

The van der Waals component of the interfacial bending moment

1. Contribution of the pressure tensor tails

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Abstract

The main purpose of this study is to find explicit expressions for the interfacial bending moment and for the Tolman length in terms of the interfacial tension at the flat interface and of the Hamaker constants of the two neighboring fluid phases. For that purpose a model expression for the anisotropy of the pressure tensor in the vicinity of a spherical interface is obtained by utilizing the Irving and Kirkwood formula in conjunction with some general thermodynamic restrictions. In particular, asymptotic expressions for the pressure tensor tails are derived. The results allow calculation of the curvature dependence of the interfacial tension due to the van der Waals interaction. They are applicable to microemulsions, critical emulsions and homogeneous nucleation.

1. INTRODUCTION

The physical dependence of interfacial tension, γ , on the curvature of a fluid/liquid interface can be described by means of the Tolman equation [1,2]

$$\gamma = \gamma_0 \left(1 - \frac{2\delta_0}{a} + \dots \right) \quad (1.1)$$

where γ_0 is the tension of the flat interface, a is the radius of the equimolecular dividing surface and δ_0 is the so-called Tolman length. If

$$\delta = a - a_s \quad (1.2)$$

is the distance between the equimolecular dividing surface and the surface of tension, then δ_0 is the limiting value of δ for a flat interface [2]:

$$\delta_0 = \lim_{1/a \rightarrow 0} \delta(a) \quad (1.3)$$

The radii a_s and a are defined by means of the equations [2,3]

$$\left(\frac{\partial\gamma}{\partial a_x}\right)_{a_x=a_0}=0 \quad (1.4)$$

and

$$\left(\frac{\partial\gamma}{\partial a_x}\right)_{a_x=a}=\frac{\partial\gamma}{\partial a} \quad (1.5)$$

where the derivatives in parentheses correspond to formal variation of the dividing surface radius, a_x , at a fixed physical state of the system (see Ref. [4]). To find the next term in the expansion (1.1) one has to know the dependence of δ on a .

The Tolman equation (1.1) provides a thermodynamic basis for calculation of the curvature dependence of interfacial tension. The next step is to determine δ_0 for a specified system by means of a statistical mechanical model. Kirkwood and Buff [5] calculated $\delta_0=3.63 \text{ \AA}$ for the surface of liquid argon at 90 K. They used a modified Lennard–Jones potential along with an analytical expression for the pair correlation function based on experimental data from X-ray diffraction. For the same system, Hill [6] calculated $\delta_0=2.81 \text{ \AA}$ by utilizing an alternative quasi-thermodynamic approach. Plesner and Platz [7] have used the procedure of Hill in combination with a different equation of state. They calculated $\delta_0=2.01 \text{ \AA}$ for liquid argon at 84 K. Toxvaerd determined values of δ_0 for Lennard–Jones fluids on the grounds of a quasi-thermodynamical approach [8] and of a statistical-mechanical approach [9]. The latter approach yields δ_0 twice as great as the former. This difference is due to some peculiarities in the pressure tensor profile obtained in Ref. [9], which are not confirmed by the molecular dynamics computer simulations [10].

The theoretical models of different authors cited above predict not only values for δ_0 , but also for γ_0 . The latter as a rule are in poor agreement with the experimental values of the interfacial tension. Most probably this is due to different simplifications adopted in the models in question. As far as we know, the first statistical mechanical model providing an excellent agreement with the experiment (with respect to γ_0) is that of Croxton and Ferrier [11]. These authors calculated also $\delta_0=3.84 \text{ \AA}$ for liquid argon at 84.3 K.

Rusanov and Brodskaya [12,13] investigated the surface tension of very small drops by the molecular dynamics method. In their computer simulations they used no more than 500 molecules incorporated in a spherical droplet. They used the intermolecular Lennard–Jones potential and confirmed that the interfacial tension decreases with decreasing droplet radius, i.e. δ_0 is positive. Thompson et al. [10] also used the method of molecular dynamics in conjunction with the “shifted” Lennard–Jones potential but they studied larger droplets — up to 2048 molecules. These authors calculated more precise pressure tensor distributions and dependences of the surface tension on curvature, con-

firming the results in Ref. [13]. A positive δ_0 was obtained also in the computer simulations by Powles et al. [14], who introduced an alternative approach connected with the Kelvin formula for the vapor pressure of small drops.

A different approach to the same problem was developed by Falls et al. [15]. They used the van der Waals equation of state together with a statistical model based on the gradient approximation [16] to calculate the pressure tensor distribution, $\gamma(a_s)$ and $\delta(a_s)$. The main results are in qualitative agreement with the data from the molecular dynamics quoted above.

Hemingway et al. [17,18] developed the penetrable-sphere model, for which δ can be obtained explicitly in the mean-field approximation. Surprisingly, this model yielded negative values of δ_0 which could be due to the admittedly unrealistic Hamiltonian. These results led the authors to some doubts about the validity of Eqn (1.3). Fisher and Wortis [19] studied the problem and concluded that within the approximations of Landau theory there seems to be no reason to doubt the validity of Eqn (1.3).

