Switch of lamellae orientation in slits

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Abstract

Effect of hydrophilicity of the confining walls on lamellar phases in oil-water-surfactant mixtures is studied in a slit geometry. In contrast to strongly hydrophilic or hydrophobic walls, which induce parallel orientation of lamellae, the lamellae can be oriented perpendicularly to the neutral walls when the material properties and the thermodynamical state of the sample are suitably chosen. When the elastic energy associated with compression or decompression of the lamellae parallel to very weakly hydrophilic walls is sufficiently large, then changes of the film thickness lead to a switch from the parallel to the perpendicular orientation of the lamellae. Our general arguments are confirmed by explicit mean-field calculations in a lattice vector model.

In self-assembling systems such as diblock copolymer melts, binary or ternary surfactant mixtures, lipids etc., various ordered structures occur spontaneously on a nanometer length scale [1–3]. The most common is the lamellar phase [4]. In ternary surfactant mixtures the lamellar phase consists of oil- and water-rich layers separated by monolayers of surfactant. It is natural to expect that the layers are parallel to the confining walls and the parallel orientation of lamellae is commonly assumed. Indeed, near a strongly hydrophilic or hydrophobic wall a water-rich or an oil-rich layer is adsorbed at the surface respectively, by which the orientation of the subsequent layers is fixed [5–8]. However, when the surface is neutral, i.e., it is neither hydrophilic nor hydrophobic, then neither component is favored and no orientation of amphiphiles is preferred near the wall. Therefore perpendicular rather than parallel orientation of the lamellar phase may be stable between two parallel surfaces that are neither hydrophilic nor hydrophobic (see Fig.1). In the case of very weakly hydrophilic walls perpendicular orientation was indeed observed in Monte Carlo simulations [8] of the phenomenological Landau-Ginzburg model [3]. Perpendicular orientation should be favoured when the distance between the walls and the period of the lamellar phase do not match. On the other hand, when the distance between the lamellae fits the distance between the weakly hydrophilic walls, parallel orientation can be stable.

Films with the lamellae oriented parallelly or perpendicularly to the walls have different mechanical, electrical, optical etc. properties. Therefore the possibility of inducing a switch between the two orientations by changing a control parameter such as the distance between the walls \( L \) is potentially very important for various applications. For example, when some electrolyte is added, the electrical conductivity between the confining walls is high in the perpendicular orientation, whereas the parallel orientation resembles a sequence of capacitors. The switch of the lamellae orientation leads also to an abrupt change of the refraction
index and the reflectivity, and of elastic properties of the film. A lamellar film containing a few lamellae has the thickness $L \sim 30 \div 100\text{nm}$. Such a lamellar film would correspond to a switch of a mesoscopic size—a device which may be useful for modern nanotechnologies. In this letter we show under what circumstances such a switch from the parallel to the perpendicular orientation of the lamellae can occur.

The confined fluid induces the solvation force between the walls\cite{10},

$$fA = -\left(\frac{\partial \Omega}{\partial L}\right)_{\mu,T,A} - p A,$$

where $\Omega, p, A, T$ and $\mu$ are the grand thermodynamic potential, the bulk pressure, the area of the confining walls, the temperature and the chemical potential respectively. $f$ can be directly measured in surface force apparatus experiments\cite{3,7,11–14}. In simple fluids oscillating $f$ reflects packing effects of molecules for $L$ up to several molecular diameters, since the stretched or shrunk confined fluid tends to assume the bulk structure. Similarly, but on a much larger length scale, $f$ reflects packing effects of oil- and water-rich domains in the complex fluids. For $L \geq 3\lambda$, where $\lambda$ is the period in the bulk phase, lamellae are parallel to the strongly hydrophilic (or hydrophobic) walls\cite{3,4,9}. When $L$ and $\lambda$ do not match, the lamellar structure is stretched for $L > L_N$ or shrunk for $L < L_N$ where $L_N = N\lambda + \lambda/2$ denotes the equilibrium thickness, corresponding to no stress, for a given number $N$ of periods of the confined phase. For $L \neq L_N$ the confined lamellar phase responds elastically to the stress strain, just like joined strings, each string representing one period of the lamellar phase\cite{7}. The elastic contribution to the excess thermodynamic potential

$$\Omega_{\text{ex}} A = \Omega - \omega_b L A,$$

where $\omega_b$ is the bulk thermodynamic-potential density, has a form

$$\Omega_{\text{ex}}^{\text{el}} = B \Delta L^2 / 2L_N,$$

with $\Delta L = L - L_N$. The elastic modulus $B$ depends on the amphiphilicity of the surfactant and on the thermodynamic state\cite{7}.

