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Gaussian random fields with two level-cuts—Model for asymmetric microemulsions with nonzero spontaneous curvature?

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The microstructure of a microemulsion is dominated by the thermodynamics of the surfactant interface between the oil and water domains. As the spontaneous curvature of this surfactant interface is strongly temperature dependent the microstructure of microemulsions also becomes temperature dependent. In the present work we have assumed that the thermodynamics of the interface is determined by the Helfrich Hamiltonian and that the interface can be described by two appropriately chosen level-cuts of a Gaussian random field. It is then possible to express the free energy density of the interface as a functional of the spectral distribution of the Gaussian random field so that the microstructure which minimizes the free energy can be determined by performing a functional minimization of the free energy with respect to the spectral distribution of the Gaussian random field. The two level-cuts are an important feature of the model since they allow us to model microemulsions with nonzero spontaneous curvature and with unequal volume fractions of water and oil. This again makes it possible to simulate the temperature driven phase inversion of the microemulsions described above. The model furthermore allows us to predict the microstructure of the microemulsion for a given composition of water, oil and surfactant and input parameters H_0 , κ and $\bar{\kappa}$ as well as to predict direct space structures and scattering structure factors. Microemulsions with bicontinuous structures, droplet structures or swollen sponge-like structures are predicted dependent on the input parameters and represented in direct and inverse space. Dilution plots for scattering peak positions are in good agreement with experimental results. © 2001 American Institute of Physics. [DOI: 10.1063/1.1388558]

I. INTRODUCTION

Experimental work on ternary microemulsion systems via measurements of scattering, conductivity and diffusion coefficients indicates the existence of a microstructure of well-defined oil and water domains with typical length scales of 100–500 Å. The domains are subject to fluctuations on the nanosecond scale, but their average shape cannot yet be predicted for any composition¹ and the development of predictive models is still a major objective of the physics of complex fluids. It is generally accepted that for a system of soft interfaces—i.e., a system where the bending energy is low compared to the thermal energy and where there are no important long range electrostatic or steric interactions, the physics is dominated by the Hamiltonian of the surfactant interface between the oil and water domains. This can to a first order be approximated by an effective Hamiltonian of a curvature–elastic interface:²

$$\mathcal{H} = \int_S dA [\kappa(H - H_0)^2 + \bar{\kappa}K], \quad (1)$$

where S denotes the interface manifold. H is the mean cur-

vature which is given by $\frac{1}{2}(c_x + c_y)$, where c_x and c_y are the local principal curvatures. H_0 is the spontaneous curvature, i.e., the preferred curvature of the unconstrained surfactant film. K is the Gaussian curvature, which is given by the product $c_x c_y$. The bending elastic constant κ and the Gaussian bending elastic constant $\bar{\kappa}$ have the units of kT and relate the curvatures to energy. A self consistent form for a Helfrich Hamiltonian which also includes a spontaneous Gaussian curvature has been suggested by Fogden *et al.*³ Even though it cannot generally be assumed that the spontaneous Gaussian curvature is negligible, we have, for the present work, decided to omit the contributions to the Helfrich Hamiltonian due to this term.

About ten years ago, Strey and coworkers showed that the phase behavior of microemulsions made out of single chain linear nonionic surfactants, water and oil can be represented by a generic phase prism.⁴ The cut of the phase prism at equal volume fractions of water and oil has become a popular way of representing the phase behavior of the ternary systems. The cut is for obvious reasons often referred to as “the fish” (see Fig. 1). Varying the temperature and surfactant concentration at a constant water to oil ratio allows the two basic variables: H_0 , the spontaneous curvature and ϕ_s , the surface area per unit volume to be varied. The loca-

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FIG. 1. The fish plot. A schematic representation of the phase behavior dependence of temperature and surfactant concentration for a ternary system of water, oil and nonionic surfactant. 1 denotes the one-phase region where the microemulsion is formed, w/o denotes the water-in-oil structure and o/w denotes the oil-in-water structure. In between the bicontinuous microemulsion is formed. $\bar{2}$ denotes the part of the two-phase region where the system separates into an w/o microemulsion and an excess water phase. $\bar{2}$ denotes the part of the two-phase region where the system separates into an o/w microemulsion and an excess oil phase. 3 denotes the three-phase region where the system separates into a microemulsion and excess water and oil phases.

tion of the relevant expected microstructures are sketched in Fig. 1.

According to this description, the system will at low temperatures, either phase separate into an oil phase and a microemulsion phase or form a stable microemulsion dependent on the surfactant concentration. In both cases the surfactant film is curved towards the oil domains which yields a continuous water domain. The spontaneous curvature of the surfactant film approaches zero at higher temperatures which leads to a set of different possible structures of the system. At high surfactant concentration a lamellar structure (L_α) is sometimes formed, whereas at lower surfactant concentration a so-called bicontinuous structure is preferred. The bicontinuous structure is a structure where both water and oil domains are continuous. If the surfactant concentration drops below a certain concentration, the microemulsion can separate into a three-phase system consisting of an oil phase, a microemulsion phase and a water phase. For even higher temperatures the surfactant film will start to curve towards the water regions, which, dependent of the surfactant concentration, leaves a possibility of either a one-phase water-in-oil microemulsion or a two-phase system of water and a water-in-oil microemulsion. The critical point γ_0 where the one-phase, two-phase and three-phase regions meet is sometimes called the point of maximal solubilization. At the corresponding temperature, $\tilde{T}$, the spontaneous curvature of the surfactant film is zero. For systems of equal volume fractions of water and oil the mean curvature of the surfactant film will also be zero.

In the present paper a structure we have chosen to denote the diluted bicontinuous structure will be discussed. This structure can be obtained by taking a bicontinuous microemulsion with equal volume fractions of water and oil and

zero mean curvature and diluting it with either water or oil. As the composition of the diluted bicontinuous structure is asymmetric in water and oil the mean curvature of the surfactant film is nonzero even though the spontaneous curvature of the film is zero. In Sec. V it will be discussed in more detail how the diluted bicontinuous structure and the regular droplet structure differ.

The phase diagram in Fig. 1 represents a microemulsion formed with a general nonionic surfactant. Microemulsions with ionic surfactants generally show an inverse dependence on temperature with water-in-oil microemulsions at low temperatures and oil-in-water microemulsions at high temperatures.⁴

A number of different models for microemulsions have been suggested over the years. When comparing the different models it is important to keep in mind that they have been made with very different foci. Some models have been developed for describing the droplet structures while other models describe the bicontinuous structures. Furthermore some models have been developed in order to get tools for analyzing, e.g., small-angle scattering data while others have been developed for explaining the phase behavior of microemulsions.

A. Models based on theory from liquid state physics

This group contains several different models which are reviewed in more detail in Ref. 5. The models all have in common that they describe the microstructure of discrete particles (mono- or polydisperse spheres, ellipsoidal particles) interacting with different kinds of potentials (hard spheres, attractive or repulsive). The liquid state physics models describe the small-angle scattering from droplet microemulsions as for example the ionic AOT [bis(2-ethylhexyl)sulfosuccinate sodium salt] microemulsions very successfully⁶ and allow information about the size, polydispersity and sometimes the shape of microemulsions droplets and the type of interaction between them to be deduced from scattering data. As the models are based on liquid state theory and have no direct connection to the Helfrich formalism, there are only indirect ways of getting information about the bending elastic constants^{7–11} whereas no general information can be obtained about the spontaneous curvature.