There have been several attempts at the experimental measurement of δ_0 . In all of them some indirect data for the curvature dependence of the interfacial tension are processed in accordance with the Tolman equation [Eqn (1.1)]. Nielsen et al. [20,21] determined δ_0 for some emulsion systems containing water, oil and alcohol; in particular they found $\delta_0 = 2.4 \text{ \AA}$ for tribromomethane/water-methanol and $\delta_0 = -1.3 \text{ \AA}$ for 1,2-dichlorobenzene/water-methanol. Fisher and Israelachvili found a change of γ with a , with $\delta > 0$, for cyclohexane [22], but could detect no change with water [23]. Wingrave et al. [24] calculated curvature-dependent surface tensions for hydrodynamic liquid imbibition in initially evacuated mesoporous Vycor spheres. These authors found δ_0 ranging from 1 \AA to 10 \AA for the various liquids studied.

A new interest in the curvature effects on interfacial tension was awakened by the experiments with microemulsions (see the work by Overbeek et al. [25] and the references therein). The microemulsion droplets not only have high curvature, but also they exhibit a very low interfacial tension. Therefore the curvature effect turns out to be important.

An approach to the curvature effect on the interfacial tension, which can be applied to microemulsions, is connected with the so-called interfacial bending moment, B (see for example Refs [26,27]). Its limiting value for a flat interface is simply connected with the Tolman length [28,29]:

$$B_0 = 2\gamma_0\delta_0 \quad (1.6)$$

The electrostatic, van der Waals and steric interactions yield contributions to the total bending moment B . For a typical microemulsion B can be represented in the form [29]

$$B = B_s + B_c + B_e + B_p \quad (1.7)$$

where the four terms in the right-hand side account for the contribution of the

surfactant, cosurfactant, electrolyte and the two pure immiscible liquids (oil and water). The last contribution, B_p , which is due to the van der Waals interaction between the two liquids, can be of the order of the electrostatic contribution [29], but it has not been accounted for in the available theories of microemulsions [25].

Our aim in the present series of two papers is to express explicitly the interfacial bending moment, B , and the Tolman length, δ , for the interface between two immiscible fluids (without adsorbed surfactants) through the Hamaker constants of the two liquids and the interfacial tension, γ_0 , of the flat interface. In other words, our purpose is to calculate B and δ , but not γ_0 (the value of γ_0 is usually available by experiment). For that purpose we will use the expressions

$$\gamma = \frac{1}{3} \int_0^{\infty} \Delta P(r) \left(\frac{2a_x}{r} + \frac{r^2}{a_x^2} \right) dr \quad (1.8)$$

and

$$B = \frac{2}{3} \int_0^{\infty} \Delta P(r) \left(\frac{a_x^2}{r} - \frac{r^2}{a_x} \right) dr \quad (1.9)$$

derived in Ref. [27]. Here a_x is the radius of an arbitrary dividing surface and

$$\Delta P = P_N - P_T \quad (1.10)$$

represents the anisotropy of the pressure tensor with P_N and P_T being its normal and transversal components (see for example Refs [2,30]). Equations (1.8) and (1.9) are generalized for arbitrarily curved (non-spherical) interfaces in Ref. [31].

One can check that γ and B in Eqns (1.8) and (1.9) satisfy the relation [26]

$$B = a_x^2 \left(\frac{\partial \gamma}{\partial a_x} \right) \quad (1.11)$$

Equation (1.11) can be considered as a thermodynamic definition for the interfacial bending moment. In particular, Eqns (1.4) and (1.11) show that B is identically zero for the surface of tension.

It is worthwhile noting that the presence of the interfacial bending moment leads to a difference between the thermodynamical and mechanical interfacial tensions, γ and σ :

$$\sigma = \gamma + \frac{B}{2a_x} \quad (1.12)$$

(see Ref. [27] for more details). By substitution from Eqns (1.8) and (1.9) into Eqn (1.12), one can represent the mechanical interfacial tension also in

the form of an integral over the pressure tensor anisotropy ΔP (see Eqn (2.4) below).

There are different statistical models for calculation of the pressure tensor [3,32–34]. They differ because of the different choices of the contour joining two interacting molecules. Some authors [3,17] interpret this fact as an arbitrariness in the definition of the pressure tensor, leading to arbitrariness in the mechanical definition of the Tolman length. Our viewpoint is somewhat different. The validity of many results in molecular physics (like the expressions for the pressure tensor) is limited to the reliability of the statistical model used. In such a situation only experiment can decide which is the best model expression for the pressure tensor. In as far as an experimental indication is still missing, we will make use below of the conceptually most simple expression of Irving and Kirkwood [32].

Our approach for determining ΔP consists of the following. The asymptotic behavior of ΔP far from the interface is determined by means of the Irving–Kirkwood expression along with the attractive part of the Lennard–Jones intermolecular potential. (This is done in the present paper.) A model expression for the behavior of ΔP close to the interface is constructed under the thermodynamic restriction to yield γ , satisfying Eqn (1.5) for all radii a and $\gamma = \gamma_0$ for a flat interface (cf. also Eqn (1.8)). In the second part [35] of this study the resulting expression for ΔP is applied to calculate the interfacial bending moment B and the Tolman length δ for various liquid/gas and oil/water interfaces. Of course, this calculation gives only the contribution of the van der Waals forces to the interfacial bending moment of a microemulsion droplet, denoted by B_p in Eqn (1.7). The other terms in Eqn (1.7) can be calculated as explained in Ref. [29].

