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A General Method for Calculating Bending Moduli and Spontaneous Curvature of Polymer Brushes in Terms of Local Density Functional Theory

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ABSTRACT: A general method for calculating the spontaneous curvature and the bending modulus of surfactant monolayers or grafted polymer brushes is presented which is based on a density functional theory, where the bending parameters and the spontaneous curvature are *analytically* represented in terms of integral moments of the solution for the flat geometry. The novelty here is that the problem is solved for an arbitrary form of the free energy density function with the only requirement being that the energy functional is local. The difference compared to other approaches is that for the case of local density functional theories; the lateral pressure and its derivatives with respect of curvature could be expressed analytically in terms of the density profiles of the flat geometry. This general approach enables a variety of problems involving polymer brushes, surfactants, and amphiphilic diblock copolymers to be treated directly and has direct application in modeling the phase behavior of microemulsions and surfactant solutions. As particular examples we consider the cases of low-density arbitrary solvent, arbitrary density in ideal solvent and Θ solvent of a polymer brush and an amphiphilic diblock copolymer.

1. Introduction

The properties of microemulsions are determined by bending energy and entropic contributions. It has long ago[1] been recognized that the properties of the microscopic surfactant film control to a great extent the type of microstructure formed. The Helfrich phenomenological model[2] for the curvature energy of amphiphilic structures proved quite successful in reducing the number of natural parameters used to describe the phase behavior and microstructural characteristics of complex systems like microemulsions, vesicles, mixtures of surfactants, and polymers, and biological membranes. A comprehensive review of curvature and elastic properties of monolayers and membranes is given by Petrov et al.[3] The statistical mechanics approach of Ben-Shaul et al.[4] was used by Szleifer et al.[5,6] to develop a molecular theory of the curvature elasticity in surfactant films and monolayers. Barneveld et al.[7,8] have applied the self-consistent field lattice approach of Scheutjens and Fleer[9] to develop a numerical scheme for evaluating the spontaneous curvature and the bending elasticity parameters for both bilayers and monolayers of alkyl polyethylene-glycols. Safran[10] developed a simple model for low-density grafted polymer brushes based on stretching and osmotic contributions, which was used latter by Paunov et al.[11] for C_iE_j monolayers at an alkane−water interface. Milner and Witten[12] used the self-consistent field (SCF) theory to represent the stretching contribution in the energy functional of grafted polymer brushes. Milner and Safran[13] applied this approach with an optimization with respect to the area per molecule at the surface. Clement et al.[14] used a nonlocal form of the density functional to calculate the bending constants of the adsorbed polymer layer which gives a different result compared to refs 11 and 12 due to the differences in the density functional form.

The major problem that other approaches face when calculating bending constants from density functional theory (see, e.g., ref 15) is that the bending moduli, κ and $\bar{\kappa}$, and the spontaneous curvature H_0 are given in terms of the second correction of the density profiles in the curved geometry (or curvature derivatives of lateral pressure), which must be calculated explicitly for any specific case. We show here that the first curvature correction of the density profile could be calculated for any *local* density functional in explicit and analytical form provided that it satisfies certain boundary conditions and normalization, which leads to expression for the elastic modulus expressed in the terms of solution of the density functional for a *flat geometry*.

2. Bending Elasticity Parameters at Constant Area per Molecule

The free energy density functional of a system of polymer chains grafted on a flat interface and a solvent can be represented as follows

$$F = A\int_0^H Q(\varphi(x), x)\,\mathrm{d}x, \quad A\int_0^H \varphi(x)\,\mathrm{d}x = CM \quad (1)$$

where A is the total area of the interface, C is a normalizing constant, and H is the thickness of the polymer brush. In eq 1, $Q(\varphi(x), x)$ is the local free energy density and $\varphi(x)$ is the local volume fraction of polymer segments which satisfies the boundary conditions $Q(\varphi(H), H) = 0$ and $\varphi(H) = 0$. For small but finite curvature (see Figure 1a) of the interface, the functional

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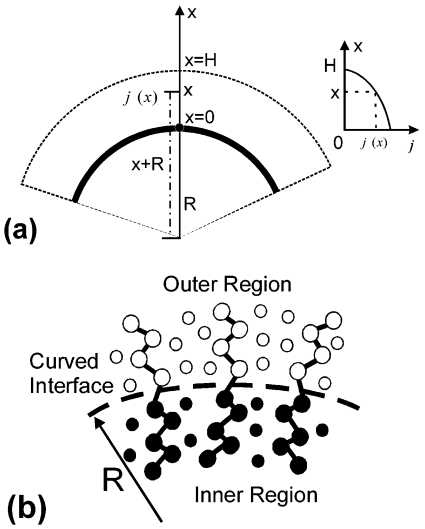

Figure 1. (a) Schematic representation of the polymer brush layer at curved surfaces. (b) Sketch of the monolayer of nonionic surfactant (diblock copolymer) at the interface between oil and water. The nonionic surfactant molecule consists of a hydrophobic and hydrophilic block, like C_iE_j surfactant. The free energy of mixing of both blocks of the surfactant molecule with the adjacent solvent depends on the curvature of the interface.

