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From monolayers to bilayers: Effective rigidity and compressibility in asymmetric ternary amphiphilic systems

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Fluctuation effects in lamellar phases of ternary asymmetric amphiphilic systems are considered. These systems are characterized by two length scales corresponding to the thickness of the oil and water layers. For large separations between the amphiphilic layers, the dominant contribution to the free energy can be written in the Helfrich form if an effective bending rigidity is introduced that is allowed to depend on the water and oil layer thicknesses. The scaling form of this effective rigidity is determined from Monte Carlo simulations of an asymmetric three-layer system. An expression for the effective layer compressibility is derived, which can be expressed in terms of the effective bending rigidity. These effects lead to pronounced corrections of the scattering exponents η_m, which can be measured in scattering experiments.

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I. INTRODUCTION

One of the rather intriguing structures obtained upon mixing an amphiphilic material with water and oil is the lamellar phase, in which alternating layers of oil and water are separated by monomolecular layers of amphiphilic molecules [1,2]. The origin of this mesostructure lies in the physical properties of the amphiphilic molecules, which are composed of both a hydrophilic and a hydrophobic part, thus preferring to be located at a boundary between water and oil regions. This phase has been obtained in several theoretical treatments starting from microscopic Hamiltonians [3] and generalized Landau-Ginsburg free energies [4]. A rather complimentary route derives effective free energies for lamellar and other phases [5] from the well-known expression for the bending energy of thin sheets [6]. The dominant contribution to the effective free energy in the lamellar phase is due to thermal fluctuations and results mainly from the loss of configurational entropy of amphiphilic layers in the presence of impenetrable neighboring layers. For a single pair of layers with mean separation ℓ, this free energy can be shown to behave like [7]

$$V_{fl}(\ell) \approx \frac{c_{fl}T^2}{K\ell^2} \tag{1}$$

for large separations ℓ between neighboring membranes with K being the bending modulus of a single lamella and T the temperature. In previous treatments of the lamellar phase, the free energy per separation coordinate has usually been taken to be (1) independent of the total number of layers in the stack, thereby neglecting possible corrections for the coefficient c_{fl} [8]; the justification for this procedure has been given only recently and consists of the quasiseparability of a symmetric, constrained stack of membranes (or amphiphilic sheets) [9]. The form of the fluctuation potential $V_{fl}(\ell)$ as given by (1) has been verified experimentally by small-angle x-ray scattering experiments on swollen stacks of surfactant bilayers [10,11].

In fact, the simple superposition procedure of calculating the total free energy of a multilamellar stack by simply adding the free energies of the individual pairs of amphiphilic layers each assumed to be given by (1) fails if the stack becomes asymmetric, i.e., if the separations between individual amphiphilic sheets are not the same throughout the system. This is the case in asymmetric ternary lamellar systems, for which the amounts of water and oil are unequal. To understand how this failure comes about, consider a stack of $N+1$ amphiphilic layers, each parametrized by a displacement field $l_n(\mathbf{x})$. The relative displacement fields, or separations between the lamellae, are denoted by $\delta l_n \equiv l_{n+1} - l_n$ and are always positive, thus taking into account the impenetrability of individual layers. The mean separation, given by a thermal average, is denoted by $\ell_n \equiv \langle \delta l_n \rangle$. A symmetric stack is defined by $\ell = \ell_n$ for all n and is realized for a ternary system in the lamellar phase region with equal amounts of water and oil (neglecting boundary effects). Consider now deviations from this symmetric case by changing the relative amounts of water and oil. Clearly, for the extreme case of no oil present at all, one is left with a bilayer system, in which case the fluctuation interaction for the displacement field equivalent to the thickness of a water layer should be given by (1), but with a bending constant K twice as large as for the monolayer case. This stands in vivid contrast to the simple superposition principle outlined above. For asymmetric systems with varying oil and water thicknesses, the fluctuation potential will show a smooth crossover from the behavior of symmetric systems [with only small corrections to (1)] to the behavior of the limiting bilayer case.

