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Mean-field description of the structure and tension of curved fluid interfaces

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Citation

Kuipers, J. (2009, December 16). *Mean-field description of the structure and tension of curved fluid interfaces*. Retrieved from <https://hdl.handle.net/1887/14517>

Version: Corrected Publisher's Version

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Chapter 2

Thermodynamic Expressions for the Tolman length

ABSTRACT

The Tolman length measures the extent to which the surface tension of a small droplet deviates from its planar value. Recent thermodynamic treatments have proposed a relation between the Tolman length and the isothermal compressibility of the liquid phase at two-phase coexistence, $\delta \approx -\sigma\kappa_\ell$. In this chapter we review this analysis and show how it relates to earlier thermodynamic expressions. Its applicability is discussed in the context of van der Waals' square-gradient theory. It is found that the relation is semiquantitatively correct for this model unless one is too close to the critical point.

2.1 Introduction

When we consider a simple liquid in equilibrium with its vapour, one thermodynamic parameter, the surface tension σ , is sufficient to describe the planar interface between both phases. The grand potential for such a situation can be written as

$$\Omega = -pV_\ell - pV_v + \sigma A, \quad (2.1)$$

where V_ℓ, V_v denote the volumes of the liquid and vapour phase respectively, p is the pressure (at mechanical equilibrium the same throughout the system) and A denotes the interfacial area. The exact position of the dividing surface is not known since on a molecular scale the interface is rough and fluctuating, however the area A and total volume ($V_\ell + V_v$) in Eq. (2.1) are invariant to the choice of the dividing surface so σ in Eq. (2.1) is well-defined.

The situation for curved interfaces is somewhat different. Curved interfaces appear when considering nucleation, where small vapour/liquid droplets are being formed or when fluids are being confined, for example. The pressures in both phases are now not equal and both the sum ($p_\ell V_\ell + p_v V_v$) and A are no longer invariant anymore upon changing the location of the dividing surface.

Gibbs [30] formulated a major part of the novel thermodynamics of curved surfaces but it was Tolman [22] who took the ideas of Gibbs further and worked them out extensively for spherical surfaces. Tolman realized that the surface tension for small droplets needs curvature corrections [22]. To leading order in an expansion in curvature $1/R$, where R is given by the equimolar radius of the droplet, it is given by,

$$\Delta p = \frac{2\sigma}{R} \left(1 - \frac{\delta}{R} + \dots \right), \quad (2.2)$$

where $\Delta p = p_\ell - p_v$ is the pressure difference between the inside and outside of the drop and σ is the surface tension of the planar interface. The first term in Eq.(2.2) is the well-known Laplace equation [15] with the leading order term in curvature defining the Tolman length δ . Alternatively, one can expand the surface tension itself to leading order in curvature $1/R$ in terms of the droplet radius R :

$$\sigma(R) = \sigma \left(1 - \frac{2\delta}{R} + \dots \right). \quad (2.3)$$

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.(2.2), 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 [31, 32]. 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.(2.3) 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 dependence of the surface tension influences the nucleation rate exponentially, experimental interest has come from the description of nucleation phenomena [33].

From a theoretical side the Tolman length has been studied by many people but some (still) unresolved issues arise. We will now briefly discuss four such issues.

Critical Exponents It is well established that the mean-field exponent for the Tolman length has the borderline value of zero [34]. What that implies for the behaviour 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 Mohanty [35] argued that it diverges in the same manner as the correlation length ($t^{-\nu}$), but most authors now believe that if the Tolman length diverges, it does so with an exponent close to zero [34,36,37]. Using complete scaling Anisimov [38] recently showed that the Tolman length diverges more strongly than expected upon approach to the critical point depending on the degree of asymmetry between the liquid and vapour phase. We will come back to this point in the discussion.

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 [31,32,39–49]. 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 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 [50–53].

Recent MD simulations furthermore indicate that the Tolman length sensitively depends on the interaction potential [54]. The discrepancy in sign and its dependence on the interaction potential is not understood. Further MD simulations should help to resolve these issues.