form of the local free energy density Q remains the same and the density functional problems can be written as

$$F = \beta R^{\alpha} \int_0^H Q(\varphi(x), x)\left(1 + \frac{x}{R}\right)^{\alpha} dx, \qquad \beta R^{\alpha} \int_0^H \varphi(x)\left(1 + \frac{x}{R}\right)^{\alpha} dx = MC = \text{const} \tag{2}$$

where $\alpha = 1$, $\beta = 2\pi L$ for a cylindrical curved interface and $\alpha = 2$, $\beta = 4\pi$ for a spherical interface; M is the total number of "polymeric molecules". In terms of the area per molecule $\sigma = \beta R^{\alpha}/M$ the normalizing condition in eq 2 can be rewritten as $\sigma\int_0^H \varphi(x)(1 + x/R)^{\alpha}\, dx = C$. Here it is assumed that the area per molecule σ does not change with the curvature of the interface. Then the free surface energy $\gamma(R) = F/\beta R^{\alpha}$ can be expanded in power series of the curvature $(1/R)$

$$\gamma(1/R) = \int_0^{H(1/R)} Q(\varphi(x, 1/R), x)\left(1 + \frac{x}{R}\right)^{\alpha} dx \approx \gamma(0) + \frac{\gamma'(0)}{R} + \frac{\gamma''(0)}{2R^2} \tag{3}$$

where the coefficients $\gamma'(0)$ and $\gamma''(0)$ can be expressed in terms of integral moments of the equilibrium distribution $\varphi(x)$ for the case of flat interface. Using eqs 2 and 3, the solution of the constrained minimizing condition of the functional, $\delta Q(\varphi,x)/\delta\varphi = \mu$, and the boundary conditions, one obtains

$$\frac{d\gamma}{d(1/R)} = \alpha\int_0^H (Q(\varphi(x), x) - \mu\varphi(x))\left(1 + \frac{x}{R}\right)^{\alpha-1} x\, dx \tag{4}$$

Using eq 2, for the second derivative, one obtains

$$\frac{d^2\gamma}{d(1/R)^2} = \alpha(\alpha - 1)\int_0^H (Q(\varphi(x), x) - \mu\varphi(x)) \times \left(\frac{R + x}{R}\right)^{\alpha-2} x^2\, dx - \alpha\frac{\partial\mu}{\partial 1/R}\int_0^H \varphi(x)\left(\frac{R + x}{R}\right)^{\alpha-1} x\, dx \tag{5}$$

Since the "chemical potential" μ does not depend on x, using $\partial\mu/\partial(1/R) = (\delta^2 Q/\delta\varphi^2)\partial\varphi/\partial(1/R)$, one gets

$$\frac{\partial\mu}{\partial 1/R} = -\alpha\int_0^H \varphi(x)\left(1 + \frac{x}{R}\right)^{\alpha-1} x\, dx \Big/ \int_0^H \left(\frac{\delta^2 Q}{\delta\varphi^2}\right)^{-1}\left(1 + \frac{x}{R}\right)^{\alpha} dx \tag{6}$$

This is the main result in this paper, which allows direct calculation of the bending constants. In the next section (variable area per molecule), a similar approach will be used to calculate the derivatives with respect to the area per molecule. If this approach is not used, one cannot represent the results in the terms of the solution for a flat interface and to estimate its moments. Combining eqs 5 and 6, one gets

$$\gamma''(0) = \alpha(\alpha - 1)\int_0^H (Q(\varphi(x), x) - \mu\varphi(x))x^2\, dx + \alpha^2\left(\int_0^H \varphi x\, dx\right)^2 \Big/ \int_0^H \left(\frac{\delta^2 Q}{\delta\varphi^2}\right)^{-1} dx \tag{7}$$

The comparison between eq 3 and Helfrich's expression for the free energy of the curved system

$$\gamma(1/R) = \gamma(0) - \frac{\alpha\kappa H_0}{R} + \frac{\alpha(2(\alpha - 1)\bar{\kappa} + \alpha\kappa)}{2R^2} \tag{8}$$

gives

$$2H_0 = I_2/I_1, \quad \kappa = I_1, \quad \bar{\kappa} = I_3 \tag{9}$$

$$I_1 = \left(\int_0^H \varphi x\, dx\right)^2 \Big/ \int_0^H \left(\frac{\delta^2 Q}{\delta\varphi^2}\right)^{-1} dx, \qquad I_2 = \int_0^H (\mu\varphi - Q(\varphi, x))\, x\, dx, \qquad I_3 = -\int_0^H (\mu\varphi - Q(\varphi, x))\, x^2\, dx \tag{10}$$

Note that eqs 9 and 10 allow one to calculate the κ, $\bar{\kappa}$, and H_0 in terms of moments of the flat profile distribution, $\varphi(x)$; i.e., it is not necessary to solve the density functional problem in different geometries. This result can also be generalized for the case of amphiphilic diblock copolymers (like C_iE_j) adsorbed at the interface between two immiscible phases (see Figure 1b). Then the two polymer volume fraction distributions φ^{out} and φ^{in} at both sides of the interface can be determined from the local free energy density functions, $Q^{\text{out}}(\varphi^{\text{out}}, x)$ and $Q^{\text{in}}(\varphi^{\text{in}}, x)$, following the same route to obtain

$$2H_0 = (I_2^{\text{out}} - I_2^{\text{in}})/(I_1^{\text{out}} + I_1^{\text{in}}), \quad \kappa = I_1^{\text{out}} + I_1^{\text{in}}, \quad \bar{\kappa} = I_3^{\text{out}} + I_3^{\text{in}} \tag{11}$$

