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Measurement of the Gaussian curvature of the surfactant film in an isometric bicontinuous one-phase microemulsion

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Small-angle x-ray and neutron-scattering (SAXS and SANS) measurements are made of a three-component isometric microemulsion, $C_{10}E_4$-D_2O-octane, in the one-phase channel around the hydrophile-lipophile balance temperature of the system. A previous SANS contrast variation experiment indicated that the microstructure of this isometric microemulsion is bicontinuous in water and oil, with the surfactant film having a zero mean curvature. We analyze the SAXS and SANS data taken with a bulk contrast in terms of a modified Berk's random wave model. We choose a spectral function which is an inverse sixth-order polynomial, with three parameters a, b, and c, as introduced by Lee and Chen earlier. This three-parameter spectral function is then used in conjunction with Cahn's clipping scheme to obtain the Debye correlation function for the microemulsion. The analysis gives an excellent agreement with the intensity data in an absolute scale. We then use the three parameters so obtained to calculate the mean Gaussian curvature of the surfactant film. We also show a three-dimensional-reconstructed morphology of the microemulsion. [S1063-651X(96)01712-6]

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I. INTRODUCTION

Recently, Lee and Chen [1] proposed a contrast variation method in conjunction with the small-angle neutron-scattering (SANS) technique to measure both the mean and Gaussian curvatures of surfactant film in a bicontinuous three-component microemulsion directly. The method consists of accurate, independent measurements of three interfacial areas: the water surfactant, the oil surfactant and the midplane of the surfactant film. From these three areas and the effective surfactant film thickness, including the degree of water and oil penetration into the film, they showed that, in principle, one can calculate both the mean and Gaussian curvatures.

For a determination of both the magnitude and sign of the mean curvature, they were able to demonstrate the feasibility of the method by showing the linear relationship between the curvature and the temperature deviation from the hydrophile-lipophile balance (HLB) temperature within the one-phase channel. In essence, they succeeded in directly confirming the inversion of the curvature from an oil-in-water type (negative) at low temperatures to a water-in-oil (positive) type at high temperatures. The degree of accuracy in the areas and the surfactant film thickness determinations allowed them to detect the sign and magnitude of the mean curvature $\langle H \rangle$ at the lowest limit of 1×10^{-3} Å^{-1}. However the overall accuracy of the measurements was not sufficient to determine the sign or magnitude of the Gaussian curvature. This *limitation* is related to an intrinsic *inaccuracy* of the SANS method in the determination of the interfacial areas, and in particular to the degrees of solvent penetration into the surfactant film. It is, in the author's judgement, impossible to determine the Gaussian curvature using this method with the present state-of-the-art SANS technique.

However, there is an alternative route to calculate the Gaussian curvature through the analysis of the SANS or small-angle x-ray (SAXS) data. This is through the use of the random wave model of Berk [2,3]. In the Berk model, one considers the microstructure of a bicontinuous microemulsion to be a result of a microphase separation of water and oil. From the SANS scattering length density contrast point of view, if one deuterates water, the hydrophobic and hydrophilic portions of the surfactant molecules are respectively included as part of the oil and part of the water. The boundary between the two regions of different scattering length densities is then located somewhere within the surfactant film. Bicontinuous microemulsions can be considered as effectively microphase-separated liquids, because numerous SANS and SAXS experiments [4,5], together with freeze fracture electron micrographs [6], revealed that there were interpenetrating mesoscopic domains of nearly pure water and pure oil existing in these liquids. The morphology of a bicontinuous microemulsion is in many ways similar to that of a phase-separated binary alloy observed in a late stage of spinodal decomposition [7].

Cahn in 1965 proposed [8] a scheme for generating a three-dimensional morphology of a phase-separated A-B alloy by clipping a Gaussian random field generated by superimposing many isotropically propagating sinusoidal waves with random phases. The Gaussian random field can be normalized in such a way that it fluctuates continuously between −1 and +1. One then realizes the two-phase morphology by clipping the continuous random process, namely, by assigning, say, 0 to all negative signals representing A, and +1 to all positive signals representing B. In this scheme, the essential feature of the morphology depends only on the spectral function, which is the three-dimensional Fourier transform of the two-point correlation function of the Gaussian random field. The spectral function gives the distribution of the magnitudes of the propagating wave vectors of the sinusoidal waves.

