Wetting and capillary condensation in self-assembling systems

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Results obtained within Ciach-Høye-Stell model of oil-water-surfactant mixtures in restricted geometry are reviewed. Special attention is paid to phase transitions in semiinfinite and in slit geometries. Similarities and differences between simple fluids and self-assembling systems are highlighted.

1. INTRODUCTION

Mixtures of polar and nonpolar liquids, such as water and oil, phase separate at room temperatures. Amphiphiles added to such mixtures self-assemble into monolayers, separating the oil- and water- rich regions. In microemulsion the monolayers are not localized in space, and their formation is reflected in the form of the water-water (or oil-oil) density correlation function, which exhibits damped oscillations with the decay rate $\xi$ and periodicity $\lambda = 10nm$. For distances $1 < r/\lambda < 10$ this correlation function resembles the density-density correlation function in simple fluids for $1 < r/\sigma < 10$ [12]. For $r/\lambda < 1$ the shape of the correlation functions in microemulsion is different than in simple fluids for $r/\sigma < 1$, and reflects the fact that the water- or oil-rich domains of mesoscopic size, surrounded by amphiphilic monolayers, are soft and compressible rather than rigid. In ordered phases $\xi \rightarrow \infty$, and the structure is periodically repeated in one (lamellar phase) two (hexagonal phase) or three dimensions (cubic phases). 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, they resemble solids of very large unit cells, where hard atoms are replaced by soft domains, surrounded by monolayers which behave as elastic membranes [2,3].
A single external surface (e.g. 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 $\xi$. For this reason confinement plays a significant role when the size of the system becomes comparable to $\xi$. The structure in self-assembling systems is characterized by large typical lengths, often two orders of magnitude larger than the molecular sizes [1,4]. The deformations of the structure are thus expected for distances from the wall two or three orders of magnitude larger than in simple fluids, and the finite size effects are expected for much larger systems. Effects of boundaries are particularly strong close to phase transitions. Discontinuous transitions in the bulk are accompanied by wetting and capillary condensation phenomena in confinement. The latter phenomena in simple fluids have drawn much attention in the recent years [5-7].

Here we describe ordering and disordering effects of a single planar wall and of slit-like geometry on self-assembling systems. We pay particular attention to lamellar phases and lamellar-microemulsion or lamellar-water/oil phase boundaries. In confinement the tendency for formation of various ordered periodic structures can be enhanced or de-enhanced depending on chemical nature, shapes, structure or size of the boundaries of the system. In the lamellar phases the planes describing average positions of surfactant monolayers are parallel to each other. The monolayers undulate, and near a coexistence with microemulsion numerous passages between the nearest monolayers are formed. In microemulsions the monolayers strongly fluctuate and are interconnected, so that the whole system is isotropic. This very complex structure makes the problem of effect of boundary conditions very difficult.

We shall discuss wetting and capillary condensation on general gronds. The self-assembly of amphiphiles into monolayers occurs in a broad class of systems. Remarkable similarity between particular properties of all such systems can be observed, provided that one end of the solute particles attracts polar and repulses nonpolar particles, whereas the other end does the opposite. This property of the interactions is necessary and sufficient for self-assembly into bilayers or monolayers, if the amphiphilic interactions are sufficiently strong. The features common for the whole class of the self-assembling systems should be described by generic models in which the irrelevant details of the interactions are just disregarded. We choose the lattice CHS model [9] described in sec 2.

We shall discuss wetting and capillary condensation on general grounds in the following section. In sec. 2 we describe the CHS model and the calculation method which allows to verify our predictions by direct calculations. The paper is closed with a short discussion.
2. SELF-ASSEMBLING SYSTEMS IN RESTRICTED GEOMETRY; MODEL-INDEPENDENT CONSIDERATIONS

A. Wetting. Consider first an attractive wall in contact with a gas phase. If the transition to liquid is approached, then a liquid-like layer is formed near the surface, and its thickness grows as

$$\Gamma = \log |\Delta \mu|$$  \hspace{1cm} (1)

where $\Delta \mu$ is a chemical-potential distance from the gas-liquid coexistence. The above relation holds for any order-disorder transition in uniform systems exposed to a wall [5,6,16], and follows from the Landau-Ginzburg functional of the form

$$F[\eta] = \int d^{d-1} r \int_0^\infty dz \left[ \frac{1}{2} (\nabla \eta)^2 + \frac{1}{4} \eta^2 + \frac{1}{6} \eta^4 + \delta(z) \left( h + c \eta \right) \right]$$  \hspace{1cm} (2)

where $\eta$ is a suitable order-parameter (OP) for the corresponding order-disorder transition. In the case of the gas-liquid transition $\eta$ is identified with the difference between liquid and gas densities. A crucial quantity for studying the wetting is the so called adsorption or coverage,

$$\Gamma = \int_0^\infty dz (\eta(z) - \eta(\infty))$$  \hspace{1cm} (3)

proportional to the thickness of the wetting layer. In the context of the liquid-gas coexistence $\Gamma$ describes the total amount of adsorbed liquid per area $A$ of the confining surface.

