1-1-2005

Brownian dynamics of mixed surfactant micelles

Georgui K. Bourov
University of Central Florida

Aniket Bhattacharya
University of Central Florida

Find similar works at: <https://stars.library.ucf.edu/facultybib2000>

University of Central Florida Libraries <http://library.ucf.edu>

This Article is brought to you for free and open access by the Faculty Bibliography at STARS. It has been accepted for inclusion in Faculty Bibliography 2000s by an authorized administrator of STARS. For more information, please contact STARS@ucf.edu.

Recommended Citation

Bourov, Georgui K. and Bhattacharya, Aniket, "Brownian dynamics of mixed surfactant micelles" (2005).
Faculty Bibliography 2000s. 4641.
<https://stars.library.ucf.edu/facultybib2000/4641>

Brownian dynamics of mixed surfactant micelles

Cite as: J. Chem. Phys. **123**, 204712 (2005); <https://doi.org/10.1063/1.2125687>

Submitted: 14 April 2005 . Accepted: 26 September 2005 . Published Online: 23 November 2005

Georgui K. Bourov, and Aniket Bhattacharya

View Online

Export Citation

ARTICLES YOU MAY BE INTERESTED IN

[Determination of the critical micelle concentration in simulations of surfactant systems](#)

The Journal of Chemical Physics **144**, 044709 (2016); <https://doi.org/10.1063/1.4940687>

[Confinement effects on micellar systems with a hydrogen-bonding solvent](#)

The Journal of Chemical Physics **145**, 164902 (2016); <https://doi.org/10.1063/1.4965817>

[Rheological characterizations of wormlike micellar solutions containing cationic surfactant and anionic hydrotropic salt](#)

Journal of Rheology **59**, 1229 (2015); <https://doi.org/10.1122/1.4928454>

Lock-in Amplifiers up to 600 MHz

starting at

\$6,210

Zurich
Instruments

Watch the Video

Brownian dynamics of mixed surfactant micelles

Geuorgui K. Bourov and Aniket Bhattacharya^{a)}

Department of Physics, University of Central Florida, Orlando, Florida 32816-2385

(Received 14 April 2005; accepted 26 September 2005; published online 23 November 2005)

We investigate micelle formation in a system containing two or more different amphiphiles with different geometries using a stochastic molecular-dynamics (MD) simulation method. For a binary system containing two amphiphiles, we calculate the critical micelle concentration (CMC) and cluster distribution for the mixture at several mole fractions and compare the simulation results with those predicted by analytic theories in the dilute limit and with experiments. We find that the CMC obtained from molecular mean-field theory agrees well with our simulation results. Motivated by the industrial use of mixed surfactant systems, we then extend our studies to a system containing six different chain lengths drawn from a Poisson distribution. We find that unlike a binary mixture of amphiphiles, the different species cancel the effects of each other so that the cluster distribution for the mixture has a shape of a system consisted entirely of amphiphiles of length equal to the mean chain length of the Poisson distribution. © 2005 American Institute of Physics.

[DOI: [10.1063/1.2125687](https://doi.org/10.1063/1.2125687)]

I. INTRODUCTION

A mixture of surfactants quite often give rise to enhanced performance over its individual components in industrial and technological applications.^{1,2} Surfactants have natural polydispersity in length when they are produced with chain polymerization; therefore, obtaining a pure system requires additional processing and can be more expensive to produce. Moreover, for many applications additives are needed for better stability and control of the physical properties. Thus, a surfactant mixture with a distribution of lengths, or a mixture of two or more different type of surfactants (e.g., neutral and charged) often is a more desirable product for the industry.

At a fundamental level studies of mixed surfactant systems may serve as platforms to explore coexistence and transitions among different exotic phases in soft matter systems.³ For example, a mixed surfactant system consisting of positively and negatively charged hydrophilic heads has been experimentally found to produce vesicles in aqueous solution.⁴ The transition from spherical micelles, which is the characteristic of pure aqueous solution of each species, to vesicles is important in a number of practical applications and has been recently investigated with scattering probes.⁵ A routine way to produce vesicles of desired size and shape will be an extremely useful technology, as synthetic, biocompatible vesicles can be used as carriers of drugs. A mixed cationic and anionic surfactant system is capable of producing wormlike micelles⁶ which have been used for linear polymers and polyelectrolytes. Recently, shear-induced morphologies and near Maxwellian rheological behavior of these mixed surfactant systems have attracted a lot of attention both from academic and applied perspectives.