3. Variation of the Surface Area with Curvature

As one could see from the results in the previous section, the values of the bending constants will strongly depend on the adsorption (surface coverage). On the other hand, they will depend strongly on the way in which the radius of curvature is determined, which affects the location of the surface separating the two phases. However, for any "reasonable" choice of the location of this dividing surface the result should not affect measurable physical quantities. From the Helfrich expression (eq 8), one observes directly that if the radius R of either the spherical or cylindrical surface is shifted by a microscopic distance d, the coefficients in the expansion in $1/R$ will change. One can show that the leading coefficients in the expansion are unaffected by this shift, but the second-order coefficients, the rigidity constants κ and $\bar{\kappa}$, indeed are dependent on the choice of the location of the dividing surface. Only if the surface tension and κH_0 vanish are the rigidity constants independent of the choice of the location of the dividing surface. Thus, both the surface coverage and the position of the dividing interface are influencing the values of the bending constants. Until now we did not consider the connection between surface curvature and adsorption, assuming that one could control independently the adsorption and the position of the dividing interface (curvature). However, for a real system, not all combinations of mathematical curvature (position of the dividing interface) and surface coverage are physically acceptable. One should accept only these combinations, which ensure that the free energy of the system is at a minimum. The minimum condition applied for such a case gives a connection between the curvature of the interface and surface coverage (adsorption). This means that if one fixes the curvature (i.e., position of the dividing interface), then the surface coverage will change (compared to the flat geometry case), which is due to the change of the chemical potential due to the curvature. Thus, to ensure that the chemical potentials of the curved and the flat systems are equal (and equal to the bulk one), some of the molecules should desorb/adsorb from the interface. Instead of using a constant chemical potential like a constraint condition, we chose to use a minimum of the surface free energy with respect of the area per molecule.[10,13] Of course both of them are equivalent, and our choice is motivated only by computational efficiency. We have fixed the dividing interface position to be the interface between two bare fluid phases, assuming that the polymer brush thickness (or specific range of the interaction of local DFT) is much higher than the thickness of the bare interface. Another possibility is to fix the adsorption (saying that the surfactant is strongly attached to the interface) and then to adjust the position of the dividing interface so the mathematical and physical interface to coincide. We did not choose this route of calculation because the first one is more physically reasonable. For instance for a surfactant monolayer at the oil−water interface, the area per surfactant molecule changes with the curvature of the interface.

In this section, we will consider the area per molecule as a parameter that is to be accounted for when minimizing the free energy and in the calculating of the bending elasticity.[10,13] In this case, the total free energy could be written as

$$F = \gamma_{\mathrm{L}} A + F_{\mathrm{mol}} \tag{12}$$

where γ_{L} is the interfacial surface tension of the bare liquid−liquid interface and F_{mol} is the free energy of the molecules given by eq 1. Minimizing the area per molecule with respect to the total area A is equivalent to minimizing the energy per molecule with respect to the area per molecule

$$f = \gamma_0(\sigma) + \gamma_1(\sigma)/R + \gamma_2(\sigma)/R^2 \tag{13}$$

where $\gamma_0(\sigma) = \gamma_{\mathrm{L}}\sigma + \gamma(0, \sigma)\sigma$, $\gamma_1(\sigma) = \gamma'(0, \sigma)\sigma$, and $\gamma_2(\sigma) = \gamma''(0, \sigma)\sigma/2$ are the expansion coefficients obtained in the previous section, but at a fixed total area per molecule. The condition for minimizing the free surface energy is $(\partial f/\partial\sigma)|_{\sigma_0^R} = 0$, where σ_0^R is the optimum value of the area per molecule for curved interface, while σ_0 is its counterpart for a flat surface. Assuming that they are related as $\sigma_0^R = \sigma_0 + \Delta/R + O(1/R^2)$ one can expand the minimum energy condition around the "flat" state to get

$$\frac{\partial\gamma_0}{\partial\sigma}\Big|_{\sigma_0{}^R} = \gamma_{\mathrm{L}} + \gamma(0, \sigma_0) + \sigma_0\frac{\partial\gamma(\sigma, 0)}{\partial\sigma}\Big|_{\sigma_0} = 0,$$
$$\Delta = -\frac{\partial\gamma_1}{\partial\sigma}\Big|_{\sigma_0}\left(\frac{\partial^2\gamma_0}{\partial\sigma^2}\Big|_{\sigma_0}\right)^{-1} \tag{14}$$

Further, we expand the free energy with respect to the curvature by taking into account that in the equilibrium the area per molecule is a function of the curvature as well. Since we consider only a linear correction of the area per molecule, this correction will influence the second-order term of free energy curvature expansion.

