Monte Carlo study of interfacial properties in an amphiphilic system

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A three-component model representing a balanced, amphiphilic system at a three-phase coexistence of oil-, water-rich, and disordered phases is simulated, and interfacial tensions between all phases are obtained from histogram methods. We find that the disordered phase wets the oil-water interface, and that its tension is reduced due to the presence of the amphiphile by a factor of 93. The determination of the structure function shows that the system is between disorder and Lifshitz lines. These three factors are all consistent with the simulated amphiphile being weak. Fluctuations do not reduce the tension significantly from mean-field estimates, but do alter the location of the wetting transition. The latter is in accord with the expected behavior of a system in which the interfacial tension is small.

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One of the most intriguing features of simple mixtures of oil, water, and amphiphile is that, under appropriate conditions, the interfacial tension between oil and water can be reduced by several orders of magnitude [1]. Some systematics of this reduction are well established. First, the tension is lowest when the concentrations of oil and of water are approximately equal, and the system is said to be balanced. Second, in a balanced system, the tension decreases as the concentration of amphiphile increases. There is a limiting value of amphiphile concentration, however, beyond which the oil- and water-rich phases become unstable to the formation of a uniform disordered phase. The lowest tension is therefore attained at the triple point of the three phases. Finally, the tension between a given oil and water can be reduced still further by employing increasingly efficient amphiphiles, i.e., ones that bring about the uniform phase with a smaller and smaller concentration of amphiphile. This latter correlation between efficient amphiphiles and low oil-water tensions can be understood [2] if one pictures the uniform phase as consisting of coherent regions of oil and water separated by sheets of amphiphiles with an average spacing l. Assuming that the amphiphile sheets in the disordered phase are essentially the same as that at an oil-water interface, the Gibbs free energy per unit volume of the disordered phase in the balanced system, g_{dis}, can be written

$$g_{dis} = \tfrac{1}{2}(g_{oil} + g_{water}) + \tfrac{1}{l}(\sigma_{ow} - |g_{int}(l)|) , \qquad (1)$$

where g_{oil}, g_{water} are the Gibbs free energy of the oil- and water-rich regions, σ_{ow} is the oil-water interfacial tension, and $g_{int}(l)$ is the interaction between amphiphilic sheets at the distance l, which is assumed to be attractive.

At three-phase coexistence, $g_{oil} = g_{water} = g_{dis}$ from which it follows that $\sigma_{ow} = |g_{int}(l)|$. At large separations l, the interaction between amphiphilic sheets must be a decreasing function of the distance, so that the tension decreases with increasing l. Further, the larger the distance between sheets, the less amphiphile there is per unit volume, so that the amphiphile is more efficient. Hence, the interfacial tension decreases as the efficiency of the amphiphile increases. In the water and octane system, for example [3], the concentration of the n-akyl polyglycol ether C_5E_2 needed to bring about the disordered phase is 46.6 wt. %, and the interfacial tension is 0.36 erg/cm^2, compared to the typical value of 50 erg/cm^2 in the absence of amphiphile. Thus the tension is reduced by a factor of 130. The more efficient C_8E_4 brings about the disordered phase with only 24.4 wt. % and reduces the tension to 0.041 erg/cm^2, a reduction by a factor of 1250. From the above argument, it would seem that thermal fluctuations might be important in bringing about the low tensions as they cause an entropic repulsion [4] between the sheets of amphiphiles, which would cause l to increase and the tension to decrease.

Fluctuations may also play an important role in the wetting phenomenon in these systems. The experimental observations are that the disordered phase wets the oil-water interface when the amphiphile is weak, whereas it does not do so when the amphiphile is strong [3,5]. This correlation was explained using a Landau theory of an amphiphilic system with short-range interactions [6] that showed that a transition from a wet to a nonwet interface should occur at the disorder line [7], the line at which the large distance behavior of the water-water correlation functions changes from monotonic to nonmonotonic decay. The former behavior characterizes the disordered phase brought about by weak amphiphiles; the latter is characteristic of a microemulsion, the disordered phase produced by strong amphiphiles. The effect of long-range van der Waals forces is to cause the wetting transition to be first order and to occur on the nonmonotonic decay side of the disorder line [6]. these predictions have been verified by experiment [8]. Although fluctuations

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<u>49</u>   494

are not expected to alter the first-order nature of the transition, they certainly can affect the location of the transition. The relative importance of such fluctuations is usually gauged by the dimensionless ratio $w \equiv k_b T_w / 4\pi\sigma\xi^2$, where T_w is the wetting temperature, and ξ, the bulk correlation length [9]. In most systems, this ratio is of order unity. In the systems under consideration, however, this ratio is orders of magnitude larger due to the extremely small value of the interfacial tension. The expected effect [10] of the fluctuations in such a system is to cause the wetting transition to occur on the microemulsion side of the disorder line even in the absence of van der Waals forces. The inclusion of such forces would be to cause the transition to occur even farther on the microemulsion side.