A very natural and tempting idea is to extend basic ther-

modynamic theory of self-assembly⁷ to a mixture of surfactants and to treat micelles as a separate phase under the assumption that mixing is ideal, which renders the analytic treatment simple. This method, aptly known as the pseudophase separation model, was the first theoretical tool applied to the ideal mixing of binary nonionic amphiphilic systems.^{8–10} A disadvantage of this method is that, since the theory treats each micelle as a single phase (“pseudophase”), it is incapable of furnishing information regarding aggregate sizes and their distribution, etc. In more explicit molecular approaches,^{11,12} the free-energy contributions from different molecular interactions are taken into account. Thus, the macroscopic properties, e.g., the size of aggregates, the CMC of the mixture, etc., can be linked to the characteristics of the individual amphiphilic molecule, e.g., size, type of hydrophilic head group, ratio of the hydrophilic to hydrophobic segments, etc.

Computer simulation has played a major role in studying the properties of self-assembling amphiphilic systems. The great advantage of simulation studies is that one can obtain a microscopic understanding of the thermodynamic properties and a detailed picture of the self-assembled phases from the characteristic features of a single amphiphile and the interaction parameters of the models. The simulation results have been very useful for further refinement of theoretical models and understanding their limitations as well. Surprisingly, despite increased interest in mixed surfactant systems, compared with studies of the bulk properties of amphiphiles of a given type using Monte Carlo^{13–20} (MC) and molecular-dynamics^{21–29} methods, simulation studies are relatively few.^{30,31} Recently Gharibi *et al.*,³⁰ and Zaldivar and Larson³¹ studied binary amphiphilic systems using lattice Monte Carlo method. Both groups have studied the correlation between interaction energy parameter representing

^{a)}Author to whom correspondence should be addressed. Electronic mail: aniket@physics.ucf.edu

nonideal behavior among different species and aggregation properties of the binary mixture. There has been no report of simulation on the off-lattice models so far.

In this work we report the Brownian dynamics simulation results on mixed surfactant systems using a Grest-Kremer-type bead-spring model for the surfactants.³² First we study a series of binary systems of amphiphiles and focus on how geometry itself introduces nonideality. Then we go beyond binary mixtures and study a more realistic system where the lengths of the amphiphiles are drawn from a Poisson distribution which mimics the distribution obtained during a synthesis process. The outline of our paper is as follows. In the next section we review some of those theoretical predictions which we will later compare with our simulation results. The model and simulations strategies are outlined in Sec. III. Section IV is devoted to the results that we obtained using Brownian dynamics simulation. Section V deals with the summary and discussion.

II. THEORY

For a binary mixture denoting the molar concentrations of two types of amphiphilic molecules in solution as X_1 and X_2 , respectively, the mole fraction x_1 for the amphiphile of type 1 in the solution is given by

$$x_1 = \frac{X_1}{X_1 + X_2}. \quad (1)$$

The mole fraction x_2 for the amphiphile of type 2 is then

$$x_2 = 1 - x_1. \quad (2)$$

Evidently, the micellization of both amphiphiles is affected by the presence of the other type of molecule. This leads to new aggregation properties. One of the most important characteristics of the mixture is its critical micelle concentrations (CMC). If the CMC of pure amphiphiles are known, then according to the molecular theory model,¹² the CMC of the mixed system C_M can be obtained as

$$\frac{1}{C_M} = \frac{x_1}{f_1 C_1} + \frac{1-x_1}{f_2 C_2}. \quad (3)$$

Here C_1 and C_2 are the CMC for the type-1 and type-2 amphiphiles, respectively, and f_1 and f_2 are the activity coefficients of the amphiphiles taking into account the nonideality of the interactions between molecules of different types.

For a multicomponent system Eq. (3) can be generalized as follows:

$$\frac{1}{C_M} = \sum_{i=1}^n \frac{x_i}{f_i C_i}. \quad (4)$$

We will use the above two equations to compare the CMC for a mixed amphiphilic system obtained from our simulation. In this paper, we restrict our studies to mixtures of neutral amphiphilic molecules with the same type of interactions, and therefore the activity coefficients for all components are unity.

TABLE I. Interaction parameters for the amphiphiles.