In this article it is shown that the general form of the repulsion interaction (1) can still be maintained in the general case of asymmetric ternary amphiphilic systems upon introduction of an effective bending rigidity K^{eff} that depends on the individual thicknesses of the water and oil layers. The explicit scaling form of this effective rigidity is determined using Monte Carlo simulations of a stack of elastic layers. It is further shown how these new effects modify the layer compressibility modulus $\mathcal{B}$ of an asymmetric system. This, in turn, leads to pronounced and experimentally accessible variations of the exponents η_m, governing the algebraic decay of the mth quasi-Bragg peak. These results should also be of importance for the calculation of phase diagrams of amphiphilic systems featuring the microemulsion phase and disordered phases in addition to the lamellar phase; a dependence of the effective rigidity on the asymmetry will influence the mutual stability of different phases.

II. ASYMMETRIC LAMELLAR AMPHIPHILIC SYSTEMS

Asymmetric amphiphilic systems are characterized by unequal amounts of water and oil. In the lamellar phase, one thus obtains water and oil layers of different thicknesses. For the general case, the fluctuation free energy of the nth displacement field can, in analogy to (1), be written as

$$V_{fl}^{(n)}(\{\ell_N\}) \approx \frac{c_{fl}T^2}{K_n^{eff}(\{\ell_N\})\ell_n^2} \ , \tag{2}$$

which can be viewed as a *definition* of the effective bending rigidity K_n^{eff} of the nth displacement field [12]. The usefulness of this definition lies in the accessibility of K_n^{eff} and its predictive power, as will be demonstrated in later sections. This effective rigidity in the most general case depends on all mean separations in the stack. For the symmetric case, it has been shown that $K_n^{eff} \approx K$ to a very good approximation [9], where K stands for the bending rigidity of a single layer, or the constant entering (1) for the case of a single pair of layers.

For the restricted case of a ternary amphiphilic system, one has $\ell_n = \ell_{n+2}$ for all n, so that, in this case, one can write

$$K_n^{eff}(\{\ell_N\}) = \mathcal{K}^{eff}(\ell_{n+1}/\ell_n, \ell_n), \tag{3}$$

neglecting the dependence on the total number of layers N, which is very small [9]. In Sec. II C the scaling function $\mathcal{K}^{eff}(x,y)$ is extracted from Monte Carlo simulations of three elastic layers.

A. Line shapes of quasi-Bragg peaks

Experimentally, the interactions between fluctuating layers in a stack can be determined using small-angle x-ray scattering. In these experiments, the separation between the lamellae is fixed by the amount of solvent added. Due to the large fluctuations in these systems, the Bragg peaks are replaced by power law singularities $|q_{\|} - q_m|^{\eta_m - 2}$ centered around $q_m = 2\pi m/d$ and characterized by exponents [14]

$$\eta_m = \frac{Tq_m^2}{8\pi\sqrt{\mathcal{B}\kappa}}, \tag{4}$$

where $\mathcal{B}$ and κ are the compressibility and bending volume moduli, respectively, given by

$$\kappa \equiv K/d, \tag{5}$$

$$\mathcal{B} \equiv d\frac{\partial^2 F(d)}{\partial d^2}. \tag{6}$$

The repeat distance d is defined as the sum of the separation ℓ between layers and the layer thickness δ,

$$d \equiv \ell + \delta. \tag{7}$$

For lamellar systems that are above their unbinding temperature and thus can, in principle, be swollen indefinitely, short-ranged forces are rather unimportant and only lead to correction terms to (1) for small separations between the layers [15]. For symmetric systems, the dominant contribution to the interaction free energy $F(d)$ is thus given by (1), in which case the exponents η_m turn out to be

$$\eta_m = \frac{\pi m^2}{2\sqrt{6c_{Fl}}}\left(1-\frac{\delta}{d}\right)^2 = \eta^\infty m^2\left(1-\frac{\delta}{d}\right)^2. \tag{8}$$

Taking the Helfrich estimate $c_{fl} = 3\pi^2/128$ [6], one obtains $\eta^\infty = 4/3$, which is in quantitative agreement with experimental results. Extensive Monte Carlo simulations point to a value of c_{fl} half as large [9,16,17], a discrepancy not satisfactorily resolved so far [15,18]. The effects considered in this article show that the exponents η_m should, in fact, depend *continuously* on the thickness ratio of the oil and water layers, leading to a decrease of the values of η_m. Since the experiments were actually done for various ratios of water and oil layer thicknesses [10,11], this could explain the disagreement between measurements and theoretical predictions using Monte Carlo estimates of c_{fl}.

