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1994 J. Phys.: Condens. Matter 6 L173

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LETTER TO THE EDITOR

The surface tension and Tolman’s length of a drop

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Received 4 February 1994

**Abstract.** We examine the surface tension and Tolman’s length of a spherical drop using the simplified Cahn–Hilliard model which has been used previously by the author to calculate the homogeneous nucleation rate. It is found that the Tolman’s length is given by the difference of the bulk correlation lengths of the liquid and vapour phases, and is negative for normal liquids. We discuss briefly the difficulty of estimating the Tolman’s length from computer simulations.

In a recent publication [1] (hereafter denoted paper I), we discussed the homogeneous nucleation rate of critical spherical drops using the simplified Cahn–Hilliard model [1–3]. In this letter, we will discuss the magnitude of the Tolman’s length [4] using the expression for the surface tension derived in paper I.

In this model, the radius  $r_0$  of the spherical nucleus is a function of the chemical potential  $\Delta\mu$  measured from the value at the two-phase coexistence (for a liquid drop  $\Delta\mu > 0$ , and for a vapour bubble  $\Delta\mu < 0$ ). The equation which determines the radius  $r_0$  of a liquid drop is given by (see paper I, equations (2.13) and (2.14))

$$1 + \frac{\rho_m - \rho_v}{\rho_l - \rho_m} + \frac{\lambda_v(\rho_m - \rho_v)}{\lambda_l(\rho_l - \rho_m)}(\lambda_l r_0) = (\lambda_l r_0) \coth(\lambda_l r_0) \tag{1}$$

where the densities  $\rho_i$  ( $i = 1, m, v$ ) are functions of the chemical potential. Their definitions are given in paper I. We will use the same notation as paper I.  $\lambda_l$  and  $\lambda_v$  are the inverse bulk correlation lengths of liquid phase and vapour phase respectively. They are proportional to the isothermal compressibility. In our model they are the only parameters which characterize the bulk thermodynamics. In general, we have

$$\lambda_l < \lambda_v. \tag{2}$$

The surface tension  $\gamma_s$  of the spherical drop with radius  $r_0$  divided by the surface tension  $\gamma_\infty$  of the planar interface becomes (see paper I, equations (2.16) and (2.17))

$$\frac{\gamma_s}{\gamma_\infty} = \frac{(\rho_m - \rho_v)(\rho_l - \rho_v)}{(\rho_m - \rho_{v0})(\rho_l - \rho_{v0})} \left( 1 + \frac{1}{r_0 \lambda_v} \right). \tag{3}$$

At the (gas) spinodal  $\Delta\mu = \Delta\mu_v$ , we have  $\gamma_s = 0$  because  $\rho_v = \rho_m$  at this point. In the limit of planar interface  $r_0 \rightarrow \infty$ ,  $\Delta\mu \rightarrow 0^+$  and hence  $\rho_v \rightarrow \rho_{v0}$ , we have  $\gamma_s/\gamma_\infty \rightarrow 1$ . For the weak supersaturation  $\Delta\mu \rightarrow 0^+$ , the radius diverges according to

$$r_0 \rightarrow (1/\lambda_v)(\Delta\mu_v/\Delta\mu) \tag{4}$$

hence, the surface tension (2) is given approximately by

$$\frac{\gamma_s}{\gamma_\infty} \simeq 1 + \frac{\lambda_v - \lambda_l}{\lambda_l} \left( \frac{\Delta\mu}{\Delta\mu_v} \right) - \frac{\lambda_v}{\lambda_l} \left( \frac{\Delta\mu}{\Delta\mu_v} \right)^2 \quad (5)$$

or, using the radius  $r_0$ , by

$$\frac{\gamma_s}{\gamma_\infty} \simeq 1 + \left( \frac{1}{\lambda_l} - \frac{1}{\lambda_v} \right) \frac{1}{r_0} - \frac{1}{\lambda_l \lambda_v} \frac{1}{r_0^2} \quad (6)$$