B. Models of the Talmon–Prager type

This category includes a number of different models all having in common that they fill space with different shaped and sized polyhedra, normally cubes or Voronoï-cells.^{12–15} The polyhedra are randomly filled with water or oil according to the composition of the modeled sample. The surfactant interface is assumed to be modeled by the interface between cells with oil and water. In this way the Talmon–Prager type of models gives a primitive description of the microstructure of bicontinuous or diluted bicontinuous microemulsions which can be used for explaining some of the very basic features of both the behavior and the small-angle scattering patterns of microemulsions.

C. Disordered open connected (DOC) models

This category of models contains both the original DOC model^{16,17} suggested by Zemb *et al.* and a model of similar type suggested recently by Tlustý *et al.*¹⁸

The DOC (Disordered Open and Connected) model takes as the Talmon–Prager model its starting point in a Voronoï tessellation of space. The Helfrich Hamiltonian is minimized under the constraints of constant area per unit volume and constant sample composition and assuming that κ and $\bar{\kappa} \gg kT$. In order to avoid unphysically high curvatures, the distance between the points used for generating the Voronoï construction is equal to at least twice the surfactant length. The model constraints are satisfied in two limiting cases where the interior phase of the microemulsion is placed along either the edges (DOC-cylinders model) or the facets (DOC-lamellar model) of the Voronoï-cells depending on whether the microemulsion has very strong or very weak curvature towards water. In the DOC-cylinders model (strong spontaneous curvature) the structure is described by droplets coalescing via short cylinders¹⁹ and a connected network structure can be formed. In the DOC-lamellar model (vanishingly low spontaneous curvature) the structure is described by connected random bilayers and different bilayer structures including symmetric and asymmetric sponges can be modeled.²⁰ An analytic expression for the maximum in the scattering structure factor as well as numerical calculations of the full scattering curve are available.²¹

Within the frame of the DOC model, the microstructure as well as the connectivity can be predicted, as long as the bending elastic constants remain much larger than kT . However, the “stiff interface” condition is not generally fulfilled and the model breaks down in the case of short single chain surfactants, where the bending elastic constants are close to $1 kT$.

Tlustý *et al.*¹⁸ have suggested a model, which as the DOC-cylinders model is based on a picture of the microemulsion as having a branched tubular structure. The model expression for the free energy takes into account the contributions to the curvature energy of the tubes and the junctions as well as entropy contributions from the junctions and their distributions. By changing the microemulsion composition the predicted network becomes denser and some of the scaling phenomena observed in the three-phase region of the microemulsion phase diagram can be explained. No direct space structures nor scattering structure factors are predicted by the model. This has the consequence that the model is yet to be tested *quantitatively* against, e.g., scattering data or microscopy pictures. However, *qualitative* comparisons with pictures of microemulsions obtained by cryogenic temperature transmission electron microscopy have been made.²² These pictures of nonionic microemulsion systems of $C_{12}E_5$ /water/*n*-octane show that at certain compositions and temperatures the microemulsion indeed has a microstructure of interconnected oil-swollen cylinders.

A disadvantage of both the original DOC model and the model by Tlustý *et al.* is that only asymmetric bicontinuous microemulsions are predicted, i.e., bicontinuous microemulsions with nonzero mean curvature. This implies that the bicontinuous microemulsion with zero mean curvature ob-

served around $\tilde{T}$ cannot be explained by the models.

D. Random surface models

This category of models is based on the ideas of Cahn²³ and Berk.^{24,25} Cahn suggested that the structure of a liquid that undergoes spinodal decomposition could be described in terms of a superposition of standing sinusoidal waves of fixed wavelength but random amplitude, direction and phase. By attributing a level-cut value to the hilly landscape thus obtained and assuming that one of the two phases was given by all the domains above the level-cut value and the other given by all domains below the level-cut value he achieved a model for the structure that bore great resemblance with pictures of phase-separating glasses.²³

Berk²⁴ adopted this idea and made plausible that it could also be used it as a model for bicontinuous microemulsion systems. He showed how to Fourier transform structures generated according to Cahn’s scheme in order to determine the scattering patterns and discussed the influence of generating the field by means of a Gaussian distribution of wavelengths instead of a single wavelength. The same year Teubner and Strey²⁶ derived the so-called Teubner–Strey model from Landau theory. In both of these papers the scattering peak observed for microemulsions was explained and in the following years the Teubner–Strey model has been widely applied when analyzing scattering data on microemulsions (see, e.g., Ref. 27).

Teubner²⁸ proved that the structures generated according to the procedures suggested by Cahn and Berk were actually realizations of Gaussian random fields and this allowed him to derive analytical expressions of the mean curvature $\langle H \rangle$, the mean squared curvature $\langle H^2 \rangle$ and the Gaussian curvature $\langle K \rangle$ in terms of the level-cut value of the Gaussian random field.

Shortly after Pieruschka and Marčelja^{29,30} showed how the expression for the free energy corresponding to the Helfrich Hamiltonian could be expressed in terms of level-cut Gaussian random fields generated from the spectrum $\nu(k)$. From a variational minimization of the obtained expression for the Helfrich free energy, they showed that if the physics of the microemulsion system is governed by the Helfrich Hamiltonian, then the Gaussian random field that models the microemulsion system should be generated by a spectrum $\nu(k)$ that has the same functional form as the Teubner–Strey model.

Compared to the previously mentioned models the Gaussian random field model has the advantage that it is directly based on the physics contained in the Helfrich Hamiltonian. The structures predicted by the model are not constrained to be either tubular or lamellar as in the models of the DOC type, but can be varied to some extent by changing the spectral density of the generating random field. However, in its present form the Gaussian random field model still shares the great disadvantage with the models of the Talmon–Prager and DOC type that the curvature can only be changed continuously by changing the composition of the system.

The intention of the present work is to use the formalism developed by Teubner, Marčelja, and Pieruschka to set up a model for microemulsions where both the spontaneous curvatures and the volume fractions of water, oil and surfactant can be varied. We will show how it becomes possible to model a phase inversion of the microemulsion microstructure from oil droplets in water through bicontinuous to water droplets in oil simply by changing the spontaneous curvature. Direct space structures and scattering structure factors are calculated for different sets of values for the bending elastic constant, κ , the Gaussian bending elastic constant, $\bar{\kappa}$, and the spontaneous curvature, H_0 . Furthermore, predictions of the microemulsion microstructure as a function of these parameters are made.

II. BASIC IDEAS

We assume that the physics of the microemulsion is described by the Helfrich Hamiltonian and that the surfactant interface can be described by appropriate level-cuts α and β of a Gaussian random field:

$$s(\mathbf{r}) = \int d\mathbf{k} s(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (2)$$

where the amplitudes $s(\mathbf{k})$ are taken from a Gaussian distribution centered at zero with standard deviation given by the function $\nu(\mathbf{k})$:

$$p(s(\mathbf{k})) = \frac{1}{\sqrt{2\pi\nu(\mathbf{k})}} e^{-|s(\mathbf{k})|^2/(2\nu(\mathbf{k}))}. \quad (3)$$

The level-cuts α and β determine the representation of the microemulsion from the underlying Gaussian random field. We have assumed that the water and oil domains are bounded as follows:

$$\begin{aligned} \mathbf{r} \text{ is a water domain if } & \begin{cases} s(\mathbf{r}) \geq \alpha \text{ or } s(\mathbf{r}) \leq \beta, & \text{for } \alpha > \beta; \\ s(\mathbf{r}) \geq \alpha \text{ and } s(\mathbf{r}) \leq \beta, & \text{for } \alpha < \beta; \end{cases} \\ \mathbf{r} \text{ is an oil domain elsewhere} & \end{aligned} \quad (4)$$

The definitions are illustrated for a two-dimensional field in Fig. 2. The bicontinuous microemulsion with zero mean curvature modeled in the one-level cut case^{29,30} is obtained with equal volume fractions of water and oil and in the limit $\alpha=0$ and $\beta=\pm\infty$. By allowing both the possibility $\alpha>\beta$ and $\alpha<\beta$ it becomes furthermore possible to simulate a continuous transition from positive mean curvature to negative mean curvature of the surfactant film. This corresponds to a transition from water droplets in oil to oil droplets in water. It should be noted that for a given composition of the microemulsion, the constraint of the fixed volume fraction of the water has the consequence that β is a function of α (or the opposite). It should also be noted that even though the level cut values α and β provide a bridge between the Gaussian random field and the picture of the microemulsion they do not play a role on their own and are not experimentally observable parameters in real systems.