Interaction	r_{ij}^c / σ_{ij}	σ_{ij}	ϵ_{ij}
Head-head	$2^{1/6}$	$1.5\sigma_{tt}, 2.0\sigma_{tt}, 3.0\sigma_{tt}$	1.0
Head-tail	$2^{1/6}$	$(\sigma_{hh} + \sigma_{tt}/2)$	1.0
Tail-tail	2.5	1.0	1.0

III. MODEL AND METHOD

The details of the model and the method are given in Refs. 28 and 29. Here we briefly mention the information pertinent to the choices for the mixed micellar system. An amphiphile is represented as $h_m t_n$ with m hydrophilic head (h) and n hydrophobic tail (t) beads connected by $m+n-1$ bonds. We use a Grest-Kremer-type model³² so that the non-bonded potential acting between any two beads is chosen to be a Lennard-Jones (LJ) interaction and the interaction between successive beads is given by a finite-extendable nonlinear elastic (FENE) potential as given below.

$$U_{LJ}^{ij}(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 - \left(\frac{\sigma_{ij}}{r_{ij}^c} \right)^{12} + \left(\frac{\sigma_{ij}}{r_{ij}^c} \right)^6 \right], \quad r \leq r_{ij}^c, \quad (5a)$$

$$U_{chain}(r_{ij}) = -\frac{1}{2} k R_{ij}^2 \ln \left[1 - \left(\frac{r_{ij}}{R_{ij}} \right)^2 \right], \quad (5b)$$

where r_{ij}^c is the cutoff distance beyond which the LJ interaction is set to be zero, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ and $\mathbf{r}_i, \mathbf{r}_j$ are the locations of the i th and the j th monomers, respectively. *Amphiphilicity* in this model is introduced by a repulsive cutoff distance for the head-head and head-tail interactions ($r_{hh}^c = 2^{1/6}\sigma_{hh}$, $r_{ht}^c = 2^{1/6}\sigma_{ht}$), and an attractive cutoff for the tail-tail interaction ($r_{tt}^c = 2.5\sigma_{tt}$). k and R_{ij} are the force constant and the length parameters of the FENE potential. We have chosen $k = 30(\epsilon_{tt}/\sigma_{tt}^2)$, $R_{ij} = 1.5\sigma_{ij}$ and $\epsilon_{ij} = 1$. The choice of the LJ parameters are summarized in Table I. Each monomer is coupled to a heat bath and its equation of motion is

$$m_i \ddot{\mathbf{r}}_i = -\nabla U_i - \Gamma \dot{\mathbf{r}}_i + \mathbf{W}_i(t), \quad (6)$$

where

$$U_i = \sum_{j \neq i} \left(U_{LJ}^{ij}(r_{ij}) + \sum_{j=i \pm 1} U_{chain}(r_{ij}) \right),$$

m_i is the mass of the i th particle, Γ is the monomer friction coefficient, and $\mathbf{W}_i(t)$ describes the random force of the heat

TABLE II. Types of amphiphilic molecules studied.

Type	Configuration	Head Size	Length
1	$h_1 t_4$	1.5	5
2	$h_1 t_4$	2.0	5
3	$h_1 t_6$	1.5	7
4	$h_1 t_6$	2.0	7
5	$h_1 t_6$	3.0	7
6	$h_1 t_8$	2.0	9
7	$h_1 t_8$	3.0	9

FIG. 1. Concentration of free amphiphiles X_1 as a function of the total concentration X for a mixture of h_1t_4 and h_1t_6 for several mole fraction x_1 for h_1t_4 . The knee of the curve is used to extract the CMC.

bath acting on each monomer as a Gaussian white noise with zero mean satisfying the fluctuation-dissipation relation

$$\langle \mathbf{W}_i(t) \cdot \mathbf{W}_j(t') \rangle = 6m_i k_B T \delta_{ij} \delta(t - t').$$

The stationary solutions of the above equations of motion produce a Boltzmann distribution, and therefore the simulated system represents a canonical ensemble. Additionally, we use reduced units throughout this study; the unit of length is σ_{tt} , the unit of time is $\tau = \sigma_{tt}(m/\varepsilon_{tt})^{1/2}$, and the unit of temperature is ε_{tt}/k_B where k_B is the Boltzmann constant. All beads have equal mass which is set to unity. The parameter $\Gamma=1.0$, and the integration time step $\Delta t=0.01\tau$. We have kept the reduced temperature at $T\varepsilon/k_B=0.9$ for all the results reported here.

