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Thermodynamic expressions for the Tolman length

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The Tolman length δ [J. Chem. Phys. **17**, 333 (1949)] measures the extent by which the surface tension of a small liquid drop deviates from its planar value. Despite increasing theoretical attention, debate continues on even the sign of Tolman's length for simple liquids. Recent thermodynamic treatments have proposed a relation between the Tolman length and the isothermal compressibility of the liquid at two-phase coexistence, $\delta \approx -\kappa_t \sigma$. Here, we review the derivation of this relation and show how it is related to earlier thermodynamic expressions. Its applicability is discussed in the context of the squared-gradient model for the liquid-vapor interface. It is found that the relation is semiquantitatively correct for this model unless one is too close to the critical point.

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I. INTRODUCTION

The Tolman length δ was introduced in 1949 to describe the curvature dependence of the surface tension of a small liquid droplet.¹ It is conveniently defined in terms of an expansion in $1/R$, with $R=R_e$ the equimolar radius of the liquid drop, of the pressure difference across the droplets surface:

$$\Delta p = \frac{2\sigma}{R} \left(1 - \frac{\delta}{R} + \cdots \right). \quad (1.1)$$

In this expression $\Delta p = p_\ell - p_v$ is the pressure difference between the (bulk) pressure of the liquid inside and the pressure of the vapor outside, and σ is the surface tension of the planar interface. The first term on the right-hand side of Eq. (1.1) is the familiar Laplace equation² with the leading-order correction defining the Tolman length δ . Another way to define the Tolman length is to consider the radius dependence of the surface tension, $\sigma(R)$. To leading order in $1/R$ one has

$$\sigma(R) = \sigma \left(1 - \frac{2\delta}{R} + \cdots \right). \quad (1.2)$$

Note that $\sigma(R)$ denotes the surface tension of a liquid drop with radius R , whereas σ denotes its value in the planar limit. In this definition, and the one in Eq. (1.1), the Tolman length is defined as a coefficient in an expansion in $1/R$ and therefore does not depend on R . In the literature one may find definitions of the Tolman length in which $\delta = \delta(R)$ to account not only for deviations with the planar limit to *leading order* in $1/R$ but to *all order* in $1/R$. A legitimate question then addresses the accuracy of truncating the expansion at first order.^{3,4} Here, we shall not pursue this line of research limiting our discussion strictly to the limit $\delta = \lim_{R \rightarrow \infty} \delta(R)$, so to say, keeping in mind that in this limit results should be consistent.

The definition in Eq. (1.2) shows that the surface tension deviates from its planar value when the droplet radius is of the order of Tolman's length. Since any (small) radius depen-

dence of the surface tension influences the nucleation rate exponentially, experimental interest has come from the description of nucleation phenomena.⁵ From a theoretical side, the Tolman length has received a lot of attention but, surprisingly, some issues remain completely unresolved. We briefly discuss four issues that are or have been controversial.

A. Critical exponent

It is well established that the mean-field exponent for the Tolman length has the borderline value of zero.⁶ What that implies for the behavior of the Tolman length near the critical point for a real fluid is therefore quite sensitive to the value of the critical exponent going beyond mean field. The Tolman length might diverge algebraically, diverge logarithmically, become zero, or reach some finite value. Phillips and Mohanty⁷ argued that it diverges in the same manner as the correlation length ($\xi^{-\nu}$), but most authors now believe that if the Tolman length diverges, it does so with an exponent close to zero.^{6,8,9}

B. Sign of δ for a simple liquid

Of late, much theoretical work on the Tolman length has been carried out in the context of density-functional theories.^{3,4,10–20} These theories give consistent results with regard to the mean-field value of the Tolman length for simple liquids: it is only weakly temperature dependent reaching a value at the critical point which is small (a fraction of a molecule's diameter) and *negative*. The few molecular-dynamics (MD) simulations that have been carried out for a Lennard-Jones system, however, seem to indicate that the Tolman length is *positive* although of the same order of magnitude as in the density-functional theories.^{21–24} Recent MD simulations furthermore indicate that the Tolman length sensitively depends on the interaction potential.²⁵ The discrepancy in sign and its dependence on the interaction potential is not understood. Further MD simulations should help us to resolve these issues.

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C. Mechanical expressions

For the numerical evaluation of the surface tension, computer simulations have used the pressure tensor approach. In this method, the tangential and normal components of the pressure tensor are evaluated through the interfacial region, and the integral over its difference then yields the surface tension.² It was furthermore shown that different expressions for the pressure tensor (which is not uniquely defined²⁶) all yield the same value for the surface tension.² A similar approach was suggested for the evaluation of the Tolman length, but now as *the first moment* of the excess tangential pressure of a planar interface. However, already in 1982 Henderson and Schofield²⁷ and Schofield and Henderson²⁸ showed that the first moment of the excess tangential pressure depends on the form of the pressure tensor used and is therefore ill defined. Later it was also shown that the Tolman length evaluated in this way using the “normal” Irving-Kirkwood form for the pressure tensor is inconsistent with a more direct virial approach which avoids the use of a pressure tensor.²⁹

It is now well established that the mechanical expression for the Tolman length is not well defined.^{29–31} However, in the context of *local theories*, i.e., theories in which the free energy depends only on one position, and not, as for the pressure tensor, on two positions (the positions of the two interacting molecules), the Tolman length can indeed be written as the first moment of the surface free-energy density.³² An example of such an expression is given in Sec. I D.