Berk in 1987 further developed the idea of Cahn mathematically for the purpose of analyzing scattering data. In particular, he derived an important relation connecting the two-point correlation function and the Debye correlation function. In his original paper, however, Berk discussed only a spectral function which is a δ function. This resulted in generating a morphology which is only partially disordered. Chen, Chang, and Strey [4] later pointed out that a broader but peaked spectral function is necessary to generate a more disordered morphology which will reproduce SANS intensity distributions. In particular, the spectral function should be chosen such that it has the second moment to ensure a finite interfacial area per unit volume. This point can be easily appreciated by the following argument.

II. THEORETICAL BACKGROUND

The intensity distribution of SAXS and SANS from an isotropic two-component porous material can be calculated generally from a Debye correlation function $\Gamma(r)$ by the following formula [9]:

$$I(Q)=\langle \eta^2\rangle \int_0^\infty dr\, 4\pi r^2 j_0(Qr)\Gamma(r), \tag{1}$$

where $\langle \eta^2\rangle=\varphi_1\varphi_2(\rho_1-\rho_2)^2$, φ_1 and φ_2 refer to the volume fractions of components 1 and 2, and ρ_1 and ρ_2 refer to the corresponding scattering length densities. In addition to the two physical boundary conditions—that the Debye correlation function is normalized to unity at the origin and that it should go to zero at infinity—the most important property of the correlation function is that it has a linear term in the small r expansion of the form

$$\Gamma(r\rightarrow 0)=1-\frac{1}{4\varphi_1\varphi_2}\frac{S}{V}r+\cdots , \tag{2}$$

where S/V is the total interfacial area per unit volume.

In the random wave model of Berk [2], a Gaussian random field $\psi(\mathbf{r})$ is constructed by superposition of a large number of cosine waves:

$$\psi(\mathbf{r})=\frac{\sqrt{2}}{\sqrt{N}}\sum_{i=1}^{N}\cos(\mathbf{k}_i\cdot\mathbf{r}+\varphi_i), \tag{3}$$

where directions of the wave vector $\mathbf{k}_i$ are sampled isotropically over a unit sphere, and the phase φ_i is distributed randomly over the interval $(0,2\pi)$. The statistical properties of a Gaussian random process is completely characterized by giving its two-point correlation function.

We define a two-point correlation function $g(|\mathbf{r}_1-\mathbf{r}_2|)=\langle\psi(\mathbf{r}_1)\psi(\mathbf{r}_2)\rangle$ and the associated spectral function $f(k)$ by a Fourier transform relation

$$g(|\mathbf{r}_1-\mathbf{r}_2|)=\int_0^\infty 4\pi k^2 j_0(k|\mathbf{r}_1-\mathbf{r}_2|)f(k)dk. \tag{4}$$

This continuous random process is then clipped and transformed into a two-state discrete random process. Then the Debye correlation function for this discrete random process for the isometric case, namely, $\varphi_1=\varphi_2$, is given exactly as [2]

$$\Gamma(r)=\frac{2}{\pi}\sin^{-1}g(r). \tag{5}$$

This remarkably simple result comes about because one clips the Gaussian random field given in Eq. (3).

From the relation in Eq. (4), one has a small-r expansion of $g(r)$ of the form

$$\begin{aligned} g(r)&=\int_0^\infty 4\pi k^2[1-\tfrac{1}{6}k^2r^2+\cdots]f(k)dk\\ &=1-\tfrac{1}{6}\langle k^2\rangle r^2+\cdots , \end{aligned} \tag{6}$$

where we used the normalization condition $g(0)=1$. Note that this expansion has a quadratic dependence on r in the second term. Use the result of Eq. (6) in Eq. (5), we obtain a correct expansion

$$\Gamma(r\rightarrow 0)=1-\frac{2}{\pi\sqrt{3}}(\langle k^2\rangle)^{1/2}r+\cdots . \tag{7}$$

