Density functional theory of a curved liquid–vapour interface: evaluation of the rigidity constants

Edgar M Blokhuis\textsuperscript{1} and Alan E van Giessen\textsuperscript{2}

\textsuperscript{1} Colloid and Interface Science, Leiden Institute of Chemistry, Gorlaeus Laboratories, PO Box 9502, 2300 RA Leiden, The Netherlands
\textsuperscript{2} Hobart and William Smith College, Department of Chemistry, Geneva, NY 14456, USA

E-mail: e.blokhuis@chem.leidenuniv.nl

Received 7 February 2013, in final form 12 April 2013
Published 3 May 2013
Online at stacks.iop.org/JPhysCM/25/225003

Abstract

It is argued that to arrive at a quantitative description of the surface tension of a liquid drop as a function of its inverse radius, it is necessary to include the bending rigidity $k$ and Gaussian rigidity $\bar{k}$ in its description. New formulae for $k$ and $\bar{k}$ in the context of density functional theory with a non-local, integral expression for the interaction between molecules are presented. These expressions are used to investigate the influence of the choice of Gibbs dividing surface, and it is shown that for a one-component system, the equimolar surface has a special status in the sense that both $k$ and $\bar{k}$ are then the least sensitive to a change in the location of the dividing surface. Furthermore, the equimolar value for $k$ corresponds to its maximum value and the equimolar value for $\bar{k}$ corresponds to its minimum value. An explicit evaluation using a short-ranged interaction potential between molecules shows that $k$ is negative with a value around minus 0.5–1.0 $k_B T$ and that $\bar{k}$ is positive with a value that is a bit more than half the magnitude of $k$. Finally, for dispersion forces between molecules, we show that a term proportional to $\log (R^2/R)$ replaces the rigidity constants and we determine the (universal) proportionality constants.

1. Introduction

The surface tension of a simple drop of liquid has captured the imagination of scientists dating back to the pioneering work of Gibbs [1]. This interest continues, with the main focus of attention directed towards the description of the deviation of the surface tension from its planar value when the radius of the liquid droplet becomes smaller. Such a deviation is especially important in the theoretical description of nucleation phenomena [2]. The homogeneous nucleation of a liquid from a supersaturated vapour follows via the formation of small liquid droplets, and the nucleation time and energy depend sensitively on the precise value of the droplet’s surface tension.

A key quantity in quantifying the extent by which the surface tension of a liquid drop deviates from its planar value is the Tolman length introduced by Tolman in 1949 [3]. It can be defined in two equivalent ways. In the first way, one considers the radial dependence of the surface tension of a (spherical) liquid droplet defined as the excess grand free energy per unit area,

$$\Omega = -p_V V_\ell - p_v V_v + \sigma_s(R) A.$$  \hspace{1cm} (1)

When the radius $R$ of the droplet is large, the surface tension can be expanded in the inverse radius,

$$\sigma_s(R) = \sigma - \frac{2\delta\sigma}{R} + \ldots,$$  \hspace{1cm} (2)

where $\sigma$ is the surface tension of the planar interface and $\delta$ is the leading order correction defines the Tolman length $\delta$. In the second route to define the Tolman length, one considers the pressure difference $\Delta p = p_\ell - p_v$ between the pressure of the liquid inside and the pressure of the vapour outside the droplet. For large radii of curvature, $\Delta p$ is expanded in $1/R$,

$$\Delta p = \frac{2\sigma}{R} - \frac{2\delta\sigma}{R^2} + \ldots.$$  \hspace{1cm} (3)

$$\Delta p = \frac{2\sigma}{R} - \frac{2\delta\sigma}{R^2} + \ldots.$$  \hspace{1cm} (3)
The first term on the right hand side is the familiar Laplace equation [4] with the leading order correction giving Tolman’s original definition of the Tolman length [3]. It is important to note that this correction only takes on the form in equation (3) when the equimolar radius \([1]\) is taken as the radius of the liquid drop, i.e. \(R = R_s\). Furthermore, with this choice of the (Gibbs) dividing surface, terms of order \(O(1/R^4)\) are absent and the dots represent terms of order \(O(1/R^3)\). When the location of the droplet radius is chosen away from the equimolar radius, the Tolman length correction to the Laplace equation has a form different from that shown in equation (3).

For instance, the radius corresponding to the so-called surface of tension \((R = R_s)\) is defined such that equation (3) appears as \(\Delta p = 2\sigma(R_s)/R_s\).

The determination of the value of the Tolman length for a simple drop of liquid has proved to be not without controversy (recent reviews are given in [5, 6]). This is mainly due to two reasons. Firstly, one of the first microscopic expressions for the Tolman length was formulated in the context of a mechanical approach, which led to an expression for the Tolman length in terms of the first moment of the excess tangential pressure profile of a planar interface [7]. However, it was pointed out by Henderson and Schofield in 1982 that such an expression depends on the form of the pressure tensor used and is therefore not well-defined [8–11]. Furthermore, even the evaluation of the Tolman length using the usual Irving–Kirkwood [12] form for the pressure tensor leads to incorrect results [13], and the use of the mechanical expression is now (mostly) abandoned.

A second origin of controversy is simply due to the fact that for a regular liquid–vapour interface the Tolman length is small (a fraction of the molecular diameter), since it measures the subtle asymmetry between the liquid and vapour phases. Straightforward squared-gradient theory with the familiar tanh-profile for the density profile leads to a zero value of the Tolman length [14, 15] and it remains a challenge to distinguish its value from zero in computer simulations [16–20]. Nowadays, those computer simulations that have succeeded in obtaining a value different from zero indicate that its value is negative, with its magnitude around one tenth of a molecular diameter [21–26] and error bars usually somewhat less than half that number.

The sign and magnitude of the Tolman length for a regular liquid–vapour interface are corroborated by a large number of different versions of density functional theory (DFT), which has proved to be an invaluable tool in the theoretical description of inhomogeneous systems [27–30]. Quite surprisingly, the details of the density functional theory at hand do not seem to matter that much [6, 31] and one ubiquitously finds that the Tolman length is negative with a magnitude comparable to that obtained in simulations. This includes results for the Tolman length from van der Waals squared-gradient theory [32, 33], density functional theory with a non-local, integral expression for the interaction between molecules (DFT-LDA) [6, 34–37], density functional theory with weighted densities (DFT-WDA) [31] and density functional theory using Rosenfeld’s [38] fundamental measure theory for the hard-sphere free energy (DFT-FMT) [23–25, 39].

All in all, there now seems to be the same level of agreement between simulations and DFT for the Tolman length as exists for the surface tension, with the exception of one particular type of simulation result. In [21–26] the Tolman length is determined in computer simulations of liquid droplets for various (large) radii of curvature, but in a different set of simulations the Tolman length is extracted from computer simulations of a planar interface [40, 41], using a virial expression for the Tolman length [42]. The simulations of the planar interface lead to a Tolman length that has the same order of magnitude as the simulations of the liquid droplets but now with the opposite sign. It has been suggested that, since the interfacial area is much larger in the simulations of the planar interface, the presence of capillary waves might play an important role [21]. However, it is difficult to imagine that this would change the sign of the Tolman length so that the resolution to this problem remains uncertain.

