

Swollen lamellar phases confined in capillarylike pores

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Structure and mechanical properties of swollen lamellar phases confined in square-base pipes are studied in a mesoscopic lattice model for oil-water-surfactant mixtures. Structure depends crucially on a thermodynamic state and is quite different far and close to the coexistence with a uniform phase. Lamellar domains with different orientations of lamellas are formed in most cases, and the mechanics is determined mainly by domain-wall energies. Shift of phase equilibria in square-base pipes compared to the bulk is just opposite to the shift in slits. We find capillary delamellarization for short-period and for swollen phases, for hydrophilic and for neutral external surfaces.

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I. INTRODUCTION

In systems self-assembling in periodic structures on the nanometer length scale the effects of confinement are much stronger than in simple fluids. In particular, in the lamellar phase the phenomena known for confined simple fluids are present for much larger systems, up to $0.1-1\ \mu\text{m}$. Moreover, new effects of confinement occur, because in the lamellar phase the translational and rotational symmetries are broken. The confined lamellar phases were studied experimentally [1] and theoretically [2–4] mainly in the slit geometry. Other geometries, such as long pores with small bases (“pipes”), may lead to different mechanical and thermodynamic properties, due to deformations of the structure which in the slits are absent. The effects of confinement on mechanics and structure in square-base long pipes were studied in Ref. [5] for short-period lamellar phases. However, from the results obtained for slits [2,4], and described briefly below, it follows that the effects of confinement on the swollen and short-period lamellar phases are significantly different, and it is not justified to assume that in pipes those effects are similar. Separate studies are necessary for a determination of the effects of confinement in pipes on the mechanics and structure of the swollen lamellar phases. This is the first purpose of our work. Our second purpose concerns phase equilibria in pipes. In Ref. [3] the effect of capillary lamellarization, analogous to capillary condensation, was investigated in the slit geometry. Similar effect of capillary smectization was investigated recently in liquid crystals [6]. Our purpose here is to find out how the effect of capillary lamellarization, found in slits in Ref. [3], is modified in pipes. In fact we find instead a capillary delamellarization for all kinds of surfaces for short-period as well as for swollen lamellar phases.

Let us briefly summarize the mechanical and structural properties of the swollen and short-period lamellar phases confined in slits. Theoretical studies [4] for a model system indicate that lamellas in the swollen lamellar phases are parallel to all types of flat surfaces, and under expansion (compression) uniformly swell (shrink) until a new lamella is introduced (removed), and $N \rightarrow N+1$ ($N \rightarrow N-1$), where N denotes the number of confined lamellas. Mechanically such

phases with N lamellas are analogous to a series of N joint springs with a very small modulus of elasticity B . At the equilibrium distances $L=L_N$ there is no stress in the system and $L_{N+1}-L_N=\lambda$, the period of the lamellar structure. B decreases with the increasing period of the bulk lamellar phase λ [2,7]. Such a theoretically predicted behavior agrees with experimental results [1].

In the short-period phases the orientation of the lamellas depends on the chemistry (hydrophilicity) of the confining surfaces. For neutral surfaces the lamellas are perpendicular to the confining walls. Between weakly hydrophilic surfaces a switch of the orientation of the lamellas occurs when the slit is expanded (compressed), and the width of the slit changes from the values commensurate to the values incommensurate with λ . Such a switch was predicted in the lattice model of oil-water-surfactant mixtures [4] and for copolymers [8]. For the latter case the phenomenon was also observed experimentally [9]. For strongly hydrophilic surfaces the expansion of the slit leads to localized deformations of the structure, and to a nonelastic response [2,4].

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. In Ref. [5] it has been observed that for strongly hydrophilic walls the structure in the square-base pipes is quite different than in the slits. A quasionion structure is formed, and the lamellar domains parallel to the external surfaces form domain walls along the diagonals of the square base. In Ref. [5] the response of the confined system to an increase of the thickness of the capillary (with conserved symmetry) was also studied. When L is increased compared to the equilibrium side length $L=L_N$, for which no stress is present, a thin water or oil cylinder coated with surfactant is inserted into

the center of the pore, and further expansion leads to an increase of the thickness of the central layer, until the next equilibrium width $L=L_{N+1}$ is reached [5]. Then the procedure is repeated. Insertion of the new layer is associated with a large stress, which then slowly releases under expansion. The behavior is thus inelastic.

As already discussed for the slit geometry, the swollen lamellar phases may behave in quite a different way. Neither the structure nor the mechanical properties in long capillaries can be deduced from the behavior of the short-period phases. In particular, some other deformations of the lamellar structure may occur in the square-base capillaries with hydrophilic surfaces, and they may be associated with a different mechanical response to the compression or expansion of the capillary compared to its equilibrium width $L=L_N$. Determination of the structure and mechanical properties of the swollen lamellar phases in long pores is the first purpose of this work.

Let us summarize the phase equilibria of self-assembling systems in confinement. The elastic contribution to the thermodynamic potential influences the transition between the uniform and the lamellar phase. In slits the shift of the phase transition depends on the width of the slit L , and can be described by the modified Kelvin equation [3]. In the modified Kelvin equation the phenomenological parameters are the solute density difference in the two coexisting phases and the difference between the wall-fluid surface tensions, as in simple fluids. In addition, the shift of the transition depends on the modulus of elasticity B and on λ . To the best of our knowledge the shift of the phase equilibria in pipes was not yet studied for any lamellar system. It may differ from the behavior predicted for the slits, due to additional deformations of the structure. In principle, the large energy of deformations may suppress the stabilization of the periodic phase in the capillary, even when the lamellar phase is stable in the bulk and the planar surfaces favor the lamellar phase. The second purpose of this work is a determination of the shift of the uniform–lamellar phase transition in square-base capillaries for short-period and for swollen lamellar phases, for hydrophilic and neutral surfaces.

For systems with $L \gg \lambda$ determination of the structure, mechanics, and phase equilibria from realistic microscopic models is very difficult. However, lamellar phases in systems as diverse as oil-water-surfactant mixtures, block copolymers, or liquid crystals (smectic phase) have very similar properties on the mesoscopic length scale. These properties depend more on the ratio between the period of the structure and the thickness of the monolayer, than on the substance forming the lamellar phase. The details of the molecular structure are not of primary importance for the general features of the phase equilibria or the structure on the length scale much larger than the atomic size. For this reason mesoscopic models can provide a valuable insight and first semiquantitative results, which can stimulate experimental or theoretical studies with more realistic models. In fact predictions of the Ciach, Høye, and Stell (CHS) model [2] for the slit geometry agree quite well with experimental results [1]. In this work we study the effects of confinement in square-base capillaries on the swollen lamellar phases in the CHS model.

