

## Description of the Fluctuating Colloid-Polymer Interface

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To describe the full spectrum of surface fluctuations of the interface between phase-separated colloid-polymer mixtures from low scattering vector  $q$  (classical capillary wave theory) to high  $q$  (bulklike fluctuations), one must take account of the interface's bending rigidity. We find that the bending rigidity is negative and that on approach to the critical point it vanishes proportionally to the interfacial tension. Both features are in agreement with Monte Carlo simulations.

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One of the outstanding theoretical problems in the understanding of the structure of a simple liquid surface is the description of the full spectrum of surface fluctuations obtained in light scattering experiments [1,2] and computer simulations [3–5]. Insight into the structure of a simple liquid surface is provided by molecular theories [6,7], such as the van der Waals squared-gradient model, on the one hand, and the capillary wave model [8,9] on the other hand. The theoretical challenge is to incorporate both theories and to describe the spectrum of fluctuations of a liquid surface from the molecular scale to the scale of capillary waves.

Here, we report on a theoretical description of Monte Carlo (MC) simulations [4] of a system consisting of a mixture of colloidal particles with diameter  $d$  and polymers with a radius of gyration  $R_g$ . The presence of polymer induces a depletion attraction [10] between the colloidal particles which may ultimately induce phase separation [11,12]. The resulting interface of the demixed colloid-polymer system is studied for a number of polymer concentrations and for a polymer-colloid size ratio  $\varepsilon \equiv 1 + 2R_g/d = 1.8$ .

The quantity studied in the simulations is the (surface) density-density correlation function:

$$S(r_{\parallel}) \equiv \frac{1}{(\rho_{\ell} - \rho_v)^2} \int_{-L}^L dz_1 \int_{-L}^L dz_2 \langle [\rho(\vec{r}_1) - \rho_{\text{step}}(z_1)] \times [\rho(\vec{r}_2) - \rho_{\text{step}}(z_2)] \rangle, \quad (1)$$

where  $\rho(\vec{r})$  is the colloidal density,  $\vec{r}_{\parallel} = (x, y)$  is the direction parallel to the surface, and where we have defined  $\rho_{\text{step}}(z) \equiv \rho_{\ell} \Theta(-z) + \rho_v \Theta(z)$  with  $\Theta(z)$  the Heaviside function and  $\rho_{\ell, v}$  the bulk density in the liquid and vapor region, respectively, where by “liquid” we mean the phase relatively rich in colloids and by “vapor” the phase relatively poor in colloids. Its Fourier transform is termed the *surface structure factor*

$$S(q) = \int d\vec{r}_{\parallel} e^{-i\vec{q} \cdot \vec{r}_{\parallel}} S(r_{\parallel}). \quad (2)$$

In Fig. 1, MC simulation results [4] for  $S(q)$  are shown for various values of the integration limit  $L$ . The figure shows that the contribution to  $S(q)$  from short wavelength fluctuations (high  $q$ ) increases with  $L$ .

To analyze  $S(q)$ , one needs to model the density fluctuations in the interfacial region. In the capillary wave model (CW) [8], the fluctuating interface is described in terms of a two-dimensional surface height function  $h(\vec{r}_{\parallel})$

$$\rho(\vec{r}) = \rho_0(z) - \rho'_0(z)h(\vec{r}_{\parallel}) + \dots, \quad (3)$$

where  $\rho_0(z) = \langle \rho(\vec{r}) \rangle$ . In the *extended* capillary wave model (ECW), the expansion in gradients of  $h(\vec{r}_{\parallel})$  is continued [13–15]:

$$\rho(\vec{r}) = \rho_0(z) - \rho'_0(z)h(\vec{r}_{\parallel}) - \frac{\rho_1(z)}{2} \Delta h(\vec{r}_{\parallel}) + \dots \quad (4)$$