Another feature that ubiquitously results from the computer simulations and DFT calculations of liquid droplets is that the surface tension is not monotonic as a function of the (inverse) radius (for a recent review, see [6]). A maximum in the surface tension of a liquid droplet occurs, which suggests that the surface tension is qualitatively better approximated by a parabola rather than by a straight line with its slope given by the Tolman length. This means that one needs to include higher order terms, going beyond the level of the Tolman length, in the expansion of the surface tension in equation (2). Such an expansion was first provided in the ground-breaking work by Helfrich in 1973 [43]. The form for the free energy suggested by Helfrich is the most general form for the surface free energy of an isotropic surface expanded to second order in the surface’s curvature [43],

\[
\Omega_H = \int dA \left[ \sigma - \delta \sigma J + \frac{k}{2} J^2 + \tilde{k} K + \cdots \right],
\]

where \(J = 1/R_1 + 1/R_2\) is the total curvature, \(K = 1/(R_1 R_2)\) is the Gaussian curvature and \(R_1, R_2\) are the principal radii of curvature at a certain point on the surface. The expansion defines four curvature coefficients: \(\sigma\), the surface tension of the planar interface; \(\delta\), the Tolman length [3]; \(k\), the bending rigidity; and \(\tilde{k}\), the rigidity constant associated with Gaussian curvature. The original expression proposed by Helfrich [43] features the radius of spontaneous curvature \(R_0\) as the linear curvature term \((\delta \sigma \rightarrow 2k/R_0) [5, 13]\), but in honour of Tolman we stick to the notation in equation (4).

For surfaces for which the curvatures \(J\) and \(K\) are constant, the Helfrich free energy per unit area reduces to

\[
\Omega_H/A \equiv \sigma(J, K) = \sigma - \delta \sigma J + \frac{k}{2} J^2 + \tilde{k} K + \cdots,
\]

which for a spherically or cylindrically shaped surface takes the form

\[
\sigma_s(R) = \sigma - \frac{2 \delta \sigma}{R} + \frac{(2k + \tilde{k})}{R^2} + \cdots \quad \text{(sphere)};
\]

\[
\sigma_c(R) = \sigma - \frac{\delta \sigma}{R} + \frac{k}{2R^2} + \cdots \quad \text{(cylinder)}.
\]
These expressions indicate that the second order coefficients, which express the non-monotonicity of the surface tension as observed in simulations and DFT calculations of liquid drops, are given by the combination of the rigidity constants $2k + \bar{k}$ and the bending rigidity $k$. Our goal in this paper is to provide general formulae for the bending rigidities $k$ and $\bar{k}$ using density functional theory (DFT-LDA). This work extends previous work by us [34], by Koga and Zeng [44], by Barrett [45] and by Baidakov et al [46]. Our formulae are subsequently applied to explicitly evaluate the bending rigidities and it is determined how well they can be used to describe the surface tension of a liquid drop (or vapour bubble).

The expansion of the surface tension of a liquid drop to second order in $1/R$ has not been without controversy [47–49]. Two issues have played a role here. The first issue concerns the fact that when the interaction between molecules is sufficiently long-ranged, the expansion in $1/R$ may not be analytic beyond some term [42, 50, 51]. In particular, for dispersion forces the second order correction has the form $\log(R)/R^2$ rather than $1/R^2$, and one could argue that the rigidity constants are ‘infinite’. Nowadays, this point is well-appreciated and no longer a source of controversy. In this paper we come back to this issue and provide explicit expressions for the second order correction to replace the expansion in equation (6) or (7) for dispersion forces.

A second issue is the argument that even for short-ranged interactions, which are mostly considered in simulations and DFT calculations, the second order term might pick up a logarithmic correction of the form $\log(R)/R^2$ [47–49]. The reasoning behind this focuses on the fact that for a spherical droplet, the second order contribution to the free energy, i.e. the expression in equation (6) multiplied by the area $A = 4\pi R^2$ is independent of $R$, which might be an indication that it should be replaced by a logarithmic term. The most compelling argument against this reasoning lies in the fact that the same argument applied to a cylindrical interface would lead to the conclusion that already the linear term in $1/R$ (Tolman length) would pick up logarithmic corrections. Although the issue is not completely settled, the presence of a logarithmic correction for short-ranged interaction has not been observed in simulations or demonstrated in calculations either in mean-field theory (DFT) or in statistical mechanics [42]. Also, in this paper, we inspect (numerically) the possible presence of a logarithmic correction to the second order term in the expansion of the free energy of a liquid drop and find no evidence for its presence.

Our paper is organized as follows. In section 2 we discuss the density functional theory that is considered (DFT-LDA) and use it to determine the surface tension $\sigma_s(R)$ of a liquid drop and vapour bubble. In section 3, the free energy is expanded to second order in $1/R$ for a spherical and cylindrical interface, which allows the formulation of new, closed expressions for the rigidity constants $k$ and $\bar{k}$ [34, 45]. An important feature addressed is the consequence of the choice made for the location of the dividing surface (the value of $R$) on the values of the bending rigidities. The formulae for $k$ and $\bar{k}$ are explicitly evaluated using a cut-off and shifted Lennard-Jones potential for the attractive part of the interaction potential. Since the evaluation of these expressions requires numerical determination of the density profile, we supply in section 4 an accurate approximation based on squared-gradient theory to evaluate $\delta, k$ and $\bar{k}$ from the parameters of the phase diagram only. In section 5 we consider the full Lennard-Jones interaction potential and determine its consequences for the expansion of the free energy in $1/R$. We end with a discussion of results.

2. Density functional theory

The expression for the (grand) free energy in density functional theory is based on the division into a hard-sphere reference system plus attractive forces described by an interaction potential $U_{at}(r)$. It is the following functional of the density $\rho(\vec{r})$ [27–30]:

$$\Omega[\rho] = \int d\vec{r} [f_{hs}(\rho) - \mu(\rho, T, \rho)] + \frac{1}{2} \int d\vec{r}_1 \int d\vec{r}_2 U_{at}(\rho) \rho(\vec{r}_1) \rho(\vec{r}_2),$$

where $\mu$ is the chemical potential. For the free energy of the hard-sphere reference system $f_{hs}(\rho)$, we take the well-known Carnahan–Starling form [52],

$$f_{hs}(\rho) = k_B T \rho \ln(\rho) + k_B T \rho \frac{(4\eta - 3\eta^2)}{(1 - \eta)^2},$$

where $\eta \equiv (\pi/6) \rho d^3$, with $d$ the molecular diameter. The Euler–Lagrange equation that minimizes the free energy in equation (8) is given by

$$\mu = f'_{hs}(\rho) + \int d\vec{r}_1 U_{at}(\rho) \rho(\vec{r}_2).$$

For a uniform system, the Euler–Lagrange equation becomes

$$\mu = f'_{hs}(\rho) - 2a \rho,$$

with the van der Waals parameter $a$ explicitly expressed in terms of the interaction potential as

$$a \equiv -\frac{1}{2} \int d\vec{r}_1 U_{at}(\rho).$$

Using the expression for the chemical potential in equation (11), the bulk pressure is obtained from $\Omega = -pV$, leading to the following equation of state:

$$p = \frac{k_B T \rho (1 + \eta + \eta^2 - \eta^3)}{(1 - \eta)^3} - a \rho^2.$$
\[ \rho(\vec{r}) = \rho_\text{\tiny coex}(z). \] In planar geometry, the Euler–Lagrange equation in equation (10) becomes

\[ \mu_{\text{\tiny coex}} = f'_{\text{\tiny hs}}(\rho_0) + \int d\vec{r}_2 \ U_{\text{\tiny att}}(r) \rho_0(z_2). \] (14)