In order to carry out simulations of mixed micellar systems, we have chosen various combinations of hydrophilic and hydrophobic segments which are summarized in Table II. First we study a binary mixture of amphiphiles. Then we extend our studies to amphiphiles whose lengths are drawn from a Poisson distribution.

IV. RESULTS

The simulations are carried out in a $32 \times 32 \times 32$ box with periodic boundary conditions. Typical length of the runs are $(5-10) \times 10^6$ MD steps excluding 10^6 equilibrating MD steps. The maximum number of chains in the box is 1920. We have used a link-cell list and a fast Gaussian random number generator to expedite the calculations.

A. Critical micelle concentration

First we consider a mixture of two amphiphilic molecules with the same length but different head sizes. Previously we have studied how the hydrophilic head group geometry affects the CMC, shape, and sizes of the cluster distribution.^{28,29} Here we extend this calculation for a mixture of these two types of amphiphiles of same tail length but with different head sizes. We chose molecules of type 1 and type 2 to be amphiphiles with head sizes $1.5\sigma_{tt}$ and $2.0\sigma_{tt}$, respectively. The total concentration of amphiphiles in the

FIG. 2. A comparison of the CMC for h_1t_4 . Data from Fig. 1 are used to obtain CMC from simulations (squares). The corresponding theoretical curve (dotted line) is calculated using Eq. (3).

solution is kept constant at $X=0.7\%$. From our previous studies we found that larger head group implies a higher value of the CMC.^{28,29} Here we notice that as we increase the molar fraction of the amphiphiles with smaller head group, the CMC of the mixture systematically decreases and interpolates between the CMC of two pure systems. This is shown in Fig. 1.

From Fig. 1 we can calculate the CMC for the mixed system for various mole fractions for the type-1 molecules. From simulation results for the pure systems we find the CMC for type 1 and type 2 to be $C_1=0.0025$ and $C_2=0.0037$, respectively. We then calculate the CMC of the mixture from Eq. (3). This comparison is shown in Fig. 2. Theoretical predictions are within the error interval of the simulation results.

B. Cluster distribution

Now we systematically study the effect of mixing two different amphiphiles on the cluster distribution. First, we keep the hydrophobic tail part of the molecules the same and only vary hydrophilic head sizes. In previous papers^{28,29} we reported how the shape and peak of the cluster distribution are affected by the head group geometry. Here we extend similar analysis for a mixture of amphiphiles only differing

FIG. 3. Cluster distributions for a binary mixture of h_1t_4 -type amphiphiles with $\sigma_{hh}=1.5\sigma_{tt}$ and $\sigma_{hh}=2.0\sigma_{tt}$ at different molar concentrations.

FIG. 4. Cluster distribution for a 50-50 mixture of h_1t_4 ($\sigma_{hh}=1.5\sigma_{tt}$) and h_1t_6 with $\sigma_{hh}=2.0\sigma_{tt}$ (circles) and $\sigma_{hh}=3.0\sigma_{tt}$ (squares).

in the hydrophilic head size. In particular, we show results for a binary mixture of two h_1t_4 differing only in their hydrophilic head sizes chosen to be $\sigma_{hh}=1.5\sigma_{tt}$ and $\sigma_{hh}=2.0\sigma_{tt}$, respectively.

The cluster distribution depends on the composition and is plotted in Fig. 3 for total molar concentration $X=0.7\%$. The composition $x_1=0.0$ and 1.0 corresponds to the pure systems amphiphiles with head $\sigma_{hh}=2.0\sigma_{tt}$ and $\sigma_{hh}=1.5\sigma_{tt}$, respectively. Earlier we found that amphiphiles with bigger head group have sharper distribution peaked at a smaller value of the cluster size. We notice that by mixing the two surfactants with $\sigma_{hh}=1.5\sigma_{tt}$ and $\sigma_{hh}=2.0\sigma_{tt}$ one can interpolate between the limits. This may be a useful information for synthesis of surfactant mixtures.

