



ELSEVIER

Physica A 304 (2002) 85–92

PHYSICA A

www.elsevier.com/locate/physa

# The existence of three length scales and their relation to the interfacial curvatures in bicontinuous microemulsions

S.M. Choi<sup>a,1</sup>, S.H. Chen<sup>a</sup>, T. Sottmann<sup>b</sup>, R. Strey<sup>b,\*</sup>

<sup>a</sup>Department of Nuclear Engineering, 24-209, MIT, Cambridge, MA 02139, USA

<sup>b</sup>Institut für Physikalische Chemie, Universität Köln, D-50939 Köln, Germany

---

## Abstract

A clipped random wave model (CRW) with an inverse 8th-order polynomial spectral density function (SDF) is proposed for the analysis of small-angle neutron scattering intensities from isometric bicontinuous microemulsions. The spectral density function contains three basic length scales which are essential in describing mesoscopic scale structures of porous materials. The scattering intensities from ionic and non-ionic bicontinuous microemulsions were analyzed using the model to obtain the average Gaussian and square mean curvatures, the specific interfacial area and the bending rigidity constant. © 2002 Published by Elsevier Science B.V.

PACS: 62.10.-m; 82.70.Kj

Keywords: Microemulsions; Scattering

---

Mixtures of oil, water, and surfactant exhibit a rich variety of phases with corresponding characteristic internal structures. The amphiphilic nature of surfactant molecules allow themselves to form interfacial monolayers between oil and water domains, making the originally immiscible two bulk liquids soluble to each other. Depending on the composition, temperature and salinity, these three component solutions exhibit various conformation of interfaces with a mesoscopic length scale of the order of 100 Å. Therefore, the study of the microstructure of a microemulsion is to understand the

---

\* Corresponding author.

<sup>1</sup> Present address: Department of Nuclear Engineering, Korea Advanced Institute of Science and Technology, 373-1 Kusong-dong, Yusong-gu, Taejeon, 305-701, South Korea.

distribution of two-dimensional interfaces in three-dimensional space. From topological point of view, the local shape of an interface can be completely described by a Gaussian curvature,  $K$ , and a mean curvature,  $H$ , which are defined as  $K = 1/(R_1R_2)$  and  $H = 1/2(1/R_1 + 1/R_2)$ ,  $R_1$  and  $R_2$  being the two principal radii of curvatures. The overall structure of the interface can be described in terms of the average Gaussian curvature,  $\langle K \rangle$ , and the average mean curvature,  $\langle H \rangle$ , which are averages over the whole interface. These interfacial curvatures are the important quantities defining the bending free energy of the interface. In case  $\langle H \rangle = 0$ , the higher order curvature  $\langle H^2 \rangle$  becomes important. This average square mean curvature is related to the fluctuation of the interface which can be used to define the persistence length of the interface. Knowledge of these average interfacial curvatures allow us to describe the morphology of a porous medium in a quantitative way as well as to extract the physical property such as the bending rigidity constant. In this letter, we present the measurements of the average Gaussian and square mean curvatures, the specific interfacial area (SIA), and the bending rigidity constant in bicontinuous microemulsions by analyzing SANS data with the CRW model. The SDF used in the CRW model contains three basic length scales, the inter-domain distance (water to water or oil to oil)  $d$ , the coherence length  $\xi$  of the local domain order, and the surface roughness parameter  $\delta$ . SANS experiments were performed for both the ionic and non-ionic bicontinuous microemulsions.

