Effects of confinement on self-assembling systems

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Abstract

Systems in which particles can self-assemble into mono- or bilayers can form variety of stable and metastable structures on a nanometer length scale. For this reason confinement has a particularly strong effect on such systems. We discuss in some detail effects of confinement on lamellar and cubic phases with double-diamond structure. Structural deformations in slit geometry are described for large and small unit cells of the structure (in units of the thickness of the monolayer) and for various strengths of interactions with the confining surfaces. We show how the structural changes of the confined fluid are reflected in the measurable solvation force between the confining walls.

KEY WORDS: Surfactant solution; microemulsions; membrane; lattice model; phase transitions; density profile; surface phenomena; confined system; solvation force.

I. INTRODUCTION

Confinement plays a significant role when the size of the system becomes comparable to a typical length characterizing the structure of the confined fluid. Usually the typical length is related to an average distance between particles, and the effects of confinement manifest themselves in systems whose sizes are of order of several molecular diameters. The characteristic lengths, such as the correlation length, become large close to phase transitions, and in such cases the effects of confinement are found in much larger systems. Large typical lengths, often two orders of magnitude larger than the molecular sizes, characterize the structure in self-assembling systems. The typical length \( \lambda \) corresponds to the size of correlated domains (for example micelles or lamellae) and is reflected in the form of correlation functions. On the length scale set by \( \lambda \) the domains play a similar role as particles on the molecular length scale. Because of the presence of the structure on the nanometer length scale, the finite size effects are expected for system sizes two or three orders of magnitude larger than in simple fluids, even far from phase transitions.

Bulk phase diagrams in self-assembling systems are very rich due to stability of liquid-crystalline phases with different symmetry. Because phases with different structure, symmetry and characteristic length are stable or metastable in the bulk, the structure of the confined system may depend significantly on the size and shape of the container. The increase of the free energy of the stable or metastable phase, which is associated with structural
deformations induced by the confinement, is much larger if the bulk structure is strongly incompatible with the shape and the size of the container. As a result it may happen that the structure of the confined system is significantly different (for example has a different symmetry) than the structure of the bulk phase, because some phase which is metastable in the bulk may become stable in the confinement, if its structure fits better the geometry of the system. Such phenomenon resembles capillary condensation in simple fluids.

To summarize, we note that the structure on the nanoscale in the self-assembling systems can play a role analogous to the structure on the microscale in simple fluids, therefore one can expect similarities between properties of the confined complex fluids on the nanoscale and properties of confined simple fluids on the microscale. On the other hand, various stable and metastable phases with quite different structures are present in the bulk self-assembling systems, in contrast to the simple fluids. This difference between the complex and the simple fluids may result in variety of phenomena in confined self-assembling systems which in confined simple fluids are absent.

II. SELF-ASSEMBLING SYSTEMS

In the systems containing amphiphilic particles (lipids, surfactants, copolymers) one observes a spontaneous formation of phases exhibiting a short- or a long-range order on a length scale one or two orders of magnitude larger than the size of the amphiphiles. Amphiphilic molecules are typically elongated, and their two ends are of quite different nature. One end is polar, whereas the other one is non-polar and typically consists of a hydrocarbon chain. When the amphiphiles are dissolved in a polar or a non-polar solvent, then a self-assembly of amphiphiles into bilayers takes place. This end of the amphiphile, which is repulsed by the solvent, is hidden inside the bilayer, by which the contacts between the polar and non-polar particles and particle parts are avoided. Mixtures of polar and non-polar liquids, such as water and oil, phase separate at room temperatures. Amphiphiles added to such mixtures self-assemble into monolayers, separating the oil- and water-rich regions. The polar (non-polar) end of the amphiphiles forming the monolayer is oriented towards the polar (non-polar) solvent (Fig. 1). Again, in ternary mixtures the unfavorable contacts between the polar and non-polar particles or particle parts are avoided when the self-assembly into monolayers occurs. Both the bilayers and the monolayers can assume various shapes (Fig. 1). The surface describing the center of the bilayers or monolayers can be closed as in micelles or inverse micelles, or not, as in lamellar and bicontinuous phases. The latter phases are formed if there is no appreciable asymmetry with respect to the shapes and interactions between the two different parts of amphiphiles. In the lamellar phases the monolayers and bilayers fluctuate around their average positions, described by flat, parallel surfaces. In the bicontinuous phases short- or long-range order is present on the length scale set by the size of the water-rich domains. In the sponge-phase or in the microemulsion the actual monolayers are described by surfaces characterized by very large and negative Euler characteristics [1], but their average positions are not localized. The presence of the structure on the mesoscopic length scale is reflected only in the form of the water-water density correlation function [2]\(\lambda\). This correlation function exhibits a damped oscillatory behavior with the period of oscillations \(\lambda\) related to the size of the water-rich domains. Its form for distances \(r/\lambda > 1\) resembles the density-density correlation function in simple fluid
fluids for $r/\sigma > 1$, where $\sigma$ is a microscopic length comparable to the size of molecules. For $r/\lambda < 1$ the shape of the correlation functions in microemulsion and sponge phases is different than in simple fluids for $r/\sigma < 1$, and reflects the fact that the domains are soft and compressible rather than rigid. Hence on the mesoscopic length scale the water-rich domains play a role analogous to particles on the molecular length scale, except that the domains are soft rather than rigid and under an external stress can change their shape and volume. There also exist bicontinuous structures exhibiting a long-range order [4,5]. In such phases the surfaces describing the average position of the centers of bilayers or monolayers are periodic, that is a certain unit cell is infinitely repeated in space. An example of such unit cell is shown in Fig.2 for the double-diamond (D) phase.