III. DETERMINATION OF THE GAUSSIAN RANDOM FIELD AND THE LEVEL-CUT VALUES

The free energy density of the Gaussian random field with level-cuts that approximates the bending Hamiltonian given by Eq. (1) can be approximated by^{31,32}

$$f_{\text{free}} \approx \frac{S}{V} [2\kappa \langle (H - H_0)^2 \rangle + \bar{\kappa} \langle K \rangle] - \frac{1}{2\pi^2} \int_k dk k^2 \ln \nu(k) \\ = \frac{S}{V} [2\kappa \langle H^2 \rangle - 4\kappa H_0 \langle H \rangle + 2\kappa \langle H_0^2 \rangle + \bar{\kappa} \langle K \rangle] \\ - \frac{1}{2\pi^2} \int_k dk k^2 \ln \nu(k), \quad (5)$$

where S/V is the surface to volume ratio of the system. The brackets $\langle \dots \rangle$ denote the average taken over the Gaussian random field. The first four terms of Eq. (5) thus contain the contributions to the surface energy whereas the last term is our ansatz for the entropy term.

For a two-level-cut model with level-cuts α and β the surface to volume ratio is given by

$$\frac{S}{V} = \frac{2}{\pi} \sqrt{\frac{\langle k^2 \rangle}{3}} [e^{-\alpha^2} + e^{-\beta^2}] \equiv \frac{2}{\pi} \sqrt{\frac{\langle k^2 \rangle}{3}} [A] \equiv \phi_s, \quad (6)$$

where $[A]$ is an abbreviation of $[e^{-\alpha^2} + e^{-\beta^2}]$. This expression is just a generalization of the expression given by Teubner in Ref. 28 for the one-level-cut model. ϕ_s is the volume fraction of the surfactant. Strictly speaking the relation between ϕ_s and the surface to volume ratio is given by

$$\frac{S}{V} = \frac{\phi_s}{d_s}, \quad (7)$$

where d_s is the thickness of the surfactant layer. This relation will later allow us to attribute an absolute length scale to the system.

The moment $\langle k^n \rangle$ is in 3-dimensional space calculated as follows:

$$\langle k^n \rangle = \frac{1}{2\pi^2} \int_0^{k_c} dk k^{2+n} \nu(k). \quad (8)$$

As the distribution function $\nu(k)$ should be normalized to unity, we have the following constraint:

$$\langle k^0 \rangle = \langle 1 \rangle = \frac{1}{2\pi^2} \int_0^{k_c} dk k^2 \nu(k) = 1. \quad (9)$$

The surface to volume ratio is fixed in a thermodynamically stable microemulsion so we get an additional constraint on $\nu(k)$ from (6):

$$\langle k^2 \rangle = 3 \left(\frac{\phi_s \pi}{[A]2} \right)^2 = \frac{1}{2\pi^2} \int_0^{k_c} dk k^4 \nu(k). \quad (10)$$

The averages $\langle H \rangle$, $\langle H^2 \rangle$ and $\langle K \rangle$ for the two-level-cut model are generalized from the expressions for the one-level-cut model²⁸ as follows:

$$\langle x \rangle_{\alpha+\beta} = \frac{\langle x \rangle_{\alpha} \frac{S_{\alpha}}{V} + \langle x \rangle_{\beta} \frac{S_{\beta}}{V}}{\frac{S_{\alpha}}{V} + \frac{S_{\beta}}{V}} = \frac{\langle x \rangle_{\alpha} e^{-\alpha^2/2} + \langle x \rangle_{\beta} e^{-\beta^2/2}}{e^{-\alpha^2/2} + e^{-\beta^2/2}}, \quad (11)$$

where $\langle x \rangle_{\alpha}$ denotes the average of x of the surface given by the α -level-cut. S_{α}/V is the surface to volume ratio of the surface given by the α -level-cut, it is proportional to the surface area of the α surface and is therefore used as a weight factor in the averaging procedure. This means that $\langle H \rangle$, $\langle H^2 \rangle$ and $\langle K \rangle$ are given by

$$\langle H \rangle = \frac{1}{2} \sqrt{\frac{\pi}{6} \langle k^2 \rangle} \left[\frac{\alpha e^{-\alpha^2/2} - \beta e^{-\beta^2/2}}{e^{-\alpha^2/2} + e^{-\beta^2/2}} \right] \equiv \frac{1}{2} \sqrt{\frac{\pi}{6} \langle k^2 \rangle} [B], \quad (12)$$

$$\langle H^2 \rangle = \frac{1}{6} \langle k^2 \rangle \left[\frac{\alpha^2 e^{-\alpha^2/2} + \beta^2 e^{-\beta^2/2}}{e^{-\alpha^2/2} + e^{-\beta^2/2}} + \frac{6}{5} \frac{\langle k^4 \rangle}{\langle k^2 \rangle^2} - 1 \right] \\ \equiv \frac{1}{6} \langle k^2 \rangle [[B^2] - 1] + \frac{1}{5} \frac{\langle k^4 \rangle}{\langle k^2 \rangle}, \quad (13)$$

and

$$\langle K \rangle = \frac{1}{6} \langle k^2 \rangle \left[\frac{\alpha^2 e^{-\alpha^2/2} + \beta^2 e^{-\beta^2/2}}{e^{-\alpha^2/2} + e^{-\beta^2/2}} - 1 \right] \equiv \frac{1}{6} \langle k^2 \rangle [[B^2] - 1], \quad (14)$$

where $[B]$ is an abbreviation of $[(\alpha e^{-\alpha^2/2} - \beta e^{-\beta^2/2})/(e^{-\alpha^2/2} + e^{-\beta^2/2})]$ and $[B^2]$ is an abbreviation of $[(\alpha^2 e^{-\alpha^2/2} + \beta^2 e^{-\beta^2/2})/(e^{-\alpha^2/2} + e^{-\beta^2/2})]$. By inserting (12), (13) and (14) in (5) and using (8) the free energy can be expressed as a functional of $\nu(k)$. In order to determine the spectrum $\nu(k)$ which minimizes the free energy given by Eq. (5), a variational minimization of f_{free} with respect to $\nu(k)$ is performed. The two constraints (9) and (10) are taken into account in the minimization via Lagrange multipliers. The result of the variational minimization is that $\nu(k)$ has the same functional form as in the case of one-level-cut Gaussian random fields,³⁰ namely

$$\nu(k) = \frac{a}{k^4 - b k^2 + c}, \quad (15)$$

where the constants a , b and c are modified according to the two-level-cut model as follows:

$$a = \frac{\pi^2 15 \phi_s}{16 \kappa [A]^2}, \quad (16)$$

$$b = - \frac{([B^2] - 1) \phi_s^2 \pi^2 15}{16 [A]^2} + \frac{2 [A]^2 \langle k^4 \rangle}{3 \pi^2 \phi_s^2} \\ + \frac{5 [B] \pi^{3/2} \phi_s H_0}{2 \sqrt{2} [A]} - \frac{5}{2} H_0^2 \\ - \frac{15 \phi_s^2 \pi^2 ([B^2] - 1) \bar{\kappa}}{32 \kappa [A]^2} - \frac{5 \lambda_1}{4 \kappa}, \quad (17)$$