II. PHENOMENOLOGY

We start with a brief description of thermodynamic properties of a system confined in a box with the edges of lengths L_α with $\alpha=x,y,z$. We assume that the system is in equilibrium with a reservoir, and that the temperature T and the chemical potentials μ_i of all components are fixed. The increment of the grand thermodynamic potential can be written as

$$d\Omega = \omega_b d(L_x L_y L_z) + 2\sigma_x d(L_y L_z) + 2\sigma_y d(L_x L_z) + 2\sigma_z d(L_x L_y) + f_x L_y L_z dL_x + f_y L_x L_z dL_y + f_z L_x L_y dL_z. \quad (1)$$

ω_b is the bulk thermodynamic potential density, σ_x , σ_y , and σ_z are the wall-fluid surface tensions for walls perpendicular to \hat{x} , \hat{y} , and \hat{z} , respectively, while f_x , f_y , and f_z are related to the excess pressure in the direction denoted by the subscripts. For fixed $L_z \gg L_x, L_y$, the above simplifies to

$$d(\Omega/L_z) = \omega_b d(L_x L_y) + 2\sigma_x dL_y + 2\sigma_y dL_x + f_x L_y dL_x + f_y L_x dL_y. \quad (2)$$

In the rest of this work we shall focus on the case of long pores with $L_z \rightarrow \infty$ and will consider $\Omega^z = \Omega/L_z$.

A. Mechanical properties

The excess pressure in the x direction is defined as

$$\Pi_x = - \left(\frac{\partial \Omega_{ex}}{\partial V} \right)_{L_y, L_z} = - \frac{1}{L_y} \left(\frac{\partial \Omega_{ex}^z}{\partial L_x} \right), \quad (3)$$

where V is the volume, and the excess grand thermodynamic potential of the system confined in the box with $L_z \rightarrow \infty$ is

$$\Omega_{ex} = \Omega_{ex}^z L_z = (\Omega^z - \omega_b L_x L_y) L_z. \quad (4)$$

Π_y is defined in a similar way. For a square-base pore $L_x=L_y=L$, symmetry conserving compressions or expansions are associated with the excess pressure given by

$$\Pi = - \left(\frac{\partial \Omega_{ex}}{\partial V} \right)_{L_z} = - \frac{1}{2L} \left(\frac{\partial \Omega_{ex}^z}{\partial L} \right). \quad (5)$$

Ω_{ex} , and consequently the excess pressure, depend significantly on the structure of the confined fluid. For periodic structures Ω_{ex} contains a term associated with the energy of deformations of the periodic structure when its period λ is incommensurate with L . For swollen lamellar phases in slit geometry this contribution has the form characteristic for elastic systems [2],

$$\Omega_{el}^z = B_l (L - L_N)^2 L / 2L_N, \quad (6)$$

where for $L=L_N$ the slit contains N undeformed lamellar units. The period of density oscillations in the undeformed lamellar structure is the same as in the bulk. Let us first focus on the lamellar structure of the confined fluid. We assume that the lamellas are parallel to the x direction, and the period of density oscillations is $\lambda \ll L$. For the square-base pores, and deformations that conserve this symmetry, the excess pressure (5) for the confined lamellar phase can be written as [5]

$$\Pi(L) = -\frac{1}{L}(\sigma_{\parallel} + \sigma_{\perp}) - \frac{B_l(L-L_N)}{2L_N} \left(1 + \frac{L-L_N}{2L}\right) \quad (7)$$

$$(L_N^t < L < L_{N+1}^t),$$

where $\sigma_{\parallel} = \sigma_x$ and $\sigma_{\perp} = \sigma_y$. The second term in Eq. (7) represents the elastic contribution (6), and vanishes for $L=L_N$. For $L=L_{N+1}^t$ a new lamella is introduced into the expanding pore $N \rightarrow N+1$ and for the confined lamellar structure $L_{N+1}^t - L_N^t = \lambda$. The instabilities at $L=L_N^t$ lead to an additional contribution to $\Pi(L)$ of the form $\sum_{N=N_o} a_N \delta(L-L_N^t)$.

For $L_N \gg \lambda$ Eq. (7) may be expanded as

$$\Pi(L) + \frac{1}{L}(\sigma_{\parallel} + \sigma_{\perp}) = -\frac{B_l}{2}x - \frac{B_l}{4}x^2 + \frac{B_l}{4}x^3 + O(x^4) \quad (8)$$

$$(L_N^t < L < L_{N+1}^t),$$

where $x=(L-L_N)/L_N$. For short-period phases the lamellar structure was found to be stable in square-base capillaries with neutral walls [5].

In the square-base pores with identical hydrophilic walls the directions x and y are equivalent. The lamellas should be parallel to the strongly hydrophilic surfaces. In Ref. [5] it is shown that this is indeed the case for short-period phases. In the resulting quasionion structure domain walls between perpendicularly oriented lamellas are formed along the diagonals, and intersect at the center of the square. The domain walls are associated with additional contributions to Ω_{ex}^z , which are present even in the absence of compression or expansion of the layers (i.e., for $L=L_N$). For $L=L_N$ we assume that for the quasionion structure

$$\Omega_{ex}^z(L_N) = 4L_N\sigma_{\parallel} + 2\sqrt{2}L_N\gamma_o + \delta, \quad (9)$$

where γ_o is the surface tension associated with the surface along which the perpendicularly oriented lamellas form a domain wall, and δ is the line tension along the line where the domain walls intersect. If, in addition, we assume that the elastic contribution (6) is also present, then for the quasi onion structure we obtain

$$\Pi(L) = -\frac{1}{L}(2\sigma_{\parallel} + \sqrt{2}\gamma_o) - \frac{B_o(L-L_N)}{2L_N} \left(1 + \frac{L-L_N}{2L}\right) \quad (10)$$

$$(L_N^t \leq L < L_{N+1}^t),$$

where B_o denotes the modulus of elasticity of the onion structure. Similarly as in the case of the lamellar structure, the instabilities at $L=L_N^t$, associated with the contribution to $\Pi(L)$ of the form $\sum_{N=N_o} b_N \delta(L-L_N^t)$ are also present.

In Ref. [5] it was shown that in the stiff, short-period lamellar phases the onion structures are semielastic, i.e., $\Omega_{ex}^z(L-L_N) - 4L\sigma_{\parallel} - 2\sqrt{2}L\gamma_o$ has a nearly parabolic shape only for $L-L_N < 0$ (and for $|L-L_N|$ sufficiently small), i.e., for compression. For small positive values of $L-L_N > 0$ (i.e., for expansion) $\Omega_{ex}^z(L-L_N) - 4L\sigma_{\parallel} - 2\sqrt{2}L\gamma_o$ rapidly increases due to insertion of the new cylinder in the center of the pipe.