The self-assembly of amphiphiles into bilayers or monolayers, which then assume different shapes on the mesoscopic length scale, occurs in a large class of systems. The details of inter-particle interactions in different systems exhibiting self-assembly can be quite different. Despite these differences remarkable similarity between properties of all such systems can be observed, provided that one end of the solute particles (i.e. amphiphiles) attracts polar and repulses non-polar particles, whereas the other end does the opposite. This property of the interactions is necessary and sufficient for self-assembly into bilayers or monolayers if the amphiphilic interactions are sufficiently strong, and the other details of the interactions are irrelevant for the structure formation on the mesoscopic length scale and for other properties common for all self-assembling systems, such as the very low surface tension between some of the phases. The features common for the whole class of the self-assembling systems are also shared by the members of the class in which the inter-particle interactions are particularly simple. The universal properties of the self-assembling systems should be described by generic models in which the irrelevant details of the interactions are just disregarded. Here we use the generic model introduced by Ciach, Høye and Stell (CHS) [6] to study the universal effects of confinement.

III. MODEL

The CHS model [3] was introduced for description of balanced ternary systems. In such systems symmetric amphiphiles form monolayers with vanishing spontaneous curvature and the volume fractions of oil and water are equal. The model can be easily generalized for unbalanced systems. In particular binary water-surfactant mixtures can be described by a generalized version of the CHS model. Here we concentrate on the case with the highest symmetry. We assume a symmetry with respect to a replacement of the polar particles and particle parts by non-polar particles and particle parts and vice versa. It means that if all the amphiphiles change their orientations into the opposite ones and simultaneously water particles replace the oil particles and vice versa, the energy of the system is unchanged. In the simplest case the model is defined on a simple cubic lattice and close packing is assumed. The length unit is set by the lattice constant $a$, assumed to be equal to the length of the amphiphile. Each lattice cell can be occupied by either a water, an oil or a surfactant particle. Different orientations of the latter are treated as different components having the same chemical potential. A typical configuration is shown in Fig.3. Non-vanishing interactions are determined by the polar-nonpolar symmetry and by the interactions shown in Fig.3. We assume nearest-neighbor interactions. In the simplest version of the model, except from the
water-water (oil-oil) interaction $-b$ only the water-amphiphile (oil-amphiphile) interaction $-c\Delta r \cdot \hat{u} (+c\Delta r \cdot \hat{u})$ is assumed, with $\hat{u}$ describing the orientation of the amphiphile located at the distance $\Delta r$ from the water (oil) particle. In the extended model one assumes in addition the amphiphile-amphiphile interaction $g[(\hat{u} \times (r' - r)) \cdot (\hat{u'} \times (r - r'))]$, where $\hat{u}$ ($\hat{u'}$) is the orientation of the amphiphile located at $r$ ($r'$). The above interaction supports formation of flat monolayers, with amphiphiles parallel to each other and perpendicular to the surface they occupy. If $g \neq 0$, the stability region of the lamellar phase enlarges.

The CHS model can be further simplified if one requires that $\hat{u}$ is reduced to $\pm \hat{e}_i, i = 1, \ldots, d$, where $\hat{e}_i$ are the unit lattice vectors. If only one dimensional lamellar phase is stable for given thermodynamic conditions, then $\hat{u}$ can be projected onto the direction $\hat{n}$ perpendicular to the lamellae (from water towards oil). In this case one can distinguish two states of amphiphiles, one with $(\hat{u} \cdot \hat{n}) > 0$, the other one with $(\hat{u} \cdot \hat{n}) < 0$.

The model is relatively simple and can be considered as a generic, semi-microscopic model for the self-assembling systems. Having the property that one end of the solute (amphiphilic) particles attracts water and repulses oil and the other one does the opposite, the model is a member of the class of the self-assembling amphiphilic systems and can reliably describe those properties which are shared by all the members of this class. Although quite simple, the model can be solved exactly only in one-dimensional systems. Therefore a mean-field (MF) approximation has been applied for studying the bulk phase behavior and structure of various phases. Fluctuations that are left out from the MF calculations can change the quantitative results. Fluctuation-induced first-order phase transitions can occur instead of continuous transitions found in the MF approximation. Moreover, fluctuations can destroy the order. Monte Carlo simulations performed for some other models of self-assembly show however that the regions of stability of the ordered phases shrink in the presence of fluctuations, but the ordered phases do not disappear. Thus, the MF approximation gives qualitatively correct phase diagrams for such complex systems.

