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Theory of interfacial bending constants

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Abstract

We critically work over the density functional theoretical foundation of the interfacial free energy with curvature terms. For a spherical interface described by a free-energy functional with square-gradient and square-Laplacian terms we find that the grand potentials of the stationary states are given exactly (and only) by pressure–volume and interfacial tension contributions. On the other hand, when the density functional is partially optimized in the subspace of densities with fixed interface position, the resulting effective interface potential acquires in the limit of large radius the customary form of Helfrich. We illustrate our findings with a description for the nucleation of micelles.

1. Introduction

Microemulsions and related lyotropic liquid-crystalline phases possess a mesoscopic structure consisting of immiscible solvent regions bordered by thin fluctuating amphiphile interfaces, and the shape properties of these internal interfaces appear to be essential in determining the macroscopic phase behaviour [1]. In view of this, much theoretical work has been carried out viewing mixtures of amphiphiles with otherwise immiscible solvents as systems of interfacial films where the supporting solvents participate through certain film parameters [1]. Because interfaces formed by amphiphiles often have very small or vanishing tensions, it is important to incorporate in the free energy the contribution from interfacial bending. Consequently, the interfacial free energy is given by the following expression:

$$F_H = \int dS [\gamma - 2\kappa c_0 J + \kappa J^2 + \bar{\kappa} K] \quad (1.1)$$

where dS is the element of area, $J/2$ and K , are, respectively, the mean and the Gaussian curvatures of the surface that represents the interface, and γ , c_0 , κ and $\bar{\kappa}$ are, respectively, the interfacial tension, the spontaneous curvature, the bending rigidity and the saddle-splay constant. (Note that our definition of κ differs from that given in some of the references below by a factor of two.) The Helfrich free energy [2], as equation (1.1) is known, is usually derived, phenomenologically, under the assumption that the bending properties of the interface are those of a continuum thin elastic plate. Equation (1.1) can be viewed as a functional of the

surface curvatures from which equilibrium shapes can be determined. Thus, for given values of the coefficients γ , c_0 , κ and $\bar{\kappa}$, the equilibrium shape of the interfacial film is obtained by minimization of F_H over all possible surface shapes.

There have been several attempts [3, 4] to give a statistical-mechanical foundation to the Helfrich free energy, and the density functional approach has proved to be a powerful tool for achieving this end [4]. The prototypical density functionals in these studies contain terms proportional to the square gradient and the square Laplacian of (one, scalar) order parameter that can be thought to represent the local difference in concentration of the two solvents. As a result of these studies, expressions have been obtained for the quantities involved, such as the spontaneous curvature and the bending rigidities [4]. However, it has been found that in the absence of approximations the equilibrium interfacial coefficients appear defined locally across the interface [4], and that they have a characteristic dependence on the local curvature [4], of the type previously found a long time ago for the surface tension and measured by the length of Tolman [5, 6].

Here we discuss further the nature of the statistical-mechanical basis for the free energy of a curved interface. For concreteness and simplicity of presentation, we describe our analysis in terms of a spherical interface although our derivations apply to more general geometries. We first investigate whether the model free-energy functional complies with the known phenomenological rules for the moments of the pressure tensor that are related to the Laplace equation and to the torque on a slice of the interface [6]. For this purpose we determine exactly the normal and tangential components of this tensor by considering a general deformation of the inhomogeneous fluid [7], and find that the grand potential Ω_{eq} of the equilibrium (or, more generally, for other stationary) states consists of only two terms, a pressure–volume term and an interfacial tension term. The values for the interfacial tension and the position of the Gibbs dividing surface R are fixed by the moment rules. Closer examination of the expression for the equilibrium interfacial tension reproduces the Helfrich form with locally defined interfacial coefficients (i.e. for each position across the interface).

A different approach that we also follow here is that of optimizing the density functional in two steps. In the first step optimization is carried out within the subspace of interfacial order parameter profiles $\phi(r)$ with a fixed value ϕ_R at position R , and we obtain an effective potential $\Omega(R)$ that reproduces for large R the conventional global form of Helfrich. This procedure is similar to that devised some years ago [8] for interfaces near a planar wall and that led to the development of effective interfacial potentials for the study of wetting phenomena [8]. Technically, the grand potential functional contains, in addition to the chemical potential μ (associated with a uniform field), another Lagrange multiplier ν associated with a delta-like potential that fixes the position of the interface. The interfacial coefficients in $\Omega(R)$ have a strong dependence on the choice of the reference value ϕ_R of the order parameter.

We illustrate our findings with a description for the nucleation of micelles. We use a local free-energy density with three minima [9] and find for a suitable model parameter region the occurrence of two nucleation radii, R_1 and R_2 , and a metastable micelle of intermediate radius R_m which may be nucleated from fluctuations within $R_1 < R < R_2$. (The stable phase is a uniform phase.) The stability analysis of these spherical objects has been studied recently [10] for the same model free energy, and agreement with the predictions of that study and those from the effective potential $\Omega(R)$ is obtained.

The outline of the rest of the article is as follows. In the next section we recall the properties of the moments of the pressure tensor for a spherical interface. In section 3 we derive the pressure tensor \mathbf{p} from the grand potential functional $\Omega[T, \mu; \phi(r)]$, where T is the temperature. We obtain the exact expression for the equilibrium grand potential $\Omega_{eq}(T, \mu)$, as well as those for the pressure difference across the interface and the position of the Gibbs

dividing surface. In section 4 we perform the partial optimization of the modified functional $\Omega[T, \mu, \nu; \phi(r; R)]$ and obtain the effective potential $\Omega(R)$, and describe its properties for large R . In section 5 we present a description for the nucleation of micelles in terms of $\Omega(R)$. Section 6 contains a brief discussion.