For ionic microemulsions, we used an ionic surfactant AOT (sodium-bis-ethylhexylsulfho-succinate),  $D_2O$  and H-decane system. To realize a bicontinuous structure in this system, small amount of salt has to be added [1]. Therefore, the three parameters which control the phase behavior of microemulsions are temperature, salinity, and composition. In this study we choose a phase diagram in the salinity–surfactant volume fraction plane at isometric composition (equal volume fractions of aqueous and oily components) at a fixed temperature close to HLB (hydrophilic–lipophilic balanced) temperature. The phase diagram of AOT/ $D_2O$ (NaCl)/H-decane system at a temperature  $45^\circ C$  is shown in Fig. 1a. The one-phase and three-phase regions are where the bicontinuous microemulsions are formed. To perform the bulk contrast SANS experiments, we match the scattering length density of decane (a mixture of H-decane, 94.99 wt%, and D-decane, 5.01 wt%) with that of hydrocarbon tail of AOT. The volume fraction of  $D_2O$  plus head group of AOT was maintained at 0.5 for all surfactant volume fractions, i.e.,  $\varphi_1 = \varphi_{D_2O} + \beta\varphi_s = 0.5$ , where  $\beta$  ( $=0.1064$ ) is the volume fraction of head group in AOT. Therefore, from the neutron scattering point of view, the three component ionic microemulsion under study was reduced to an isometric ( $\varphi_1 = \varphi_2 = 0.5$ ) binary system. SANS measurements were performed at  $45^\circ C$  for six different points in the one-phase region close to lamellar phase boundary, which are indicated as crosses in the phase diagram. Since the average mean curvature of lamellar phase is known to be zero, the average mean curvature at the points close to lamellar phase are expected to be very close to zero.

For non-ionic microemulsions, we used 18 different  $C_iE_j/D_2O/n$ -alkane systems [2]. The phase behavior of these systems have been thoroughly discussed [3]. In all samples, volume fractions of water and oil were maintained equal. Since volume fractions of head group and tail group of non-ionic surfactants under study are approximately

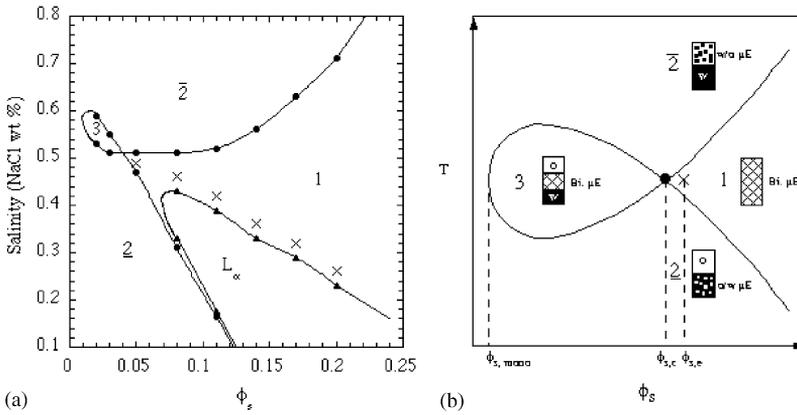


Fig. 1. The phase diagrams of: (a) AOT/brine/H-decane system and; (b)  $C_1E_j$ /water/n-alkane systems (schematic). The crosses are the points where SANS measurements were performed.

equal, the three component non-ionic microemulsions were reduced to effective isometric binary systems. Fig. 1b shows a schematic phase diagram of isometric non-ionic microemulsions in temperature–surfactant volume fraction plane. The fish tail indicated as solid circle is a minimal specific interface point where the microemulsion is bicontinuous and its average mean curvature is known to be zero. In order to be able to maintain a stable, one-phase microemulsion during SANS experiments, measurements were performed at a point denoted by  $X$ . In every case, the difference between the surfactant volume fractions at the fish tail and the point  $X$ , ( $\phi_{s,f} - \phi_{s,e}$ ), is  $< 0.01$ . For the exact volume fraction of the surfactants residing at the interfaces, the monomeric solubility of surfactant in the subphase,  $\phi_{s,m}$ , was accounted for.

The SANS intensities of ionic microemulsions were measured using SAND at Argonne National Laboratory (ANL). Non-ionic microemulsions were measured using NG7 SANS station at National Institute of Standards and Technology (NIST), and D11 small-angle diffractometer at Institute Laue Langevin (ILL) in Grenoble, France.

SANS intensity distribution from an isotropic, disordered two-component porous material is proportional to a three-dimensional Fourier transform of a scalar Debye correlation function  $\Gamma(r)$  [4]. To calculate the Debye correlation function for bicontinuous microemulsions, we adopt the CRW model. The CRW model was an idea originally introduced by Cahn [5] to describe morphology of spinodally decomposed binary alloys and was implemented for the case of bicontinuous microemulsions by Berk [6] using a simple SDF. In this method, one first generates a random field by superposition of large number of cosine waves by

$$\psi(\vec{r}) = \sqrt{2/N} \sum_{i=1}^N \cos(\vec{k}_i \cdot \vec{r} + \phi_i),$$

