Functional Langevin models for the mesoscopic dynamics of surfactant aggregation in solution

B. A. C. van Vlimmeren, M. Postma, P. Huetz, A. Brisson, and J. G. E. M. Fraaije
BIOSON Research Institute & Groningen Biomolecular Sciences and Biotechnology Institute, Department of Biophysical Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
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We discuss a time-dependent potential model for the simulation of surfactant aggregation in solution. The numerical model is derived from a generalization of time-dependent Ginzburg-Landau theory for conserved order parameters. An element in our coarse-grained approach is that we retain important aspects of molecular detail by inclusion of single-chain density functionals. Representative results of simulations of concentrated dioctadecylamine solutions are discussed. We find that multicomponent coarse-grained simulations are indeed feasible, and may increase our understanding of a wide variety of mesoscopic aggregation processes in complex surfactant solutions. A conspicuous result is that thermal fluctuations greatly influence the formation of the aggregate structures. [S1063-651X(96)12811-7]

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I. INTRODUCTION

Functional Langevin models offer a natural way to describe slow diffusive and hydrodynamic mesoscale phenomena in many complex fluids [1–5]. A general Z-component evolution equation for coarse-grained diffusive relaxation of conserved order parameters is

$$\frac{\partial \rho_I(\mathbf{r})}{\partial t} = \sum_{J=1}^{Z} \int_V \mathcal{D}_{IJ}(\mathbf{r},\mathbf{r}_1)\mu_J(\mathbf{r}_1)d\mathbf{r}_1 - \beta^{-1}\sum_{J=1}^{Z}\int_V \frac{\delta \mathcal{D}_{IJ}(\mathbf{r},\mathbf{r}_1)}{\delta \rho_J(\mathbf{r}_1)}\, d\mathbf{r}_1 + \eta_I(\mathbf{r},t),$$
$$\mathcal{D}_{IJ}(\mathbf{r},\mathbf{r}_1) = \boldsymbol{\nabla}_{\mathbf{r}} \cdot \Lambda_{IJ}(\mathbf{r},\mathbf{r}_1)\boldsymbol{\nabla}_{\mathbf{r}_1}, \tag{1}$$

with spatial vectors $\mathbf{r}$ and $\mathbf{r}_1$, particle concentration fields $\rho_I(\mathbf{r})$ $(I=1,\ldots,Z)$, transport coefficients Λ_{IJ}, intrinsic chemical potentials $\mu_I(\mathbf{r}) \equiv \delta F/\delta \rho_I(\mathbf{r})$ (F is the free energy), and noise fields $\eta_I(\mathbf{r},t)$. $\beta^{-1}=k_BT$. The first term is the systematic diffusion, the second term counterbalances spurious drift, and the third term introduces thermal fluctuations into the system. The noise has a Gaussian distribution with moments dictated by the fluctuation-dissipation theorem [6,7]. This model is a generalization of model **B** [4,8].

In the cited papers [1–5,8] and references cited therein, one can find numerous examples of computer simulations of time-dependent Ginzburg-Landau models for two-component incompressible liquids with linear transport coefficients and relatively simple fourth-order phenomenological expansion models for the free energy. The goal of mesoscopic modeling would be a theory of ordering phenomena in complex fluids, based on an atomic description and including molecular shape, packing effects, and charges. We use a free energy functional, derived for a collection of Gaussian chains in a mean-field environment. In this approach we try to retain as much as possible of the underlying molecular detail, i.e., the architecture and composition of the chain molecules are important. To this end, we do not use an expansion of the free energy in the order parameters, as is commonly done in Ginzburg-Landau models, but rather use a single chain inverse density-functional description for the chemical potentials. Previously, we studied the random term [9], the Gaussian chain density functional [10], and the relation with fourth-order expansions [11]. Some results of numerical calculations of phase separation in block copolymer melts are discussed in Ref. [12].

