PHYSICAL REVIEW E VOLUME 49, NUMBER 5 MAY 1994

Charge-frustrated model of bicontinuous phases

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(Received 12 January 1994)

A nonlinear field theoretic model for surfactant self-assembly is described and applied to bicontinuous phases. The anharmonic model treats bonding constraints and the resulting frustration of phase separation in terms of an electrostatic analogy. The model does not assume self-assembly, and it accounts for all long-wavelength density fluctuations. A renormalized harmonic approximation is used to predict scattering curves. With physically reasonable values for the parameters that characterize the model, the predictions of the theory compare favorably with experiment and are consistent with Porod's law in the small angle region.

PACS number(s): 82.70.Kj, 05.20.−y, 61.20.Gy, 61.25.Em

I. INTRODUCTION

This and the following paper [1] address the nature of bicontinuous phases. The analysis is carried out within the framework of a field theoretic electrostatic analogy of oil-water-surfactant systems. The present paper is devoted to the demonstration that the theory, the so-called "charge-frustrated" model, is capable of predicting bicontinuity with physically reasonable microscopic parameters. An analysis of whether the ubiquitous interfaces in such systems are thick or thin is presented in the following paper.

A variety of lattice models have been introduced to account for the wide range of possible equilibrium microemulsion behavior [2]. Treated in the mean-field approximation, these models have yielded phase diagrams. In some cases, correlation functions and structure factors have been predicted [3]. There have been molecular thermodynamic approaches to surfactant self-assembly as well [4]. Finally, phenomenological approaches to structure factor calculation have been suggested, from Landau-Ginzberg expansions [5] to random wave algorithms [6–8]. Most of this work assumes from the outset that the amphiphilic interfaces separating oil and water are thin. The exception is the recent phenomenological model of Gompper and Kraus [9], in which bicontinuity is found to possibly coincide with broad interfaces — a conclusion we also reach in our second paper [1].

The approach we take is different from these earlier works. We do not assume a particular interfacial structure. We adopt a model in which molecular parameters are related to known physical properties of the disassociated system — the average length of the surfactant molecules and the surface tension of a surfactant-free oil-water interface, for example. Since the elementary constituents of the model are the disassembled species, the theory does not presuppose the existence of self-assembled structures. Rather it aims at predicting such formation.

Thus we are not attempting to replace the phenomenological models. Rather the ultimate goal is to provide additional predictive power for these models with a foundation that relates the phenomenological parameters (e.g., curvature energies) to microscopic properties (e.g., lengths of surfactant molecules).

The model we use is nonlinear. It augments a standard field theoretic Hamiltonian with a contribution that accounts for the constraints of bonding between the head (waterlike) and tail (oil-like) groups comprising the surfactants. This augmenting term will be demonstrated to be of the form of an electrostatic potential energy, hence the terminology "electrostatic analogy." In the absence of surfactant there is no electrostatic term and the Hamiltonian is of the Ising universality class. It predicts the demixing and interfacial fluctuations of an oil-water mixture below its critical temperature. In this region, the parameters characterizing the model can be related to the surface tension of an oil-water interface in the absence of surfactant. With surfactant present, however, the constraint of electrostatic neutrality imposed by the augmenting term frustrates this phase separation. The extent of the frustration depends, in part, upon the magnitude of an effective charge. This magnitude is a function of the microscopic length of a surfactant, i.e., the length scale of the bonding constraint. It is also a function of temperature and surfactant concentration. The full Hamiltonian is virtually identical to the free energy functional used by Stillinger in his mean-field analysis of self-assembly [10]. It is also closely related to models employed in the study of diblock copolymers [11].

We motivate the anharmonic Hamiltonian in Sec. II. Specifically, we consider the energetics of long-wavelength fluctuations of a nearly homogeneous oil-water-surfactant system. It is not altogether surprising that an electrostatic analogy would arise from such an analysis. The constraints of stoichiometry imply the constancy of some linear combination of density fields in the zero wave vector limit $k \to 0^+$. As such, for small displacements from homogeneity, the restoring force will have an infinite force constant in this limit. The assumption of analyticity therefore implies a contribution to the Hamiltonian quadratic in densities with a coefficient diverging at least as fast as k^{-2} as $k \to 0^+$. This form is the Coulomb potential. By constraining the form of the Hamiltonian, we show that this potential appears in a more general anharmonic model valid for sharply inhomogeneous systems. Monte Carlo calculations with this anharmonic Hamiltonian [12] have shown that the model does predict self-assembly in a variety of forms (e.g., lamellar phases and micelles of various shapes). This provides some justification of our assumed form of the Hamiltonian.

In Sec. III we discuss the physical meaning and order of magnitude values for the parameters in our model. Section IV details our variational treatment of the nonlinear model. We compare the bulk scattering curves from the model with those from experiment in Sec. V. Section VI discusses the model, as fit to experiment. In particular, we show the model is consistent with Porod's law, consistent with demixing if the surfactant is removed, and consistent with pure oil-water surface tensions. Section VII provides a brief summary of our conclusions. An Appendix presents the details of the variational renormalization calculation.