Mechanical expressions When obtaining the surface tension from computer simulations one often falls back to the use of mechanical expressions relating the surface tension to the integral of the difference between the normal and tangential components of the pressure tensor [15]. There is no unique choice for the pressure tensor [55] but it was shown that the actual choice did not alter the values of the surface tension [15]. In the same line of thought a similar method for the Tolman length was devised relating the surface tension to an integral of the first moment of the excess

tangential pressure of a planar interface. However, it was shown by Henderson and Schofield [56,57] that the first moment is dependent on the actual choice of the pressure tensor and this makes such a mechanical expression for the Tolman length not well 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 [58].

It is now well-established that the mechanical expression for the Tolman length is not well-defined [58–60]. 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 [61]. An example of such an expression is given in section 2.4.

Fluctuation route – Triezenberg-Zwanzig Examining the liquid interface from a completely different perspective, in 1972 Triezenberg and Zwanzig derived a formal expression for the surface tension expressing it in terms of the direct correlation function in the two-phase region by examining the restoring force associated with thermal fluctuations of the interface [62]. As of yet, no analog prescription for the Tolman length exists and this lead people to believe [56,59,60] that this “fluctuation route” is fundamentally different for curved interfaces than for planar ones.

It is now known that different thermodynamic conditions to induce interfacial curvature may lead to different values for curvature coefficients not only for the Tolman length, but also for the second order curvature coefficients [63,64]. From quite a different perspective, Helfrich expanded the surface free energy of an arbitrarily curved surface to second order in the curvature [23]

$$F_H = \int dA \left[\sigma - 2 \frac{k}{R_0} J + \frac{k}{2} J^2 + \bar{k} K \right]. \quad (2.4)$$

In this expression $J = \frac{1}{R_1} + \frac{1}{R_2}$, the total curvature, $K = \frac{1}{R_1 R_2}$, the Gaussian curvature with R_1 and R_2 the radii of curvature at a point on the surface. The expansion coefficients 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. Many people have shown Eq.(2.4) to be a suitable choice in describing systems where the surface tension does not play a dominant role [23, 26, 65].

Even though it was set up in a different context, the Helfrich expansion is analogous to the expansion made by Tolman to first order and for a spherical surface (where $J = \frac{2}{R}$) comparing the first order terms in Eqs.(2.2) and ??eq:sigmaR) one finds [58]

$$\sigma \delta = \frac{2k}{R_0}. \quad (2.5)$$

This equation connects the Tolman length to the radius of spontaneous curvature. Assuming a positive rigidity ($k > 0$), a positive Tolman length would imply positive

values for R_0 which indicates a preferred curvature towards the liquid phase whereas negative values for the Tolman length would result in a tendency for the interface to curve toward the vapour phase.

The Tolman length can also be related to the *surface of tension* [15,22], the surface for which the Laplace equation holds exactly for all drop radii:

$$\Delta p = \frac{2\sigma_s}{R_s}, \quad (2.6)$$

where $\sigma_s = \sigma(R = R_s)$ is the surface tension at the surface of tension. Tolman himself showed [22] that the Tolman length could be related to the adsorbed amount at the interface at coexistence

$$\delta = \frac{\Gamma}{\Delta\rho_0}, \quad (2.7)$$

with $\Delta\rho_0 = \rho_{0,\ell} - \rho_{0,v}$ where the subscript zero denotes the value of the density at two-phase coexistence. In the next section we will show that this results leads to another definition of the Tolman length:

$$\delta = \lim_{R \rightarrow \infty} (R - R_s) = z_e - z_s, \quad (2.8)$$

where the heights z_e and z_s denote the locations of the equimolar surface and the surface of tension respectively. Although these definitions do not lend themselves well for direct numerical results without a specific microscopic model, it does connect the Tolman length to different thermodynamic quantities (radius of spontaneous curvature, adsorption, etc.).