D. Fluctuation route: Triezenberg-Zwanzig

A formal expression for the surface tension was derived by Triezenberg and Zwanzig in 1972 by considering the restoring force or free energy associated with a thermal fluctuation of the surface.³³ This so-called Triezenberg-Zwanzig expression for the surface tension features the direct correlation function in the two-phase region. An analogous formula for the Tolman length has thus far not been obtained and it was suggested^{27,30,31} that the “fluctuation route” is fundamentally different for curved surfaces than it is for planar surfaces. This problem is not yet resolved although it is now well understood that different thermodynamic conditions to induce a curvature of the interface lead to different values for the curvature coefficients not only for the Tolman length but also for the coefficients in a further curvature expansion.^{34,35}

These last two issues on “mechanical” expressions and fluctuation route expressions bear an issue also on curvature coefficients in a *further* expansion in the curvature, in particular, the second-order coefficients. From quite a different perspective than Tolman, Helfrich expanded the surface free energy of an arbitrarily shaped surface to second order in the curvature,³⁶

$$F_H = \int dA \left[\sigma - 2 \frac{k}{R_0} J + \frac{k}{2} J^2 + \bar{k} K \right]. \quad (1.3)$$

In this expression $J=1/R_1+1/R_2$ is the total curvature, and $K=1/(R_1R_2)$, the Gaussian curvature, with R_1 and R_2 the radii of curvature at a point on the surface. The coefficients in the expansion are R_0 , the radius of spontaneous curvature,

k , the rigidity constant associated with bending, and \bar{k} , the rigidity constant associated with Gaussian curvature. Helfrich and many authors after him showed that the above free energy can be used to describe systems where surface tension is not the dominating factor such as in membranes and surfactant systems.^{36,37}

Even though the Helfrich free energy was introduced in a different context, it is analogous to the expansion made by Tolman to first order for the surface tension of a liquid droplet in Eq. (1.2). Comparing the leading-order terms in Eqs. (1.2) and (1.3), with $J=2/R$, one immediately finds that²⁹

$$\delta\sigma = \frac{2k}{R_0}. \quad (1.4)$$

Any results given for the Tolman length are therefore directly relevant to the radius of spontaneous curvature R_0 . One finds that a positive value for the Tolman length corresponds to a positive R_0 (assuming $k>0$) which indicates that the interface tends to curve toward the liquid phase, whereas a negative Tolman length implies a negative R_0 and a preferred curvature toward the vapor phase.

Apart from being related to the radius of spontaneous curvature, the Tolman length can also be linked to the so-called *surface of tension*.^{1,2} The surface of tension, positioned at R_s , is defined as the surface for which the Laplace equation holds exactly for all droplet radii,

$$\Delta p = \frac{2\sigma_s}{R_s}, \quad (1.5)$$

where $\sigma_s=\sigma(R=R_s)$ is the surface tension at the surface of tension. Using the Gibbs adsorption equation, Tolman himself showed¹ that the Tolman length can be expressed in terms of the adsorbed amount at the surface of tension at coexistence,

$$\delta = \frac{\Gamma_s}{\Delta\rho_0}, \quad (1.6)$$

where $\Delta\rho_0=\rho_{\ell,0}-\rho_{v,0}$; the subscript zero to the density denotes the value at two-phase coexistence. In the next section we come back to Tolman’s derivation of Eq. (1.6) and also show that it leads to

$$\delta = \lim_{R \rightarrow \infty} (R - R_s) = z_e - z_s, \quad (1.7)$$

where the height’s z_e and z_s are the locations of the equimolar surface and the surface of tension in the planar limit, respectively. Tolman thus showed in a pure thermodynamic approach that the Tolman length is related to the adsorption at the surface of tension [Eq. (1.6)] and can be directly expressed as the *distance* between the surface of tension and the equimolar surface [Eq. (1.7)]. Although such a thermodynamic approach does not yield numerical results, unless a certain microscopic model is considered, it is thus able to provide a link between different thermodynamic quantities.