from which we see that the surface tension becomes a maximum at approximately the chemical potential

$$(\Delta\mu/\Delta\mu_v)_{\max} \simeq (\lambda_v - \lambda_l)/2\lambda_v \quad (7)$$

or at the radius

$$(r_0)_{\max} \simeq 2/(\lambda_v - \lambda_l) \quad (8)$$

provided that  $\Delta\mu/\Delta\mu_v \ll 1$ . From equation (5) the maximum value of  $\gamma_s/\gamma_\infty$  is given by

$$\left( \frac{\gamma_s}{\gamma_\infty} \right)_{\max} \simeq 1 + \frac{\lambda_l \lambda_v}{2} \left( \frac{1}{\lambda_l} - \frac{1}{\lambda_v} \right)^2 > 1 \quad (9)$$

because of the inequality (2). Therefore, as the chemical potential  $\Delta\mu$  increases from  $0^+$ , and the radius of the drop shrinks, the surface tension  $\gamma_s$  reaches a maximum greater than  $\gamma_\infty$  at the finite value of  $\Delta\mu$ . In a symmetric fluid with  $\lambda_l = \lambda_v$ , the surface tension  $\gamma_s$  reaches a maximum  $\gamma_\infty$  at exactly  $\Delta\mu = 0$ . In this special case the surface tension  $\gamma_s$  of a spherical drop is a monotonic decreasing function of  $\Delta\mu$  and is always lower than  $\gamma_\infty$ .

As  $r_0 \rightarrow \infty$ , equation (6) becomes

$$\gamma_s = \gamma_\infty \left( 1 - \frac{2\delta}{r_0} \right) \quad (10)$$

which is the so-called Tolman's formula [4]. From equation (6), Tolman's length  $\delta = \delta_{\text{liq}}$  for the liquid drop is given by the difference of the correlation lengths of bulk as

$$\delta_{\text{liq}} = \frac{1}{2} \left( \frac{1}{\lambda_v} - \frac{1}{\lambda_l} \right) < 0 \quad (11)$$

which is negative because of (2). In a symmetric fluid with  $\lambda_l = \lambda_v$ ,  $\delta_{\text{liq}} \equiv 0$  from (11), which has been proved by general argument in [5].

When we approach the (gas) spinodal  $\Delta\mu \rightarrow \Delta\mu_v^-$ , the radius of the drop vanishes according to

$$r_0 \rightarrow \sqrt{\frac{3}{\rho_v(\rho_l + \rho_v)} \left( 1 - \frac{\Delta\mu}{\Delta\mu_v} \right)}. \quad (12)$$

Similarly the surface tension also vanishes

$$\frac{\gamma_s}{\gamma_\infty} \rightarrow \sqrt{\frac{\rho_v(\rho_l + \rho_v)}{3\rho_l^2} \left( 1 - \frac{\Delta\mu}{\Delta\mu_v} \right)}. \quad (13)$$

So far, only the liquid drop formation has been considered. We can obtain similar formulae for a bubble by interchanging the subscripts l and g in the formulae for the drop. However, equation (5), for example, remains unchanged. Since the bubble  $\Delta\mu < 0$ , the surface tension of the bubble is always lower than the surface tension of the plane. Instead of equation (11), Tolman's length for the bubble is now given by

$$\delta_{\text{gas}} = \frac{1}{2} \left( \frac{1}{\lambda_l} - \frac{1}{\lambda_v} \right) > 0 \quad (14)$$

which is always positive, and satisfies a relation  $\delta_{\text{liq}} = -\delta_{\text{gas}}$ .