Comparing this with Eq. (2), we arrive at the useful relation we set out to derive:

$$\frac{S}{V}=\frac{2}{\pi\sqrt{3}}(\langle k^2\rangle)^{1/2}. \tag{8}$$

We next consider a random surface generated by the level set

$$\psi(\mathbf{r})=\psi(x,y,z)=0. \tag{9}$$

Teubner [10] has proved a remarkably elegant theorem that for this random surface the mean curvature is zero, and that the Gaussian curvature $\langle K\rangle$ is negative and given by

$$\langle K\rangle=-\tfrac{1}{6}\langle k^2\rangle=-\frac{\pi^2}{8}\left(\frac{S}{V}\right)^2. \tag{10}$$

Since for an isometric, bicontinuous microemulsion the level surface defined by Eq. (9) is approximately the midplane of the surfactant monolayer in a bulk contrast experiment, the Gaussian curvature of the surfactant monolayer can be computed once the spectral function can be found. The choice of the spectral function can be based on a criterion such that when it is substituted into Eqs. (4), (5), and (1), it would give an intensity distribution which agrees with SANS or SAXS data.

A suitable form of the spectral function was proposed by Lee and Chen [11], which is an inverse sixth-order polynomial in k, and which contains three parameters a, b, and c. It is

$$f(k)=\frac{8\pi b[a^2+(b+c)^2]/(2\pi)^3}{(k^2+c^2)[k^4-2(a^2-b^2)k^2+(a^2+b^2)^2]}. \tag{11}$$

This form is an extension of the well-known structure factor proposed by Teubner and Strey [12] for bicontinuous microemulsions, and which possesses a definite second moment. The corresponding two-point correlation function can also be written down analytically, and has a quadratic term in the small-r expansion:

$$\begin{aligned} g(r) &= \frac{1}{a^2+(c-b)^2}\left\{(a^2+c^2-b^2)\,\frac{\sin(ar)}{ar}\,e^{-br} \right. \\ &\quad \left. +2b\,\frac{e^{-cr}-e^{-br}\cos(ar)}{r}\right\} \\ &= 1-\frac{1}{6}\left\{\frac{(a^2+b^2)^2+c^2(a-b)(a+3b)}{a^2+(c-b)^2}\right\}r^2+\cdots \\ &= 1-\frac{1}{6}\langle k^2\rangle r^2+\cdots \\ &= 1\langle K\rangle r^2+\cdots . \end{aligned} \tag{12}$$

The first two parameters a and b have their approximate correspondences in the Teubner-Strey (TS) theory [4]. In the TS theory, the Debye correlation function is given by $\Gamma_{\mathrm{TS}}(r)=e^{-r/\xi}[\sin(2\pi r/d)/(2\pi r/d)]$. The correspondences are $a\approx 2\pi/d$ and $b=1/\xi$, where d is the interdomain (water-water or oil-oil) repeat distance, and ξ the coherence length of the local order [4]. The parameter c controls the large-Q behavior of the scattering intensity distribution, the existence of which is essential for the good agreement of the theory and experiment at large Q, as will be seen below.

From Eq. (12), we finally identify the central result of this paper:

$$\langle K\rangle = -\frac{1}{6}\left\{\frac{(a^2+b^2)^2+c^2(a-b)(a+3b)}{a^2+(c-b)^2}\right\}. \tag{13}$$

III. EXPERIMENTS

SANS experiments for $C_{10}E_4$-D_2O-octane microemulsion system were carried out both at the NSF 30-m SANS instrument in the Cold Neutron Research Facility at NIST, and, the H9B Biology Low Angle Diffractometer at Brookhaven High Flux Beam Reactor. We used $\lambda=6$ Å, $\Delta\lambda/\lambda=15\%$ at the former, and $\lambda=5$ Å, $\Delta\lambda/\lambda=10\%$ at the latter. The Q range covered in the measurements was from 0.004 to 0.35 Å^{-1}. Detailed descriptions of the experiments were given in Ref. [1].