and

$$c = \frac{15\lambda_2\pi^2\phi_s}{16\kappa[A]^2}. \quad (18)$$

The constant a depends only on the level-cut parameters α and β and known parameters. The constants b and c depend on the undetermined Lagrange multipliers λ_1 and λ_2 . b and c can be determined by solving the equation system given by (9) and (10) using the expression for $\nu(k)$ given by Eq. (15). Integration of (9) leads to the equation

$$0 = \frac{\sqrt{b - \sqrt{b^2 - 4c}} \tanh^{-1} \left(\frac{\sqrt{2k_c}}{\sqrt{b - \sqrt{b^2 - 4c}}} \right)}{\sqrt{2}\sqrt{b^2 - 4c}} - \frac{\sqrt{b + \sqrt{b^2 - 4c}} \tanh^{-1} \left(\frac{\sqrt{2k_c}}{\sqrt{b + \sqrt{b^2 - 4c}}} \right)}{\sqrt{2}\sqrt{b^2 - 4c}} - \frac{2\pi^2}{a}. \quad (19)$$

Similarly, integration of (10) leads to the equation

$$0 = -\frac{8\kappa\phi_s\pi^2}{5} + k_c + \frac{\sqrt{2}(b - \sqrt{b^2 - 4c})^{3/2} \tanh^{-1} \left(\frac{\sqrt{2k_c}}{\sqrt{b - \sqrt{b^2 - 4c}}} \right)}{4\sqrt{b^2 - 4c}} - \frac{\sqrt{2}(b + \sqrt{b^2 - 4c})^{3/2} \tanh^{-1} \left(\frac{\sqrt{2k_c}}{\sqrt{b + \sqrt{b^2 - 4c}}} \right)}{4\sqrt{b^2 - 4c}}. \quad (20)$$

Here (19) and (20) are transcendental equations in b and c and have to be solved numerically for each choice of the level-cuts α and β . When this is done we have an expression for the spectrum $\nu(k)$ that minimizes the free energy for a given set of level-cuts α and β . From $\nu(k)$ we are able to calculate the free energy, which is then easy to minimize numerically with respect to the values of level-cuts. It is noted that the integral in (10) is not convergent for the spectral distribution given by (15). As in earlier work, a cut-off value k_c is therefore needed. k_c equals $2\pi/\lambda_c$, where λ_c , physically, is the shortest wavelength where the first order expansion for the elastic theory can be applied. We believe that $k_c = 1 \text{ nm}^{-1}$ corresponding to a λ_c of about ten molecular widths is a reasonable cut-off value.

IV. CALCULATION OF STRUCTURE FACTORS

Reports of experimental studies of microemulsion systems refer to the concentrations of surfactants (and sometimes co-surfactants), water (including soluble species such as salt) and oil. Then a procedure for splitting the space occupied by the microemulsion into polar and apolar vol-

umes relies on identifying a “polar head” and a “hydrophobic chain” of the surfactant molecule. For the model calculations in the present study we have assumed that half the surfactant molecule is polar and the other half is apolar. The volume fraction of oil referred to in the text, ϕ_o , refers to the total apolar volume, that is the volume fraction of the pure oil and half the volume fraction of the surfactant. Similarly, the volume fraction of water, ϕ_w , refers to the total polar volume. This means that $\phi_o + \phi_w$ adds up to unity.

Once the spectrum $\nu(k)$ with level-cuts α and β that minimizes the Helfrich free energy is found, we obtain a representation of the structure of the microemulsion both in direct and in inverse space.

A. Representation in direct space

In direct space the representation is obtained from the equation (2) where the $\nu(k)$ enters through the distribution $s(k)$ and from the level-cut values α and β . The software that has been used for generating the direct space representations of the microemulsions in Fig. 6 and 7 was written by Roberts.³³

B. Representation in reciprocal space

The reciprocal space representations of the microemulsion are the structure factors that can be obtained in a scattering experiment. The structure factor is calculated from $\nu(k)$ according to the following procedure:²⁹ $\nu(k)$ is Fourier transformed and the correlation function, $g(r)$, is obtained. The correlation function of the random Gaussian field with level-cuts α and β , $\Gamma^{\alpha\beta}$, is calculated from $g(r)$. $\Gamma^{\alpha\beta}$ is Fourier transformed and the structure factor, $s(q)$, is obtained. The integrations necessary to determine $\Gamma^{\alpha\beta}$ from $g(r)$ and to Fourier transform $\Gamma^{\alpha\beta}$ are carried out numerically using the very robust Fortran subroutines from the Quadpack library.³⁴

C. Conformations with similar free energy

The variational minimization of the free energy only determines the minimizing spectrum $\nu(k)$. We obtain no information about how sharp the minimum is and therefore no information about what the energy cost of perturbing this minimal conformation would be. As the minimization of the free energy with respect to the level-cut values α and β is carried out separately after the variational minimization has been performed, it is possible to get an estimate of the Boltzmann distribution of the conformations given by the different level-cuts α and β . We have calculated the Boltzmann factors of the different conformations using the following expression:

$$P_B(\alpha) = \frac{e^{[(F_{\text{free}}(\alpha) - F_{\text{free}}(\alpha_{\text{min}}))/\pi\xi^3/6]}}{\int e^{[(F_{\text{free}}(\alpha) - F_{\text{free}}(\alpha_{\text{min}}))/\pi\xi^3/6]} d\alpha}, \quad (21)$$

i.e., as the difference between the free energy per unit volume of the conformation given by the level-cut value α and the free energy per unit volume of the minimal energy conformation. The unit volume is taken to be the volume of a

sphere with diameter equal to the correlation length ξ of the structure, where ξ is calculated from the factors b and c in the $\nu(k)$ using the following expression:²⁶

$$\xi = \frac{1}{\sqrt{\frac{1}{2}\sqrt{c} + \frac{b}{4}}}. \quad (22)$$

In Ref. 35 this approach has been called conformational diffusion. However, it does not give the full Boltzmann distribution over all conformations but only the Boltzmann distribution over the conformations given by the different level-cut values. In spite of this, the averaging provides an idea about the effect of conformations with similar free energies and we have included it in the calculations of the reciprocal space structure factors presented in the following section.

V. RESULTS

Minimization of the free energy, Eq. (5), tells us which microstructure is the preferred for one given sample composition and set of parameters κ , $\bar{\kappa}$ and H_0 . The sample composition is fixed once the volume fraction of the water phase ϕ_w (or alternatively the oil phase ϕ_o) and the surface to volume ratio ϕ_s are fixed. This gives us five possible parameters to vary when we want to study the behavior of the free energy. With this large parameter space it is an impossible task to give a complete account of all model predictions, but in the following we will show some examples. In the model predictions we have chosen to focus on $\kappa=1$ kT and $\kappa=2$ kT since most experimental studies of microemulsion systems indicate that these values are typical for the bending elastic constants. We will show examples of calculations on microemulsions with both symmetric and asymmetric compositions.

A. Examples of model predictions

Figure 3 contains diagrams of the microemulsion structure as function of H_0 for a microemulsion with equal volume fractions of water and oil but varying ϕ_s , where ϕ_s is directly proportional to the surfactant volume fraction.³⁶ In the microemulsion part of the three-phase region (see Fig. 1) the mean curvature $\langle H \rangle$ has been shown to be proportional to $(\tilde{T}-T)$ around $\tilde{T}$.⁴ In this part of the phase diagram the mean curvature attempts to follow the spontaneous curvature H_0 . This means that it is reasonable to assume that H_0 is also proportional to $(T-\tilde{T})$ around $\tilde{T}$. As the temperature dependence of H_0 is intrinsic for the surfactant³⁷—in contrast to the temperature dependence of $\langle H \rangle$ which depends on both the surfactant and the composition—it is furthermore reasonable to assume that the proportionality between H_0 and $(T-\tilde{T})$ extends into the one-phase region of the phase diagram. This implies that the H_0 - ϕ_s cut through phase space shown in Fig. 3 is comparable to the traditional “fish”-cut shown in Fig. 3. However, as the model cannot (yet) be used for predicting the phase transition lines between one-phase and two- or three-phase regions, Fig. 3 is only a diagram of what the microstructure will be if the system forms a microemulsion.