Even though the effect of fluctuations may be important to the reduction of the interfacial tension and to the wetting temperature of amphiphilic systems, it has been little studied. Monte Carlo simulation of a Ginzburg-Landau model has been used to relate the near vanishing of the interfacial tension to the location of the triple line [11]. The absolute reduction in interfacial tensions, however, is not obtainable from such models. Very recently, a lattice model was simulated, and the interfacial tension between the oil-rich phase and the disordered phase was calculated [12]. The effects of finite size on the result were not estimated. A reduction in the oil-water tension of a factor of 500 can be inferred from the results. From the experimental observations above, this is a reasonable number for a strong amphiphile. Whether or not the model oil-water interface was not wetted by the middle phase, as would be expected for a strong amphiphile, was not addressed. However, from the simulation results, which do not appear to show a large probability for the occurrence of an unwetted interface, one concludes that the interface was wetted by the middle phase, contrary to expectations.

We have examined the reduction in oil-water tension and the state of the oil-water interface by Monte Carlo simulation of a three-component model, which has been extensively analyzed previously by mean-field theory [13]. A system not far from the four-phase point was examined in detail, and the interfacial free energies between oil and middle phases, and between oil and water phases, were calculated independently using histogram methods [14] and reweighting techniques [15,16]. Finite-size effects were found to be important. The tension of the oil-water interface in the pressure of amphiphile is reduced by a factor of 93 with respect to its value in the absence of amphiphile. This is not a spectacular reduction, but one that is fully consistent with our result that the oil-water interface is wetted by the middle phase. Hence, the particular system studied represents a weak amphiphile. Finally, by calculating the correlation functions of the system, we determine that the middle phase is on the microemulsion side of the disorder line. Thus the transition from wet to not wet must occur on this side, as is found in experiment [8]. That the fluctuations alter the location of the wetting transition from the mean-field location of the disorder line is in agreement with theoretical expectations of the behavior of this system characterized by such

a small interfacial tension [10].

The three-dimensional, cubic-lattice model that we have employed is one in which an oil or water or amphiphile molecule is present at every site. The Hamiltonian that governs the system is

$$\mathcal{H} = -\sum_\alpha \sum_\beta \sum_{\langle i,j \rangle} E_{\alpha\beta}^{ij} P_i^\alpha P_j^\beta - \sum_\alpha \mu_\alpha \sum_i P_i^\alpha + \mathcal{H}_{amp} \ , \quad (2)$$

where $P_i^\alpha = 1$ if the ith site is occupied by species α and is zero otherwise. The index α takes the values a, b, and c, representing water, oil, and amphiphile, respectively. The first term is simply the sum of all distinct pair interactions between particles. We assume nearest-neighbor interactions only. Because of the constraint that there must be a molecule of some kind in each cell, there are only three independent nearest-neighbor pair interactions, which we take to be J, K, and C defined by

$$E_{aa} + E_{bb} - 2E_{ab} = 4J \ ,$$
$$E_{aa} + E_{cc} - 2E_{ac} = J + K + 2C \ , \quad (3)$$
$$E_{bb} + E_{cc} - 2E_{bc} = J + K - 2C \ .$$

The parameter

$$4C = 2(E_{bc} - E_{ac}) - (E_{bb} - E_{aa}) \quad (4)$$

is related to the difference between the interaction of amphiphile and water and of amphiphile and oil. In a balanced system $C = 0$. The second term in Eq. (2) contains the chemical potentials. Due to the constraint, there are only two independent ones, which we take to be

$$H = \tfrac{1}{2}(\mu_a - \mu_b) + 3(E_{ac} - E_{bc}) \ , \quad (5)$$

and

$$\Delta = \mu_c - \tfrac{1}{2}(\mu_a + \mu_b) - 3(E_{ac} + E_{bc} - 2E_{cc}) \ . \quad (6)$$

The third term in (1) distinguishes molecule c as an amphiphile in that the energy decreases by $|L|$ if it sits between an a and b and increases by the same amount if it sits between two a or two b;

$$\mathcal{H}_{amp} = -L \sum_{i,j,k} (P_i^a P_j^c P_k^a + P_i^b P_j^c P_k^b - P_i^a P_j^c P_k^b - P_i^b P_j^c P_k^a) \ ,$$

$$(7)$$

where the sum is over all triplets of adjacent sites in a line, and $L < 0$.