As we will show later, some of the results of Ref. [5] do not apply to the swollen phases. More complex structures stabilize in pipes with hydrophilic surfaces when the lamellar phase is stable in the bulk (off phase coexistence with the uniform phase). Lamellar domains assume different shapes for different values of L , and different orientations of lamellas with respect to the domain walls occur. For more complex structures $2\sqrt{2}\gamma_o L$ should be replaced by the sum of surface energies of all the domain walls that are formed in the capillary, and Eqs. (9) and (10) should be modified accordingly. Because different structures occur, it is more convenient to consider the overall domain-wall energy per area of one external wall,

$$\sigma_{dw} = \lim_{L \rightarrow \infty} \Omega_{ex}^z(L)/L - 4\sigma_{\parallel}. \quad (11)$$

In the particular case of the onion structure $\sigma_{dw} = 2\sqrt{2}\gamma_o$.

B. Phase equilibria

Let us focus on phase equilibria between the lamellar and uniform phases in a system confined in a square-base pipe. Consider first a simple fluid at fixed thermodynamic conditions that is close to the bulk transition to the phase which is preferred by the walls. In the slit the phase transition occurs for a particular wall separation. The phenomenon is known as the capillary condensation or evaporation, when the liquid-wall or the gas-wall surface tension is lower respectively. In Ref. [3] the effect of confinement in the slit on the phase equilibria between uniform and lamellar phases was studied. It was found that the elastic contribution to Ω leads to a significant modification of the Kelvin equation for the capillary lamellarization. Namely, when one of the phases is periodic, then at fixed thermodynamic conditions close to the bulk coexistence a sequence of transitions between the two phases occurs for a sequence of wall separations [3].

In pipes we can expect similar effects as in the slits. In addition, formation of the quasionion structure may play a role for the shift of the phase transition. Let us briefly repeat the derivation of the modified Kelvin equation [3] for the quasionion structure, i.e., for Ω_{ex}^z given in Eqs. (9) and (10). For concreteness let us focus on oil-water-surfactant mixtures. We shall also limit ourselves to symmetric (equal oil and water chemical potentials) and incompressible (fixed total density) mixtures, where only the chemical potential difference between water and surfactant, μ , is relevant. For the chemical potential $\mu = \mu_{coex}$ and the temperature T corresponding to the bulk coexistence, the bulk densities of the grand thermodynamic potential Ω^z for the two phases are equal,

$$\omega_b^p(\mu_{coex}, T) = \omega_b^u(\mu_{coex}, T), \quad (12)$$

where the superscripts p and u denote the periodic and the uniform phase, respectively. At the capillary lamellarization in the square-base pipe of the length L , for $\mu_{cc} = \mu_{coex} + \Delta\mu$, and fixed T we have

$$\Omega^p(\mu_{cc}, T, L) = \Omega^u(\mu_{cc}, T, L). \quad (13)$$

Let us assume that the phase stable in the bulk is uniform, and the phase condensing in the capillary responds elasti-

cally to the compression and/or expansion. For the uniform phase the solvation force can be neglected, and for sufficiently small $\Delta\mu$ we can expand $\Omega^{(p,u)}(\mu_{coex} + \Delta\mu, T, L)$ about μ_{coex} . The resulting modified Kelvin equation has the form

$$\Delta\mu = \frac{\Delta\bar{\sigma}}{(\rho^u - \rho^p)L} - \frac{B(L - L_N)^2}{2(\rho^u - \rho^p)LL_N}, \quad (14)$$

where $\rho^{(p,u)}$ are *thermodynamic* solute densities satisfying the relation $(\partial\omega/\partial\mu)_{T,N} = \rho$. In ordered phases containing surfactants or lipids ρ^p corresponds to space-averaged solute densities. For the equilibrium wall separations $L = L_N$, corresponding to no stress, the second term in (14) vanishes and (14) reduces to the usual Kelvin equation. In the case of the quasionion structure, however, in addition to the wall-fluid surface tension, also the domain-wall energy contribution should be included, and

$$\Delta\bar{\sigma} = 4\Delta\sigma + 2\sqrt{2}\gamma_o, \quad (15)$$

where $\Delta\sigma = \sigma^p - \sigma^u$ and $\sigma^{p,u}$ corresponds to the wall-fluid surface tension for the corresponding phase. For more complex structures $2\sqrt{2}\gamma_o$ should be replaced by σ_{dw} , and Eq. (15) should be modified accordingly. Note the crucial role of the sign of $\Delta\bar{\sigma}$ for the type of the phase transition, i.e., whether the lamellarization (analog of condensation) or delamellarization (analog of evaporation) occurs. Recall that μ is the difference between the chemical potentials for water and for the surfactant, so μ increases for decreasing surfactant density. Usually $\rho^u - \rho^p < 0$, and when the periodic phase is preferred by the walls, $\Delta\sigma < 0$, so $\Delta\mu > 0$ at the transition, i.e., the transition occurs at lower surfactant density than in the bulk. However, in principle, $\Delta\bar{\sigma}$ can become positive for sufficiently large values of the domain-wall energy σ_{dw} . In such a case the analog of evaporation would occur, i.e., the stability region of the uniform phase would be enlarged in the square-base capillary, even though the planar walls prefer the lamellar phase. Within the phenomenological theory we cannot predict the sign of $\Delta\bar{\sigma}$ in particular experimental or model systems. Therefore the question whether the stability of the periodic phase in capillaries occurs before or after the bulk transition when the surfactant density is increased, can be answered by experiments or by calculations for some model systems. Here we consider the phase equilibria in square-base pipes for short-period and for swollen lamellar phases for hydrophilic and neutral surfaces in the CHS model described in the next section.

III. MODEL

The CHS model was introduced by Ciach, Høye, and Stell [10] 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 [11]. For determination of the excess grand potential and the correspond-

ing structure of the confined system we use a mean-field approximation and for the grand thermodynamic potential we assume the following expression:

$$\Omega = H_{MF}[\rho_i(\mathbf{r})] - TS, \quad (16)$$

where

$$H_{MF}[\hat{\rho}_i(\mathbf{r})] = \frac{1}{2} \sum_{\mathbf{r} \in V} \sum_i \phi_i(\mathbf{r}) \hat{\rho}_i(\mathbf{r}) - \mu \sum_{\mathbf{r} \in V} [\hat{\rho}_1(\mathbf{r}) + \hat{\rho}_2(\mathbf{r})] + \sum_{\mathbf{r} \in \partial V} \sum_i h_i \hat{\rho}_i(\mathbf{r}) \quad (17)$$

is the Hamiltonian in the mean-field approximation, the lattice constant a is comparable to the length of amphiphilic molecules,

$$\phi_i(\mathbf{r}) = \sum_{\mathbf{r}'} \sum_j u_{ij}(\mathbf{r} - \mathbf{r}') \rho_j(\mathbf{r}') \quad (18)$$

is the mean field, 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

$$\rho_i(\mathbf{r}) = \langle \hat{\rho}_i(\mathbf{r}) \rangle_{MF} \quad (19)$$

is the mean-field average of the microscopic densities $\hat{\rho}_i(\mathbf{r})$. 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. 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}' . 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, oriented 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 above-described interactions with water particles located at the surface. Decreased or increased hydrophilicity of the external surfaces can also be considered. 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.