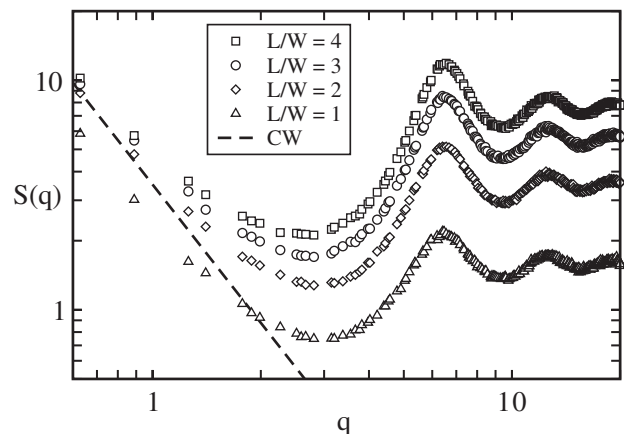


FIG. 1. MC simulation results for the surface structure factor (in units of  $d^4$ ) versus  $q$  (in units of  $1/d$ ) for various values of the integration limit  $L/W = 1, 2, 3, 4$  [4]. The dashed line is the capillary wave model. In this example  $\varepsilon = 1.8$ ,  $\eta_p = 1.0$ .

The function  $\rho_1(z)$  is identified as the correction to the density profile due to the *curvature* of the interface,  $\Delta h(\vec{r}_{\parallel}) \approx -1/R_1 - 1/R_2$ , with  $R_1$  and  $R_2$  the (principal) radii of curvature.

With Eq. (4) inserted into Eq. (1), we find that  $S(q)$  equals the *height-height correlation function*,  $S(q) = S_{hh}(q)$ , where

$$S_{hh}(q) \equiv \int d\vec{r}_{\parallel} e^{-i\vec{q}\cdot\vec{r}_{\parallel}} \langle h(\vec{r}_{1,\parallel}) h(\vec{r}_{2,\parallel}) \rangle. \quad (5)$$

Here we have assumed that the location of the interface, as described by the height function  $h(\vec{r}_{\parallel})$ , is given by the *Gibbs equimolar surface* [16], which gives for  $\rho_0(z)$  and  $\rho_1(z)$ :

$$\int dz [\rho_0(z) - \rho_{\text{step}}(z)] = 0, \quad \int dz \rho_1(z) = 0. \quad (6)$$

Naturally, other choices are possible [5] and equally legitimate as long as they lead to a location of the dividing surface that is “sensibly coincident” [16] with the interfacial region.

The height-height correlation function  $S_{hh}(q)$  is determined by considering the free energy  $\Delta\Omega$  associated with a surface fluctuation [8,9]. The inclusion of a curvature correction to the free energy is described by the Helfrich free energy [17]. It gives for  $\Delta\Omega$

$$\Delta\Omega = \frac{1}{2} \int \frac{d\vec{q}}{(2\pi)^2} \sigma(q) q^2 h(\vec{q}) h(-\vec{q}), \quad (7)$$

with

$$\sigma(q) = \sigma + kq^2 + \dots \quad (8)$$

The coefficient  $k$  is identified as Helfrich’s *bending rigidity* [17,18]. It is important to realize that the bending rigidity, defined by Eqs. (7) and (8), depends on the choice made for the location of the dividing surface (here, the Gibbs equimolar surface for the colloid component).

Using Eq. (7), the height-height correlation function can be calculated [18]

$$S_{hh}(q) = \frac{k_B T}{\sigma(q) q^2} = \frac{k_B T}{\sigma q^2 + k q^4 + \dots}. \quad (9)$$

Without bending rigidity ( $k = 0$ ) this is the classical capillary wave result in the absence of gravity (dashed line in Fig. 1). When  $L$  is sufficiently large, the capillary wave model accurately describes the behavior of  $S(q)$  at low  $q$ .

To model  $S(q)$  in the *whole*  $q$  range, we also include bulklike fluctuations to the density:

$$\rho(\vec{r}) = \rho_0(z) - \rho'_0(z) h(\vec{r}_{\parallel}) - \frac{\rho_1(z)}{2} \Delta h(\vec{r}_{\parallel}) + \delta\rho_b(\vec{r}). \quad (10)$$

Inserting Eq. (10) into Eq. (1), one now finds that

$$S(q) = S_{hh}(q) + \mathcal{N}_L S_b(q). \quad (11)$$

The second term is derived from an integration into the

bulk regions (to a distance  $L$ ) of the bulk structure factor  $S_b(q)$

$$S_b(q) = 1 + \rho_b \int d\vec{r}_{12} e^{-i\vec{q}\cdot\vec{r}_{12}} [g(r) - 1]. \quad (12)$$

The density correlation function  $g(r)$  differs in either phase, but here we take for it  $g_\ell(r)$  of the bulk *liquid*. This approximation may be justified by arguing that close to the critical point there is no distinction between the two bulk correlation functions, whereas far from the critical point the contribution from the bulk vapor can be neglected since  $\rho_v \approx 0$ . The error is further reduced by fitting the  $L$ -dependent prefactor  $\mathcal{N}_L$  to the limiting behavior of  $S(q)$  at  $qd \rightarrow \infty$ .