It is convenient to reformulate the three-component mixture in the language of a spin-1 magnetic system. To do so, we define the spin variable S_i at the ith site via

$$P_i^a = S_i(1 + S_i)/2 \ ,$$
$$P_i^b = -S_i(1 - S_i)/2 \ , \quad (8)$$
$$P_i^c = 1 - S_i^2 \ ,$$

so that $S_i = 1, -1, 0$ corresponds to the presence at site i of a molecule of type a, b, or c, respectively. In terms of the spins, the Hamiltonian of Eq. (2) takes the form

$$\mathcal{H} = - \sum_{\langle i,j \rangle} [JS_iS_j + KS_i^2S_j^2 + C(S_iS_j^2 + S_i^2S_j)]$$

$$- \sum_i (HS_i - \Delta S_i^2) - L \sum_{\langle i,j,k \rangle} S_i(1 - S_j^2)S_k , \qquad (9)$$

to within a constant. The first sum is over all pairs, the second over all sites, and the third over all groups of three neighboring sites, which are in a line.

We have studied the model with parameters (all in units of J) $C = H = 0$, corresponding to a balanced system, and $K = 0.5$, and at temperature $T = 2.78$. The phase diagram as a function of Δ, the amphiphile chemical potential, and L, the strength of the amphiphilic interaction, is shown in Fig. 1. For very weak amphiphiles ($|L|$ small), there is a region of oil-water coexistence for small Δ, corresponding to low amphiphile concentration. As the concentration increases, a continuous transition to the disordered state is encountered. No lamellar phase appears. For stronger amphiphiles ($|L|$ larger), the transition to the disordered phase becomes first order, and a lamellar phase is encountered at larger concentrations of amphiphile. The disordered phase exists in the narrow region between the line of three-phase coexistence and the lamellar phase. At a sufficiently large negative value, $L_4 = -5.5 \pm 0.2$, the four-phase point is encountered, below which oil and water coexist with the lamellar phase. We have examined the interfacial properties in detail at the value $L = -5$. The mean-field phase diagram at the same temperature is shown, for comparison, in Fig. 2. One notes that the region in which the disor-
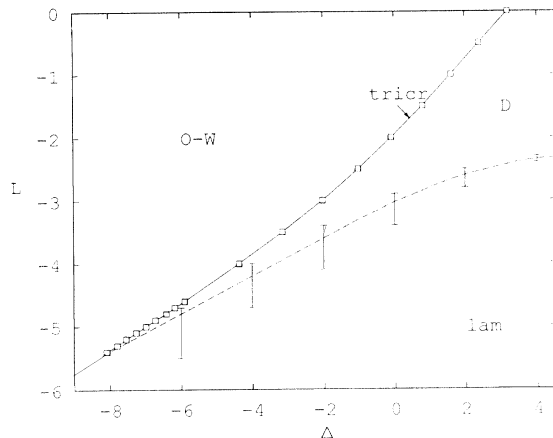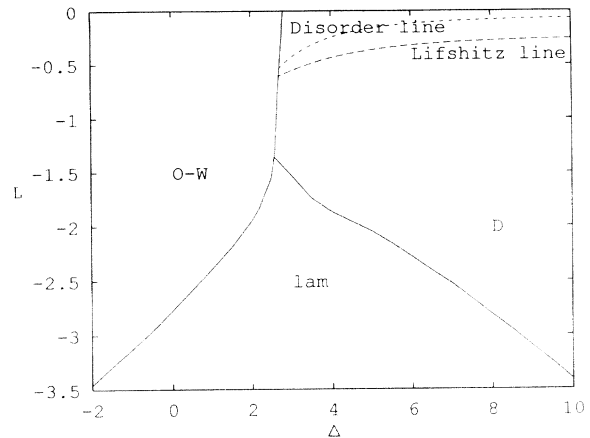

FIG. 2. Phase diagram of the same system as in Fig. 1, but as obtained from mean-field theory. The disorder and Lifshitz lines are shown with short and long dashes, respectively.

dered phase intrudes between oil-water coexistence and the lamellar phase is increased significantly. This is in agreement with other studies [11,17].