The surface tension of the planar interface is the surface free energy per unit area \((\sigma = (\Omega + pV)/A)\) [4],

\[ \sigma = -\frac{1}{4} \int_{-\infty}^{\infty} dz \int d\vec{r}_2 \ U_{\text{\tiny att}}(r) r^2 (1-s^2) \rho_0'(z_1) \rho_0'(z_2), \] (15)

where \(z_2 = z_1 + sr \) and \(s = \cos \theta_{12}. \)

2.2. A spherical drop of liquid

When the chemical potential \(\mu\) is varied to a value off-coexistence, spherically shaped liquid droplets in metastable equilibrium with a bulk vapour phase may form. Such droplets are termed critical droplets. The radius of the liquid droplet is taken to be equal to the equimolar radius, \(R = R_c\) [1], which depends on the value of the chemical potential chosen, and is defined as

\[ 4\pi \int_0^r dr \ r^2 [\rho_s(r) - \rho_v] = \frac{4\pi}{3} R_c^3 (\rho_c - \rho_v). \] (16)

The (grand) free energy for the formation of the critical droplet is given by

\[ \frac{\Delta \Omega}{A} = \frac{\Omega + p_v V}{A} = -\frac{\Delta \rho \rho_c}{3} + \sigma_s(R), \] (17)

with \(p_v\) the vapour pressure outside the droplet and \(p_c = p_v + \Delta \rho\) the liquid pressure inside (see the remark below, however). The surface tension of the critical droplet is the quantity that we wish to study, and this equation provides a way to determine it from \(\Delta \Omega.\)

In spherical geometry, the free energy density functional in equation (8) is given by

\[ \frac{\Delta \Omega[\rho_s]}{A} = \int_0^r dr_1 \left( \frac{r_1}{R} \right)^2 [f'_{\text{\tiny hs}}(\rho_s) - \mu \rho_s(r_1)] \]
\[ + \frac{1}{2} \int_0^r dr_1 \left( \frac{r_1}{R} \right)^2 \]
\[ \times \int d\vec{r}_2 \ U_{\text{\tiny att}}(r) \rho_s(r_1) \rho_s(r_2), \] (18)

with the Euler–Lagrange equation that minimizes the above free energy equal to

\[ \mu = f'_{\text{\tiny hs}}(\rho_s) + \int d\vec{r}_2 \ U_{\text{\tiny att}}(r) \rho_s(r_2). \] (19)

The procedure to determine \(\sigma_s(R)\) as a function of \(R\) is as follows.

(1) First, the bulk densities \(\rho_{0,\ell}\) and \(\rho_{0,v}\) and the chemical potential at two-phase coexistence \(\mu_{\text{\tiny coex}}\) are determined by solving the following set of equations:

\[ f'_{\text{\tiny hs}}(\rho_{0,v}) = \mu_{\text{\tiny coex}}, \quad f'_{\text{\tiny hs}}(\rho_{0,\ell}) = \mu_{\text{\tiny coex}}, \]
\[ f(\rho_{0,v}) - \mu_{\text{\tiny coex}} \rho_{0,v} = f(\rho_{0,\ell}) - \mu_{\text{\tiny coex}} \rho_{0,\ell}. \] (20)

(2) Next, the chemical potential \(\mu\) is varied to a value off-coexistence, \(\mu > \mu_{\text{\tiny coex}}\), to obtain bubbles of vapour \((R > 0)\) and when \(\mu < \mu_{\text{\tiny coex}}\) we obtain droplets \((R < 0)\). For a given temperature and chemical potential \(\mu\) the liquid and vapour densities \(\rho_L\) and \(\rho_v\) are then determined by solving the following two equations:

\[ f'(\rho_L) = \mu, \quad f'(\rho_v) = \mu, \] (21)

with the corresponding bulk pressures calculated from

\[ p_v = -f'(\rho_v) + \mu \rho_v, \quad p_L = -f'(\rho_L) + \mu \rho_L. \] (22)

It should be remarked that far outside the droplet \((r \rightarrow \infty)\), the density (or pressure) is equal to that of the bulk, \(\rho_s(\infty) = \rho_v\), but only for large droplets is the density inside the droplet \((\rho_s(r = 0) = \rho_v)\) equal to its bulk value \((\rho_v)\).

(3) Finally, the Euler–Lagrange equation for \(\rho_s(r)\) in equation (19) is solved numerically with the boundary condition \(\rho_s(\infty) = \rho_v\). The resulting density profile \(\rho_s(r)\) is inserted into equation (16) to determine \(\Delta \Omega\) and thus \(\sigma_s(R)\).

This procedure is carried out using a cut-off and shifted Lennard-Jones potential for the attractive part of the interaction potential,

\[ U_{\text{\tiny att}}(r) = \begin{cases} U_{1,3}(r_{\text{\tiny min}}) - U_{1,3}(r_c), & 0 < r < r_{\text{\tiny min}}, \\ U_{1,3}(r) - U_{1,3}(r_c), & r_{\text{\tiny min}} < r < r_c, \\ 0, & r > r_c, \end{cases} \] (23)

where \(U_{1,3}(r) = 4\epsilon [(d/r)^{12} - (d/r)^{6}]\) and \(r_{\text{\tiny min}} = 2\frac{1}{3} d\).

Figure 1 shows the resulting phase diagram as a function of reduced density \(\rho^* = \rho d^3\) and reduced temperature \(T^* = k_B T / \epsilon\). The solid lines are the liquid–vapour densities for two
values of the LJ cut-off radius; the square symbols are recent computer simulation results taken from [53].

In figure 2, we show the pressure difference multiplied by $R/2\sigma$ as a function of the reciprocal radius. The circular symbols are previous simulation results [21] that were used to determine the Tolman length from (minus) the slope at $1/R = 0$ ($\delta \approx -0.10d$ [21]). For comparison, we show the result of DFT calculations as the solid line, where we have taken the pressure at the centre of the droplet as the liquid pressure. The excellent agreement in figure 2 is somewhat misleading since the corresponding values of the surface tension differ by as much as 50%. The results of DFT calculations using $p_l$ from equation (22) as the liquid pressure are plotted as square symbols to show that the slight difference between $p_l(0)$ and $p_l$ for small droplets has no consequences for the determination of $\delta$.

In figure 3, a typical example of the surface tension of a spherical liquid drop (or vapour bubble) is shown as a function of $1/R$, with $R$ the equimolar radius of the droplet. The symbols are the values for $\sigma_s(R)$ calculated using DFT. The solid line is the parabolic approximation in equation (6) with values for the coefficients $\sigma, \delta$ and $2k + \tilde{k}$ calculated from formulae presented in section 3. The behaviour of the surface tension is characterized by a positive first derivative at $1/R = 0$, which indicates that the Tolman length is negative, and a negative second derivative, which indicates that the combination $2k + \tilde{k}$ is also negative. It is concluded that the parabolic approximation gives a quantitatively accurate description of the surface tension for a large range of reciprocal radii. The determination of the full $\sigma_s(R)$ is usually quite elaborate and it therefore seems sufficient to only determine the coefficients in the parabolic approximation to $\sigma_s(R)$ as a function of $1/R$. This is carried out in section 3.