2. THERMODYNAMIC DESCRIPTION OF THE SYSTEM

The system under consideration consists of a spherical drop (or bubble), phase I, surrounded by another fluid phase (phase II). We will suppose that the phase I is composed only of pure component 1 and phase II is composed only of pure component 2. Then at constant temperature the Gibbs adsorption equation reads [2,4]

$$d\gamma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 + \left(\frac{\partial \gamma}{\partial a_x} \right) da_x \quad (2.1)$$

As earlier, a_x is the radius of an arbitrarily chosen spherical dividing surface; Γ_1 and Γ_2 are the respective adsorptions of the two components; μ_1 and μ_2 are their chemical potentials.

Let us choose a_x to be equal to the radius, a , of the equimolecular dividing surface with respect to the component 1. In other words a is defined in such a way that

$$\Gamma_1|_{a_x=a} = 0 \quad (2.2)$$

We will consider changes in a at constant chemical potential in the outer phase, i.e.

$$\mu_2 = \text{constant} \quad (2.3)$$

The substitution from Eqns (2.2) and (2.3) into Eqn (2.1) leads to Eqn (1.5). Our purpose below is to examine the restrictions implied on a model expression for $\Delta P(r, a)$ by the general thermodynamic equation (1.5).

From Eqns (1.8), (1.9) and (1.12) it follows that

$$\sigma(a_x) = \int_0^{\infty} \Delta P(r, a) \frac{a_x}{r} dr \quad (2.4)$$

Besides, Eqns (1.8) and (2.4) yield

$$\gamma(a_x) = \frac{2}{3} \sigma(a_x) + \frac{1}{3} J(a_x) \quad (2.5)$$

where

$$J(a_x) = \int_0^{\infty} \Delta P(r, a) \frac{r^2}{a_x^2} dr \quad (2.6)$$

From Eqns (2.4) and (2.6) one easily derives

$$\sigma(a_x) = \frac{a_x}{a} \sigma(a) \quad J(a_x) = \frac{a^2}{a_x^2} J(a) \quad (2.7)$$

The derivative $(\partial\gamma/\partial a_x)$ in the left-hand side of the Eqn (1.5) corresponds to differentiation with respect to a_x when all physical parameters, including a , are constant. Then from Eqns (2.5) and (2.7) one derives

$$\left(\frac{\partial\gamma(a_x)}{\partial a_x} \right)_{a_x=a} = \frac{2}{3} \frac{1}{a} (\sigma(a) - J(a)) \quad (2.8)$$

On the other hand, a substitution $a_x = a$ in Eqn (2.5) followed by differentiation yields

$$\frac{\partial\gamma}{\partial a} = \frac{2}{3} \frac{d\sigma(a)}{da} + \frac{1}{3} \frac{dJ(a)}{da} \quad (2.9)$$

Finally, from Eqns (1.5), (2.8) and (2.9) one obtains

$$J(a) + \frac{1}{2} a \frac{dJ(a)}{da} = \sigma(a) - a \frac{d\sigma(a)}{da} \quad (2.10)$$

Having in mind Eqns (2.4) and (2.6) one can conclude that Eqn (2.10) imposes a restriction on the function $\Delta P(r,a)$.

Let b be a parameter characterizing the width of the transition region between the phases I and II. Then

$$\epsilon = b/a \quad (2.11)$$

will be a small parameter for not too small radii a . In view of (2.11), Eqn (2.10) can be transformed to read

$$J - \frac{1}{2}\epsilon \frac{dJ}{d\epsilon} = \sigma + \epsilon \frac{d\sigma}{d\epsilon} \quad (2.12)$$

In general, one can seek $J(\epsilon)$ and $\sigma(\epsilon)$ in the form of asymptotic expansions

$$J(\epsilon) = \sum_{n=0}^{\infty} J_n g_n(\epsilon) \quad \sigma(\epsilon) = \sum_{n=0}^{\infty} \sigma_n g_n(\epsilon) \quad (2.13)$$

for small ϵ . Here $g_n(\epsilon)$ where $n=0, 1, 2, \dots$, is an asymptotic sequence of gauge functions (see for example Ref. [36] for the general theory of asymptotic expansions); J_n and σ_n are coefficients. The substitution from Eqn (2.13) into Eqn (2.12), in principle, provides a series of equations for determining J_n and σ_n . Such an approach based on Eqn (2.12) is applied in the second part of this study [35]. Below we will investigate the asymptotic behavior of $\Delta P(r,a)$ far from the interface. This investigation will enable us to find the gauge functions $g_n(\epsilon)$ where $n=0, 1, 2, \dots$.

3. OUTER AND INNER REGIONS

It is known [2,3,30] that in the narrow transition zone between two fluid phases the density deviates from its values in the bulk of the phases. Below we will call the "inner" region the interfacial region where the density substantially changes. Besides, we will suppose that this inner region is contained in the interval $a-b \leq r \leq a+b$, where r is a radial coordinate accounted from the center of the spherical drop. $2b$ characterizes the width of the inner region with respect to the density profile. Alternatively, the region $0 \leq r < a-b$ of phase I and the region $a+b < r < \infty$ of phase II will be called "outer" regions I and II, respectively. The changes in the density are negligible in the outer regions.