where  $|\vec{k}_i|$  is sampled from the SDF  $f(k)$  and the direction of  $\vec{k}_i$  is uniformly distributed over a unit sphere and the random phase  $\phi_i$  over an interval  $(0, 2\pi)$ .  $\psi(\vec{r})$  is a Gaussian

random field due to the central limit theorem. The statistical properties of a Gaussian random field  $\psi(\vec{r})$  is completely characterized by its SDF or the two-point correlation function. The two-point correlation function is defined as  $g(|r_1 - r_2|) = \langle \psi(\vec{r}_1)\psi(\vec{r}_2) \rangle$ , and can be given as a three-dimensional Fourier transform of the SDF. To realize the morphology of a two-phase porous material, the continuous random field  $\psi(\vec{r})$  is then clipped at some level  $\alpha$ . By clipping, we mean a non-linear transformation which assign a value 1 to the field when its value is greater or equal to a level  $\alpha$  and a value zero otherwise. The Debye correlation function for this two-state discrete random field can be written as an analytical function of  $g(r)$ . In particular, for isometric case ( $\alpha = 0$ ), it can be shown that the Debye correlation function is given by a simple relation  $\Gamma(r) = 2/\pi \sin^{-1}(g(r))$  [7].

A random interface between the two components in an isometric system is generated by a level set,  $\psi(\vec{r})=0$ , which defines the dividing surface between the aqueous region and the oily region where the Gaussian random field changes its sign. It was shown by Teubner [7] that for this random interface (with  $\langle H \rangle = 0$ ), the average Gaussian and square mean curvatures are given in terms of the two lower-order moments of the SDF as  $\langle K \rangle = -\frac{1}{6}\langle k^2 \rangle$  and  $\langle H^2 \rangle = \frac{1}{6}\langle k^2 \rangle (\frac{6}{5}\langle k^4 \rangle / \langle k^2 \rangle^2 - 1)$ . Therefore, once the SDF of the system is given, all the interfacial curvatures can be calculated.

The applicability of the CRW model depends on a choice of a physically reasonable form of the SDF. In the analysis of a scattering intensity from a bicontinuous microemulsion, Teubner–Strey (T–S) structure factor which contains two basic length scales, the inter-domain distance  $d$  and the coherence length  $\xi$  of the local domain order, has been widely used [8,9]. Derivation of the T–S model; however, does not involve a process such as clipping which realizes the interface between micro-phase separated sub-phases. The model, therefore, cannot provide information on the interfacial curvatures and the correct SIA. This is the reason why, while the T–S model fits the scattering intensity very well at low  $Q$ -region where there is a peak, it shows poor agreement with the scattering intensity at large  $Q$ -region where a transition to Porod behavior occurs. As a consequence, although T–S intensity formula goes asymptotically as  $Q^{-4}$  at large  $Q$ , it gives a SIA as much as a factor two lower than the correct value (see Fig. 2). The small  $r$  expansion of the Debye correlation function in the T–S model contains a linear and a square terms while the Debye correlation function for a binary system with a sharp interface is known to have an expansion with a linear and a cubic terms, the latter contains information on curvatures [10]. Therefore, the two parameter T–S structure factor is incomplete for representing the true structure of a bicontinuous microemulsion.

To be able to reproduce the whole scattering intensity distribution and to extract the correct SIA and the interfacial curvatures, we choose a SDF, which is an inverse 8th-order polynomial with three length scales, by considering the fundamental requirements for a physically reasonable SDF. As mentioned above, the average Gaussian and square mean curvatures are determined by the 2nd and 4th moments of SDF. In order to have finite 2nd and 4th moments, the SDF should be at least an inverse 8th-order polynomial in  $k$ . The SDF chosen in this study is

$$f(k) = \frac{bc(a^2 + (b + c)^2)^2 / (b + c)\pi^2}{(k^2 + c^2)^2(k^4 + 2(b^2 - a^2)k^2 + (a^2 + b^2)^2)} \quad (1)$$