In this paper we present an application of the method to the aggregation processes in surfactant solutions. A few representative results of simulations in two dimensions (2D) are presented. Since the present version of the model neglects hydrodynamic effects, we discuss concentrated surfactant solutions only. The particular system we studied is an aqueous solution of dioctadecylamine [DODA, $(C_{18}H_{37})_2NH$]. This surfactant is a precursor for soft templates in (membrane-)protein crystallization [13,14]. The comparison with the experimental data [14] shows that the particular density functional we have chosen needs further improvement to describe the strong liquid crystalline-type ordering in surfactant membranes, especially with respect to chain-chain correlations. Nevertheless, our main conclusion is that the inclusion of molecular detail in functional Langevin models via density-functional methods is in principle possible. This may lead to the description of a wide variety of interesting mesoscale phenomena in self-assembling systems. In addition, it seems that thermal fluctuations greatly influence the aggregate structures.

II. MODEL DESCRIPTION

We study a system with volume V containing n_S solvent molecules and n_D surfactant molecules. Each surfactant molecule is defined as a triblock copolymer Gaussian chain, with composition $T_{N_T}H_{N_H}T_{N_T}$ (total number of beads $N=2N_T+N_H$), where T is a ''tail'' and H is a ''head'' bead. We assume for simplicity that the system is incompressible and that the bead volumes of the chain and the molecular volume of the solvent molecules are the same, i.e.,

$$\rho_T(\mathbf{r})+\rho_H(\mathbf{r})+\rho_S(\mathbf{r})=\nu^{-1}, \tag{2}$$

where ν is the average volume that is available per bead. The subscript denotes tail beads (T), head beads (H), or solvent molecules (S). We assume furthermore that the dynamics is controlled by a local exchange mechanism and that the mobilities M of the beads and solvent molecules are identical. In this case, the spurious drift term is zero and the general Langevin model Eq. (1) reduces to three coupled stochastic partial differential equations (omitting space and time coordinates):

$$\frac{\partial \rho_I}{\partial t} = \sum_J \nabla \cdot \Lambda_{IJ} \nabla \mu_J + \eta_I, \tag{3}$$

where $I,J = H$, T, or S. The kinetic coefficients are (in matrix notation)

$$\mathbf{\Lambda} = M\nu \begin{pmatrix} \rho_T(\nu^{-1}-\rho_T) & -\rho_T\rho_H & -\rho_T\rho_S \\ -\rho_H\rho_T & \rho_H(\nu^{-1}-\rho_H) & -\rho_H\rho_S \\ -\rho_S\rho_T & -\rho_S\rho_H & \rho_S(\nu^{-1}-\rho_S) \end{pmatrix}, \tag{4}$$

where M is the mobility coefficient. The thermal noise is

$$\eta_I = \nabla \cdot C_{IJ} \mathbf{w}_J, \tag{5}$$

where $\mathbf{w}_J$ are Gaussian distributed random vector fields

$$\langle w_{Jx_j}(\mathbf{r},t) \rangle = 0, \tag{6}$$

$$\langle w_{Jx_i}(\mathbf{r},t) w_{Jx_j}(\mathbf{r}_1,t) \rangle = \delta(t-t')\,\delta(\mathbf{r}-\mathbf{r}_1)\,\delta^K_{IJ}\delta^K_{ij}, \tag{7}$$

where $x_i = x,y,z$. The noise correlation coefficients C_{IJ} are related to the kinetic coefficients via

$$\mathbf{C}\mathbf{C}^T = 2\beta^{-1}\mathbf{\Lambda}. \tag{8}$$

The application of the fluctuation-dissipation theorem and the numerical calculation of the random fields are discussed further in [9].

The intrinsic chemical potentials are obtained by a density functional argument for a collection of ideal Gaussian chains in a mean-field environment. Basically, the idea is that on a coarse-grained time scale the collective statistical distribution function Ψ of all surfactant and solvent molecules is such that the free energy functional $F[\Psi]$ is minimal in each time interval, given the spatially varying density pattern. The variation of the free energy with respect to the distribution function Ψ, under the constraint that the statistical average of the microscopic density operators is the reference density pattern, leads directly to an expression for the intrinsic chemical potentials. A detailed analysis of the application of the method to copolymer melts can be found in [12]; here we summarize the results for surfactant solutions. The chemical potentials are defined by