As shown schematically in Fig. 1 the anisotropy of the pressure tensor is well pronounced in the inner region (see for example Refs [2,9,10,15]). The anisotropy vanishes in the outer regions, which contain only the "tails" of ΔP . As discussed by Rusanov [37] the width of the region, where the anisotropy of ΔP is not negligible, is one order of magnitude larger than $2b$. Therefore the contribution of the outer regions to the integrals σ and J in Eqns (2.4) and (2.6) cannot be a priori neglected. Accordingly, one can write

$$\sigma(a) = \sigma^I(a) + \sigma^{\text{in}}(a) + \sigma^{\text{II}}(a) \quad (3.1)$$

$$J(a) = J^I(a) + J^{\text{in}}(a) + J^{\text{II}}(a) \quad (3.2)$$

where

$$\sigma^I(a) = \int_0^{a-b} \Delta P^I(r,a) \frac{a}{r} dr \quad J^I(a) = \int_0^{a-b} \Delta P^I(r,a) \frac{r^2}{a^2} dr \quad (3.3)$$

$$\sigma^{\text{in}}(a) = \int_{a-b}^{a+b} \Delta P^{\text{in}}(r,a) \frac{a}{r} dr \quad J^{\text{in}}(a) = \int_{a-b}^{a+b} \Delta P^{\text{in}}(r,a) \frac{r^2}{a^2} dr \quad (3.4)$$

$$\sigma^{\text{II}}(a) = \int_{a+b}^{\infty} \Delta P^{\text{II}}(r,a) \frac{a}{r} dr \quad J^{\text{II}}(a) = \int_{a+b}^{\infty} \Delta P^{\text{II}}(r,a) \frac{r^2}{a^2} dr \quad (3.5)$$

Here the superscripts "I", "II" or "in" denote the values of $\Delta P(r,a)$ in the

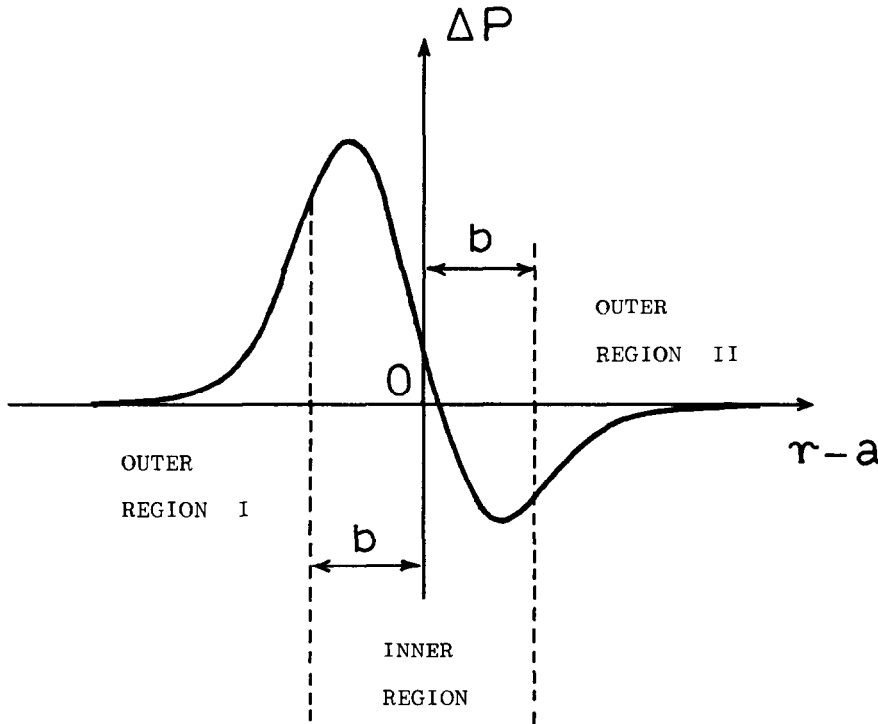


Fig. 1. Sketch of the anisotropy of the pressure tensor distribution, $\Delta P = P_N - P_T$, as a function of the distance to the equimolecular dividing surface, in a system of two neighboring fluid phases; b represents the half-width of the transition region.

respective regions. Model expressions for ΔP^I and ΔP^{II} are derived below, whereas ΔP^{in} is considered in the second part [35] of this study. The parameter b is also liable to determination in the framework of our model: values of b for different liquid–liquid interfaces are listed in Tables 2 and 3 of Part II [35].

4. MODEL FOR CALCULATION OF ΔP^I AND ΔP^{II}

A rigorous asymptotic expression for ΔP far from a flat interface was derived by Kuni and Rusanov [38,39] for van der Waals interactions. The leading term of this asymptote (in our notation) reads

$$\Delta P^I = \frac{1}{8\pi} A_1 \frac{1}{y^3} \quad (4.1)$$

$$\Delta P^{II} = \frac{1}{8\pi} A_2 \frac{1}{y^3} \quad (4.2)$$

where y is the absolute value of the distance to the interface and

$$A_1 = \pi^2 (\alpha_{11}\rho_1^2 - \alpha_{12}\rho_1\rho_2) \quad (4.3)$$

$$A_2 = \pi^2 (\alpha_{22}\rho_2^2 - \alpha_{12}\rho_1\rho_2) \quad (4.4)$$

with ρ_1, ρ_2 being the number densities of the two bulk phases and α_{ij} ($i, j = 1, 2$) being the London constants of interaction between two molecules from the respective components (phases). It should be noted that some approximate statistical theories yield an exponential decay both of the pressure tensor and of the density profile (see for example [40]). However, as pointed out by many authors [41], exponential tails are not the correct behavior for both these profiles. The right asymptotes decay proportionally to y^{-3} (see Ref. [39]).

