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Phase transitions in confined lamellar phases

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Abstract. Effects of confinement on mechanical, structural and thermodynamic properties of uniform fluids are very well understood. In contrast, a general theory based on statistical thermodynamics for confined nonuniform and non-isotropic phases, such as the lamellar phase, is in its infancy. In this review we focus on the lamellar phase confined in a slit or in a pipe in order to illustrate various effects of confinement. We limit ourselves to the results obtained by M. Tasinkevych, V. Babin and the author for lamellar phases in oil-water-surfactant mixtures within a generic semi-microscopic model, using a mean-field approximation. We show that compared to isotropic fluids the excess grand potential contains additional terms associated with structural deformations. These terms depend on the type of the confining walls, the shape of the container and on the thickness of the lamella. As a result of the dependence of the structure of the confined lamellar phase on the shape of the container, capillary lamellarization and capillary delamellarization is found in slits and in pipes respectively.

Key words: lamellar phases, confinement, phase transitions.

1. Introduction

Amphiphilic molecules self-assemble into mono- or bilayers, which surround mesoscopic liquid domains of a size $\lambda \sim 10-100$ nm. In certain conditions the liquid domains and the amphiphilic membranes surrounding them form a pattern inside a unit cell, and this pattern is periodically repeated in space. The resulting ordered phases can be periodic in one-, two-, or in three dimensions. Such phases are soft, because the shape of the mesoscopic liquid domains can be deformed, when an external stress is applied. On the other hand, the response to the external stress depends on the direction of the applied force with respect to the symmetry elements (axes and/or planes) of the ordered phase. Due to anisotropy and periodic order of these phases on the one hand, and their softness and liquid nature inside the domains on the other hand, their response to expansion or compression is much more complex, and much less studied than in liquids and solids. Only recently confined self-assembling systems draw increasing attention [1–12]. The experimental studies focused mainly on the mechanical properties of the confined self-assembling systems and on the structure of thin films formed on solid substrates. The effect of a confinement on phase transitions between the lyotropic liquid crystals and uniform phases was studied in Refs. [10–12]. In Refs. [13,14] similar effects in termotropic liquid crystals were considered. In this mini-review we restrict our attention to the most frequently found lamellar phases, and for concreteness we choose ternary oil-water-surfactant mixtures. Based on the theoretical results obtained in Refs. [9–12], general properties of nonuniform and non-isotropic phases in confinement are summarized. Features that are absent in confined uniform fluids are emphasized.

A wall of a container disturbs the structure of the fluid in the near-surface layer of a thickness comparable to a bulk correlation length ξ. Far from phase transitions $\xi \sim R$, where R is the molecular diameter. For this reason confinement plays a significant role when the size of the fluid system is up to about $10R$. The domains surrounded by mono- or bilayers in the self-assembling systems resemble soft particles. Thus, the confinement plays a significant role at least for the wall separation $\sim 10\lambda$, therefore properties of the confined system may be significantly different than in the bulk on the nanometer scale. In particular, biologically relevant self-assembled systems are confined in organelle whose size is $\sim 10\lambda$, and the whole cell is surrounded by the cell membrane, whose size is about two orders of magnitude larger than the domain size λ. The confinement may also play a very important role in systems relevant for nanotechnology.

Because of the broken translational and rotational symmetries of the lamellar phase, its structure in confinement may depend on the geometry of the container and on the hydrophilicity of surfaces. The structural deformations expected in the confined system are associated with stress, i.e. with additional contributions to the grand potential. As a consequence, the phase equilibria between lamellar and disordered phases may be significantly affected by confinement, and this effect may depend on the shape of the container. To verify whether the shape of the container may indeed influence the phase transitions, we consider phase equilibria between lamellar and uniform phases in a slit and in a channel of square cross-section. We shall use the word ‘pipe’ in the latter case for the sake of brevity. The two cases are shown in Fig. 1.

Determination of the large-scale properties of self-assembled systems from a microscopic Hamiltonian is

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not feasible, since thousands of complex molecules are involved. However, remarkable similarity between many such systems can be observed. For example, elastic properties of the lamellar phases depend on λ/ℓ, where ℓ is the bare thickness of the mono-layer which is comparable to the length of amphiphilic molecules. The precise chemical structure of amphiphilic molecules is less important for elastic properties of the lamellar phase with given λ/ℓ.