In order to explore the effect of the head group geometry further, next we simulate a 50-50 mixture of h_1t_4 ($\sigma_{hh}=1.5\sigma_{tt}$) and h_1t_6 for $\sigma_{hh}=1.5\sigma_{tt}$ and $\sigma_{hh}=2.0\sigma_{tt}$, respectively. The cluster distributions are shown in Fig. 4. It is notable that the difference in cluster distribution arises solely due to different head sizes ($\sigma_{hh}=1.5\sigma_{tt}$ and $\sigma_{hh}=2.0\sigma_{tt}$ for h_1t_6) as the contribution from h_1t_4 remains the same in both

FIG. 5. Cluster distribution for a 50-50 mixture of h_1t_4 ($\sigma_{hh}=1.5\sigma_{tt}$) and h_1t_8 with $\sigma_{hh}=2.0\sigma_{tt}$ (circles) and $\sigma_{hh}=3.0\sigma_{tt}$ (squares).

FIG. 6. Comparison of cluster distributions for (a) h_1t_6 with $\sigma_{hh}=1.5\sigma_{tt}$, (b) h_1t_8 with $\sigma_{hh}=2.0\sigma_{tt}$, and (c) a 50-50 mixture of these two species; the inset shows the ratio of chains of each species in a given cluster as a function of cluster size.

cases. Even within a mixture, the larger head group produces a sharper distribution, a conclusion that we obtained before in the case of pure surfactants.^{28,29} A similar study is also made for a 50-50 mixture of h_1t_4 and h_1t_8 shown in Fig. 5 to see the effect of the longer chain. One notices that the cluster distributions for the amphiphilic mixture show multiple peaks.

Figure 6 shows a comparison of the cluster distributions of two pure systems consisting of h_1t_6 with $\sigma_{hh}=1.5\sigma_{tt}$ and h_1t_8 with $\sigma_{hh}=2.0\sigma_{tt}$ and a 50-50 mixture of these two species. The cluster distribution for the binary mixture is significantly different from those of the pure systems. Positions of the peaks are shifted. How do the surfactants mix in different clusters? Figure 7 shows a typical snapshot for a mixture of h_1t_6 with $\sigma_{hh}=1.5\sigma_{tt}$ and h_1t_8 with $\sigma_{hh}=2.0\sigma_{tt}$. It appears from the picture that the two species mix equally. The inset of Fig. 6(c) shows the ratio $P_1(N)/P_2(N)$, where

$$P_1(N) = \frac{N_1}{N} \text{ and } P_2(N) = \frac{N_2}{N},$$

and N_1 and N_2 are the number of two types of surfactant chains present in a cluster of size $N=N_1+N_2$. For larger clus-

FIG. 7. Snapshot of mixed micelles formed from a 50-50 mixture of h_1t_6 with $\sigma_{hh}=15\sigma_{tt}$ and h_1t_8 with $\sigma_{hh}=2.0\sigma_{tt}$. The simulation is done at total amphiphile concentration $X=0.007$.

ters, the ratio stays close to unity implying that both surfactants participate equally in the formation of mixed micelles.

C. Amphiphilic mixture with the poisson distribution

The commercial applications of surfactants typically involve a mixture of surfactants as they can be produced at a relatively lower cost, and often outperform single surfactant solutions. Synthesis via chemical reactions leads to a mixture of molecules with various degrees of polymerization. Therefore, for realistic modeling of surfactants it is more important to study the aggregation properties of a mixture of surfactants with a certain distribution of lengths to mimic the experiments more closely. A typical distribution of length N in the polymerization process of amphiphiles can be characterized by the Poisson distribution given by

$$P_N = \frac{\lambda^N e^{-\lambda}}{N!}, \quad (7)$$

where λ is the mean degree of polymerization.

We have simulated two systems where the chain lengths are sampled from a Poisson distribution with mean degree of

TABLE III. Characteristics of amphiphilic molecules with Poisson distribution of the length.