Asymptotes similar to Eqns (4.1), (4.2) have been derived by Kuni and Rusanov [39,42] for the case of slightly curved interfaces ($b \ll y \ll a$), which is not the case considered here. In our case $b \ll a$ but y and a are quantities of comparable magnitude. We will derive expressions for $\Delta P^I(r, a)$ and $\Delta P^{II}(r, a)$ by using the Irving–Kirkwood equation for the pressure tensor [2,3,32]:

$$\mathbf{P}(\mathbf{r}) = k_B T \sum_{i=1}^2 \rho_i(\mathbf{r}) \mathbf{U} - \frac{1}{2} \sum_{i,j=1}^2 \int d\mathbf{R} \int_0^1 d\eta \frac{\mathbf{R}\mathbf{R}}{R} \frac{d\varphi_{ij}}{dR} \rho_{ij}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \quad (4.5)$$

Here \mathbf{U} is a three-dimensional idemfactor, k_B is the Boltzmann constant, T is temperature, ρ_i and $\rho_{ij}^{(2)}$ are the singlet and pair distribution functions for the respective components, \mathbf{R} is a vector connecting two molecules of components i and j having a potential energy of the van der Waals interaction

$$\varphi_{ij} = -\frac{\alpha_{ij}}{R^6} \quad (4.6)$$

$$R = |\mathbf{R}| = |\mathbf{r}_1 - \mathbf{r}_2| \quad (4.7)$$

(see Fig. 2). The position vectors

$$\mathbf{r}_1 = \mathbf{r} - \eta \mathbf{R} \quad \mathbf{r}_2 = \mathbf{r} + (1 - \eta) \mathbf{R} \quad (4.8)$$

determine the location of the two molecules. By definition [43]

$$\rho_{ij}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \rho_i(\mathbf{r}_1) \rho_j(\mathbf{r}_2) g_{ij}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \quad (4.9)$$

where $g_{ij}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ is the pair correlation function.

It should be noted that the integral term in Eqn (4.5) corresponds to a specified model for calculation of the contribution of the intermolecular interaction to the pressure tensor \mathbf{P} . Other possible models are considered in the works by Kirkwood and Buff [5], Harasima [33], Schofield and Henderson [34]. The different models correspond to different choices of a contour joining the interacting molecules. The expression of Irving and Kirkwood (4.5), corresponding to a straight line (Fig. 2), is the most natural, and the one generally used [3].

In the case of a spherical drop it is convenient to introduce spherical integral variables R , θ , φ (see Fig. 2). By carrying out the integration with respect to the azimuthal angle φ one can derive from Eqns (1.10), (4.5) and (4.6)

$$\Delta P(\mathbf{r}) = 3\pi \int_{-1}^1 d\beta (1 - 3\beta^2) \int_0^1 d\eta \int_0^\infty \frac{dR}{R^4} \hat{\rho}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \quad (4.10)$$

where

$$\hat{\rho}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i,j=1}^2 \alpha_{ij} \rho_{ij}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$$

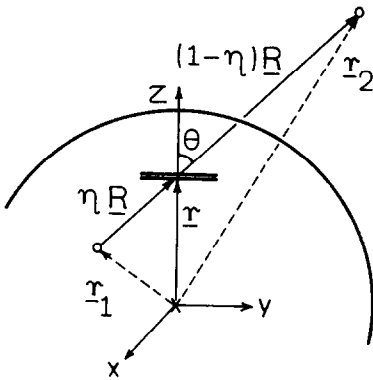


Fig. 2. Sketch for calculation of the Irving-Kirkwood pressure tensor in a two-phase system of spherical symmetry, at the point specified by the position vector \mathbf{r} . The two interacting points \mathbf{r}_1 and \mathbf{r}_2 are connected by the vector \mathbf{R} , the latter passing through the point \mathbf{r} .

and $\beta = \cos\theta$ (the angle θ is shown in Fig. 2). We will use also the notation

$$r = |\mathbf{r}| \quad r_1 = |\mathbf{r}_1| \quad r_2 = |\mathbf{r}_2| \quad (4.11)$$

To determine $\Delta P(\mathbf{r})$ from Eqn (4.9) one needs a model expression for $\hat{\rho}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$. Since we seek asymptotic formulae for ΔP in the outer regions, where $|r-a| \gg b$, we will use the following model expression:

$$\hat{\rho}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \begin{cases} \alpha_{11}\rho_1^2\theta(R-\delta_1) & \text{for } r_1, r_2 < a \\ \alpha_{22}\rho_2^2\theta(R-\delta_2) & \text{for } r_1, r_2 > a \\ \alpha_{12}\rho_1\rho_2 & \text{for } r_i > a, r_j < a; i \neq j; i, j = 1, 2 \end{cases} \quad (4.12)$$

$$\hat{\rho}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \begin{cases} \alpha_{22}\rho_2^2\theta(R-\delta_2) & \text{for } r_1, r_2 > a \\ \alpha_{12}\rho_1\rho_2 & \text{for } r_i > a, r_j < a; i \neq j; i, j = 1, 2 \end{cases} \quad (4.13)$$

$$\hat{\rho}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \begin{cases} \alpha_{12}\rho_1\rho_2 & \text{for } r_i > a, r_j < a; i \neq j; i, j = 1, 2 \end{cases} \quad (4.14)$$

Here δ_1 and δ_2 characterize the distance of the closest approach of two molecules of the component 1 or 2, and

$$\theta(x) = \begin{cases} 1 & \text{for } x > 0 \\ 0 & \text{for } x < 0 \end{cases} \quad (4.15)$$

is the step-wise function of Heaviside. ρ_1 and ρ_2 are the number densities in the respective bulk phases.