II. NONLINEAR MODEL

Here we motivate a Hamiltonian valid in the long-wavelength limit that can describe surfactant self-assembly. This Hamiltonian controls the fluctuation statistics of our system. Consideration will be directed to microemulsions of the oil, water, and surfactant type. Specifically there will be four density fields $\{\rho_i(\mathbf{r})\}$, where $\rho_1(\mathbf{r})$ is the water, $\rho_4(\mathbf{r})$ is the oil, $\rho_2(\mathbf{r})$ is the surfactant head, and $\rho_3(\mathbf{r})$ is the surfactant tail field. There are n_i segments in a molecule containing groups of type i. For example, the bulk density of oil segments ρ_4 is n_4 times the bulk density of oil molecules. Similarly, ρ_3 is n_3 times the bulk density of surfactants. The bulk densities and the number of segments per molecule will be specified when actual experimental systems are examined.

It is reasonable to assume that in the long-wavelength limit, the Hamiltonian for a field theoretic model of this system can be written as ($\beta^{-1} = k_B T$)

$$\begin{aligned}\beta H[\{\rho_i(\mathbf{r})\}] &= \sum_i \int d\mathbf{r} f_i(\rho_i(\mathbf{r})) \\ &\quad -\frac{1}{2}\sum_{i,j}\int\int d\mathbf{r}d\mathbf{r}'\delta\rho_i(\mathbf{r})c_{ij}(|\mathbf{r}-\mathbf{r}'|)\delta\rho_j(\mathbf{r}') , \end{aligned} \tag{1}$$

where $f_i(\rho_i(\mathbf{r}))$ is a nonlinear yet local function of $\rho_i(\mathbf{r}) = \delta\rho_i(\mathbf{r}) + \rho_i$. The nonlocal coupling function $c_{ij}(r)$ is independent of the instantaneous density and is thus a property of a statistically isotropic fluid mixture. The terms linear in the density are not explicitly included in Eq. (1) since they simply determine the average value of the density fields, and the average densities will be specified in actual applications. Equation (1) can be rewritten as

$$\begin{aligned}\beta H[\delta\hat{\rho}_i(\mathbf{k})] &= \frac{1}{2(2\pi)^3}\sum_{ij}\int d\mathbf{k}\,\delta\hat{\rho}_i(-\mathbf{k}) \\ &\quad \times[\delta_{ij}f_i'' - \hat{c}_{ij}(k)]\delta\hat{\rho}_j(\mathbf{k}) + O(\delta\hat{\rho}^3) , \end{aligned} \tag{2}$$

where

$$\delta\hat{\rho}_i(\mathbf{k}) = \int d\mathbf{r}\,\delta\rho_i(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{r}} \tag{3}$$

is the Fourier transform of the density function.

In a compact notation, Eq. (2) can be written as

$$\begin{aligned}\beta H[\delta\hat{\boldsymbol{\rho}}(\mathbf{k})] &= \frac{1}{2(2\pi)^3}\int d\mathbf{k}\,\delta\hat{\boldsymbol{\rho}}^{\top}(-\mathbf{k})\hat{\mathbf{M}}^{-1}(k)\delta\hat{\boldsymbol{\rho}}(\mathbf{k}) \\ &\quad +O(\delta\rho^3) , \end{aligned} \tag{4}$$

where the 4×4 matrix $\hat{\mathbf{M}}^{-1}(k)$ has elements

$$\hat{M}_{ij}^{-1}(k) = \delta_{ij}f_i'' - \hat{c}_{ij}(k) \tag{5}$$

and $\delta\boldsymbol{\rho}(\mathbf{r})$ is a four-component vector symbolizing fluctuations in the four field components $\{\rho_i(\mathbf{r})\}$. Terms higher order than quadratic in $\delta\hat{\rho}$ have been omitted from Eq. (4). To the extent that those omitted terms are negligible, one may compute the density-density correlation function

$$\langle\delta\rho_i(\mathbf{r})\delta\rho_j(\mathbf{r}')\rangle = \frac{\int\mathcal{D}\boldsymbol{\rho}(\mathbf{r})\delta\rho_i(\mathbf{r})\delta\rho_j(\mathbf{r}')e^{-\beta H}}{\int\mathcal{D}\boldsymbol{\rho}(\mathbf{r})e^{-\beta H}} \tag{6}$$

by performing Gaussian integrals. The result is [13]

$$\int d(\mathbf{r}-\mathbf{r}')\langle\delta\rho_i(\mathbf{r})\delta\rho_j(\mathbf{r}')\rangle e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} = \hat{M}_{ij}(k) . \tag{7}$$

The quantity measured in kinematical diffraction studies [14] is therefore given in the quadratic approximation by the inverse of the coupling matrix in Eq. (4).

The functions $f_i(\rho)$ and $c_{ij}(r)$ in Eq. (2) are determined by ensuring that Eqs. (5) and (7) are correct sufficiently close to homogeneity. In that regime, the Fourier transform of the density-density correlation functions for the fields associated with surfactants at a bulk density ρ_S has the inverse

$$\begin{aligned}\hat{M}_{ij}^{-1}(k) &= \rho_S^{-1}\hat{\omega}_{ij}^{-1}(k) - \Delta\hat{c}_{ij}(k) \\ &= n_i^{-2}\rho_S^{-1}\delta_{ij} - \hat{c}_{ij}^{(0)}(k) - \Delta\hat{c}_{ij}(k) , \quad i = 2,3 \end{aligned} \tag{8}$$

where use is made of both the intramolecular coupling function $\hat{c}_{ij}^{(0)}(k)$ and the intermolecular coupling function $\Delta\hat{c}_{ij}(k)$. Equation (8) is a contracted form of Chandler and Andersen's equation [15] used in the polymer reference interaction site model (RISM) theory [16]. In that context, $\Delta c_{ij}(r)$ is the so-called "site-site" direct correlation function. It is expected to be short ranged.