3. Curvature expansion

In this section, we consider spherically and cylindrically shaped liquid droplets and expand the free energy and density profile systematically to second order in $1/R$. An important feature of our analysis will be to not restrict ourselves to a particular choice of the dividing surface, but to instead leave the radius $R$ unspecified. This will allow us to derive new, more general expressions and will allow for a new investigation of the consequences of varying the choice for the location of the dividing surface. To second order in $1/R$, the expansion of the density profile of the spherical droplet reads

$$\rho_s(r) = \rho_0(z) + \frac{1}{R} \rho_{s,1}(z) + \frac{1}{R^2} \rho_{s,2}(z) + \cdots,$$

where $z = r - R$. The leading order correction to the density profile of the spherical interface is twice that of the cylindrical interface, so it is convenient to define $\rho_1(z) \equiv \rho_{s,1}(z) = 2\rho_{c,1}(z)$. We shall consider the expansion of the free energy of the spherical and cylindrical droplets separately.

3.1. Spherical interface

The coefficients in the curvature expansion of the density are determined from the curvature expansion of the Euler–Lagrange equation in equation (19). The result is that the (planar) density profile $\rho_0(z)$ is determined from equation (14), and $\rho_1(z)$ follows from solving

$$\mu_1 = f'_{\rho_0}(\rho_0) \rho_1(z) + \int d\vec{r}_{12} U_{at}(r) \times \left[ \rho_1(z) + \frac{r^2}{2(1 - s^2)} \rho_0'(z) \right],$$

where $\mu_1 = 2\sigma/\Delta p$ [5, 15]. For the evaluation of the curvature coefficients it turns out to be sufficient to determine the density profiles $\rho_0(z)$ and $\rho_1(z)$ only.
The analysis for the cylindrical interface is analogous to that for the spherical interface. Following the same procedure as for the spherical interface, the expressions for $\sigma$ and $\delta\sigma$ in equations (26) and (27) are recovered and one obtains as an expression for the bending rigidity $k$

$$k = \frac{1}{8} \int_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U_{\text{int}}(r)^2 (1 - s^2) \rho_0(z_1) \rho_0(z_2)$$

$$+ \frac{1}{8} \int_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U_{\text{int}}(r)^4 (1 - s^2)^2 \rho_0(z_1) \rho_0(z_2)$$

$$+ \int_{-\infty}^{\infty} dz \left[ \frac{\mu_1}{4} z \rho_0'(z) + \frac{\mu_1}{2} z^2 \rho_0(z) + 2 \mu_{c,2} z \rho_0'(z) \right],$$

where $\mu_{c,2} = -\sigma \Delta p_1/(2 \Delta \rho)^2$ [5, 15]. An expression for the rigidity constant associated with Gaussian curvature is then obtained by combining equations (28) and (29),

$$\bar{k} = -\frac{1}{4} \int_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U_{\text{int}}(r)^2 (1 - s^2) \rho_0'(z_1) \rho_0'(z_2)$$

$$- \frac{1}{8} \int_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U_{\text{int}}(r)$$

\[
\times r^4 (1 - s^2) (1 - s^2) \rho_0'(z_1) \rho_0'(z_2) + (\mu_{s,2} - 4 \mu_{c,2}) \int_{-\infty}^{\infty} dz \rho_0'(z). \quad (30)
\]

The expressions for $k$ and $\bar{k}$ differ somewhat in two ways from previous expressions derived by us in [34]. Firstly, they are rewritten in a more compact form with a printing error in [34] corrected (as noted by Barrett [45]). Secondly, these expressions are derived without reference to a particular choice for the location of the dividing surface, i.e. for the location of the $z = 0$ plane. This feature allows us to investigate the influence of the choice for the location of the dividing surface. As already known, the surface tension and Tolman length are independent of this choice but $k$ and $\bar{k}$ do depend on it.

### 3.3. Choice for the location of the dividing surface

We first consider the density profile of the planar interface, obtained by solving the differential equation in (14), to investigate the consequences of the choice for the location of the dividing surface for $\delta$ and $\bar{k}$. One may verify that when $\rho_0(z)$ is a particular solution of the differential equation in equation (14), then the shifted density profile

$$\rho_0(z) \to \rho_0(z - z_0)$$

is also a solution for arbitrary value of the integration constant $z_0$. However, since the expressions for $\delta$ and $\bar{k}$ feature $z$ (or $z_1$) in the integrand, such a shift has consequences for the different contributions to $\delta$ and $\bar{k}$. To investigate this in more detail, we first place the dividing surface of the planar system at the equimolar surface, $z = z_e$, which is defined such that the excess density is zero [1],

$$\int_{-\infty}^{\infty} dz \left[ \rho_0(z) - \rho_{0,1} \Theta(z - z) - \rho_{0,2} \Theta(z - z) \right] = - \int_{-\infty}^{\infty} dz \left[ z - z_e \right] \rho_0'(z) = 0,$$

where $\Theta(z)$ is the Heaviside function. When all distances to the surface are measured with respect to the equimolar plane, we need to replace $z$ by $z - z_e$ in the expressions for $\delta$ and $\bar{k}$. For the Tolman length in equation (27) we then find that

$$\delta \sigma = \frac{1}{4} \int_{-\infty}^{\infty} dz_1 \int d\vec{r}_{12} U_{\text{int}}(r)^2 (1 - s^2)$$

$$\times (z_1 - z_e) \rho_0'(z_1) \rho_0'(z_2),$$

where we have used equation (32). Now, to investigate the consequences of shifting the dividing surface away from the equimolar surface by a distance $\Delta$, we replace $z \to z - (z_e + \Delta)$ in the expression for the Tolman length in equation (27). One may easily verify that on account of the fact that $\mu_1 = 2\rho/\Delta \rho$ the Tolman length then again reduces to the expression in equation (33), which proves that the Tolman length is independent of the choice for the location of the dividing surface.
Replacing \( z \rightarrow z - z_c \) in the expression for the rigidity constant associated with Gaussian curvature in equation (30), we find that \( \tilde{k} \) simplifies to

\[
\tilde{k}_{\text{equimolar}} = -\frac{1}{3} \int_{-\infty}^{\infty} dz_1 \int d\tilde{r}_{12} U_{\text{att}}(r) r^2 (1 - s^2) \times (z_1 - z_e)^2 \rho_0'(z_1) \rho_0'(z_2)
\]

\[
- \frac{1}{9} \int_{-\infty}^{\infty} dz_1 \int d\tilde{r}_{12} U_{\text{att}}(r) r^4 (1 - s^2) \times (1 - 5s^2) \rho_0'(z_1) \rho_0'(z_2).
\]

(34)

Again, we may investigate the consequence of shifting the dividing surface by replacing \( z \rightarrow z - (z_c + \Delta) \) in the expression for \( \tilde{k} \) in equation (30). We then find that

\[
\tilde{k} = \tilde{k}_{\text{equimolar}} + \sigma \Delta^2.
\]

(35)

This equation shows that \( \tilde{k} \) does depend on the choice for the location of the dividing surface. It also shows that \( \tilde{k} \) evaluated for the equimolar surface (\( \Delta = 0 \)) corresponds to the lowest possible value for \( \tilde{k} \) and is the least sensitive to a shift in the location of the dividing surface.