Recently, one such thermodynamic treatment was postulated by Bartell [66], in which an approximate expression for the Tolman length was derived in terms of the isothermal macroscopic compressibility of the liquid phase, κ_ℓ , at liquid-vapour coexistence:

$$\delta \approx -\kappa_\ell \sigma. \quad (2.9)$$

In this chapter we will show how this expression relates to previous thermodynamic expressions and we will test its validity in the context van der Waals' square-gradient theory.

In the next session we start by a review of Tolman's thermodynamic analysis and we will present a formal systematic expansion in curvature in order to link the Tolman length to the second order coefficient of the chemical potential in an expansion in curvature. In section 2.3 we will review the connection between the Tolman length and the isothermal compressibility of the liquid phase and in section 2.4 the applicability of these expressions is tested using a van der Waals liquid-vapour system as an example. We finish with some conclusions.

2.2 Thermodynamics

Figure 2.1 shows the appropriate thermodynamic conditions in a schematic way. Shown is the two-phase coexistence line as a function of chemical potential and tem-

perature along which $\mu = \mu_{\text{coex}}(T)$. At two-phase coexistence both phases have the same chemical potential and bulk pressure and there they coexist with a planar interface between them. By raising the chemical potential at constant temperature (depicted by the dashed arrow in Figure 2.1) the liquid phase will become the more stable phase. In this region we will consider the formation of a critical nucleus with an equimolar radius of R and surrounded by metastable vapour. This is the typical situation considered in the description of nucleation [33]. While making sure we do

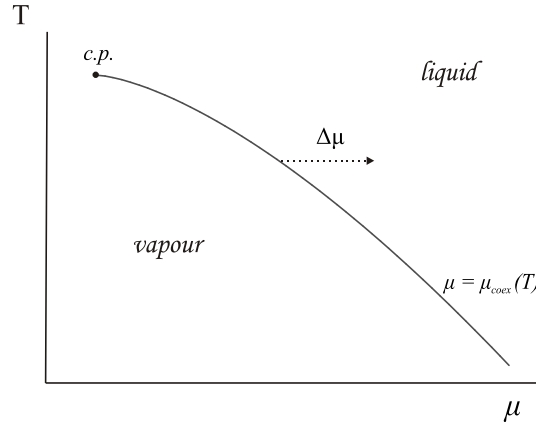


Figure 2.1 Schematic phase diagram for a liquid-vapour system as a function of μ and T . The solid line is the locus of liquid-vapour coexistence, $\mu = \mu_{\text{coex}}(T)$, ending at the critical point ($\mu = \mu_c$, $T = T_c$). The dashed line is a path in the phase diagram for fixed temperature and varying chemical potential $\Delta\mu = \mu - \mu_{\text{coex}}$, along which a liquid droplet in a metastable vapour is considered.

not cross the spinodal, the radius R is well defined in this region approaching infinity when $\mu \rightarrow \mu_{\text{coex}}$. This suggests that instead of μ we could take $1/R$ as variable to indicate the amount we are brought off-coexistence.

Thermodynamics relates the density to changes in the chemical potential when changing pressure:

$$\frac{1}{\rho} = \left(\frac{\partial \mu}{\partial p} \right)_T. \quad (2.10)$$

Alternatively, when changing the chemical potential along the path depicted in Figure 2.1, the pressure in either phase changes according to

$$dp_{\ell,v} = \rho_{\ell,v} d\mu, \quad (2.11)$$

where the subscripts ℓ, v denote the liquid or vapour phase respectively. The pressure difference across the droplet is then given by

$$d(\Delta p) = \Delta \rho d\mu, \quad (2.12)$$

This expression is valid along the whole path sketched in Figure 2.1 but we now consider the case where $\Delta\mu$ is small, i.e. we consider changes infinitesimally close to the coexistence line. Inserting Eq.(2.6) and the Gibbs adsorption equation $d\sigma_s = -\Gamma_s d\mu$ (chosen at the surface of tension) in Eq.(2.12) one finds

$$d\left(\frac{2\sigma_s}{R_s}\right) = -\frac{\Delta\rho}{\Gamma_s} d\sigma_s. \quad (2.13)$$

To leading order in $1/R_s$ this becomes

$$d\left(\frac{2\sigma}{R_s} + \dots\right) = -\left(\frac{\Delta\rho_0}{\Gamma_s} + \dots\right) d\left(\sigma - \frac{2\delta\sigma}{R_s} + \dots\right). \quad (2.14)$$

So that

$$\delta = \frac{\Gamma_s}{\Delta\rho_0}, \quad (2.15)$$

which is the same definition Tolman used in his original work [22]. Note that Γ_s is the adsorption at the surface of tension at two-phase coexistence.

