a flat liquid–vapor interface and curvature corrections to this profile was used to examine the variation of surface tension with the drop radius using the Yukawa and Lennard-Jones potentials.

INTRODUCTION

The objective of this work is to describe the thermodynamic properties of large drops in the density-functional approach. The radius of drops is taken to be large enough that the surface tension can be described by the first and second terms in the expansion of surface tension in terms of the surface curvature. As is well known, the first term of this expansion represents Tolman's correction. Thus, one of our purposes is to determine the sign and magnitude of the limiting Tolman length. In addition, we calculate the coefficient of the next term in the expansion of the surface tension (effective rigidity constant), which, in turn, allows the Tolman length to be evaluated as a function of the interface curvature.

DENSITY PROFILE AT A LARGE DROP RADIUS

The solution is sought in the density-functional approach [1]. Note that the version employed here relies on the local, heard-sphere description of the contribution related to intermolecular repulsion and nonlocal description of long-range attraction, with no allowance for long-range correlations (random-phase approximation).

The equation of the density profile in a spherically symmetric system has the form [1, 2]

$$\mu_h[\rho(r)] - \mu + \int_V dr' \rho(r') w(|\mathbf{r} - \mathbf{r}'|) = 0, \qquad (1)$$

where $\rho(r)$ is the particle-number density profile for a spherically symmetrical liquid–vapor system, $\mu_h[\rho]$ is the chemical potential of the rigid-sphere system in the Carnahan–Starling formulation [1, 2], μ is the chemical potential of the system, $w(r)$ is the long-range part of the intermolecular interaction potential, and the integral is taken over the volume V of the system.

To describe the limiting case of a flat liquid–vapor interface, it is convenient to introduce the variables $\tilde{r} \equiv |\mathbf{r} - \mathbf{r}'|$, $s = \cos\theta$ (θ is the angle between vectors $\mathbf{r}$ and $\mathbf{r}' - \mathbf{r}$), and $z = r - R$ (R is the radius of curvature of the drop surface). To find the solution to equation (1) in the limit of a large drop, we use the procedure proposed by Blokhuis and Bedeaux [3, 4], who used the small parameter d/R, where d is the rigid-sphere diameter. The solution of (1) is sought in the form of expansion $\rho(r) = \rho_0(z) + \rho_1(z)/R + \rho_2(z)/R^2 + \dots$, where $\rho_0(z)$ is the density profile for a flat interface, and $\rho_1(z)$, $\rho_2(z)$, ... are corrections for curvature. The chemical potential of the system also has the form $\mu = \mu_\infty + \mu_1/R + \mu_2/R^2 + \dots$, where μ_∞ is the chemical potential of saturated vapor over a flat interface, and μ_1, μ_2, ... are the corresponding corrections for curvature. Thus, equation (1) yields a system of coupled equations. The first and second equations of this system have the form

$$\mu_h[\rho_0(z)] - \mu_\infty + 2\pi \int_0^\infty d\tilde{r}\, \tilde{r}^2 w(\tilde{r}) \int_{-1}^1 ds\, \rho_0(z + s\tilde{r}) = 0, \quad (2)$$

$$\left.\frac{\partial\mu_h}{\partial\rho}\right|_{\rho=\rho_0(z)} \rho_1(z) - \mu_1$$
$$+ 2\pi \int_0^\infty d\tilde{r}\, \tilde{r}^2 w(\tilde{r}) \int_{-1}^1 ds\, (\rho_0(z + s\tilde{r}) s\tilde{r} + \rho_1(z + s\tilde{r})) = 0. \quad (3)$$

The density profile $\rho_0(z)$ and surface tension σ_∞ of a flat interface can be found by solving equation (2). The solution to this equation was found earlier for the Yukawa potential and the Lennard-Jones potential in the Wicks–Chandler–Anderson formulation [1, 2].