Combining eqs 1 and 12 with eq 14, one can also express all derivatives of the respective energy functional

$$\gamma(0, \sigma_0) = \int_0^H Q(\varphi(x), x)\,\mathrm{d}x,$$
$$\sigma_0\frac{\partial\gamma(\sigma, 0)}{\partial\sigma}\Big|_{\sigma_0} = \mu\sigma_0\int_0^H \frac{\partial\varphi}{\partial\sigma}\,\mathrm{d}x \tag{15}$$

$$\sigma\int_0^H \frac{\partial\varphi}{\partial\sigma}\,\mathrm{d}x = -\int_0^H \varphi\,\mathrm{d}x, \quad \frac{\partial\gamma(\sigma,0)}{\partial\sigma}\Big|_{\sigma_0} = -\mu\int_0^H \varphi\,\mathrm{d}x \tag{16}$$

The substitution of eq 15 and 16 into eq 14 gives

$$\frac{\partial\gamma_0}{\partial\sigma}\Big|_{\sigma_0{}^R} = \gamma_{\mathrm{L}} + \int_0^H[Q(\varphi(x), x) - \mu\varphi(x)]\,\mathrm{d}x = 0 \tag{17}$$

Since $\gamma_0(\sigma_0) = \sigma_0\gamma_{\mathrm{L}} + \sigma_0\int_0^H Q(\varphi(x), x)\,\mathrm{d}x = \sigma_0\mu\int_0^H \varphi(x)\,\mathrm{d}x$, for the surface tension of the system one obtains $\gamma_0(\sigma_0)/\sigma_0 = \mu\int_0^H \varphi(x)\,\mathrm{d}x = \mu C/\sigma_0$. The second derivative can also be calculated as follows

$$\frac{\partial^2\gamma_0}{\partial\sigma^2}\Big|_{\sigma_0} = -\frac{\partial\mu}{\partial\sigma}\int_0^H \varphi(x)\,\mathrm{d}x \tag{18}$$

Similar to eq 5, one gets

$$\frac{\partial\mu}{\partial\sigma} = -\int_0^H \varphi\,\mathrm{d}x/\sigma_0\int_0^H\left(\frac{\delta^2 Q}{\delta\varphi^2}\right)^{-1}\mathrm{d}x \tag{19}$$

$$\frac{\partial^2\gamma_0}{\partial\sigma^2}\Big|_{\sigma_0} = [\int_0^H \varphi\,\mathrm{d}x]^2/\sigma_0\int_0^H\left(\frac{\delta^2 Q}{\delta\varphi^2}\right)^{-1}\mathrm{d}x \tag{20}$$

$$\frac{\partial\gamma_1}{\partial\sigma}\Big|_{\sigma_0} = \alpha\int_0^H(Q(\varphi(x), x) - \mu\varphi(x))\,x\,\mathrm{d}x -$$
$$\sigma\alpha\frac{\partial\mu}{\partial\sigma}\int_0^H \varphi(x)\,x\,\mathrm{d}x \tag{21}$$

Using eqs 19, 20, and 21, one derives

$$\frac{\partial\gamma_1}{\partial\sigma}\Big|_{\sigma_0} = \alpha\int_0^H(Q(\varphi, x) - \mu\varphi)\,x\,\mathrm{d}x + \alpha[\int_0^H \varphi\,\mathrm{d}x] \times$$
$$[\int_0^H \varphi x\,\mathrm{d}x]/\int_0^H\left(\frac{\delta^2 Q}{\delta\varphi^2}\right)^{-1}\mathrm{d}x \tag{22}$$

Thus, the corrected (due to the curvature dependence of the area per molecule) expansion of the free energy per unit molecule can be represented by the form

$$f = \gamma_0(\sigma_0) + \left\{\gamma_1(\sigma_0) + \Delta\frac{\partial\gamma_0(\sigma)}{\partial\sigma}\bigg|_{\sigma_0}\right\}/R + \left\{\gamma_2(\sigma_0) + \Delta\frac{\partial\gamma_1(\sigma)}{\partial\sigma}\bigg|_{\sigma_0} + \frac{\Delta^2}{2}\frac{\partial\gamma_0(\sigma)}{\partial\sigma}\bigg|_{\sigma_0}\right\}/R^2 \quad (23)$$

By using the condition for the free energy minimum for the flat interface in eq 23, one obtains

$$f = \gamma_0(\sigma_0) + \gamma_1(\sigma_0)/R + \left\{\gamma_2(\sigma_0) - \frac{\Delta^2}{2}\frac{\partial\gamma_0(\sigma)}{\partial\sigma}\bigg|_{\sigma_0}\right\}/R^2 \quad (24)$$

Using eqs 14, 20, 22, and 24, one finally derives

$$f = \mu C - \alpha\sigma_0 I_2/R + \alpha\sigma_0\left\{(\alpha - 1)I_3 + \alpha I_1 - \alpha I_1\left(1 - \frac{I_2 I_4 \sigma_0}{C I_1}\right)^2\right\}/(2R^2) \quad (25)$$

where $I_4 = \int_0^H \varphi(x)x\, dx$ and the area per molecule is determined from the condition

$$\gamma_L = I_0 = \int_0^H [\mu\varphi(x) - Q(\varphi(x), x)]\, dx \quad (26)$$

Comparing the results with eq 8, one obtains new expressions for the bending constants of monolayer, which now account for the fact that the area per molecule is adjusted in the process of curving the interface

$$2H_0 = \frac{C}{I_4\sigma_0\left(2 - \frac{I_2 I_4 \sigma_0}{I_1 C}\right)}, \quad \kappa = \frac{I_2 I_4 \sigma_0}{C}\left(2 - \frac{I_2 I_4 \sigma_0}{C I_1}\right), \quad \bar{\kappa} = I_3 \quad (27)$$