B. Effective compressibility

In this section the effective compressibility $\mathcal{B}^{eff}$ for an asymmetric amphiphilic system is calculated, which will be needed for the evaluation of η_m. As noted above, ternary systems are completely specified by the two separations corresponding to the water and oil layer thicknesses. The free energy for a subsystem consisting of only three neighboring layers (envisioned to be embedded in an infinite stack) can be written as

$$F(\delta l_1, \delta l_2) = \frac{c_{fl}T^2}{K_1^{eff}\delta l_1^2} + P_1\delta l_1 + \frac{c_{fl}T^2}{K_2^{eff}\delta l_2^2} + P_2\delta l_2 \ , \tag{9}$$

where δl_1 and δl_2 are the displacement fields corresponding to the water and oil layer thicknesses, or vice versa. The Lagrange multipliers P_1 and P_2 have been introduced in order to vary the mean separations independently and correspond to pressure variables. The mean separations ℓ_α (with $\alpha = 1, 2$) follow from minimizing the expression (9) and are given by

$$\ell_\alpha = \left(\frac{2c_{fl}T^2}{K_\alpha^{eff}P_\alpha}\right)^{1/3}. \tag{10}$$

For the calculation of the effective layer compressibility, it is useful and sufficient to expand (9) up to second order in δl_α, leading to

$$F(\delta l_1,\delta l_2) = \frac{3c_{fl}T^2}{K_1^{eff}}\left(\frac{1}{\ell_1^2}+\frac{(\delta l_1-\ell_1)^2}{\ell_1^4}\right) +\frac{3c_{fl}T^2}{K_2^{eff}}\left(\frac{1}{\ell_2^2}+\frac{(\delta l_2-\ell_2)^2}{\ell_2^4}\right). \tag{11}$$

The repeat distance for vanishing layer thickness is defined by $d=\delta l_1+\delta l_2$ (the case of finite thickness will be considered only at the end); minimizing the free energy expression (11) with respect to the water and oil layer thicknesses δl_1 and δl_2 at fixed repeat distance d, one finally obtains the expression

$$F(d) = 3c_{fl}T^2\left(\frac{1}{K_1^{eff}\ell_1^2}+\frac{1}{K_2^{eff}\ell_2^2} +\frac{(d-\ell_1-\ell_2)^2}{K_1^{eff}\ell_1^4+K_2^{eff}\ell_2^4}\right). \tag{12}$$

From this expression and the definition (6), the effective compressibility is easily identified to be

$$\mathcal{B}^{eff} = \frac{6c_{fl}dT^2}{K_1^{eff}\ell_1^4+K_2^{eff}\ell_2^4}, \tag{13}$$

thus depending on the effective bending rigidities for the two inequivalent separations.

A related expression for the effective compressibility is obtained if the layers themselves are compressible, which could be due to the intrinsic fluidity of the amphiphilic layers or due to adsorbed polymers. In all these cases, the free energy for a system of two layers including the compressibility of the layers, characterized by a modulus γ, can, in analogy to (9), be written as

$$F = \frac{\gamma}{2}(\delta-\delta_0)^2+\frac{c_{fl}T^2}{K\delta l^2}+P\delta l, \tag{14}$$

where δ_0 is the equilibrium thickness of the layer. Defining the repeat distance as $d\equiv\delta l+\delta$ and repeating the calculation that lead to (13), one obtains for the free energy in this case

$$F = \frac{3c_{fl}T^2}{K\ell^2}+\frac{(d-\ell-\delta_0)^2}{2/\gamma+K\ell^4/3c_{fl}T^2}. \tag{15}$$

The effective compressibility in this case can be seen to be

$$\frac{1}{\mathcal{B}^{eff}} = \frac{1}{\gamma d}+\frac{1}{\mathcal{B}^0} \tag{16}$$

with the bare compressibility according to (6) and (7) given by

$$\mathcal{B}^0 = \frac{6c_{fl}dT^2}{K\ell^4}. \tag{17}$$

The compressibility modulus $\mathcal{B}^{eff}$ can thus be considerably decreased, depending on the actual value of the layer compressibility modulus γ. The expected values for the exponents η_m will thus increase, see (4); however, this will make the discrepancy between the measured exponents and the theoretical predictions using the Monte-Carlo value for c_{fl} only larger. With a different starting point for a similar idea, the opposite conclusion was drawn in Ref. [18].