To address the influence of the dividing surface on the value of the bending rigidity \( k \), we need to consider the properties of the density profile \( \rho_1(z) \) as well. One may verify that when \( \rho_1(z) \) is a particular solution of equation (25) then also

\[
\rho_1(z) \rightarrow \rho_1(z) + \alpha \rho_0'(z)
\]

(36)

is a solution for arbitrary value of the integration constant \( \alpha \). Now, one may easily verify by inserting equation (36) into (29) that \( k \) is independent of the value of the integration constant. This means that just like \( \tilde{k} \) and \( k \) we only need to consider the influence of the choice for the location of the dividing surface of the planar density profile \( \rho_0(z) \). For the equimolar surface, the expression for the bending rigidity in equation (29) reduces to

\[
k_{\text{equimolar}} = 4 \int_{-\infty}^{\infty} dz_1 \int d\tilde{r}_{12} U_{\text{att}}(r) r^2 (1 - s^2) \rho_0'(z_1) \rho_1(z_2)
\]

\[
+ \frac{1}{18} \int_{-\infty}^{\infty} dz_1 \int d\tilde{r}_{12} U_{\text{att}}(r) r^4 (1 - s^2)^2 \rho_0'(z_1) \rho_0'(z_2)
\]

\[
+ \frac{\mu_1}{4} \int_{-\infty}^{\infty} dz_1 (z - z_e) \rho_0'(z_1) + 2 (z - z_e)^2 \rho_0'(z_2).
\]

(37)

Shifting the dividing surface by replacing \( z \rightarrow z - (z_c + \Delta) \) in the expression for \( k \) in equation (29), we then find that

\[
k = k_{\text{equimolar}} + \sigma \Delta^2.
\]

(38)

It is concluded that also the bending rigidity \( k \) does depend on the choice for the location of the dividing surface. The bending rigidity evaluated for the equimolar surface (\( \Delta = 0 \)) now corresponds to the largest possible value for \( k \) but it is again the least sensitive to a shift in the location of the dividing surface.

The procedure to determine the curvature coefficients \( \sigma, \delta, k \) and \( \tilde{k} \) is now as follows. The planar profile \( \rho_0(z) \) is first determined from the differential equation in equation (14), with \( \rho_{0,\ell}, \rho_{0,\ell}, \nu_{\text{corex}} \) and \( \nu_{\text{corex}} \) derived by solving the set of equations in equation (20). From \( \rho_0(z) \), the location of the equimolar plane \( z = z_e \) is determined from equation (32) and the curvature coefficients \( \sigma, \delta \) and \( \tilde{k} \) are evaluated from the integrals in equations (26), (33) and (34), respectively. The constant \( \mu_1 \) is subsequently determined from \( \mu_1 = 2 \sigma/\Delta \rho \), which allows us to determine the bulk density values \( \rho_{1,\ell} \) and \( \rho_{1,\ell} \) from \( \rho_{1,\ell} = \mu_1 f''(\rho_{0,\ell})/f'(\rho_{0,\ell}) \). For given \( \rho_0(z) \) and \( \mu_1 \), the differential equation for \( \rho_1(z) \) in equation (25) is solved with the boundary conditions \( \rho_1(-\infty) = \rho_{1,\ell} \) and \( \rho_1(\infty) = \rho_{1,\ell} \). Finally, with \( \rho_1(z) \) determined, \( k \) can be evaluated from the integral in equation (37).

This procedure is carried out (again) using the cut-off and shifted Lennard-Jones potential in equation (23) for the attractive part of the interaction potential. Figure 4 shows the surface tension and Tolman length \( \delta \) (in units of \( \sigma \)) as a function of reduced temperature. The circular symbols are the results of the full DFT calculations in equations (26) and (27). The solid lines are the squared-gradient approximations of section 4. The square symbols are simulation results for \( \sigma \) from [53] and for \( \delta \) from [21] (solid square) and [24] (two open squares).

Figure 4. Surface tension \( \sigma \) (in units of \( k_B T/\ell^2 \)) and Tolman length \( \delta \) (in units of \( \sigma \)) as a function of reduced temperature. The circular symbols are the results of the full DFT calculations in equations (26) and (27). The solid lines are the squared-gradient approximations of section 4. The square symbols are simulation results for \( \sigma \) from [53] and for \( \delta \) from [21] (solid square) and [24] (two open squares).
In figure 5, the bending rigidity $k$, the Gaussian rigidity $\bar{k}$ and the combination $2k + \bar{k}$ are shown as a function of temperature. The rigidity constants are evaluated using the equimolar surface for the location of the dividing surface. The circular symbols are the values for $k$ and $\bar{k}$ calculated using DFT for two values of the reduced LJ cut-off radius, $r_c = 2.5$ and 7.5, with the solid lines the corresponding squared-gradient approximations determined in section 4. Also shown are simulation results by the group of Binder [24]. Although a detailed comparison of the DFT and simulation results is not really appropriate due to a difference in cut-off used, the agreement in sign and order of magnitude is rather satisfactory.

### 4. Squared-gradient expressions

The evaluation of $\delta$, $k$ and $\bar{k}$ requires the full numerical evaluation of the density profiles $\rho_0(z)$ and $\rho_1(z)$ from the differential equations in (14) and (25). This procedure is quite elaborate, prompting a need for simple formulae that provide (approximate) numbers for the various coefficients. In this section we provide a rather accurate approximation scheme based on the squared-gradient approximation which only requires the calculation of the phase diagram as input.

The squared-gradient theory for surfaces dates back to the work of van der Waals in 1893 [54]. Its free energy functional is derived from equation (8) by assuming that gradients in the density are small so that $\rho(\vec{r}_2)$ may be expanded around $\rho(\vec{r}_1)$. This leads to

$$\Omega[\rho] = \int d\vec{r} \left[ m \left( \vec{\nabla} \rho(\vec{r}) \right)^2 + f(\mu) - \mu \rho(\vec{r}) \right],$$

where the squared-gradient coefficient $m$ is given by

$$m \equiv -\frac{1}{12} \int d\vec{r}_{12} r^2 U_{alt}(r).$$

Expressions for the curvature coefficients in squared-gradient theory were formulated some time ago. For the surface tension of the planar interface, we have the familiar expression given by van der Waals [54],

$$\sigma = 2m \int_{-\infty}^{\infty} dz \, \rho_0(z)^2.$$  \hspace{1cm} (41)

For the Tolman length, Fisher and Wortis derived the following expression [14]:

$$\delta \sigma = -2m \int_{-\infty}^{\infty} dz \, (z - z_0) \rho_0(z)^2.$$ \hspace{1cm} (42)