2. Phenomenological theory

The pressure tensor across an spherical interface has the form

$$\mathbf{p} = p_n \hat{r} \hat{r} + p_t (\hat{\theta} \hat{\theta} + \hat{\varphi} \hat{\varphi}) \quad (2.1)$$

where p_n and p_t are the components along its normal (\hat{r}) and tangential ($\hat{\theta}$, $\hat{\varphi}$) directions, respectively. We recall [6] that the vanishing divergence $\nabla \cdot \mathbf{p} = 0$ implies that

$$\frac{d}{dr} r^k p_n = r^{k-1} ((k-2)p_n + 2p_t) \quad k = 0, 1, \dots \quad (2.2)$$

where r is the radial direction, and from this expression the following properties are obtained. First, integration of equation (2.2) when $k = 0$ yields

$$p_n(0) - p_n(L) = P_{in} - P_{out} = 2 \int_0^L dr r^{-1} (p_n - p_t) \quad (2.3)$$

where L is the linear size of the system and P_{in} and P_{out} are the pressures inside and outside of the spherical droplet, respectively. For equation (2.3) to be in correspondence with the Laplace equation, the ratio of the tension σ to the radius R of the droplet must be

$$\sigma/R = \int_0^L dr r^{-1} (p_n - p_t). \quad (2.4)$$

(Notice that we have used here a different notation for the interfacial tension from that of the previous section: σ instead of γ .) Next, we consider $k = 2$, and note that the force per unit angle on a wedge of the sphere is given by

$$\int_0^L dr r p_t = \frac{1}{2} L^2 P_{out} \quad (2.5)$$

which can be rewritten, after addition and subtraction of equation (2.3), multiplied by $R^2/2$, and use of equation (2.4), as

$$\int_0^L dr r p_t = \frac{1}{2} (L^2 - R^2) P_{out} + \frac{1}{2} R^2 P_{in} - \sigma R. \quad (2.6)$$

Equation (2.6) states that the force evaluated through integration of $r p_t$ is equivalent to the force obtained from three contributions, two from the constant pressures inside and outside the sphere and the third from the interfacial tension. Finally, the case $k = 3$ relates to the moment of the force per unit angle on the wedge:

$$\int_0^L dr r^2 p_t = -\frac{1}{3} \int_0^L dr r^2 (p_n - p_t) + \frac{1}{3} L^3 P_{out} \quad (2.7)$$

which can be rewritten, after addition and subtraction of equation (2.3), multiplied by $R^3/3$, and use of equation (2.4), as

$$\int_0^L dr r^2 p_t = \frac{1}{3} (L^3 - R^3) P_{out} + \frac{1}{3} R^3 P_{in} - \frac{1}{3} \int_0^L dr r^2 (p_n - p_t) - \frac{2}{3} \sigma R^2. \quad (2.8)$$

If we require that the total torque on the wedge consists of a pressure term and an interfacial tension term, i.e.

$$\sigma R^2 = \int_0^L dr r^2 (p_n - p_t) \quad (2.9)$$

equation (2.8) becomes

$$\int_0^L dr r^2 p_t = \frac{1}{3}(L^3 - R^3)P_{out} + \frac{1}{3}R^3 P_{in} + \sigma R^2. \quad (2.10)$$

The values of σ and R can be determined from equations (2.4) and (2.9) provided $0 < \sigma < \infty$ and $0 < R < \infty$; they are

$$\sigma = \left(\int_0^L dr r^2 (p_n - p_t) \right)^{1/3} \left(\int_0^L dr r^{-1} (p_n - p_t) \right)^{2/3} \quad (2.11)$$

and

$$R = \left(\int_0^L dr r^2 (p_n - p_t) \right)^{1/3} \left(\int_0^L dr r^{-1} (p_n - p_t) \right)^{-1/3}. \quad (2.12)$$

When R is large, σ is given by

$$\sigma = \int_{-R}^{L-R} dz (p_n - p_t) \quad (2.13)$$

and R is obtained from the condition

$$\int_0^L dr (r - R)(p_n - p_t) = 0 \quad (2.14)$$

where $r = R + z$. We recognize in equations (2.13) and (2.14) the customary ‘mechanical’ expressions for the surface tension and for the position of the Gibbs dividing surface of a spherical interface [6]. We will return to the expressions for the moments of the pressure tensor components given by equations (2.7) and (2.10) in the next section where we determine the pressure tensor components for our model free-energy functional.

3. Density functional theory

Consider the following form for the grand potential density functional, $\Omega = \int dr \omega(\phi)$, of a single (scalar) order parameter $\phi(\mathbf{r})$:

$$\Omega[\phi(\mathbf{r})] = \int dr \left\{ f(\phi(\mathbf{r})) + \frac{1}{2}A(\phi(\mathbf{r}))(\nabla\phi(\mathbf{r}))^2 - \frac{1}{4}B(\phi(\mathbf{r}))(\nabla^2\phi(\mathbf{r}))^2 - \mu\phi(\mathbf{r}) \right\} \quad (3.1)$$

where $f(\phi)$ is the free-energy density of the uniform system, μ is the chemical potential conjugate to ϕ , and the quantities $A(\phi)$ and $B(\phi)$ are, respectively, proportional to the second and fourth moments of the direct pair correlation function [4]. Our method for deriving an expression for the pressure tensor \mathbf{p} from equation (3.1) is based [7] on the determination of the change in grand potential $\Delta\Omega_V$ that takes place in a subsystem with volume V of the fluid as a vector deformation $\delta\mathbf{r}$ is applied to it. From $\Delta\Omega_V$, obtained in the form of an integral over V of the strain, $\boldsymbol{\varepsilon} = \nabla\delta\mathbf{r}$, times \mathbf{p} , we obtain the sought for expression for the pressure tensor. When the functional contains only the traditional squared gradient term, we recover the known symmetric form for \mathbf{p} [11]. There are two sources for the change $\Delta\Omega_V$: one due to a change in V , $\Delta_V\Omega$, and the other due to a change in ϕ , $\Delta_\phi\Omega$. We can immediately write

