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Correspondence between the pressure expressions and van der Waals theory for a curved surface

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We investigate the apparent contradiction between the pressure expressions, or ‘‘mechanical expressions,’’ and the van der Waals squared-gradient expressions for the curvature coefficients k/R_0, k, and $\bar{k}$. We show that, in the context of the mean-field theory discussed, both types of expression are indeed equivalent, with the differences only being caused by the thermodynamic conditions used to vary the curvature.
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I. INTRODUCTION

The introduction of the Helfrich expression for the curvature free energy[1] has led to an important advancement in the theoretical understanding of complex interfaces.[2,3] In terms of two elasticity or rigidity constants, k and $\bar{k}$, as well as the radius of spontaneous curvature R_0, the Helfrich free energy has been used to describe the shape, fluctuations, and free energy of membranes, vesicles, microemulsions, etc.[2] It has the following form:

$$F_H = \int dA \left[\sigma - \frac{2k}{R_0} J + \frac{k}{2} J^2 + \bar{k} K \right], \tag{1.1}$$

where σ is the surface tension of the *planar* surface, $J = 1/R_1 + 1/R_2$ is the total curvature, $K = 1/(R_1 R_2)$ is the Gaussian curvature, and R_1 and R_2 are the principal radii of curvature at a certain point on the surface A.

The Helfrich expression is, however, phenomenological in nature: no information is provided on the *value* of the parameters σ, k/R_0, k, and $\bar{k}$ and a lot of theoretical work has therefore been devoted to the determination of these parameters in the context of a more microscopic theory.[4–8] We should mention that Eq. (1.1) can be viewed in two, equivalent, ways. In the approach by Romero-Rochín, Varea and Robledo,[7] Eq. (1.1) is the expression for an *arbitrarily* shaped surface with curvature dependent coefficients σ, k/R_0, k, and $\bar{k}$. In the approach considered here, Eq. (1.1) is viewed as an expansion in curvature with the coefficients σ, k/R_0, k, and $\bar{k}$ curvature *independent*.

Inspection of the form of the Helfrich free energy in Eq. (1.1) shows that the theoretical determination of k/R_0, k, and $\bar{k}$ requires the variation of the free energy with *curvature*. The coefficients are then related to the first and second derivatives of the free energy with respect to the curvature. The way one varies the curvature depends very much on the system at hand. In the following we discuss three types of interfaces; those made of surfactant monolayers or bilayers, the solid–liquid interface, and the liquid–vapor interface.

We first discuss the case in which the surface is made of surfactant (or lipid) bilayers or monolayers. This is the system for which Helfrich originally wrote down his free energy, i.e., for the interface between two immiscible fluids where the specific molecules at the interface (e.g., the surfactant or lipid molecules) are the ones responsible for the strength of the rigidity constants. In this case one may change, for instance, the amount ($\Gamma_{\rm surf}$) or chemical potential ($\mu_{\rm surf}$) of the component that is predominantly adsorbed at the interface in order to vary the curvature. In fact, Porte and Ligoure[9] investigated the influence of either changing the chemical potential or the composition on the value of the rigidity constants for these systems.

The result of changing only the properties of the surfactant molecules at the interface is that the thermodynamic state of the bulk regions away from the surface is *unaffected*. For such a system Helfrich supplied formulas for the calculation of the curvature coefficients. Using ‘‘mechanical’’ arguments he derived expressions for k/R_0 and $\bar{k}$ in terms of moments of the transverse pressure profile,[4] $\Pi_0(z)$, of the planar surface, analogous to Buff’s[10] ‘‘mechanical’’ expression for the surface tension, σ, as the zeroth moment of the transverse pressure profile [see Eq. (1.2) below]. He added, however, that the expression for k/R_0 is only valid for a *tensionless* interface ($\sigma = 0$) and the expression for $\bar{k}$ is only valid for a *tensionless*, *symmetric* interface ($\sigma = 0$, $k/R_0 = 0$). Later, Szleifer and coworkers[5] extended the analysis of Helfrich, in the context of mean-field theory, to go beyond the mechanical arguments by Helfrich and showed that Hel-

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[a)] Electronic mail: e.blokhuis@chem.Leidenuniv.nl frich's expressions are correct also when $\sigma \neq 0$ and $k/R_0 \neq 0$. Furthermore, Szleifer and coworkers provided an expression for the rigidity constant k. The expressions by Helfrich[4] and Szleifer *et al.*[5] read

$$\sigma = -\int_{-\infty}^{\infty} dz\, \Pi_0(z), \quad \frac{2k}{R_0} = \int_{-\infty}^{\infty} dz\, z\, \Pi_0(z),$$
$$\bar{k} = -\int_{-\infty}^{\infty} dz\, z^2\, \Pi_0(z), \quad k = -\frac{1}{2}\int_{-\infty}^{\infty} dz\, z\, \Pi_{s,1}(z), \tag{1.2}$$

where z is the coordinate normal to the interface. Since these expressions are derived using arguments beyond the mechanical arguments by Helfrich, we will refer to these expressions as the **pressure expressions**[11] (rather than the ''mechanical expressions''). The expression for k features $\Pi_{s,1}(z)$, the first order coefficient of the lateral pressure profile of a spherical interface, $\Pi_s(r;R)$, in an expansion in $1/R$, the reciprocal radius,

$$\Pi_s(r;R) = \Pi_0(z) + \frac{1}{R}\Pi_{s,1}(z) + \cdots, \tag{1.3}$$

where the radial distance $r \equiv R+z$. $\Pi_{s,1}$ is the leading order change in the lateral pressure profile due to bending of the interface. Here it is expressed in terms of the lateral pressure profile of the *spherical* interface, but we should keep in mind that we could equally well have expressed it in terms of the lateral pressure profile of a *cylindrical* interface replacing $\Pi_{s,1}$ by $2\,\Pi_{c,1}$, or in general replace $\Pi_{s,1}$ by $2(\partial \Pi/\partial J)$. In the following the subscript s refers to the spherical surface and the subscript c to the cylindrical surface. The additional number to s and c (e.g., s,1) refers to the coefficient in an expansion in $1/R$ to that order.