Recently, another such thermodynamic treatment was given by Bartell³⁸ in which an approximative expression for the Tolman length is derived in terms of the *isothermal com-*

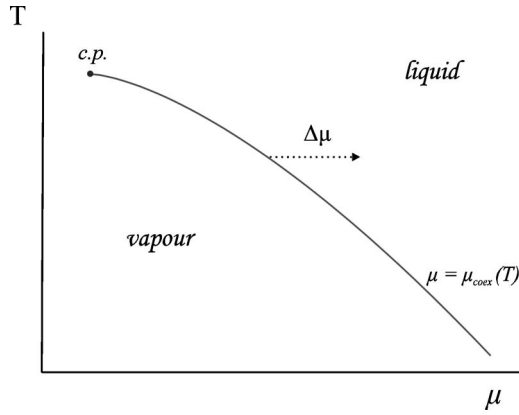


FIG. 1. Schematic phase diagram for a liquid-vapor system as a function of μ and T . The solid line is the locus of liquid-vapor coexistence, $\mu = \mu_{\text{coex}}(T)$, ending at the critical point ($\mu = \mu_c$, $T = T_c$). The dashed line is a path in the phase diagram for fixed temperature and varying chemical potential $\Delta\mu = \mu - \mu_{\text{coex}}$, along which a liquid droplet in a metastable vapor is considered.

pressibility of the liquid phase, κ_ℓ , at liquid-vapor coexistence,

$$\delta \approx -\kappa_\ell \sigma. \quad (1.8)$$

Our goal is to show how this approximation is related to earlier thermodynamic expressions and then to test its validity in the context of the van der Waals squared-gradient model.

We start in the next section by reviewing the previous thermodynamic analysis by Tolman and discuss a formal thermodynamic treatment in which a systematic expansion in curvature is made relating the Tolman length to the second-order coefficient of the chemical potential in an expansion in curvature. In Sec. III we review the different derivations in the literature for the relation between the Tolman length and the isothermal compressibility of the liquid phase, and discuss in Sec. IV the applicability of these expressions taking a van der Waals liquid-vapor system as an example. We end with a discussion of results in Sec. V.

II. THERMODYNAMICS

The appropriate thermodynamic conditions are depicted schematically in Fig. 1. As a function of chemical potential and temperature, a typical phase diagram is shown with $\mu = \mu_{\text{coex}}(T)$, the locus of two-phase coexistence. At two-phase coexistence we have two bulk phases, liquid and vapor, coexisting with a planar interface in between. In the following we keep temperature constant and increase the chemical potential above μ_{coex} into a region where the liquid is the stable phase. In this region, we consider the formation of a critical nucleus (liquid droplet), with equimolar radius R , surrounded by the (metastable) vapor phase. This is the typical situation considered in the description of nucleation.⁵ For any $\mu > \mu_{\text{coex}}$, but not beyond the spinodal, the equimolar radius R is well defined approaching infinity when $\mu \rightarrow \mu_{\text{coex}}$. This means that instead of μ we may also take $1/R$ as our thermodynamic variable to vary our position in the phase diagram in Fig. 1.

Thermodynamics relates the density to the change in chemical potential with pressure at constant temperature,

$$\frac{1}{\rho} = \left(\frac{\partial \mu}{\partial p} \right)_T. \quad (2.1)$$

So, for any infinitesimal change in μ along the path in Fig. 1, the pressure in either phase varies according to

$$dp_{\ell,v} = \rho_{\ell,v} d\mu, \quad (2.2)$$

where the subscripts ℓ and v refer to the liquid or vapor phase, respectively. The change in pressure difference between the liquid inside and the vapor outside the critical nucleus is therefore given by

$$d(\Delta p) = \Delta \rho d\mu. \quad (2.3)$$

This expression holds along the whole path sketched in Fig. 1, but we next consider only the case where the changes are made infinitesimally close to two-phase coexistence, i.e., $\Delta\mu = \mu - \mu_{\text{coex}}$ is small. First we use Eq. (2.3) to relate the Tolman length to the surface of tension, and then use Eq. (2.3) to relate the Tolman length to the chemical potential.

Inserting $\Delta p = 2\sigma_s/R_s$ [Eq. (1.5)] and the Gibbs adsorption equation $d\sigma_s = -\Gamma_s d\mu$ (taking the surface to be located at the surface of tension) into Eq. (2.3), we have

$$d\left(\frac{2\sigma_s}{R_s}\right) = -\frac{\Delta \rho}{\Gamma_s} d\sigma_s. \quad (2.4)$$

To leading order in $1/R_s$ this gives

$$d\left(\frac{2\sigma}{R_s} + \dots\right) = -\left(\frac{\Delta \rho_0}{\Gamma_s} + \dots\right) d\left(\sigma - \frac{2\delta\sigma}{R_s} + \dots\right). \quad (2.5)$$

So that¹

$$\delta = \frac{\Gamma_s}{\Delta \rho_0}, \quad (2.6)$$

where it is understood that Γ_s is the adsorption at the surface of tension at two-phase coexistence. This is the result in the original paper by Tolman¹ defining the quantity δ that later became known as the Tolman length.