In view of Eqs. (5) and (8), we have $f_i''(\rho_i) = 1/n_i^2\rho_S = 1/n_i\rho_i$ and thus

$$f_i(\rho_i(\mathbf{r})) = \frac{1}{n_i}\{\rho_i(\mathbf{r})\ln[\rho_i(\mathbf{r})] - \rho_i(\mathbf{r})\} . \tag{9}$$

This equation is the standard Flory free energy of mixing applied to an inhomogeneous fluid [17].

While we expect the intermolecular contribution to the nonlocal $c_{ij}(|\mathbf{r}-\mathbf{r}'|)$ to be short ranged, the intramolecular contribution to $c_{ij}^{(0)}(r)$ has a long-ranged component. It arises because of the conservation law of stoichiometry, and it is what is derived in Refs. [10,12]. Specifically,

$$\hat{c}_{ij}^{(0)}(k) = -\frac{4\pi\beta z_i z_j}{n_i n_j k^2} + O(k^0),$$
$$z_2 = -z_3 = \left[\frac{3}{4\pi\beta\rho_s\Delta^2}\right]^{\frac{1}{2}} \equiv z \ . \tag{10}$$

The length Δ in Eq. (10) is roughly the root-mean-square separation between the head and the tail groups of a surfactant molecule.

A similar comparison between the quadratic field theoretic Hamiltonian and the correlation functions for the oil and water components produces additional diagonal Flory free energy of mixing terms as well as short-ranged direct correlation function interactions. There is no nonlocal stoichiometric constraint governing the $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ fields, however, and thus there are no additional effective Coulombic interactions. Assuming the surfactant and oil-water cross terms are also short ranged, the final long-wavelength Hamiltonian is

$$\beta H[\{\rho_i(\mathbf{k})\}] = \sum_i \int d\mathbf{r}\ \frac{1}{n_i}\rho_i(\mathbf{r}) \ln\left[\rho_i(\mathbf{r})\right] + \frac{\beta}{2(2\pi)^3}\int d\mathbf{k}\ \delta\hat{\boldsymbol{\rho}}^{\top}(-\mathbf{k}) \times \left[\mathbf{J} + \mathbf{G}k^2 + \mathbf{C}\ \frac{4\pi z^2}{k^2}\right]\delta\hat{\boldsymbol{\rho}}(\mathbf{k}) \ , \tag{11}$$

where again the terms linear in the density have been left out. The elements of the matrices $\mathbf{J}$ and $\mathbf{G}$ give the coefficients of the small k expansion of the $\Delta\hat{c}_{ij}(k)$ functions, and $C_{ij} = z_i z_j / z^2 n_i n_j$ (the nonsurfactant components of which are zero). The terms of $O(k^0)$ and $O(k^2)$ in the bonding free energy terms have also been neglected. This Fourier space representation is, of course, equivalent to the real-space representation

$$\beta H[\{\rho_i(\mathbf{r})\}] = \sum_i \int d\mathbf{r} \frac{1}{n_i}\rho_i(\mathbf{r}) \ln\left[\rho_i(\mathbf{r})\right] + \frac{\beta}{2}\int d\mathbf{r}\ \delta\boldsymbol{\rho}^{\top}(\mathbf{r})[\mathbf{J} - \mathbf{G}\nabla^2]\delta\boldsymbol{\rho}(\mathbf{r}) + \frac{\beta}{2}\int\int d\mathbf{r}d\mathbf{r}'\delta\boldsymbol{\rho}^{\top}(\mathbf{r})\ \frac{z^2}{|\mathbf{r}-\mathbf{r}'|}\ \mathbf{C}\ \delta\boldsymbol{\rho}(\mathbf{r}') \ . \tag{12}$$

We assume that the net total density is fixed, i.e.,

$$\rho_1(\mathbf{r}) + \rho_2(\mathbf{r}) + \rho_3(\mathbf{r}) + \rho_4(\mathbf{r}) \equiv \rho_0 \tag{13}$$

is a constant. This local incompressibility is plausible for long wavelengths. A reasonable and simplest approximation for the short-ranged interactions of the surfactant head and tail density fields is that they are the same as those for oil and water density fields. If this similarity were strictly true, the short-ranged interactions would be independent of concentrations. The Hamiltonian thus reduces to one involving three independent fields and two parameters

$$\beta H[\{\rho_i(r)\}] = \sum_i \int d\mathbf{r}\ \frac{1}{n_i}\rho_i(\mathbf{r}) \ln \rho_i(\mathbf{r}) + \frac{\beta}{2(2\pi)^3}\int d\mathbf{k}\ \delta\hat{\boldsymbol{\rho}}^{\top}(-\mathbf{k}) \times \left[(j + gk^2)\mathbf{D} + \frac{4\pi z^2}{k^2}\mathbf{C}\right]\delta\hat{\boldsymbol{\rho}}(\mathbf{k}) \ , \tag{14}$$

where vector $\delta\boldsymbol{\rho}(\mathbf{r})$ is now a three-component vector symbolizing fluctuations in $\rho_1(\mathbf{r})$, $\rho_2(\mathbf{r})$, and $\rho_3(\mathbf{r})$. The matrices $\mathbf{C}$ and $\mathbf{D}$ are 3×3: $D_{ij} = 0$ if $i = 3$ or $j = 3$, and $D_{ij} = 1$ otherwise; $C_{ij} = 0$ if $i = 1$ or $j = 1$, and $C_{ij} = (-1)^{i+j}/n_i n_j$ otherwise. The energy parameters are defined by

$$j = J_{11} + J_{22} - 2J_{12},$$
$$g = G_{11} + G_{22} - 2G_{12}. \tag{15}$$

In the summation, it is now understood that the fourth field $\rho_4(\mathbf{r})$ is computed from Eq. (13). Our field theoretic Hamiltonian Eq. (14) is virtually identical to that used by Stillinger in a variational density-functional calculation [10].