FIG. 3. A model prediction of the phase behavior dependence of ϕ_s and H_0 for microemulsions with equal volume fractions of water and oil. For non-ionic microemulsions $H_0 \propto (\tilde{T}-T)$ for which reason the H_0 -scale has been reversed. (a) The phase behavior of a system with $\kappa=1$ kT and a number of different values for $\bar{\kappa}$ has been plotted. (b) A similar plot but for $\kappa=2$ kT. The label “bicontinuous” refers to a bicontinuous structure with zero mean curvature, while w/o (or o/w) refers to a structure of water droplets in oil (respectively, oil droplets in water).

In Fig. 3(a) the bending elastic constant κ is fixed at 1 kT and in 3(b) $\kappa=2$ kT, the Gaussian bending elastic constant $\bar{\kappa}$ has been set to a number of different values. The diagram should be read as follows: Say $\bar{\kappa}=0$, find the upper and lower transition line corresponding to $\bar{\kappa}=0$. Everywhere between the two lines the microemulsion has a bicontinuous structure with zero mean curvature. In this region the microstructure of the microemulsion will not change as temperature changes. Above the upper line the microemulsion forms water droplets in oil and below the lower line the microemulsion forms oil droplets in water. In the model the distinction between bicontinuous and droplet microemulsions are given by the set of level-cut values (α, β) that minimizes the free

energy. If $(\alpha, \beta) = (0, \infty)$ the microemulsion is bicontinuous with zero mean curvature. If α and β have other values say $(\alpha, \beta) = (0.67, -0.67)$ the microemulsion forms droplets. Figures 6(a) and 6(b) are two-dimensional cuts through the Gaussian random field models of bicontinuous and droplet structures generated for $\kappa = 1$ kT. Figures 7(a) and 7(b) are projections of the corresponding 3D structures. Note that the bicontinuous structure given here is in principle similar to the bicontinuous structure previously described by Pieruschka and Marčelja.²⁹ Comparing Figs. 3(a) and 3(b) we observe that a larger κ gives rise to a more narrow bicontinuous microemulsion region.

If $\bar{\kappa}$ is negative the bicontinuous structure is only favored for low ϕ_s and close to $H_0 = 0$. The introduction of spontaneous curvature quickly leads to the formation of droplets. The local stability limit evaluated in the absence of spontaneous curvature, $-\bar{\kappa} < 2\kappa$, is never reached.³⁸

A positive $\bar{\kappa}$ would favor a bicontinuous structure in a larger part of the phase space if the structure remained stable. This is not surprising when inspecting the expression for the Helfrich free energy, Eq. (5). The mean Gaussian curvature $\langle K \rangle$ will be negative for bicontinuous structures and positive for droplet structures and the sign of $\bar{\kappa}$ therefore determines which of these structures has the lowest free energy. However, when $\bar{\kappa} > 0$ the free energy is lower for structures of high absolute value of $\langle K \rangle$, and the system is likely to phase separate.

The model predicts a first order phase transition from the bicontinuous domain to the droplet domain. The transition takes place in a transition region where both phases coexist and which lies outside the transition line marked on the figure. For low values of ϕ_s the transition region is quite extended. With increasing $|H_0|$ the droplet domains are gradually closed and the droplets become more and more monodisperse. The free energy is only weakly dependent on the level-cut values (α, β) in a rather wide region around the level-cut values that minimize the free energy. This gives rise to the easy coexistence of conformations ranging from the bicontinuous structure with zero mean curvature to the most monodisperse and curved structure the model can produce. As ϕ_s increases the transition region become gradually more and more narrow, the dependence between the free energy and the level-cut values become more pronounced and fewer conformations are available to the system. For high ϕ_s the transition region is very narrow and a large morphological change is induced by a small increase in $|H_0|$. In the transition region the volume fraction of microemulsion with a zero mean curvature bicontinuous structure quickly drops while the volume fraction of the most monodisperse droplets the model can produce $((\alpha, \beta) = (0.67, -0.67))$ increases correspondingly. The bending elastic constant κ also plays an important role for how the bicontinuous to droplet transition occurs. A higher κ generally gives rise to a more narrow transition region.

Figure 4 contains a similar diagram but for a diluted version of the microemulsion from Fig. 3, where the volume fraction of the apolar phase (oil plus the apolar part of the surfactant) is set to $\phi_o = 0.25$ while the remaining part, ϕ_w , is constituted by water and the polar part of the surfactant.

FIG. 4. A similar plot as in Fig. 3 but for a system with asymmetric composition, $\phi_o = 0.25$ and $\phi_w = 0.75$. (a) $\kappa = 1$ kT and (b) $\kappa = 2$ kT. The structures labeled “diluted bicontinuous,” “symmetric sponge,” and “asymmetric sponge” are explained in the text. “o/w” refers to the structure of oil droplets in water also explained in the text.

This asymmetric microemulsion can take three different types of structures.

For large positive spontaneous curvatures the microemulsion will form oil droplets in water which are as monodisperse and regular shaped as the model allows them to be. This region is labeled o/w in the figure. In Figs. 6(c) and 7(c) a Gaussian random field model of the droplet structure is shown in two dimensions and three dimensions, respectively. On the surface of the droplets small local inclusions/protrusions of a much smaller size than an average droplet can be observed. These are allowed as long as the bending constants are not too high and they consume a significant part of the available interface.

In a region around $H_0 = 0$ the microemulsion forms a structure we have chosen to call “diluted bicontinuous” as mentioned in the introduction. Figures 6(d) and 7(d) show

the Gaussian random field model of the droplet structure in two and three dimensions, respectively. Due to the conflict between a low spontaneous curvature and the asymmetric composition of the sample, an o/w structure with larger and more irregular shaped droplets than in the droplet microemulsion is formed. Everywhere inside the diluted bicontinuous region $(\alpha, \beta) = (0.67, \infty)$, so one of the level-cuts is infinite as in the bicontinuous microemulsion with zero mean curvature. However, as the sample composition is asymmetric, bicontinuity is not generally guaranteed. The mean curvature of this diluted bicontinuous structure is positive, but significantly lower than the mean curvature of the droplet structure described above.

If the spontaneous curvature is large and negative there will be a competition between the o/w structure preferred by the asymmetric sample composition and the w/o structure preferred by the spontaneous curvature of the surfactant film. This leads to a peculiar structure: water-droplets with negative curvature start to grow inside the oil-droplets in order to minimize the curvature contribution to the free energy and a microstructure that resembles vesicles with an oil-swollen double layer is obtained [Figs. 6(e) and 7(e)]. The structure can also be described as an asymmetric sponge structure and is comparable to the multiple emulsion structures (with droplets inside droplets) observed on a larger scale. With increasingly negative H_0 the size of these objects grow and in the limiting case a symmetric swollen sponge structure with $\alpha = -\beta$ is formed [Figs. 6(f) and 7(f)]. It should be noted that this structure is similar to the swollen L3 structure discussed in Ref. 39. Comparing Figs. 4(a) and 4(b) we note again that a higher κ leads to a more narrow region of the diluted bicontinuous structure.