In order to study the interfacial properties, we simulated systems that were $2L \times L \times L$ with periodic boundary conditions in all directions. This geometry was chosen because two interfaces will be present at oil-water coexistence, and several internal interfaces are expected in the disordered phase. It was necessary to allow the system adequate room to create these interfaces. As the interface that is most energetically favored is the (111) interface, the lattice is constructed so that the (111) planes are perpendicular to the long axis of the system. In order that finite-size effects could be examined, we took $L = 10$, 12, 14, 16, and 20. We determined interfacial free energies using an extended version of the histogram method of Binder [14]. Let Φ be some extensive quantity, whose distribution function $\mathcal{N}(\Phi)$ has two distinct peaks of height N_{max} at two-phase coexistence. The method assumes that the main contribution to the minimum N_{min} of $\mathcal{N}$ between the two peaks arises from configurations with two interfaces separating one-phase regions. Hence the interfacial tension is given by

$$f_s/k_BT = -\frac{1}{2A} \ln \left[\frac{N_{min}}{N_{max}} \right] , \qquad (10)$$

where A is the interfacial area.

At three-phase coexistence, two-dimensional histograms have to be analyzed. From it, all interfacial tensions are obtained. Because in this kind of analysis, the statistics of the histograms need to be reasonably good even in regions in which the value of the distribution function is small, we used a non-Boltzmann weighting scheme [15,16] in part of the simulations: configurations $\mathcal{C}$ are distributed according to

$$N_0(\mathcal{C}) \propto P_{Boltzmann}(\mathcal{C}) W(M,Q) , \qquad (11)$$

where $M = \sum_i S_i / \sum_i 1$, $Q = \sum_i S_i^2 / \sum_i 1$, $P_{Boltzmann}$ is the standard grand canonical distribution, and the additional weighting factor W favors configurations with interfaces.

FIG. 1. Phase diagram at $T = 2.78$ in the plane of the amphiphilic chemical potential, Δ, and strength, L, as determined by histograms obtained from Monte Carlo simulation of a $20 \times 10 \times 10$ system. The transition from the disordered middle phase (D) to coexisting oil- and water-rich phases (O-W) is shown by a full line. It is second order down to a tricritical point located between $-1.5 > L > -2.0$, and first order beyond. The approximate position of the tricritical point is shown with an arrow. The line of these transitions ends at $L = -5.5 \pm 0.2$, at which a transition to a lamellar phase (lam) is encountered. The dashed line shows the approximate location of first-order transitions from middle phase to lamellar phase, determined in an $8 \times 8 \times 8$ system.

A suitable choice for W requires some knowledge of the distribution function $\mathcal{N}(M,Q)$ beforehand. We obtained good results with $W \propto 1/\mathcal{N}$ in the neighborhood and between the three one-phase peaks in the (M,Q) plane. In practice, we started with an initial guess for the distribution function that was based on the results at smaller system sizes. Within three or four iteration steps we then systematically improved W, until it was good enough that data could be collected. Going from one iteration step to the other, we used directly the measured distribution function to construct the new weighting factor, without fitting it to some smooth function. The noise in W therefore induces some additional noise in the raw data, which mostly cancels out in the reweighting process (Fig. 4). Furthermore, we used histogram extrapolation [18] in Δ in order to locate the three-phase point and to evaluate the histograms there. We checked whether the usage of this method is justified at small system size ($L=10$). The histograms are fairly smooth in the M,Q plane, and the locations of the maxima do not change very much as the parameters are varied. We note that the situation is entirely different for histograms in the internal energy U, and extrapolation in temperature already fails for very small temperature steps. We define the three-phase point to be that point at which the distribution function $\mathcal{N}_1(Q) \equiv \sum_M \mathcal{N}(M,Q)$ has two peaks of equal height. The value of Δ at the triple point is $\Delta = -7.00 \pm 0.02$ for all system sizes.