Equation (3) was solved by an iteration procedure [2]. Typical $\rho_1(z)$ profiles at different temperatures are displayed in Fig. 1. A noteworthy feature of these data is that the $\rho_1(z)$ curves show a sharp minimum ($\rho_1(z) < 0$)
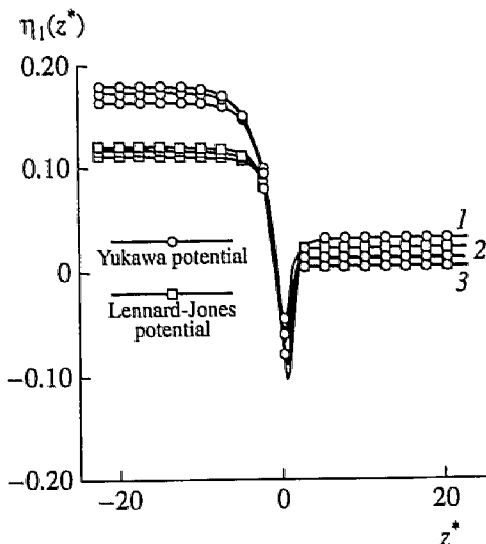
Fig. 1. First-order curvature corrections to the density profile for a flat interface ($\eta_1 \equiv \pi d^2 \rho_1/6$, $z^* \equiv z/d$); the origin of coordinates is on the equimolecular interface; $T = (I)\ 0.7T_c$, (2) $0.6T_c$, and (3) $0.5T_c$, where T_c is the critical temperature.

at $z \simeq 0$ (transition layer). This implies that, around the transition layer, the density profile for a slightly curved surface lies below that for of a flat interface. A similar behavior was reported by Blokhuis and Bedeaux [4], who used, however, the gradient expansion method and Landau φ^4 theory and, hence, obtained symmetric $\rho_0(z)$ and $\rho_1(z)$ profiles, resulting in zero Tolman length.

COEFFICIENTS IN THE EXPANSION OF SURFACE TENSION IN TERMS OF CURVATURE

At large radii of curvature of the interface, R, the variation of surface tension with R is described by Tolman's formula, $\sigma(R) = \sigma_\infty(1 - 2\delta_\infty/R)$, where δ_∞ is the limiting Tolman length for $R \longrightarrow \infty$. The thermodynamic definition of the Tolman length is

$$\delta = \Gamma(R_s)/(\rho_l - \rho_v), \tag{4}$$

where $\Gamma(R_s)$ is the amount of adsorption on the tension surface of radius R_s, and ρ_l and ρ_v are, respectively, the volume densities of the liquid and vapor phases at a given chemical potential. In the limit of large R_s, we obtain from (4) the most often used expression for δ_∞:
$\delta_\infty = (R_e - R_s)|_{R_s \to \infty}$, where R_e is the radius of curvature of the equimolecular interface, for which $\Gamma(R_e) = 0$. R_s can be found as

$$R_s^3 = -2R_e^3 + 6R_e^2\sigma_e(R_e)/(\rho_l - \rho_v), \tag{5}$$

where ρ_l and ρ_v are pressures in the liquid and vapor phases, respectively.

Tolman's formula holds for any interface, and the limiting Tolman length is independent of the interface. If not only first-order but also second-order terms are retained in the expansion of surface tension in terms of curvature, the coefficients of the second term in the expansion will be different for the equimolecular and tension surfaces. The surface tension on the equimolecular interface can be written as

$$\sigma_e(R_e) = \sigma_\infty(1 - 2\delta_\infty/R_e + \kappa/R_e^2). \tag{6}$$

Blokhuis and Bedeaux [3] obtained integral relations for the limiting Tolman length δ_∞ and effective rigidity constant κ. For δ_∞, they obtained two expressions:

$$\delta_\infty = -\frac{\pi}{4\sigma_\infty} \int\limits_{-\infty}^{\infty} dz \int\limits_{0}^{\infty} d\tilde{r}\,\tilde{r}^3 \frac{dw(\tilde{r})}{d\tilde{r}}$$
$$\times \int\limits_{-1}^{1} ds(1 - 3s^2)\rho_1^{(2)}(z, z + s\tilde{r}, \tilde{r}), \tag{7}$$

$$\delta_\infty = -\frac{\pi}{4\sigma_\infty} \int\limits_{-\infty}^{\infty} dz \int\limits_{0}^{\infty} d\tilde{r}\,\tilde{r}^3 \frac{dw(\tilde{r})}{d\tilde{r}}$$
$$\times \int\limits_{-1}^{1} ds(1 - 3s^2)(2z + s\tilde{r})\rho_0^{(2)}(z, z + s\tilde{r}, \tilde{r}), \tag{8}$$

where $\rho_0^{(2)}(z, z + s\tilde{r}, \tilde{r})$ and $\rho_1^{(2)}(z, z + s\tilde{r}, \tilde{r})$ are, respectively, the zero-order and first-order terms in the expansion of the two-particle distribution function in terms of $1/R_e$. For κ, they obtained

$$\kappa = \frac{\pi}{4\sigma_\infty} \int\limits_{-\infty}^{\infty} dz \int\limits_{0}^{\infty} d\tilde{r}\,\tilde{r}^3 \frac{dw(\tilde{r})}{d\tilde{r}}$$
$$\times \int\limits_{-1}^{1} ds\left[(1 - 3s^2)(2z + s\tilde{r})\rho_1^{(2)}(z, z + s\tilde{r}, \tilde{r}) \right. \tag{9}$$
$$\left. - \frac{\tilde{r}^2 s^2}{3}(3 - 5s^2)\rho_0^{(2)}(z, z + s\tilde{r}, \tilde{r})\right].$$