A second class of systems, for which the Helfrich free energy has been used, are those in contact with a solid curved wall. Several authors[12–15] have calculated the electrostatic contribution to the curvature coefficients using double layer theory for a charged solid wall,[16] while recently Clement and Joanny[17] calculated the curvature energy associated with polymer adsorption onto a curved substrate. In these systems the curvature of the interface is varied simply by changing the radius of the solid wall. As in the case described above, the thermodynamic state of the system away from the surface is *unaffected* by the variation of the curvature of the interface. The result is that the curvature coefficients can be calculated using the pressure expressions in Eq. (1.2) with the only difference that the integration over z runs from the hard wall (at $z=0$) to infinity.

A third route to the calculation of the curvature coefficients has used van der Waals' squared-gradient expression for the surface free energy[8,18,19] of a simple liquid–vapor interface,

$$F[\rho] = \int d\vec{r}\,[m|\vec{\nabla}\rho(\vec{r})|^2 + f(\rho) - \Delta\mu\,\rho(\vec{r})], \tag{1.4}$$

where m is the usual coefficient of the squared-gradient term, $f(\rho)$ is the free energy density for a fluid constrained to have uniform density ρ, and $\Delta\mu$ is the chemical potential difference between the chemical potential of the curved surface and that of the planar surface ($\Delta\mu = \mu - \mu_{\mathrm{coex}}$). Using the above expression for the free energy, Gompper and Zschocke[8] and Blokhuis and Bedeaux[19] derived the following formulas for the curvature coefficients:

$$\begin{aligned}
\sigma &= 2m\int_{-\infty}^{\infty} dz[\rho_0']^2,\\
\frac{2k}{R_0} &= -2m\int_{-\infty}^{\infty} dz\, z[\rho_0']^2\\
&\quad + \frac{1}{2}\Delta\mu_{s,1}\int_{-\infty}^{\infty} dz[\rho_0 - \rho_{0,\mathrm{bulk}}],\\
\bar{k} &= 2m\int_{-\infty}^{\infty} dz\, z^2[\rho_0']^2\\
&\quad + (4\,\Delta\mu_{c,2} - \Delta\mu_{s,2})\int_{-\infty}^{\infty} dz[\rho_0 - \rho_{0,\mathrm{bulk}}],\\
k &= -m\int_{-\infty}^{\infty} dz\,\rho_0'\rho_{s,1} - \frac{1}{4}\Delta\mu_{s,1}\int_{-\infty}^{\infty} dz[\rho_{s,1} - \rho_{s,1,\mathrm{bulk}}]\\
&\quad - \Delta\mu_{s,1}\int_{-\infty}^{\infty} dz z[\rho_0 - \rho_{0,\mathrm{bulk}}]\\
&\quad - 2\,\Delta\mu_{c,2}\int_{-\infty}^{\infty} dz[\rho_0 - \rho_{0,\mathrm{bulk}}].
\end{aligned} \tag{1.5}$$

In the above formulas is $\rho_0 = \rho_0(z)$ the density profile of the planar interface and $\rho_{s,1}(z)$ the first order correction to the density profile of the spherical interface in an expansion in $1/R$. The subscript ''bulk'' refers to the bulk value extrapolated to the surface at $z=0$ so that for example $\rho_{0,\mathrm{bulk}} = \rho_{0,l}\,\theta(-z) + \rho_{0,v}\,\theta(z)$.

Comparing the expressions in Eqs. (1.2) and (1.5) it is not obvious that the pressure expressions and the expressions derived from van der Waals theory are in agreement. Yet the validity of both expressions seems well established. The van der Waals expressions in Eq. (1.5) were derived independently by Gompper and Zschocke[8] and by Blokhuis and Bedeaux.[19] Furthermore the result for k/R_0 agrees with an earlier expression by Fisher and Wortis.[18] Also, these expressions can be derived from the virial expressions for the curvature coefficients[6] by making a mean-field approximation to the pair density.[19,20]

On the other hand, it is well established by various authors[12–15] that the expressions for the electrostatic contribution to the curvature coefficients in double layer theory calculated directly via the free energy are the same as when the pressure expressions are used. This was shown by Winterhalter and Helfrich[12] using the Debye–Hückel theory, by Lekkerkerker[13] and by Mitchell and Ninham[14] using Poisson–Boltzmann theory in excess salt, and by Fogden, Daicic, and coworkers[15] using Poisson–Boltzmann theory with an arbitrary amount of added salt. Our object in this article is to establish in more detail the correspondence between the expressions in Eqs. (1.2) and (1.5). It will be shown that, keeping the thermodynamic conditions under which the surface is bend in mind, that Eqs. (1.2) and (1.5) are indeed equivalent.