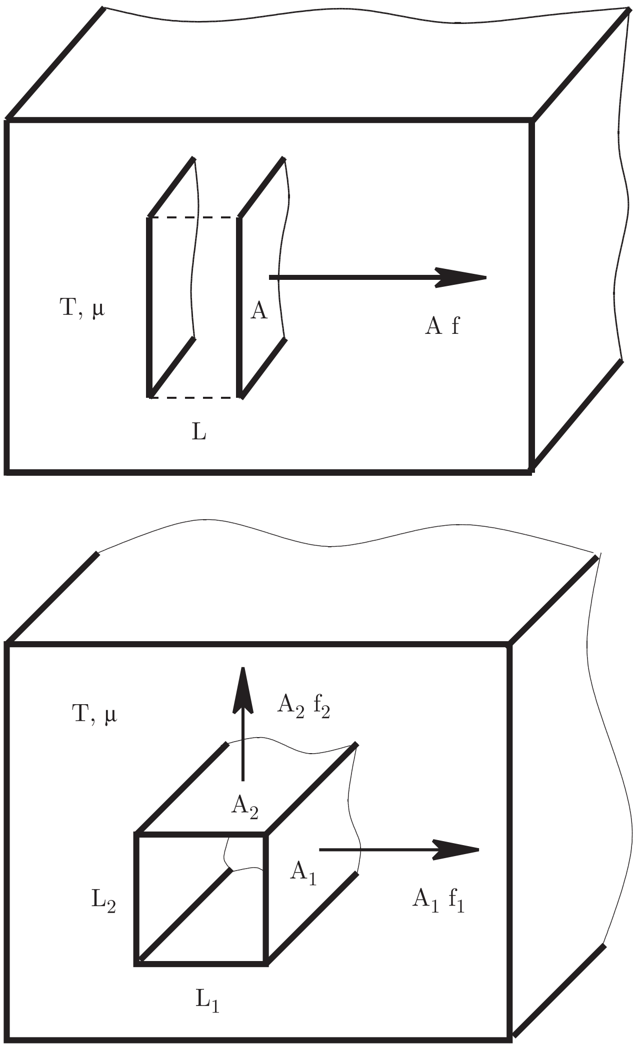


Fig. 1. The slit (up panel) and the pipe (down panel) geometry. The systems inside the slit and inside the pipe are in contact with reservoirs, and T and μ are fixed. f is the force applied externally in order to fix the desired wall separation L

The features common for a family of systems can be described by a highly simplified, effective coarse-grained Hamiltonian, in which the irrelevant details of the interactions are just disregarded. We choose the lattice CHS model [15], which predicts stability of the lamellar phases in the bulk. Most of our general results, however, should be valid also for other systems forming the lamellar phases. When the distance between the confining surfaces, L, is much larger that the size of amphiphiles ℓ, then compression/expansion should not lead to deformations of the shape of molecules, since the energy required for such deformations is larger than the energy associated with rearrangement of the positions of molecules inside the liquid domains. Hence, we can assume that the bulk and confined systems can be described by the same generic model.

In the next section the CHS model and the methods of obtaining the thermodynamic and mechanical quantities are briefly described. Next we present the results for phase coexistence in the slit and in the pipe. In the last section we summarize the contributions to the grand potential associated with different structural deformations of the confined lamellar phase.

2. CHS model and calculation methods

2.1. The model. The CHS model was introduced by Ciach, Høye and Stell [15] to describe universal properties of oil–water–surfactant solutions. We assume that the space can be divided into cells of a simple cubic lattice, and that the cells are occupied by clusters of molecules of the same type. The clusters of surfactant molecules are oriented, and can be described by a unit vector showing an average direction from a head to a tail of amphiphiles. For a detailed description see [10,11,15]. For determination of the excess grand potential and the corresponding structure of the confined system we use a mean-field approximation and for the grand thermodynamic potential we assume the following expression

$$\Omega = H_{MF}\left[\rho_i(\mathbf{r})\right] - TS, \tag{1}$$

where

$$\begin{aligned} H_{MF}\left[\hat\rho_i(\mathbf{r})\right] = {} & \frac{1}{2}\sum_{\mathbf{r}\in V}\sum_i \phi_i(\mathbf{r})\hat\rho_i(\mathbf{r}) \\ & - \mu\sum_{\mathbf{r}\in V}\left(\hat\rho_1(\mathbf{r})+\hat\rho_2(\mathbf{r})\right) + \sum_{\mathbf{r}\in\partial V}\sum_i h_i\hat\rho_i(\mathbf{r}) \end{aligned} \tag{2}$$

is the Hamiltonian in the mean-field approximation, V is the system-volume, ∂V is the system boundary, the lattice constant is $a \sim \ell \sim 2$ nm,

$$\phi_i(\mathbf{r}) = \sum_{\mathbf{r}'}\sum_j u_{ij}\left(\mathbf{r}-\mathbf{r}'\right)\rho_j(\mathbf{r}') \tag{3}$$

is the mean-field acting on the specie i, μ is the water-surfactant chemical-potential difference, $S = -k_b\sum_{\mathbf{r}}\rho_i(\mathbf{r})\ln\rho_i(\mathbf{r})$ is the ideal entropy of mixing and