III. MICROSCOPIC ENERGY AND LENGTH SCALES

The model Hamiltonian Eq. (14) contains several parameters. They are the net total density ρ_0, the j and g energy parameters, the frustrating charge magnitude z, and an implicit short-wavelength cutoff k_c. Physically reasonable values of each of these quantities are known. For example, net total particle density should be close to that appropriate for water at standard conditions $\rho_0 \approx 1/30$ Å^{-3}. In our numerical work, we adopt precisely this value. The Hamiltonian in Eq. (14), being a functional of density fields, cannot apply on truly atomistic length scales. A short-wavelength cutoff is therefore required. This cutoff excludes from consideration those density fields with density variations on too short a length scale. A surfactant length is an appropriate value for this minimal level of resolution, and the cutoff should be roughly $\pi/20$ Å$\cong 0.15$ Å^{-1}. This is the value we will use.

The energy parameter j represents the unfavorable oil-water contact energy times an oil segment or water molecule volume. Presumably, therefore, $j\rho_0$ is in the range of -3 to $-10k_BT$. Thus we expect j to be of the order of $-10^2 k_BT$ Å^3. Similarly the ratio $-g/j$ represents the cross-sectional area of a typical segment. The g parameters should thus be of the order of $(10^2 - 10^3)k_BT$ Å^5.

With these typical values, a surfactant-free oil-water system would phase separate in a mean-field approximation to our Hamiltonian (14). The surface tension in a phase-separated oil-water mixture (with no surfactant) can in fact, be deduced from our model. Since we make the simplifying assumption that the short-ranged interactions of surfactant head and tail segments are identical to those of water and oil, the result of applying our theory to a pure oil-water mixture will still be Eq. (14). But there is then just one field $\rho_1(\mathbf{r})$; D is unity and C is zero. To calculate an approximate surface tension, we have performed mean-field (maximum term) calculations on Eq. (14) specialized to an oil-water mixture in the presence of an interface [18]. That is, we constrained the system to variations in one direction only and found the two density configurations that correspond to the two states of broken symmetry. The mean-field convexity condition for phase separation is identical to the $\det[\hat{\boldsymbol{\chi}}(0)] \geq 0$ stability condition for the Gaussian theory. These two bulk configurations were then used as boundary conditions, and the density profile that minimized the Hamiltonian in Eq. (14) was determined. The excess energy associated with this profile relative to the energy of the uniform state is the surface tension.

The equation for the surface tension thus calculated is [18]

$$\sigma = \int_{\rho^{(\alpha)}}^{\rho^{(\gamma)}} [-2gW(\rho)]^{1/2} d\rho \ , \tag{16}$$

where $\rho^{(\alpha)}$ and $\rho^{(\gamma)}$ are concentrations of water in the two separated phases, and $-W(\rho)$ is the excess free energy density of the homogeneous phase over that of the separated phases. In particular,

$$\begin{aligned} -W(\rho) = \psi(\rho) &+ \psi(\rho^{(\alpha)})(\rho - \rho^{(\gamma)})/(\rho^{(\gamma)} - \rho^{(\alpha)}) \\ &-\psi(\rho^{(\gamma)})(\rho - \rho^{(\alpha)})/(\rho^{(\gamma)} - \rho^{(\alpha)}) \ , \end{aligned} \tag{17}$$

where

$$\begin{aligned} \psi(\rho) &= j\rho^2 + \rho[\ln\rho - 1]/\beta n_1 \\ &\quad + (\rho_0 - \rho)[\ln(\rho_0 - \rho) - 1]/\beta n_2 \end{aligned} \tag{18}$$

is the local part of the nonsurfactant contribution to the free energy density from Eq. (14). The correct order of magnitude for the surface tension, $\sim 0.1 k_B T/\text{Å}^2$, is obtained from Eq. (16) with the parameters discussed above.

The presence of the surfactant in a microemulsion mixture tends to frustrate the oil-water phase separation. The size of the frustrating charge, z in Eq. (10), leads to a pair interaction between neighboring surfactant particles of typical size $z^2\rho_s^{1/3}/n_i n_j$. The concentration of surfactant in bicontinuous phases are generally in the range of $x_s = \rho_s/\rho_0$ between 0.05 and 0.5. The length of a surfactant molecule Δ is about 20 Å and n_i is in the range 1–10. With these parameters, one finds that $z^2\rho_s^{1/3}/n_i n_j$ is in the range 10^{-3}–$10^{-1} k_B T$. Thus, the frustration makes a small contribution to the local free energetics. It is the cumulative effect, i.e., the contributions to small k in Eq. (14), that can lead to mesoscopic self-assembly.