Figure 5 contains diagrams of how the microstructure changes with temperature for a system with fixed oil to surfactant ratio $\phi_o/\phi_s = 2.5$ and varying oil-droplet concentration ϕ_o . Again there are three characteristic structures: At low negative H_0 the water in oil structure is preferred, at high positive H_0 the oil in water structure is preferred, and in between there is a bicontinuous or diluted bicontinuous domain [i.e., $(\alpha, \beta) = (c, \infty)$, where the constant c depends on ϕ_o]. We observe that depending on the value of H_0 and κ one can obtain an increase or a decrease in the connectivity of the water domains with increasing oil contents contents. A similar behavior has been observed experimentally by Rushforth *et al.* in a series of conductivity measurements on ionic microemulsions.⁴⁰

Figure 6, which we have already referred to above, contains examples of some of the different structures the microemulsion system can take. The plots are 2D cross sections of the three-dimensional Gaussian random fields generated from the spectrum $\nu(k)$ with the level-cuts α and β which minimize the expression for the free energy of the microemulsion system [Eq. (5)]. Figure 7 contains projections of the full 3D field of the same structures as Fig. 6.

Figure 8 contains examples of the structure factors the different structures would give rise to in a scattering experiment with bulk contrast. Figure 8(a) shows the scattering from a bicontinuous structure formed in a system with equal volume fractions of water and oil. The scattering curves are

FIG. 5. A plot of the microstructure dependence on the oil contents ϕ_o and spontaneous curvature H_0 for a system with fixed $\phi_o/\phi_s = 2.5$. The microstructure is indicated for a number of different values of κ . (a) $\kappa = 1$ kT. (b) $\kappa = 2$ kT.

calculated for $\kappa = 1$ kT and $\kappa = 2$ kT. It is seen that the lower κ value gives rise to a more smooth scattering peak.

Figure 8(b) shows the scattering from the droplet structures formed in the same systems for higher $|H_0|$. For $\kappa = 2$ kT and with increasing $|H_0|$ the transition from the bicontinuous to the most monodisperse o/w structure takes place in a very narrow transition region. The scattering pattern from the droplet structure is shown. For $\kappa = 1$ kT the transition region is more extended. Gradually the large irregular shaped regions formed in the bicontinuous region become more and more monodisperse. The scattering patterns resulting from the droplet structures formed for two different values of H_0 are shown. An important feature of the droplet structure factors is that the scattering peak observed for the bicontinuous system disappears as the structure become more and more droplet-like. This was at first quite surprising

FIG. 6. The 2D cross sections of the direct space representation of microemulsions with different compositions and spontaneous curvatures H_0 as predicted by the Gaussian random field model. For the illustrations water is black and oil is white. The side lengths of the figures are $320 \pi \text{\AA} \approx 1000 \text{\AA}$. (a) Bicontinuous microemulsion, $\phi_w = \phi_o$, $\phi_s = 0.2$, $\kappa = 1 \text{ kT}$, $\bar{\kappa} = -0.5 \text{ kT}$, $H_0 = 0 \text{ 1/\AA}$. (b) Droplet microemulsion, $\phi_w = \phi_o$, $\phi_s = 0.2$, $\kappa = 1 \text{ kT}$, $\bar{\kappa} = -0.5 \text{ kT}$, $H_0 = 0.075 \text{ 1/\AA}$. (c) Droplet microemulsion, $\phi_o = 0.25$, $\phi_s = 0.1$, $\kappa = 1 \text{ kT}$, $\bar{\kappa} = -0.5 \text{ kT}$, large positive H_0 . (d) Diluted bicontinuous microemulsion, $\phi_o = 0.25$, $\phi_s = 0.1$, $\kappa = 1 \text{ kT}$, $\bar{\kappa} = -0.5 \text{ kT}$, $H_0 = 0 \text{ 1/\AA}$. (e) Swollen vesicles/asymmetric sponge, $\phi_o = 0.25$, $\phi_s = 0.1$, $\kappa = 1 \text{ kT}$, $\bar{\kappa} = -0.5 \text{ kT}$, $H_0 = -0.05 \text{ 1/\AA}$. (f) Sponge structure, $\phi_o = 0.25$, $\phi_s = 0.1$, $\kappa = 1 \text{ kT}$, $\bar{\kappa} = -0.5 \text{ kT}$, large negative H_0 .

to us because real droplet microemulsions at these compositions normally exhibit a strong scattering peak (see, e.g., Ref. 6). However, the scattering peak observed in real droplet microemulsions with bulk-contrast arises from droplet-droplet correlations which are usually due to steric or electrostatic interactions between the droplets.⁵ Such interactions are not contained in the Gaussian random field model. Furthermore, since the picture of the droplets is based on a Gaussian random field, once a droplet is observed, the possibility of observing another droplet is larger close to the droplet than far away from it. This implies that the spatial distribution of droplets in the model becomes different from that of real droplet microemulsions in such a way that no scattering peak is produced. We refer here to the peak occurring from the repulsive interaction between droplets. The po-

sition of this maximum is nearly identical for x-ray and neutron scattering. This has to be distinguished from the secondary maximum, mainly visible in systems of spherical objects with shell contrast. The position of this secondary maximum is related to the form factor and is independent of the concentration of surfactant.⁴¹ Since the droplets modeled in the present case have bulk contrast and are both non-spherical and relatively polydisperse this secondary maximum is not visible.

Figure 8(c) shows how the structure factor evolves with H_0 for a microemulsion with a volume fraction of oil, $\phi_o = 0.25$ and $\kappa = 1 \text{ kT}$. Again a clear scattering peak is observed for the bicontinuous structure. As for the $\phi_o = \phi_w$ case this scattering peak is gradually reduced as H_0 increases and smaller and more monodisperse droplets are formed. A similar trend is seen when H_0 decreases. The scattering peak is still present for the swollen vesicles/asymmetric sponge but vanishes gradually as the structure with decreasing H_0 approaches the symmetric sponge structure. Experiments show that real sponge structures also exhibit a scattering peak²⁰ which is due to film-film correlations arising from a relatively well-defined thickness of the surfactant bilayer. The thickness of the bilayer simulated by the Gaussian random field model apparently fluctuates more than that of real bilayers and the scattering peak disappears.

The interaction between adjacent interfaces in the two level-cut model is a contact repulsion, instead of having some spatial range. Broad peaks are that are observed in real systems where repulsive interaction is felt at distances typically 1–2 nm from the oil/water interface are not reproduced because of this deficiency in the free energy expression of the model.

Finally Fig. 8(d) shows how the structure factor of the bicontinuous/diluted bicontinuous structure evolves with the varying volume fraction of the oil for a system with fixed $\phi_s = 0.1$. We observe that the scattering peak gradually moves to higher and higher scattering angles as the volume fraction of the oil decreases. This is in good agreement with the smaller and smaller domain size.

B. Validity of the model

Israelachvili, Mitchell and Ninham suggested in the 1970s that the so-called surfactant packing parameter $p = v/al$ —where v is the volume, a is the area per head group and l is the length of the surfactant—is crucial for the shape of surfactant aggregates.^{42,43} When p decreases from one towards zero the surfactant aggregates will pass through a sequence of shapes starting with being locally flat as in bilayers or vesicles, to form cylindrical micelles for intermediary values of p and finally to form spherical micelles for low values of p .