Since the Cahn-Hilliard model is equivalent to the Landau-Ginzburg model, the above result for Tolman's length can also be derived directly from a general formula for the latter model [5]:

$$\delta = \frac{\int_{-\infty}^{\infty} dz z \rho'_0(z)}{\int_{-\infty}^{\infty} dz \rho'_0(z)} - \frac{\int_{-\infty}^{\infty} dz z [\rho'_0(z)]^2}{\int_{-\infty}^{\infty} dz [\rho'_0(z)]^2} \quad (15)$$

where  $\rho'_0(z) = d\rho_0(z)/dz$  is the derivative of the density profile of the flat interface. With the density profile  $\rho_0(z) \sim \exp(\eta_l z)$  ( $z < 0$ ) and  $\rho_0(z) \sim \exp(-\eta_g z)$  ( $z > 0$ ) from this double-parabola approximation, we can directly calculate equation (11). Fisher and Wortis [5] have estimated Tolman's length of drop using the Landau-type density expansion of the free energy near the critical point, and have shown that it is related to the fifth-order expansion coefficient. They have applied this result to a van der Waals fluid and predicted a negative Tolman's length.

In figures 1 and 2, we show the ratio  $\gamma_s/\gamma_\infty$  as functions of the chemical potential  $\Delta\mu(\beta)$  and the radius  $r_0$  ( $x_0 = \lambda_l r_0$ ) of a drop or a bubble;  $\beta > 0$  represents a drop and  $\beta < 0$  a bubble. We have followed paper I and defined non-dimensional parameters  $\alpha$  and  $\beta$  as

$$\alpha = \lambda_l/\lambda_v \quad (16a)$$

$$\beta = 4\Delta\mu/\lambda^2\Delta\rho_0 \quad (16b)$$

where

$$\Delta\rho_0 = \rho_{l0} - \rho_{v0}$$

$$2/\lambda = 1/\lambda_l + 1/\lambda_v.$$

We note that  $\alpha < 1$  because of inequality (2).

Figures 1 and 2 (right portions) display non-monotonic behaviour approximately described by the quadratic equations (5) and (6). Such non-monotony has already been discovered in the local density-functional theories [6, 7] numerically (see e.g. figure 5 of [7]). Since Tolman's length is given by the difference of two bulk correlation lengths in (11), it is obvious from our analysis that such non-monotony is more remarkable when the parameter  $\alpha = \lambda_l/\lambda_v$  is smaller (figure 1 and 2), or the asymmetry between bulk liquid and vapour phases is larger. This tendency is also visible in a recent density-functional calculation of a liquid drop in a spherical cavity using the more sophisticated weighted-density approximation (WDA) (see figure 3(a) of [8]). It is also clear from figure 1 that the series expansion (5) is fairly accurate.

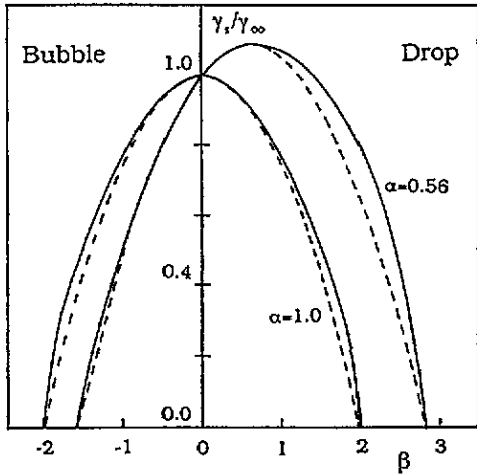


Figure 1. The surface tension  $\gamma_s$  divided by  $\gamma_\infty$  as a function of supersaturation  $\beta$  (—), compared with the approximate quadratic polynomial (5) (---). This figure is essentially the same as figure 5 of paper I. Note that in a normal fluid with  $\alpha < 1$ ,  $\gamma_s$  becomes greater than  $\gamma_\infty$ . The polynomial (5) is fairly accurate over the whole range of supersaturation.