In Fig. 2, we show the result from Fig. 1 for  $L/W = 3$ . For  $qd \ll 1$  the results asymptotically approach the capillary wave model (dotted line). The dashed line is the result of adding the bulklike fluctuations to the capillary waves:

$$S(q) = \frac{k_B T}{\sigma q^2} + \mathcal{N}_L S_b(q). \quad (13)$$

Figure 2 shows that Eq. (13) already matches the simulation results quite accurately except at intermediate values of  $q$ ,  $qd \approx 1$ .

Finally, we include a bending rigidity in  $S(q)$ :

$$S(q) = \frac{k_B T}{\sigma q^2 + k q^4 + \dots} + \mathcal{N}_L S_b(q). \quad (14)$$

The value of the bending rigidity is extracted from the behavior of  $S(q)$  at low  $q$ . The fact that the simulation results in Fig. 2 are systematically *above* the capillary wave model in this region indicates that the bending rigidity thus obtained is *negative*,  $k < 0$ . Unfortunately, a negative bending rigidity prohibits the use of  $S(q)$  in Eq. (14) to

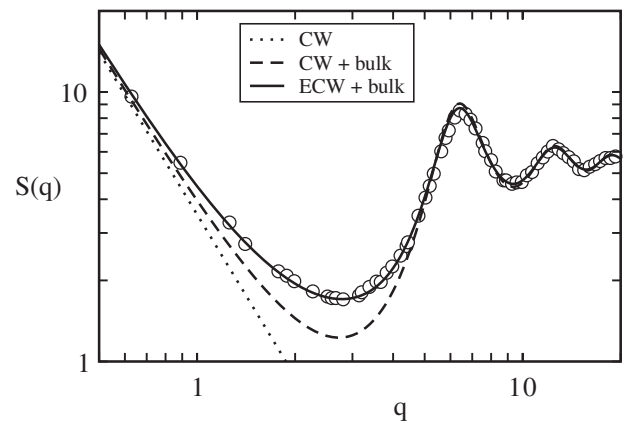


FIG. 2. MC simulation results [4] (circles) for the surface structure factor (in units of  $d^4$ ) versus  $q$  (in units of  $1/d$ ). The dotted line is the capillary wave model; the dashed line is the combination of the capillary wave model and the bulk correlation function; the solid line is the combination of the extended capillary wave model and the bulk correlation function. In this example  $\varepsilon = 1.8$ ,  $\eta_p = 1.0$ ,  $L/W = 3$ .

fit the simulation results in the *entire*  $q$  range, since the denominator becomes zero at a certain value of  $q$ . It is therefore convenient to rewrite the expansion in  $q$  in Eq. (14) as

$$S(q) = \frac{k_B T}{\sigma q^2} \left( 1 - \frac{k}{\sigma} q^2 + \dots \right) + \mathcal{N}_L S_b(q), \quad (15)$$

which is equivalent to Eq. (14) to the order in  $q^2$  considered, but which has the advantage of being well behaved in the entire  $q$  range. The above form for  $S(q)$ , with the bending rigidity used as an adjustable parameter, is plotted in Fig. 2 as the solid line. Exceptionally good agreement with the MC simulations is now obtained for all  $q$ . In Table I, we list the fitted values for the bending rigidity for a number of different polymer concentrations.

Next, we investigate whether the value and behavior of  $k$  can be understood from a molecular theory. One should then consider a microscopic model for the free energy  $\Omega$  to determine the density profiles  $\rho_0(z)$  and  $\rho_1(z)$ . Here, we consider the free energy density functional based on a *squared-gradient* expansion [7,13,14,19]:

$$\Omega[\rho] = \int d\vec{r} \left[ m |\vec{\nabla} \rho(\vec{r})|^2 - \frac{B}{4} [\Delta \rho(\vec{r})]^2 + g(\rho) \right], \quad (16)$$

where the coefficients  $m$  and  $B$  are defined as

$$m \equiv -\frac{1}{12} \int d\vec{r}_{12} r^2 U(r), \quad B \equiv -\frac{1}{60} \int d\vec{r}_{12} r^4 U(r). \quad (17)$$