C. Scaling form of the effective rigidity

In this section the explicit scaling function $\mathcal{K}^{eff}(x,y)$ of the effective bending rigidity is determined. The minimal system where this can be done is an asymmetric stack of three layers, which is studied by extensive Monte Carlo (MC) simulations. The effective Hamiltonian for such a system can be written as

$$\mathcal{H}\{l_1,l_2,l_3\} = \int d^2\mathbf{x}\left\{\sum_{n=1}^{3}\left[\frac{K}{2}\left[\nabla^2 l_n(\mathbf{x})\right]^2\right] +P_1[l_2(\mathbf{x})-l_1(\mathbf{x})] +P_2[l_3(\mathbf{x})-l_2(\mathbf{x})]\right\}, \tag{18}$$

where the displacement field $l_n(\mathbf{x})$ parametrizes the shape of the nth membrane. The bending energies are approximated by the layer curvatures, and the pressures P_1 and P_2 are introduced so as to produce finite and different separations between the layers. The spontaneous curvature has not been included in the effective Hamiltonian; it does not effect the phase behavior because the integral over such a term vanishes for the lamellar topology [19]. The hard-wall interaction is implicitly embodied by the constraint $l_1<l_2<l_3$. After discretization of the coordinate $\mathbf{x}$ with lattice constant $a_\parallel$ and using the dimensionless continuous height variables $z_n\equiv l_n\sqrt{K/T}/a_\parallel$, the only remaining parameters are the rescaled pressures $p_\alpha\equiv P_\alpha a_\parallel^3/\sqrt{KT}$. The MC simulations typically consisted of 10^7 MC steps using square lattices with up to 12 500 sites [20,21].

Three series of simulations at fixed reduced pressures of $p_1=0$, $p_1=0.01$, and $p_1=0.1$ were performed, where the other pressure p_2 was varied over four orders of magnitude. The first series with $p_1=0$ corresponds to a system of only two layers since, in this case, the layer parametrized by l_1 is unbound from the other two layers and consequently has not been included in the simulation. In Figs. 1(a) and 1(b) the results for the separations $\langle\delta z_2\rangle\equiv\langle z_3-z_2\rangle$ and $\langle\delta z_1\rangle\equiv\langle z_2-z_1\rangle$ are shown as a function of p_2. The mean separation $\langle\delta z_2\rangle$, which is coupled to p_2, scales accurately like $\sim p_2^{-1/3}$ for all three values of p_1, in agreement with (10) and denoted by the straight line in the double-logarithmic plot in Fig. 1(a). For $p_1=0.01$ (open squares) and $p_1=0.1$ (open circles)

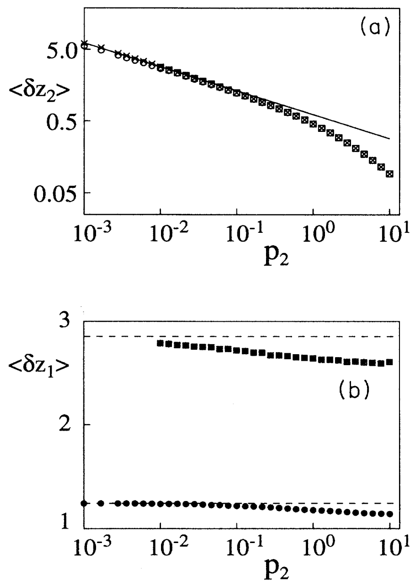

FIG. 1. Mean separations $\langle \delta z_\alpha \rangle$ in a stack of three layers as a function of the pressure p_2 for fixed pressure $p_1 = 0$ (crosses), $p_1 = 0.01$ (squares), and $p_1 = 0.1$ (circles). (a) Results for $\langle \delta z_2 \rangle$ in a double-logarithmic plot, scaling like $\sim p_2^{-1/3}$ for sufficiently small pressure p_2; the asymptotic scaling is denoted by a straight line. (b) Results for $\langle \delta z_1 \rangle$ on a linear vertical scale, approaching constant values (denoted by broken lines) as $p_2 \to 0$. The statistical errors are denoted by vertical bars which are omitted if smaller than the symbol size.