The MF Hamiltonian for the CHS model has the form

$$H^{MF} = \sum_r \sum_{i=1}^{2+2d} \phi_i(r) \left( \hat{\rho}_i(r) - \frac{1}{2} \rho_i(r) \right) - \mu \left( \hat{\rho}_1(r) + \hat{\rho}_2(r) \right),$$

where $\hat{\rho}_i(r)$ is the microscopic density such that $\hat{\rho}_i(r) = 1(0)$ if the site $r$ is (is not) occupied by the specie $i$, where $i$ refers to water, oil and surfactant in different orientations. $\rho_i(r)$ is the equilibrium density of the state $i$ at $r$. The $u_{ij}(r - r')$ is the described above interaction energy between the specie $i$ at $r$ and the specie $j$ at $r'$. Probability distribution for $\hat{\rho}_i(r)$ is given by the Boltzmann factor $P^{MF} \propto e^{-H^{MF}}$, where $\rho_i(r)$ are to be found by solving self-consistent set of equations $\rho_i(r) = \langle \hat{\rho}_i(r) \rangle_{MF}$, where $\langle \ldots \rangle_{MF}$ means averaging with $P^{MF}$. Self-consistent solutions of the above equations are equivalent to finding local minima of

$$\Omega^{MF} = \frac{1}{2} \sum_{r, r'} \sum_{i,j=1}^{2+2d} u_{ij} (r - r') \rho_i(r) \rho_j(r')$$

$$+ \sum_r \left\{ kT \sum_{i=1}^{2+2d} \rho_i(r) \ln \rho_i(r) - \mu \left( \rho_1(r) + \rho_2(r) \right) \right\}.$$  

(3)
The stable structure is identified with the global minimum of $\Omega^{MF}$.

The CHS model predicts stability and coexistence of various phases in the bulk. Already in its simplest, one dimensional version oil-rich, water-rich, microemulsion and lamellar phases can be stable. The lamellar phases range from phases with short periods (high surfactant concentration) to highly swollen phases. When 6 orientations of amphiphiles, corresponding to $\pm \hat{e}_i$, $i = 1, 2, 3$ are allowed, then a cubic bicontinuous phase D with double-diamond symmetry is stable in addition to the above mentioned phases. For continuous $\hat{u}$ also cubic G (gyroid), P (simple cubic) and close-packed micelles and reverse micelles occur. Because of the rich phase behavior and relative simplicity of interactions, the model can be applied for studying the effects of confinement on the microemulsion, lamellar and cubic phases. The results obtained within the MF approximation for the lamellar and the D phases are described below.

**IV. SLIT GEOMETRY**

We will focus on two parallel walls between which the system under consideration is confined. We assume that the distance $L$ between the walls is small i.e. $L^2 \ll A$, where $A$ is the area of each wall (Fig. 4). The grand thermodynamic potential of the confined system has the form

$$\Omega = \omega_b AL + \Omega_{ex},$$

where $\omega_b$ is the bulk grand-thermodynamic potential density, and where $\Omega_{ex}$ is the excess potential due to the presence of the confining walls. The confinement leads to additional terms in $d\Omega$, which for the slit geometry is given by

$$d\Omega = -SdT - Nd\mu - pdV + 2\sigma dA - f dL,$$

where $\sigma$ is the wall-fluid surface tension, and $fA$ is the force which has to be applied externally to keep the walls at the distance $L$,

$$f = -\frac{1}{A} \left( \frac{\partial \Omega}{\partial L} \right)_{\mu,T,A} - p = -\frac{1}{A} \left( \frac{\partial \Omega_{ex}}{\partial L} \right) = f_{ww}(L) + f_s(L, \mu, T).$$

The $f$ consists of the direct force between the walls, $f_{ww}$, present for $L$ comparable to a range of intermolecular interactions, and of the solvation force, $f_s$, induced by the confined fluid. In simple fluids the solvation force reflects packing effects of particles. When in the confined liquid the average distance between particles is larger (smaller) than in the bulk, then attraction (repulsion) between the confining walls results, since the confined fluid tends to assume the equilibrium bulk structure. When the wall separation increases and the average distance between particles starts to exceed 1.5 times the bulk equilibrium distance, a new layer of particles is introduced into the slit and the attractive solvation force abruptly changes into the repulsive one. Due to the analogy between the particles on the microscale and the water-rich domains on the mesoscale, similar packing effects of domains can be expected on the length scale set by the size of the domains. As the size of the domains is $\propto 10 - 100$ nm, the packing effects of domains should lead to oscillating
solvation force (repulsive for compressed domains and attractive for expanded domains) for quite large separations between the confining walls, even up to micrometers. On the other hand, one cannot expect complete analogy between the confined self-assembling system on the mesoscale and the confined simple fluid on the microscale. An important difference between the simple fluid on the microscale and the self-assembling system on the mesoscale is the presence of variety of stable and metastable phases with different symmetries and sizes of the unit cell in the latter. As we show later, a symmetry of the ordered phases plays a very important role for the form of the solvation force. Also, various deformed structures can occur, since the domains are flexible and can change the shape and volume, unlike the particles, which are rigid and of a fixed size.