SAXS measurements were conducted with an apparatus having an 18-kW rotating-anode x-ray generator as the source. A graphite monochromator was used to select Cu $K\alpha$ radiation at $\lambda=1.542$ Å. The sample-to-detector distance was 198.8 cm, and this path was evacuated. A one-dimensional position sensitive proportional counter was used as a detector. A Q range of 0.009–0.2 Å^{-1} was covered. Measured intensities were corrected for absorption, sample thickness, slit height, and slit width smearings, and the thermal diffuse scattering arising from density fluctuations. SAXS profiles were taken over a temperature range from 19.5 to 24.5 °C, with an increment of 0.5 °C.

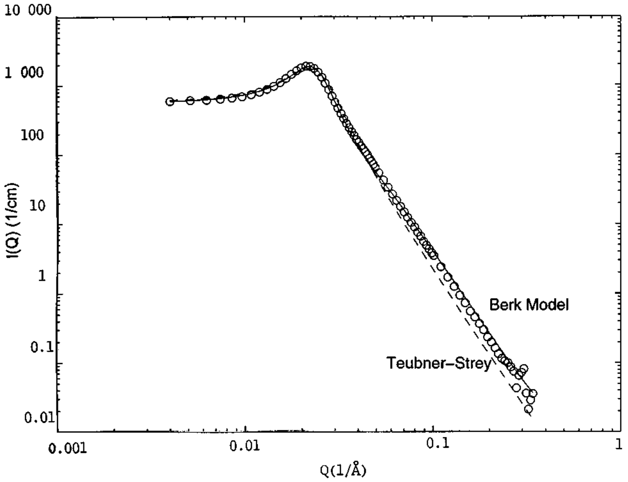

FIG. 1. Normalized SANS scattering intensity, or the differential scattering cross section per unit volume, of an isometric one-phase bicontinuous microemulsion composed of $C_{10}E_4$-D_2O-octane. Volume fractions of the components are $\varphi_s=0.132$ and $\varphi_w=\varphi_0=0.434$. It is at the hydrophile-lipophile-balance temperature (22 °C), near the fish tail of the one-phase channel. Open circles are the SANS data, and solid and dashed lines, respectively, are the fits using the modified Berk model [11] and the Teubner-Strey model [12].

IV. DISCUSSION OF THE RESULTS

In this paper, we only report SANS and SAXS results for a microemulsion, $C_{10}E_4$-D_2O-octane, having a composition $\phi_s=0.132$ and $\varphi_w=\varphi_0=0.434$, in a temperature range where the sample is in one phase. This corresponds to phase points near the so-called ‘‘fish tail’’ of the one-phase channel. At this surfactant volume fraction, the one-phase region spans a gap of 5.7 °C. Within this gap, our previous SANS investigation [1] indicated that the mean curvature is $\langle H\rangle=0\pm0.0025$ Å^{-1}, effectively zero.

Figure 1 shows a SANS intensity distribution taken at the HLB temperature $T_b=22$ °C of the sample. The intensity is given in unit of a differential cross section per unit sample volume (cm^{-1}) denoted here by $S(Q)$, which we called $I(Q)$ in Eq. (1). Open circles are the data points, and the solid line is the fit using the modified Berk (MB) model described above. For the sake of comparison, we also show a best fit, using the two-length-scale TS model, by a dashed line. It can be seen that the MB model fits the data in the high-Q region much better than the TS model. The best-fit MB parameters are

$$a=2.30\times10^{-2}\ \text{Å}^{-1},\quad b=6.01\times10^{-3}\ \text{Å}^{-1},$$

$$c=7.54\times10^{-1}\ \text{Å}^{-1},$$

from which one obtains, with the help of Eq. (13), $\langle K\rangle=-1.34\times10^{-4}$ Å^{-2}. This is the mean Gaussian curvature of the effective oil-water interface, which is an interface running somewhere through the middle of the surfactant monolayer located at the oil-water interface. Since, in Eq. (13), the numerical value of the second term in the numerator dominates that of the first, and the numerical value of param-