$$\rho_i(\mathbf{r}) = \langle\hat\rho_i(\mathbf{r})\rangle_{MF} \tag{4}$$

is the mean-field average of the microscopic densities $\hat\rho_i(\mathbf{r})$, i.e. the Boltzmann factor is $\propto \exp(-\beta\Omega[\hat\rho_i(\mathbf{r})])$. Microscopic densities are defined such that $\hat\rho_i(\mathbf{r}) = 1(0)$ if the site $\mathbf{r}$ is (is not) occupied by the specie i, where i refers to water, oil and surfactant particles in different orientations. Different orientations of the latter are treated as different components having the same chemical potential. Density fluctuations are neglected (close packing is assumed), and $\sum_i \hat\rho_i(\mathbf{r}) = 1$. Due to the close packing there is only one independent chemical potential. The $u_{ij}(\mathbf{r}-\mathbf{r}')$ is the interaction energy between the specie i at $\mathbf{r}$ and the specie j at $\mathbf{r}'$. Recall that in the generic model representing a wide class of physical systems we consider effective interactions between clusters of molecules; in particular cases the physical origin of the effective interactions can be different, including (screened) electrostatic interactions, H-bond formation and entropic effects. We only take into account three features of the inteaction potentials: (i) oil and water do not mix (except for $T\to\infty$) (ii) one end of the amphiphilic molecule is preferably oriented toward water-, while the other end is preferably oriented toward oil molecule (iii) amphiphiles preferably form monolayers where they are parallel to each other.

Such a semi-phenomenological theory is suitable only for a description of collective phenomena in which a large number of molecules is involved, such as phase equilibria, response to an external stress or correlations at distances substantially larger than ℓ. There is some analogy between the level of description in our theory (and our parameters), and in the van der Waals theory (and its famous parameters).

Based on the above features we construct a minimal model of effective interactions. We assume oil-water symmetry and nearest-neighbor interactions: the water-water (oil-oil) interaction $-b$, the water-amphiphile (oil-amphiphile) interaction $-c\Delta\mathbf{r}\cdot\hat{\mathbf{u}}$ $(+c\Delta\mathbf{r}\cdot\hat{\mathbf{u}})$, with $\hat{\mathbf{u}}$ describing the orientation of the amphiphile located at the distance $\Delta\mathbf{r}$ from the water (oil) particle, and finally the amphiphile-amphiphile interaction $g[(\hat{\mathbf{u}}\times(\mathbf{r}'-\mathbf{r}))\cdot(\hat{\mathbf{u}}'\times(\mathbf{r}-\mathbf{r}'))]$, where $\hat{\mathbf{u}}$ $(\hat{\mathbf{u}}')$ is the orientation of the amphiphile located at $\mathbf{r}$ $(\mathbf{r}')$. The latter interaction supports formation of flat monolayers (vanishing spontaneous curvature). Because of the oil-water symmetry the model is designed for a description of balanced systems. We require that $\hat{\mathbf{u}}$ is reduced to $\pm\hat{\mathbf{e}}_i, i=1,2,3$, where $\hat{\mathbf{e}}_i$ are the unit lattice vectors. Finally, h_i is the surface contact field, corresponding to the interaction with water particles located at the surface. We will also consider decreased or increased hydrophilicity of the external surfaces. In such a case the interactions between the wall and any component of the mixture are uniformly decreased or increased (multiplied by $0<h_s<1$ or by $h_s>1$) compared to the interactions between the clusters of molecules of water and the chosen specie.

2.2. The method. The natural physical length is the bare thickness of the monolayer, $\ell\sim a$. As the energy unit we can choose the water-water (oil-oil) interaction energy b, representing the oil-water surface tension for $T\to 0$. The dimensionless temperature is defined as kT/b, and similarly the dimensionless chemical potential is μ/b.

Local minima of (1) correspond to self-consistent solutions of the equations (4). Comparing the values of Ω obtained for different local minima we can find the global minimum, identified with the stable phase. At coexistence between two phases Ω assumes the same values at the two corresponding minima, and the value of Ω at the remaining minima is larger. Because of the assumed symmetry of the interaction potentials, the uniform water- and oil rich phases coexist.

In confinement the grand potential can be written in the form

$$\Omega=\omega_b V+\Omega_{ex}, \tag{5}$$

where V is the volume, and $\omega_b=-p$ is the density of the grand potential in the bulk. The form of Ω_{ex} depends on both the confined phase and the properties of the container. In order to calculate ω_b we consider one unit cell of the periodic phase and impose periodic boundary conditions. In any semi-infinite system Ω_{ex} contains a contribution from the wall-fluid surface energy. The effect of a single wall is determined from a slit with identical surfaces of area A separated by a distance $L_N>L_{N_0}$, corresponding to N undeformed lamellas, such that $\Omega-\omega_b A L_N$ is independent of N for $N>N_0$; the surface energy σ is $2\sigma A=\Omega-\omega_b A L_N$. The lamellas are undeformed, when the structure of the confined system far from the boundaries is the same as in the bulk. The wall-fluid surface energy depends on orientation of the external surface with respect to symmetry elements of the phase whose rotational symmetry is broken.

Let us consider

$$\Omega_s=\Omega-\omega_b V-\sum_i\sigma_i A_i, \tag{6}$$

where σ_i and A_i denote the surface tension and area of the i-th surface respectively, and the summation runs over all external surfaces. Eq.(6) represents the contribution to the grand potential associated with mutual effects of different walls. The dependence on the shape of the container is included in this term.