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

$$\Gamma_s = \int_{-\infty}^{\infty} dz [\rho_0(z) - \rho_{\ell,0}\Theta(-z + z_s) - \rho_{v,0}\Theta(z - z_s)], \quad (2.16)$$

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) interface and we adopt the convention that the integration runs from the liquid phase ($z = -\infty$) to the vapour phase ($z = \infty$). If we let z_e denote the location the equimolar surface, we have

$$\Gamma_e \equiv 0 = \int_{-\infty}^{\infty} dz [\rho_0(z) - \rho_{\ell,0}\Theta(-z + z_e) - \rho_{v,0}\Theta(z - z_e)]. \quad (2.17)$$

Subtracting these two expressions for the adsorption and carrying out the integration over z yields

$$\Gamma_s = \Delta\rho_0(z_e - z_s). \quad (2.18)$$

Inserting this into Eq.(2.15) one arrives at:

$$\delta = (z_e - z_s), \quad (2.19)$$

which is the same result as Eq.(2.8).

Starting with Eq.(2.12) one can also expand to second order in $1/R$ to obtain

$$\begin{aligned} & d\left(\frac{2\sigma}{R} - \frac{2\sigma\delta}{R^2} + \dots\right) \\ &= \left(\Delta\rho_0 + \frac{\Delta\rho_1}{R} + \dots\right) d\left(\mu_{\text{coex}} + \frac{\mu_1}{R} + \frac{\mu_2}{R^2} + \dots\right). \end{aligned} \quad (2.20)$$

After some regrouping the two leading order terms in $1/R$ are

$$\begin{aligned}\mu_1 &= \frac{2\sigma}{\Delta\rho_0} \\ \mu_2 &= -\frac{2\sigma\delta}{\Delta\rho_0} - \frac{\mu_1\Delta\rho_1}{2\Delta\rho_0}.\end{aligned}\quad (2.21)$$

The latter can be rewritten as

$$\mu_2 = -\frac{2\sigma\delta}{\Delta\rho_0} - \frac{\sigma\Delta\rho_1}{(\Delta\rho_0)^2}.\quad (2.22)$$

We now have found an expression for the Tolman length:

$$\delta = -\frac{\Delta\rho_1}{2\Delta\rho_0} - \frac{\mu_2\Delta\rho_0}{2\sigma}.\quad (2.23)$$

This derivation appeared previously in the literature starting from the free-energy density [34, 67, 68]. We give a a brief summary of this alternative derivation in appendix A.

Just as a microscopic model is needed to evaluate the location of the surface of tension in order to make use of the definition in Eq.(2.19), Eq.(2.23) requires the knowledge of μ_2 in order to calculate δ . In the next section we will focus on the necessary approximations in order to link the Tolman length to the isothermal compressibility.

2.3 Relation with the isothermal compressibility of the liquid

The isothermal compressibility κ in the fluid phase reads

$$\kappa \equiv \frac{1}{\rho} \left(\frac{\partial\rho}{\partial p} \right)_T = \frac{1}{\rho^2} \left(\frac{\partial\rho}{\partial\mu} \right)_T.\quad (2.24)$$

Again we consider an infinitesimal change from two-phase coexistence along the path sketched in Figure 2.1. To leading order in $1/R$ one finds that

$$\left(\frac{\partial\rho}{\partial\mu} \right) = \frac{\rho_1}{R} / \frac{\mu_1}{R} = \frac{\rho_1}{\mu_1}.\quad (2.25)$$