It is the way the surfactant monolayers are arranged in space, which distinguishes between the microemulsion and lamellar phases. A question that arises is whether the planar, hydrophilic surface leads to a formation of a lamellar layer, and whether the thickness of this layer grows according to Eq. (1), when the phase transition from microemulsion to the lamellar phase is approached. Recall the analogy between the complex system on the mesoscopic length scale and a simple fluid on the atomic length scale discussed in Introduction. On the length scale of the size of atoms the simple fluid exhibits the structure described by the pair-correlation function, and only on the larger length scale it is uniform. Similarly, on the length scale of $=100$ Å the complex system exhibits the structure as described by density distributions, and on the length scales larger than the period of density oscillations it is seen as a uniform
fluid. In the simple fluids the order parameter is the deviation of the local density from the average value in a region of a molecular size. By analogy, the order parameter in the complex system should be identified with a suitable description of the deviations of the density from the average value in a region of a linear size of the period of oscillations. In $s$-component systems exhibiting lamellar ordering the density of every component $i$ of the mixture, $\rho_i(z)$, oscillates around the average value $\bar{\rho}_i = \int_{z}^{z+\lambda} \rho_i(z') dz'$, where $z$ is the direction and $\lambda$ is the period of the density oscillations. In Ref.[10,11] the OP for one-dimensional structures (lamellar order) and for $s$-component mixtures is defined as

$$\eta(z) = \left[ \int_{z}^{z+\lambda} \sum_{i=1}^{s} \left( \rho_i(z') - \bar{\rho}_i \right)^2 \right]^{1/2}$$

In the bulk lamellar phase the shapes of $\rho_i(z)$ are the same in the whole sample, and $\eta(z)$ is a positive constant, proportional to the amplitude of the density oscillations. By definition, $\eta(z) = 0$ in the uniform phase. We have reduced the degrees of freedom related to the density profiles to just one number. This is analogous to reducing the atomic degrees of freedom on the atomic length scale to the local density deviations from the average value. Based on this analogy and following the general arguments of Landau, it is postulated in Ref.[10] that in the semi-infinite geometry the functional of $\eta$ should have the form given by (2), but with the length unit equal to the period of the density oscillations, rather than to molecular size.

The hypothesis that all the degrees of freedom except for $\eta$ given by (4) are irrelevant for the general features of the surface phenomena in the systems exhibiting self-assembly on the nanometer length scale leads to the same behavior of $\Gamma$ as in simple fluids, i.e. the thickness of the lamellar wetting layer grows according to Eq. (1). The predictions of the functional (2) can be explicitly tested for $\eta$ and $\Gamma$ defined as discrete versions of Eqs. (4) and (3) respectively in the CHS model, as we describe in sec. 3.

**B. Capillary condensation.** When the gas-liquid coexistence is approached from the gas side, condensation of a liquid-like phase takes place in narrow pores with adsorbing walls. At the capillary condensation the deviation of the chemical potential from the value at the bulk coexistence is related to the size of the slit-like pore $L$ by the Kelvin equation [7]. In simple fluids the Kelvin equation is obeyed even for quite small pore sizes[8]. Simple generalizations of
the Kelvin equation are valid in other uniform systems, for example in liquid mixtures, when a single order-parameter is relevant for the considered transition.

Phenomena analogous to the capillary condensation occur also in complex systems. When a transition to a periodic structure is approached, it may condense in a pore for a particular chemistry of the confining walls. For example, a capillary condensation of a lamellar phase in water-surfactant mixtures was observed experimentally in slit-like pores when the sponge phase was stable in the bulk[12,13].

The ordered phases are nonuniform on the nanometer length scale. The nonuniformity of the ordered phases is certainly important for slits such that \( L = \lambda \). The simple fluids are also nonuniform on the molecular length scale, still the Kelvin equation remains valid even up to molecular distances. Based on the analogy with simple fluids on the molecular length scale we postulate that the thermodynamic considerations should remain valid for the nonuniform phases for \( l \gg L \), provided that the density in the periodic structure is identified with the space-averaged density.