$$\mu_I(\mathbf{r}) \equiv \frac{\delta F}{\delta \rho_I(\mathbf{r})} = -U_I(\mathbf{r}) + \sum_J \int_V \epsilon_{IJ}(|\mathbf{r}-\mathbf{r}_1|)\rho_J(\mathbf{r}_1)d\mathbf{r}_1, \tag{9}$$

where the $\epsilon_{IJ}(|\mathbf{r}-\mathbf{r}'|)$ are mean-field interactions between component I and J. The external potentials $U_I(\mathbf{r})$ are related to the density fields through a bijective density-functional relation [12]. For the solvent molecules with no internal structure this is a simple normalized Boltzmann weight:

$$\rho_S[U_S](\mathbf{r}) = n_S \frac{e^{-\beta U_S(\mathbf{r})}}{\int_V e^{-\beta U_S(\mathbf{r})} d\mathbf{r}}. \tag{10}$$

The corresponding single chain density functional of the surfactant molecules relates the two external fields $U_T(\mathbf{r})$ and $U_H(\mathbf{r})$ to the two density fields $\rho_T(\mathbf{r})$ and $\rho_H(\mathbf{r})$. For example, the density functional for the head beads reads

$$\rho_H[U_T,U_H](\mathbf{r}) = n_D \sum_{s=1}^{N} \delta^K_{Hs} \frac{\int_{V^N} f_B \delta(\mathbf{r}-\mathbf{R}_s) d\mathbf{R}_1 \cdots d\mathbf{R}_N}{\int_{V^N} f_B d\mathbf{R}_1 \cdots d\mathbf{R}_N}, \tag{11}$$

where the Kronecker delta δ^K_{Hs} is 1 when bead s is of the head type and 0 otherwise. The Boltzmann factor is given by

$$f_B \equiv \exp\left\{ -\frac{3}{2a^2} \sum_{s'=2}^{N} (\mathbf{R}_{s'} - \mathbf{R}_{s'-1})^2 - \beta \sum_{s'=1}^{N} U_{s'}(\mathbf{R}_{s'}) \right\}.$$

$\mathbf{R}_s$ is the position of bead s and a is the Gaussian bond length parameter. The expression for the tail functional is similar.

At this point, the mean-field kernel is still unspecified. Since the statistical units of the chain molecules each sample a volume $\sim a^3$, we use a Gaussian kernel with width a [12]:

$$\epsilon_{IJ} = \epsilon^0_{IJ} \left(\frac{3}{2\pi a^2} \right)^{3/2} e^{-(3/2a^2)(\mathbf{r}-\mathbf{r}_1)^2}.$$

The diffusion equations together with the density functionals and the expression for the mean-field form a closed set, which can be solved efficiently by a finite difference method on a cubic mesh [12,15]. There are six dimensionless parameters in the numerical calculations: the dimensionless time $\tau = \beta^{-1} M h^2 t$, the noise scaling parameter $\Omega = \nu^{-1} h^3$ (the variance of the dimensionless noise scales with $\Delta\tau/\Omega$, where $\Delta\tau$ is the time step), the ratio $a h^{-1}$ of bond length a and of mesh size h, and three exchange interaction parameters χ_{HT}, χ_{HS}, and χ_{TS}, where $\chi_{IJ} = (\beta\nu^{-1}/2)[\epsilon^0_{IJ} + \epsilon^0_{JI} - \epsilon^0_{II} - \epsilon^0_{JJ}]$.

III. RESULTS AND DISCUSSION

We used a $T_8H_3T_8$ Gaussian chain as the model for DODA. The chain was selected using a simple fitting procedure, where we compared the single-chain Gaussian chain two-body correlation functions with the corresponding functions from a force field molecular model of DODA. The functions of the Gaussian chain were calculated analytically with the random-phase approximation method [16]. The correlator functions for the molecular model were calculated by a Monte Carlo method ($T = 298$ K), using the GROMOS force field [17]. The fit consists of matching the minima of the inverse structure factors in Fourier space of the molecular model and the Gaussian chain. A good fit was obtained by representing 16 carbon atoms of each tail of the molecular model by 8 beads in each tail of the Gaussian chain; the amine head and on each side two adjacent carbon atoms are represented by the three head beads. The fitted bond length parameter of the Gaussian chain is $a = 0.58$ nm. We will