V. CONFINED LAMELLAR PHASES

A. strongly hydrophilic walls

Walls which are strongly hydrophilic attract polar particles or particle parts. Therefore either a water-rich or an amphiphilic layer is adsorbed near each wall, by which the orientation of the subsequent layers is fixed. One can expect that the average densities of all the components are constant in the planes parallel to the confining walls and the density profiles $\rho_i(z)$ depend only on a distance $z$ of one arbitrarily chosen wall, say the left one. [Later we show that this assumption is wrong in the case of lamellar phases with very short periods.] Because the orientation of the lamellae is fixed, one can consider the simplest version of the CHS model, with only 4 states, namely water, oil and surfactant with the head or the tail oriented towards the left wall. The interactions between the $i$-th component and the wall are assumed to be the same as between the $i$-th component and water. In fact we consider water-covered walls.

1. swollen lamellar phases

The swollen lamellar phases confined between strongly hydrophilic walls have been studied experimentally by the surface force apparatus (SFA) measurements [10–15]. The results of the experiments show that for the distance between the walls $L \geq 5\lambda$, where $\lambda$ is the period of the bulk lamellar phase, the film responds elastically to the applied stress. For $N$ periods of the lamellar phase the confined fluid behaves in the same way as a series of $N$ joint identical springs with low elastic modulus. Such behavior was observed for different substances, and should be thus reproduced in any generic model of self-assembling systems.

We begin our study of the effects of confinement on the self-assembling systems by considering the swollen lamellar phases confined between parallel hydrophilic walls. This will serve as a test of the applicability of the CHS model for confined water-oil-surfactant mixtures. We choose model parameters such that the period of the bulk phase in the units of the thickness of the monolayer, $a$, is $\lambda \approx 10$ [16], since it is in the same range as the periods in the experimentally studied systems (in the same physical units) [13]. The excess thermodynamic potential per unit area, $\Omega_{ex}/A$, and the solvation force, $f$, obtained for $\lambda = 13$ in Ref. [16] are shown in Fig.5. For $L = L_N = N\lambda + \lambda/2 + 1$ (in $a$ units) the
\( \Omega_{ex} \) assumes minima, which correspond to \( N \) lamellar layers confined between the walls, and the period in the confined system is the same as in the bulk equilibrium. For \( L \neq L_N \) the periods of the confined and the bulk phase are different at the same thermodynamic conditions. We should stress that in the case of the swollen lamellar phases the water (and oil) rich layers are sufficiently thick to be compressible in a way similar to the bulk fluid. This fact corresponds to metastability of lamellar phases with different periods (different thicknesses of the water- and oil-rich layers) in the bulk. The metastable phases become stable under external stress, i.e. between the parallel walls a distance \( L \neq L_N \) apart. When the slit is expanded, \( L_N \to L_N + \Delta L \), then a new lamellar layer is introduced into the slit for \( \Delta L > \lambda/2 \), and the attractive solvation force abruptly changes into the repulsive one (see Fig. 5.b).

For large separations between surfaces (\( N > 4 \)) the second derivative of \( \Omega_{ex} \) with respect to \( L \), calculated at \( L = L_N \), \( B = \Omega''_{ex}(L_N) \), is well approximated by a straight line \( B = \bar{B}/L_N \) as a function of \( 1/N \) (see Fig. 6), where \( \bar{B} \) is a modulus of compressibility. Hence the response of the system to compression or decompression is elastic, and analogous to the behavior of a series of identical joined springs. \( \bar{B} \) as a function of \( P = \lambda/2 \) for a three-dimensional system is shown in Fig. 7 (open circles) together with the phenomenological curves [17] for two values of a membrane rigidity, \( \kappa \), between which the results are located [16]. The phenomenological curves are obtained for a lamellar phase modeled as a stack of elastic, undulating membranes with the bending elastic modulus \( \kappa \). The membranes represent surfactant monolayers. The discrepancy between the results of the CHS and the membrane models results probably from deformations, such as passages or droplets, neglected in the latter case. The agreement with experiments [13], on the other hand, is very good. We obtain semi-quantitative agreement between the model and the experimental results once the periods of the bulk phase in units of the thickness of the monolayer are the same in the two cases [16]. Note that the model parameters are chosen such that the bulk structures in the model and experiment agree, and then no parameters are fitted in the case of the confinement.

For the surface separations for which the number of adsorbed layers is \( N \leq 3 \), the stretch strain of layers releases by formation of the uniform water-rich film for \( N = 1, 3 \) (see Fig. 8a), and oil-rich film for \( N = 2 \) (see Fig. 8b) in the middle of the slit. The formation of the uniform films inside the slit is reflected in the saturated-like behavior of \( \Omega_{ex} \) and considerably low \( f \) for the corresponding surface separations. For such separations the central, uniform layer grows and the near-surface lamellar structure remains unchanged when the slit is expanded. The growth of the uniform water- or oil-rich central layer is not accompanied by the elastic response. Note that for \( L < 5\lambda \) removing one layer, \( L \to L - \lambda \), results in a large deformation, that is \( \lambda \to \lambda + \Delta \lambda \) with \( \Delta \lambda/\lambda > 20\% \). On the other hand, the swollen lamellar phases are stable close to the coexistence with the uniform water-/oil-rich phases (water-oil symmetry was assumed). Close to the coexistence the bulk density of the grand thermodynamic potential in the stable lamellar phase and the metastable oil- or water-rich phases are only slightly different. Moreover, the surface tension between the uniform and the swollen lamellar phases is very low. Thus, when the near-surface lamellar films have the same structure as the bulk phase, the cost of nucleation of a uniform layer in the center of the slit is lower, than the elastic-energy cost associated with large deformation, \( \Delta \lambda/\lambda > 20\% \), of the lamellar structure throughout the whole slit.
2. Short-period lamellar phases