The integration over  $\vec{r}_{12}$  is restricted to the attractive part ( $r > d$ ) of the interaction potential  $U(r)$ , for which we consider the Asakura-Oosawa-Vrij depletion interaction potential [10]:

$$U(r) = \frac{-k_B T \eta_p}{2(\varepsilon - 1)^3} \left[ 2\varepsilon^3 - 3\varepsilon^2 \left( \frac{r}{d} \right) + \left( \frac{r}{d} \right)^3 \right], \quad (18)$$

where the intermolecular distance is in the range  $1 < r/d < \varepsilon$ . For explicit calculations,  $g(\rho)$  is taken to be of the Carnahan-Starling form:

$$g(\rho) = k_B T \rho \ln(\rho) + k_B T \rho \frac{(4\eta - 3\eta^2)}{(1 - \eta)^2} - \mu \rho - a \rho^2, \quad (19)$$

TABLE I. MC simulation results [4] for the polymer volume fraction  $\eta_p$ , liquid and vapor colloidal volume fractions,  $\eta_\ell$  and  $\eta_v$ , surface tension  $\sigma$  (in units of  $k_B T/d^2$ ), bending rigidity  $k$  (in units of  $k_B T$ ; in parenthesis the estimated error in the last digit), and  $\sqrt{-k/\sigma}$  (in units of  $d$ ).

$\eta_p$	$\eta_\ell$	$\eta_v$	$\sigma$	$k$	$\sqrt{-k/\sigma}$
0.9	0.2970	0.0141	0.1532	-0.045 (15)	0.54
1.0	0.3271	0.0062	0.2848	-0.07 (2)	0.50
1.1	0.3485	0.0030	0.4194	-0.10 (3)	0.49
1.2	0.3647	0.0018	0.5555	-0.14 (3)	0.50

where  $\eta \equiv (\pi/6)\rho d^3$ ,  $\pi = \mu_{\text{coex}}$ , and the van der Waals parameter  $a$  is given by

$$a \equiv -\frac{1}{2} \int d\vec{r}_{12} U(r). \quad (20)$$

The surface tension, to leading order in the squared-gradient expansion, can be determined from the usual expression [7]

$$\sigma = 2\sqrt{m} \int_{\rho_v}^{\rho_\ell} d\rho \sqrt{g(\rho) + p}. \quad (21)$$

In the inset of Fig. 3, the surface tension is shown as a function of the colloidal volume fraction difference,  $\Delta\eta \equiv \eta_\ell - \eta_v$ . The squared-gradient expression (solid line) is in satisfactory agreement [20] with the MC simulations.

The (planar) density profile  $\rho_0(z)$  is determined from minimizing the free energy functional  $\Omega[\rho]$  in Eq. (16) in planar symmetry. To also determine the density profile  $\rho_1(z)$  from a minimization procedure, one should consider the energetically most favorable density profile for a *given* curvature of the surface. To set the curvature to a specific value, one adds to the free energy in Eq. (16) an external field  $V_{\text{ext}}(\vec{r})$  that acts a Lagrange multiplier. Different choices for  $V_{\text{ext}}(\vec{r})$  can then be made, but we choose it such that it acts only in the interfacial region:

$$V_{\text{ext}}(\vec{r}) = \lambda \rho'_0(z) \Delta h(\vec{r}_\parallel), \quad (22)$$

with the Lagrange multiplier  $\lambda$  set by the imposed curvature. This choice for  $V_{\text{ext}}(\vec{r})$  constitutes our fundamental “ansatz” for the determination of  $\rho_1(z)$ . It improves on earlier choices made [13,14,21] in the sense that the bulk densities are equal to those at coexistence and the density profile remains a continuous function.

The minimization of the free energy, with the above external field added, using the fluctuating density in Eq. (4) yields the following Euler-Lagrange (EL) equations