Next, we write out the definition of the adsorption Γ_s in terms of the density profile $\rho_0(z)$ at two-phase coexistence,

$$\Gamma_s = \int_{-\infty}^{\infty} dz [\rho_0(z) - \rho_{\ell,0}\Theta(-z+z_s) - \rho_{v,0}\Theta(z-z_s)], \quad (2.7)$$

where $\Theta(x)$ is the Heaviside function and z_s denotes the location of the surface of tension. The coordinate z is the direction perpendicular to the (planar) surface with the convention that the integration runs from the liquid phase (at $z = -\infty$) to the vapor phase (at $z = +\infty$). If we let z_e denote the location of the *equimolar surface*, we also have

$$\Gamma_e \equiv 0 = \int_{-\infty}^{\infty} dz [\rho_0(z) - \rho_{\ell,0}\Theta(-z+z_e) - \rho_{v,0}\Theta(z-z_e)]. \quad (2.8)$$

Subtracting these two expressions for the adsorption and carrying out the integration over z , one readily finds that

$$\Gamma_s = \Delta\rho_0(z_e - z_s). \quad (2.9)$$

Inserting this into Eq. (2.6) one then finally arrives at

$$\delta = z_e - z_s, \quad (2.10)$$

which is the relation given in Eq. (1.7).

Starting with Eq. (2.3), one might also expand to *second order* in the curvature ($1/R$),

$$\begin{aligned} d\left(\frac{2\sigma}{R} - \frac{2\delta\sigma}{R^2} + \dots\right) \\ = \left(\Delta\rho_0 + \frac{\Delta\rho_1}{R} + \dots\right) d\left(\mu_{\text{coex}} + \frac{\mu_1}{R} + \frac{\mu_2}{R^2} + \dots\right). \end{aligned} \quad (2.11)$$

Collecting terms of the same order in $1/R$, the two leading terms then give that

$$\mu_1 = \frac{2\sigma}{\Delta\rho_0}, \quad (2.12)$$

$$\mu_2 = -\frac{2\delta\sigma}{\Delta\rho_0} - \frac{\mu_1\Delta\rho_1}{2\Delta\rho_0}.$$

The latter can thus be rewritten as

$$\mu_2 = -\frac{2\delta\sigma}{\Delta\rho_0} - \frac{\sigma\Delta\rho_1}{(\Delta\rho_0)^2}. \quad (2.13)$$

So that we find the following expression for the Tolman length:

$$\delta = -\frac{\Delta\rho_1}{2\Delta\rho_0} - \frac{\mu_2\Delta\rho_0}{2\sigma}. \quad (2.14)$$

This is an *exact* thermodynamic relation for δ . It has been derived before in the literature starting from the free-energy density.^{6,39,40} A brief summary of this alternative derivation is given in the Appendix.

It should be stressed that although both results for δ in Eqs. (2.10) and (2.14) are derived thermodynamically without making any approximations, we have only shown that the problem of evaluating δ can be *shifted* to finding the location of the surface of tension or to the determination of μ_2 . In other words, nothing is really *solved*.

Next, we turn to an analysis in which certain approximations are made which result in linking the Tolman length to the isothermal compressibility of the liquid.

III. RELATION WITH THE ISOTHERMAL COMPRESSIBILITY OF THE LIQUID

We are reminded that the general definition of the isothermal compressibility κ in a bulk fluid reads

$$\kappa \equiv \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p} \right)_T = \frac{1}{\rho^2} \left(\frac{\partial \rho}{\partial \mu} \right)_T. \quad (3.1)$$

Next, we consider the compressibility of the bulk liquid and vapor *at two-phase coexistence*, and consider again an infinitesimal change along the path shown in Fig. 1. To leading order in $1/R$, we have that $(\partial\rho/\partial\mu) = (\rho_1/R)/(\mu_1/R) = \rho_1/\mu_1$ so that Eq. (3.1) can be written as

$$\kappa_\ell = \frac{1}{\rho_{\ell,0}^2} \frac{\rho_{\ell,1}}{\mu_1} = \frac{\rho_{\ell,1}\Delta\rho_0}{2\sigma\rho_{\ell,0}^2}, \quad (3.2)$$

$$\kappa_v = \frac{1}{\rho_{v,0}^2} \frac{\rho_{v,1}}{\mu_1} = \frac{\rho_{v,1}\Delta\rho_0}{2\sigma\rho_{v,0}^2},$$

where $\kappa_{\ell,v}$ denotes the compressibility of the bulk liquid or vapor phase at coexistence, and where we made use of the expression for μ_1 in Eq. (2.12). We may use Eq. (3.2) to rewrite $\Delta\rho_1 = \rho_{\ell,1} - \rho_{v,1}$ as

$$\Delta\rho_1 = \frac{2\sigma}{\Delta\rho_0} [\rho_{\ell,0}^2\kappa_\ell - \rho_{v,0}^2\kappa_v]. \quad (3.3)$$

Inserting Eq. (3.3) into the expression for δ in Eq. (2.14) gives

$$\delta = -\frac{\sigma}{(\Delta\rho_0)^2} [\rho_{\ell,0}^2\kappa_\ell - \rho_{v,0}^2\kappa_v] - \frac{\mu_2\Delta\rho_0}{2\sigma}. \quad (3.4)$$

In this expression for δ , which is still thermodynamically exact, the compressibility of the bulk phases is featured instead of $\Delta\rho_1$. In the remainder of this section, we revisit a thermodynamic analysis made by Bartell,³⁸ which itself is inspired by an earlier analysis by Laaksonen and McGraw,⁴¹ that proposes an approximate relation for the Tolman length involving the isothermal compressibility of only the liquid phase.