The short-period lamellar phases are stable for rather high surfactant concentration. The water- and oil-rich layers are thin in this case, and do not behave as the bulk fluid layers, in contrast to the layers in the swollen lamellar phases. When the layers of water and oil are incompressible, the phases other than the lamellar phase with one specified period are unstable in the bulk. Actually, all the phases except for the lamellar phase with \( \lambda = 4 \) are unstable in a certain region of the phase space in the CHS model \([16]\). The lack of metastability of the other phases has a strong effect on the structure of the confined lamellar phase, especially when the size of the system and the period of the only stable phase are incompatible. In the absence of metastable phases with different periods we cannot expect that the period of the confined phase will increase or decrease under expansion or compression of the slit. Also, the nucleation of a layer of a uniform phase in the center of the slit, found in the case of the swollen lamellar phases, cannot take place when the uniform phases are not metastable in the bulk. Hence, some other kinds of deformations can be expected. The short-period lamellar phases resemble smectic liquid crystals, which show Helfrich \([18–21]\) undulation instability under external stress. We should thus take into account a possibility of a similar behavior in oil-water-surfactant mixtures. The undulating structures are no longer one-dimensional, and we shall thus assume, as in Ref. \([22]\), that the densities have at least a two-dimensional structure and depend on two space variables, \((x, z)\) (in directions given by \(\hat{e}_i\) with \(i = 1, 3\)), where \(z\) is a distance from one wall and \(x\) is a coordinate in the direction parallel to the walls. We assume that in the other direction parallel to the walls the densities are constant. When the orientation of the lamellae is no longer fixed, then the assumption of only two relevant orientations of the amphiphiles is no longer justified. We thus assume that the orientations of the amphiphiles are restricted to \(\pm \hat{e}_i\) with \(i = 1, 3\), when the densities change in the two corresponding directions.

We choose the model parameters and the thermodynamical state such that the lamellar phase with the period \( \lambda = 4 \) is stable and no metastable phases are present \([22]\). By numerical minimization of \( \Omega_{ex} \) we found in Ref. \([22]\) that the structures corresponding to the global minimum of \( \Omega \) for \( L \neq L_N \) show the following pattern. For \( L = L_N + 1 \) the central water- or oil-rich layer is twice as thick as the corresponding boundary layers. For \( L = L_N + 2 \) the structure shown in Fig.\(9.a\) occurs. This structure strongly resembles the Helfrich undulation instability in smectic liquid crystals. For very thin layers of oil and water between the monolayers of amphiphiles the lamellar phase should indeed be very similar to a smectic liquid crystal. For \( L = L_N + 3 \) we observe a formation of lamellar layers near each wall, whereas in the center of the slit the lamellae are oriented perpendicularly to the confining walls (Fig.\(9.b\)). For the perpendicular orientation there is no constrain on the period of the lamellar phase within the central lamellar layer. The structures shown in Fig.\(9.c\) consist of domains of the lamellar phase having the bulk structure, and of layers of deformations separating them. The thickness of the layers of deformations is comparable to the lattice constant, which in this case is the characteristic structural length.
B. Neutral and weakly hydrophilic walls

When the confining walls are strongly hydrophilic, the lamellae are parallel to them, since the wall-fluid surface tension in a semi-infinite system is lower for this orientation than for any other one. For other orientations of the lamellae either the unfavorable contacts between the polar and nonpolar particles and/or particle parts, or deformations of the structure cannot be avoided. For a perfectly neutral wall, however, neither component nor orientation of amphiphiles is favored near the wall and one cannot a priori assume that the lamellae should be parallel to the walls. In fact in the previous section we have observed that a perpendicular orientation of lamellae stabilizes in the center of the slit, by which the deformations of the lamellar structure within the central layer are avoided. The lamellar layers formed near each wall can be considered as a kind of ‘external walls’ for the central layer of perpendicularly oriented lamellar phase. The water concentration at the surface which is in contact with the central layer is lower than at the surface covered by pure water, and this surface can be considered as a weakly hydrophilic one. Lamellae perpendicular to very weakly hydrophilic walls were also observed in Monte Carlo simulations of a Landau model of microemulsions [23]. Based on the above observations we can expect that the perpendicular orientation of the lamellae is more favorable than the parallel one for very weakly hydrophilic or perfectly neutral walls. We have found [24] that indeed, the perpendicular orientation stabilizes between neutral walls, but only for small periods of the lamellar phase, which correspond to the surfactant volume fraction $\rho_s \geq 1/3$. For swollen lamellar phases we always find stability of lamellar phases parallel to the walls in the CHS model [24].

In order to study the case of weakly hydrophilic walls, we have to define the interactions between the surface which is considered as a weakly hydrophilic one and all the components of the mixture. We assume that the interactions between each specie in the mixture and the wall are uniformly decreased compared to the interactions between this specie and the water particle. To obtain the interactions between each component and the weakly hydrophilic wall we multiply the bulk interactions between each component and the water particle by the same factor $0 < h < 1$.