3. Lamellar phases in slits

3.1. Mechanical properties. There are two distinguished orientations of the lamellas with respect to the confining surfaces: perpendicular, ⊥, and parallel, ∥. The corresponding surface energies are denoted by $\sigma_\perp$ and $\sigma_\parallel$ respectively (Fig. 2).

If the lamellas 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 λ, and in this case

$$\Omega_\perp^{ex}/A\approx 2\sigma_\perp \tag{7}$$

independently of L, provided that L is sufficiently large, $L>3\lambda$ [10]. Hence, $\Omega_s\approx 0$ for sufficiently large slits.

For the parallel orientation $\Omega_s(L)$ assumes minima for $L=L_N$, where L_N corresponds to a slit containing N undeformed layers, and for such separations no stress is present in the system. When the slit is expanded (compressed) compared to $L=L_N$, and $|L-L_N|$ is sufficiently large, a new lamellar layer is introduced into (removed from) the system, and $N\to N+1$ $(N\to N-1)$.

The large-period phases are soft, and the short-period phases are stiff. It is well known from experiments that the same external pressure induces large and small deformation in the first and in the second case respectively.

Deformations of the stiff, short-period phases for $L \neq L_N$ were studied in Ref. [10]. Far from phase coexistence with the uniform phases these deformations are shown in Fig. 3.

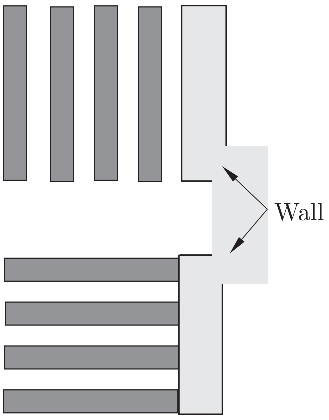


Fig. 2. Two orientations of the lamellas with respect to the external wall, associated with different values of the surface energy σ

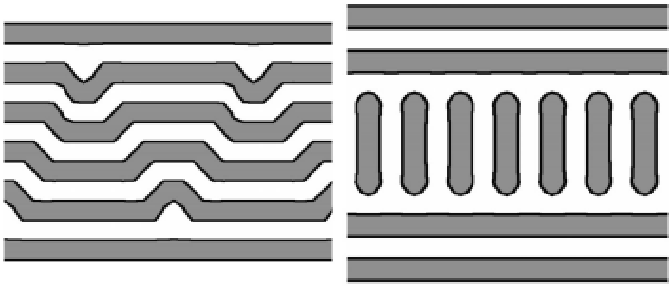


Fig. 3. Cross-section of the slit for $kT/b = 2.5$, $\mu/b = 1$, $c/b = 2.5$, $g/b = 1$ and $h_s = 1$ (far from the coexistence with the uniform phase), obtained by numerical minimization of Eq.(1) with respect to concentration profiles in Ref. [10]. Shaded regions represent oil-rich domains and white regions represent water-rich domains. Thick lines represent the local interfaces $\rho_w(x,z) - \rho_o(x,z) = 0$, where ρ_w, ρ_o are the MF averaged densities of water and oil respectively. The distance between the walls is equal to $25a$ and to $26a$ in the left- and in the right panel respectively

For sufficiently large λ/a, and for large separations between surfaces, ($L \geq 4\lambda$), quite different deformations are found. Namely, the lamellar layers swell or shrink respectively [1,2,9]. The subsequent minima of $\Omega_s(L)$ are well approximated by parabolic curves, even for quite large deviations from $L = L_N$, i.e.

$$\Omega^{ex}_{\parallel}/A \approx \sigma_{\parallel} + \frac{B}{2L_N}(L - L_N)^2, \tag{8}$$

where $|L - L_N| \leq \lambda/2$. Hence, the response of the system to compression or expansion is analogous to the behavior of a series of N identical joined springs. For the case considered in Ref. [9], $B = 0.003(k_bT/a^3)$. The compressibility modulus measured in Ref.[1] ranges for different substances from 0.003 to 0.027, when expressed in units of k_bT/ℓ^3, where the small value of B corresponds to $\lambda/\ell \sim 10$, as in Ref. [9]. For decreasing λ/ℓ a rapid increase of B was found in the CHS model [9]. Our description gives thus results consistent with experiments.

In the case of hydrophilic walls deviations from the elastic response were found in Ref.[9], and were also observed in experiments [1] for $L < 4\lambda$. Sufficiently close to the phase coexistence the associated structural deformations correspond to swelling of the central water- or oil-rich layer, whose composition is the same as in the corresponding metastable uniform phase. The N near-surface lamellas have the same thickness as in the bulk. Thus, the inelastic response to expansion or compression is associated with a different form of Ω_s, namely

$$\Omega_s/A = \Delta\omega_b(L - N\lambda) + 2\sigma_{\ell w}, \tag{9}$$

where $\Delta\omega_b$ is the difference between the grand potential densities in the metastable uniform and the stable lamellar phases, and $\sigma_{\ell w}$ is the surface tension between the lamellar phase at the walls and the water (or oil) rich phase in the center of the slit.