The expressions (4.12)–(4.14) call for some discussion. As far as the outer regions are considered, a step-wise density profile is supposed in Eqn (4.9). (Such a profile is not appropriate for the inner region, which is considered separately in Part II [35].) The correlation function in Eqn (4.9) is taken to be equal to unity in accordance with the outer asymptotic expansion [39,44,45]

$$g(R) = 1 + O\left(\frac{1}{R^6}\right)$$

for the van der Waals interaction. δ_1 and δ_2 play the role of cut-off parameters, accounting for the short range repulsion in the correlation function. (Note that φ_{ij} in Eqn (4.6) is divergent for $R \rightarrow 0$.) It is not necessary to introduce a similar cut-off parameter in Eqn (4.14) because one molecule of component 1 situated in the outer region I cannot be in close contact with a molecule of component 2 from the other phase II and vice versa. In other words, the width of the transition region b is greater than δ_i ($i=1, 2$); this is a natural assumption [37]. We will note in advance that the resulting expressions for ΔP^I and ΔP^{II} , which follow from Eqns (4.12)–(4.14), do not depend on δ_1 and δ_2 , as could be anticipated (see Eqns (5.5) and (6.5) below). (Indeed, an outer asymptotic expression accounting for the long-range interactions cannot depend on the short-range repulsion, characterized by δ_1 and δ_2 .)

The introduction of new integration variables

$$s = \eta R \quad t = (1 - \eta)R \quad (4.16)$$

in Eqn (4.10) leads to

$$\Delta P(\mathbf{r}) = 6\pi \int_0^1 d\beta (1 - 3\beta^2) \int_0^\infty ds \int_0^\infty dt \frac{1}{(s+t)^5} \hat{\rho}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \quad (4.17)$$

It follows from Eqns (4.8), (4.11) and (4.16) that

$$r_1^2 = r^2 + s^2 - 2\beta rs \quad (4.18)$$

$$r_2^2 = r^2 + t^2 + 2\beta rt \quad (4.19)$$

The substitution from Eqns (4.12)–(4.14) into (4.17) provides simple explicit expressions for ΔP^I and ΔP^{II} , which are derived below.

5. OUTER REGION I

The outer region I corresponds to

$$0 < r < a - b \quad (5.1)$$

In view of Eqns (4.18) and (4.19) one has $r_1^2 = r_1^2(s)$ and $r_2^2 = r_2^2(t)$ at constant r and β . These two functions are sketched in Figs. 3(a) and 3(b).

$$s_0 = \beta r + \sqrt{\beta^2 r^2 + a^2 - r^2} \quad (5.2)$$

and

$$t_0 = -\beta r + \sqrt{\beta^2 r^2 + a^2 - r^2} \quad (5.3)$$

are roots of the equations $r_1^2(s) = a^2$ and $r_2^2(t) = a^2$. The lines $s = s_0$ and $t = t_0$ divide the integration domain ($s > 0, t > 0$) in Eqn (4.17) into four parts: (11), (12), (21) and (22) (see Fig. 3(c)). In the part (11), $\hat{\rho}^{(2)}$ is to be calculated by using Eqn (4.12); in the part (22), by using Eqn (4.13), and in the parts (12) and (21), by using Eqn (4.14). Then Eqn (4.17) for $r < a - b$ can be transformed to read

$$\begin{aligned} \Delta P^I(r, a) = & 6\pi \int_0^1 d\beta (1 - 3\beta^2) \left\{ \alpha_{11} \rho_1^2 \int_0^{s_0} \int_0^{t_0} \theta(s+t-\delta_1) \right. \\ & + \alpha_{12} \rho_1 \rho_2 \left[\int_0^{s_0} \int_{t_0}^\infty + \int_{s_0}^\infty \int_0^{t_0} \right] + \alpha_{22} \rho_2^2 \int_{s_0}^\infty \int_{t_0}^\infty \left. \right\} \frac{ds dt}{(s+t)^5} \quad (5.4) \end{aligned}$$

All integrals in Eqn (5.4) can be solved in terms of elementary functions. The result reads

$$\Delta P^I(r,a) = -\frac{1}{8\pi a^3} \left\{ A_1 \left[\frac{3-8k^2-3k^4}{k^2(1-k^2)^3} + \frac{3}{2k^3} \ln \frac{1-k}{1+k} \right] - \frac{A}{2} \left[\frac{3-2k^2}{k^2(1-k^2)} + \frac{3}{2k^3} \ln \frac{1-k}{1+k} \right] \right\} \quad (5.5)$$