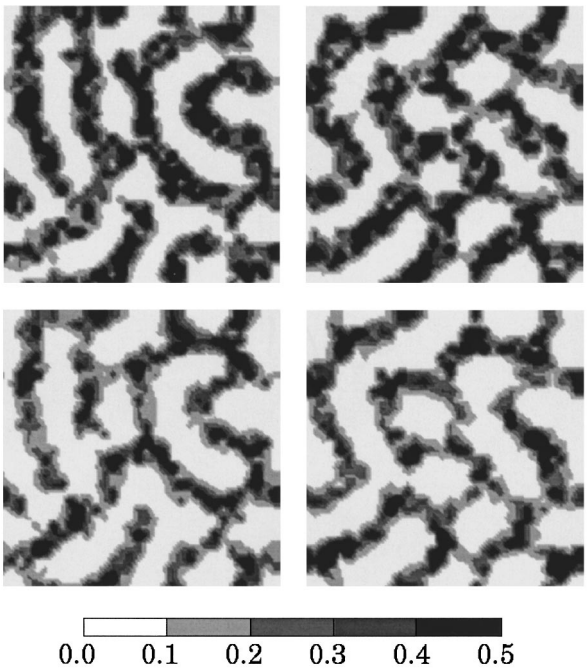

FIG. 1. Time-dependent morphologies of concentrated surfactant in solution (90% v/v dioctadecylamine in 10% v/v water), $\tau=5000$ (left) and $\tau=10\,000$ (right). Concentration of heads (upper) and solvent (lower). The noise level parameter $\Omega=2.1$. This is the value determined by the fluctuation dissipation theorem.

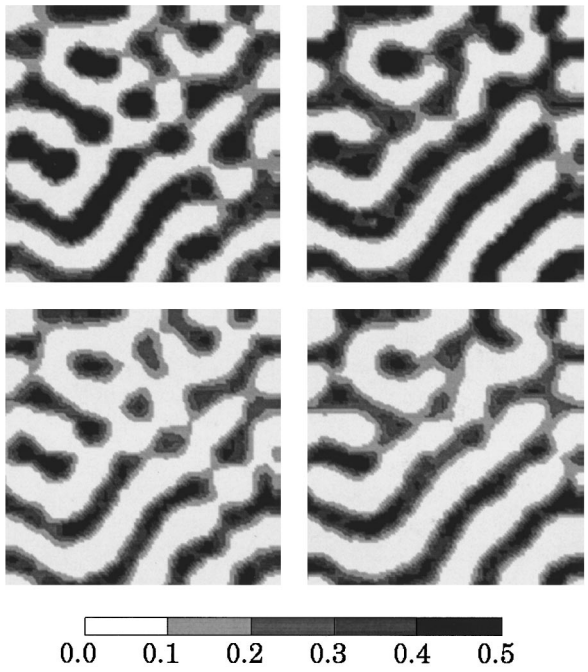

FIG. 2. As Fig. 1, except with $\Omega=52.5$.

discuss the fitting procedure in more detail elsewhere.

For the interaction parameters we used $\epsilon_{II}^{0}=0$, $\nu^{-1}\epsilon_{HT}=\nu^{-1}\epsilon_{WT}=10$ kJ mol^{-1}, and $\nu^{-1}\epsilon_{HS}=-3$ kJ mol^{-1}, corresponding to effective exchange interactions of only a few k_BT: $\chi_{HT}=\chi_{WT}=4$, $\chi_{HS}=-1.2$. The molecular volume parameter was estimated from the density of pure *dioctylamine* (0.8 g cm^{-3}) [18] as $\nu=0.057$ nm^3. The mesh width in the simulations is $h=0.5$ nm.