To address whether the physically reasonable molecular parameters in our model do indeed lead to such a large length scale structure, we use a variational treatment of the Hamiltonian (14). We turn to that treatment now.

IV. VARIATIONAL TREATMENT FOR BULK CORRELATIONS

The free energy of mixing terms, the $\rho_i(\mathbf{r})\ln\rho_i(\mathbf{r})$ terms, are not quadratic in the density field variables. The Hamiltonian is thus not amenable to exact analytical treatment. We use the Gibbs-Bogoliubov-Feynman variational bound to determine the optimal harmonic reference system for the Hamiltonian [19]. This variational method makes use of the bound for the partition function,

$$Z \geq Z_G \exp[-\beta\langle H - H_G\rangle_G] \equiv e^{-\beta A_1} \ . \tag{19}$$

Here Z_G denotes the partition function with the Gaussian Hamiltonian

$$\beta H_G = \frac{1}{2(2\pi)^3}\int d\mathbf{k}\, \hat{\boldsymbol{\rho}}^{\top}(-\mathbf{k})\hat{\mathbf{G}}(k)\hat{\boldsymbol{\rho}}(\mathbf{k}) \ , \tag{20}$$

where irrelevant terms linear in the density have been dropped. The averaging, $\langle\,\rangle_G$, is done with the Gaussian weight implied by this reference Hamiltonian.

The variational procedure identifies the coupling matrix as

$$\hat{\mathbf{G}}(k) = \beta\left((j + gk^2)\mathbf{D} + \frac{4\pi z^2}{k^2}\mathbf{C}\right) + 2\boldsymbol{\xi}_1. \tag{21}$$

The $\boldsymbol{\xi}_1$ term arises from the $\rho_i(\mathbf{r})\ln\rho_i(\mathbf{r})$ terms in Eq. (14). The variational approach deals with this nonlinearity by enforcing a self-consistency condition on $\boldsymbol{\xi}_1$. As $\boldsymbol{\xi}_1$ is independent of k, this result can be viewed as a renormalization of the $\mathbf{J} = j\mathbf{D}$ matrix.

This procedure, which requires use of the high wave vector cutoff k_c, leads to wave vector independent coefficients in the quadratic Hamiltonian that are somewhat different than those arrived at through a truncated Taylor expansion. The differences, or renormalization, account for the anharmonic contributions to the Hamiltonian. The details of this calculation relevant to the present field theoretic Hamiltonian Eq. (14) are presented in the Appendix.

This variational approach is identical to a self-consistent first-order theory for the density-density correlation function. As such, it should provide a good approximate bulk scattering curve that can be compared with experiment.

V. COMPARISON WITH EXPERIMENT

We have fit the structure factor predicted by the variational treatment of the Hamiltonian Eq. (14) to small angle scattering data. To carry out the fit, we varied the j and g parameters. The experimental data we considered are all of the bulk-contrast type, so that the experimental scattering intensity $i(k)$ is proportional to the

TABLE I. The results of fitting the model Hamiltonian to the SANS data of Ref. [22]. The data are for the cosurfactant 1-octanol. The energy units are k_BT and the length units are Å, except for f, which has units of Å^3/cm. The value of ρ_0 is 1/30 Å^3.

$\rho_2+\rho_3$	ρ_1	ρ_4	n_1	n_2	n_3	n_4	Δ	f	g	j	k_c
0.010667	0.008333	0.014333	1	1	10	15	8.0	7.13	768	-298	0.15
0.011333	0.006667	0.015333	1	1	10	15	8.0	9.77	957	-359	0.15
0.011667	0.005667	0.016	1	1	10	15	8.0	11.75	1043	-399	0.15
0.012333	0.004667	0.016333	1	1	10	15	8.0	9.38	1262	-436	0.15

water-water structure factor [20] given in the theory by Eq. (A12). The proportionality constant is

$$f=(n_O-n_W)^2/\rho_0^2, \tag{22}$$

where n_O and n_W are, respectively, the oil and water scattering length densities (not to be confused with the segment numbers n_i). In all the fitting, we take $\rho_0 = 1/30$ Å^{-3}, the molecular density of water at normal conditions. This f factor should be constant within an experiment that varies only composition, and for typical scattering length densities it should be approximately 4 Å^3/cm. In our fitting, however, we varied f along with j and g. The fit was accomplished by Powell's modified quadratically convergent method [21]. Additional quantities appearing in the Hamiltonian (14) were fixed at physically reasonable values, as noted in Table I.

The results of the fits to the ionic surfactant system D_2O-$C_{16}H_{34}$-potassium oleate-1-$H(CH_2)_iOH$ studied by Caponetti *et al.* are indicated in Fig. 1 [22]. These authors studied four systems, differing only in cosurfactant. The authors suggest that the microemulsion is in a random configuration. Only the fit for the 1-octanol cosurfactant system is displayed in Fig. 1. The scattering data were all taken at the constant sample temperature of 25 °C. The parameters of the fits are listed in Table I. The parameter f is predicted to be 4.2 Å^3/cm in this experiment. In this four-component system, the alcohol cosurfactant has been assumed to be part of the surfactant when calculating ρ_S. Any long-range component to the direct correlation function that is due to the electrostatic interactions of the polar surfactant is, of course, not included in the model Hamiltonian Eq. (14).