For the bending and Gaussian rigidity, one has [15]

$$k = -m \int_{-\infty}^{\infty} dz \, \rho_0(z) \rho_1'(z)$$

$$+ \int_{-\infty}^{\infty} dz \left[ \frac{\mu_1}{4} z \rho_1'(z) + \frac{\mu_1}{2} z^2 \rho_0'(z) + 2\mu_2 z \rho_0(z) \right],$$

$$\bar{k} = 2m \int_{-\infty}^{\infty} dz \, z^2 \rho_0(z)^2 + \left( \mu_{c2} - 4\mu_{c1} \right) \int_{-\infty}^{\infty} dz \, z \rho_0(z),$$

$$k_{\text{equimolar}} = -m \int_{-\infty}^{\infty} dz \, \rho_0(z) \rho_1'(z)$$

$$+ \frac{\mu_1}{4} \int_{-\infty}^{\infty} dz \left( z - z_e \right) \rho_1'(z) + 2(z - z_e)^2 \rho_0'(z),$$

$$\bar{k}_{\text{equimolar}} = 2m \int_{-\infty}^{\infty} dz \, (z - z_e)^2 \rho_0(z)^2.$$ \hspace{1cm} (43)

which, evaluated using the equimolar surface for the location of the dividing surface, reduce to

$$k_{\text{equimolar}} = -m \int_{-\infty}^{\infty} dz \, \rho_0(z) \rho_1'(z)$$

$$+ \frac{\mu_1}{4} \int_{-\infty}^{\infty} dz \left( z - z_e \right) \rho_1'(z) + 2(z - z_e)^2 \rho_0'(z),$$

$$\bar{k}_{\text{equimolar}} = 2m \int_{-\infty}^{\infty} dz \, (z - z_e)^2 \rho_0(z)^2.$$ \hspace{1cm} (44)
To evaluate these expressions, the density profiles $\rho_0(z)$ and $\rho_1(z)$ still need to be determined from the expanded Euler–Lagrange equation,

$$f'(\rho_0) = \mu_{\text{coex}} + 2m \rho_0''(z), \quad (45)$$

$$f''(\rho_0) \rho_1(z) = \mu_1 + 2m \rho_1'(z) + 4m \rho_0'(z). \quad (46)$$

In order to solve these equations, it is useful to assume proximity to the critical point so that the free energy density may be approximated by the usual double-well form

$$f(\rho) - \mu_{\text{coex}} \rho + p_{\text{coex}} = \frac{m}{(\Delta \rho)^2} \xi^2 (\rho - \rho_0) (\rho - \rho_0 \xi)^2, \quad (47)$$

where the bulk correlation length $\xi$ is related to the second derivative of $f(\rho)$ evaluated at either bulk density. Solution of the Euler–Lagrange equation in equation (45) then leads to the usual tanh-form for the planar density profile [4],

$$\rho_0(z) = \frac{1}{2} \left( \rho_{0,\ell} + \rho_{0,\ell} - \Delta \rho \right) \tanh((z - z_c)/2\xi). \quad (48)$$

One may verify that solution of the Euler–Lagrange equation in equation (46) gives the following general solution for $\rho_1(z)$ [15]:

$$\rho_1(z) = \frac{1}{2} m (\Delta \rho)^2 \xi + \alpha \rho_0'(z). \quad (49)$$

As already discussed, the rigidity constant is independent of the integration constant $\alpha$. Inserting these profiles into the expressions for $\sigma, k$ and $k$ in equations (41) and (44), one finds [15]

$$\sigma = \frac{m (\Delta \rho)^2}{3 \xi}, \quad (50)$$

$$k_{\text{equimolar}} = \frac{1}{\xi^2} \left( \frac{2}{\pi^2} - 3 \right) m (\Delta \rho)^2 \xi, \quad (51)$$

For the symmetric double-well form for $f(\rho)$, the Tolman length is identically zero. To obtain an estimate for $\delta$ it is therefore necessary to consider leading order corrections to the double-well form for $f(\rho)$ in equation (47) [14, 34]. This leads to the following (constant) value for the Tolman length [34]:

$$\delta = -0.286565 \sqrt{m/a}. \quad (52)$$

The prefactor depends on the precise form for $f(\rho)$, and the number quoted is specific to the Carnahan–Starling equation of state [3].

All these formulae are derived assuming proximity to the critical point, but it turns out that they also provide a good approximation in a wide temperature range when the value of $\xi$ is chosen judiciously. This is achieved by using the fact that in squared-gradient theory the surface tension $\sigma$ may be determined from $f(\rho)$ directly without the necessity to determine the density profile $\rho_0(z)$ [4],

$$\sigma = 2 \sqrt{m} \int_{\rho_{0,\ell}}^{\rho_{0,\ell}} d\rho \sqrt{f(\rho) - \mu_{\text{coex}} \rho + p_{\text{coex}}}. \quad (53)$$

An effective value for $\xi$ may now be chosen such that the two expressions for the surface tension in equations (50) and (52) are equal. This gives for $\xi$

$$\xi \mapsto \xi_{\text{eff}} = \frac{m (\Delta \rho)^2}{3 \sigma}, \quad (54)$$

with $\sigma$ given by equation (52).

The procedure to determine the solid lines in figures 4 and 5 is now as follows. For a certain interaction potential, such as the Lennard-Jones potential in equation (23), the interaction parameters $\alpha$ and $m$ are calculated. Next, as a function of temperature, the bulk thermodynamic variables $\rho_0, \rho_0, \xi, \mu_{\text{coex}}$, and $p_{\text{coex}}$ are derived by solving the set of equations in equation (20). The surface tension is then calculated from equation (52) and $\xi$ from equation (53). With all parameters known, the curvature coefficients are finally calculated from equations (50) and (51).

5. Long-ranged interactions: dispersion forces

The surface tension, Tolman length and rigidity constants have all been explicitly evaluated using a Lennard-Jones potential that is cut-off beyond a certain distance $r_c$. In this section we address the consequences of using the full Lennard-Jones potential. It is easily verified that the phase diagram in figure 1 remains essentially the same when the cut-off is changed from $r_c = 7.5$ to $\infty$, but that the shift in surface tension and Tolman length is increasingly noticeable (see figure 4). An inspection of the explicit expressions for the rigidity constants in equations (29) and (30) teaches us that both $k$ and $\bar{k}$ diverge when $r_c$ increases to infinity [42, 51]. This divergence is an indication that the expansion of the free energy is no longer of the form in equation (6) or (7), and it has to be replaced by

$$\sigma_{\text{S}}(R) = \sigma - \frac{2 \delta \sigma}{R} + (2 \kappa_s + \bar{k}_s) \frac{\log(d/R)}{R^2} + \cdots, \quad (55)$$

$$\sigma_{\text{c}}(R) = \sigma - \frac{\sigma}{R} + \kappa_{s} \frac{\log(d/R)}{2R^2} + \cdots, \quad (55)$$

where the dots represent terms of $O(1/R^2)$. The coefficients of the logarithmic terms may be extracted from the expressions for $k$ and $\bar{k}$ in equations (29) and (30). They depend on the tail of the interaction potential, but are otherwise quite universal,

$$\kappa_s = \frac{\pi}{8} \varepsilon \delta (\Delta \rho)^2, \quad (56)$$

$$\bar{k}_s = -\frac{\pi}{12} \varepsilon \delta (\Delta \rho)^2. \quad (57)$$

This expression for $\kappa_s$ is equal to that obtained in a DFT analysis of the singular part of the wavevector dependent surface tension of the fluctuating interface [55]. These expressions can also be derived from virial expressions for the rigidity constants when a sharp-kink approximation [51] is made for the density profile [4]. The form for $2 \kappa_s + \bar{k}_s$ obtained by combining equations (56) and (57) was first derived by Hooper and Nordholm in [50].
To demonstrate the divergence of the second order term in equation (54), the surface tension of a spherical liquid droplet as a function of the radius is determined for three values of the reduced LJ cut-off \( r_c = 2.5, 7.5 \) and \( \infty \). The regular contributions to \( \sigma_s(R) \) from \( \sigma \) and \( \delta \) are subtracted, so that we may define

\[
(2k + \bar{k})(R) \equiv (\sigma_s(R) - \sigma) R^2 + 2\delta \sigma R. \tag{58}
\]

This quantity is defined such that when the expansion in equation (6) for short-ranged forces is inserted, it reduces to \( 2k + \bar{k} \) in the limit that \( R \to \infty \). For long-ranged forces \( (r_c = \infty) \), insertion of equation (54) into (58) gives a logarithmic divergence in this limit. This is verified by the DFT calculations shown in figure 6 as the various symbols. For \( r_c = 2.5 \) and 7.5, the results indeed tend to the values obtained from the direct evaluation of \( 2k + \bar{k} \) calculated from equations (34) and (37) (solid circles). For \( r_c = \infty \) (triangular symbols) a slight divergence can be made out. This divergence is consistent with the dashed line, which is the divergence as described by combining the coefficients in equations (56) and (57).