In calculations by formulas (7)–(9), we use the $\rho_0(z)$ and $\rho_1(z)$ profiles obtained in this work. In the random-phase approximation, the two-particle distribution functions can be represented as

$$\rho_0^{(2)}(z, z + s\tilde{r}, \tilde{r}) \simeq \rho_0(z)\rho_0(z + s\tilde{r}), \tag{10}$$
$$\rho_1^{(2)}(z, z + s\tilde{r}, \tilde{r}) \simeq \rho_0(z)\rho_1(z + s\tilde{r}) + \rho_1(z)\rho_0(z + s\tilde{r}).$$

CALCULATION RESULTS AND CONCLUSIONS

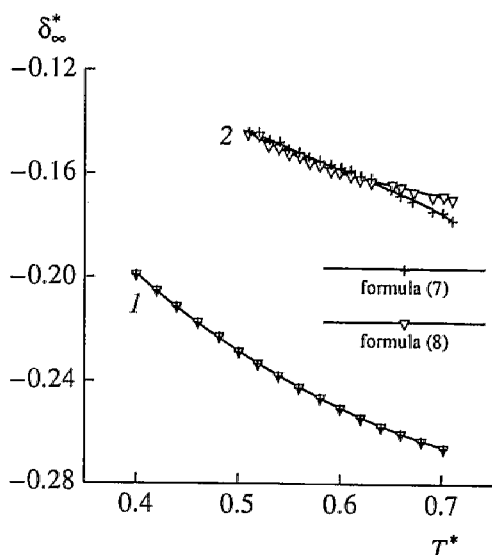Figure 2 displays the temperature dependences of δ_∞ calculated for a wide temperature range below the

Fig. 2. Tolman length, $\delta_\infty^* \equiv \delta_\infty/d$, as a function of temperature, $T^* = T/T_c$: (1) Yukawa potential, (2) Lennard-Jones potential.
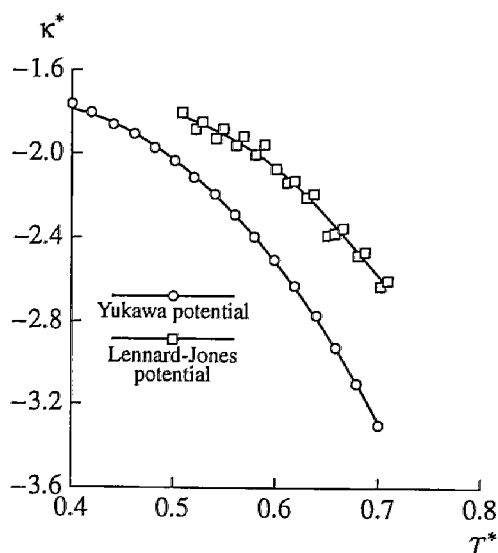

Fig. 3. Effective rigidity constant, $\kappa^* \equiv \kappa/d^2$, as a function of temperature T^*.

critical point by formulas (7) and (8) with consideration for (10). The results are seen to coincide within the calculation accuracy. A similar variation in δ_∞ was reported by Van Giessen *et al.* [5], who used only one formula, which can be reduced to (8). Our results demonstrate that δ_∞ is small and negative and rises slightly in magnitude with temperature. This implies that the *surface tension approaches the limiting value from above*, as pointed out earlier in [2, 5–7]. Moreover, the calculated δ_∞ values agree with those obtained by Koga *et al.* [6], who calculated the entire dependence of surface tension on drop curvature. All of the present formulas for δ_∞ were calculated in the random-phase approximation, which was, however, differently introduced. The fact that these formulas yield identical results within the calculation accuracy suggests that the random-phase approximation provides a sufficiently accurate value of the limiting Tolman length in the framework of the density-functional method.