When the walls are weakly hydrophilic (or hydrophobic) then in a semi-infinite system the parallel orientation of the lamellar phase is preferable, because the unfavorable contacts between the polar and the nonpolar particles or particle parts are avoided, in contrast to the perpendicular orientation of the lamellae. On the other hand, when the width of the slit and the period of the lamellar phase do not match, the lamellar structure parallel to the walls is deformed. The deformation of the structure leads to the elastic contribution to the free energy, as in the case of the strongly hydrophilic walls. For the parallel orientation $\Omega_{ex}$ contains the surface tension contribution $\sigma_\parallel A$ and the elastic energy contribution $\bar{B}(L - L_N)^2/2L_N$. The latter vanishes in the case of no stress ($L = L_N$) and assumes a maximum for the most deformed structure ($L - L_N = \lambda/2$). When the lamellar phase is oriented perpendicularly to the confining walls there is no constrain on the period of the structure, which can be the same as in the bulk and there is no elastic contribution to $\Omega_{ex}$, i.e. $\Omega_{ex} \approx \sigma_\perp A$. The surface tension in this case is larger than in the case of the parallel orientation. In the absence of the deformations of the structure, i.e. for $L = L_N$, the parallel orientation should be thus stable in the slit. However, when the elastic modulus $\bar{B}$ is sufficiently large,
the elastic energy of deformations may be larger than the difference between the surface
tensions $\sigma_\perp - \sigma_\parallel$ for wall separations $L \neq L_N$, corresponding to a strong stress. For such
wall separations a switch to the perpendicular orientation may occur.

We have observed this switch in our model \[22,24\] for the surfactant volume fraction
$\rho_s = 1/3$ and for very weakly hydrophilic walls, for example for $h_s = 0.015$ (Fig.10). Lamellar
phase with the surfactant volume fraction $\rho_s = 1/3$ is stable at room temperatures for
example in water, decane and $C_{10}E_5$ [25].

The switch should lead to an abrupt change of electrical conductivity, reflectivity, elastic
properties (large solvation force for the parallel and almost vanishing for the perpendicular
orientation). Thus by slight changes of the control parameter such as the width of the slit
we can induce abrupt, qualitative changes of various physical properties of the system.

VI. CONFINED CUBIC Bicontinuous Structure With
Double-Diamond Symmetry

The cubic phase with the double-diamond structure, D, is stable in the CHS model with 6
allowed orientations of amphiphiles, $\hat{u} = \pm \hat{e}_i$, $i = 1, 2, 3$. For sufficiently strong amphiphilic
interactions $c/b$ the D phase is stable in an extended region of the $(\mu_s, T)$ phase diagram ($\mu_s$
is the surfactant chemical-potential and $T$ is the temperature). The size of the unit cell, $\lambda$,
can be large close to the coexistence with the oil- and the water-rich phases. The $\Omega_{ex}$ was
obtained in [23] for a system confined between water-covered walls and for the parameters
Corresponding to a stability of the bulk phase with the size of the unit cell $\lambda = 8$ (Fig.11).
Note that for sufficiently large $L$ the period of $\Omega_{ex}$ is equal to $\lambda/4$, whereas in the case of
the lamellar phase the period of $\Omega_{ex}$ is equal to the period of the bulk lamellar structure.
The relation between the characteristic length of the structure, which for the ordered phases
can be identified with the size of the unit cell $\lambda$, and the response of the confined system
to the external stress is thus essentially different for the two phases. This difference follows
from different symmetries of the phases in question. Note that in the case of the lamellar
phase the whole period of the structure has to be introduced into the slit, if the unfavorable
contacts between the polar and nonpolar particles and/or particle parts are to be avoided.
It is not the case for the D structure, because it has a different symmetry. To see the
role of the symmetry of the D phase, let us examine Fig.12, where the central parts of the
water- and the oil-rich channels are shown schematically for the unit cell. The D structure
consists of the water- and the oil-rich channels and the junctions between them. In each
junction 4 water-rich or 4 oil-rich channels ('legs') are connected with each other and form
a tetrahedron. There are 4 layers of junctions in the unit cell (Fig.12). In each layer of
junctions there are 2 water and 2 oil junctions. The structure in each layer of junctions can
be obtained from the structure of the previous layer by a symmetry operation (a rotation
and a translation). The interaction energy between the infinite hydrophilic surface and the
infinite periodic structure is thus the same regardless of which layer of junctions forming the
unit cell is exposed to the surface (Fig.12). Therefore under the expansion of the slit a single
layer of junctions is introduced into the system, by which large structural deformations are
avoided. Since the thickness of the single layer of junctions is $\lambda/4$, also the period of $\Omega_{ex}$
is equal to $\lambda/4$, as we have found by numerical minization of $\Omega_{ex}$ in the CHS model.
Because the period of $\Omega_{ex}$ is small compared to $\lambda$, we have to consider large unit cells to
verify whether the response to the compression or expansion is elastic and how large (or small) is the elastic modulus compared to the lamellar phase with the same period. This work is in progress \[26\]. For other cubic phases we expect similar relation between the period of $\Omega_{ex}$ (and also the measurable solvation force) and the symmetry of the unit cell of the bulk structure.