In the slit the globally stable orientation of the lamellas is determined by the sign of the difference $\Omega^{ex}_{\parallel} - \Omega^{ex}_{\perp}$. In the case of hydrophilic surfaces the energy is lower in the parallel orientation. However, only in the parallel orientation there is a translational entropy loss, and in addition the elastic contribution to Ω occurs for $L \neq L_N$. It is not possible to predict apriori the sign of $\Omega^{ex}_{\parallel} - \Omega^{ex}_{\perp}$ in particular conditions. In Ref.[9,10] it was found by numerical minimization of Eq.(1) that in the case of the swollen lamellar phases the parallel orientation is globally stable for any kind of confining surfaces, and for any value of $L > 4\lambda$. In contrast, the perpendicular orientation is globally stable in the case of the short-period phases ($\lambda/\ell \approx 4$) even between surfaces that are weakly hydrophilic. When the hydrophilicity of the surfaces is suitably adjusted to the period of the lamellar phase, then expansion of the slit leads to a switch between the parallel and the perpendicular orientations, provided that $\lambda/\ell \leq 6$. Similar switch has been predicted [4–7] and observed [3] in block co-polymers.

3.2. Capillary lamellarization in slits.

In the case of uniform fluids the confinement-induced shift of the phase coexistence is given by the Kelvin equation [16]. Let us focus on the phase transition between the uniform and the lamellar phases in a slit. Because in the confined lamellar phase the external stress is not released even for large $L \neq L_N$, the assumptions leading to the Kelvin equation (negligible stress) are not satisfied. For the chemical potential μ_{coex} and the temperature T corresponding to the bulk coexistence, the bulk densities of the grand thermodynamic potential Ω for the two phases are equal,

$$\omega^{(1)}_b(\mu_{coex}, T) = \omega^{(2)}_b(\mu_{coex}, T). \tag{10}$$

In the slit of the width L and fixed T the coexistence between phases 1 and 2 occurs for $\mu_{cc} = \mu_{coex} + \Delta\mu$ such that

$$\Omega^{(1)}(\mu_{cc}, T, L) = \Omega^{(2)}(\mu_{cc}, T, L). \tag{11}$$

Let us assume that the phase stable in the bulk is uniform, and the phase condensing in the slit responds elastically to the compression/expansion (see Eq. (8)). For the uniform phase the stress can be neglected, and for sufficiently small $\Delta\mu$ we can expand $\Omega^{(1,2)}(\mu_{coex} + \Delta\mu, T, L)$ about μ_{coex}. The resulting modified Kelvin equation has the form

$$\Delta\mu = \frac{2\Delta\sigma}{\Delta\rho L} - \frac{B(L - L_N)^2}{2\Delta\rho L L_N}, \tag{12}$$

where $\Delta\rho = \rho^{(1)} - \rho^{(2)}$, and $\rho^{(1,2)}$ are *thermodynamic* densities at the bulk coexistence between phases 1 and 2, satisfying the relation $\left(\frac{\partial\omega}{\partial\mu}\right)_{T,N} = \rho$. In ordered phases containing surfactants or lipids $\rho^{(1,2)}$ correspond to space-averaged solute densities. For $L = L_N$ Eq. (12) reduces to the usual Kelvin equation. For fixed μ we obtain in a similar way a shift of temperature at the transition in the slit

$$\Delta T = \frac{2\Delta\sigma}{\Delta s L} - \frac{B(L - L_N)^2}{2\Delta s L L_N}, \tag{13}$$

where Δs is the difference between entropy per unit volume in the two phases at their bulk coexistence.

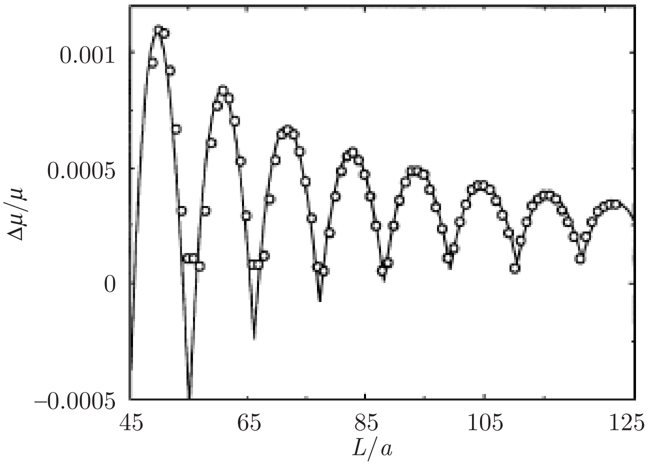
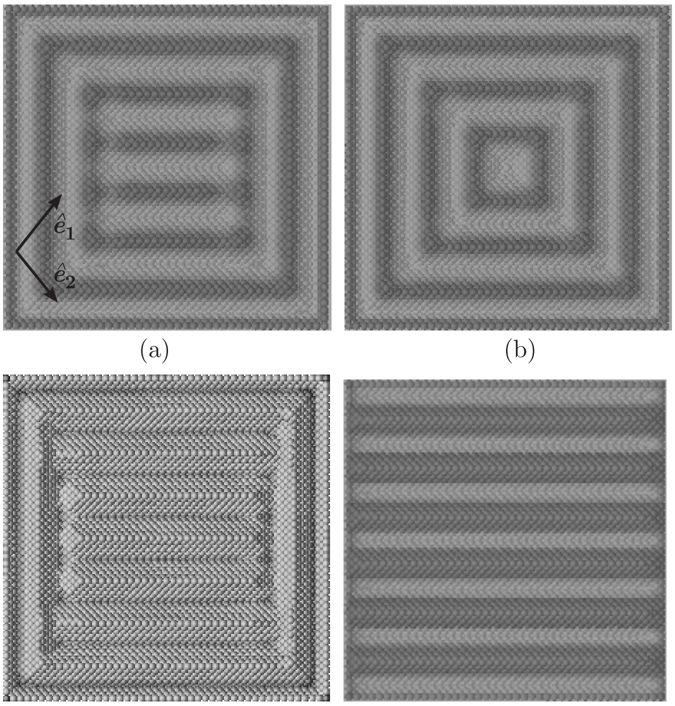