For microemulsion systems the situation is more complicated as the structure also depends on the composition and the bending elastic constants κ and $\bar{\kappa}$ and in parallel to the Helfrich formalism, both the mean packing parameter p and a spontaneous packing parameter p_0 has to be taken into account. In the following discussion we will restrain ourselves to microemulsions with equal volume fractions of water and oil. For microemulsions p and p_0 are generally re-

FIG. 7. The same structures as in Fig. 6 but projections of the full 3D fields. Note that the side lengths of the cubes in (a) and (b) are only $160 \pi \text{\AA}$, i.e., half the side lengths of the squares in Fig. 6(a) and 6(b). The side lengths of (c)–(f) are $320 \pi \text{\AA}$ as in Figs. 6(c)–6(f).

FIG. 8. Predictions of the scattering functions for different microemulsion structures. (a) A bicontinuous structure with $\phi_w = \phi_o$, $\phi_s = 0.2$, plotted for $\kappa = 2$ kT and $\kappa = 1$ kT. (b) Droplet structure with $\phi_w = \phi_o$, $\phi_s = 0.2$, plotted for $\kappa = 2$ kT and $H_0 = 0.025$ 1/Å, for $\kappa = 1$ kT and $H_0 = 0.025$ 1/Å and for $\kappa = 1$ kT and $H_0 = 0.075$ 1/Å. (c) The different structures of a microemulsion with asymmetric composition $\phi_o = 0.25$ and $\phi_s = 0.1$ plotted for a symmetric sponge structure, large (negative) H_0 , a structure with swollen vesicles, $H_0 = -0.05$ 1/Å, a diluted bicontinuous, $H_0 = 0.0$ 1/Å and for a droplet structure, large (positive) H_0 . (d) Dilution series, bicontinuous and diluted bicontinuous structures, for fixed $\phi_s = 0.1$ and $H_0 = 0.0$ 1/Å. ϕ_o varies from 0.5 to 0.1.

placed by the mean and spontaneous curvatures H and H_0 using the equalities $p = 1 + Hl + Kl^2/3$ and $p_0 = 1 + H_0l$, where l is the surfactant length, but as a rule of thumb the sequence of preferred conformations still goes from locally flat structures such as bicontinuous microemulsions with zero mean curvature, through locally cylindrical or tubular structures, to structures with almost spherical droplets as $|H_0|$ increases from 0 to larger values. Structures which are locally cylindrical cannot be modeled within the Gaussian random field formalism. Instead, an increasing H_0 , drives the microemulsion from a bicontinuous structure with zero mean curvature, through a transition region with large irregular shaped and sized droplets to a structure with as spherical and monodisperse droplets as the model can produce.

For low values of H_0 where structures which minimize the mean curvature are favored we expect our model to give a more realistic description of the microemulsion structure than the models of the DOC-type^{17,18} which describe the structures as locally cylindrical or lamellar. But as H_0 increases to larger values and more curved structures are formed, the description of surface conformations by level-cuts of Gaussian random fields becomes increasingly inaccurate and we expect the DOC-type of models to give a better description of the microstructure of the microemulsions. For even larger values of H_0 where almost spherical, monodisperse droplet structures are formed,^{6,7,11} other factors than the physics of the surfactant interface start to play an impor-

tant role for the microemulsion microstructure and the Helfrich formalism is no longer the best choice for describing the microemulsion.

The structures of the microemulsions depend on several parameters and the value of H_0 for which we expect the model to be unrealistic depends totally on these parameters. For this reason it is impossible to give a general quantitative measure for the value of H_0 where the model breaks down. However, in a system with equal volume fractions of water and oil and $\bar{\kappa} = 0$ a "low value of H_0 " would refer to situations where $H_0^2 < \langle H^2 \rangle$. In practice, H_0 is imposed by salinity, temperature etc., while H is imposed by the volume fraction of the components.

C. Comparison to experimental data

In Fig. 9 a part of the temperature versus ϕ_s phase diagram for $\phi_w = \phi_o$ (the fish-cut) of the H₂O–octane–C₁₂E₅ system (reproduced from Ref. 4) have been plotted. The temperature scale normally used in this kind of phase diagrams is converted to a $\langle H_0 \rangle$ scale using the expression⁴

$$\langle H_0 \rangle = 1.22 \times 10^{-3} (\tilde{T} - T) \text{ Å}^{-1}, \quad (23)$$

where it is assumed that $\langle H_0 \rangle$ has the same temperature dependence as $\langle H \rangle$ around $\langle H \rangle = 0$. The bending moduli of the surfactant film in this particular system has been determined

FIG. 9. The temperature- ϕ_s phase diagram of the H_2O -octane- C_{12}E_5 system plotted together with the model predictions of the microstructure. The temperature scale of the original fish plot is converted to a H_0 -scale. μ_E denotes the microemulsion region. L_α denotes the lamellar region. 3 denotes the three-phase region.

to $\kappa=1.0$ kT and $\bar{\kappa}=-0.36$ kT.⁴⁴ The phase diagram has been plotted together with the diagram of the microstructure for a system with similar parameters.

It is seen that, according to the model, a bicontinuous structure is favored in the majority of the one-phase region. Only for very high ϕ_s a droplet-structure will be favored. This has the consequence that a phase inversion in the one-phase region, from o/w through bicontinuous to w/o, is only predicted for high ϕ_s in the water/octane/ C_{12}E_5 microemulsion. This is in very good agreement with scattering measurements of the temperature dependence in the one-phase region of the very similar D_2O -decane- C_{12}E_5 system.⁴⁵ The measurements demonstrate that $I(q)$ is basically unchanged over a range of temperatures covering the one-phase region.

Most of the scattering data from nonionic microemulsions published in the literature are measured on systems with bending moduli and sample compositions not too different from the water/octane/ C_{12}E_5 microemulsion system, where the bicontinuous structure is stable over a large range of temperatures in the one-phase region.⁴⁴ This probably explains why, to our knowledge, there are no reports in the literature showing experimental evidence for a temperature driven structural inversion from o/w through bicontinuous to w/o within the one-phase region, with an associated change in the structure factors measured by small-angle scattering. In order to measure such a transition it will, according to our predictions, be necessary to find a microemulsion system where it is possible to go to high ϕ_s in the one-phase region without getting in conflict with the lamellar region. Or to find a system with a sufficiently large (negative) $\bar{\kappa}$.

Extensive work have been done by Strey and co-workers to study the behavior of the microemulsion phase in the three-phase region (the body of the fish) and in the two-phase regions below and above the three-phase region.^{4,27,44} Upon changing the temperature the composition of the mi-

croemulsion phase changes from being more water-rich at low temperatures to be symmetric in water and oil at $\tilde{T}$ and to be more oil-rich at high temperatures. The so-called characteristic length scale, ξ_{TS} , of the microemulsion domain size has been determined as a function of temperature by fitting the small-angle scattering data with the Teubner-Strey expression.^{4,44} Below and above $\tilde{T}$, ξ_{TS} is relatively small, then ξ_{TS} increases and reaches a maximum at $\tilde{T}$.⁴ In terms of the position of the scattering peak this has the effect that the peak moves smoothly from high scattering vectors at low temperatures to a low scattering vector at $\tilde{T}$ and back to high scattering vectors at high temperatures. These measurements are in good agreement with the model. As seen from Figs. 3, 4 and 9 a bicontinuous or diluted bicontinuous structure is favored for sample parameters similar to the ones in the three-phase region and as seen from Fig. 8(d) the change in composition of the diluted bicontinuous sample will give rise to a scattering peak which moves to low scattering vectors as the sample composition approaches $\phi_o = \phi_w$. Freeze-fracture electron microscopy (FFEM) pictures of the microemulsion phase in the three-phase regions⁴ confirm that the oil domains at low temperatures and the water domains at high temperatures are relatively large and irregular shaped whereas a bicontinuous structure is observed for intermediate temperatures. This is in very good agreement with the bicontinuous/diluted bicontinuous structure predicted by our model. FFEM pictures of microemulsions in the one-phase region at temperatures close to $\tilde{T}$ and with fixed surfactant volume fraction and varying oil-water ratio confirm a similar picture with a microstructural change from bicontinuous to droplets as the sample composition changes from being symmetrical to be asymmetrical in water and oil.⁴⁶

An effective test of a structural model for microemulsions consists in comparing the scaled peak position, $P_s = 2\pi\phi_s/q_{\text{max}}l$, from experiments and model in a dilution plot,^{17,47} where l is the surfactant length. Figure 10 shows such a dilution plot. The scaled peak positions of the Gaussian random field model for bicontinuous and diluted bicontinuous microemulsions are plotted for $\kappa=1$ kT and $\kappa=2$ kT, respectively. For the calculations ϕ_s is kept fixed at 0.1 while ϕ_o and ϕ_w vary.