When we compare Eqs. (1.2) and (1.5) some similarities are apparent. Suppose that we set $\Delta\mu_s = \Delta\mu_c = 0$ so that $\Delta\mu_{s,1} = \Delta\mu_{c,1} = 0$ and $\Delta\mu_{s,2} = \Delta\mu_{c,2} = 0$, and, furthermore, identify $\Pi_0(z)$ as $\Pi_0(z) = -2m(\rho_0')^2$, then already we see that the pressure expressions for σ, k/R_0, and $\bar{k}$ reduce exactly to the squared-gradient expressions. The correspondence between the two expressions for k is less clear but still, this is very encouraging and we now first wonder whether we can understand why there is no contribution from the change in chemical potential in the pressure expressions. In order to do this we first need to consider the thermodynamic circumstances.

II. THERMODYNAMIC CONDITIONS

In the van der Waals squared-gradient theory as used by Gompper and Zschocke,[8] Fisher and Wortis,[18] and Blokhuis and Bedeaux,[19] a spherical (cylindrical) drop of liquid is considered surrounded by a vapor phase. The two phases are not in coexistence when the radius $R < \infty$, and the distance to two-phase coexistence is determined by the chemical potential difference $\Delta\mu_s \equiv \mu_s - \mu_{\text{coex}}$ (or $\Delta\mu_c$ for the cylindrical interface). The droplet radius is determined by $\Delta\mu_s$ and when we consider the variation of the free energy with the radius we *really* are considering the variation of the free energy with the chemical potential. The Laplace equation enables us to relate directly the expansion coefficients of the chemical potential ($\Delta\mu_{s,1}, \Delta\mu_{s,2}, \ldots$) to the radius. In order to show this a bit more explicitly, we need to consider the Laplace equation for a spherical and cylindrical interface:

$$\begin{aligned} \Delta p &= \frac{2\sigma}{R} - \frac{4k}{R_0}\frac{1}{R^2}, \quad \text{spherical interface,} \\ \Delta p &= \frac{\sigma}{R} - \frac{k}{2}\frac{1}{R^3}, \quad \text{cylindrical interface,} \end{aligned} \tag{2.1}$$

which are both derived from the generalized Laplace equation,

$$\Delta p = \sigma J - \frac{4k}{R_0}K - \frac{k}{2}J^3 + 2kJK - k\Delta_s J. \tag{2.2}$$

In this equation $\Delta p \equiv p_l - p_v$ is the pressure difference between the liquid inside the droplet (cylinder) and the vapor outside, and Δ_s is the surface Laplacian which is important when the curvature varies from point to point on the surface. For the spherical and cylindrical interface we consider in this analysis, the curvature is constant along the surface so that $\Delta_s J = 0$.

Since the pressure difference is directly related to the chemical potential, one can show that[19]

$$\begin{aligned} \Delta\mu_{s,1} &= 2\,\Delta\mu_{c,1} = \frac{2\sigma}{\Delta\rho_0}, \\ \Delta\mu_{s,2} &= -\frac{\sigma}{(\Delta\rho_0)^2}\Delta\rho_{s,1} - \frac{4k}{R_0}\frac{1}{\Delta\rho_0}, \\ \Delta\mu_{c,2} &= -\frac{1}{4}\frac{\sigma}{(\Delta\rho_0)^2}\Delta\rho_{s,1}, \end{aligned} \tag{2.3}$$

with $\Delta\rho = \rho_l - \rho_v$ the density difference between the liquid and the vapor phase.

To summarize, in the derivation of the van der Waals expressions the radius R is varied by varying the chemical potential. The variation of the chemical potential leads to the presence of additional terms in the squared-gradient expressions in Eq. (1.5) with the explicit value of the coefficients of these terms given in Eq. (2.3).

Next, we now consider the thermodynamic conditions that are used in the calculation of the curvature coefficients of a fluid in contact with a hard wall. Here the situation is somewhat simpler. A rigid sphere (colloidal particle) is considered with a certain *fixed* radius R. The variation of the radius *does not* influence the thermodynamic state of the fluid outside with fixed density ρ_l and pressure p_l. Terms connected with the expansion of the chemical potential in the radius are therefore not present so that as a consequence,

$$\begin{aligned} \Delta\mu_{s,1} &= \Delta\mu_{c,1} = 0, \\ \Delta\mu_{s,2} &= \Delta\mu_{c,2} = 0. \end{aligned} \tag{2.4}$$

To show the correspondence between the van der Waals expressions and pressure expressions in more detail, we calculate the curvature coefficients with the only assumption that the free energy density is some function of the density $\rho(\vec{r})$ and the gradient of the density $\vec{\nabla}\rho(\vec{r})$ (to keep the calculation as general as possible). This is done under the conditon that the chemical potential is varied to vary the curvature (Sec. III) and under the condition that the chemical potential is constant (Sec. IV).