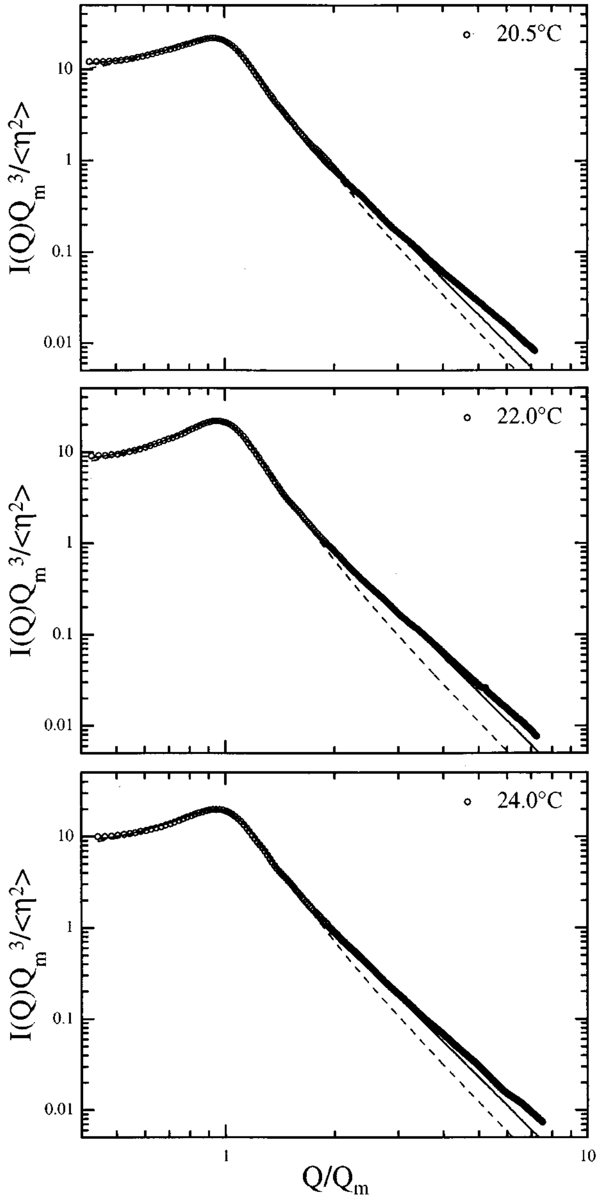

FIG. 2. Normalized SAXS intensities of the same microemulsion as described in Fig. 1 taken at three temperatures, 20.5, 22.0, and 24.0 °C. The intensity is normalized to a nondimensional quantity $I(Q)Q_m^3/\langle\eta^2\rangle$, where Q_m is the magnitude of the Q vector corresponding to the maximum intensity, and $\langle\eta^2\rangle$ is the invariant given in Eq. (1). Open circles are the SAXS data, and solid and dashed lines, respectively, are the fits using the modified Berk model [11] and the Teubner-Strey model [12].

eter c is the largest of the three, the resultant value of the Gaussian curvature is insensitive to the small variation of c.

We also checked second equality in Eq. (10). In our previous interface contrast measurement at a similar temperature, we obtained $(S/V)=0.0095\pm0.0001$ Å^{-1}. From this value we use Eq. (10) to calculate $\langle K\rangle=-1.11\times10^{-4}$ Å^{-2}. As will be seen in the following, this value agrees with that by SAXS.

We next turn to analyses of SAXS data. Our measurements cover a temperature range from 19.5 to 24.5 °C in steps of 0.5 °C. Figure 2 shows three typical normalized intensities at 20.5, 22.0, and 24.0 °C. The intensity is normalized by the invariant $\langle\eta^2\rangle$ and multiplied by a cube of Q_m, the Q position of the maximum intensity. This dimensionless quantity is then plotted as a function of a dimensionless coordinate Q/Q_m. This plot would be universal with respect to a variation of environmental factors such as temperature, if the electron-density fluctuation contains only one length scale. The figures show that this is approximately so, indicating that there are hidden relations between the three length scales $1/a$, $1/b$, and $1/c$. The open circles are the experimental data, the solid lines the MB fits, and the dashed lines the TS fits. We again note that the MB theory is much superior to TS theory at large Q, indicating the importance of the clipping performed in the former theory. A possible explanation of the excess scattering at large Q can be the diffuse electron-density distribution at the oil-water interface due to the existence of the surfactant monolayer. In this respect, it should be commented that the scattering length density distributions seen by neutrons and x-rays is not quite the same in a bicontinuous microemulsion. The three parameters extracted from the fits are listed in Table I. It can be seen from the table that, at 22 °C, the three parameters extracted from SAXS and SANS, previously given, are not exactly the same. First of all, since SANS and SAXS experiments were carried out at two widely separated times, one should not expect the phase diagrams of samples for the two respective experiments to be identical. Even allowing for this difficulty, there are still discrepancies which can be traced to the above mentioned experimental uncertainties. The a and b parameters from the two experiments are in reasonable agreement. The parameter c has a large discrepancy due to the difference in large-Q behavior of intensities from SANS and SAXS. Fortunately, the Gaussian curvature is rather insensitive to the values of c, provided that it is large enough. We can thus use SAXS data to look at the temperature dependence of the Gaussian curvature.