$$\Delta_V\Omega = \int_S d\mathbf{r} \omega = \int_S d\mathbf{S} \cdot \delta\mathbf{r} \left[f - \mu\phi + \frac{1}{2}A(\nabla\phi)^2 - \frac{1}{4}B(\nabla^2\phi)^2 \right] \quad (3.2)$$

where S is the surface that encloses V . And by considering that the surfaces $\phi(\mathbf{r}) = \text{constant}$ are moved by the displacement vector $\delta\mathbf{r}$ from $\mathbf{r} - \delta\mathbf{r}$ to \mathbf{r} and that

$$\phi(\mathbf{r} - \delta\mathbf{r}) \simeq \phi(\mathbf{r}) - \nabla\phi \cdot \delta\mathbf{r}$$

we have

$$\begin{aligned} \Delta_\phi\Omega &= \int_V d\mathbf{r} \left(\frac{\partial f}{\partial \phi} - \mu \right) \nabla\phi \cdot \delta\mathbf{r} \\ &\quad - \int_V d\mathbf{r} A \nabla\phi \cdot \nabla(\nabla\phi \cdot \delta\mathbf{r}) + \frac{1}{2} \int_V d\mathbf{r} B \nabla^2\phi \nabla^2(\nabla\phi \cdot \delta\mathbf{r}). \end{aligned} \quad (3.3)$$

After integration by parts and use of the Euler–Lagrange equation associated with equation (3.1) we obtain [7]

$$\begin{aligned} \Delta\Omega_V &\equiv \Delta_V\Omega + \Delta_\phi\Omega = \int_S d\mathbf{S} \cdot \delta\mathbf{r} \cdot \omega(\phi_{st})\mathbf{1} - \int_S d\mathbf{S} \cdot \delta\mathbf{r} \cdot \nabla\phi_{st} A \nabla\phi_{st} \\ &\quad + \frac{1}{2} \int_S d\mathbf{S} \cdot \nabla\nabla\phi_{st} B \nabla^2\phi_{st} \delta\mathbf{r} - \frac{1}{2} \int_S d\mathbf{S} \cdot \nabla\phi_{st} \nabla(B \nabla^2\phi_{st}) \cdot \delta\mathbf{r} \\ &\quad + \frac{1}{2} \int_S d\mathbf{S} \cdot B \nabla^2\phi_{st} \nabla\delta\mathbf{r} \cdot \nabla\phi_{st} \end{aligned} \quad (3.4)$$

where ϕ_{st} is a stationary solution of equation (3.1) and where $\mathbf{1}$ is the unit tensor. This last equation can be cast into the form [7]

$$\Delta\Omega_V = - \int_V d\mathbf{r} \varepsilon : \mathbf{p} + \int_S d\mathbf{S} \varepsilon : \boldsymbol{\tau} \quad (3.5)$$

where \mathbf{p} and $\boldsymbol{\tau}$ are the symmetric tensors

$$\begin{aligned} \mathbf{p} &= -\omega(\phi_{st})\mathbf{1} + \nabla\phi_{st} A \nabla\phi_{st} + \frac{1}{2} \nabla\phi_{st} \nabla(B \nabla^2\phi_{st}) + \frac{1}{2} \nabla(B \nabla^2\phi_{st}) \nabla\phi_{st} \\ &\quad - \frac{1}{2} \nabla(B \nabla^2\phi_{st}) \cdot \nabla\phi_{st} \mathbf{1} - \frac{1}{2} \nabla^2\phi_{st} B \nabla^2\phi_{st} \mathbf{1} \end{aligned} \quad (3.6)$$

and

$$\boldsymbol{\tau} = \frac{1}{2} B \nabla^2\phi_{st} (\hat{\mathbf{n}} \nabla\phi_{st} + \nabla\phi_{st} \hat{\mathbf{n}}) - \frac{1}{2} (\hat{\mathbf{n}} \cdot \nabla\phi_{st}) B \nabla^2\phi_{st} \mathbf{1} \quad (3.7)$$

where $\hat{\mathbf{n}}$ is the unit tensor normal to $\phi_{st}(\mathbf{r}) = \text{constant}$, and where the property $\nabla \cdot \mathbf{p} = 0$ holds. Also, if the strain takes place only in the interior of the region of volume V , i.e. $\delta\mathbf{r} = \text{constant}$ on S , the strain tensor ε vanishes on S and the surface term in $\Delta\Omega_V$ does likewise.

For a spherical interface, equation (3.6) becomes

$$\begin{aligned} \mathbf{p} &= -\omega\mathbf{1} + \hat{\mathbf{r}} A (\phi')^2 \hat{\mathbf{r}} + B \hat{\mathbf{r}} \phi' \frac{d}{dr} \left(\frac{2}{r} \phi' + \phi'' \right) \hat{\mathbf{r}} \\ &\quad - \frac{1}{2} B \left[\phi' \frac{d}{dr} \left(\frac{2}{r} \phi' + \phi'' \right) + \left(\frac{2}{r} \phi' + \phi'' \right)^2 \right] \mathbf{1} \end{aligned} \quad (3.8)$$

where the primes denote differentiation with respect to r . Thus, the normal and tangential components of \mathbf{p} are explicitly given by

$$p_n = -\omega + A(\phi')^2 - \frac{1}{2} B \left[-\phi' \frac{d}{dr} \left(\frac{2}{r} \phi' + \phi'' \right) + \left(\frac{2}{r} \phi' + \phi'' \right)^2 \right] \quad (3.9)$$

and

$$p_t = -\omega - \frac{1}{2}B \left[\phi' \frac{d}{dr} \left(\frac{2}{r} \phi' + \phi'' \right) + \left(\frac{2}{r} \phi' + \phi'' \right)^2 \right]. \quad (3.10)$$