Figure 3 shows the histogram for system size $L=12$. One clearly discerns the three peaks corresponding to oil-rich, water-rich, and middle phases. In addition, one sees a broad band extending over nearly the whole range of M at $Q \simeq 0.94$. Because the corresponding total number of amphiphiles $N \cong 200$ is approximately that needed for two (incomplete) planes of amphiphile in the system, we attribute this band to configurations with two interfaces. The way the histograms are analyzed quantitatively is illustrated in Fig. 4. We form $\mathcal{N}_1(Q)$, as in Fig. 4(a), the analogous $\mathcal{N}_2(M) \equiv \sum_Q \mathcal{N}(M,Q)$, as in Fig. 4(b), and the cut of the histogram $\mathcal{N}(0,Q)$, as in Fig. 4(c). For comparison, we also show that the corresponding raw
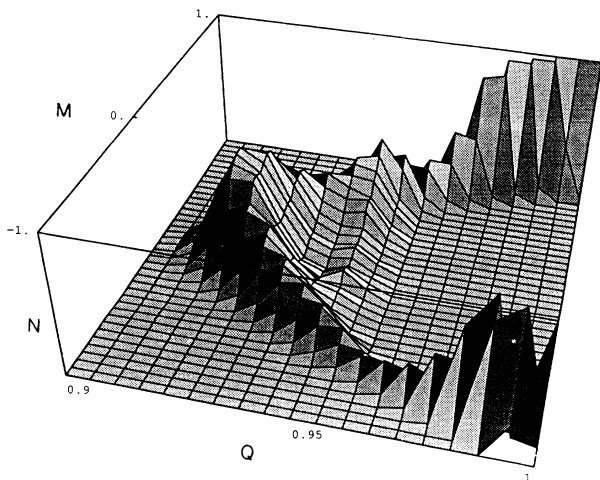
data are not yet corrected for the reweighting factor W, nor extrapolated to the value of Δ best describing three-phase coexistence.

The interfacial tension between middle phase and oil or water can readily be extracted from the maximum and minimum values of $\mathcal{N}_1(Q)$: $\sigma_{mo}(L)a^2/k_B/T = -(1/2\sqrt{3}L^2)\ln(N_{1,\min}/N_{1,\max})$, where a is the lattice
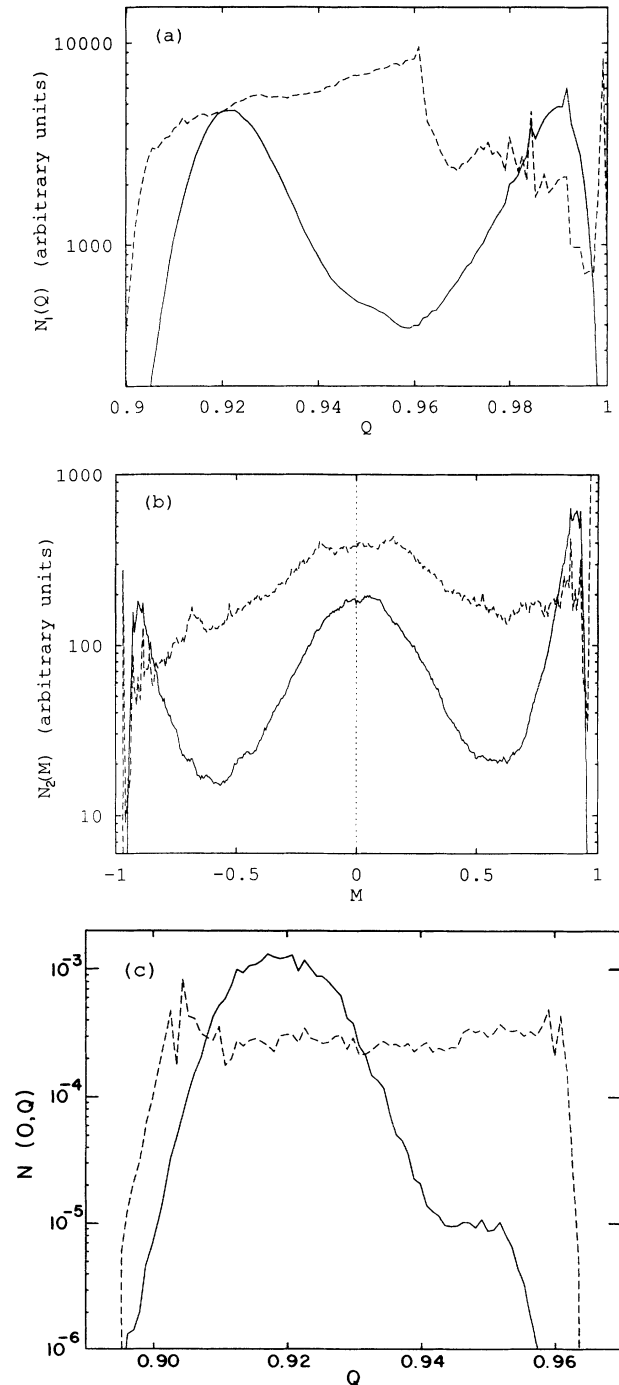