III. VARIABLE CHEMICAL POTENTIAL

The surface free energy is written in the following general way:

$$F[\rho] = \int d\vec{r}\,[-\Pi(\rho,\vec{\nabla}\rho) - \Delta\mu\,\rho(\vec{r})], \tag{3.1}$$

where it is supposed that the free energy in the bulk region is subtracted so that the above free energy is an *excess* free energy. Furthermore $\Pi(\rho,\vec{\nabla}\rho)$ is the (grand) free energy density and is some function of $\rho(\vec{r})$ and $\vec{\nabla}\rho(\vec{r})$. In van der Waals' squared-gradient theory, for instance, it has the following form [cf. Eq. (1.4)]:

$$\Pi(\rho,\vec{\nabla}\rho) = -m|\vec{\nabla}\rho(\vec{r})|^2 - f(\rho) + \mu_{\text{coex}}\,\rho(\vec{r}), \tag{3.2}$$

but we leave it unspecified in the remainder of this section. Several authors[7,8,19] have included besides a squared-gradient term a squared Laplacian term to the above free energy. The inclusion of such a term in Eq. (3.1) leads to the presence of additional terms in the Euler–Lagrange equations below with the consequence that the identification in Eqs. (3.8) and (3.10) below needs to be modified. In the following it should therefore be realized that the conclusions drawn only apply to mean-field theories whose free energy is of the form of Eq. (3.1).[20,21]

The Euler–Lagrange equation to the surface free energy in Eq. (3.1) reads

$$\frac{\partial}{\partial \rho}\Pi(\rho,\vec{\nabla}\rho)=\vec{\nabla}\cdot\frac{\partial}{\partial\vec{\nabla}\rho}\Pi(\rho,\vec{\nabla}\rho)-\Delta\mu. \tag{3.3}$$

In the following, we expand the surface free energy around the planar interface and compare the results with the surface free energy expression by Helfrich [Eq. (1.1)] which for a spherical and cylindrical geometry read

$$\begin{aligned}\frac{F_s}{A}&=\sigma-\frac{4k}{R_0}\frac{1}{R}+(2k+\bar{k})\frac{1}{R^2},\\ \frac{F_c}{A}&=\sigma-\frac{2k}{R_0}\frac{1}{R}+\frac{k}{2}\frac{1}{R^2}.\end{aligned}\tag{3.4}$$

Expanding the surface free energy for the spherical and cylindrical interface to second order in $1/R$ gives

$$\begin{aligned}\frac{F_s}{A}=\int_{-\infty}^{\infty}dz\left(1+\frac{z}{R}\right)^2\Bigg[&-\Pi_0-\frac{1}{R}\Pi_1\,\rho_{s,1}-\frac{1}{R}\Pi_2\,\rho'_{s,1}\\ &-\frac{1}{R^2}\Pi_1\,\rho_{s,2}-\frac{1}{R^2}\Pi_2\,\rho'_{s,2}-\frac{1}{2R^2}\Pi_{11}\,\rho^2_{s,1}\\ &-\frac{1}{R^2}\Pi_{12}\,\rho_{s,1}\rho'_{s,1}-\frac{1}{2R^2}\Pi_{22}(\rho'_{s,1})^2-\frac{1}{R}\Delta\mu_{s,1}\,\rho_0\\ &-\frac{1}{R^2}\Delta\mu_{s,1}\,\rho_{s,1}-\frac{1}{R^2}\Delta\mu_{s,2}\,\rho_0-\text{B.T.}\Bigg],\\ \frac{F_c}{A}=\int_{-\infty}^{\infty}dz\left(1+\frac{z}{R}\right)\Bigg[&-\Pi_0-\frac{1}{R}\Pi_1\,\rho_{c,1}-\frac{1}{R}\Pi_2\,\rho'_{c,1}\\ &-\frac{1}{R^2}\Pi_1\,\rho_{c,2}-\frac{1}{R^2}\Pi_2\,\rho'_{c,2}-\frac{1}{2R^2}\Pi_{11}\,\rho^2_{c,1}\\ &-\frac{1}{R^2}\Pi_{12}\,\rho_{c,1}\rho'_{c,1}-\frac{1}{2R^2}\Pi_{22}(\rho'_{c,1})^2-\frac{1}{R}\Delta\mu_{c,1}\,\rho_0\\ &-\frac{1}{R^2}\Delta\mu_{c,1}\,\rho_{c,1}-\frac{1}{R^2}\Delta\mu_{c,2}\,\rho_0-\text{B.T.}\Bigg],\end{aligned}\tag{3.5}$$

where the subscripts 1 and 2 to Π refer to a differentiation with respect to the first or second argument evaluated at the planar interface, e.g., $\Pi_1\equiv(\partial/\partial\rho_0)\,\Pi(\rho_0,\rho'_0)$. Π_0 is simply defined as $\Pi_0\equiv\Pi(\rho_0,\rho'_0)$. The abbreviation B.T. stands for the *boundary terms* at $z=\pm\infty$ which are to be subtracted.

The Euler–Lagrange equation (3.3) is expanded in the curvature for the spherical and cylindrical interface. To first order the following equations result:

$$\begin{aligned}&\Pi_1=\frac{\partial}{\partial z}\Pi_2,\\ &\Pi_1\rho_{s,1}-\Pi_2\rho'_{s,1}=2\Pi_2+\frac{\partial}{\partial z}(\Pi_{12}\,\rho_{s,1}-\Pi_{22}\,\rho'_{s,1})-\Delta\mu_{s,1},\\ &\Pi_1\rho_{c,1}-\Pi_2\,\rho'_{c,1}=\Pi_2+\frac{\partial}{\partial z}(\Pi_{12}\,\rho_{c,1}-\Pi_{22}\,\rho'_{c,1})-\Delta\mu_{c,1}.\end{aligned}\tag{3.6}$$

The first equation determines the profile $\rho_0(z)$ of the planar interface while the latter two determine the profiles $\rho_{s,1}(z)$ and $\rho_{c,1}(z)$. One immediately notices that since $\Delta\mu_{s,1}=2\,\Delta\mu_{c,1}$ one has that $\rho_{s,1}(z)=2\rho_{c,1}(z)$.