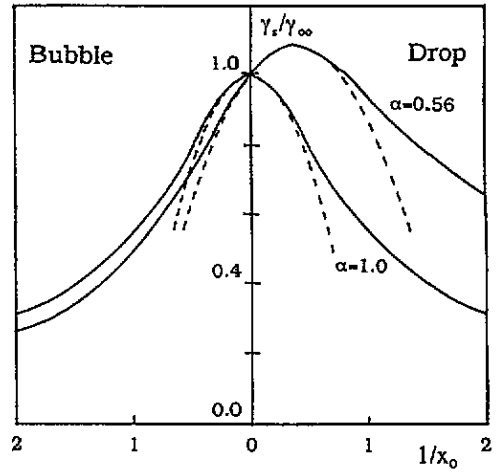


Figure 2. The surface tension  $\gamma_s$  divided by  $\gamma_\infty$  as a function of the inverse of the radius  $x_0$  (—), compared with (6) (---). Tolman's formula (10) is valid only in the limit  $1/x_0 \rightarrow 0$ .

In contrast with the liquid drop, the surface tension of the vapour bubble is always lower than the surface tension of the flat interface (left portions of figures 1 and 2), and decreases monotonically (figure 1).

For a sufficiently large radius  $r_0$ , the surface tension  $\gamma_s$  of a drop is given by the Tolman's [4] formula (10), and Tolman's length  $\delta$  becomes *negative* ( $\delta_{\text{liq}} < 0$ ). However, for a smaller radius (larger  $1/x_0$ ), the surface tension  $\gamma_s$  becomes lower than  $\gamma_\infty$  of the flat interface (figure 2). From the curve in this region one might erroneously conclude that the Tolman's length is *positive* ( $\delta_{\text{liq}} > 0$ ). Furthermore, it is clear from figure 2 that the region where the surface tension  $\gamma_s$  exceeds  $\gamma_\infty$ , and the apparent length  $\delta_{\text{liq}}$  becomes negative, is rather narrow on the scale  $1/x_0$ . Therefore, it might be difficult to extract a true negative Tolman's length from a diagram like figure 2 numerically by computer simulations. In fact, a few molecular-dynamics simulations have been performed for the liquid drop with the truncated Lennard-Jones potential using both the canonical ensemble [9] and the grand canonical ensemble [10, 11], but all these calculations indicate only a small *positive* Tolman's length.

It is possible to estimate numerically the magnitude of the Tolman's length  $\delta_{\text{liq}}$  in our model once we know the inverse correlation length  $\lambda_l$  and  $\lambda_v$ . If the fluid is a van der Waals fluid, from equation (11), Tolman's length, for example, at  $T = 0.8T_c$  ( $T_c$  is the critical temperature) becomes

$$\delta_{\text{liq}} \simeq -0.38d \quad (17)$$

where  $d$  is the hard-sphere diameter, and we have used  $\lambda_l^{-1} = 1.73d$  and  $\lambda_v^{-1} = 0.97d$ , therefore  $\alpha \simeq 0.56$ , at this temperature [13]. This value (17) is close to  $\delta_{\text{liq}} = -0.3d \pm 0.9d$  deduced by Nijmeijer *et al* [11] using the molecular dynamics for a truncated Lennard-Jones system at  $T^* = 0.9$  close to  $T = 0.8T_c$  (the critical point is  $T_c^* \simeq 1.09$  on this scale). Their

conclusion  $|\delta_{\text{liq}}| < 0.7d$  is consistent with our result. This negative value (17) is also close to the theoretical value  $\delta_{\text{liq}} = -0.35d$  calculated by Guermeur *et al* [7] using the local square-gradient model, and is also close to the value published by Hemingway *et al* [14] for the penetrable-sphere model.

In this letter, we have used the simplified Cahn–Hilliard model to discuss the surface tension and Tolman’s length of a spherical drop. The surface tension becomes an approximate quadratic function of the chemical potential. Tolman’s length is given by the difference of the correlation lengths of two bulk phases, and is shown to be negative. This result will be useful to estimate roughly the magnitude of Tolman’s length.

The author is grateful to Professor David W Oxtoby (University of Chicago) for providing him with reference [3] prior to publication.

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