6. Discussion

In the context of density functional theory, we have shown that the surface tension of a spherical liquid droplet as a function of its inverse radius is well-represented by a parabola with its second derivative related to the rigidity constants \( k \) and \( \bar{k} \). Compact formulae for the evaluation of \( k \) and \( \bar{k} \) are derived in terms of the density profiles \( \rho_0(z) \) and \( \rho_1(z) \), which are in line with previous formulae presented by us [34] and by Barrett [45]. A number of conclusions can be made with regard to these formulæ.

- The rigidity constants \( k \) and \( \bar{k} \) depend on the choice for the location of the dividing surface of the planar density profile \( \rho_0(z) \). This dependence reflects the fact that when the location of the radius \( R \) is chosen differently, the curve of \( \sigma_s(R) \) versus \( 1/R \) changes somewhat and the second derivative \( (2k + \bar{k}) \) naturally needs to be amended.

- The most natural choice for a one-component system is to locate the dividing surface of the planar interface according to the equimolar surface. For this choice both \( k \) and \( \bar{k} \) are the least sensitive to a change in the location of the dividing surface. Furthermore, the equimolar value for \( k \) corresponds to its maximum value and the equimolar value for \( \bar{k} \) corresponds to its minimum value.

- The bending rigidity \( \bar{k} \) depends on the density profile \( \rho_1(z) \), which measures the extent to which molecules rearrange themselves when the interface is curved. The bending rigidity is, however, independent of the choice made for the location of the dividing surface of \( \rho_1(z) \) (value of \( \alpha \) in equation (36)) \(^5\).

Using a cut-off and shifted Lennard-Jones potential for the attractive part of the interaction potential, the Tolman length and rigidity constants have been calculated, with the result that \( \delta \) is negative with a value of minus 0.1–0.2. \( k \) is also negative with a value around minus 0.5–1.0 \( k_B T \) and \( \bar{k} \) is positive with a value of a bit more than half the magnitude of \( k \). It is not expected that these results will depend sensitively on the type of density functional theory used, and we have shown that even an approximation scheme based on squared-gradient theory is quantitatively accurate.

Our DFT results are expected to give an accurate qualitative description of the rigidity constants determined in experiments or computer simulations. The first results of computer simulations by the group of Binder [24], shown in figure 5, seem to support this expectation, but further computer simulations are necessary. The agreement should cease to exist close to the critical point, however. Since the DFT calculations are all mean-field in character, the critical exponents obtained for both rigidity constants are the mean-field values of 1/2, which indicates that both \( k \) and \( \bar{k} \) are zero at \( T_c \). Although it has not been proved rigorously, one expects that in reality the rigidity constants are finite at the critical point, \( k, \bar{k} \propto k_B T_c \). The situation is somewhat more subtle for the rigidity constant associated with the description of surface fluctuations. Then, the bending rigidity is again negative but it vanishes on approach to the critical point with the same exponent as the surface tension [55].

Inspection of the explicit expressions presented for the rigidity constants is the most convincing method to investigate the possible presence of logarithmic corrections [47–49], to replace the rigidity constants. For short-ranged interactions between molecules, the rigidity constants are definitely finite, but for an interaction potential that falls off as \( 1/r^6 \) for large intermolecular distances (dispersion forces), the rigidity constants are infinite, indicating that the \( 1/R^2 \) term in the expansion of the surface tension needs to be

\(^5\) In the notation of [15] the crossing constraint \((cc)\) and both integral constraints \((ic\) and \(ic')\) for \( \rho_1(z) \) all lead to the same value of the bending rigidity.
replaced by a logarithmic term proportional to $\log(R)/R^2$. The proportionality constants of the logarithmic corrections are found to be quite universal since they probe the system’s long-distance behaviour and are in agreement with previous analyses [42, 50, 51] (see footnote 4).

**Acknowledgment**

AЕvG acknowledges the generous support from an American Chemical Society Petroleum Research Fund.

**Appendix. Alternative DFT expressions**

It may be useful to re-express the curvature coefficients $\delta, k$ and $\tilde{k}$ such that any reference to the chemical potential is absent. For the Tolman length, the expression for $\mu_1$ in equation (25) may be used to rewrite equation (27) as

$$\delta \sigma = \frac{1}{2} \int_{-\infty}^{\infty} dz_1 \int d\bar{r}_{12} U_{\text{att}}(r) r^2 (1 - s^2) \rho_0'(z_1) \rho_1'(z_2).$$

(A.1)

This expression is quite useful since it can be used to verify that the density profile $\rho_1(z)$ determined numerically by solving the differential equation in (25) leads to the same value for the Tolman length when evaluated using equation (27).

In order to transform the rigidity constants in a similar manner, we first need to expand the Euler–Lagrange equation in (19) to second order in $1/R$. For the spherical interface, one finds

$$\mu_{s,2} = f_{\text{hs}}(\rho_0) \rho_{s,2}(z_1) + \frac{1}{2} f_{\text{hs}}''(\rho_0) \rho_1(z_1)^2$$

$$+ \int d\bar{r}_{12} U_{\text{att}}(r) \left[ \rho_{s,2}(z_2) + \frac{r^2}{2} (1 - s^2) \rho_1'(z_2) \right]$$

$$- \frac{r^2}{2} (1 - s^2) z_2 \rho_0'(z_2)$$

$$+ \frac{r^4}{8} (1 - s^2)^2 \rho_0''(z_2).$$

(A.2)

The analogous expansion for the cylindrical interface gives

$$\mu_{c,2} = f_{\text{hc}}(\rho_0) \rho_{c,2}(z_1) + \frac{1}{2} f_{\text{hc}}''(\rho_0) \rho_1(z_1)^2$$

$$+ \int d\bar{r}_{12} U_{\text{att}}(r) \left[ \rho_{c,2}(z_2) + \frac{r^2}{8} (1 - s^2) \rho_1'(z_2) \right]$$

$$- \frac{r^2}{4} (1 - s^2) z_2 \rho_0'(z_2)$$

$$+ \frac{3r^4}{64} (1 - s^2)^2 \rho_0''(z_2).$$

(A.3)