As discussed above, this correction is equivalent to a constant chemical potential case. Another comment we would like to make is about the correction due to the surface area adjustments (second term in the second equation in eq 27). This is manifestation of the fact that the soluble layer (molecules could adjust their surface area) is less rigid upon bending compared to the layer with grafted molecules (no surface area adjustment). So in this case, the bending constant, in certain cases, could change its sign, which of course means that higher order expansions ($1/R^4$) of the free energy and surface area corrections should be taken into account. The latter makes all the consideration much more complex, which goes beyond the scope of this article.

Similarly, one could generalize the result for the case of a diblock amphiphilic polymer

$$\kappa = \{(C_{out}/I_4^{out} + C_{in}/I_4^{in})^2 I_1^{in} I_1^{out} + \sigma_0[I_2^{out} - I_2^{in}] \times \{2(I_1^{out}C_{out}/I_4^{out} - I_1^{in}C_{in}/I_4^{in}) - \sigma_0[I_2^{out} - I_2^{in}]\}\}/\{I_1^{in}(C_{in}/I_4^{in})^2 + I_1^{out}(C_{out}/I_4^{out})^2\} \quad (28)$$

$$\bar{\kappa} = I_3^{out} + I_3^{in},\ 2H_0 = (I_2^{out} - I_2^{in})/\kappa \quad (29)$$

where equilibrium area per molecule is given with $\gamma_L = I_0^{in} + I_0^{out}$. Note that a similar approach could be applied to any Landau–Ginsburg type of functional.

4. Application of the Method to Grafted Polymer Brushes

A general form of the density functional of the polymer brush has the following form:

$$\Phi(\varphi(x), x) = \frac{kT}{v_0}\left\{\frac{v_0}{v_w}[(1 - \varphi(x))\ln(1 - \varphi(x)) + \chi\varphi(x)(1 - \varphi(x))] + K_s x^2 \varphi(x)\right\} \quad (30)$$

Here $K_s = 3\pi^2/8N^2l^2$ is the elastic constant, N is the number of segments of the polymer, v_0 is the volume of the polymer segment, v_w is the volume of the solvent molecule, χ is the Flory–Huggins parameter of interaction between polymer monomer and solvent molecule, l is the Kuhn length of the polymer segment, and φ is the volume fraction of polymer segments. The constant volume normalizing conditions is

$$\sigma\int_0^H \varphi(x)\, dx = C = Nv_0 \quad (31)$$

where $\sigma = A/M$ is the area per polymer molecules and M is the total number of polymers in the system while A is the total area of the layer. We will use the approach described in the previous section to calculate the bending elasticity moduli and spontaneous curvature of the system, which obey this type of functional. We consider several different cases, which correspond to a different volume fraction and different solvent quality (controlled via Flory parameter).

4.1. Low Volume Fraction Arbitrary Solvent. We will consider only the case of low polymer coverage, as originally done by Milner and Safran.[13] For this case the SCF theory gives

$$Q(\varphi(x), x) = \frac{kT}{v_0}\left\{\frac{1}{2}B\varphi(x)^2 + K_s x^2 \varphi(x)\right\} \quad (32)$$

where $B = (1 - 2\chi)v_0/v_m$. There is also a linear term $\varphi(x)(\chi - 1)v_0/v_m$ in eq 30 in ref 13, which due to the normalizing condition integrates to a constant; i.e., it contributes to$\gamma(0)$ but not to the bending moduli. We will use the approach described in the previous section to calculate the bending elasticity moduli and the spontaneous curvature of the system. The solution of this DFT[13] is, $\varphi(x) = K_s(H^2 - x^2)/B$, $H = (3Bv_0N/2K_s\sigma)^{1/3}$. Using eqs 10, 26, and 27, one directly obtains

$$I_0 = \frac{4kTK_s^2H^5}{15v_0B} = \gamma_L, \quad I_1 = \frac{kTK_s^2H^7}{16v_0B}, \quad I_2 = \frac{kTK_s^2H^6}{12v_0B}, \quad I_3 = -\frac{4kTK_s^2H^7}{105v_0B}, \quad I_4 = \frac{K_sH^4}{4B} \quad (33)$$

For the case of constant area per molecule[11] one gets

$$\kappa = \frac{kTK_s^{\,2}H^7}{16v_0B},\quad \bar{\kappa} = -\frac{4kTK_s^{\,2}H^7}{105v_0B},\quad \kappa/\bar{\kappa} = -105/64,\qquad H_0 = \frac{2}{3H} \quad (34)$$

For the case of adjusted surface tension[13] and single chain, however, one has $2I_2I_4\sigma_0 = v_0NI_1$ which gives a correction of $\kappa_{\mathrm{adj}} = ({}^3/_4)\kappa_{\mathrm{non-adjust}}$ (see refs 12 and 13). For the case of diblock polymers adjusting their surface area one can also reproduce the results of Milner et al.[12] After substituting the value of H in eq 29, for the "lamellar" regime ($H_0 = 0$) one gets $B_{\mathrm{out}}N_{\mathrm{out}}^{\,2} = B_{\mathrm{in}}N_{\mathrm{in}}^{\,2}$ as obtained by Paunov et al.[11] Another interesting conclusion is that the PIT criteria[11] does not depend on the area per molecule but depends on the interactions of the chains with the solvents (B) and the length of the chains (N).