The distance between the confining walls can be varied by a small fraction of the period of the ordered phase \( \lambda \) that condenses in the slit. Only for some particular values of \( L \), namely for \( L = L_N \), corresponding to \( N \) structural layers confined between the walls, which have the same structure as in the bulk, there is no stress in the system. Deformations present when \( L \neq L_N \) correspond to swelling or shrinking of the lamellar layers when the slit is expanded or compressed compared to \( L = L_N \) [12,13]. When the expansion \( \Delta L = L - L_N \) is sufficiently large, a new lamellar layer is introduced into the system, \( N \rightarrow N + 1 \). Both experimental [12,13] and theoretical results [15-17] show elastic behavior of the swollen lamellar phases, analogous to a series of \( N \) identical joint springs for \( N \) periods of the confined lamellar phase.

Due to the elasticity of the periodic phases, the assumptions leading to the Kelvin equation (negligible solvation force) are not satisfied even for quite large pore sizes. For wall separations \( L \neq L_N \) significant violations of the Kelvin equation are to be expected. Grand thermodynamic potential in the slit of width \( l \) and surface-area \( A \) has the form

\[
\Omega / A = \omega L + \Omega_{ex}, \quad \Omega_{ex} = \sigma + \Omega_{st} (L)
\]

(5)

where \( \sigma \) is the wall-fluid surface tension. For any periodic structure responding elastically to the applied stress the \( L \)-dependent contribution to the grand thermodynamic potential of the confined system containing \( N \) structural units has the form
\[ \Omega_{N}(L) = \frac{B}{2L_N} (L - L_N)^2, \quad L_{N-1} < L < L_{N+1} \]  

(6)

where \( B \) is the modulus of elasticity. Note the very slow, \( L^{-1} \), decay of \( \Omega_{N}(L) \). Due to the long-range order of the phases which condense in the slit, for the wall distances \( L \neq L_N \) the external stress (6) is not released even for large \( L \), in contrast to simple fluids. For the chemical potential \( \mu_{\text{coex}} \) and the temperature \( T \) corresponding to the bulk coexistence the bulk densities of the grand thermodynamic potential \( \Omega \) for the two phases are equal,

\[ \omega^u(\mu_{\text{coex}}, T) = \omega^p(\mu_{\text{coex}}, T) \]  

(7)

Superscripts \( u \) and \( p \) correspond to the uniform and the periodic phase respectively. At the capillary condensation in a slit of width \( L \), for \( \mu_{\text{coex}} = \mu_{\text{coex}} + \Delta \mu \),

\[ \Omega^u(\mu_{\text{coex}}, T, L) = \Omega^p(\mu_{\text{coex}}, T, L) \]

For the uniform phase the solvation force can be neglected, and for sufficiently small \( \Delta \mu \) we obtain

\[ \Omega^u / A = L \left[ \omega^u(\mu_{\text{coex}}, T) + \rho^u(\mu_{\text{coex}}, T) \Delta \mu \right] + 2 \sigma^u(\mu_{\text{coex}}, T), \]

\[ \Omega^p / A = L \left[ \omega^p(\mu_{\text{coex}}, T) + \rho^p(\mu_{\text{coex}}, T) \Delta \mu \right] + 2 \sigma^p(\mu_{\text{coex}}, T) + \frac{B}{2L_N} (L - L_N)^2 \]  

(9)

where \( \sigma^{u,p} \) denotes the surface tension between the wall and the respective phase. The \( \rho^{u,p} \) are thermodynamic densities satisfying the relation \( (\partial \omega / \partial \mu)_{T,N} = \rho \). In incompressible mixtures (for example in solutions containing surfactants or lipids) \( \rho^{u,p} \) correspond to space-averaged solute densities. From (9) we obtain the modified Kelvin equation

\[ \Delta \mu = \frac{2 \Delta \sigma - \frac{B}{2L_N} (L - L_N)^2}{\Delta \rho L} \]  

(10)
where $\Delta \sigma = \sigma^- - \sigma^+$ and $\Delta \rho = \rho^- - \rho^+$. The above MKE should be valid for any elastic system condensing in slit-like pores.

For the equilibrium wall separations, $L = L_0$, corresponding to no stress, the second term in (10) vanishes and (10) reduces to the usual Kelvin equation.