Figure 3 shows plots of two quantities as a function of temperature. The open circles represent the Gaussian curvatures, their numerical values referring to the left-hand-side ordinate scale. The solid circles represent the ‘‘disorder parameter’’ b/a [13], referring to the right-hand-side ordinate scale. The disorder parameter, expressed in the context of the TS theory, is $(1/2\pi)(d/\xi)$. Since d is the repeat distance of the domains, and ξ is the coherent length of the local order, if this ratio is large, the local order is short ranged compared to the periodicity of the order. The graph shows that while the disorder parameter is at a minimum at the HLB temperature, the Gaussian curvature has a peculiar variation with the temperature. It shows the most negative value at 20.5 °C and the least negative value at 23.5 °C, while it takes an average value -1.12×10^{-4} Å^{-2} at the HLB temperature. But considering the fact that the variation of the Gaussian curvature over this temperature range is no more than 6%, and the difference between the SANS and SAXS values at the HLB temperature is as much as 17%, one may consider this peculiar variation within the experimental uncertainty. In any event, one can safely take the Gaussian curvature at the HLB temperature to have an experimental value $-(1.23\pm0.11)\times10^{-4}$ Å^{-2}.

TABLE I. Three parameters a, b, and c extracted from the fits.

Temperature (°C)	$a\times10^2$ (Å^{-1})	$b\times10^3$ (Å^{-1})	$c\times10^2$ (Å^{-1})	b/a	$\langle K\rangle\times10^4$ (Å^{-2})
19.5	1.98	6.16	3.14	0.311	−1.14
20.0	2.04	5.98	2.65	0.293	−1.18
20.5	2.10	5.77	2.65	0.275	−1.21
21.0	2.11	5.54	2.72	0.263	−1.20
21.5	2.10	5.37	3.27	0.256	−1.18
22.0	2.07	5.26	4.53	0.254	−1.12
22.5	2.06	5.17	4.94	0.251	−1.10
23.0	2.05	5.19	5.09	0.252	−1.09
23.5	2.03	5.38	5.94	0.265	−1.06
24.0	2.00	5.65	4.00	0.282	−1.09
24.5	2.02	6.11	3.75	0.303	−1.15

We may now consider the implication of this numerical value of the Gaussian curvature. Since at HLB temperature, the mean curvature is zero, we have $\langle 1/R_1\rangle = -\langle 1/R_2\rangle$. Hence

$$\langle K\rangle = \left\langle \frac{1}{R_1R_2}\right\rangle \approx -\left\langle \frac{1}{R_1}\right\rangle \left\langle \frac{1}{R_2}\right\rangle = -\left\langle \frac{1}{R_1}\right\rangle^2 = -1.23\times10^{-4}\ \text{Å}^{-2}$$

From this, we may estimate a mean domain size, if it were spherical, of 180 Å. On the other hand, we know the repeat distant of two similar domains, $d=2\pi/a=2\pi/2.07\times10^{-2}=304$ Å. Because the water and oil domains are equivalent in an isometric microemulsion, we can take the mean domain size to be 152 Å. The fact that this latter value is 18% smaller than the former indicates that the domains are in fact highly nonspherical, which is consistent with a locally saddle configuration implied by the negative Gaussian curvature.