4.2. Θ-Solvent (χ = ½) and Low Volume Fractions. In this case $\chi = {}^1/_2$ and $B = v_0/v_{\mathrm{m}}(1 - 2\chi) = 0$, so the quadratic part of the FT is zero and one needs to take into account the higher order term in the expansion of the logarithmic term in the osmotic part of the free energy. So the DF has the following form

$$\Phi(\varphi(x), x) = \frac{kT}{v_0}\left\{\frac{1}{3}w_1\varphi(x)^3 + K_sx^2\varphi(x)\right\} \qquad (35)$$

where $w_1 = 1/2\ v_0/v_{\mathrm{w}}$. The solution of DF in this case is

$$\frac{\delta\Phi}{\delta\varphi} = \frac{kT}{v_0}(w_1\varphi(x)^2 + K_sx^2) = \mu = \frac{kT}{v_0}K_sH^2,\qquad \varphi(x) = \sqrt{K_s(H^2 - x^2)/w_1} \quad (36)$$

Using the solution, eq 36, one determines all moments necessary for the calculation of the elastic constants:

$$\int_0^H \varphi(x)\,\mathrm{d}x = \sqrt{\frac{K_s}{w_1}}\frac{\pi H^2}{4} = \frac{Nv_0}{\sigma},$$

$$H = 2\left(\frac{w_1}{K_s}\right)^{1/4}\left(\frac{Nv_0}{\pi\sigma}\right)^{1/2},\quad \left(\int_0^H \varphi(x)x\,\mathrm{d}x\right)^2 = \frac{K_sH^6}{9w_1},$$

$$\mu\varphi(x) - \Phi(\varphi(x), x) = \frac{2kT}{3v_0}w_1\varphi(x)^3,$$

$$\frac{\delta^2\Phi}{\delta\varphi^2} = \frac{2kTw_1}{v_0}\varphi(x),\quad \int_0^H\left(\frac{\delta^2\Phi}{\delta\varphi^2}\right)^{-1}\mathrm{d}x = \frac{\pi v_0}{4kTw_1}\sqrt{\frac{w_1}{K_s}},$$

$$I_1 = \frac{4kT\mathrm{H}^6}{9\pi v_0}\sqrt{\frac{K_s^{\,3}}{w_1}},$$

$$I_2 = \int_0^H(\mu\varphi(x) - \Phi(\varphi(x), x))x\,\mathrm{d}x = \frac{2kT\mathrm{H}^5}{15v_0}\sqrt{\frac{K_s^{\,3}}{w_1}},$$

$$I_3 = -\int_0^H(\mu\varphi(x) - \Phi(\varphi(x), x))x^2\,\mathrm{d}x = -\frac{\pi kT\mathrm{H}^6}{48v_0}\sqrt{\frac{K_s^{\,3}}{w_1}} \quad (37)$$

Thus, for the bending moduli for the case of single-side brush (constant area per molecule), we obtain the following expressions:

$$\kappa = \frac{4kT\mathrm{H}^6}{9\pi v_0}\sqrt{\frac{K_s^{\,3}}{w_1}},\quad \bar{\kappa} = -\frac{\pi kT\mathrm{H}^6}{48v_0}\sqrt{\frac{K_s^{\,3}}{w_1}},\qquad \kappa/\bar{\kappa} = -64/(3\pi^2),\quad H_0 = \frac{3\pi}{20H} \quad (38)$$

For the case when area per molecule changes with curvature, the result could also be calculated straightforwardly.

4.3. Good Solvent (χ = 0), Arbitrary Volume Fractions. In this case, we will assume that we have a good solvent ($\chi = 0$), which gives the following function for DF of SCF:

$$\Phi(\varphi(x), x) = \frac{kT}{v_0}\left\{\frac{v_0}{v_{\mathrm{w}}}(1 - \varphi(x))\ln(1 - \varphi(x)) + K_sx^2\varphi(x)\right\} \quad (39)$$

The solution of this problem is

$$\frac{\delta\Phi}{\delta\varphi} = \frac{kT}{v_0}\left(-\frac{v_0}{v_{\mathrm{w}}}(\ln(1 - \varphi(x)) + 1) + K_sx^2\right) = \mu = \frac{kT}{v_0}\left(-\frac{v_0}{v_{\mathrm{w}}} + K_sH^2\right),$$

$$\varphi(x) = 1 - \exp[-\alpha^2(1 - x^2/H^2)] \quad (40)$$

where

$$\alpha = H\sqrt{\frac{v_{\mathrm{w}}K_s}{v_0}}$$

and

$$\int_0^H \varphi(x)\,\mathrm{d}x = H(1 - D(\alpha)/\alpha) = \frac{Nv_0}{\sigma},\qquad \left(\int_0^H \varphi(x)x\,\mathrm{d}x\right)^2 = \frac{H^4}{4\alpha^4}(\mathrm{e}^{-\alpha^2} + \alpha^2 - 1)^2 \quad (41)$$