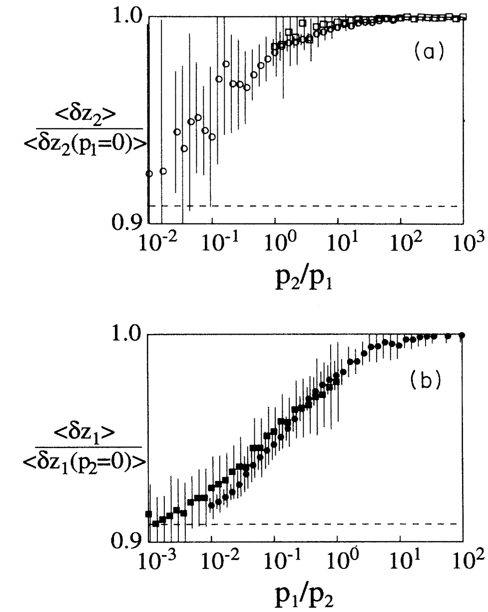

FIG. 2. Same data as in Fig. 1 now plotted as ratios of (a) $\langle \delta z_2(p_1,p_2)\rangle$ and $\langle \delta z_2(0,p_2)\rangle$ as a function of p_2/p_1 and (b) ratios of $\langle \delta z_1(p_1,p_2)\rangle$ and $\langle \delta z_1(p_1,0)\rangle$ as a function of p_1/p_2. The two different sets of data agree within the numerical errors and approach the value $(3/4)^{1/3}$, which is denoted by broken lines; see text.

there are only very small deviations from the results for $p_1 = 0$ (crosses), which have to be attributed to changes in the effective rigidity. The straight line has been drawn using the value $c_{fl} = 0.1161$, which is the best estimate for c_{fl} available [9]. In Fig. 1(b) one sees that there are small deviations of $\langle \delta z_1 \rangle$ from the asymptotic value (obtained for $p_2 = 0$ and denoted by broken lines) for $p_1 = 0.01$ (filled squares) and $p_1 = 0.1$ (filled circles) as the pressure p_2 increases.

In order to extract the influence of one fluctuating separation coordinate on the other, which is the mechanism for changes in the effective bending rigidity, one divides the data of Fig. 1 by the separation of a single pair of layers at corresponding pressures; the result of this procedure is shown in Fig. 2. It is evident that the separation ratios for $p_1 = 0.01$ and $p_1 = 0.1$ (denoted by squares and circles, respectively) scale similarly with a proper rescaling of the pressure variable, accomplished by choosing p_2/p_1 or p_1/p_2 as plot parameters. The broken lines drawn in Figs. 2(a) and 2(b) denote the expected separation ratios in the limits $p_2/p_1 \to 0$ and $p_1/p_2 \to 0$, respectively, given by $(3/4)^{1/3}$, as follows from the following argument: In either of these limits, one pair of layers is much closer together than the other, and behaves effectively like a single layer with a bending rigidity of $2K$. The effective bending rigidity of the separation coordinate of the other pair is then given by $2K/3$ [22]. Since the bending rigidity of the separation coordinate of a pair of two single membranes (with rigidity of K each) is given by $K/2$, one obtains for the ratio of the mean separations each given by (10) the value $(3/4)^{1/3}$. This asymptotic value is approached already for pressure ratios of $\simeq 1/1000$, as can be seen from Fig. 2(b).