Interesting structural deformations occur for narrow slits, $L < 2\lambda$. First, for $L < \lambda$ a capillary condensation of water, which is stable in the bulk for slightly smaller $\mu_s$, occurs. For $\lambda < L < \frac{4}{3}\lambda$ a single layer of parallel oil-rich channels is formed. In Fig.13 the oil-water interface is shown for $L = \frac{2}{3}\lambda$. Formation of a layer of cylinders (‘wheels’) can be important for lubrication of the two surfaces put into motion in direction perpendicular to the axes of the cylinders. Further expansion of the slit leads to a formation of two layers of channels near the two walls. In each layer the channels are parallel to each other and perpendicular to the channels in the other layer. The oil-rich channels perpendicular to each other are connected in a single layer of junctions, which is formed in the center of the slit (Fig.14). The resulting quasi two-dimensional bicontinuous structure looks like a nanoscopic sieve. As in the bulk D phase, there are 4 ‘legs’ merging in each junction. Unlike in the bulk, however, the channels are nearly parallel to the external walls, whereas in the bulk they form a tetrahedron.

For larger wall separations a second layer of junctions of the oil-rich channels is formed, and then further expansion leads to a formation of a third, fourth etc. layer of junctions. The channels located close to the confining walls remain parallel to them for arbitrary $L$. For an odd (even) number of layers of junctions in the confined system the channels near one external surface are perpendicular (parallel) to the channels near the other external surface. We expect such a behavior for D phases with large periods, i.e. for relatively small $\mu_s$.

VII. SUMMARY

We reviewed the results obtained in the CHS model for the lamellar and the D phases confined between two parallel walls \[16, 22, 24, 26\]. The results show that there is indeed a similarity between the confined complex fluids on the mesoscopic length scale and the confined simple fluids on the molecular length scale. Namely, the solvation force oscillates in each case with the periodicity related to a typical structural length. While in the simple fluids the typical length is related to the average distance between particles, in the case of the complex fluids the typical structural length depends on the symmetry and the anisotropy of the ordered phase. In the case of the lamellar phase the characteristic structural length is equal to the period of the lamellar phase, i.e. to the size of the unit cell $\lambda$. In the case of the D phase the structural unit corresponds to the single layer of junctions of the water- and oil-rich channels, and its thickness is equal to a quarter of the size of the unit cell, $\lambda/4$.

There are other important differences between the confined simple fluids and the confined complex fluids with different symmetries. Let us first describe the differences related to the anisotropy of the ordered phases. The anisotropy plays an important role for the slit geometry. The elastic properties of the film of an anisotropic sample depend on the orientation of the anisotropy axis with respect to the confining walls. Here we have described a switch of the lamellae orientation induced by compression or expansion of the lamellar film.
confined between very weakly hydrophilic walls. This phenomenon is associated with the anisotropy of the lamellar phase.

Another important property of the confined self-assembling systems is the close relation between the structures which can be stabilized between the confining walls and metastability of various phases in the bulk. We have described this relation in some detail in the case of the lamellar phases. The structure of the confined system is determined by a single phase metastable in the bulk if its structure fits the size of the slit and is not much different than the structure of the bulk phase (i.e. $\omega_b$ has almost the same value for the two phases). In the case of stabilization in the slit of metastable lamellar phases with different periods for different $L$, we observe an elastic response to the applied stress.

For narrow slits it turns out that a nucleation of a single layer of a uniform phase between two near-surface lamellar layers is more preferable than stabilization of a highly deformed lamellar structure in the whole slit. The lamellar phase with a significantly different period has a significantly higher $\omega_b$ than the equilibrium bulk phase. The uniform phase is also metastable in the bulk, and the surface tension between it and the lamellar phase is low. For more complex shapes of the confining walls one should thus take into account a possibility of stabilization of two or more metastable phases separated by interfaces, if there are many metastable phases in the bulk and the surface tensions between some of them are low.

If there are no metastable phases in the bulk, essentially different behavior is found in confinement. Domains of the bulk structure are formed, and the shapes of the boundaries and the orientations of the domains are adjusted to the size and the shape of the container. A confined system with dislocation-like deformations or with domains of a uniform structure does not respond elastically to the applied stress.

For the D phase we find stabilization of elementary structural units in the narrow slits. First a layer of channels is formed, then a single layer of junctions. For other cubic bicontinuous phases we may expect similar stabilization of elementary units.

The properties of the confined self-assembling systems may be important for various applications. Templates for various ordered structures are formed spontaneously and one can control the structures by controlling the thermodynamic conditions. Some of the structures, such as the layer of cylinders or the sieve-like structure, as well as transitions between them, such as the switch of the lamellae orientation, may be important for modern technologies.

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FIGURES

FIG. 1. Schematic representation of the self-assembly in the ternary oil-water-surfactant mixtures.

FIG. 2. Unit cell of the cubic D phase (the oil-water interface, separating the oil- and water-rich domains is shown).