To understand the derivation made by Bartell,³⁸ we first turn to the integral form of Eq. (2.1) for the liquid phase,

$$\Delta\mu = \mu - \mu_{\text{coex}} = \int_{p_{\text{coex}}}^{p_\ell} dp \left(\frac{1}{\rho_\ell} \right). \quad (3.5)$$

Again, we investigate only small deviations from two-phase coexistence. To leading order, which we take to be as leading order in $1/R$, one may approximate the liquid density by its coexistence value, $\rho_\ell \approx \rho_{\ell,0}$, and use the Laplace equation for $p_\ell \approx p_v + 2\sigma/R$, so that

$$\Delta\mu \approx \frac{1}{\rho_{\ell,0}} \left(\frac{2\sigma}{R} + p_v - p_{\text{coex}} \right) \quad \text{correct to } \mathcal{O}\left(\frac{1}{R}\right). \quad (3.6)$$

If one now considers also the next-to-leading-order term, one needs to take into account that the liquid density varies as a function of R , and that the Laplace equation carries the Tolman correction. One may then write³⁸

$$\begin{aligned} \Delta\mu \approx \frac{1}{2} \left(\frac{1}{\rho_\ell} + \frac{1}{\rho_{\ell,0}} \right) \left(\frac{2\sigma}{R} - \frac{2\delta\sigma}{R^2} + p_v - p_{\text{coex}} \right) \\ \text{correct to } \mathcal{O}\left(\frac{1}{R^2}\right). \end{aligned} \quad (3.7)$$

The approach by Bartell³⁸ next makes two assumptions. First, one neglects the density of the vapor compared to that of the liquid. As a result, we may also neglect any curvature dependence of the pressure and density in the vapor phase. One expects this assumption to hold as long as one is not too close to the critical point.

Second, it is argued that the expression in Eq. (3.6) somehow has a wider range of validity than to just first order

in $1/R$. In fact, it is argued³⁸ that the expression for $\Delta\mu$ in Eq. (3.7) should reduce to that in Eq. (3.6). The result is that the Tolman correction should cancel the leading curvature variation of the liquid density. Neglecting the vapor density and equating Eqs. (3.6) and (3.7) then give³⁸

$$\delta \approx -\frac{\rho_{\ell,1}}{2\rho_{\ell,0}}. \quad (3.8)$$

If we now also use Eq. (3.2)

$$\kappa_\ell = \frac{\rho_{\ell,1}\Delta\rho_0}{2\sigma\rho_{\ell,0}^2} \approx \frac{\rho_{\ell,1}}{2\sigma\rho_{\ell,0}}, \quad (3.9)$$

we arrive at the final expression for δ presented in the analysis of Bartell,³⁸

$$\delta \approx -\kappa_\ell\sigma. \quad (3.10)$$

This result may also be derived considering the thermodynamically exact relation for δ in Eq. (3.4). The argument that the expression for $\Delta\mu$ in Eq. (3.7) should reduce to that in Eq. (3.6) amounts to stating that the second-order correction in Eq. (3.7) should vanish, i.e., $\mu_2 \approx 0$. If, furthermore, the vapor density is neglected, one may verify that Eq. (3.10) immediately results when one sets $\rho_v=0$ and $\mu_2=0$ in Eq. (3.4).

To get more insight into especially the latter of these two approximations (i.e., $\mu_2 \approx 0$), we evaluate the Tolman length in the context of van der Waals' squared-gradient theory in the next section.

IV. RESULTS USING THE VAN DER WAALS EQUATION OF STATE

In this section we turn to the explicit evaluation of δ in the context of the van der Waals squared-gradient theory² in order to gain numerical insight into the thermodynamic relation $\delta \approx -\kappa_\ell\sigma$.

In squared-gradient theory, the grand free energy is a functional of the density $\rho(\mathbf{r})$,²

$$\Omega[\rho] = \int d\mathbf{r} [m|\nabla\rho(\mathbf{r})|^2 + g(\rho)], \quad (4.1)$$

where m is the usual coefficient of the squared-gradient term and $g(\rho)$ is the grand free energy density for a fluid constrained to have uniform density ρ .