Type	Configuration	Length	Molecules
1	h_1t_5	6	261
2	h_1t_6	7	330
3	h_1t_7	8	361
4	h_1t_8	9	361
5	h_1t_9	10	330
6	h_1t_{10}	11	277

FIG. 8. Poisson distribution for $\lambda=9$. The shaded region represents the area covered by the six values of length (n) chosen in our simulation. The tail lengths of surfactants chosen in our simulation satisfy this distribution.

polymerization $\lambda=9$. We compare the cluster distributions obtained for these mixed surfactant systems with those obtained for the pure systems. For the pure system simulations we chose amphiphiles h_1t_8 (type 6 and 7 in Table II) of chain length 9 with different hydrophilic head sizes $\sigma_{hh}=2\sigma_{tt}$ and $\sigma_{hh}=3\sigma_{tt}$, respectively. For simulating the mixed system we have chosen six different chain lengths drawn from the Poisson distribution as expressed in Eq. (7). The characteristics of the surfactants are summarized in Table III. It is worth mentioning that since only six lengths are chosen from an infinite number of chain lengths, this does not reflect a true Poisson distribution. As shown in Fig. 8 we only sample points from the shaded area of the given Poisson distribution for $\lambda=9$. The total number of chains in the simulation was

FIG. 9. Cluster distribution for a pure and a mixed amphiphilic system with Poisson distribution of the lengths for two different head sizes.

1920 with six different chain lengths weighted according to Fig. 8. For example, the total number of chains for length 8 and 9 is 361 while the total number of chains for length 6 is 261. The number of chains for the other lengths are chosen in a similar manner.

The cluster distributions obtained in our simulation are shown in Fig. 9. In the same figure we show the cluster distribution for the chain length corresponding to the mean degree of polymerization $\lambda=9$. We notice that the cluster distribution of a mixed system of chains with a Poisson distribution of lengths is close to the cluster distribution of the pure system with a length equal to the mean length of the Poisson distribution. We find it to be true for two different systems. Unlike binary mixture of amphiphiles, the distribution remains practically unaffected. The presence of shorter and longer chains somehow cancel out the effect of each other. It will be very interesting to verify this result experimentally and for other distributions as well.

V. CONCLUSION

In summary, in this paper we report Brownian dynamics simulation of mixed micelles. This is, to the best of our knowledge, the first systematic study of mixed amphiphilic systems in continuum. We first calculate the CMC for a binary mixture of amphiphiles as a function of the mole fractions for one of the components and compare our result with those obtained from molecular mean-field theory. Our results are consistent with the theoretical predictions. Next we have studied several other binary mixtures of amphiphiles specifically addressing the role of hydrophilic head size. We notice that a larger hydrophilic head still produces a sharper peak in the cluster distribution for the mixture. In other words, just by changing the volume of the hydrophilic head (this implies attaching different hydrophilic moiety which is not difficult to engineer) one can change the peak of the cluster distribution. In general, we find that for a simple binary mixture of amphiphiles, changing the hydrophilicity affects both the distribution and the CMC.

We then extended the study to amphiphiles whose lengths are drawn from a Poisson distribution. Unlike a binary mixture, we find that the cluster distribution does not show any characteristic feature; instead it roughly follows the cluster distribution of the corresponding mean length of the distribution. It will be nice to see some experimental work along this line.

Finally, in this work we specifically addressed the case where the intrachain and interchain interaction parameters are identical. This study is important to carry out, because it shows only the effects of excluded volume and entropy. Breaking this symmetry will certainly have interesting non-trivial effects which are currently under investigation. There are a number of important issues in mixed amphiphilic system that need to be addressed. For example, simulation studies of transition from micelle to vesicle is an interesting problem. In general, a thorough study of the phase diagram

of amphiphiles³³ will be very interesting from both fundamental and technological perspectives. We will report some of these studies in future publications.

ACKNOWLEDGMENTS

The research reported here is supported from the National Science Foundation NIRT (ENG/ECS and CISE/EIA) under Grant No. 0103587. We thank Weili Luo and Kevin Belfield for numerous discussions.