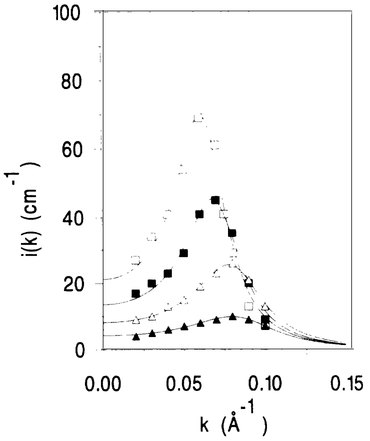

FIG. 1. The SANS data of Ref. [22] for the cosurfactant 1-octanol are compared with the fit of Table I. The peak intensity decreases with increasing ρ_S.

Six additional sets of scattering data from disordered isotropic microemulsions [6,23–27] were fit, however, by a straightforward quadratic expansion of Eq. (14) about average densities. That is, only the first term in Eq. (A11) was used. All these fits were successful, but the parameters determined are not quantitatively accurate since this approach neglects the nonlinear effects in Eq. (14). Unless otherwise noted, our discussion will pertain only to the results of the variational calculation.

VI. DISCUSSION OF RESULTS

These microemulsion systems possesses a wide range of characteristic lengths. The scattering peak typically corresponds to a distance of 300 Å, surfactant lengths are about 20 Å, and atomic details are of the order of 1 Å. The great disparity between the first length scale and the other two is what allows for a successful small-k field theoretic description of the system. The Hamiltonian Eq. (14) is specialized to a very simple model of a three-component surfactant system. Explicit consideration of the cosurfactant is not included, for example. Additionally the long-ranged Coulombic interactions present in ionic and polar surfactants are not included. In the systems examined, however, these interactions are screened by ionic density fluctuations, and the assumption of effectively short-ranged interactions should be appropriate.

The assumption of the very simple forms for the small k intermolecular couplings is perhaps the least tenable. This assumption is what leads to the presence of only two adjustable parameters in the model, j and g. These parameters are, in fact, not constant with varying oil, water, and surfactant volume fractions. The square-gradient coefficient g increases with ρ_S and the bulk term j decreases with ρ_S within a series of experiments on a single surfactant system. This variability should not be surprising considering the true difference between oil and water and the surfactant tail and head groups. Contrast variation experiments that probe the fluctuations of more than one independent field will indicate further failings due to the simple assumption that **J** and **G** matrices are characterized by only two parameters j and g.

As seen in Table I, the variational treatment produces scaling factors f that are nearly constant with changing system composition. These scaling factors should be constant with changing system composition, and this result is another indication of the importance of the nonlinear response in Eq. (14), which is incompletely accounted for in the variational treatment.

A test of the model would be to allow the surfactant length Δ to vary. Since this length is precisely defined, allowing it to be optimized should not lead to a result substantially different from that assumed in the table. In all cases, the optimized length is within a factor of 2 of the value initially assumed, and the quality of the fit was not improved significantly upon optimization of the surfactant length. It seems, therefore, that the parameter Δ appearing in Eq. (10) has been correctly defined. It is not, for example, necessary to renormalize it to account for effects that have been neglected in the Hamiltonian Eq. (14).

Another test of the model is to remove the surfactant and determine where the system phase separates, as an oil and water mixture should. We have computed the densities of oil and water that would be present if the surfactant were removed, scaling them up so as to maintain the constant density ρ_0. In all cases, a quadratic treatment predicts that the model does, in fact, phase separate with the j parameter found from fitting the diffraction data.

As another test of the model, we consider the oil-water surface tension for this phase separated system in the absence of surfactant. The surface tensions computed as discussed in Sec. III with the parameters determined by the variational treatment are in the range 0.17–0.28 $k_BT/\text{Å}^2$. A typical oil-water surface tension is $0.12k_BT/\text{Å}^2$ [28]. This rough agreement with the variational estimate supports the model that underlies our analysis. The associated calculation for the density profiles gives interfacial widths of roughly 10 Å.

To the extent that a bicontinuous phase is a correlated microphase separated material with isotropically fluctuating interfaces of negligible width, the scattering curve decays as $1/k^4$ for large k [29,30]. This decay is known as Porod's law. The authors of Refs. [6,24,25] report that this law is observed in the range just beyond the peak in the small-angle neutron scattering (SANS) data for bicontinuous phases. A plot of $\ln i(k)$ versus $\ln k$ shows a $1/k^4$ decay for the structure factors predicted by some of the fits (both variational and nonvariational) in the same range in which the experiments observe the $1/k^4$ decay. Figure 2 displays such plots for some of the fits. The first two curves in Fig. 2 decay with a slope of -4.0 ± 0.1, whereas the last two curves decay with slopes of -4.5 and -5.2. In fact, all of the other fits lead to such approximate $1/k^4$ decays, with three exceptions. These exceptions occur in studies for which bicontinuous structures were not postulated.

While the k^{-4} decay does follow from the presence of thin interfaces, our theoretical results based upon a Gaussian approximation that does not support thin interfaces demonstrate that the converse is not necessarily true. More generally, the k^{-4} decay is a manifestation of large domains, rich in either oil or water. Such structures can be well described by a Gaussian field theory, as evidenced by the curves shown in Fig. 2. Whether or not the interfaces separating these domains are sharp can be discerned from the correlations between surfactants. This issue, studied experimentally by film scattering, is outside the realm of a Gaussian model, since that class of models is not applicable to microphase separated systems at the small lengths associated with a narrow interface [31]. The analysis of this issue and the corresponding bimodality of density distributions is given in our subsequent companion paper [1].