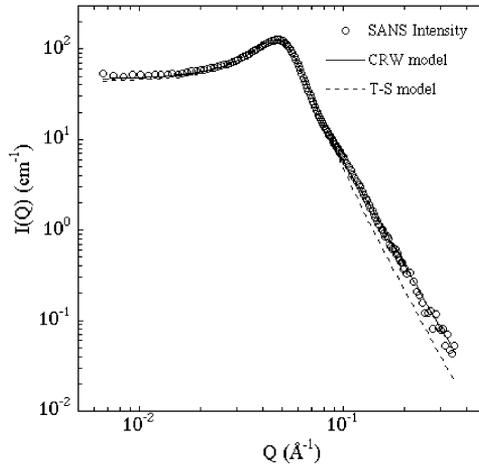


Fig. 2. A typical analysis of SANS intensity. The data shown here is taken from AOT/brine(NaCl = 0.26 wt%)/H-decane system at  $\phi_s = 0.20$ . The solid line is the CRW model and the dotted line is the T–S model. The parameters used in the CRW model are  $d = 126.5 \text{ \AA}$ ,  $\xi = 68.5 \text{ \AA}$  and  $\delta = 4.8 \text{ \AA}$ , and in the T–S model  $d = 128.5 \text{ \AA}$  and  $\xi = 63.4 \text{ \AA}$ .

which has  $g(r)$  in an analytical form [11]. This SDF contains three parameters  $a$ ,  $b$ , and  $c$  which are related to the three basic length scales, the inter-domain distance  $d$ , the coherence length  $\xi$  of the local domain order, and the surface roughness parameter  $\delta$ , respectively,  $d = 2\pi/a$ ,  $\xi = 1/b$ , and  $\delta = 1/c$ . Compared with the T–S model, we have one additional length scale  $\delta$  which defines the roughness of interface. The smaller  $\delta$  means rougher (more wrinkled) interface and the larger  $\delta$  smoother interface. The  $\delta$  controls the large  $Q$ -behavior of SANS intensities and is essential to properly explain the Porod's regime in which the T–S model shows poor agreement with experiments. Fig. 2 shows a typical scattering intensity and its analysis. Solid line is the CRW model with the SDF given in Eq. (1) and dotted line is the T–S model. Note that the CRW model agrees with the experiment over the entire  $Q$ -range very well while the T–S model shows clear deviation from the experiments at large  $Q$ . This suggests that we need at least three length scales to properly describe the internal structure of bicontinuous porous material.

Since the average Gaussian and square mean curvatures are described by the 2nd and 4th moment of the SDF, they can be explicitly expressed in  $a$ ,  $b$ , and  $c$  [11]. Having acquired the three parameters  $a$ ,  $b$ , and  $c$ , i.e.,  $d$ ,  $\xi$ , and  $\delta$  from data analysis, the average Gaussian curvatures were calculated. From the small  $r$  expansion of the Debye correlation function, it can be shown that the SIA is given by,  $(S/V) = (2/\pi\sqrt{3})\sqrt{\langle k^2 \rangle}$ . If all surfactant molecules reside at the interface, we can also show a simple relation,  $(S/V) = (\phi_s/\Delta)$ . Since the average Gaussian curvature in an isometric system is proportional to  $\langle k^2 \rangle$ , we have a scaling relation of the form,

$$\Delta^2 \langle K \rangle = -(\pi^2/8)\phi_s^2. \quad (2)$$

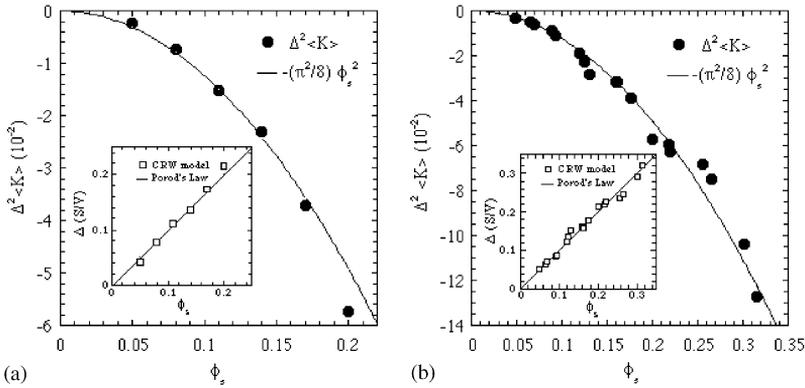


Fig. 3. Scaled Gaussian curvature and SIA as a function of  $\phi_s$ ; (a) AOT/brine/H-decane system; (b)  $C_iE_j$ /water/n-alkane systems. The solid line in (a) is a parabola with a coefficient  $-(\pi^2/8)$ . The insets show the SIA by the CRW model and by Porod's law (solid line).