We can now evaluate the moments discussed in the previous section for our model. At the outset we notice that

$$4\pi \int_0^L dr r^2 p_t = -4\pi \int_0^L dr r^2 \omega = -\Omega_{eq} \quad (3.11)$$

which by comparison with equation (2.10) implies that

$$\Omega_{eq} = -P_{in} V_{in} - P_{out} V_{out} + \sigma S \quad (3.12)$$

where $V_{in} = (4\pi/3)R^3$, $V_{out} = (4\pi/3)(L^3 - R^3)$ and $S = 4\pi R^2$. This is the main (and exact) result of this section. That is, for this model the equilibrium grand potential consists of only two types of contribution, the pressure–volume terms $-P_{in} V_{in}$ and $-P_{out} V_{out}$ and the interfacial tension term σS , where σ and R are given by equations (2.11) and (2.12). This result applies generally to all of the stationary states of the grand potential, i.e. the solutions of the Euler–Lagrange equation associated with equation (3.1). We also have

$$4\pi \int_0^L dr r^2 p_n = -P_{in} V_{in} - P_{out} V_{out} \quad (3.13)$$

since

$$4\pi \int_0^L dr r^2 (p_n - p_t) = \sigma S. \quad (3.14)$$

Use of equations (3.9) and (3.10) in equation (3.14), and integration by parts, implies

$$\sigma S = 4\pi \int_0^L dr r^2 [A(\phi')^2 - B(\phi'')^2 + 2B\phi'\phi''/r - 3B(\phi')^2/r^2]. \quad (3.15)$$

This equation can be put in a form similar to that of the Helfrich free-energy equation (1.1) except that the interfacial coefficients are defined locally, i.e.

$$\sigma S = 4\pi \int_0^L dr r^2 [\gamma(r) - 2(\kappa c_0)(r)J + \kappa(r)J^2] \quad (3.16)$$

where the local curvatures are $J = 2/r$ and $K = 1/r^2$ and the local coefficients are

$$\gamma(r) = A(\phi')^2 - B(\phi'')^2 \quad (3.17)$$

$$2(\kappa c_0)(r) = B\phi'\phi'' \quad (3.18)$$

and

$$\kappa(r) = -\bar{\kappa}(r) = -B(\phi')^2. \quad (3.19)$$

As for the pressure difference across the interface, we obtain from

$$2 \int_0^L dr r^{-1} (p_n - p_t) = P_{in} - P_{out} \quad (3.20)$$

the expression

$$P_{in} - P_{out} = \int_0^L dr \left[\frac{2}{r} (A(\phi')^2 - B(\phi'')^2) - \frac{2}{r^2} B\phi'\phi'' - \frac{3}{r^3} B(\phi')^2 \right]$$

or

$$P_{in} - P_{out} = \int_0^\infty dr \left[\frac{2}{r} \gamma(r) + \frac{1}{r^2} (\kappa c_0)(r) + \frac{4}{r^3} \kappa(r) \right]. \quad (3.21)$$

Equations (3.15) and (3.21) have been derived previously by different routes [4, 12]. The position of the Gibbs dividing surface is given by

$$R = \left\{ \int_0^L dr r^2 [A(\phi')^2 - B(\phi'')^2 + 2B\phi'\phi''/r - 4B(\phi')^2/r^2] \right\}^{1/3} \\ \times \left\{ \int_0^L dr \left[\frac{1}{r} (A(\phi')^2 - B(\phi'')^2) - \frac{1}{r^2} B\phi'\phi'' - \frac{2}{r^3} B(\phi')^2 \right] \right\}^{-1/3}. \quad (3.22)$$

4. Effective interface potential

In view of the results presented in the previous section for the equilibrium properties of the spherical interface, it is not essential to derive a Helfrich-type functional to obtain the same results through its optimization. Nevertheless, it is not only instructive but of potential use to do so. Therefore, in order to derive a Helfrich free-energy expression with global coefficients from equation (3.1), we optimize this functional partially, only within the subspace of order parameter profiles $\phi(r)$ with given reference value $\phi_R \equiv \phi(r = R)$, i.e. with fixed interfacial position R . The result $\Omega(R)$ can then be optimized with respect to R to recover the expression for the equilibrium grand potential Ω_{eq} derived in the previous section. Our procedure is best performed by introducing a Lagrange multiplier ν for the constraint ϕ_R , and we consider now our starting free-energy functional to be

$$\Omega[\phi(r; R)] = \Omega[\phi(r)] - \nu R^2 \phi(r = R) = \int dr r^2 (\omega - \nu \delta(r - R) \phi) \quad (4.1)$$

i.e. we seek solutions for the inhomogeneous fluid in the presence of an external potential with the shape of a Dirac delta function at R . For the spherical interface that we are considering, the Euler–Lagrange equation associated with equation (4.1) is

$$\frac{df}{d\phi} - \mu + \frac{dA}{d\phi} (\phi')^2 - \frac{1}{r^2} \frac{d}{dr} (Ar^2 \phi') - \frac{B}{2r^2} \frac{d^2}{dr^2} \left[r^2 \left(\phi'' + \frac{2}{r} \phi' \right) \right] \\ + \frac{B}{r^2} \frac{d}{dr} \left[r \left(\phi'' + \frac{2}{r} \phi' \right) \right] = \nu \delta(r - R). \quad (4.2)$$