FIG. 4. Histogram $\mathcal{N}(M,Q)$ at $L=14$ (a) summed over M (b) summed over Q (c) cut at $M=0$. Dashed lines show raw data, solid lines show the histograms after having been corrected for the reweighting factor W and extrapolated from $\Delta = -7.0$ to -6.99.

FIG. 3. Histogram in Q and M at $L=12$, $\Delta = -7.0$.

constant. Obtaining σ_{ow}, the tension between oil-rich and water-rich phases, is complicated by the fact that there are two interfaces separating these phases because of the periodic boundary conditions, and the contribution to the histogram from these configurations is, for small systems sizes, not far from the peak in the histogram representing the middle phase. The desired contribution appears as a shoulder on the larger peak in $\mathcal{N}(0,Q)$ in Fig. 4(c). We calculate the interfacial tension by comparing the area, $N_{2,\min}$ under that shoulder to the height of the peaks $N_{2,\max}$ representing the oil or water phase in $\mathcal{N}_2(M)$: $\sigma_{ow}(L)a^2/k_BT = -(1/2\sqrt{3}L^2)\ln(N_{2,\min}/N_{2,\max})$. Note that the value of $N_{2,\min}$ has a large uncertainty due to the fact that we do not know how far the shoulder extends into the middle phase peak. However, since we are only interested in the logarithm of $N_{2,\min}$, the error in $\sigma_{ow}(L)$ is not large.

The results are listed in Table I. The values of the interfacial tensions change dramatically as the system size increases, and these changes affect the perceived wetting properties. The simulations at $L=10$ and 12 indicate that the middle phase does not wet the oil-water interface $[\sigma_{ow}(L)<2\sigma_{mo}(L)]$, while in the larger samples it is clearly seen that this is not the case. The system passes from one behavior to the other at a characteristic length $L_w \simeq 12$.

In order to relate this wetting behavior to the degree of internal structure of the microemulsion, we calculated correlation functions $G(n)$ and structure functions $\Gamma(q)$ in the (111) direction in the disordered phase ($\Delta=-6.9$, very close to three-phase coexistence).

$$G(n)=\langle S_0 S_p \rangle \ , \quad \mathbf{p}=na(\hat{\mathbf{x}}+\hat{\mathbf{y}}+\hat{\mathbf{z}}) \ , \tag{12}$$

$$\Gamma(q)=\left\langle \left| \sum_r e^{i\mathbf{q}\cdot\mathbf{r}}S_r \right|^2 \right\rangle \ , \quad \mathbf{q}=\frac{q}{\sqrt{3}}(\hat{\mathbf{x}}+\hat{\mathbf{y}}+\hat{\mathbf{z}}) \ . \tag{13}$$

Samples with dimensions $L\times L\times L$, $L=16$, 32, and 40, with the (100), (010), and (001) directions parallel to the edges of the cube were used.

The results are shown in Figs. 5 and 6. The correlation function clearly oscillates, and its period is approximately $d/a=12\pm2$. Note that due to the periodic boundary conditions, the oscillations are squeezed or dilated depending on how well the system size matches the oscilla-

tion length, and that this will also affect the amplitudes. From the decay of the correlation function over the first six lattice sites, one can extract a correlation length $\xi/a=1\pm0.1$. This yields the ratio $2\pi\xi/d=0.52$. Thus the system is between the disorder line, $2\pi\xi/d=0$, and the Lifshitz line, $2\pi\xi/d=1$. At the latter, the peak in the structure functions first moves off of zero wave vector. The period of the oscillations turns out to be the same as the characteristic length L_w mentioned earlier. This may be coincidental. However, it suggests an intuitive picture for the finite-size behavior of the interfacial tensions. On a small scale, less than the oscillation length of the correlation function, the oil and water regions appear to be coexisting bulk phases separated by a single sheet of amphiphiles. However, on a larger scale, these regions are seen to be oil and water domains of the middle phases, which wet the interface.