Fig. 4. Shift of the first-order transition between water-rich and lamellar phases as a function of the wall separation L/a, where a is the lattice constant. The solid line is the curve given by (12) with L replaced by $L - 2l_s$. The optimal value of the fitting parameter l_s/a is 6.205. $\Delta\sigma = 0.000527b/a^2$, $\Delta\rho = 0.003124$ have been obtained by independent calculations of the surface tensions and the space-averaged densities at the bulk phase-coexistence. The temperature of the system is $k_bT/b = 2.7$ and the material constants are $c/b = 2.4$, $g/b = 0.15$. The bulk first-order transition is at $\mu_{coex}/b = 4.1541978$

When the water-rich phase is stable in the slit, a single lamella of thickness l_s is adsorbed at the hydrophilic surface. In this case the region which can be filled with water is effectively thinner than the whole slit. The simple thermodynamic prediction agrees quite well with the numerical results obtained in the CHS model [12] (see Fig. 4), provided that L is sufficiently large, $L > 4\lambda$, and is replaced by $L - 2l_s$ in (12).

4. Lamellar phases in pipes

There is only one distinguished orientation in slits – the one perpendicular to the confining surfaces. This is no longer the case for pipes. For the square-base pipes two perpendicular orientations, corresponding to two pairs of the walls, are equivalent. Thus, for identical hydrophilic surfaces two orientations of the lamellas are equally probable. If the surface energy of the lamellar phase perpendicular to the hydrophilic surface is large, then the lamellar structure may not be stable in the square-base capillary. On the other hand, when near all surfaces the parallel lamellas are formed, deformations of the structure inside the pore must be present for all wall separations (see Fig. 5).



(a) (b)

(c) (d)

Fig. 5. Cross-sections through the pipe with water-covered walls far from the coexistence with the uniform phase for (a) $L/d = 82$, b) $L/d = 84$ and c) $L/d = 90$, obtained in Ref. [11] by numerical minimization of Eq. (1) with respect to concentration profiles. Light and dark regions correspond to the water- and oil-rich layers respectively. Note different domain-walls, where lamellas with different orientations are in contact. No stress is present in the case (c). (d) Cross-sections through the pipe with neutral walls for $L/d = 82$. The thermodynamic variables $kT/b = 2.65, \mu/b = 4.6$ and material constants $c/b = 2.5, g/b = 1$ correspond to a stable lamellar phase with the period $\lambda/d = 12$, far from the coexistence with the uniform phase. In the case of the swollen phases the unit vector normal to the lamellas is $\hat{\boldsymbol{n}} = \frac{1}{\sqrt{2}}(\hat{\boldsymbol{e}}_1 + \hat{\boldsymbol{e}}_2)$, where the unit lattice vectors $\hat{\boldsymbol{e}}_i$ are shown in the panel (a). As a consequence, in this case $l \sim d = a/\sqrt{2}$

The results obtained in Ref. [11] for the CHS model show that the morphology in the pipe depends on thermodynamic conditions. Far from the coexistence with the uniform phases the lamellar structure is stable for neutral walls, and Ω_s has a similar form as in the slits. For hydrophilic walls the structures are more complex, as shown in Fig. 5, and additional contribution to Ω_s appears. This new contribution is associated with the domain-walls surface energy.

Because different structures occur for different L, the ratio between the area of the domain walls and the area of the external wall is different in different cases. Moreover, the angle between the vectors normal to the lamellas and to the domain wall is different in Fig. 5a and in Fig. 5b, and the associated domain wall energy is also different. The corresponding contribution to Ω_s has the form $\sum_j \sigma^j_{dw} A^j_{dw}$, where all domain-walls are included (Fig. 5).