In the next step the effective bending rigidity of a separation coordinate is determined from the Monte Carlo data. Using definition (2) and relation (10), one obtains

$$\frac{K_\alpha^{eff}}{K} = \left[2 \left(\frac{\langle \delta z_\alpha(p_\alpha, p_\beta)\rangle}{\langle \delta z_\alpha(p_\alpha, 0)\rangle} \right)^3 - 1 \right]^{-1}, \qquad (19)$$

which is plotted in Fig. 3 as a function of $\langle \delta z_\beta \rangle / \langle \delta z_\alpha \rangle$, with the symbols retaining their previous definitions. This graph corresponds to a plot of the scaling function $\mathcal{K}^{eff}(x,y)$ as a function of x only. The dependence on the second argument is negligible over the length scales considered in the simulation, as follows from the good agreement between the data for $p_1 = 0.01$ (squares) and $p_1 = 0.1$ (circles). The solid line in Fig. 3 denotes the scaling function

$$\frac{\mathcal{K}^{eff}(x,y)}{K} \simeq \frac{\mathcal{K}^{eff}(x)}{K} = 2 - \frac{x^\mu}{x^\mu + x_0^\mu}, \qquad (20)$$

with the fit value $x_0 = 0.3 \pm 0.005$ and the exponent

$$\mu = 3/2 \pm 0.2 . \qquad (21)$$

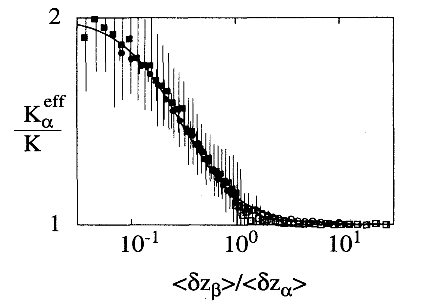

FIG. 3. Rescaled effective bending rigidity K_α^{eff}/K as a function of $\langle\delta z_\beta\rangle/\langle\delta z_\alpha\rangle$, which corresponds to a plot of the rescaled scaling function $\mathcal{K}^{eff}(x,y)/K$ defined by (3) as a function of x only. The dependence on the second argument is small and can be neglected for the range of length scales considered here. The solid curve is the heuristic scaling given by (20) and agrees with the data over the whole range of length scales. To the left, the effective bending rigidity corresponds to the case of bilayers given by $K^{eff}/K = 2$, to the right one recovers the behavior of monolayers characterized by $K^{eff}/K = 1$.

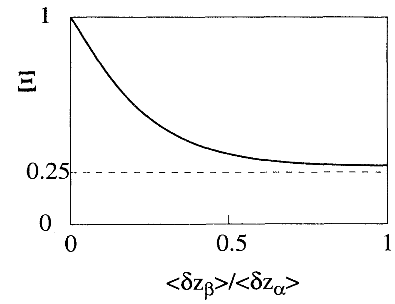

FIG. 4. Correction factor of the exponents η_m as a function of the oil-water layer thickness ratio. For bilayer systems, i.e., for $\langle\delta z_\beta\rangle/\langle\delta z_\alpha\rangle = 0$, the factor is 1 and one recovers the original result. For symmetric systems with $\langle\delta z_\beta\rangle/\langle\delta z_\alpha\rangle = 1$ the correction is roughly 1/4.

The agreement with the data is satisfactorily over the whole range of data. The dependence on the second argument y seems to be very small and is not detectable for the length scales considered numerically.

D. Effective exponents η_m

The closed form result for the effective bending rigidity (20) allows one to calculate the exponents η_m for the case of asymmetric amphiphilic systems. The starting point is expression (4), in which the effective compressibility modulus $\mathcal{B}^{eff}$ given by (13) has to be inserted. The volume bending modulus κ is not modified by the fluctuation effects considered here and is given by $2K/d$, independent of the separations between the layers. Taking into account the finite thickness δ of a monolayer, the final result for the exponents can, in analogy to (8), be written as

$$\eta_m = \eta^\infty m^2 \Xi(\ell_1,\ell_2)\left(1-\frac{2\delta}{d}\right)^2 \tag{22}$$

with the correction factor given by

$$\Xi(\ell_1,\ell_2) = \left(\frac{K_1^{eff}\ell_1^4 + K_2^{eff}\ell_2^4}{2K(\ell_1+\ell_2)^4}\right)^{1/2}. \tag{23}$$