In order to estimate the values of the interfacial tensions in the limit of infinite sample size, a rigorous finite-size scaling analysis would be desirable. Unfortunately, finite-size scaling of interfacial tensions in three dimensions is nontrivial even in simple systems, because finite-size corrections proportional to $L^{-2}\ln L$ and to L^{-2} both

TABLE I. Results for the interfacial tensions between oil and middle phases, $\sigma_{om}(L)$, and between oil and water phases, $\sigma_{ow}(L)$ calculated in systems of size $L\times L\times 2L$ for various system sizes. The value of the chemical potential of the amphiphile, Δ, at three-phase coexistence, and the number of Monte Carlo steps (MCS) per site is shown.

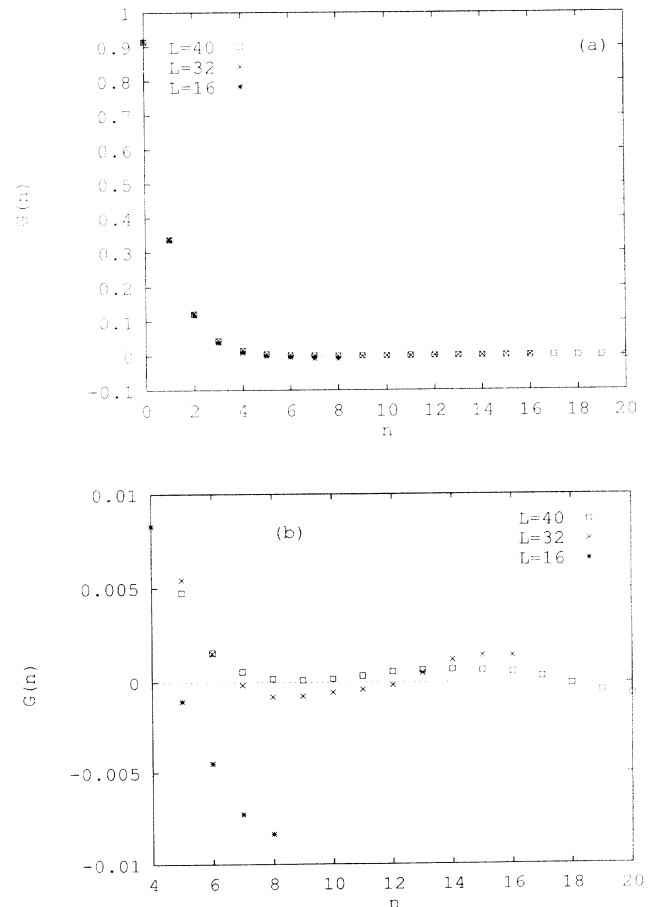| L	$a^2\sigma_{om}(L)/k_BT$	$a^2\sigma_{ow}(L)/k_BT$	Δ	MCS
10	0.0064 ± 0.001	0.0023 ± 0.002	-6.98	2.5×10^6
12	0.0049 ± 0.0006	0.0046 ± 0.002	-6.99	2.0×10^6
14	0.0038 ± 0.0006	0.0087 ± 0.002	-6.99	4.0×10^6
16	0.0029 ± 0.0006	0.0092 ± 0.002	-6.995	6.0×10^6
20	0.0029 ± 0.0006		-6.998	3.6×10^6

FIG. 5. Correlation function $G(n)$ in the (111) direction. A portion of the function in (a) is shown magnified in (b) so that the oscillations are more clearly seen.
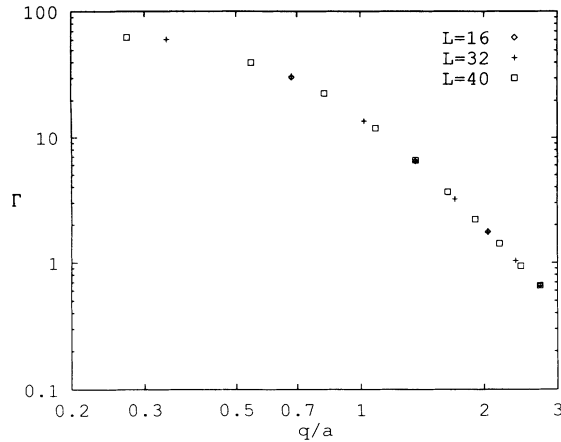
FIG. 6. Structure function $\Gamma(q)$ for q in the (111) direction.