The surface tension and Tolman length can be expressed in terms of $\rho_0(z)$ which is the density profile at two-phase coexistence obtained by a functional minimization of $\Omega[\rho]$,^{2,39}

$$\begin{aligned} \sigma &= 2m \int_{-\infty}^{\infty} dz [\rho'_0(z)]^2, \\ \delta\sigma &= 2m \int_{-\infty}^{\infty} dz (z - z_e) [\rho'_0(z)]^2. \end{aligned} \quad (4.2)$$

The location of the equimolar surface, z_e , is determined by the condition in Eq. (2.8).

To obtain the density profile $\rho_0(z)$, a certain form for the grand-free energy density has to be assumed. Before taking

for $g(\rho)$ the form given by the van der Waals equation of state, it is instructive to consider the results for σ and δ , when one assumes for $g(\rho)$ a double parabola,

$$g(\rho) + p_{\text{coex}} = \begin{cases} \frac{1}{2\rho_{v,0}^2\kappa_v}(\rho - \rho_{v,0})^2 & \text{when } \rho < \rho_m \\ \frac{1}{2\rho_{\ell,0}^2\kappa_\ell}(\rho - \rho_{\ell,0})^2 & \text{when } \rho > \rho_m, \end{cases} \quad (4.3)$$

where ρ_m is the density where the two parabola meet. The curvature of the parabola is directly related to the compressibility, $g'' = 1/(\rho^2\kappa)$. Iwamatsu¹⁰ determined the surface tension and Tolman length taking this form for the free-energy density,

$$\begin{aligned} \sigma &= \left(\frac{m}{2}\right)^{1/2} \frac{(\Delta\rho_0)^2}{(\rho_{\ell,0}\sqrt{\kappa_\ell} + \rho_{v,0}\sqrt{\kappa_v})}, \\ \delta &= \left(\frac{m}{2}\right)^{1/2} (\rho_{v,0}\sqrt{\kappa_v} - \rho_{\ell,0}\sqrt{\kappa_\ell}). \end{aligned} \quad (4.4)$$

For the purely quadratic form for $g(\rho)$ in Eq. (4.3), one may show that $\mu_2=0$. The result is that if one also neglects the vapor density in the above set of equations, one may immediately verify that $\delta = -\kappa_\ell\sigma$ holds for this model.

The double-well formula gives reasonable results for low temperatures but is not suited to describe the behavior near the critical point. The van der Waals form for the free energy *does* describe the critical point, albeit in a mean-field fashion. It is given by

$$g(\rho) = -k_B T \rho \ln\left(\frac{1/\rho - b}{\Lambda^3/e}\right) - a\rho^2 - \mu_{\text{coex}}\rho, \quad (4.5)$$

where a and b are the usual van der Waals parameters and Λ is the de Broglie thermal wavelength. We have solved for the density profile using the above van der Waals free energy numerically, and plotted the result for δ as a function of temperature as the solid line in Fig. 2. At the critical point δ reaches a finite, negative value^{6,11}

$$\begin{aligned} \delta &= -\frac{1}{12} \left(\frac{2m}{a}\right)^{1/2} (T \rightarrow T_c), \\ \sigma &= \sigma_0 t^{3/2} = \frac{16a}{27b^2} \left(\frac{2m}{a}\right)^{1/2} t^{3/2}, \end{aligned} \quad (4.6)$$

where $t \equiv 1 - T/T_c$ is the reduced temperature distance to the critical point. We may also write $\delta = -\sigma_0/(192p_c)$ for the value of the Tolman length at the critical point, where $p_c = a/(27b^2)$ is the critical pressure for a van der Waals fluid (this prefactor of $-1/192$ differs from that quoted in Ref. 42).

The dotted curve in Fig. 2 gives the contribution to δ derived from setting $\mu_2=0$ in Eq. (3.4),

$$\delta \approx -\frac{\sigma}{(\Delta\rho_0)^2} [\rho_{\ell,0}^2\kappa_\ell - \rho_{v,0}^2\kappa_v]. \quad (4.7)$$

One concludes from Fig. 2 that this approximation describes the qualitative features of δ rather well and that it is quanti-