Inserting the above expressions for Π_1 into the surface free energy and integrating by parts gives, after some algebra, the following results for the surface free energy of the sphere and the cylinder:

$$\begin{aligned}\frac{F_s}{A}=&\int_{-\infty}^{\infty}dz[-\Pi_0]\\ &+\frac{1}{R}\int_{-\infty}^{\infty}dz[-2z\,\Pi_0-\Delta\mu_{s,1}(\rho_0-\rho_{0,\text{bulk}})]\\ &+\frac{1}{R^2}\int_{-\infty}^{\infty}dz\Bigg[-z^2\Pi_0+\Pi_2\rho_{s,1}-2\,\Delta\mu_{s,1}z\,(\rho_0-\rho_{0,\text{bulk}})\\ &-\frac{1}{2}\Delta\mu_{s,1}(\rho_{s,1}-\rho_{s,1,\text{bulk}})-\Delta\mu_{s,2}(\rho_0-\rho_{0,\text{bulk}})\Bigg],\\ \frac{F_c}{A}=&\int_{-\infty}^{\infty}dz[-\Pi_0]\\ &+\frac{1}{R}\int_{-\infty}^{\infty}dz[-z\,\Pi_0-\Delta\mu_{c,1}(\rho_0-\rho_{0,\text{bulk}})]\\ &+\frac{1}{R^2}\int_{-\infty}^{\infty}dz\Bigg[\tfrac{1}{2}\Pi_2\,\rho_{c,1}-\Delta\mu_{c,1}z(\rho_0-\rho_{0,\text{bulk}})\\ &-\frac{1}{2}\Delta\mu_{c,1}(\rho_{c,1}-\rho_{c,1,\text{bulk}})-\Delta\mu_{c,2}(\rho_0-\rho_{0,\text{bulk}})\Bigg].\end{aligned}\tag{3.7}$$

Comparing Eqs. (3.7) and (3.4) allows us to identify the curvature coefficients as

$$\begin{aligned}\sigma&=-\int_{-\infty}^{\infty}dz\Pi_0,\\ \frac{2k}{R_0}&=\int_{-\infty}^{\infty}dz\left[z\,\Pi_0+\frac{1}{2}\Delta\mu_{s,1}(\rho_0-\rho_{0,\text{bulk}})\right],\\ \bar{k}&=\int_{-\infty}^{\infty}dz[-z^2\Pi_0+(4\,\Delta\mu_{c,2}-\Delta\mu_{s,2})(\rho_0-\rho_{0,\text{bulk}})],\\ k&=\int_{-\infty}^{\infty}dz\Bigg[\frac{1}{2}\Pi_2\,\rho_{s,1}-\Delta\mu_{s,1}\,z\,(\rho_0-\rho_{0,\text{bulk}})\\ &\qquad-\frac{1}{4}\Delta\mu_{s,1}(\rho_{s,1}-\rho_{s,1,\text{bulk}})-2\,\Delta\mu_{c,2}(\rho_0-\rho_{0,\text{bulk}})\Bigg],\end{aligned}\tag{3.8}$$

where we have used that $\Delta\mu_{s,1}=2\,\Delta\mu_{c,1}$ and $\rho_{s,1}=2\rho_{c,1}$. As a final step we rewrite the expression for k somewhat by using that

$$\begin{aligned}\int_{-\infty}^{\infty}dz\,z\Pi_{s,1}&=\int_{-\infty}^{\infty}dz[z\Pi_{s,1}\,\rho_{s,1}+z\Pi_2\,\rho'_{s,1}]\\ &=\int_{-\infty}^{\infty}dz[-\Pi_2\,\rho_{s,1}],\end{aligned}\tag{3.9}$$

so that

$$k=\int_{-\infty}^{\infty}dz\Bigg[-\frac{z}{2}\Pi_{s,1}-\Delta\mu_{s,1}\,z(\rho_0-\rho_{0,\mathrm{bulk}})-\frac{1}{4}\Delta\mu_{s,1}\,(\rho_{s,1}-\rho_{s,1,\mathrm{bulk}})-2\,\Delta\mu_{c,2}\,(\rho_0-\rho_{0,\mathrm{bulk}})\Bigg].\tag{3.10}$$

We have thus derived in Eqs. (3.8) and (3.10) the pressure expressions for the curvature coefficients in the case that the chemical potential is varied to change the curvature of the interface. The pressure Π was identified as the (grand) free energy density defined by Eq. (3.1). One may verify that these pressure expressions are *equivalent* to the van der Waals squared-gradient expressions in Eq. (1.5) when one inserts the explicit expressions for Π_0 and $\Pi_{s,1}$,

$$\begin{aligned}\Pi_0&=-m\,(\rho_0')^2-f(\rho_0)+\mu_{\mathrm{coex}}\,\rho_0=-2m\,(\rho_0')^2,\\ \Pi_{s,1}&=-2m\,\rho_0'\rho_{s,1}'-f'(\rho_0)\rho_{s,1}+\mu_{\mathrm{coex}}\,\rho_{s,1}\\ &=-2m\,\rho_0'\rho_{s,1}'-2m\,\rho_0''\rho_{s,1},\end{aligned}\tag{3.11}$$

derived using the form for $\Pi(\rho,\vec{\nabla}\rho)$ in Eq. (3.2).