turn out to be relevant [16,19]. Obviously the quality of our data is not good enough to allow for a three-parameter fit, as would be required. On the other hand, we found that the two values of $\sigma_{mo}(L)$ for the largest two values of L for which it was obtained, $L = 16$, 20, were essentially the same, as were the two values of $\sigma_{ow}(L)$ for the two largest values of L, 14 and 16, for which it was calculated. A similar analysis in the three-dimensional Ising model showed that the values of the interfacial tensions at $L = 16$ differed from their asymptotic values by less than 20%. Therefore we believe that $\sigma_{om}a^2/k_BT = 2.9 \times 10^{-3} \pm 0.6 \times 10^{-3}$ is a realistic estimate for the interfacial tension between middle phase and oil or water [20], and $9.2 \times 10^{-3} \pm 2 \times 10^{-3}$ for the analogous dimensionless free energy per unit area of a single sheet of amphiphile separating bulk oil and water phases. Because the middle phase wets the oil-water interface, the macroscopic interfacial tension between oil and water is just twice σ_{om}, i.e., $\sigma_{ow}a^2/k_BT = 5.8 \times 10^{-3} \pm 1.2 \times 10^{-3}$. Without any amphiphile, the model reduces to a simple three-dimensional Ising model, which, at $T/J = 2.78$, has the interfacial tension $\sigma_I a^2/k_BT = 0.54$ [21]. This is the tension of a (100) interface, but as this temperature is well above the roughening temperature the interfacial free energy is expected to depend only weakly on orientation.

Thus the amphiphile reduces the interfacial tension by a factor of 93. This is consistent with the interface being wetted by the middle phase as a comparison with the system, water, octane, C_4E_1 shows [3]. In that system, the oil-water interfacial tension is reduced by a factor of 130, and the interface is wetted by the middle phase. The presence of a lamellar phase in our system, however, is not consistent with the weak amphiphile C_4E_1, which produces no such phases.

It is not simple to compare our results for the interfacial tension directly with those of mean-field theory, because the phase diagram is altered significantly by the presence of fluctuations, as indicated by the comparison of Figs. 1 and 2. Nonetheless, reductions in the interfacial tension calculated within mean-field theory for the same model in systems near the four-phase point have ranged [13] from 30 to 100. It would appear, therefore, that fluctuations are not responsible for the low tensions calculated in model systems with short-range interactions. We infer that this is also the case in physical systems. It could be argued that fluctuations offset the effect of attractive long-range interactions that, according to Eq. (1) and the argument following, tend to increase the magnitude of the interfacial tension, and we cannot rule this out.

What is clearer, however, is that fluctuations affect the location of the wetting transition. As do long-range forces, fluctuations drive the transition from the disorder line, the location predicted by mean-field theory, to the microemulsion side of it, the location where it is, in fact, observed experimentally.

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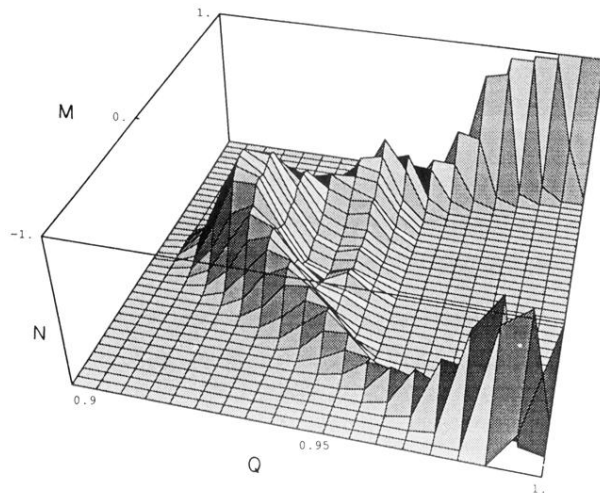
FIG. 3. Histogram in Q and M at $L=12$, $\Delta=-7.0$.