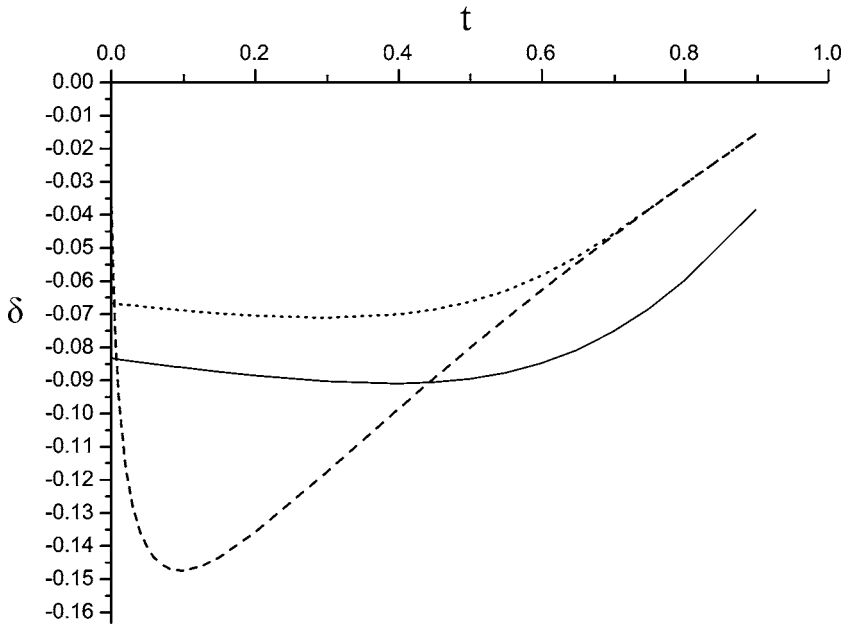


FIG. 2. Tolman length in units of $(2m/a)^{1/2}$ as a function of reduced temperature $t \equiv 1 - T/T_c$. The solid line is the result obtained from the numerical solution of the squared-gradient model using the van der Waals equation of state. The dotted line is the approximate expression for δ in Eq. (4.7). The dashed line is the approximation $\delta \approx -\kappa_\ell \sigma$ with κ_ℓ taken from the van der Waals equation of state.

tatively accurate within 25% in the entire temperature domain, including the critical point where $\delta = -(1/15) \times (2m/a)^{1/2}$.

Far from the critical point, we may neglect the vapor density compared to the liquid density so that Eq. (4.7) reduces to the formula proposed by Bartell,³⁸

$$\delta \approx -\kappa_\ell \sigma. \quad (4.8)$$

This relation is shown as the dashed curve in Fig. 2. It is clear that the approximation breaks down close to the critical point, but it is qualitatively accurate away from it. Both approximations in Eqs. (4.7) and (4.8) thus capture the order of magnitude and sign of the full mean-field solution.

V. DISCUSSION

In this article, we have reviewed the thermodynamic relations for the Tolman length. Such relations are useful in providing a framework for mathematical modeling. We have investigated the expressions for the Tolman length that involve the isothermal compressibility of the liquid, and tested their applicability in the context of the squared-gradient model for the liquid-vapor interface. The main results of this investigation are shown in Fig. 2. It should be kept in mind that any conclusions drawn from this figure are made strictly in the context of the mean-field model. An important observation is that the approximate expressions for δ in Eqs. (4.7) and (4.8) do capture the order of magnitude and sign of the full mean-field solution. In these expressions the *sign* of Tolman's length is determined by the difference between the liquid and vapor phases of the symmetrized compressibility $\chi \equiv \rho^2 \kappa$; since $\chi_\ell > \chi_v$ the Tolman length is negative. This observation was first made by Iwamatsu¹⁰ using the double-well form for the free-energy density for which the approximation Eq. (4.7) holds exactly.

It is tempting to infer from the expression for δ in Eq. (4.7) the critical behavior of Tolman's length beyond mean-field theory. The assumption then implicitly made is that the

term involving μ_2 in the full expression for δ in Eq. (3.4) is subdominant near the critical point, or—as is the case for the squared-gradient mean-field model—has the same leading critical behavior as the contribution to δ in Eq. (4.7). The critical behavior of the compressibility χ in the coexisting liquid and vapor phases is described by the following form:⁴³

$$\chi_\ell = \chi_0 t^{-\gamma} (1 + \alpha_\ell t^{-\Delta} + \dots), \quad (5.1)$$

$$\chi_v = \chi_0 t^{-\gamma} (1 + \alpha_v t^{-\Delta} + \dots).$$

The leading critical behavior of the symmetrized compressibility, as described by the prefactor χ_0 and the critical exponent $\gamma \approx 1.24$, is the same for χ_ℓ and χ_v . Since $\delta \propto \chi_v - \chi_\ell$, the critical behavior of the Tolman length is determined by the leading-order corrections, as described by the dimensionless prefactors α_ℓ and α_v and the gap-exponent $\Delta \approx -0.50$.⁴³ We thus find from Eq. (4.7)

$$\delta \propto t^{\mu-2\beta-\gamma-\Delta} \propto t^{-\Delta-\nu} \propto t^{-0.13}, \quad (5.2)$$

where $\mu \approx 1.26$, $\nu \approx 0.63$, and $\beta \approx 0.325$ are the usual critical exponents for the surface tension, correlation length, and density difference, respectively.²

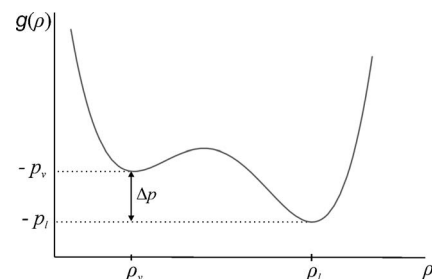


FIG. 3. Typical shape of the grand free-energy density $g = \Omega/V$ as a function of density. It describes the situation of a liquid droplet (with $\rho = \rho_\ell$ and $p = p_\ell$) in a metastable vapor phase (with $\rho = \rho_v$ and $p = p_v$).