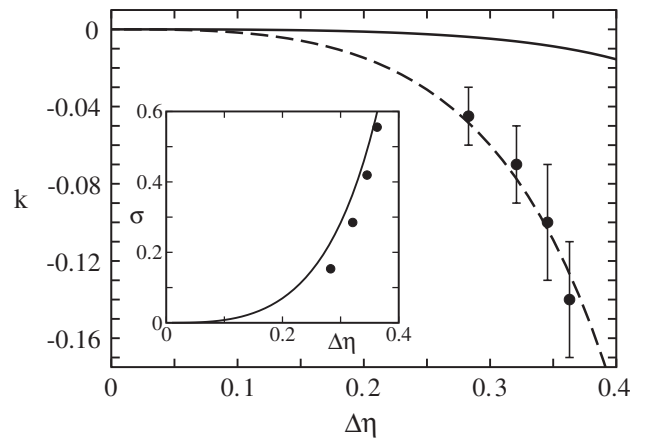


FIG. 3. Bending rigidity in units of  $k_B T$  versus the volume fraction difference  $\Delta\eta$ . The inset shows the surface tension in units of  $k_B T/d^2$ . The solid lines are the gradient expansion approximation; filled circles are the results from the MC simulations; the dashed line is the fit  $\sqrt{-k/\sigma} \approx 0.47d$ .

for  $\rho_0(z)$  and  $\rho_1(z)$ :

$$\begin{aligned} g'(\rho_0) &= 2m\rho_0''(z), \\ g''(\rho_0)\rho_1(z) &= 2m\rho_1''(z) + 4m\rho_0'(z) \\ &\quad + 2B\rho_0'''(z) + 2\lambda\rho_0'(z). \end{aligned} \quad (23)$$

The change in free energy  $\Delta\Omega$  due to a certain density fluctuation is determined by inserting  $\rho(\vec{r})$  in Eq. (4) into the expression for  $\Omega$  in Eq. (16). One finds that  $\Delta\Omega$  is then given by the expression in Eq. (7), with the bending rigidity [14]

$$k = -2m \int dz \rho_1(z) \rho_0'(z) - \frac{B}{2} \int dz \rho_0'(z)^2, \quad (24)$$

where we have used the EL equations in Eq. (23).

To determine  $\rho_0(z)$  we assume proximity to the *critical point* where  $g(\rho)$  takes on the usual double-well form. The solution of the EL equation in Eq. (23) then gives [7]:

$$\rho_0(z) = \frac{1}{2}(\rho_\ell + \rho_v) - \frac{\Delta\rho}{2} \tanh(z/2\xi), \quad (25)$$

where  $\xi$  is a measure of the interfacial thickness which we shall define as  $\xi \equiv m(\Delta\rho)^2/(3\sigma)$ , with the value of  $\sigma$  given by Eq. (21). To determine  $\rho_1(z)$  the differential equation in Eq. (23) is solved using the tanh profile for  $\rho_0(z)$ , yielding:

$$\rho_1(z) = \frac{3B}{10m} \frac{\Delta\rho}{\xi} \frac{\{1 - \ln[2 \cosh(z/2\xi)]\}}{\cosh^2(z/2\xi)}, \quad (26)$$

where we have used that  $\lambda = -2m + B/(5\xi^2)$ .

Inserting Eq. (26) into Eq. (24), one finds for  $k$

$$k = -\frac{B(\Delta\rho)^2}{60\xi} = -\frac{B\sigma}{20m}. \quad (27)$$

This expression indicates that the bending rigidity vanishes near the critical point with the same exponent as the surface tension, i.e.,

$$k \propto \frac{B\sigma}{m} \propto \sigma d^2. \quad (28)$$

This scaling behavior should be contrasted to the usual assumption that  $k \propto \sigma\xi^2$ , i.e., that  $k$  approaches a finite, nonzero limit at the critical point [18,21].

In Fig. 3, the gradient expansion result in Eq. (27) for the bending rigidity is shown as the solid line. The bending rigidity is *negative*, in line with the simulation results, although the magnitude is significantly lower.

To summarize, we have shown that to account for the simulated scattering function over the whole range of scattering vector  $q$ , including the intermediate range between low  $q$  (classical capillary wave theory) and high  $q$  (bulklike fluctuations), one must take account of the interface's *bending rigidity*. Two of the important results are that the bending rigidity  $k$  for the interface between phase-

separated colloid-polymer mixtures is *negative*, and that on approach to the critical point it vanishes proportionally to the interfacial tension rather than, as had often been supposed, varying proportionally to the product of the tension and the square of the correlation length, thereby approaching a finite, nonzero limit. Both features of  $k$  are in accord with what is found in the simulations. The magnitude of  $k$  obtained from the molecular theory is lower ( $\sqrt{-k/\sigma} \approx 0.13d$ ) than in the simulations ( $\sqrt{-k/\sigma} \approx 0.47d$ ; dashed line in Fig. 3).

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