Fig. 3a and b show the scaled average Gaussian curvature as a function of  $\phi_s$  for the ionic and non-ionic microemulsions, respectively. The effective chain length  $\Delta$  for each surfactant is extracted from the SIA determined through an independent analysis of the Porod region. It is striking to see that when all the average Gaussian curvatures are scaled with  $\Delta^2$ , they show a parabolic dependence on surfactant volume fraction with a coefficient  $-(\pi^2/8)$  (solid line). This good agreement between experimental results and the theoretical expectation tells us that our method of extracting the average Gaussian curvature from SANS intensity is a consistent and reliable procedure.

Fig. 4 shows the square mean curvature  $\langle H^2 \rangle$  of AOT/brine/H-decane as a function of  $\phi_s$ . In typical bicontinuous microemulsions, the parameter  $c$  is much larger than  $a$  and  $b$  and it can be shown that  $\langle H^2 \rangle$  mainly depends on  $c$ ,  $\langle H^2 \rangle \approx c^2/5 = \delta^{-2}/5$ . Points are also shown for  $(\delta^{-2}/5)$ . They agree with  $\langle H^2 \rangle$  fairly well, confirming the physical meaning of  $\delta$ .

While, according to Gauss–Bonnet theorem,  $\langle K \rangle$  is a topological constant related to the number of passages per unit interfacial area in this locally saddle point structure,  $\langle H^2 \rangle$  is the fluctuation of the mean curvature ( $\langle H \rangle = 0$  in this study) thus relating to the persistence length of the interface. According to DeGennes and Taupin [12], the persistence length of interface is an exponential function of the bending rigidity constant of the surfactant monolayer. Interpreting the inverse of the root mean square fluctuation of the mean curvature,  $1/\sqrt{\langle H^2 \rangle}$ , as the persistence length of the random interface, we have a relation

$$\frac{\delta}{\sqrt{5}} \approx \frac{1}{\sqrt{\langle H^2 \rangle}} = \Delta \exp\left(\frac{4\pi\kappa}{3k_B T}\right), \tag{3}$$

where  $\kappa$  is the bending rigidity constant,<sup>2</sup>  $k_B$  the Boltzmann constant, and  $T$  the temperature. Since we can measure  $\langle H^2 \rangle$ , the bending rigidity constant  $\kappa$  can be calculated

<sup>2</sup> Kappa depends on (chain length)<sup>3</sup>; see Ref. [13].

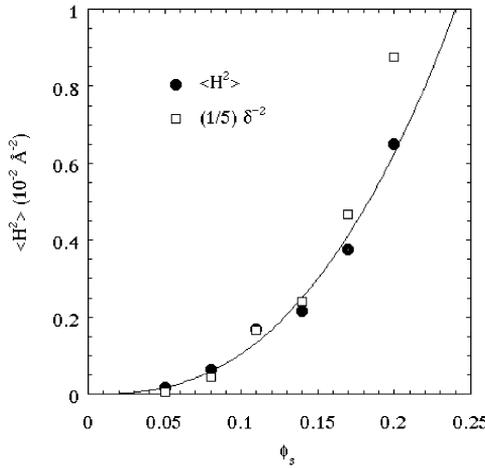


Fig. 4. Square mean curvature  $\langle H^2 \rangle$  (solid circles) of AOT/brine/H-decane system as a function of  $\phi_s$ . Squares represent  $(1/5)\delta^{-2}$ . The solid line is a guide to show the variation of  $\langle H^2 \rangle$  in  $\phi_s$ .