Now Eq.(2.24) can be written as

$$\begin{aligned}\kappa_\ell &= \frac{1}{\rho_{\ell,0}^2} \frac{\rho_{\ell,1}}{\mu_1} = \frac{\rho_{\ell,1}\Delta\rho_0}{2\sigma\rho_{\ell,0}^2}, \\ \kappa_v &= \frac{1}{\rho_{v,0}^2} \frac{\rho_{v,1}}{\mu_1} = \frac{\rho_{v,1}\Delta\rho_0}{2\sigma\rho_{v,0}^2},\end{aligned}\quad (2.26)$$

where $\kappa_{\ell,v}$ denotes the isothermal compressibility in the bulk liquid and vapour phases respectively at coexistence. We may use Eq.(2.26) to rewrite $\Delta\rho_1 = \rho_{\ell,1} - \rho_{v,1}$ as

$$\Delta\rho_1 = \frac{2\sigma}{\Delta\rho_0} \left[\rho_{\ell,0}^2 \kappa_{\ell} - \rho_{v,0}^2 \kappa_v \right]. \quad (2.27)$$

Inserting Eq. (2.27) into the definition of δ in Eq. (2.23) one obtains

$$\delta = -\frac{\sigma}{(\Delta\rho_0)^2} \left[\rho_{\ell,0}^2 \kappa_{\ell} - \rho_{v,0}^2 \kappa_v \right] - \frac{\mu_2 \Delta\rho_0}{2\sigma}. \quad (2.28)$$

This thermodynamically exact relation describes δ in terms of the compressibility of the bulk phases instead of $\Delta\rho_1$.

The remainder of this section deals with the analysis made by Bartell [66], which in turn is inspired by a previous analysis done by Laasonen and McGraw [69], that proposes an approximate expression for the Tolman length in terms of the isothermal compressibility of only the liquid phase.

In order to understand the derivation made by Bartell [66] we turn to the integral form of Eq.(2.10) in the liquid phase:

$$\Delta\mu = \mu - \mu_{\text{coex}} = \int_{p_{\text{coex}}}^p dp \left(\frac{1}{\rho_{\ell}} \right). \quad (2.29)$$

When we consider infinitesimal changes from coexistence (i.e. $\Delta\mu$ small) one may approximate the bulk liquid density by its value at two-phase coexistence to leading in $1/R$ by, $\rho_{\ell} \approx \rho_{\ell,0}$ and use the Laplace equation for the pressure in the liquid phase, $p_{\ell} \approx p_v + \frac{2\sigma}{R}$ so that,

$$\Delta\mu \approx \frac{1}{\rho_{\ell,0}} \left(\frac{2\sigma}{R} + p_v - p_{\text{coex}} \right) \quad \text{correct to } \mathcal{O}\left(\frac{1}{R}\right). \quad (2.30)$$

When considering the next-to leading order term, the Laplace equation gets a correction and the liquid density becomes a function of R . We find

$$\Delta\mu \approx \frac{1}{2} \left(\frac{1}{\rho_{\ell}} + \frac{1}{\rho_{\ell,0}} \right) \left(\frac{2\sigma}{R} - \frac{2\sigma}{R^2} + p_v - p_{\text{coex}} \right) \quad (2.31)$$

correct to $\mathcal{O}\left(\frac{1}{R^2}\right)$.

Next, the analysis by Bartell [66] introduces two assumptions. First the vapour density is neglected. As a consequence any curvature dependence of the pressure and density in the vapour phase also disappears. One would expect this assumption to break down in the vicinity of the critical point. Second, it is argued [66] that Eq.(2.29) has a wider range of validity than just to first order in $1/R$. The result is that the Tolman length should cancel the leading curvature variation of the liquid

density. Neglecting the vapour density and equating Eqs.(2.29 and 2.30) then result in [66]

$$\delta \approx -\frac{\rho_1}{2\rho_{0,\ell}}. \quad (2.32)$$

If we now employ the same assumptions on the compressibility of the liquid phase, Eq.(2.24) we have