With the spectral function completely determined from SANS and SAXS experiments, we can then plot out the three-dimensional picture of the level surface. This is done using Eq. (9), which defines the level surface, in conjunction with the definition Eq. (3) and the spectral distribution function Eq. (11) [4]. The surface so obtained is unique in a statistical sense, i.e., *equivalent surfaces generated by different sampling of random k-vectors satisfying the fitted spectral function are statistically equivalent*. This surface represents the effective oil-water interface, or the mid-plane of the surfactant monolayer. Figure 4 is such a three-dimensional rendering of the microemulsion at the HLB temperature. In the figure, the edge of the cube is 600 Å. We see that the water and oil domains are intertwined with each other, and that the geometry of the surfactant sheet is locally in a saddle

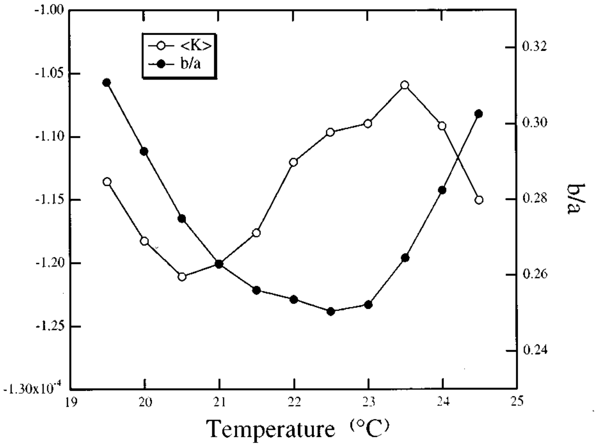

FIG. 3. Calculated average Gaussian curvatures and the disorder parameters (defined in the text) as functions of temperature, using the three parameters a, b, and c extracted from SAXS data.

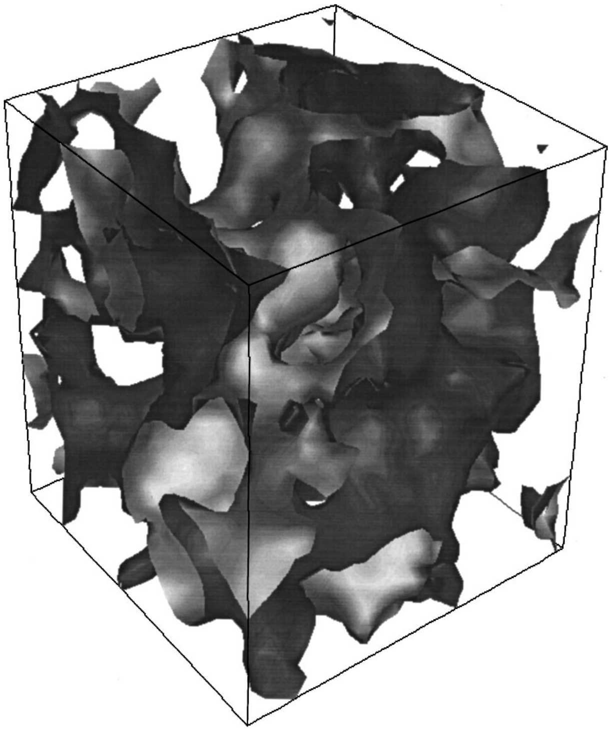

FIG. 4. A three-dimensional morphology of the isometric bicontinuous microemulsion at the HLB temperature exhibited through a $\psi(x,y,z)=0$ level surface generated by using the spectral function Eq. (11) in conjunction with three parameters $a=2.30\times10^{-2}$ Å^{-1}, $b=6.01\times10^{-3}$ Å^{-1}, and $c=7.54\times10^{-1}$ Å^{-1}. The cubic box has a dimension $600\times600\times600$ Å^3.

configuration. An interdomain distance of 304 Å is also consistent with the picture.

V. CONCLUSION

We propose a practical scheme for extracting the Gaussian curvature of the water-oil interface from SANS and SAXS intensities in a bulk contrast. This method is at present feasible only for isometric bicontinuous microemulsions, where the mean curvature is approximately zero. We show the three-dimensional morphology of an isometric, bicontinuous microemulsion which is completely consistent with SANS and SAXS data. We are looking forward to extending this method to the case of nonisometric microemulsions in the near future.

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