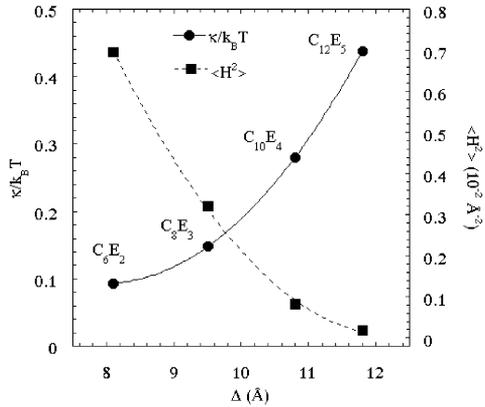


Fig. 5. Square mean curvature  $\langle H^2 \rangle$  (solid squares) and bending rigidity constant  $\kappa$  (solid circles) of  $C_iE_j$ /water/n-octane system as a function of  $\Delta$ .  $\kappa$  is calculated according to  $\kappa/k_B T = (3/8\pi) \ln(\Delta^2 \langle H^2 \rangle)^{-1}$ .

from Eq. (3).  $\langle H^2 \rangle$  and  $\kappa$  of four different non-ionic microemulsions are presented in Fig. 5. In these microemulsions, while the same oil (H-octane) and water ( $D_2O$ ) are used, the effective chain length of each surfactant is different. When plotted against  $\Delta$ ,  $\langle H^2 \rangle$  decreases and  $\kappa$  increases with  $\Delta$  both quadratically. This is a physically reasonable results.

In summary, a novel method for SANS data analysis is proposed which enables one to compute both the average Gaussian and square mean curvatures, and SIA in an isometric bicontinuous porous structure. The new ingredient is the introduction of the three length scales into the procedure. The method is applied to six different phase

points of an isometric ionic microemulsion system (AOT/D<sub>2</sub>O/H-decane) along a line of zero mean curvature and 18 different non-ionic microemulsion systems ( $C_iE_j/D_2O/n$ -alkane) at their respective minimal specific interface points. Scaling the measured Gaussian curvatures with  $\Delta^2$  determined independently from Porod's law, we found a parabolic relation between the scaled average Gaussian curvature and the surfactant volume fraction. Interpreting the inverse of the root mean square fluctuation of the mean curvature as the persistence length for the random interface, the measured average square mean curvature allows us to estimate the bending rigidity constant of the surfactant monolayer. The bending rigidity constant shows a parabolic dependence on the effective chain length  $\Delta$ .

### Acknowledgements

We are very happy to contribute this paper to the Proceedings of the International Workshop on Scattering Studies of Mesoscopic Scale Structure and Dynamics in Soft Matter, Messina Italy, November 22–25, 2000, which was held in the honor of the 65th birthday of Professor Sow-Hsin Chen whose enthusiasm and contribution to soft matter has been always inspiring and remarkable.

We are grateful to Dr. Charlie Glinka at the NIST Center For Neutron Research and Dr. Papanan Thyagarajan at the Intense Pulsed Neutron Source in ANL for the use of their SANS instruments. This research was supported by grants from the Material Science Division of the US Department of Energy and the US National Science Foundation under agreement number DMR-9986442.

### References

- [1] S.H. Chen, S.L. Chang, R. Strey, *J. Chem. Phys.* 93 (1990) 1907–1917.
- [2] T. Sottmann, R. Strey, S.H. Chen, *J. Chem. Phys.* 106 (15) (1997) 6483.
- [3] M. Kahlweit, R. Strey, B. Busse, *J. Phys. Chem.* 94 (1990) 3881. *Phys. Rev. E* 47 (1993) 4197.
- [4] P. Debye, H.R. Jr. Anderson, H. Brumberger, *J. Appl. Phys.* 28 (1957) 679.
- [5] J.W. Cahn, *J. Chem. Phys.* 42 (1965) 93.
- [6] N.F. Berk, *Phys. Rev. Lett.* 58 (1987) 2718. *Phys. Rev. A* 44 (1991) 5069.
- [7] M. Teubner, *Europhys. Lett.* 14 (1991) 403.
- [8] M. Teubner, R. Strey, *J. Chem. Phys.* 87 (1987) 3195.
- [9] S.H. Chen, S.L. Chang, R. Strey, *Progr. Colloid Polym. Sci.* 81 (1990) 30.
- [10] Von R. Kirste, G. Porod, *Kolloid Z. Z. Polym.* 184 (1962) 1–7.
- [11] S.H. Chen, S.M. Choi, *J. Appl. Crystallogr.* 30 (1997) 755.
- [12] P.G. de Gennes, C. Taupin, *J. Phys. Chem.* 79 (1982) 4586.
- [13] I. Szleifer, D. Kramer, A. Ben Shaul, D. Roux, W.M. Gelbart, *Phys. Rev. Lett.* 60 (1988) 1966.