FIG. 3. CHS lattice model. Top: a typical configuration. Bottom: non-vanishing interactions.

FIG. 4. Slit geometry.

FIG. 5. a: the excess thermodynamic potential $\Omega_{ex}$ per unit surface area (in units of $b/a^2$), defined in (4), as a function of the wall separation measured in units of the lattice constant $a$. b: the solvation force $f$ (in units of $b/a^3$) as a function of the wall separation. The thermodynamic variables $\tau = kT/b$, $\mu/b$ and the material constant $c/b$ of the one-dimensional system correspond to stability of the swollen lamellar phase with $\lambda = 13a$ ($\tau = 0.84, \mu/b = 0.774, c/b = 1$); the distance from the first-order transition between the water-rich and the lamellar phases is $|\Delta \mu/b| = 0.003$. Walls are covered by water. Dashed lines are to guide the eye.

FIG. 6. The thermodynamic variables $\tau$, $\mu/b$ and the material constant $c/b$ are the same as in Fig.5. The subsequent minima of $\Omega_{ex}$ are fitted by quadratic curves $B(L - L_N)^2$, where $L_N$ is the equilibrium separation for $N$ adsorbed layers and $B$ is the coefficient in the fitting curve to the $N$-th minimum. $B$ (in units of $b/a^4$) is shown as a function of the inverse number of adsorbed layers $1/N$. Dashed line is a linear fit.

FIG. 7. Compressibility modulus $\bar{B}$ (in units of $kT/a^3$), of the swollen lamellar phases as a function of the average distance between the surfactant monolayers, $P = \lambda/2$ (in units of $a$) in the three-dimensional system. The behavior expected from the phenomenological prediction of Helfrich is shown for two values of $\kappa$: $0.5kT$ (solid line), $0.6kT$ (dashed line).

FIG. 8. One-dimensional system in the case of intermediate wall separations, $18 < L < 54$. Length is measured in units of the lattice constant $a$. The thermodynamic variables $\tau$, $\mu/b$ and the material constant $c/b$ are the same as in Fig.5. Period of the bulk lamellar phase is $\lambda = 13$. Walls are covered by water. a: the density distribution of water between the walls for the separation $L = 29$. b: the density distribution of oil between the walls for the separation $L = 39$. 

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FIG. 9. The oil-water interfaces, $\rho_1(x,z) - \rho_2(x,z) = 0$, are shown in the $(x,z)$ plane, where $\rho_1, \rho_2$ are the densities of water and oil respectively. The white (dark) regions represent the water-rich (oil-rich) domains. The values of the thermodynamic variables and the coupling constants are $\tau = kT/b = 2.5$, $\mu/b = 1$, $c/b = 2.5$, $g/b = 1$ and $h_s = 1$ and correspond to a stability of the lamellar phase with the period $\lambda = 4$ (in $a$ units). a: the distance between the walls is equal to 25 (in $a$ units). b: the distance between the walls is equal to 26 (in $a$ units).

FIG. 10. Excess grand thermodynamic potential for the parallel, $\Omega_{ex}^{\parallel}(L)$ (white circles), and the perpendicular, $\Omega_{ex}^{\perp}(L)$ (triangles down), orientations as a function of the wall separation (in units of $a$) for $c/b = 2.4$, $kT/b = 2.8$, $\mu/b = 3$ and $g/b = 0.15$. (a) $h_s = 0$ (neutral walls); (b) $h_s = 0.015$ (weakly hydrophilic walls); (c) $h_s = 1$ (strongly hydrophilic walls).

FIG. 11. $\Omega_{ex}$ for the confined D-phase as a function of the distance $L$ between confining walls (measured in $a$ units). Dark region corresponds to the water condensation in the slit. The parameters $kT/b = 2.3$, $\mu/b = 3.5$, $c/b = 2.5$, correspond to stability of the bulk D-phase with the size of the unit cell $\lambda = 8$ (in $a$ units).

FIG. 12. Schematic representation of the D phase. White (dark) cylinders represent water (oil) channels and the spheres represent the junctions. Cross-sections of the 4 layers of junctions are also shown with junctions indicated as dark and white circles.

FIG. 13. Oil-water interface of the structure formed in the slit for $L = \lambda + \lambda/8$.

FIG. 14. Oil-water interface of the structure formed in the slit. $L = \lambda + 3\lambda/8$. 
Fig. 1

micelles

bicontinuous

lamellar

\[ \lambda \approx 500 \text{ Å} \]

water

surfactant

oil

\[ a \approx 20 \text{ Å} \]
Fig. 3

\[ -g \cos \varphi \sin \vartheta_1 \sin \vartheta_2 \]
Fig. 4
Fig. 6

Graph showing the relationship between $B 10^5 (b/a^4)$ and $1/N$. The graph is a linear plot with data points connected by a dashed line.
Fig. 7

\[ B(kT/a^3) \]

\[ \kappa = 0.5kT \]

\[ \kappa = 0.6kT \]
Fig. 8

(a) and (b) show variations of \( \rho_w \) and \( \rho_o \) with \( z/a \) respectively.
Fig. 9a

periodic boundary conditions

wall separation - 25
Fig. 12

rotation + translation

rotation + translation

rotation + translation

rotation + translation