$$\kappa_\ell = \frac{\rho_{1,\ell}\Delta\rho_0}{2\sigma\rho_{\ell,0}^2} \approx \frac{\rho_{\ell,1}}{2\sigma\rho_{\ell,0}}, \quad (2.33)$$

which leads to [66]

$$\delta \approx -\sigma\kappa_\ell. \quad (2.34)$$

This is the expression derived in the analysis done by Bartell [66]. It can also be derived from the thermodynamically exact relation Eq.(2.23). The previous approximations imply setting $\mu_2 = 0$ and $\rho_v = 0$ in Eq.(2.23) to obtain the above result. In order to gain more insight in the validity of these approximations, especially setting $\mu_2 = 0$, we evaluate the Tolman length in the context of van der Waals' square-gradient theory in the next section.

2.4 The Tolman length using the van der Waals equation of state

In this section we turn to the explicit evaluation of the Tolman length in the context of van der Waals' square-gradient theory [15]. The grand free energy is given by the following functional form [15]:

$$\Omega[\rho(\mathbf{r})] = \int d\mathbf{r} [m|\nabla\rho(\mathbf{r})|^2 + g(\rho)], \quad (2.35)$$

where m is the usual coefficient of the square-gradient term and $g(\rho)$ is the grand free energy density for a fluid constrained to have uniform density ρ . The density profile $\rho_0(z)$ for the liquid and vapour at two-phase coexistence can be obtained by a functional minimization of Eq. (2.35). Then the surface tension and Tolman length can be expressed in terms of $\rho_0(z)$ [15,67]:

$$\begin{aligned} \sigma &= 2m \int_{-\infty}^{\infty} dz [\rho'_0(z)]^2, \\ \sigma\delta &= 2m \int_{-\infty}^{\infty} dz (z - z_e) [\rho'_0(z)]^2, \end{aligned} \quad (2.36)$$

where the location of the equimolar surface z_e is determined by the condition in Eq.(2.17).

In order to determine the density profile a specific model for $g(\rho)$ needs to be chosen. Before we take the van der Waals equation of state, it is instructive to consider the results when one assumes for $g(\rho)$ a double parabola.

Results for double parabola as free energy The grand free energy density is given by

$$g(\rho) + p_{\text{coex}} = \begin{cases} \frac{1}{2\rho_{v,0}^2\kappa_v} (\rho - \rho_{v,0})^2 & \text{when } \rho < \rho_m, \\ \frac{1}{2\rho_{\ell,0}^2\kappa_\ell} (\rho - \rho_{\ell,0})^2 & \text{when } \rho > \rho_m, \end{cases} \quad (2.37)$$

where ρ_m is the density where the two parabola meet. The curvature of the parabola is directly related to the compressibility, $g'' = 1/(\rho^2\kappa)$. Iwamatsu [39] used this form of the free energy to determine the surface tension and the Tolman length. They obtained

$$\begin{aligned} \sigma &= \left(\frac{m}{2}\right)^{1/2} \frac{(\Delta\rho_0)^2}{(\rho_{\ell,0}\sqrt{\kappa_\ell} + \rho_{v,0}\sqrt{\kappa_v})}, \\ \delta &= \left(\frac{m}{2}\right)^{1/2} (\rho_{v,0}\sqrt{\kappa_v} - \rho_{\ell,0}\sqrt{\kappa_\ell}). \end{aligned} \quad (2.38)$$

It can be shown that the quadratic form for the free energy in Eq.(2.37) yields $\mu_2 = 0$. If one then also neglects the vapour density (i.e. $\rho_v = 0$), it immediately follows that $\delta = -\kappa_\ell\sigma$ holds for this model.