For μ and T sufficiently close to the bulk coexistence of the uniform water/oil-rich and lamellar phases, the structure of the lamellar phase in the pipe is quite different than off coexistence. For hydrophilic as well as for neutral surfaces the onion-like structure (Fig. 5b) stabilizes for all values of $L \gg \lambda$. When L and λ are not compatible, the central part of the pipe is occupied by the uniform phase. The cross-section densities, $\rho_w - \rho_o$, as functions of x for $y = L/2$ are shown in Figs. 6 and 7.

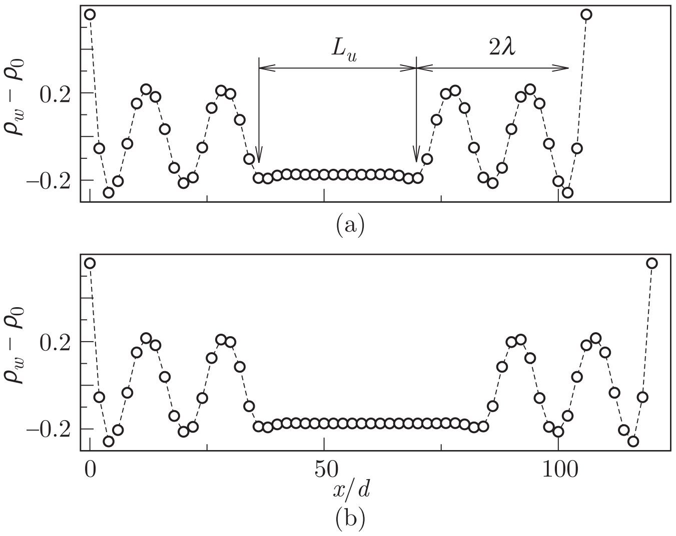


Fig. 6. The difference between densities of water and oil, $\rho_w - \rho_o$, as a function of x for $y = L/2$. (a) $L/d = 106$, and b) $L/d = 120$. There are four lamellar layers (oil and water-rich domains) absorbed at the walls, and the thickness of the central uniform oil-rich tube is $L_u \approx L - 4\lambda$. The walls are water-covered, the thermodynamic variables $kT/b = 2.65, \mu = \mu_{coex}(1 - 0.0016)$ and material constants $c/b = 2.5, g/b = 1$ are close to the bulk coexistence of the lamellar phase with the period $\lambda/d = 16$, and the uniform, oil- and water rich phases

The thickness $L_u = L - N\lambda$ of the central uniform domain, or equivalently the number of lamellar layers at the walls, N, is a function of the distance to the phase transition between the lamellar and water/oil-rich phases in the bulk. At fixed L, L_u increases discontinuously (the number of absorbed lamellar layers decreases) by approaching the coexistence, i.e. for $\mu \to \mu_{coex}$ (see Fig. 8). The water or oil densities in the center of the pore are close to those in the bulk uniform phases.

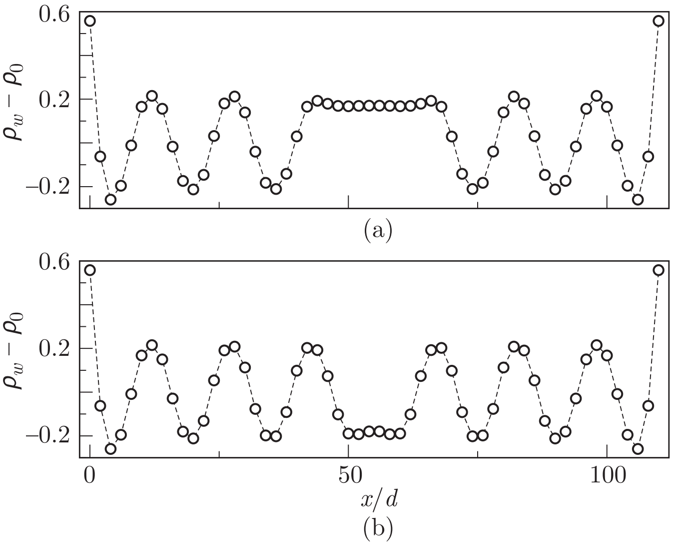


Fig. 7. The difference between densities of the water and oil, $\rho_w - \rho_o$, as a function of x for $y = L/2$ in the onion phase with a) five and b) six lamellar layers absorbed at the walls at the capillary delamellarization transition given by $kT/b = 2.65, \mu_{cc} = \mu_{coex}(1 - 0.0045)$. The pore size $L/d = 106$ and the walls are water-covered. Note that in the CHS model the water- and oil-rich phases coexist, therefore the core part can be filled either with water or with oil. The values of the thermodynamic variables and material constants $c/b = 2.5, g/b = 1$ correspond to the stability of the lamellar phase with the period $\lambda/d = 16$