With the heuristic scaling form (20), this correction factor can be calculated explicitly and is plotted in Fig. 4 as a function of the ratio of the oil and water thicknesses. As one would expect, the correction factor is invariant with respect to an interchange of the oil and water thicknesses and is one for the pure bilayer case, $\langle\delta z_\beta\rangle/\langle\delta z_\alpha\rangle = 0$, and reaches $\approx 1/4$ as the symmetric case defined by $\langle\delta z_\beta\rangle/\langle\delta z_\alpha\rangle = 1$ is approached. The value 1/4 is expected in the absence of any dependence of the effective bending rigidity K^{eff} on the number of layers N, which corresponds to $\mathcal{K}^{eff}(1,y) = 1$ for $y \to \infty$. The value $\Xi(\ell,\ell) = 1/4$ then follows for large ℓ, since the scattering at a repeat distance d for the symmetric case corresponds to the first subharmonic defined by $m = 1/2$, see (8).

III. SUMMARY AND DISCUSSION

The behavior of lamellar phases of asymmetric amphiphilic systems has been considered. Formally, these systems can be described by asymmetric stacks of elastic layers that are held together by pressures that vary between the different separation coordinates. Main consideration has been given to ternary amphiphilic systems, for which there are two inequivalent displacement fields, namely the thickness of the water and the oil layers. The behavior of such a system can, to a very good approximation, be gathered from a three-layer system with two different external pressures acting between the layers, which has been studied by extensive Monte Carlo simulations.

The fluctuation force for each separation coordinate can be written in the standard form introduced by Helfrich, given that the bare bending rigidity is replaced by an effective rigidity that is allowed to depend on the two inequivalent separations. The effective rigidity for a given separation coordinate crosses over smoothly from the bare value of an isolated layer to a value twice as large (and thus corresponding to a bilayer) as the mean value of the other separation coordinate goes to zero. For the moderate separations considered numerically, the data are accurately described by a simple scaling function for the effective bending rigidity that depends only on the ratio of the oil and water separations. These findings should have pronounced effects on the relative stability of the lamellar phase compared to other phases found for amphiphilic systems, resulting in a shift of phase boundaries. The predictions for the effective elastic moduli can be checked quantitatively by x-ray scattering experiments on asymmetric lamellar systems, which yield the exponents η_m. These exponents are predicted to be proportional to a correction factor Ξ, which has been calculated explicitly (see Fig. 4) and depends sensitively on the ratio of the oil and water layer thicknesses. In the analysis of previous experiments, this correction factor has been neglected. In one set of experiments, the separation ratio was varied between ≈ 1 and ≈ 7 [10], leading to values of the correction factor Ξ between $\approx 1/4$ and $\approx 2/3$ (see Fig. 4). In fact, if one uses the latter value of Ξ together with the Monte-Carlo estimate for the fluctuation amplitude c_{fl} instead of Helfrich's original estimate, one obtains values for the exponents η_m very close to the ones that were successfully used to fit the experimental data. Additional corrections are expected for small separations due to van der Waals attraction between the lamellae [15]. In summary, the effects discussed in this article considerably modify the fluctuation-induced interaction in asymmetric lamellar stacks. They have been neglected in the data analysis of scattering experiments so far, and might help to reconcile experimental results and theoretical estimates for the fluctuation strength c_{fl}.

The data taken numerically extend to a maximal value of $\langle \delta z \rangle \simeq 5$, which corresponds to an experimental separation of $\ell \simeq 100$ Å, using $K/T \simeq 1$ and $a_{||} \simeq 20$ Å roughly corresponding to the thickness of amphiphilic layers. Although the accuracy of the scaling function (20) has only been tested for a restricted range of separations, it is exactly this range that is accessible experimentally. Modifications to the scaling form as given by (20) could come in for much larger separations, which probably cannot be realized experimentally. The asymptotic behavior of $\mathcal{K}(x, y)$ for large y has been considered for the symmetric case characterized by $x = 1$ [9]. There it was found that the data are compatible with $\mathcal{K}(1, y)/K = 1$ for $y \rightarrow \infty$, but a slightly larger value [as suggested by the scaling function (20)] could not be ruled out due to numerical errors. Deviations from (20) would probably come in through a y dependency of x_0 and possibly also μ.

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