Multiplication of equation (4.2) by ϕ' followed by integration with respect to r gives

$$[f - \mu\phi]_a^b = \frac{1}{2} A(\phi')^2 \Big|_a^b - \frac{1}{4} B(\phi'')^2 \Big|_a^b + \frac{1}{2} B(\phi')^2 \left(\phi'' + \frac{2}{r} \phi' \right) \Big|_a^b \\ + \frac{1}{2} B\phi' \left(\phi''' + \frac{4}{r^2} \phi' \right) \Big|_a^b + \int_a^b dr \frac{2}{r} [A(\phi')^2 - B(\phi'')^2] \\ + \int_a^b dr \left[-\frac{2}{r^2} B\phi'\phi'' + \frac{4}{r^3} B(\phi')^2 \right]. \quad (4.3)$$

Evaluating this expression for $a = 0$ and $b = R$ and then for $a = R$ and $b = L$ and taking into account that the third derivative of ϕ is discontinuous at R , with

$$\frac{B}{2} [\phi'''|_{R^+} - \phi'''|_{R^-}] = \nu \quad (4.4)$$

we obtain

$$\Omega(R) = -P_{in} V_{in} - P_{out} V_{out} + 4\pi \left\{ \int_0^L dr r^2 [A(\phi')^2 - B(\phi'')^2] - \int_0^L dr r B\phi'\phi'' \right. \\ \left. + 2 \int_0^L dr \left[A(\phi')^2 - B(\phi'')^2 - \frac{1}{r} B\phi'\phi'' + \frac{2}{r} B(\phi')^2 \right] \left[\frac{R^3 - r^3}{3r} \right] \right\}. \quad (4.5)$$

This is the main result of this section. It is important to notice that the same expression was obtained in reference [12] for the equilibrium profile of the spherical interface (and for general interfacial geometry in reference [4]), but here it holds for the solutions of equation (4.2), those stationary profiles ϕ that satisfy the condition $\phi_R \equiv \phi(r = R)$. Less generally, an expansion of equation (4.5) for large R , using $r = R + z$, and $\phi = \phi_0 + \phi_1/R + \phi_2/R^2$, leads to the expression

$$\begin{aligned} \Omega(R) = & -P_{in}V_{in} - P_{out}V_{out} \\ & + S \left\{ \int_{-R}^{L-R} dz [A(\phi'_0)^2 - B(\phi''_0)^2] + \frac{2}{R} \int_0^L dz z [A(\phi'_0)^2 - B(\phi''_0)^2] \right. \\ & \left. - \frac{1}{R^2} \int dz [A\phi'_0\phi_1 - B\phi''_0\phi'_1] + \frac{1}{R^2} \int dz z^2 [A(\phi'_0)^2 - B(\phi''_0)^2] \right\}. \end{aligned} \quad (4.6)$$

Equation (4.6) is of the Helfrich form:

$$\Omega(R) = -P_{in}V_{in} - P_{out}V_{out} + [\gamma - 2\kappa c_0 J + \kappa J^2 + \bar{\kappa} K] S \quad (4.7)$$

with $J = 2/R$, $K = 1/R^2$ and $S = 4\pi R^2$, and where

$$\gamma = \int dz [A(\phi'_0)^2 - B(\phi''_0)^2] \quad (4.8)$$

$$-2\kappa c_0 = \int dz z [A(\phi'_0)^2 - B(\phi''_0)^2] \quad (4.9)$$

and

$$4\kappa + \bar{\kappa} = \int dz z^2 [A(\phi'_0)^2 - B(\phi''_0)^2] - \int dz [A\phi'_0\phi_1 - B\phi''_0\phi'_1]. \quad (4.10)$$

In obtaining equation (4.6), the following auxiliary relations were employed:

$$\int dz [A\phi'_0\phi'_1 - B\phi''_0\phi''_1] = \int dz z [A(\phi'_0)^2 - B(\phi''_0)^2] \quad (4.11)$$

$$\begin{aligned} 2 \int dz z [A\phi'_0\phi'_1 - B\phi''_0\phi''_1] = & \int dz z^2 [A(\phi'_0)^2 - B(\phi''_0)^2] \\ & - \int dz [A\phi'_0\phi_1 - B\phi''_0\phi'_1] + \int dz B(\phi'_0)^2 \end{aligned} \quad (4.12)$$

and

$$\begin{aligned} \int dz [A\phi'_0\phi'_2 - B\phi''_0\phi''_2] = & 2 \int dz z [A\phi'_0\phi'_1 - B\phi''_0\phi''_1] \\ & + \frac{1}{2} \int dz [A\phi'_0\phi_1 - B\phi''_0\phi'_1] - \frac{1}{2} \int dz [A(\phi'_1)^2 - B(\phi''_1)^2] \\ & - \int dz z^2 [A(\phi'_0)^2 - B(\phi''_0)^2] - \int dz B(\phi'_0)^2. \end{aligned} \quad (4.13)$$

These relations are obtained from the Euler–Lagrange equation (4.2) using $r = R + z$, and $\phi = \phi_0 + \phi_1/R + \phi_2/R^2$, multiplying by either $z\phi'_0$ or $z^2\phi'_0$, and integrating over z [12].

We point out that thus far, no specific choice for the position of the Gibbs dividing surface R has been introduced in deriving $\Omega(R)$ and that the equilibrium R_{eq} obtained from minimization of $\Omega(R)$ is still dependent on ϕ_R .