Here, $D(x) = \mathrm{e}^{-x^2}\int_0^x \mathrm{e}^{t^2}\,\mathrm{d}t$ is the Dawson integral. For the case of small coverage ($\alpha \approx H/Nl \ll 1$) we have $D(x) \approx x - 2x^3/3 + O(x^5)$ ($x \ll 1$), which substituted back into eq 41 gives the result from section 4.1 (after setting $w = v_0/v_{\mathrm{m}}$). For high coverage (high segment density), $H/Nl \approx 1$, the Dawson integral could be expanded for the case of high values: $D(x) \approx {}^1/_2x + {}^1/_4x^3 + O(1/x^5)$ ($x \gg 1$), and thus the first estimate for H is $H = Nv_0/\sigma$. Thus, the results can be represented in general form

$$\mu\varphi(x) - \Phi(\varphi(x), x) = -\frac{kT}{v_w}(\varphi(x) + \ln(1 - \varphi(x))), \quad (42)$$

$$I_2 = \int_0^H (\mu\varphi(x) - \Phi(\varphi(x), x))x\,dx = \frac{kTH^2}{4v_w\alpha^2}(2(1 - e^{-\alpha^2}) + \alpha^2(\alpha^2 - 2)),$$

$$\frac{\delta^2\Phi}{\delta\varphi^2} = \frac{kT}{v_w}\frac{1}{1 - \varphi(x)},$$

$$\int_0^H\left(\frac{\delta^2\Phi}{\delta\varphi^2}\right)^{-1} dx = \frac{v_w}{kT}\int_0^H (1 - \varphi(x))\,dx = \frac{v_w}{kT}\left(H - \frac{Nv_0}{\sigma}\right) = \frac{v_w HD(\alpha)}{kT\alpha},$$

$$\kappa = I_1 = \frac{kTH^3}{4v_w\alpha^3}\frac{(e^{-\alpha^2} + \alpha^2 - 1)^2}{D(\alpha)},$$

$$H_0 = \frac{I_2}{2I_1} = \frac{\alpha}{2H}\frac{(2(1 - e^{-\alpha^2}) + \alpha^2(\alpha^2 - 2))D(\alpha)}{(e^{-\alpha^2} + \alpha^2 - 1)^2},$$

$$\bar\kappa = I_3 = -\int_0^H(\mu\varphi(x) - \Phi(\varphi(x), x))x^2\,dx = \frac{kTH^3}{v_w}\left(\frac{D(\alpha)}{2\alpha^3} + \frac{1}{3} - \frac{2\alpha^2}{15} - \frac{1}{2\alpha^2}\right),$$

$$\kappa/\bar\kappa = \frac{(e^{-\alpha^2} + \alpha^2 - 1)^2}{4\alpha^3\left(\frac{D(\alpha)}{2\alpha^3} + \frac{1}{3} - \frac{2\alpha^2}{15} - \frac{1}{2\alpha^2}\right)D(\alpha)}$$

For small values of α, eqs 42 reduce to the results from section 3.1 with the substitution, $w = v_0/v_m$. For large values of α some of the asymptotic are $\kappa = kTH^3\alpha^2/2v_w$ and $\bar\kappa = -2kTH^3\alpha^2/15v_w$, while the intermediate cases are depicted in Figures 2 and 3.

4.4. Some Remarks on the General Case. Finally, we would like to make some comments concerning the most general case, which from all other cases could be extracted. In the general case, analytical solution is available and it is given with a transcendental equation:

$$\frac{v_0}{v_w}[-\ln(1 - \varphi(x)) + 2\chi\varphi(x)] + K_s x^2 = K_s H^2 = \frac{v_0}{v_w}[-\ln(1 - \varphi(0)) + 2\chi\varphi(0)] \quad (43)$$

which could be expressed also as

$$\ln\left[\frac{1 - \varphi(x)}{1 - \varphi_0}\right] + 2\chi(\varphi_0 - \varphi(x)) = \frac{v_w}{v_0}K_s x^2, \quad \text{or}$$

$$x = \sqrt{\frac{v_0}{v_w K_s}}\sqrt{\ln\left[\frac{1 - \varphi(x)}{1 - \varphi_0}\right] + 2\chi(\varphi_0 - \varphi(x))} \quad (44)$$

where $\varphi_0 = \varphi(0)$. Then the normalizing condition reads:

$$\frac{Nv_0}{\sigma} = \int_0^H \varphi(x)\,dx = -\int_0^H x\,d\varphi(x) = \sqrt{\frac{v_0}{v_w K_s}}\int_0^{\varphi_0}\sqrt{\ln\left[\frac{1 - u}{1 - \varphi_0}\right] + 2\chi(\varphi_0 - u)}\,du \quad (45)$$