The stable structure is identified with the global minimum of (16). Local minima of (16) correspond to self-consistent solutions of the equations (19). Comparing the values of Ω^z obtained for different local minima we can find the global minimum.

We assume now that $L_z \rightarrow \infty$ and that the structure in the pore is translationally invariant in the z direction. In this case

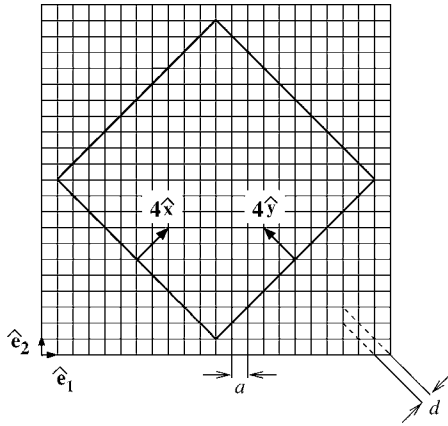


FIG. 1. The cross section through the square-base capillary. The characteristic lengths and vectors are shown. See text for more details.

the projection of the orientation of the amphiphilic molecules onto the (x, y) plane is relevant for the description of the structure. Density distributions and excess pressure in such a pore can be thus calculated in a two-dimensional version of the CHS model, where $\hat{\mathbf{u}}$ belongs to the (x, y) plane. Following Ref. [5] we project $\hat{\mathbf{u}}$ onto the unit lattice vectors in the (x, y) plane, $\hat{\mathbf{e}}_i$, $i=1, 2$, and we distinguish four different states, which can be described as $\pm\hat{\mathbf{e}}_i$, $i=1, 2$. We consider two types of boundary conditions: (i) all the walls of the pore are water covered or strongly hydrophilic; the interactions with the boundary lattice sites are the same as with the water-occupied sites in the bulk and (ii) all the walls are neutral—there is no interaction with the sites at the boundary layer. It is straightforward to write down the expressions for the external fields $h_i(\mathbf{x})$ which correspond to these boundary conditions.

The MF bulk phase diagram of an effectively two-dimensional model was found in Ref. [5] for fixed interaction constants $c/b=2.5$ and $g/b=1$. The stable phases are as follows: microemulsion, oil-rich, water-rich, a phase with two-dimensional density oscillations (“tubular phase”), the surfactant-rich phase with a smectic order, and finally the lamellar phase. In this work we choose the above values of the coupling constants. In continuous-space models all orientations of bulk lamellas are equivalent. However, on the lattice the rotational symmetry is broken. Therefore the lamellar phases on the lattice are not only characterized by the density profiles in the direction of the density oscillations, but also by the orientation of the vector normal to the layers, $\hat{\mathbf{n}}$. It turns out that in the considered model the short-period phases, with $\lambda \leq 6$, are characterized by $\hat{\mathbf{n}}=[1, 0, 0]$ or $\hat{\mathbf{n}}=[0, 1, 0]$, or $\hat{\mathbf{n}}=[0, 0, 1]$. Such phases confined in square-base capillaries were studied in Ref. [5]. In this work we focus on the swollen phases $\lambda > 6$, in which $\hat{\mathbf{n}}=[\pm 1, \pm 1, 0]$ or $\hat{\mathbf{n}}=[\pm 1, 0, \pm 1]$, etc. in the CHS model. In real systems the lamellas are parallel to strongly hydrophilic surfaces, and to model such situations for the swollen phases near a hydrophilic wall one should consider the external surfaces perpendicular to $\hat{\mathbf{n}}=[\pm 1, \pm 1, 0]$, etc.. The cross section through the square-base capillary on the lattice is shown in Fig. 1, and the schematic of the structure of the particular “frozen” swol-

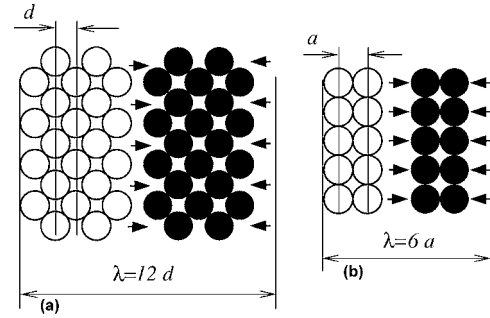


FIG. 2. (a) Schematic of the frozen lamellar structure with $\hat{\mathbf{n}}=(1, 1, 0)$ and $\lambda=12d$. (b) Schematic of the frozen lamellar structure with $\hat{\mathbf{n}}=(1, 0, 0)$ and $\lambda=6a$. The filled and open circles denote water and oil clusters, respectively, and the arrow denotes the cluster of oriented surfactant.

len and short-period lamellar phases are shown in Fig. 2, respectively.

Before presenting the numerical results we should specify the length and energy units. For the ordering in the lamellar structure, i.e., on the mesoscopic length scale, the natural physical length is the bare thickness of the monolayer, or the length of amphiphilic molecules. In the lattice model the thickness of the monolayer depends on the orientation of the lamellas. For the swollen phases the thickness of the monolayer corresponds to $d=a/\sqrt{2}$, where a is the lattice constant (see Figs. 1 and 2). For the swollen phases we shall choose d as the length unit. Typically, in the systems forming the swollen phases $d \sim 2$ nm. For the stiff short-period phases with the density oscillations in the principal directions on the lattice, the thickness of the monolayer corresponds to a (see Figs. 1 and 2). For systems forming short-period phases the thickness of the monolayer is typically smaller, and we choose $a \sim 1.5$ nm as the length unit. As the energy unit we can choose the water-water (oil-oil) interaction energy b , representing the oil-water surface tension for $T \rightarrow 0$. The dimensionless temperature is defined as kT/b , and similarly the dimensionless chemical potential is μ/b .

In order to determine the effects of confinement we first calculate ω^b characterizing the bulk, and next the surface tensions σ_{\parallel} and σ_{\perp} characterizing the semi-infinite systems. In the bulk case we consider one unit cell and impose periodic boundary conditions. The effect of a single wall is determined from the slit with identical walls. In the directions parallel to the surfaces one unit cell and periodic boundary conditions are considered. The width L is chosen sufficiently large so that for the considered box $\ell_x \times \ell_y \times L$ the calculated $\Omega - \omega_b \ell_x \ell_y L$ is independent of L within the required accuracy, and the sides ℓ_x and ℓ_y are appropriately chosen. On the lattice the excess pressure Π is obtained by replacing the derivative in Eq. (5) by the lattice first-order difference operator. More details concerning calculation methods can be found in Refs. [2,5].