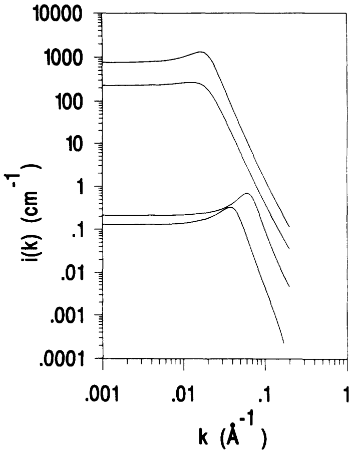

FIG. 2. The predicted scattering curves for fits to the SANS data in Refs. [24,6,22,25] are plotted on a log-log scale. The curves are divided by factors of 1, 10, 100, and 1000, respectively, to facilitate plotting.

VII. CONCLUSIONS

We have derived an anharmonic field theoretic Hamiltonian for oil, water, and surfactant systems valid from nearly homogeneous to microphase separated emulsions. With physically reasonable parameters, this model compares favorably with several sets of SANS data. The parameters in the model pertain to small length scale microscopic properties. Given the favorable comparison of theory and experiment, it appears that the charge frustrated model Eq. (14) captures the essential physical features that underlie the nature of oil-water-surfactant assemblies. In the following paper we use the model to examine specifically the formation of interfaces in bicontinuous phases.

ACKNOWLEDGMENTS

We have benefited from stimulating discussions with Berend Smit and Raymond Yee. This research has been supported by NSF. M.W.D. thanks the Fannie and John Hertz Foundation for financial support.

APPENDIX: THE OPTIMAL HARMONIC REFERENCE SYSTEM

We want to find the optimal harmonic reference system to treat Eq. (14). The Hamiltonian of Eq. (14) contains a nonquadratic local part as well as a quadratic nonlocal part. Schematically, the Hamiltonian is of the form

$$\begin{aligned}\beta H[\boldsymbol{\rho}(\mathbf{r})] &= F_1[\hat{\boldsymbol{\rho}}(\mathbf{k})] + F_2[\boldsymbol{\rho}(\mathbf{r})],\\ F_1[\hat{\boldsymbol{\rho}}(\mathbf{k})] &= \mathbf{a}\cdot\hat{\boldsymbol{\rho}}(\mathbf{0}) + \frac{1}{2V}\sum_{\mathbf{k}}\hat{\boldsymbol{\rho}}^{\top}(-\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})\hat{\boldsymbol{\rho}}(\mathbf{k}),\\ F_2[\boldsymbol{\rho}(\mathbf{r})] &= \int d\mathbf{r} f_2[\{\rho_i(\mathbf{r})\}]\ , \qquad \text{(A1)}\end{aligned}$$

where F_1 is the quadratic part of βH, F_2 is the local nonquadratic part, $\hat{\mathbf{A}}(\mathbf{k})$ is a real, symmetric, positive-definite $N \times N$ matrix, and $\mathbf{a}$ is a real, N-vector constant. In the specific case of Eq. (14), $N = 3$, $\hat{\mathbf{A}}(\mathbf{k}) = \beta[(j + gk^2)\mathbf{D} + (4\pi z^2/k^2)\mathbf{C}]$, $f_2[\{\rho_i(\mathbf{r})\}] = \sum_i n_i^{-1}\rho_i(\mathbf{r})\ln\rho_i(\mathbf{r})$, and the $\mathbf{a}$ field has been suppressed by convention. This Hamiltonian will be treated in the grand canonical ensemble. To facilitate the following manipulations, a discrete spectrum in k space is indicated in Eq. (A1). In the limit $V \to \infty$, the spectrum will become continuous.

We want to approximate (A1) by the purely harmonic reference system that has the Hamiltonian

$$\beta H_G = \mathbf{b}\cdot\hat{\boldsymbol{\rho}}(\mathbf{0}) + \frac{1}{2V}\sum_{\mathbf{k}}\hat{\boldsymbol{\rho}}^{\top}(-\mathbf{k})\hat{\mathbf{G}}(\mathbf{k})\hat{\boldsymbol{\rho}}(\mathbf{k})\ , \qquad \text{(A2)}$$

where again $\hat{\mathbf{G}}(\mathbf{k})$ is a real, symmetric, positive-definite matrix, and $\mathbf{b}$ is a real, constant vector without loss of generality if $\rho_i(\mathbf{r})$ is real. The average of the local F_2 function in the harmonic reference system defined by Eq. (A2) is denoted as

$$\langle F_2\rangle_G = V\langle f_2\rangle_G = V\xi[\mathbf{G}^{-1}(\mathbf{0}),\boldsymbol{\rho}]\ . \qquad \text{(A3)}$$

Note that the average of the local f_2 function ξ depends only upon the average density and the variance of the density in a isotropic fluid, as is indicated in Eq. (A3). From Gaussian statistics this average is given by

$$\begin{aligned}\xi[\mathbf{G}^{-1}(\mathbf{0}),\boldsymbol{\rho}] &= \xi\Big[V^{-1}\sum_{\mathbf{k}}\hat{\mathbf{G}}^{-1}(\mathbf{k}), -\hat{\mathbf{G}}^{-1}(\mathbf{0})\mathbf{b}\Big]\\ &= \xi\Big[(2\pi)^{-3}\int d\mathbf{k}\,\hat{\mathbf{G}}^{-1}(\mathbf{k}), -\hat{\mathbf{G}}^{-1}(\mathbf{0})\mathbf{b}\Big]\ . \qquad \text{(A4)}\end{aligned}$$