5. Nucleation of spherical micelles

To illustrate how the effective interface potential $\Omega(R)$ derived above actually works, we consider specific calculations for a model spherical interface. We specify further the grand potential functional $\Omega[\phi]$ in equation (3.1) by adopting the following piecewise-parabolic form for the free-energy density $f(\phi)$ [9]:

$$f = \begin{cases} \lambda_w(\phi - \phi_w)^2 & \phi < \phi_1 \\ \lambda_a\phi^2 + f_0 & \phi_1 < \phi < \phi_2 \\ \lambda_o(\phi - \phi_o)^2 & \phi_2 < \phi \end{cases} \quad (5.1)$$

where the two minima at ϕ_w and ϕ_o represent the uniform equilibrium phases when $\mu = 0$ of solvents w and o , respectively. The height of the central minima at $\phi = 0$ is controlled by the parameter f_0 and decreasing its value has an effect suggestive of addition of amphiphile to the mixture, and when $f_0 = 0$, the minimum at $\phi = 0$ corresponds to an equilibrium solution of the two solvents rich in amphiphile. We assume that A has the stepwise form

$$A = \begin{cases} A_w > 0 & \phi < \phi_1 \\ A_a < 0 & \phi_1 < \phi < \phi_2 \\ A_o > 0 & \phi_2 < \phi \end{cases} \quad (5.2)$$

and B is a constant independent of ϕ . In figure 1 we show the functions $f(\phi)$ and $A(\phi)$ that we used for our calculations described below. Recently [10], the spherical interfaces associated with this functional have been studied and their stability analysed. In a region of parameter values, three distinct solutions $\phi(r)$ are found: two of them are maxima (unstable stationary states) and one is a minimum (stable equilibrium state—actually metastable with respect to a uniform phase) of $\Omega[\phi]$. In figure 2 we show the profile $\phi(r)$ and its first two derivatives $\phi'(r)$ and $\phi''(r)$ for one equilibrium spherical interface. The radii of these solutions were investigated

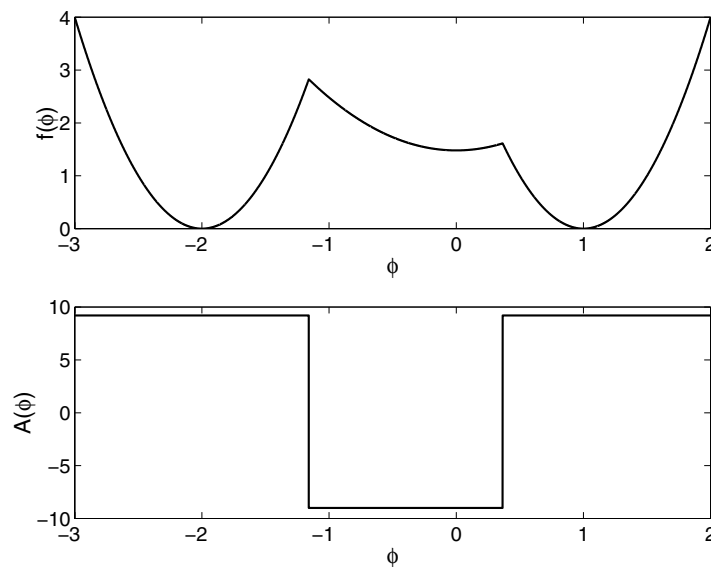


Figure 1. The functions $f(\phi)$ and $A(\phi)$ used for our calculations; $\phi_w = -2$, $\phi_o = 1$, $\lambda_w = 4.6$, $\lambda_a = -4.5$, $\lambda_o = 4.6$, $f_0 = 1.48$, $A_w = 9.2$, $A_a = -9.0$, $A_o = 9.2$, $B = -4$. The values of ϕ_1 and ϕ_2 are determined from continuity conditions for $\phi(r)$ and its derivatives.

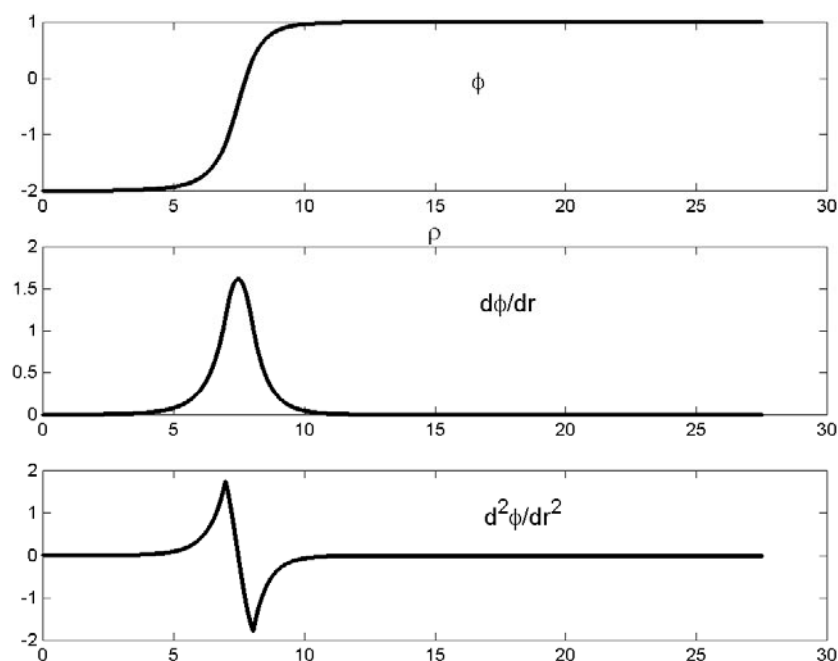


Figure 2. The profile $\phi(r)$ and its first two derivatives $\phi'(r)$ and $\phi''(r)$ for one equilibrium spherical interface with $\mu = 0$.

as functions of f_0 and μ for chosen fixed values of the other model parameters. The existence of the stable and unstable branches accounts for the occurrence of nucleation processes in the model that are descriptive of formation of spherical micelles. Thus, for example, for a fixed value of f_0 and varying μ , the stable solution has a radius R_m bounded by those of the unstable solutions R_1 and R_2 . The unstable solution with the smaller radius R_1 corresponds to the critical nucleation spherical object and the stable one, with intermediate radius R_m , to the equilibrium micelle. The other unstable branch with the larger radius R_2 corresponds to another critical sphere at which nucleation can take place of either the equilibrium micelle or of a uniform phase of infinite radius.