IV. NUMERICAL RESULTS

A. Structure and mechanical properties

In the first step we consider the structure for neutral and for water-covered walls in square-base pipes for different

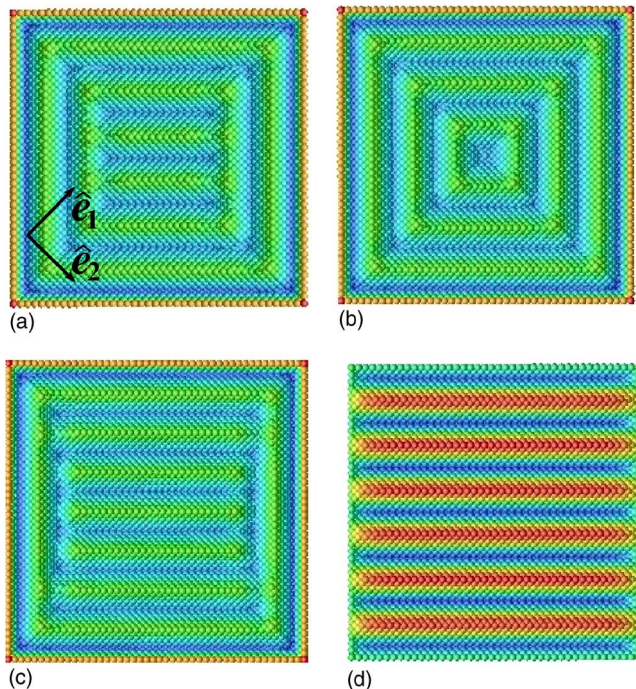


FIG. 3. (Color online) Water-covered walls, (a) $L/d=82$, (b) $L/d=84$, and (c) $L/d=90$. The case (c) corresponds to the equilibrium width with no stress, $\Pi=0$. (d) Neutral walls $L/d=82$. The thermodynamic variables $kT/b=2.65$, $\mu/b=4.6$ and material constants $c/b=2.5$, $g/b=1$ correspond to a stable lamellar phase with the period $\lambda/d=12$.

thermodynamic states. We shall focus first on the stability region of the bulk lamellar phase far from the phase transition, and next on the vicinity of the bulk coexistence of the lamellar and the uniform phases. Our results show that structure of the confined lamellar phase is quite different in the two thermodynamic states.

1. Far off the lamellar-water coexistence

For the neutral walls the lamellar structure is stable for all values of $L \gg \lambda$, as is the case for short-period phases [5]. For water-covered walls, however, the structure in the capillary is different for different values of $L_N^i \leq L < L_{N+1}^i$, as shown in Figs. 3(a)–3(c). Only for $L=L_N-6$ the quasionion structure is stable, where $L_N=6+\lambda N$ corresponds to vanishing stress. Otherwise we see the onionlike structure near the walls, and the region with lamellas in the center of the square [Figs. 3(a) and 3(c)]. Cross sections through such structures resemble cigars in a box, and we call them cigar structures. Note that in the cigar configuration in addition to the domain walls along the diagonals of the square, there are two more domain walls parallel to the walls of the long pore. The orientations of the lamellas with respect to these domain walls are different than along the diagonals of the square base, so the domain wall surface tension is also different.

Let us describe the mechanical properties of the swollen phases in thermodynamic states corresponding to the stability of the lamellar phase in the bulk (off the phase coexistence). Consider first the excess pressure for the square-base

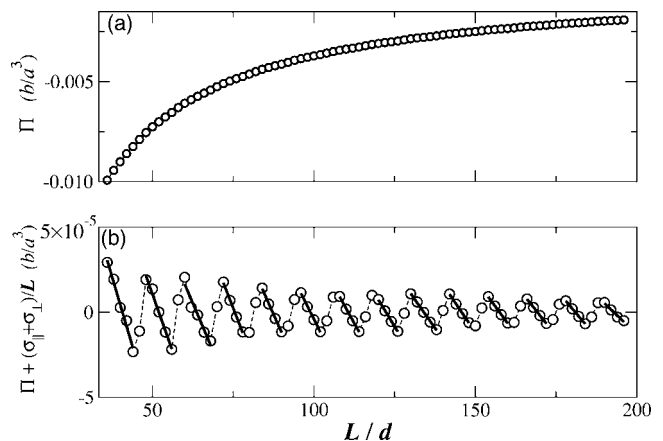


FIG. 4. (a) The excess pressure $\Pi = -(1/2L)\partial\Omega_{ex}^z/\partial L$; (b) $\Pi(L) + (\sigma_{\parallel} + \sigma_{\perp})/L$ [see Eqs. (7) and (8)] for the square-base pore with side L as functions of L . The walls are neutral (surface fields $h_i=0$). The solid lines in (b) are given by the first term on the rhs of Eq. (8) for L such that $|L-L_N|/d \leq 2$. The surface tensions are $\sigma_{\parallel}=0.190b/d^2$ and $\sigma_{\perp}=0.188b/d^2$. The optimal value of the fitting parameter B_l is $B_l=0.000\ 3kT/d^3$. 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 $\lambda/d=12$. For any value of L the square-base pore favors the lamellar structure Fig. 3(d). Lengths are measured in d units, and b is the water-water interaction energy.

capillaries with neutral walls, for which the lamellar structure shown in Fig. 3(d) is stable. Π is shown in Fig. 4(a). The contribution to the excess pressure associated with structural deformations, $\Pi(L) + (\sigma_{\parallel} + \sigma_{\perp})/L$, is shown in Fig. 4(b), where the surface tensions $\sigma_{\parallel}=0.190b/d^2$ and $\sigma_{\perp}=0.188b/d^2$ were obtained by independent calculations. The solid lines correspond to the optimal value of the fitting parameter $B_l=0.000\ 3kT/d^3$ [see Eq. (8)]. The agreement with the elastic behavior is very good. Note the very low value of the elastic constant B_l , much lower (three orders of magnitude) than in the case of the short-period lamellar phases. For the swollen phases the elastic contribution to Π is negligible compared to the surface-energy contributions [it is two orders of magnitude smaller, see Fig. 4(a)], in contrast to the case of the short-period phases, where these two contributions are comparable [5].