In models with random placement of the oil and water domains, the characteristic length scale ξ has the following dependence on the composition:⁴⁸

$$\xi = a \frac{\phi_o(1-\phi_o)}{\phi_s/l}, \quad (24)$$

where a is a numerical constant. The constant a depends weakly on the particular model of the microemulsion structure. Notice that this formula can be obtained from geometrical arguments and need not include any statistical mechanics.

The scattering peak and the corresponding characteristic length scale, ξ , have been analyzed for a number of microemulsions in the bicontinuous and diluted bicontinuous domain (see, e.g., Refs. 27,49). Fitting data with the Teubner-Strey expression for scattering intensity provides the value of the correlation length ξ_{TS} for a particular microemulsion.²⁷ If this length is accepted as the characteristic length scale ξ , the

FIG. 10. Scaled peak positions from microemulsions plotted as a function of the volume fraction of the apolar phase, ϕ_o . Full line: Gaussian random field model of diluted bicontinuous microemulsions for $\kappa=1$ kT. Dashed line: the same model for $\kappa=2$ kT. Dotted line: spheres interacting via a hard spheres potential calculated in the Percus–Yevick approximation. Dash-dotted line: curve fitted to experimental results in Ref. 49. *: average scaled peak position for a number of nonionic microemulsions according to Ref. 27. $\square$: microemulsions with SHBS (Ref. 49). $\diamond$: microemulsions with DTAB (Ref. 49). $\triangle$: microemulsions with SDS (Ref. 49).

experiments then suggest $\xi \approx \pi/q_{\max}$ as in Ref. 49. The scaled peak position is then given as $P_s \approx 2a\phi_o(1-\phi_o)$. The empirical law $\xi \approx \pi/q_{\max}$ appears natural for symmetrical microemulsion compositions where periodicity is of the order of twice the domain size. However, it does not appear natural for an imperfect distribution of droplets on a lattice of size ξ , where one normally would expect a scattering peak at $q_{\max} \approx 2\pi/\xi$. In Fig. 10 we find that the present model predicts a curve for the scaled peak positions which in its functional form is very similar to the random placement expression (24). This similarity was already noted by Pieruschka³² who compared an approximate calculation valid in the scaling regime to the model of Ref. 14 which predicts a behavior of ξ similar to (24). The empirical identification $\xi = \pi/q_{\max}$ is no longer necessary in the present model, since both ξ (or ξ_{TS}) and $q_{\max}$ are evaluated from the elastic constants.

Abillon *et al.*⁴⁹ has found a good qualitative agreement between Eq. (24) with $a=6$ and the characteristic length scales determined from peak positions for a number of microemulsions with different water to oil ratios and different ionic surfactants [respectively, dodecyl trimethyl ammonium bromide (DTAB), sodium dodecyl sulphate (SDS) and sodium hexadecyl benzene sulphonate (SHBS)].⁵⁰ The measurements of the peak positions are performed on microemulsions in the three-phase region and in the 2-phase region below and above the three-phase region. Instead of passing through these phases by varying the temperature, the authors have varied the salinity of the samples. The experimentally determined characteristic sizes are digitized from Fig. 3 in

Ref. 49, transformed into scaled peak positions and plotted in Fig. 10 together with Eq. (24) with $a=6$.

In a study of microemulsions with equal volume fractions of water and oil and different types of the nonionic C_iE_j surfactants (alkyl-ethylene-oxides) Sottman *et al.*²⁷ has determined the constant a to be 7.16 on average. The peak position corresponding to this value is also plotted in Fig. 10.

The experimental point corresponding to the peak positions from microemulsions formed in systems with a different nonionic surfactant falls well on the top of the Gaussian Random field prediction for $\kappa=1$ kT. An average value of $\kappa=1$ kT for the nonionic microemulsions is in good agreement with the experimental findings of Sottmann *et al.*⁴⁴

The experimental points for the ionic microemulsion fall in a quite wide band around Eq. (24). The experimental points coming from microemulsions formed with DTAB are in better agreement with the peak positions of the Gaussian random field model for $\kappa=2$ kT than with Eq. (24). Both the series of experimental points coming from microemulsions formed with SDS and with SHBS are asymmetrically distributed around $\phi_o=0.5$. This could be explained by a variation in the value for κ due to the variation in the salinity of the samples.⁵¹ The plot indicates that the bending rigidity κ is generally larger in the ionic microemulsions than in the nonionic microemulsions. This is in good agreement with the theoretical predictions of Daicic *et al.*⁵¹ A bending rigidity close to $\kappa=2$ kT disagrees with the experimental findings of Ref. 49. These authors have, using ellipsometry, determined the value of κ to be from 0.55 to 1 kT, dependent on the surfactant type. However, as Gradziński has pointed out recently,⁵² experimentally determined values for κ and $\bar{\kappa}$ still vary largely from one study to another.

The scaled peak positions of the structure factor of oil droplets in water formed at compositions similar to the ones used above and interacting via a hard-spheres potential calculated in the Percus–Yevick approximation⁵ are also plotted. It is interesting to note how well these peak positions compare to the experimental observations by Abillon *et al.*⁴⁹ for $\phi_o < 0.5$. As both the water to oil ratios and the amount of surfactant per unit volume are similar in the two types of calculations the models will also be similar in the Porod limits. This has the consequence that it, in this concentration range, is very difficult to distinguish a droplet structure from a bicontinuous/diluted bicontinuous structure if the scattering data are only analyzed in terms of the peak position and Porod limit.

VI. CONCLUSION

We have demonstrated that the Gaussian random field formalism together with the Helfrich Hamiltonian can be used to formulate a model for microemulsion systems with nonzero spontaneous curvature and asymmetric composition. In the model it is possible to drive a microemulsion with fixed composition from a w/o structure through a bicontinuous structure to an o/w structure by changing the spontaneous curvature H_0 .

By comparing the phase diagrams predicted by the Gaussian random field model with experimentally determined phase diagrams it is seen that for typical nonionic

microemulsions the bicontinuous or diluted bicontinuous structure is favored in a very large part of the one-phase region. This suggests why a full phase inversion of a one-phase system with fixed composition has, to our knowledge, never been measured for nonionic microemulsion systems.

The direct space microemulsion structures predicted by the model agree well with freeze fracture microscopy pictures of the microemulsion phase in the three-phase region. This suggests that the microemulsion in the three-phase region is of the bicontinuous or diluted bicontinuous kind. Plots of the position of the modeled scattering peak as a function of concentration are also in good agreement with corresponding curves determined for experimental systems.

The model is based on the Helfrich Hamiltonian and the Gaussian random field formalism. This means that we expect the model to give a good structural description for structures with low mean curvature. Film–film and droplet–droplet interactions which become significant in, respectively, sponge structures and droplet structures are not included in the Helfrich formalism. Furthermore, locally cylindrical structures cannot be described within the Gaussian random field formalism. For these structures we expect other types of models to give more realistic pictures.

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