An important issue that we have not addressed thus far is the fact that a certain arbitrariness exists in locating the exact position of the dividing surface and therefore in the exact value of the radius R.[22] The consequences hereof for the curvature coefficients can be read off from the expressions in Eq. (3.8) which are derived without specifying the location of the dividing surface. One finds that the surface tension of the planar interface σ does not depend on the location of the dividing surface. Also, the spontaneous curvature k/R_0 is *independent* of the location of the dividing surface. This can be checked by shifting the dividing surface over a distance Δ. The first contribution to k/R_0 is then changed by an amount $\sigma\Delta$, while the second contribution changes by an amount $-1/2(\Delta\rho_0)\,\Delta$. Use of Eq. (2.3) then yields that the net change in k/R_0 of shifting the dividing surface is zero. The rigidity constants, however, *do* depend on the location of the dividing surface, and when numerical values are supplied for k and $\bar{k}$ this can be done only after a certain choice for the location of the dividing surface has been made. For instance, in the derivation of the pressure equations for monolayers and bilayers by Szleifer *et al.*,[5] the location of the dividing surface was chosen to be the ''surface of inextension'' or ''neutral surface.'' This is the surface whose area is unchanged during the variation of the curvature. We refer to Ref. 5 for a more elaborate discussion of this point (see also Ref. 3). For the evaluation of the curvature coefficients in the van der Waals theory for a liquid–vapor droplet, the dividing surface was located at Gibb's equimolar surface.[19] In the next section we investigate the case of a fluid in contact with a hard spherical (cylindrical) wall. In that case the dividing surface is chosen at the hard wall.

It is noteworthy that Eqs. (3.8) and (3.10) reduce *exactly* to the pressure expressions in Eq. (1.2) when one sets $\Delta\mu_{s,1}=\Delta\mu_{c,1}=0$ and $\Delta\mu_{s,2}=\Delta\mu_{c,2}=0$. Therefore, we next look in more detail into the situation where the chemical potential is kept constant.

IV. CONSTANT CHEMICAL POTENTIAL

We now investigate the situation in which the chemical potential is fixed $(\Delta\mu=0)$ and the radius of curvature is varied independent of the thermodynamic state. Therefore we consider the surface free energy of a fluid in contact with a hard spherical (cylindrical) wall with fixed radius R,

$$F[\rho]=-\int d\vec{r}[\Pi(\rho,\vec{\nabla}\rho)\,]+A\Phi_w(\rho^w),\tag{4.1}$$

where $\Phi_w(\rho^w)$ is the interaction of the fluid with the wall at $z=0$ and is assumed to depend only on the density at the wall, ρ^w. The form of the above free energy is quite general and in the Appendix we give two examples where the free energy indeed has this form.

The Euler–Lagrange equation to the surface free energy in Eq. (4.1) reads

$$\frac{\partial}{\partial\rho}\Pi(\rho,\vec{\nabla}\rho)=\vec{\nabla}\cdot\frac{\partial}{\partial\vec{\nabla}\rho}\Pi(\rho,\vec{\nabla}\rho),\tag{4.2}$$

with the boundary condition at the wall,

$$\frac{\partial}{\partial\rho^w}\Phi_w(\rho^w)=\hat{n}\cdot\frac{\partial}{\partial\vec{\nabla}\rho^w}\Pi(\rho^w,\vec{\nabla}\rho^w).\tag{4.3}$$

In this expression $\hat{n}$ is the unit vector in the direction normal to the interface. Expanding the surface free energy for the spherical and cylindrical interface to second order in $1/R$ now gives

$$\begin{aligned}\frac{F_s}{A}=\int_0^{\infty}dz\left(1+\frac{z}{R}\right)^2\Bigg[&-\Pi_0-\frac{1}{R}\Pi_1\,\rho_{s,1}-\frac{1}{R}\Pi_2\,\rho_{s,1}'\\ &-\frac{1}{R^2}\Pi_1\,\rho_{s,2}-\frac{1}{R^2}\Pi_2\,\rho_{s,2}'-\frac{1}{2R^2}\Pi_{11}\,\rho_{s,1}^2\\ &-\frac{1}{R^2}\Pi_{12}\,\rho_{s,1}\rho_{s,1}'-\frac{1}{2R^2}\Pi_{22}\,(\rho_{s,1}')^2-\mathrm{B.T.}\Bigg],\\ &+\Phi_{w,0}+\frac{1}{R}\Phi_{w,0}'\,\rho_{s,1}^w+\frac{1}{R^2}\Phi_{w,0}'\,\rho_{s,2}^w+\frac{1}{2R^2}\Phi_{w,0}''\,(\rho_{s,1}^w)^2,\\ \frac{F_c}{A}=\int_0^{\infty}dz\left(1+\frac{z}{R}\right)\Bigg[&-\Pi_0-\frac{1}{R}\Pi_1\,\rho_{c,1}-\frac{1}{R}\Pi_2\,\rho_{c,1}'\\ &-\frac{1}{R^2}\Pi_1\,\rho_{c,2}-\frac{1}{R^2}\Pi_2\,\rho_{c,2}'-\frac{1}{2R^2}\Pi_{11}\,\rho_{c,1}^2\\ &-\frac{1}{R^2}\Pi_{12}\,\rho_{c,1}\rho_{c,1}'-\frac{1}{2R^2}\Pi_{22}\,(\rho_{c,1}')^2-\mathrm{B.T.}\Bigg]\\ &+\Phi_{w,0}+\frac{1}{R}\Phi_{w,0}'\,\rho_{c,1}^w+\frac{1}{R^2}\Phi_{w,0}'\,\rho_{c,2}^w+\frac{1}{2R^2}\Phi_{w,0}''\,(\rho_{c,1}^w)^2,\end{aligned}\tag{4.4}$$