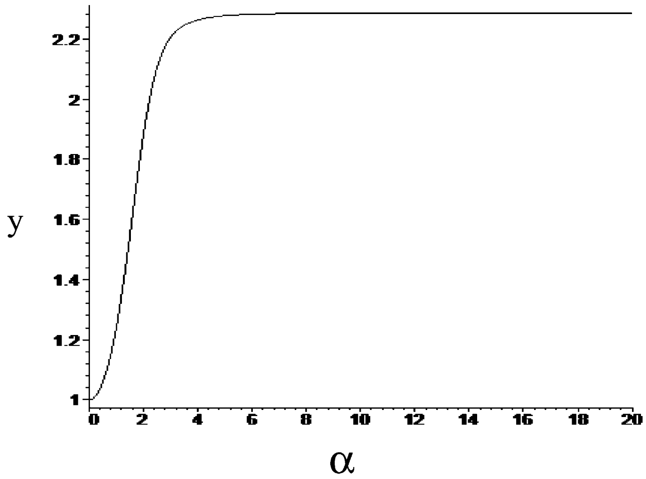

Figure 2. $y = -64\kappa/105\bar\kappa = 32(e^{-\alpha^2} + \alpha^2 - 1)^2/7(4\alpha^5 + 15(\alpha - D(\alpha)) - 10\alpha^3)D(\alpha)$ as a function of α. For small α, this function has a limit 1 while for big values (α > 4) the limit is 16/7.

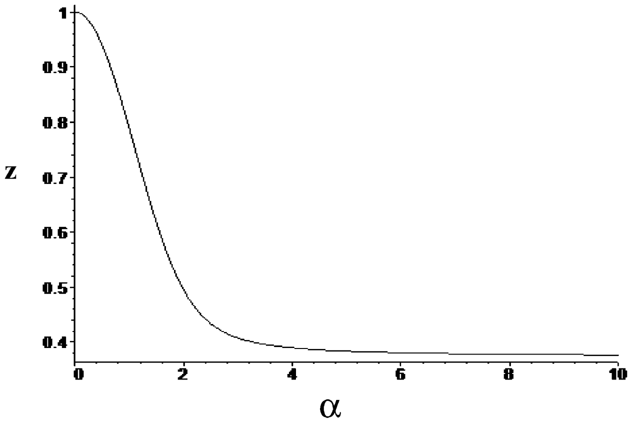

Figure 3. $z = 3H_0H/2 = 3\alpha/4\,(2(1 - e^{-\alpha^2}) + \alpha^2(\alpha^2 - 2))D(\alpha)/(e^{-\alpha^2} + \alpha^2 - 1)^2$, as a function of α. For small values, the function is 1 and for large values it goes to 3/8.

The latter should be considered as an equation for φ_0, which is independent of N. If one knows φ_0, then H can be calculated immediately from eq 43.

A more convenient form of last equation could by obtained by changing the variables: $z = z_0 + \ln(1 - u)$ with $z_0 = -\ln(1 - \varphi_0)$, which gives

$$\frac{Nv_0}{\sigma} = \sqrt{\frac{v_0}{v_w K_s}}\int_0^{z_0}\sqrt{z + 2\chi e^{z-z_0}}\,e^{z-z_0}\,dz \quad (46)$$

For the calculation of bending modulus one needs to solve integrals of the type $\int_0^H \varphi(x)x^k\,dx$. The integrals containing odd powers of k could be calculated analytically in terms of φ_0, by simple partial integration, while for the even powers integrals it could be shown that they could be expressed in terms of the normalizing integral (eq 46). Thus, if one has a good approximation for eq 46, the bending constants can be easily estimated. For the case of small z_0 the estimation is straightforward and gives the well-known result. For the case when $\chi = 0$, one can take the integral analytically in terms of Dawson functions. More problematic is calculation of the integral for big z_0. In this case the integral could be expanded by two parts: one close to z_0 (end of the chain) and one close to the wall $z = 0$. This is the same as looking for a solution of transcendental eq 43 in terms of two solutions, an inner (close to the wall) and an outer one (close to H), and a proper matching between them into the intermediate region. The latter will be the subject of a future work.

5. Conclusions

We have demonstrated that there is a very simple general method for calculation of the bending constants of grafted copolymer brushes, both for monoblock and diblock polymers (surfactants). The main advantage of the method described in the present paper is that we have expressed in closed analytical form all the elastic constants in terms of moments of the *solution for flat geometry only*. To illustrate the method, we have calculated the bending moduli of mono- and diblock polymers (surfactants) under several different conditions. For the cases when there are literature data, we have compared our calculations (see section 4.1) with the literature[13] and have demonstrated the applicability of the method. We have also calculated other two cases, which according to our best knowledge are new results. For the case of diblock polymers and surfactants, we derive simple algebraic expressions for the bending constants as functions of the corresponding moments of the single blocks. By making all possible combinations from the cases studied in this part, one can obtain plenty of new results for the case of diblock polymers. These results obtained in this chapter could be used for better prediction of phase behavior of nonionic surfactants. For example for the case of C_nE_k surfactants in ternary water/oil (hexadecanes) the Flory parameter is practically zero for the hydrophobic part of surfactant, and one can use results from section 4.3, while for ethoxylated part dissolved in water one could assume that it is close to the Θ-point and use results from cases in section 4.2. The resulting formulas may give a better description of microemulsion properties in this case than ones proposed by Wang et al.[13] and Paunov et al.[11]

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