Unfortunately, this double-well form for the free energy is not able to describe the behaviour near the critical point. The free energy derived from the van der Waals equation of state *does* describe the critical point albeit in a mean-field manner,

$$g(\rho) = -k_B T \ln\left(\frac{1/\rho - b}{\Lambda^3/e}\right) - a\rho^2 - \mu_{\text{coex}}\rho. \quad (2.39)$$

Here 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 results for δ in Figure 2.2. At the critical point δ reaches a finite negative value [34, 40]

$$\begin{aligned} \delta &= -\frac{1}{12} \left(\frac{2m}{a}\right)^{1/2} \quad (T \rightarrow T_c), \\ \sigma &= \sigma_0 t^{3/2} = \frac{16a}{27b^2} \left(\frac{2m}{a}\right)^{1/2} t^{3/2}, \end{aligned} \quad (2.40)$$

where $t \equiv 1 - T/T_c$ is the reduced temperature distance to the critical point. This result may also be written as

$$\delta = -\frac{\sigma_0}{192p_c}, \quad (2.41)$$

where the critical pressure in the fluid phase according to the van der Waals model is given by $p_c = a/(27b^2)$ (this prefactor of $-1/192$ differs from that quoted in ref. [70]). The dotted curve in Figure 2.2 gives the contribution to δ derived from setting $\mu_2 = 0$ in Eq.(2.28),

$$\delta \approx -\frac{\sigma}{(\Delta\rho_0)^2} [\rho_{\ell,0}^2\kappa_\ell - \rho_{v,0}^2\kappa_v]. \quad (2.42)$$

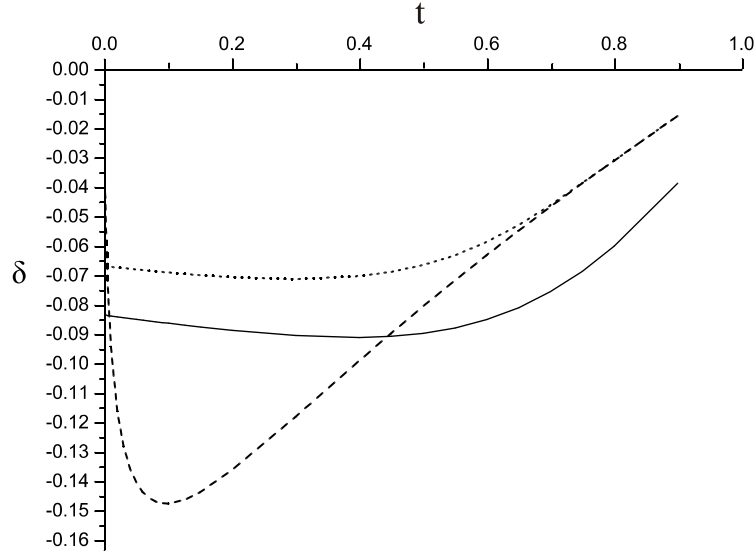


Figure 2.2 Tolman length in units of $(2m/a)^{1/2}$ as a function of reduced temperature $t \equiv 1 - T/T_c$. The solid line is the result obtained from the numerical solution of the square-gradient model using the van der Waals equation of state. The dotted line is the approximate expression for δ in Eq.(2.42). The dashed line is the approximation $\delta \approx -\kappa_\ell \sigma$ with κ_ℓ taken from the van der Waals equation of state.

One concludes from Figure 2.2 that this approximation describes the qualitative features of δ rather well and is quantitatively correct within 25% in the entire temperature range considered. Far from the critical point the vapour density becomes negligible and Eq.(2.42) reduces to the the formula proposed by Bartell [66]

$$\delta \approx -\kappa_\ell \sigma. \quad (2.43)$$

This relation is shown in Figure 2.2 as the dashed line. It is clear that the approximation breaks down close to the critical point, but it is qualitatively correct far away from it. Both approximations in Eqs.(2.42) and (2.43) thus capture the order of magnitude and sign of the full mean-field solution.

2.5 Discussion

In this chapter, we have reviewed thermodynamic relations for the Tolman length. Such relations are useful in providing a framework for mathematical modeling. We saw that the surface tension itself may depend on curvature and thermodynamics gives us the tools to provide expressions for the curvature coefficients. The validity of such an expansion in curvature can be questioned (see chapter 3), but in the

case of bringing a liquid-vapour system off-coexistence by a small amount (i.e. $\Delta\mu$ small) Tolman's expansion (truncated at the first order term) provides a satisfactory description for the liquid drop.