where we have defined $\Phi_{w,0}\equiv\Phi_w(\rho_0^w)$. The Euler–Lagrange equation (4.2) is expanded to first order in the curvature for the spherical and cylindrical interface,

$$\begin{aligned}
&\Pi_1 = \frac{\partial}{\partial z}\Pi_2, \\
&\Pi_1\,\rho_{s,1} - \Pi_2\,\rho'_{s,1} = 2\Pi_2 + \frac{\partial}{\partial z}(\Pi_{12}\rho_{s,1} - \Pi_{22}\,\rho'_{s,1}), \qquad (4.5) \\
&\Pi_1\rho_{c,1} - \Pi_2\,\rho'_{c,1} = \Pi_2 + \frac{\partial}{\partial z}(\Pi_{12}\rho_{c,1} - \Pi_{22}\,\rho'_{c,1}),
\end{aligned}$$

and so is the boundary condition in Eq. (4.3),

$$\begin{aligned}
&-\Pi_2^w = \Phi'_{w,0}, \\
&\Pi_{12}^w\,\rho_{s,1}^w - \Pi_{22}^w\,(\rho_{s,1}^w)' = \Phi''_{w,0}\,\rho_{s,1}^w, \qquad (4.6) \\
&\Pi_{12}^w\,\rho_{c,1}^w - \Pi_{22}^w\,(\rho_{c,1}^w)' = \Phi''_{w,0}\,\rho_{c,1}^w.
\end{aligned}$$

Again it is noted that $\rho_{s,1}(z) = 2\rho_{c,1}(z)$. Using Eqs. (4.5) and (4.6), the surface free energy of the sphere and cylinder can now be written as

$$\begin{aligned}
\frac{F_s}{A} &= \int_0^\infty dz[-\Pi_0] + \Phi_{w,0} + \frac{1}{R}\int_0^\infty dz[-2z\,\Pi_0] \\
&\quad + \frac{1}{R^2}\int_0^\infty dz[-z^2\Pi_0 + \Pi_2\rho_{s,1}], \\
\frac{F_c}{A} &= \int_0^\infty dz[-\Pi_0] + \Phi_{w,0} + \frac{1}{R}\int_0^\infty dz[-z\,\Pi_0] \qquad (4.7) \\
&\quad + \frac{1}{R^2}\int_0^\infty dz\left[\frac{1}{2}\Pi_2\rho_{c,1}\right],
\end{aligned}$$

so that one may identify the curvature coefficients as

$$\begin{aligned}
&\sigma = -\int_0^\infty dz[\Pi_0] + \Phi_{w,0}, \quad \frac{2k}{R_0} = \int_0^\infty dz[z\Pi_0], \\
&\bar{k} = \int_0^\infty dz[-z^2\Pi_0], \quad k = \int_0^\infty dz\left[\frac{1}{2}\Pi_2\,\rho_{s,1}\right]. \qquad (4.8)
\end{aligned}$$

Notice that all the terms involving the interaction with substrate, Φ_w, have dropped out of the expressions for k/R_0, k, and $\bar{k}$. As a final step we, again, rewrite the expression for k somewhat by using that

$$\begin{aligned}
\int_0^\infty dz\, z\Pi_{s,1} &= \int_0^\infty dz[z\Pi_1\,\rho_{s,1} + z\Pi_2\,\rho'_{s,1}] \\
&= \int_0^\infty dz[-\Pi_2\,\rho_{s,1}], \qquad (4.9)
\end{aligned}$$

so that

$$k = \int_0^\infty dz\left[-\frac{z}{2}\Pi_{s,1}\right]. \qquad (4.10)$$

Apart from the presence of $\Phi_{w,0}$ in the expression for the surface tension and the fact that the integration runs from $z = 0$ instead of $z = -\infty$, the expressions in Eqs. (4.8) and (4.10) are *exactly equal* to the pressure expressions in Eq. (1.2). Starting with the general expression for the surface free energy in Eq. (4.1) we have thus rederived all the pressure expressions for the system in which the chemical potential is fixed.

V. SUMMARY

We have investigated the apparent contradiction between the pressure expressions and van der Waals expressions for the curvature coefficients k/R_0, k, and $\bar{k}$. In the context of the mean-field theory expressed by the similar Eqs. (3.1) and (4.1), we showed that the origin of the difference between the two types of expression lies solely in the thermodynamic conditions used to vary the curvature. As we have seen, the appropriate thermodynamic conditions depend very much on the system at hand. To study, for instance, the nucleation of liquid droplets, the curvature depends on the thermodynamic distance to coexistence ($\Delta\mu = \mu - \mu_{\mathrm{coex}}$) via the Laplace equation, and the analysis in Sec. III is the appropriate one, while for the description of the electric double layer of a colloidal particle with fixed radius or the description of the adsorption of a polymer onto a curved wall, the analysis in Sec. IV is more suited. The latter analysis is also closely related to the investigation of microemulsion systems and systems containing membrane bilayers. In these cases one may, for instance, change the chemical potential of the component that is predominantly adsorbed at the interface (e.g., the surfactant or lipid molecules) in order to change the curvature. As in the case of a system in contact with a curved wall, the thermodynamic state of the system away from the surface[23,24] is unaffected.