Because neither component is favoured near the neutral wall, it has a disordering effect on the lamellar order due to the missing neighbors\cite{13}. The missing-neighbors contribution to the excess potential $\Omega^{\text{ex}}$ depends on the orientation of the lamellar phase (see Fig.1). For the parallel orientation ($||$), $\Omega^{\text{ex}} = \Omega^{\text{ex}}||$, the interactions are cut along a single layer or along an interface. For the perpendicular orientation ($\perp$), $\Omega^{\text{ex}} = \Omega^{\text{ex}}\perp$, the water-water, surfactant-surfactant and oil-oil interactions are missing at the surface in proportions depending on $\lambda$ and the thickness of the monolayer $a$. The density distributions near the surfaces tend to minimize the effect of the missing neighbors at the walls, and determine the values of the surface tensions $\sigma||$ and $\sigma\perp$. Sufficiently far from phase transitions the effect of the wall should extend to distances comparable with the characteristic length of the system, which in this case corresponds to $\lambda$. If the lamellae are perpendicular to the confining walls, there is no constrain on the period of the lamellar phase, which can be equal to the bulk value, and in this case there is no elastic contribution to $\Omega^{\text{ex}}\perp$. Thus except for narrow slits, i.e. for $L > 3\lambda$, we expect $\Omega^{\text{ex}}\perp \approx 2\sigma\perp$ independently of $L$. In the case of the parallel orientation of
lamellae, for $L \neq L_N$, there are deformations of the structure in the whole slit like in the case of the hydrophilic walls and $\Omega_{\parallel}^{ext} \approx 2\sigma_{\parallel} + \Omega_{el}^{ext}(L)$.

By suitable tuning of hydrophilicity of surfaces, amphiphilicity, $T$ and surfactant volume-fraction $\rho_s$ one could in principle obtain comparable $\sigma_{\parallel}$ and $\sigma_{\perp}$. For weakly hydrophilic walls one can expect $\sigma_{\parallel} < \sigma_{\perp}$. Thus, the parallel orientation should be stable in the case of no stress ($L = L_N$). The perpendicular orientation may be stable for slightly different wall separations, corresponding to stretched or shrunk parallel lamellar phases, if the elastic contribution to $\Omega_{\parallel}^{ext}$ is sufficiently large. According to the phenomenological theory $B = 9\pi^2(kT)^2\lambda^4/2[64\kappa(\lambda/2 - a)]^{-1}$, where $\kappa$ is the bending elasticity of monolayers. Thus the compression or decompression induced switch to the perpendicular orientation is to be expected for relatively small $\lambda$, rather than for highly swollen lamellar phases.

Whether the switch can indeed occur in particular systems should be verified either experimentally or by a more accurate analysis. The theoretical analysis should allow for a determination of $\sigma_{\perp}$, $\sigma_{\parallel}$ and $\Omega_{el}$ (or more accurately $\Omega_{\parallel}^{ext}, \Omega_{\perp}^{ext}$) in particular systems. There are several theoretical approaches to bulk self-assembling systems. The approach suitable for a particular problem depends on the relevant length scale. In our case two length ratios are important, namely $L/\lambda$ and $\lambda/a$. $L/\lambda$ is the number of oil (water) layers in the slit for the $\parallel$ orientation, and $\lambda/a$ characterizes the liquid-crystalline lamellar phases. For $\lambda/a$ sufficiently large ($\lambda/a > 4$), the water-rich layers are sufficiently thick to be compressible as in bulk liquid. Experimental results show that the lamellar phases respond to compression or decompression by shrinking or swelling the water-rich (and/or oil-rich) layers, rather than by developing deformations characteristic for solids or by deformations of the molecular structure of amphiphiles. Hence the degrees of freedom related to the structure of molecules can be neglected, as long as $L/a \gg 2$. Dislocations, frustration etc. can be expected for stiff, solid-like structures, i.e. when the water-rich (oil-rich) layers are very thin, $\lambda/a < 4$. Since for our problem the relevant length ratios are $1 < L/\lambda \leq 10$ and $4 < \lambda/a \leq 10$, the molecular degrees of freedom, frustrations etc. can be disregarded. On the other hand, the popular approaches in which the monolayers are approximated by infinitely thin mathematical surfaces may be oversimplified, particularly for comparable thicknesses of the layers of water and surfactant ($4 \leq \lambda/a \leq 6$).

In a presence of a wall the surface term describing the interaction of the surface with the water, oil, and amphiphiles in various orientations must be included. In a purely phenomenological approach one cannot apriori know what values of additional surface parameters are physical. Therefore one cannot know if the predicted phenomena, occurring for certain values of parameters, are physical or not. It is thus advantageous to consider a semi-microscopic approach and relate the interactions with the surface to the effective interactions in the bulk. For example, for the water-covered surface the interactions between various components and the surface are determined by the interactions between these components and water and there is much less ambiguity in defining the surface contribution in such an approach.