As a result we find that the Tolman length diverges weakly on approach to the critical point, which is in line with previous predictions.^{6,8,9,24} The result $\delta \propto t^{-\Delta-\nu}$ is also consistent with the mean-field critical behavior for δ in the van der Waals model, as given in Eq. (4.6) (i.e., $\delta \propto \text{const}$), when one inserts the mean-field value for the exponents $\nu=1/2$ and $\Delta=-1/2$.

APPENDIX: ALTERNATIVE THERMODYNAMIC DERIVATION OF EQUATION (2.14) IN TERMS OF THE FREE-ENERGY DENSITY

Our derivation^{6,39} starts with the grand free-energy per volume $g \equiv \Omega/V$ which is the appropriate free energy at fixed μ , V , and T . In particular, we consider $g(\rho)$ which is the grand free-energy density of a hypothetical fluid *constrained* to a certain density ρ . A typical shape for $g(\rho)$ is shown in Fig. 3. Only at its minimum (minima) does $g(\rho)$ have a clear physical meaning as the (metastable) equilibrium state. The density at the minimum defines the equilibrium density and the corresponding value of $g_{\min} = -p$, owing to the thermodynamic relation $\Omega = -pV$. In the example depicted in Fig. 3, there are two minima corresponding to a stable liquid phase and a metastable vapor phase:

$$g'(\rho_\ell) = g'(\rho_v) = 0,$$

$$g(\rho_\ell) = -p_\ell, \quad (\text{A1})$$

$$g(\rho_v) = -p_v.$$

To explicitly investigate the variation of the free energy with chemical potential, we consider the Helmholtz free-energy density $f \equiv F/V$,

$$g(\rho) = f(\rho) - \mu\rho. \quad (\text{A2})$$

The minimization equations in Eq. (A1) then become

$$f'(\rho_\ell) = f'(\rho_v) = \mu, \quad (\text{A3})$$

$$f(\rho_\ell) - \mu\rho_\ell = -p_\ell, \quad (\text{A4})$$

$$f(\rho_v) - \mu\rho_v = -p_v. \quad (\text{A5})$$

Next, we expand in $1/R$. The leading-order and next-to-leading order terms of the expansion of Eq. (A3) give

$$f'(\rho_{\ell,0}) = f'(\rho_{v,0}) = \mu_{\text{coex}}, \quad (\text{A6})$$

$$f''(\rho_{\ell,0})\rho_{\ell,1} = f''(\rho_{v,0})\rho_{v,1} = \mu_1.$$

Next, we consider $\Delta p = p_\ell - p_v$ with p_ℓ and p_v given in Eqs. (A4) and (A5). A systematic expansion to second order in $1/R$ gives

$$\begin{aligned} \Delta p = & f(\rho_v) - \mu\rho_v - f(\rho_\ell) + \mu\rho_\ell = f(\rho_{v,0}) - \mu_{\text{coex}}\rho_{v,0} - f(\rho_{\ell,0}) + \mu_{\text{coex}}\rho_{\ell,0} + \frac{1}{R}[f'(\rho_{v,0})\rho_{v,1} - \mu_{\text{coex}}\rho_{v,1} - \mu_1\rho_{v,0} - f'(\rho_{\ell,0})\rho_{\ell,1} \\ & + \mu_{\text{coex}}\rho_{\ell,1} + \mu_1\rho_{\ell,0}] + \frac{1}{R^2}\left[f''(\rho_{v,0})\rho_{v,2} - \mu_{\text{coex}}\rho_{v,2} - \mu_2\rho_{v,0} - \mu_1\rho_{v,1} + \frac{1}{2}f''(\rho_{v,0})(\rho_{v,1})^2 - f''(\rho_{\ell,0})\rho_{\ell,2} + \mu_{\text{coex}}\rho_{\ell,2} \right. \\ & \left. + \mu_2\rho_{\ell,0} + \mu_1\rho_{\ell,1} - \frac{1}{2}f''(\rho_{\ell,0})(\rho_{\ell,1})^2\right] + \dots \end{aligned} \quad (\text{A7})$$

The zeroth-order term vanishes since $p_{\ell,0} = p_{v,0} = p_{\text{coex}}$ at co-existence. Using Eq. (A6) in the remaining terms one has

$$\begin{aligned} \Delta p = & \frac{2\sigma}{R} - \frac{2\delta\sigma}{R^2} + \dots = \frac{\mu_1\Delta\rho_0}{R} + \frac{1}{R^2}\left[\mu_2\Delta\rho_0 + \frac{\mu_1}{2}\Delta\rho_1\right] \\ & + \dots \end{aligned} \quad (\text{A8})$$

Comparing the corresponding terms in the expansion in $1/R$ one recovers the results in Eqs. (2.12) and (2.14).

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