In Figs. 1 and 2, we present the results of two simulations, each system containing 90% v/v surfactant and 10% v/v solvent. We neglected the gradients in one direction and used a relatively small system of 32^2 grid points [15]. In Fig. 1 are the results of calculations using the nominal values of the noise scale parameter $\Omega=2.1$ (corresponding to the value $\nu^{-1}h^3$ as prescribed by the fluctuation dissipation theorem) and Fig. 2 shows the results using a five times reduced noise level (setting $\Omega=52.5$). We can roughly estimate the ''real'' time span in the simulations with the Stokes-Einstein relation for the diffusion coefficient $\beta^{-1}M$. Since in the concentrated surfactant solution the local viscosity will be much larger than 10^{-3} kg m^{-1} s^{-1} (the viscosity of water) one unit of τ is $\gg 1$ μs.

In both figures we observe the formation of disordered lamellae and various micellar aggregates, where the level of disorder is considerably larger in Fig. 1 with large fluctuations of the surfaces and of membrane thickness. There are a number of important results. First, the lamellar structures in the full noise simulation continuously break up and form again, thereby reducing the average size of the aggregates. Second, the solvent is in all cases closely associated with the head beads: no isolated solvent droplets can be found. Third, in the absence of solvent no stable microphases are formed with the chosen head-tail interaction parameters (simulation results not shown). Thus, the presence of a relatively small amount of solvent leads to an increase in the effective repulsion between apolar and polar parts of the surfactant molecules: in the microphase separated system, the heads protect the solvent from energetically unfavorable contacts with the tails. Finally, it should be stressed that it takes a very long time to reach fluctuation equilibrium of the collective structures. In fact, from further extensive simulations of this and similar systems in 2D and also in 3D (data not shown) we found invariably that after some time the system locks into a certain metastable arrangement of aggregate structures, from which it is difficult to escape. The effect is more pronounced if the level of the noise is lower. In the complete absence of thermal fluctuations the system would very quickly freeze into a metastable state. The abundant occurrence of metastable states in self-assembly systems is well known in the experimental literature [19]. The same type of phenomenon is also observed in the experimental data on DODA aggregation [14].

Since the level of the noise is an important factor in the aggregate formation, it is illustrative to estimate the most effective value of the noise scale parameter Ω. In the present simulations, where all beads and solvent molecules have the same size, the fluctuation dissipation theorem demands that $\Omega=\nu^{-1}h^3$. But in the real experimental system the molecular volume of solvent is somewhat smaller than the molecular volumes of the statistical units of the chain molecule. A better parametrization for the noise scale parameter could be $\Omega_{\mathrm{eff}}\approx\nu_S^{-1}h^3=4.2$, since the fluctuations are most dominant in the regions where the solvent concentration is relatively high (interfaces and bulk solvent). This would imply that the actual influence of the noise is likely to be smaller than suggested by the full noise calculation (Fig. 1), but not so small as in the reduced noise calculation (Fig. 2).

Comparison with experimental results is difficult, since all of the experimental data in [14] refer to dilute solutions. Electron micrographs show that in aqueous solutions DODA

self-assembles into square- and rectangular-shaped plates or even stacks of lamellae, depending on processing conditions. The data further suggest that the ordering of the hydrophobic tails is rather strong, almost crystallinelike. Here, we have used a single-chain density functional in a mean-field approach, and as a consequence the strong ordering effects cannot be reproduced well: the mean-field approximation for chain-chain correlations is obviously not very good for strongly ordered materials. Since the Gaussian chain model has no energetic bending terms, the molecules in our simulation are more flexible than a hydrocarbon chain. The width of the lamellae in the simulations is ~ 2 nm, which indicates that the tails of the Gaussian chain are considerably disordered. This is not in agreement with the experimental findings.

We conclude that in a qualitative sense the simulations reproduce several important aspects of aggregate formation in concentrated surfactant solutions, i.e., the effect of added solvent on the aggregate structures, and the formation of metastable states. In addition the simulations show a strong influence of the thermal noise. The accurate reproduction of crystallinelike ordering of tails is in the present model difficult to achieve, unless we find a better way to include the chain-chain correlations. It is easy to change the parameters of the Gaussian chain density functional in such a way that more complex mixtures in 2D and 3D can also be studied. We are currently investigating the application of the method to solutions of long flexible polymer surfactants that do not have crystallinelike ordering properties. In this case the mean-field approximation is much better.

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