All the above discussed requirements for the appropriate description of confined amphiphilic systems are fulfilled by the semi-microscopic CHS (Ciach, Høye and Stell) lattice model [17]. The model is described in detail in Ref. [17] and here we remind it only briefly. The microscopic states are $\hat{\rho}_i(x) = 1(0)$ if the site $x$ is (is not) occupied by the state $i$, where $i = 1, 2, ..., 2 + M$ denotes water, oil and surfactant in different orientations respectively. In
the case of close-packing and oil–water symmetry only one chemical potential variable is relevant, namely \( \mu = \mu_1 - \mu_{\text{surf}} = \mu_2 - \mu_{\text{surf}} \), with \( \mu_{\text{surf}} = \mu_i \) for \( i > 2 \). The Hamiltonian in a presence of external fields \( h_i(x) \) can be written as:

\[
H = \frac{1}{2} \sum_{x \neq x'} \sum_{i,j} \hat{\rho}_i(x) U_{ij}(x - x') \hat{\rho}_j(x') + \\
\sum_{x} \sum_i h_i(x) \hat{\rho}_i(x) - \mu \sum_x (\hat{\rho}_1(x) + \hat{\rho}_2(x)).
\]

(4)

The lattice constant \( a \equiv 1 \) is identified with the length of the amphiphiles (~2nm). Nearest-neighbor interactions are assumed and \( U_{ij}(x - x') \) vanishes for \( |x - x'| \neq 1 \). In the case of oil-water symmetry the water-water and oil-oil interactions are of the same strength \( -b \), and the water-oil interaction energy is set to zero. The interaction between an amphiphile in an orientation \( \hat{\omega} \) at \( x \) and a water (or oil) particle at \( x' \) is \(-c \hat{\omega} \cdot \Delta x \) (or \(+c \hat{\omega} \cdot \Delta x \)), where \( \Delta x = x - x' \), thus opposite orientations of amphiphiles are preferred by the water and the oil particles, as in real systems. Two amphiphiles with orientations \( \hat{\omega} \) and \( \hat{\omega}' \) at \( x \) and \( x' \) respectively contribute \(-g(\hat{\omega} \times \Delta x) \cdot (\hat{\omega}' \times \Delta x)\) to the system energy (when \( |\Delta x| = 1 \)), i.e. \( g \) supports formation of planar monolayers with amphiphiles parallel to each other and perpendicular to the surface they occupy. Explicit expressions for \( U_{ij}(x - x') \) defined above can be found in Ref. [3]. For lamellar phases the direction perpendicular to the planar layers of surfactant, oil and water is distinguished. We arbitrarily choose the orientation of the unit vector normal to the layers and denote it by \( \hat{n} \). Then all orientations of amphiphiles such that \( \hat{\omega} \cdot \hat{n} > 0 \) (or \( \hat{\omega} \cdot \hat{n} < 0 \)) are mapped onto a single state \( \rightarrow \) (or \( \leftarrow \)). Hence, once the direction of density oscillations is fixed, there are 4 states corresponding to water, oil, \( \rightarrow \) and \( \leftarrow \) at every lattice site.

The model parameters characterize the effective interactions between different components, and the interactions with the surface can be expressed in terms of these parameters. When the surface is water-covered, all the components interact with the wall in the same way as with the bulk water, and \( h_i(x) \) can be easily derived from the bulk interactions. When the hydrophilicity of the wall is decreased, the interactions with the wall can be decreased by the same factor \( h_a \) for all the components. Thus, \( 0 \leq h_a \leq 1 \) should correspond, at least qualitatively, to physical surfaces, ranging from neutral through weakly hydrophilic to strongly hydrophilic walls.

The model parameters are not directly measurable, but the calculated values for measurable quantities can be compared with experiments. For example, the model parameters can be choosen so that \( \lambda/a \) is the same as in a particular experimental system. In this way the model parameters can be related to different experimental systems in the bulk. It turns out that once the bulk properties in the model and experiments are the same, for strongly hydrophilic walls (the case with no free surface parameters) the modulus of compressibility \( B \) (in \( kT \) units) in the model and experiments agree very well [3]. Therefore, in contrast to purely phenomenological models with arbitrary parameters, the CHS model can quite reliably predict phenomena not yet studied experimentally.