In figure 3 we show the effective interface potential $\Omega(R)$ for fixed f_0 and for various values of μ ; the behaviour described above can be observed for the case where $\mu = -0.014$. In figure 4 we show the effective potential $\Omega(R)$ as calculated for both the exact equation (4.5) and the Helfrich-like large-radius approximation equation (4.6) when $\mu = -0.015$. We observe that the approximate equation (4.6) reproduces fairly accurately the exact equation (4.5) for large and moderate R , this within a large interval that includes the maximum with large radius R_2 and the minimum at R_m ; however, it fails to display the maximum at the small radius R_1 . The results obtained from the exact $\Omega(R)$ are in agreement with those obtained from the stability analysis [10] of spherical interfaces for the same density functional model.

6. Discussion

We have examined the density functional basis of the interfacial free energy with curvature terms. Our analysis was presented for a spherical interface described by a free-energy functional with square-gradient and square-Laplacian terms that is commonly used to study

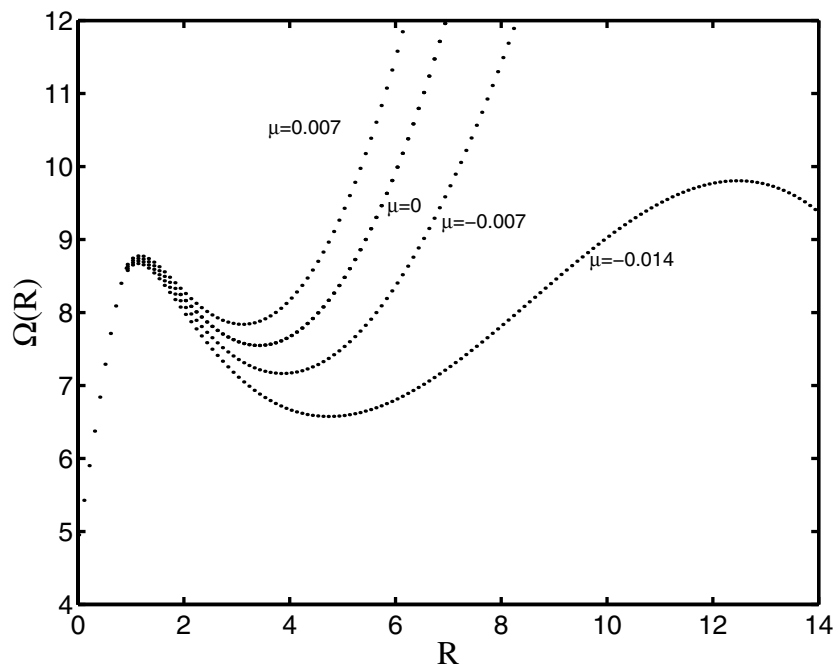


Figure 3. The exact effective interface potential $\Omega(R)$ (equation (4.5)) for $f_0 = 1.48$ and for various values of μ .

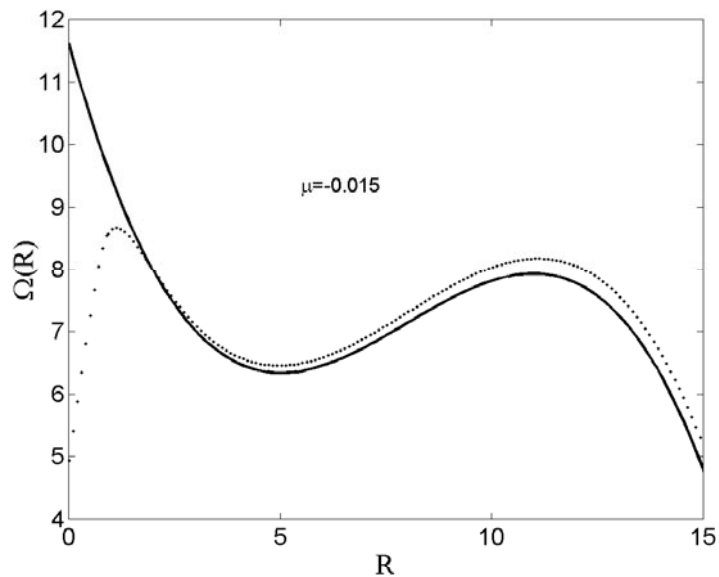


Figure 4. The effective potential $\Omega(R)$ as calculated for both the exact equation (4.5) and the Helfrich-like approximation for large R , equation (4.6), when $\mu = 0.015$.

thin amphiphilic interfaces. As one part of our study, we derived exact expressions for the components of the pressure tensor and we employed them to evaluate their moments. We found that the grand potential of the stationary states is given exactly by the sum of two terms,

i.e. pressure–volume and interfacial tension contributions. The expression for the equilibrium interfacial tension contribution has the form of an integral over the radial variable and the integrand has the Helfrich form but with locally defined interfacial coefficients [4, 13]. Similar expressions were obtained for the pressure difference across the interface [12] and for the position of the Gibbs dividing surface. These results provide a complete and exact solution for the inhomogeneous problem at hand and the method can be similarly applied to other interfacial geometries.