Let us focus now on the mechanical properties of the lamellar phase confined in square-base capillaries with hydrophilic (water-covered) walls. In Fig. 5(a) we show $[\Omega_{ex}^z(L_N) - 4\sigma_{\parallel}]/(2\sqrt{2})$, analogous to γ_o in the onion structures. The surface tension $\sigma_{\parallel}=-0.483b/d^2$ was obtained by independent calculations. Thermodynamic considerations suggest that the above line should be a straight line. Indeed, our results agree very well with the above prediction. Our result compared with the result of Ref. [5] (for $kT/b=2.1$ and $\mu/b=3.1$) shows that the values of $[\Omega_{ex}^z(L_N) - 4\sigma_{\parallel}]/(2\sqrt{2})$ for the swollen and short-period phases are identical, when expressed in the natural physical units. This result is quite surprising and shows that the domain-wall energy is much less sensitive to the period of the lamellar phase than the elastic modulus. The overall domain-wall energy per area of a single external surface defined in Eq. (11) is

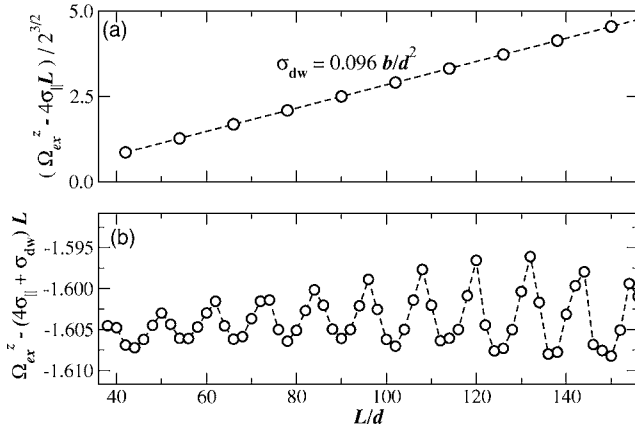


FIG. 5. (a) $[\Omega_{ex}^z(L_N) - 4\sigma_{||}L_N]/(2\sqrt{2})$ at the values of the width of the pore $L=L_N$ corresponding to no stress, $\sigma_{||} = -0.483b/d^2$. From the slope of the straight solid line we can deduce the value of $\sigma_{dw}/(2\sqrt{2})$ in the absence of the stress for the phase with $\lambda=12d$. Note that $\sigma_{dw}/(2\sqrt{2})$ is analogous to γ_o for the onion structure, and that for short-period phases the same value of $\gamma_o \approx 0.034b/d^2$ was obtained in Ref. [5] for $kT/b=2.1$ and $\mu/b=3.1$. (b) $\Omega_{ex}^z(L) - (4\sigma_{||} + \sigma_{dw})L$ for the square base pore with side L , as a function of L . The walls are water covered. The thermodynamic variables are $kT/b=2.65$, $\mu/b=4.6$ and the material constants are $c/b=2.5$ and $g/b=1$ (off phase coexistence).

$\sigma_{dw} \approx 0.096b/d^2$. From Eq. (9) and the linear fit in Fig. 5(a) we obtain the value of the sum of line tensions of intersecting domain walls, $\delta = \Omega_{ex}^z(L_N) - (4\sigma_{||} + \sigma_{dw})L_N \approx -1.608b/d$. Note that δ is negative and quite large. In the short-period lamellar phases positive value of δ with a similar magnitude was obtained [5].

In Fig. 5(b) the contribution to Ω_{ex}^z associated with structural deformations, $\Omega_{ex}^z(L) - (4\sigma_{||} + \sigma_{dw})L$, is shown. This quantity is negative, because it contains the contribution associated with the negative line tension δ in addition to the quasielastic contribution. In Fig. 6(a) we show the contributions to the excess pressure associated with the corresponding contributions to Ω_{ex}^z shown in Fig. 5. We compare the

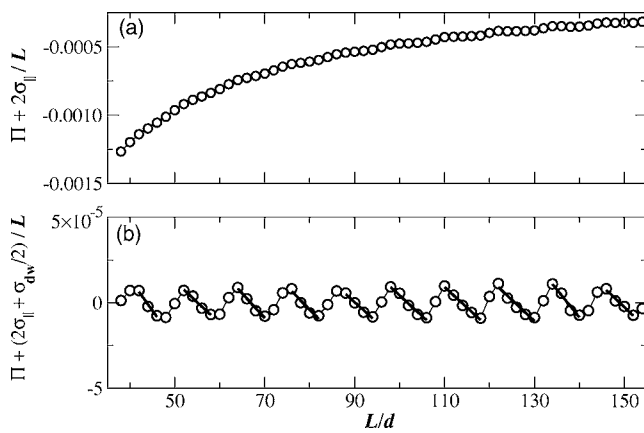


FIG. 6. (a) $\Pi(L) + 2\sigma_{||}/L$, and (b) $\Pi(L) + (2\sigma_{||} + \sigma_{dw}/2)/L$, for the square-base pore with side L , as functions of L . The walls are water covered. $\sigma_{||} = -0.483b/d^2$ and $\sigma_{dw} = 0.068\sqrt{2}b/d^2$. The solid lines are the best fits of the elastic term with $B_o = 0.0002b/d^3$. The thermodynamic variables and material constants are the same as in Fig. 5.

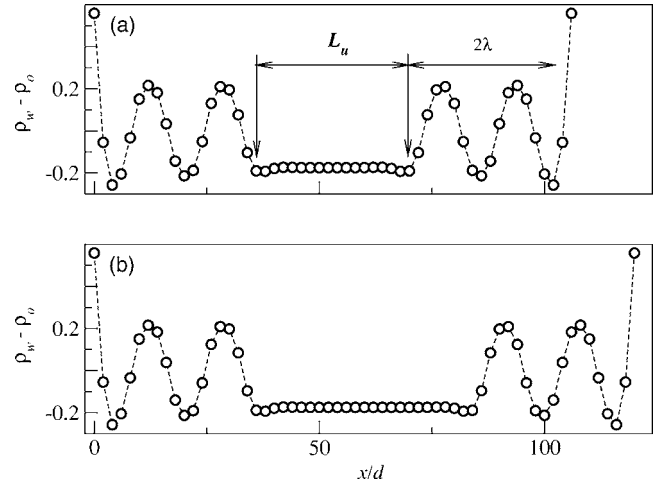


FIG. 7. The difference between densities of water and oil, $\rho_w - \rho_o$, as a function of x for $y=L/2$. (a) $L/d=L_4^1=106$, and (b) $L/d=120=L_5^1-2$. There are four lamellar layers (oil and water-rich domains) absorbed at the walls, and the thickness of the central uniform oil-rich tube is $L_u \approx L - 4\lambda$. 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.

numerical results with the elastic behavior, with the modulus of elasticity obtained by the best fit of Eq. (10) to our results, as shown in Fig. 6(b). The contribution to Π associated with structural deformation is about one order of magnitude smaller than the contributions associated with all surface energies.

2. Close to the lamellar-water coexistence

For μ and T sufficiently close to the bulk coexistence of the uniform water and/or 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 onionlike structure stabilizes for all values of $L \gg \lambda$. The cross section densities $\rho_w - \rho_o$ as functions of x for $y=L/2$ are shown in Fig. 7 for $L=106$ and $L=120$. As we show below, the thickness L_u of the central uniform domain, or equivalently the number of lamellar layers at the walls, is a function of the distance to the phase transition between lamellar and water and/or oil-rich phases. At the fixed L , L_u increases (the number of absorbed lamellar layers decreases) discontinuously by approaching the coexistence. For the structures shown in Fig. 7(b) (and analogous structures for different L) the water and oil densities in the center of the pore are close to those in the bulk uniform phase at the bulk coexistence of the uniform and lamellar phases.