- ¹B. Jönsson, B. Lindman, K. Holmberg, and B. Kronberg, *Surfactants and Polymers in Aqueous Solution* (Wiley, New York, 1998), pp. 128–132.
- ²*Mixed Surfactant Systems*, edited by P. M. Holland and D. N. Rubingh (American Chemical Society, Washington, DC, 1992).
- ³S. A. Safran, *Statistical Thermodynamics of Surfaces, Interfaces, and Membranes* (Addison-Wesley, New York, 1994).
- ⁴E. W. Kaler, A. K. Murthy, B. E. Rodriguez, and T. A. N. Zasadzinski, *Science* **245**, 1371 (1989).
- ⁵O. Söderman, K. L. Herrington, E. W. Kaler, and D. D. Miller, *Langmuir* **13**, 5531 (1997).
- ⁶B. A. Schubert, E. W. Kaler, and N. J. Wagner, *Langmuir* **19**, 4079 (2003).
- ⁷J. Israelachvili, *Intermolecular and Surface Forces* (Academic, London, 1992).
- ⁸K. Shinoda, *J. Phys. Chem.* **58**, 541 (1954).
- ⁹H. Lange and K. H. Beck, *Kolloid Z. Z. Polym.* **251**, 424 (1973).
- ¹⁰H. J. Clint, *J. Chem. Soc., Faraday Trans. 1* **71**, 1327 (1975).
- ¹¹R. Nagarajan, *Langmuir* **4**, 474 (1988).
- ¹²S. Puvvada and D. Blankschtein, *J. Phys. Chem.* **96**, 5567 (1992); **96**, 5579 (1992).
- ¹³R. G. Larson, L. E. Scriven, and H. T. Davis, *J. Chem. Phys.* **83**, 2411 (1985); R. G. Larson, *ibid.* **89**, 1642 (1988); **91**, 2479 (1989); **96**, 7904 (1992); *J. Phys. II* **6**, 1441 (1996).
- ¹⁴C. M. Care, *J. Phys. C* **20**, 689 (1987); *J. Chem. Soc., Faraday Trans. 1* **83**, 2905 (1987); D. Brindle and C. M. Care, *J. Chem. Soc., Faraday Trans.* **88**, 2163 (1994); J.-C. Desplat and C. M. Care, *Mol. Phys.* **87**, 441 (1996).
- ¹⁵P. H. Nelson, G. C. Rutledge, and T. A. Hatton, *J. Chem. Phys.* **107**, 10777 (1997).
- ¹⁶A. Bhattacharya and S. D. Mahanti, *J. Phys.: Condens. Matter* **12**, 6141 (2000).
- ¹⁷A. Bhattacharya and S. D. Mahanti, *J. Phys.: Condens. Matter* **13**, L861 (2001).
- ¹⁸M. A. Floriano, E. Caponetti, and A. Z. Panagiotopoulos, *Langmuir* **15**, 3143 (1998).
- ¹⁹A. Z. Panagiotopoulos, M. A. Floriano, and S. K. Kumar, *Langmuir* **18**, 2940 (2002).
- ²⁰S. Salaniwal, S. K. Kumar, and A. Z. Panagiotopoulos, *Langmuir* **19**, 5164 (2003).
- ²¹D. R. Rector, F. van Swol, and J. R. Henderson, *Mol. Phys.* **82**, 1009 (1994).
- ²²B. Palmer and J. Liu, *Langmuir* **12**, 746 (1996); **12**, 6015 (1996); B. Palmer, J. Liu, and J. Virden, *ibid.* **15**, 7426 (1999).
- ²³Z. Zhang, M. Horsch, M. Lamm, and S. Glotzer, *Nano Lett.* **3**, 1341 (2003).
- ²⁴P. K. Maiti, Y. Lansac, M. A. Glaser, N. A. Clark, and Y. Rouault, *Langmuir* **18**, 1908 (2002).
- ²⁵J.-B. Maillet, V. Lachet, and P. V. Coveney, *Phys. Chem. Chem. Phys.* **1**, 5277 (1999).
- ²⁶F. K. von Gottberg, K. A. Smith, and T. A. Hatton, *J. Chem. Phys.* **106**, 9850 (1997).
- ²⁷S. Bogusz, R. M. Venable, and R. Pastor, *J. Phys. Chem.* **105**, 8312 (2001).
- ²⁸G. K. Bourov and A. Bhattacharya, *J. Chem. Phys.* **119**, 9219 (2003).
- ²⁹G. K. Bourov and A. Bhattacharya, *J. Chem. Phys.* **122**, 04472 (2005).
- ³⁰H. Gharibi, S. M. Hashemianzadeh, and B. M. Razavizadeh, *Colloids Surf., A* **196**, 31 (2002).
- ³¹M. Zaldivar and R. G. Larson, *Langmuir* **19**, 10434 (2003).
- ³²G. S. Grest and K. Kremer, *Phys. Rev. A* **33**, 3628 (1986).
- ³³G. K. Bourov and A. Bhattacharya, *Bull. Am. Phys. Soc.* **50**, 556 (2005).