We followed a different procedure to obtain a Helfrich free energy from a density functional theory with the capacity of generating equilibrium interfacial shapes via a variational property. This method consisted of a partial optimization of the grand potential functional in the subspace of interfacial order parameter profiles with a fixed value at a given position R . The result is an effective interface potential $\Omega(R)$ that in the limit of large R acquires the form of Helfrich. The expressions obtained for the interfacial coefficients resemble those obtained previously by other methods [3, 12] but there are important differences that deserve mention. First, all the order parameter profiles $\phi(r)$ that make up $\Omega(R)$ correspond to the same chemical potential μ , including that for the planar interface, ϕ_0 . The equilibrium planar interface requires $\mu = 0$ and we do not introduce in our treatment a chemical potential expansion $\mu = \mu_1/R + \mu_2/R^2$ with respect to $\mu = 0$. We recall [12, 13] that expressing the equilibrium $\phi_{eq}(r)$ for the spherical interface at μ in terms of the equilibrium planar $\phi_{eq}(z)$ at $\mu = 0$ leads to Tolman [5, 6] and higher-order curvature corrections to the surface tension. Second, as a concrete example, we determined the effective potential $\Omega(R)$ for the piecewise-parabolic form of the free-energy density $f(\phi)$ and analysed the occurrence of stationary states for some range of parameters of the model. This specific calculation provided the opportunity of comparison of the exact $\Omega(R)$ with the large- R approximation, and we found that the approximate form reproduces surprisingly well the exact potential for large and intermediate values of R but not for small R where it disagrees strongly with the exact result. The extrema of the exact $\Omega(R)$ coincide with the stationary properties derived in section 3 and therefore are consistent with the Laplace equation $P_{in} - P_{out} = 2\sigma/R$. However, the stationary states of the large- R approximation satisfy a generalized Laplace equation. We recall [4, 12] that optimization of

$$\Omega(J, K) = -P_{in}V_{in} - P_{out}V_{out} + S[\gamma + 2\kappa c_0 J + \kappa J^2 + \bar{\kappa} K] \quad (6.1)$$

leads to the generalized Laplace equation

$$P_{in} - P_{out} = \gamma J_0 - 4\kappa c_0 K_0 - \kappa J_0(J_0^2 - 4K_0) \quad (6.2)$$

where J_0 and K_0 are the curvatures for the extrema of $\Omega(J, K)$. For a spherical surface one has

$$P_{in} - P_{out} = 2\gamma/R_0 - 4\kappa c_0/R_0^2 \quad (6.3)$$

where R_0 is a solution of $\partial\Omega(R)/\partial R = 0$. Therefore, optimization of equation (4.6) with respect to R for fixed coefficients as given by equations (4.8) to (4.10) automatically satisfies the generalized Laplace equation (6.3) while R_0 is still dependent on ϕ_R . Last, we comment on the dependence of the coefficients given by equations (4.8) to (4.10) on the reference value ϕ_R . This dependence can be estimated by considering a small shift in the choice of R , $R \rightarrow R + \delta$. This implies

$$\begin{aligned} \Omega(R + \delta) = & -\frac{4\pi}{3}P_{in}(R + \delta)^3 - \frac{4\pi}{3}P_{out}(L^3 - (R + \delta)^3) \\ & + 4\pi(\gamma(R + \delta)^2 - 4\kappa c_0(R + \delta) + (4\kappa + \bar{\kappa})) \end{aligned} \quad (6.4)$$

and therefore the corresponding shifts in the values of the coefficients are

$$\gamma \rightarrow \gamma + (P_{out} - P_{in})\delta \quad (6.5)$$

$$-4\kappa c_0 \rightarrow -4\kappa c_0 + 2\gamma\delta + (P_{out} - P_{in})\delta^2 \quad (6.6)$$

$$4\kappa + \bar{\kappa} \rightarrow 4\kappa + \bar{\kappa} - 4\kappa c_0\delta + \gamma\delta^2 + \frac{1}{3}(P_{out} - P_{in})\delta^3. \quad (6.7)$$

These shifts have been examined for values of δ of the order of the width of the interfacial profile and it was found that each is of the order of the value of the term in the next order in $1/R$ [12]. In figure 5 we show the dependence of the interfacial coefficients γ , $2\kappa c_0$ and $4\kappa + \bar{\kappa}$, as given by equations (4.8) to (4.10), on the value of the reference ϕ_R .

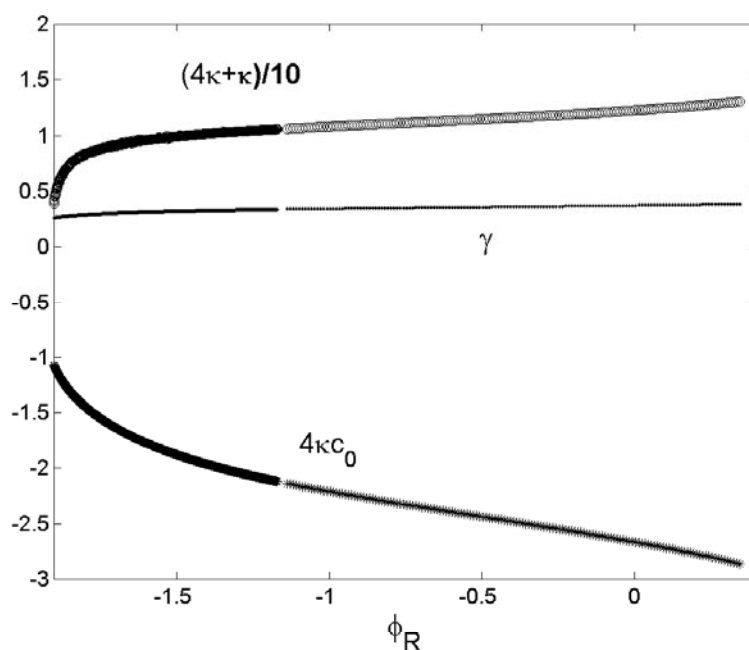


Figure 5. Dependences on the reference ϕ_R of the interfacial coefficients γ , $4\kappa c_0$ and $4\kappa + \bar{\kappa}$, as given by equations (4.8) to (4.10).

Acknowledgment

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