In Fig. 8(b) $\Omega_{ex}^z(L) - (4\sigma_{||} + \sigma_{dw})L$, which describes the contribution to Ω_{ex}^z associated with the structural deformations, is shown. The thermodynamic variables T and μ are chosen sufficiently close to the phase coexistence, and correspond to the stability of the lamellar phase with $\lambda/d=16$, and the walls of the pipe are water covered. All structural deformations are concentrated in the center of the pore (see

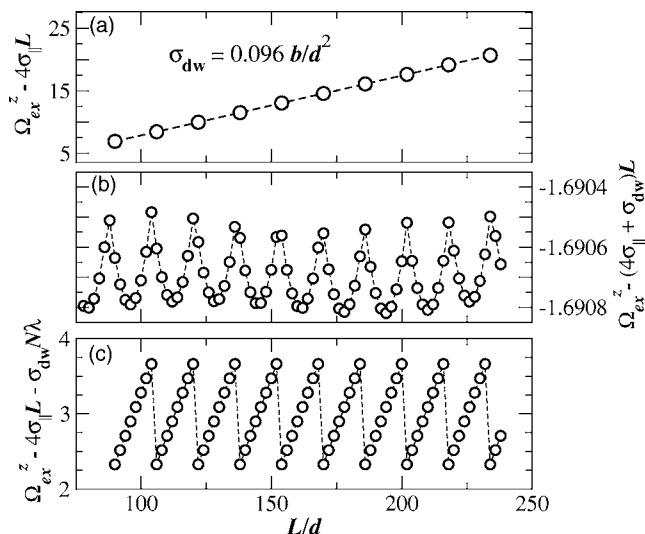


FIG. 8. (a) $\Omega_{ex}^z - 4\sigma_{||}L$ at the values of the width of the pore $L=L_N^l$ corresponding to the minimal size of the central water-, or oil-rich domain. $\sigma_{||} = -0.480b/d^2$. (b) $\Omega_{ex}^z(L) - (4\sigma_{||} + \sigma_{dw})L$; (c) $\Omega_{ex}^z(L) - 4\sigma_{||}L - \sigma_{dw}N\lambda$ for the square-base pore with the side length L , as a function of L . The walls are water covered. The thermodynamic variables $kT/b=2.65$, $\mu/b=\mu_{coex}(1-0.0016)$, and material constants $c/b=2.5$, $g/b=1$ correspond to the stability of the lamellar phase with period $\lambda/d=16$.

Fig. 7). The size L_u of the uniform water- or oil-rich central part of the pipe increases under expansion until L reaches the instability value $L_N^l - 1$, i.e., just before the insertion of a new lamellar layer at $L/d=L_N^l$. Lamellar layers which surround the water- or oil-rich central part have the same structure as in the bulk lamellar phase. Thus, the elastic contribution to the excess pressure Π , given by the second term in the Eq. (10), is not present in this case. $L=L_N^l$ corresponds to configurations with the smallest size of the central water- or oil-rich tube, which in the present case is $L_u/d=34$. When L increases, but stays below L_{N+1}^l , the thickness of the lamellar ring does not change (see Fig. 7), and also the length of the domain wall remains constant and equal to $\approx N\lambda/2$, where N is the number of oil- and water-rich layers adsorbed at the walls. Therefore, for such values of the system size the contribution to the free energy coming from the domain wall stays constant and equals to $\approx \sigma_{dw}N\lambda$. The contribution to Ω_{ex}^z for $L_N^l \leq L < L_{N+1}^l$ is related to the presence of the central water- or oil-rich domain and the water-lamellar phase interfaces (see Fig. 7). We can estimate the excess value of the grand potential on thermodynamic grounds as

$$\Omega_{ex}^z - 4\sigma_{||}L \approx \sigma_{dw}N\lambda + \Delta\omega^b(L - N\lambda)^2 + 4\sigma_{w\ell}(L - N\lambda) + \delta, \quad (20)$$

where we approximate the thickness of the central uniform tube by $L_u=L-N\lambda$ for $L_N^l \leq L < L_{N+1}^l$. In the above $\Delta\omega^b = \omega_w^b - \omega_\ell^b$ is the difference between the bulk densities of the grand potential for the water- or oil-rich and lamellar phases, and $\sigma_{w\ell}$ is the surface tension of the interface between the water and lamellar phases.

In order to verify validity of the above conjecture we plot in Fig. 8 two quantities, $\Omega_{ex}^z - 4\sigma_{||}L - \sigma_{dw}L$ and $\Omega_{ex}^z - 4\sigma_{||}L - \sigma_{dw}N\lambda$. From Eq. (20) we expect

$$\Omega_{ex}^z - 4\sigma_{||}L - \sigma_{dw}L \approx \Delta\omega^b L_u^2 + (4\sigma_{w\ell} - \sigma_{dw})L_u + \delta \quad (21)$$

and

$$\Omega_{ex}^z - 4\sigma_{||}L - \sigma_{dw}N\lambda \approx \Delta\omega^b L_u^2 + 4\sigma_{w\ell}L_u + \delta. \quad (22)$$

Close to the phase coexistence $\Delta\omega^b$ is very small, and the linear term should dominate in Eq. (22); this is indeed the case, as shown in Fig. 8(c). The quadratic term can be seen in Fig. 8(b), indicating a small value of $4\sigma_{w\ell} - \sigma_{dw}$. Note that the quadratic term in Eq. (20) has quite a different physical origin than the quadratic term in Eq. (6).

B. Phase transitions

At the bulk coexistence the uniform water-rich phase is stable in the pipe. In fact, in the uniform phase an oil-rich lamellar layer of thickness $\approx \lambda/2$ is formed near the walls, but in a substantial part of the pipe the densities are constant and assume the same values as in the bulk. This uniform structure remains stable also when the lamellar phase is stable in the bulk, until $\Delta\mu = \mu - \mu_{coex}$ assumes sufficiently low, negative value. This behavior is quite opposite to the capillary lamellarization found in slits with hydrophilic walls [3], where the lamellar phase stabilizes in slits when the uniform phase is stable in the bulk. Let us analyze the values of the wall-fluid surface tensions for the swollen phases. At the bulk coexistence the wall-water surface tension is $\sigma_w \equiv \sigma_u = -0.48036b/d^2$, and the wall-lamellar surface tension is $\sigma_{lam} \equiv \sigma_p = -0.48041b/d^2$. However, the energy density γ_o of the domain wall between different orientations of lamellas is sufficiently large, $\gamma_o \approx 0.034b/d^2$, to inhibit stabilization of the periodic structure. The difference between the surface tensions $\sigma_u - \sigma_p \approx 0.0005b/d^2$ does not compensate for the domain-wall energy density, therefore we obtain delayed condensation of the onion structures. In this case we get the capillary ‘‘evaporation’’ of the lamellar phase in the pipe with hydrophilic walls, i.e., in the region of lamellar-phase stability we observe formation in the middle of the pore of the oil- or water-rich phases with spacial extension L_u which changes with $\Delta\mu$ discontinuously. If the μ_{coex} is approached from the side of the lamellar phase the capillary ‘‘evaporation’’ of the latter occurs layer by layer. Namely, if at some value of $\Delta\mu$ there are N lamellar layers at the walls, then by decreasing the absolute value of $\Delta\mu$, the structural transition line at which N changes to $N-1$ is reached. Eventually only one oil lamellar layer stays at the walls, and this is the uniform configuration mentioned above.