With these two thermodynamic conditions, expressions for the curvature coefficients were derived. In Sec. III the curvature was varied by varying the chemical potential, while in Sec. IV the chemical potential is kept constant and the curvature is varied by varying the radius of the spherical or cylindrical substrate that is in contact with the system. The resulting expressions from the former analysis were shown to reduce to those obtained in van der Waals theory, while the results from the latter analysis were shown to be equal to the pressure expressions identifying the lateral pressure profile as the excess (grand) free energy density.

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APPENDIX: EXAMPLES OF THE FREE ENERGY AS GIVEN IN EQ. (4)

We now discuss two recent examples from the literature in which the surface free energy has the form of Eq. (4.1). In the first example, the adsorption of polymers onto a curved surface is considered, while in the second example the electric double layer theory is discussed.

1. Polymer adsorption

In the recent description of polymer adsorption onto a curved substrate by Clement and Joanny,[17] the surface free energy is a functional of ψ, which is related to the local monomer concentration c by $\psi^2=c$. It has the following form:

$$F[\psi]=\int d\vec{r}\left[|\vec{\nabla}\psi(r)|^2+\frac{1}{2}\nu(\psi^2-\psi_b^2)^2\right]-A\frac{1}{d}(\psi^w)^2, \tag{A1}$$

where d is the extrapolation length which measures the strength with which polymers are adsorbed at the wall, ν is the excluded volume parameter, and $\psi_b^2=c_b$, the local monomer concentration in the bulk. Lengths are scaled with $a/\sqrt{6}$, with a the monomer size, and energies by k_BT, with k_B Boltzmann's constant and T the absolute temperature.

When Eq. (A1) is compared to Eq. (4.1) we can identify Π and Φ_w as

$$\begin{aligned}\Pi(\psi,\vec{\nabla}\psi)&=-|\vec{\nabla}\psi(r)|^2-\tfrac{1}{2}\nu(\psi^2-\psi_b^2)^2,\\ \Phi_w(\psi^w)&=-\frac{1}{d}(\psi^w)^2.\end{aligned} \tag{A2}$$

The Euler–Lagrange equation, Eq. (4.2), and boundary condition, Eq. (4.3), now read as

$$\begin{aligned}\Delta\psi&=\nu\,\psi(\psi^2-\psi_b^2),\\ \hat{n}\cdot\vec{\nabla}\psi^w&=-\frac{1}{d}\psi^w.\end{aligned} \tag{A.3}$$

With the identification in Eq. (A2) and after solving the Euler–Lagrange equation in Eq. (A3), one is then able to calculate the curvature coefficients using the expressions in Eqs. (4.8) and (4.10).

2. Electrostatic double layer

The electrostatic contribution to the free energy of the double layer immersed in a 1–1 electrolyte has the following form:[13,25]

$$F_{\mathrm{el}}=\int d\vec{r}\left\{-\frac{1}{2}\epsilon_0\epsilon_r|\vec{\nabla}\psi(\vec{r})|^2-2n_{\mathrm{el}}k_BT\left[\cosh\left(\frac{e\psi}{k_BT}\right)-1\right]\right\}+A\sigma\,\psi^w, \tag{A4}$$

where ϵ_r is the dielectric of the aqueous medium, ϵ_0 is the permittivity of vacuum, n_{el} is the electrolyte number density, e is the elementary charge, and σ (not to be confused with the surface tension) is the surface charge density.

The electrical free energy above is written in terms of the electrostatic potential $\psi(\vec{r})$, which is to be determined by solving the *Poisson–Boltzmann* equation,

$$\Delta\Psi=\kappa^2\sinh(\Psi), \tag{A5}$$

where the dimensionless potential $\Psi\equiv e\psi/k_BT$ and inverse Debye length $\kappa\equiv(2e^2n_{\mathrm{el}}/\epsilon_0\epsilon_rk_BT)^{1/2}$ have been introduced. The requirement of constant surface charge density leads to the following boundary condition to the Poisson–Boltzmann equation:

$$\hat{n}\cdot\vec{\nabla}\Psi^w=-2p\kappa, \tag{A6}$$

where $p\equiv 2\pi Q\sigma/\kappa e$, with $Q\equiv e^2/4\pi\epsilon_0\epsilon_rk_BT$ the Bjerrum length.

In this case, the differential equation determining the profile of the order parameter, the Poisson–Boltzmann equation, is derived from electrostatics (the Poisson equation) rather than from the minimization of the free energy in Eq. (A4). In fact, in the derivation of the electrical free energy in Eq. (A4) one has already made use of the Poisson–Boltzmann equation.[25] However, the Poisson–Boltzmann equation, Eq. (A4), and boundary condition, Eq. (A5), both *do* result from the Euler–Lagrange equation treating F_{el} as if it were a functional of ψ; $F_{\mathrm{el}}=F_{\mathrm{el}}[\psi]$. The result is that if we now identify

$$\begin{aligned}\Pi(\psi,\vec{\nabla}\psi)&=\frac{1}{2}\epsilon_0\epsilon_r|\vec{\nabla}\psi(\vec{r})|^2+2\,n_{\mathrm{el}}k_BT\left[\cosh\left(\frac{e\psi}{k_BT}\right)-1\right],\\ \Phi_w(\psi^w)&=\sigma\,\psi^w,\end{aligned} \tag{A7}$$

we can again calculate the curvature coefficients using the expressions in Eqs. (4.8) and (4.10) as noted by Winterhalter and Helfrich,[12] Lekkerkerker,[13] and by Fogden, Daicic, and coworkers.[15]

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