We have investigated expressions for the Tolman length that involve the isothermal compressibility of the liquid, and tested their applicability in the context of the square-gradient model for the liquid-vapour interface. The main results of this investigation are shown in Figure 2.2. 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.(2.42) and (2.43) 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 vapour phase 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 Iwamatsu [39] using the double-well form for the free energy density for which the approximation Eq.(2.42) holds exactly.

It is tempting to infer from the expression for δ in Eq.(2.42) the critical behaviour 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.(2.28) is sub-dominant near the critical point, or – as is the case for the square-gradient mean-field model – has the same leading critical behaviour as the contribution to δ in Eq.(2.42). The critical behaviour of the compressibility χ in the coexisting liquid and vapour phase is described by the following form [71]

$$\begin{aligned}\chi_\ell &= \chi_0 t^{-\gamma} \left(1 + \alpha_\ell t^{-\Delta} + \dots \right), \\ \chi_v &= \chi_0 t^{-\gamma} \left(1 + \alpha_v t^{-\Delta} + \dots \right).\end{aligned}\tag{2.44}$$

The leading critical behaviour 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 behaviour 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 $\Delta \approx -0.50$ [71]. We thus find from Eq.(2.42):

$$\delta \propto t^{\mu-2\beta-\gamma-\Delta} \propto t^{-\Delta-\nu} \propto t^{-0.13},\tag{2.45}$$

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 [15].

As a result we find that the Tolman length diverges weakly on approach to the critical point, which is in line with previous predictions [34, 36, 37, 53]. The result $\delta \propto t^{-\Delta-\nu}$ is also consistent with the mean-field critical behaviour for δ in the van der Waals model as given in Eq.(2.40) (i.e. $\delta \propto \text{constant}$), when one inserts the mean-field value for the exponents $\nu = 1/2$ and $\Delta = -1/2$.

As a final point we like to point out the recent results given by Anisimov [38] obtained using complete scaling [72]. Starting from the generalized Laplace equation

Eq. (2.2), the pressure difference in and outside the liquid drop is separated into a symmetric and antisymmetric part ¹:

$$\Delta p = (\Delta p)_{\text{sym}} + (\Delta p)_{\text{asym}} \quad (2.46)$$

Since the Tolman length depends on the asymmetric part only to a first approximation δ can be written as

$$\frac{2\delta}{R} \simeq -\frac{(\Delta p)_{\text{asym}}}{(\Delta p)_{\text{sym}}}. \quad (2.47)$$

In the vicinity of the critical point the pressure difference scales as $(\Delta p)_{\text{crit}} \approx \chi(\Delta\mu)^2$ and accordingly the isothermal compressibility χ (the susceptibility with respect to density fluctuations) can again be separated into a symmetric and asymmetric part. Using expressions for the susceptibility obtained earlier from complete scaling allowed for the expansion of the Tolman length valid in the vicinity of the critical point:

$$\delta \propto \text{constant}_1 t^{\beta-\nu} + \text{constant}_2 t^{1-\alpha-\beta-\nu}, \quad (2.48)$$

where $\alpha \simeq 0.109$ is a universal critical Ising exponent. Since $1 - \alpha - \beta - \nu \simeq -0.065$ the first term (only present when using complete scaling) in Eq. (2.48) diverges more strongly ($\beta - \nu \simeq -0.304^2$) and will determine the leading order behaviour upon approaching the critical point. This result implies that in highly asymmetric fluids (like high molecular weight hydrocarbons or ionic fluids) the Tolman length can easily reach a substantial magnitude.

It should be kept in mind however that faraway from the critical point the Tolman's length is only a small fraction of the molecular dimensions and in order to observe noticeable changes in the surface tension one needs a nanosize droplet.

¹The part of Δp which does not depend on which fluid phase resides within or outside the droplet is the symmetric part.

²More thermodynamic quantities like the adsorption Γ diverge as $t^{\beta-\nu}$