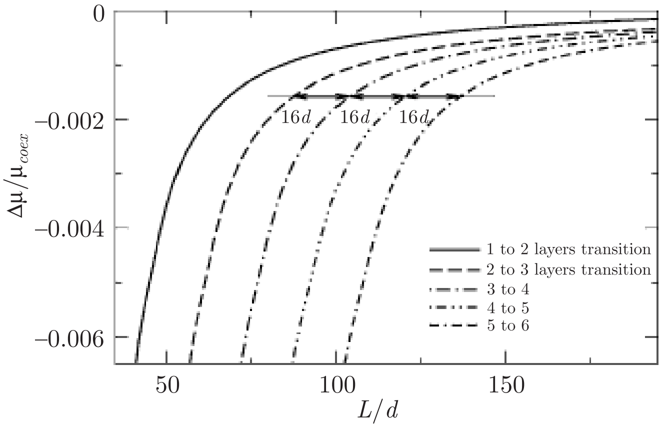


Fig. 8. Structural transitions between onion phases with different number of lamellar layers at the walls in the square-base capillary for $kT/b = 2.65$. The walls of the pore are water covered. The lines separate the stability region of the onion structures with N layers (above) from the stability region of the structures with $N+1$ layers (below in $\Delta\mu/\mu_{coex}$). The case of $1 \le N \le 5$ is shown

The phase equilibria in square-base pipes are just opposite to the phenomenon of capillary lamellarization predicted for slits [12]. Capillary delamellarization is observed in all cases, as a result of the domain-wall energy associated with formation of quasi-onion structures. We have also checked that the hydrophilicity of the external walls influences the shift of the phase coexistence in the pipes very weakly.

5. Summary

The presence of the structure on the nanometer length scale influences the effects of confinement in a very significant way. The strong dependence of the stress on the orientation and the thickness of the sample, and on thermodynamic conditions, is of crucial importance for the structure of the confined system even for $L \sim 10^2\lambda$ or larger. For given shape of the container slight changes of L may lead to abrupt changes of the structure, resulting from the tendency of the system to minimize the thermodynamic potential Ω_{ex}. In the case of broken translational and rotational symmetries Ω_{ex} contains additional terms, and these terms depend on: (i) the chemistry of the confining walls (ii) the period of the lamellar phase, because it determines the elastic modulus B (iii) the thermodynamic state (iv) the geometry of the container.

(i) The chemistry of the confining surface determines the wall-fluid surface energy. For different orientations of the lamellas the wall-fluid surface tension is different.

(ii) Theoretical studies confirm that the large-period phases respond elastically to the external stress. The elastic response is associated with uniform swelling (shrinking) of the lamellas under expansion (compression) of the sample. In the short-period phases the inelastic response is found. The inelastic response is associated with localized deformations of the structure, such as formation of domains with different orientation of the symmetry elements, or stabilization of the phase that is metastable in the bulk in some part of the confined system. The thickness of the lamellas is the same as in the bulk.

(iii) The effects of confinement are qualitatively different far from and close to the phase coexistence with uniform phases. Near the coexistence the difference between the grand potential density in the stable and the metastable phases, $\Delta\omega_b$, is small, and a part of the confined system may be filled with the uniform phase if the interface tension between the two phases is low.

(iv) When the symmetries of the container and of the bulk lyotropic liquid crystal are not compatible, domains of differently oriented lamellar phases, associated with domain-wall surface energy, may be formed in some thermodynamic states. Close to the phase coexistence we have observed formation of domain walls in the lamellar phase confined in square-base pipes for all kinds of external walls.

The above observations lead to the following form of Ω_{ex} near the coexistence with a uniform phase

$$\Omega_{ex} = \sum_i \sigma_i A_i + \sum_j \sigma^j_{dw} A^j_{dw} + \sigma_{w\ell} s + \Delta\omega_b v + \Omega_{el} \quad (14)$$

where $\sum_i \sigma_i A_i$ is the sum of wall-fluid surface tension contributions associated with all external walls; $\sigma_{dw} A_{dw}$ is the sum of all domain-wall surface energies and $\sigma_{w\ell}$ is the interface tension between the water and lamellar phases coexisting in the confined system, and s is the area of the interface. $\Delta\omega_b v$ is the contribution associated with the region of volume v occupied by the uniform phase. Finally, Ω_{el} is the elastic contribution in the case of the swollen phases, and in the case of the slit it has the form given in Eq. (8). In particular cases some of the above terms may vanish. In slits with $L > 4\lambda$ only the first and the last terms are present in the case of the swollen phases. In square-base pipes the last term vanishes (the confined lamellar phase has the same period as in the bulk). Note that $\sigma_{dw} > 0$, $\Delta\omega_b > 0$ and $\sigma_{w\ell} s > 0$. However, the deformations of the lamellar phase (and $\Omega_{el} > 0$) and/or the large wall-fluid surface tensions $\sigma_\perp$ can be avoided when these terms are present, resulting in the lowest value of Ω_{ex}.

Let us stress at the end that in periodic structures the geometry of the confining walls may play a more significant role than the hydrophilicity, or, in general, wall-fluid interaction potentials. For the same kind of walls quite opposite phenomena may occur in different geometries, as we have shown for phase equilibria. This property results from broken symmetry of the periodic phases, and we expect that other physical systems may exhibit similar behavior.

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