where

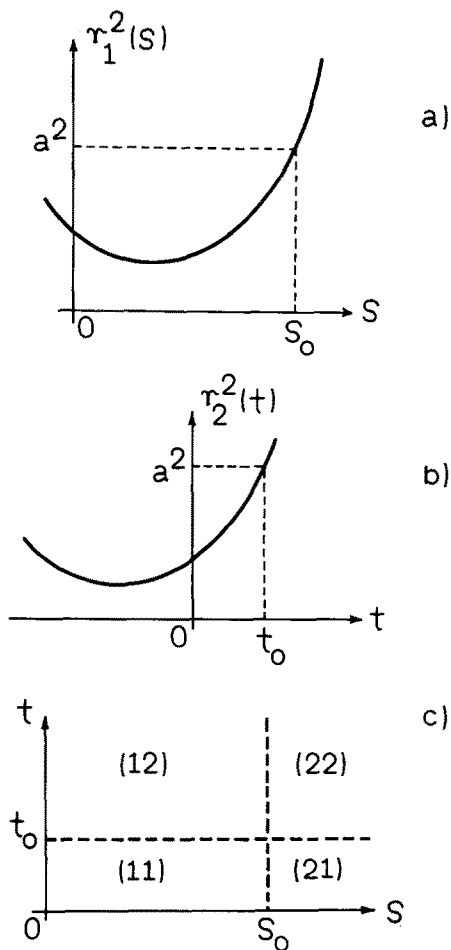


Fig. 3. Outer region I: $r < a - b$. (a) Sketch of the function $r_1^2(s)$ [Eqn (4.18)]. For $s < s_0$ the point r_1 is in the phase I; for $s > s_0$ the point r_1 is in the phase II. (b) Sketch of the function $r_2^2(t)$ [Eqn (4.19)]. For $t < t_0$ the point r_2 is in the phase I; for $t > t_0$ the point r_2 is in the phase II. (c) Parts of the integration domain in Eqn (4.17). Region (11): $r_1 < a$ and $r_2 < a$. Region (12): $r_1 < a$ and $r_2 > a$. Region (21): $r_1 > a$ and $r_2 < a$. Region (22): $r_1 > a$ and $r_2 > a$.

$$k = r/a \quad (5.6)$$

$$A = \pi^2 (\alpha_{11} \rho_1^2 + \alpha_{22} \rho_2^2 - 2\alpha_{12} \rho_1 \rho_2) \quad (5.7)$$

is the Hamaker constant and A_1 is given by Eqn (4.3). In particular, δ_1 does not take part in Eqn (5.5) because

$$\int_0^{s_0} \int_0^{t_0} \theta(s+t-\delta_1) \frac{ds dt}{(s+t)^5} = \frac{1}{12} \left[\frac{4}{\delta_1^3} - \frac{1}{s_0^3} - \frac{1}{t_0^3} + \frac{1}{(s_0+t_0)^3} \right]$$

and

$$\int_0^1 d\beta (1-3\beta^2) = 0 \quad (5.8)$$

Equation (5.5) is the sought for expression for $\Delta P^I(r, a)$. Owing to the isotropy of the pressure tensor at the drop center, one should expect that $\Delta P^I(0, a) = 0$. Indeed, from Eqn (5.5) one derives

$$\Delta P^I(r, a) = -\frac{1}{40\pi} \frac{1}{a^3} (A + 48A_1) k^2 + O(k^4) \quad (5.9)$$

for $k \ll 1$.

The limit of Eqn (5.5) for a flat interface can be obtained by substituting $k = 1 - y/a$ (with $y = a - r$) and by running a to infinity at fixed y in Eqn (5.5). As a result one obtains Eqn (4.1), as could be expected.

6. OUTER REGION II

The outer region II corresponds to

$$a + b < r < \infty \quad (6.1)$$

From Eqns (4.19) and (6.1) it follows that

$$r_2(t) > a \quad \text{for } t \geq 0 \text{ and } 0 \leq \beta \leq 1 \quad (6.2)$$

However, $r_1(s) > a$ only when $\beta < (1 - a^2/r^2)^{1/2}$ (see Fig. 4(a)). When $(1 - a^2/r^2)^{1/2} < \beta \leq 1$ the equation $r_1^2(s) = a^2$ has two roots: s_0 and s_1 (see Fig. 4(b)); s_0 is given by Eqn (5.2), and

$$s_1 = \beta r - \sqrt{\beta^2 r^2 + a^2 - r^2} \quad (6.3)$$

The vertical lines $s = s_0$ and $s = s_1$ divide the integration domain ($s > 0, t > 0$) in Eqn (4.17) into three parts (see Fig. 4(c)). Then, having in mind Eqns (4.12)–(4.14), (6.1) and Fig. 4(c), one can transform Eqn (4.17) to read

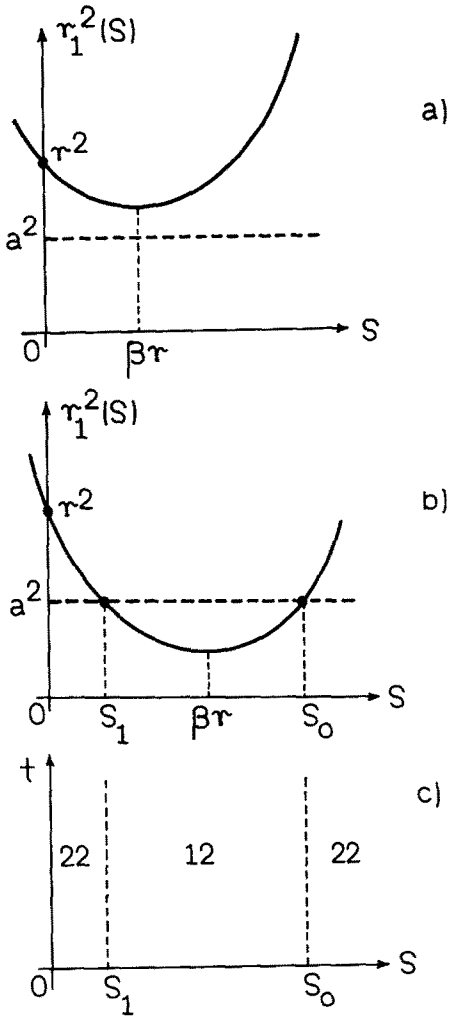


Fig. 4. Outer region II: $r > a + b$. (a) Sketch of the function $r_1^2(s)$ [Eqn (4.18)] for $\beta < (1 - a^2/r^2)^{1/2}$. The point r_1 is in the phase II. (b) Sketch of the function $r_1^2(s)$ for $\beta > (1 - a^2/r^2)^{1/2}$. When $s < s_1$ and $s > s_0$ the point r_1 is in the phase II. When $s_1 < s < s_0$ the point r_1 is in the phase I. (c) Parts of the integration domain in Eqn (4.17). Region (12): $r_1 < a$ and $r_2 > a$. Region (22): $r_1 > a$ and $r_2 > a$.