The structural transition lines are obtained for fixed temperatures by finding the value of μ for which the values of Ω^z in the confined lamellar phases with $N-1$ and N lamellar layers are equal. The structures in the lamellar phase with $N=5$ and $N=6$ at the capillary delamellarization transition in the hydrophilic pore are shown in Fig. 9. The phase diagram obtained for the swollen lamellar phase in square-base hydrophilic pipes is shown in Fig. 10. The lines presented in Fig. 10 do not end with critical points at small values of L ,

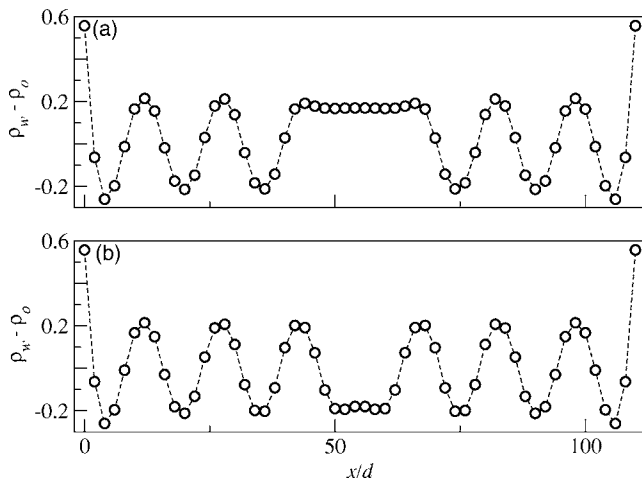


FIG. 9. The difference between densities of the water and oil, $\rho_w - \rho_o$, as a function of x for $y=L/2$ in the onion phase with (a) five and (b) six lamellar layers absorbed at the walls at the capillary delamellarization transition given by $kT/b=2.65, \mu_{cc}=\mu_{coex}(1-0.0045)$. The pore size $L/d=106$ and the walls are water covered. 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 $\lambda/d=16$.

but correspond to the structural transitions in the pipe, at which the number of absorbed water- and oil-rich layers changes from N to $N+1$ when L grows from $\approx 2N\lambda$ to $2(N+1)\lambda$. For each line there is a crossover from the above structural transitions, occurring far from the phase boundary (the almost vertical parts of the lines in Fig. 10 at small L), to the delamellarization transitions (the almost horizontal parts of the lines in Fig. 10 at large L). At the delamellarization transitions the decrease of the absolute value of $\Delta\mu$ leads for fixed L to a formation of a uniform water- or oil-rich domain in the center of the pipe. The thickness of the central uniform

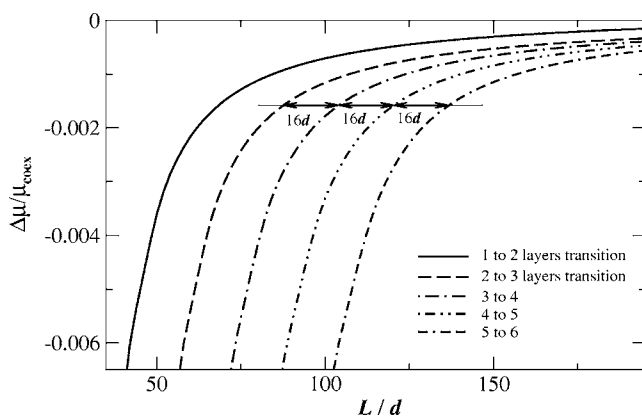


FIG. 10. Structural transitions between onion phases with different numbers of lamellar layers at the walls in the square-base capillary for $kT/b=2.65$. The walls of the pore are water covered. The lines separate the stability region of the onion structures with N layers (above) from the stability region of the structures with $N+1$ layers (below in $\Delta\mu/\mu_{coex}$). The case of $1 \leq N \leq 5$ is shown. The horizontal line corresponds to the value of the chemical potential, at which the results shown in Fig. 8 have been obtained.

part increases from $L_u(N)$ to $L_u(N-1)=L_u(N)+\lambda$ when the transition lines are crossed on approaching the stability of the bulk uniform phase. Finally, deep inside the lamellar-phase stability region (large absolute values of $\Delta\mu$) the lines meet the bulk structural transformation line at which the lamellar phases with $\lambda/d=16$ and $\lambda/d=14$ coexist.

In the case of the neutral walls the phase diagram does not show considerable changes compared to the case presented here. The phase equilibria in pipes are governed by the differences in wall-fluid surface tensions and the domain-wall energies. In contrast to the elastic properties, σ_{dw} depends very weakly on the period of the lamellar structure. Thus one could expect that formation of periodic structures in the short-period and in the swollen phases is delayed by a similar value of $\Delta\mu(L)/\mu_{coex}$.

V. SUMMARY

We investigated swollen lamellar phases in square-base capillaries. We found that the structure and mechanical properties depend very strongly on a thermodynamic state. Off phase coexistence with uniform phases the structure depends on the hydrophilicity of external surfaces. Lamellar structure is formed between neutral walls, whereas between hydrophilic walls quite complex structures, different for different widths of the pipe, are formed (see Fig. 3). Mechanical properties are determined mainly by surface tensions and domain-wall energies. The elastic (or quasielastic) contribution to the excess pressure is negligible. This is in contrast to the short-period phases, where the quasielastic contribution is significant.

Sufficiently close to the bulk coexistence with uniform phases the quasionion structure is stable in square-base pipes for all values of L regardless of the hydrophilicity of surfaces. Expansion leads to the swelling of the central water- or oil rich tube. This property is different than in the previously studied cases [1,2,5,11]. In the center of the swollen tube the densities are the same as in the bulk, i.e., two-phase coexistence inside the pipe is observed (see Fig. 7).

The phase equilibria in square-base pipes are just opposite to the phenomenon of capillary lamellarization predicted for slits [3]. Capillary delamellarization is observed in all cases, as a result of the domain-wall energy associated with formation of quasionion structures. We have also checked that the hydrophilicity of the external walls influences the shift of the phase coexistence in the pipes very weakly.

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.

ACKNOWLEDGMENTS

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