Inserting these expressions for $\mu_{s,2}$ and $\mu_{c,2}$ into equations (29) and (30), one finds

$$k = - \frac{1}{3} \int_{-\infty}^{\infty} dz_1 \int d\bar{r}_{12} U_{\text{att}}(r) r^2 (1 - s^2) \rho_0'(z_1) \rho_{s,2}'(z_2)$$

$$+ \frac{1}{2} \int_{-\infty}^{\infty} dz_1 \int d\bar{r}_{12} U_{\text{att}}(r) r^2 (1 - s^2) \rho_1'(z_1) \rho_1'(z_2),$$

$$\tilde{k} = \frac{1}{2} \int_{-\infty}^{\infty} dz_1 \int d\bar{r}_{12} U_{\text{att}}(r) r^2 (1 - s^2) \rho_0'(z_1)$$

$$\times (1 + 3s^2) \rho_0'(z_1) \rho_1'(z_2),$$

(A.4)

$$\times \left[ 4 \rho_{s,2}'(z_2) - \rho_{s,2}'(z_2) \right]$$

$$+ \frac{1}{8} \int_{-\infty}^{\infty} dz_1 \int d\bar{r}_{12} U_{\text{att}}(r) r^2 (1 - s^2) z_1^2 \rho_0'(z_1) \rho_0'(z_2)$$

$$- \frac{1}{96} \int_{-\infty}^{\infty} dz_1 \int d\bar{r}_{12} U_{\text{att}}(r)$$

$$\times r^4 (1 - s^2)(1 + 7s^2) \rho_0'(z_1) \rho_0'(z_2).$$

(A.5)

These expressions have the advantage that no reference is made to the external field used to change the curvature. It might therefore be expected that these expressions are independent of the way the interfacial curvature is varied. An important disadvantage, however, is that these expressions can only be evaluated when the second order corrections to the density profiles, $\rho_{s,2}(z)$ and $\rho_{c,2}(z)$, are determined as well.

**References**

[1] Gibbs J W 1961 *Collected Works* (New York: Dover)
[2] See e.g. Oxtoby D W 1992 *Fundamentals of Inhomogeneous Fluids* ed D Henderson (New York: Dekker) and references therein
[3] Tolman R C 1949 *J. Chem. Phys.* 17 333
[4] Rowlinson J S and Widom B 1982 *Molecular Theory of Capillarity* (Oxford: Clarendon)
[5] Blokhuis E M and Kuipers J 2006 *J. Chem. Phys.* 124 074701
[6] Malijevský A and Jackson G 2012 *J. Phys.: Condens. Matter* 24 464121
[7] Buff F P 1955 *J. Chem. Phys.* 23 419
[8] Hemingway S J, Henderson J R and Rowlinson J S 1981 *Faraday Symp. Chem. Soc.* 16 33
[9] Henderson J R and Schofield P 1982 *Proc. R. Soc. A* 380 211
[10] Schofield P and Henderson J R 1982 *Proc. R. Soc. A* 379 231
[11] Henderson J R 1986 *Fluid Interfacial Phenomena* ed C A Croxton (New York: Wiley)
[12] Irving J H and Kirkwood J G 1950 *J. Chem. Phys.* 18 817
[13] Blokhuis E M and Bedeaux D 1992 *J. Chem. Phys.* 97 3576
[14] Fisher M P A and Wortis M 1984 *Phys. Rev.* B 29 6252
[15] Blokhuis E M and Bedeaux D 1993 *Mol. Phys.* 80 705
[16] Nijmeijer M J P, Bruin C, van Woerkom A B, Bakker A F and van Leeuwen J M J 1992 *J. Chem. Phys.* 96 565
[17] ten Wolde P R and Frenkel D 1998 *J. Chem. Phys.* 109 9901
[18] El Bordoumi H, Mareschal M, Lovett R and Baus M 2000 *J. Chem. Phys.* 113 9804
[19] Lei Y A, Bykov T, YooO S and Zeng X C 2005 *J. Am. Chem. Soc.* 127 15346
[20] Horsch M, Hasse H, Shchechin A K, Agarwall A, Eckelbsch A, Vrabec J, Mülle E A and Jackson G 2012 *Phys. Rev. E* 85 031605
[21] van Giessen A E and Blokhuis E M 2009 *J. Chem. Phys.* 131 164705
[22] Schrader M, Virnau P and Binder K 2009 *Phys. Rev. E* 79 061104
[23] Sampayo J G, Malijevský A, Müller E A, de Miguel E and Jackson G 2010 *J. Chem. Phys.* 132 141101
[24] Block B J, Das S K, Oettel M, Virnau P and Binder K 2010 J. Chem. Phys. 133 154702
[25] Tröster A, Oettel M, Block B J, Virnau P and Binder K 2012 J. Chem. Phys. 136 064709
[26] Das S K and Binder K 2011 Phys. Rev. E 84 061607
[27] Sullivan D E 1979 Phys. Rev. B 20 3991
[28] Tarazona P and Evans R 1984 Mol. Phys. 52 847
[29] Evans R 1979 Adv. Phys. 28 144
[30] Evans R 1990 Liquids at Interfaces (Les Houches XLVIII (1988)) ed J Charvolin, J F Joanny and J Zinn-Justin (Amsterdam: North-Holland)
[31] Bykov T V and Zeng X C 2006 J. Chem. Phys. 125 144515
[32] Baidakov V G and Boltachev G Sh 1999 Phys. Rev. E 59 469
[33] Baidakov V G and Boltachev G Sh 2004 J. Chem. Phys. 121 8594
[34] van Giessen A E, Blokhuis E M and Bukman D J 1998 J. Chem. Phys. 108 1148
[35] Koga K, Zeng X C and Shchekin A K 1998 J. Chem. Phys. 109 4063
[36] Napari I and Laaksonen A 2001 J. Chem. Phys. 114 5796
[37] Barrett J C 2006 J. Chem. Phys. 124 144705
[38] Rosenfeld Y 1989 Phys. Rev. Lett. 63 980
[39] Li Z and Wu J 2008 Indust. Eng. Chem. Res. 47 4988
[40] Haye M J and Bruin C 1994 J. Chem. Phys. 100 556
[41] van Giessen A E and Blokhuis E M 2002 J. Chem. Phys. 116 302
[42] Blokhuis E M and Bedeaux D 1992 Physica A 184 42
[43] Helfrich W 1973 Z. Naturforsch. C 28 693
[44] Koga K and Zeng X C 1999 J. Chem. Phys. 110 3466
[45] Barrett J C 2009 J. Chem. Phys. 131 084711
[46] Baidakov V G, Boltachev G Sh and Chernykh G G 2004 Phys. Rev. E 70 011603
[47] Henderson J R 1992 Fundamentals of Inhomogeneous Fluids ed D Henderson (New York: Dekker)
[48] Rowlinson J S 1994 J. Phys.: Condens. Matter 6 A1
[49] Fisher M E 1967 Physics 3 255
[50] Hooper M A and Nordholm S 1984 J. Chem. Phys. 81 2432
[51] Naportkowski M and Dietrich S 1993 Phys. Rev. E 47 1836
[52] Biener T and Dietrich S 1998 Physica A 252 85
[53] Carnahan N F and Starling K E 1970 Phys. Rev. A 1 1672
[54] Baidakov V G, Protsenko S P, Kozlova Z R and Chernykh G G 2007 J. Chem. Phys. 126 214505
[55] van der Waals J D 1893 Verh. Kon. Akad. v Wetensch. Amst. 1 81
[56] van der Waals J D 1979 J. Stat. Phys. 20 200 (Engl. transl.)
[57] Blokhuis E M, Kuipers J and Vink R L C 2008 Phys. Rev. Lett. 101 086101
[58] Blokhuis E M 2009 J. Chem. Phys. 130 014706