$$\begin{aligned}
 \Delta P^{II}(r, a) = & 6\pi \int_0^{\beta_1} d\beta (1 - 3\beta^2) \alpha_{22} \rho_2^2 \int_0^\infty ds \int_0^\infty dt \frac{\theta(s+t-\delta_2)}{(s+t)^5} + 6\pi \int_{\beta_1}^1 d\beta (1 - 3\beta^2) \\
 & \times \int_0^\infty dt \left\{ \alpha_{22} \rho_2^2 \int_0^{s_1} ds \frac{\theta(s+t-\delta_2)}{(s+t)^5} + \alpha_{12} \rho_1 \rho_2 \int_{s_1}^{s_0} \frac{ds}{(s+t)^5} + \alpha_{22} \rho_2^2 \int_{s_0}^\infty \frac{ds}{(s+t)^5} \right\} \quad (6.4)
 \end{aligned}$$

where $\beta_1 = (1 - a^2/r^2)^{1/2}$. All integrals in Eqn (6.4) can be solved in terms of elementary functions. The result reads

$$\Delta P^{\text{II}}(r,a) = -\frac{A_2}{8\pi a^3} \left[\frac{3 - 8k^2 - 3k^4}{k^2(k^2 - 1)^3} + \frac{3}{2k^3} \ln \frac{k+1}{k-1} \right] \quad (6.5)$$

where A_2 and k are given by Eqns (4.4) and (5.6) respectively. Equation (6.5) is the sought for expression for $\Delta P^{\text{II}}(r,a)$. Far away from the spherical drop (bubble) Eqn (6.5) yields

$$\Delta P^{\text{II}}(r,a) = \frac{2A_2}{\pi a^3} \left[\frac{1}{k^6} + O\left(\frac{1}{k^8}\right) \right], \quad k \gg 1 \quad (6.6)$$

The limit of Eqn (6.5) for a flat interface can be obtained by substituting $k = y/a + 1$ (with $y = r - a$) and by running a to infinity at fixed y in Eqn (6.5). The result coincides with the known Eqn (4.2), as is required.

7. DISCUSSION AND CONCLUDING REMARKS

The main results obtained in this paper are Eqns (5.5) and (6.5) for $\Delta P^{\text{I}}(r,a)$ and $\Delta P^{\text{II}}(r,a)$ in the outer regions I and II (see Fig. 1). (According to Eqn (1.10), $\Delta P = P_{\text{N}} - P_{\text{T}}$ expresses the anisotropy of the pressure tensor.) The expressions (5.5) and (6.5), referring to a spherical interface of radius a , are exact results in the framework of a model, in which the pressure tensor is given by the Irving-Kirkwood formula, Eqn (4.5), and the (modified) pair distribution function $\hat{\rho}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ is expressed by Eqns (4.12)–(4.14). However, from a physical point of view the latter model expression for $\hat{\rho}^{(2)}$ is acceptable only at a sufficiently large distance from the interface ($|r - a| \gg b$), i.e. in the respective two outer regions I and II. In other words, Eqns (5.5) and (6.5) have asymptotic character. Mathematically this fact manifests itself in divergency both of Eqn (5.5) and of Eqn (6.5) for $r \rightarrow a$.

In spite of the fact that Eqns (5.5) and (6.5), as well as their limiting versions, Eqns (5.9) and (6.6), are results of independent interest as asymptotic expressions, they make sense in the framework of the program for calculation of the curvature effects on surface tension, proposed in the first three sections of the paper. The final goal of this program is to calculate the contribution of the van der Waals forces to the curvature effect on surface tension by using only information about the London constants α_{ij} (cf. Eqn (4.6)) and about the surface tension of the flat interface. We attempt to achieve this goal by combining some general results of thermodynamics and statistical mechanics (like Eqns (1.5), (1.8) and (1.9)) with development of an appropriate model. The first step in this direction is made in the present paper. Indeed, the substitution from Eqns (5.5) and (6.5) into Eqns (3.3) and (3.5) provides expressions for the contribution of the outer regions into the surface tension of a

spherical drop (bubble). Expansions of these expressions for small ϵ , similar to Eqn (2.13), lead to a determination of the sequence of gauge functions $\{g_n(a)\}$. Then one can find ΔP in the inner region by using asymptotic expansion with respect to the same gauge functions. This program is realized in the second part of this study [35], where the interfacial bending moment and the distance between the surface of tension and the equimolecular dividing surface are calculated for different fluid-liquid interfaces in the framework of the model. It turns out that the model is in good agreement with the numerical data for liquid argon and water as well with experimental data for the interfacial tension of liquid hydrocarbons/water emulsion interfaces.

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