Employing the variational bound Eq. (19),

$$\frac{\partial}{\partial\hat{G}_{ij}(\mathbf{k})}A_1 = \frac{\partial}{\partial b_i}A_1 \equiv 0\ , \qquad \text{(A5)}$$

one finds that the terms in the optimal harmonic reference system satisfy the equations

$$\begin{aligned}\hat{\mathbf{G}}(\mathbf{k}) &= \hat{\mathbf{A}}(\mathbf{k}) + 2\boldsymbol{\xi}_1\left(V^{-1}\sum_{\mathbf{k}}\hat{\mathbf{G}}^{-1}(\mathbf{k}), -\hat{\mathbf{G}}^{-1}(\mathbf{0})\mathbf{b}\right),\\ \mathbf{b} &= \hat{\mathbf{G}}(\mathbf{0})\hat{\mathbf{A}}^{-1}(\mathbf{0})\\ &\quad\times\left[\mathbf{a} + \boldsymbol{\xi}_2\left(V^{-1}\sum_{\mathbf{k}}\hat{\mathbf{G}}^{-1}(\mathbf{k}), -\hat{\mathbf{G}}^{-1}(\mathbf{0})\mathbf{b}\right)\right]\ , \qquad \text{(A6)}\end{aligned}$$

where the tensors $\boldsymbol{\xi}_1$ and $\boldsymbol{\xi}_2$ are the partial derivatives

$$\xi_{1_{ij}} = \partial\xi[\mathbf{W},\mathbf{y}]/\partial W_{ij},\quad \xi_{2_i} = \partial\xi[\mathbf{W},\mathbf{y}]/\partial y_i\ . \qquad \text{(A7)}$$

Equation (A6) is a simple integral equation for the renormalized harmonic coefficients. In particular, the renormalized coupling matrix can be considered to be equal to the original coupling matrix plus a self-consistent constant. In the case of Eq. (14), one can see that essentially only the matrix $j\mathbf{D}$ is renormalized in this procedure.

This result Eq. (A6) is applied to Eq. (14) by expanding the $\rho_i(\mathbf{r})\ln\rho_i(\mathbf{r})$ terms about the average density that the variational treatment would predict. That is, these terms are expanded about the average densities of the oil, water, and surfactant mixture, and a statistical mechanical treatment (via the variational bound) of the model is required to lead to the correct bulk densities. With this stipulation, only the first relation in Eq. (A6) need be considered. Specifically,

$$\begin{aligned}\xi = {}& p(\chi_{11},\rho_1)/n_1 + p(\chi_{22},\rho_2)/n_2\\ &+ p(\chi_{33},\rho_3)/n_3 + p(\chi_{44},\rho_4)/n_4\ , \qquad \text{(A8)}\end{aligned}$$

where the Gaussian average function p is given by

$$p(\chi,\rho) = \rho(\ln\rho - 1) + \chi/2\rho + \chi^2/4\rho^3 + \cdots \qquad \text{(A9)}$$

and

$$\boldsymbol{\xi}_{1_{ij}} = \delta_{ij}p_1(\chi_{ii},\rho_i)/n_i + p_1(\chi_{44},\rho_4)/n_4, \qquad \text{(A10)}$$

where the partial derivative p_1 is given by

$$2p_1(\chi,\rho) = 1/\rho + \chi/\rho^3 + \cdots\ . \qquad \text{(A11)}$$

Here $\rho_4 = \rho_0 - \rho_1 - \rho_2 - \rho_3$ and $\chi_{44} = \sum_{ij}\chi_{ij}$. The shorthand $\chi_{ij} = G_{ij}^{-1}(\mathbf{0})$ has been used for the point density-density correlations of the reference system. Both of these series Eqs. (A9) and (A11) are asymptotic expansions that have been truncated. Equation (A11) implies that there will be one term beyond that due to a pure quadratic expansion that enters in the first relation in (A6). This term will give an indication of the importance of the nonlinear response in Eq. (14). Specifically, the four p_1 functions in (A9), and hence in (A6), need to be determined self-consistently. Note that if only the first term in (A11) is employed, no self-consistency condition is enforced, and this treatment leads to a quadratic approximation to Eq. (14).

The model Hamiltonian Eq. (14), does not have a convergent value for the integral expression for the $\boldsymbol{\chi} = \mathbf{G}^{-1}(\mathbf{0})$ matrix in Eq. (A4). A cutoff is therefore employed in this small-k theory. In the case of Table I, the cutoff is 0.15 Å^{-1}. Note that the SANS intensity is given by

$$i(k) = f[\hat{\mathbf{G}}(k)^{-1}]_{11}\ . \qquad \text{(A12)}$$

Equation (A6) is solved efficiently by a globally convergent, iterative Newton-Raphson technique [32]. We find that the region of convergence for this root-finding technique is rather small when the scattering function Eq. (A12) has the peaked form typical of the bicontinuous SANS data. As a result, the j and g parameters must be varied in small increments during the fitting procedure if the root finder is to converge.

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