The small limiting Tolman length implies that, at large drop radii, σ is a weak function of R. At the same time, at small drop radii, surface tension varies substantially with R [2, 6, 7], but the Tolman formula is inapplicable because, along with the first-order correction for $\sigma(R)$, a significant role is played by higher order corrections, in particular the second-order correction with the coefficient κ in (6).

Calculations of κ by formula (9) for temperatures below the critical point (Fig. 3) show that κ is negative and rises in magnitude with temperature. Thus, the curve of surface tension for the equimolecular surface, described by formula (6), shows a maximum, in agreement with earlier data [2, 6, 7].

Baidakov and Boltachev [7], considering a van der Waals system, argued that two coefficients of the

expansion are sufficient to describe surface tension if the radius of curvature is not too small. This implies that formula (6) can be used not only in the limit of very large R_e. To check this statement, consider the $\sigma_e(R_e)$ curves (Fig. 4) plotted with the use of formula (6) and those obtained by direct calculations relying on the total density profile of a spherical drop [2] (as pointed out above, the accuracy of these calculations is fairly high at a sufficiently small drop radius). It can be seen that the curves obtained with the Lennard-Jones potential are indeed closely similar at all temperatures below the critical point.
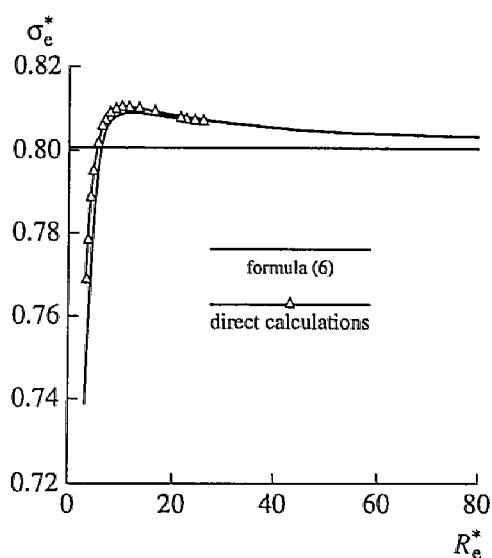

Fig. 4. Surface tension σ_e^* ($\sigma^* \equiv \pi d^2\sigma/6kT$, where k is the Boltzmann constant) vs. radius of curvature of the equimolecular interface, $R_e^* = R_e/d$, for the Lennard-Jones potential at $T = 0.51T_c$; the horizontal line indicates δ_∞^*.
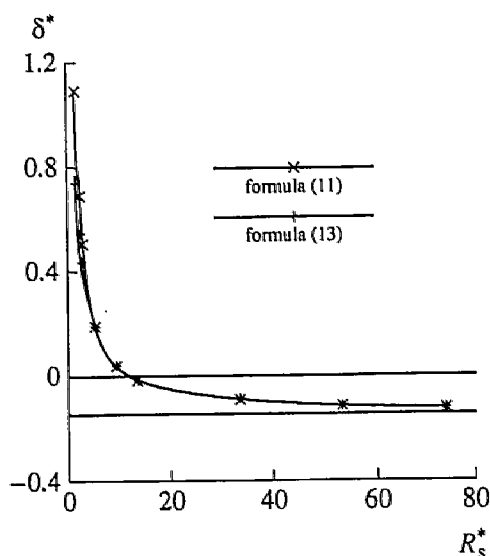
Fig. 5. Tolman length, $\delta^* \equiv \delta/d$, vs. radius of curvature of the tension surface, $R_s^* \equiv R_s/d$, for the Lennard-Jones potential at $T = 0.51T_c$; the horizontal line indicates δ_∞^*.

The Tolman length $\delta(R)$ can be calculated by two procedures: First, we write formula (4) in the form

$$\delta = (R_e^3 - R_s^3)/3R_s^2 \tag{11}$$

and use definition (5) of R_s, which can be transformed, under the assumption that formula (6) is valid at any R_e, to the form

$$R_s^3 \tag{12}$$
$$= R_e^3[-2 + 3(1 - 2\delta_\infty/R_e + \kappa/R_e^2)/(1 - 2\delta_\infty/R_e)].$$

Second, we use the approximate formula

$$\delta = R_e - R_s. \tag{13}$$

Figure 5 displays the δ plots calculated by formulas (11) and (13). It can be seen that the Tolman length tends to the negative value $\delta(R_s)$ for $R \longrightarrow \infty$; at sufficiently small R, δ_∞ becomes positive and depends on the calculation procedure.

ACKNOWLEDGMENTS

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