The structure of the stable confined lamellar phase in mean-field approximation (MF) corresponds to the global minimum of the grand-thermodynamic potential

\[
\Omega^{MF}(T, \mu, L) = \sum_x \sum_i \rho_i(x) \left( kT \ln(\rho_i(x)) + \frac{1}{2} \phi_i(x) + h_i(x) - \mu(\delta_{i1} + \delta_{i2}) \right).
\]

(5)
Measurements of the above quantities should give significantly different results for the parallel and perpendicular orientations. Reflectivity, index of refraction and electrical conductivity change abruptly with the switch of the orientation does take place. Fig. 2 refers to such a system and corresponds to the results of experiments. The effect of the correlations should not depend significantly on the kind of the confining walls and we expect that the correlations can have quantitative, but not qualitative effect on the results.

Our results show that the switch is to be expected for \( \lambda/a \approx 6 \), i.e. with the water (oil) layers twice as thick as the surfactant monolayers, and sufficiently far from phase boundaries. From the rough relation \( 2a/\lambda \approx \rho_s \), we obtain the estimation \( \rho_s \approx 0.33 \pm 0.1 \) for the surfactant volume fraction which should correspond to the occurrence of the switch. For this range of \( \rho_s \), the lamellar phase is stable at room temperatures for example for the CHS model. We consider two classes of density distributions, corresponding to the parallel and the perpendicular orientations of the lamellar phase. In the first case the two distinguished orientations of amphiphiles are \( \omega = \pm \hat{z} \). In the second case we assume that the layers are parallel to the \((y, z)\)-plane, and \( \omega = \pm \hat{x} \). The slit is infinite in directions \( x \equiv x_1 \) and \( y \equiv x_2 \). In the case of the parallel orientation of the lamellar phase \( \rho_i(x) \equiv \rho_i(z) \). In the second case, due to the deformations of the structure near the surfaces, the density distributions are \( \rho_i(x) \equiv \rho_i(x, z) \). In the direction \( x \) we assume periodic boundary conditions in a system of a size \( \lambda \), since \( \Omega_i^x \) for such system is the same as for infinite periodic structure with the period \( \lambda \) (we also considered smaller and larger sizes to be sure we find the stable structure). We use the method of finding local minima of \( \Omega^{MF} \) by solving numerically a set of self-consistent equations for densities, tested in earlier works [9]. Then we find the structures corresponding to the lowest values of \( \Omega_i^x \) and \( \Omega_i^z \), and eventually we calculate \( \Omega_i^x - \Omega_i^z \) to find the global minimum. It turns out that \( \Omega_i^x - \Omega_i^z \) depends sensitively on the hydrophilicity of the surfaces \( h_s \), on the ratio of water-surfactant \( c/b \) and surfactant-surfactant \( g/b \) interactions and on the period of the lamellar phase, which for given interactions depends on \( \mu \) (or \( \rho_s \)) and \( T \). We find that for highly swollen lamellar phases the parallel orientation is preferred, and that for smaller periods \( \lambda \) the perpendicular orientation stabilizes between neutral walls. We find that there exist systems for which the switch of the orientation does take place. Fig. 2 refers to such a system and corresponds to the stability region of the lamellar phase far from phase boundaries, with \( \lambda/a = 6 \). The switch takes place for relatively small \( \lambda \) and for weakly hydrophilic walls, as expected. Note that in the case of the neutral walls the period of \( \Omega_i^x(L) \) is \( \lambda/2 \) (Fig. 2a), since either oil- or water-rich layers can be adsorbed at the surfaces. In contrast, in the case of the hydrophilic walls only the water-rich layers are formed near the walls and the period of \( \Omega_i^x(L) \) is \( \lambda \) (see Fig. 2c).

In MF the correlations between the lamellae are neglected. Such correlations are particularly important close to the melting of the lamellar phases where they lead to creation of channels connecting the neighboring water-rich layers and eventually to the transition to the microemulsion. Far from phase boundaries, however, the correlations should play less important role. In the case of the hydrophilic walls the MF results for the CHS model agree quite well with the results of experiments. The effect of the correlations should not depend significantly on the kind of the confining walls and we expect that the correlations can have quantitative, but not qualitative effect on the results.

Various experimental methods can be used for detecting the switch, due to the abrupt change of various properties of the sample. For example, SFA measures should show vanishing force for the perpendicular orientation and elastic response for the parallel orientation. Reflectivity, index of refraction and electrical conductivity change abruptly when the switch takes place. Measurements of the above quantities should give significantly different results.
different results for the two orientations, thus allowing for observation of the phenomenon.

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Fig. 1. Schematic illustration of parallel (a) and perpendicular (b) orientations of the lamellar phase in a slit. Shaded regions represent oil-rich domains, while white regions represent water-rich layers and thick black lines represent the surfactant monolayers.
Fig. 2. $\Omega_{\|}^{ex}(L)$ (white circles) and $\Omega_{\perp}^{ex}(L)$ (triangles down) 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).