3. CHS MODEL RESULTS

Here we concentrate on the lattice model introduced by Ciach, Høye and Stell (CHS). The model is designed for a description of the balanced systems, with vanishing spontaneous curvature of the surfactant monolayer. In such systems oil and water play effectively symmetrical roles. Every lattice site is occupied by either oil-, water-, or an amphiphile. Microscopic densities are $\hat{\rho}_i(r) = 1(0)$ if the site $r$ is (is not) occupied by the specie $i$, where $i = 1, 2$ refer to water and oil respectively, and $i > 2$ refers to surfactant molecules in different orientations. In fact we consider clusters of molecules in the semimicroscopic, coarse-grained description. Close-packing and oil-water symmetry are assumed ($\mu_1 = \mu_2$). Different orientations of the surfactant particles are treated as different components having the same chemical potential $\mu_s$. Only one chemical potential variable is relevant in the case of close-packing, namely $\bar{\mu} = \mu_1 - \mu_2 = \mu_2 - \mu_2$, with $\mu_i = \mu_s$ for $i > 2$. The Hamiltonian in a presence of external fields $h(x)$ can be written as:

$$H = \frac{1}{2} \sum_{x \in \Gamma} \sum_{o} \hat{\rho}_i(x)U_o(x-x')\hat{\rho}_j(x') +$$
$$+ \sum_{x} \sum_{o} h_i(x)\hat{\rho}_i(x) - \bar{\mu} \sum_{x} (\hat{\rho}_1(x) - \hat{\rho}_2(x))$$

(11)

The $U_o(r-r')$ is the interaction energy between the specie $i$ at $r$ and the specie $j$ at $r'$. We assume nearest-neighbor interactions. Except from the water-water (oil-oil) interaction $-b$ the water-amphiphile (oil-amphiphile) interaction $-c\Delta r \cdot \hat{u} (+c\Delta r \cdot \hat{u})$ is assumed, with $\hat{u}$ describing the orientation of the amphiphile located at the distance $\Delta r$ from the water (oil) particle. The amphiphile-amphiphile interaction has the form $g[(\hat{u} \times (r-r')) \cdot (\hat{u} \times (r-r'))]$, where $\hat{u}$ ($\hat{u}'$) is the orientation of the amphiphile located at $r$ ($r'$). The above interaction supports formation of flat monolayers (vanishing spontaneous curvature), with amphiphiles parallel to each other and perpendicular to the
surface they occupy. The lattice constant is $a = 1$, and is identified with the size of the amphiphiles. Finally, the surface external field is defined as

$$h_i (\mathbf{r}) = h_i \sum_{r \in \partial V} U_{ij} (\mathbf{r} - \mathbf{r}') \rho_j (\mathbf{r}')$$

where in the above expression $\rho_j (\mathbf{r}')$ for $\mathbf{r}' \in \partial V$ are fixed, external conditions. Here we focus on $\rho_i (\mathbf{r}) = 1$, $\rho_{\alpha \beta} (\mathbf{r}) = 0$ at the walls, i.e for $\mathbf{r} \in \partial V$. $0 < h_i < 1$ describes surfaces ranging from neutral to water-covered.

In contrast to the phenomenological approach, once the interaction parameters are fixed in the CHS model, there are no other parameters which could be fitted to the experimental results. The only other parameters in this approach are the thermodynamical variables.

It is impossible to solve the CHS model exactly except for one-dimensional systems. In practice one can obtain approximate results within a mean-field (MF) theory or by MC simulations. Within the MF approximation the microscopic configurations $\hat{\rho}_i (\mathbf{x})$ occur with a probability proportional to the Boltzmann factor

$$\exp \left( - \frac{1}{k_B T} \sum_i \left( \phi_i (\mathbf{x}) (\hat{\rho}_i (\mathbf{x}) - \rho_i (\mathbf{x})) + h_i (\mathbf{x}) \hat{\rho}_i (\mathbf{x}) - \bar{\rho}_i (\mathbf{x}) \right) \right)$$

where $\phi_i (\mathbf{x}) = \sum_{x} U_{ij} (\mathbf{x} - \mathbf{x}') \rho_j (\mathbf{x}')$ is the mean field and $\rho_i (\mathbf{x})$ is the MF-average of $\hat{\rho}_i (\mathbf{x})$, introduced here to compensate for double counting of pairs of sites. The grand thermodynamic potential in MF takes the form:

$$\Omega (\tau, \mu, L) = \sum_i \sum_{\mathbf{x}} \rho_i (\mathbf{x}) \left( \tau \ln (\rho_i (\mathbf{x})) + \frac{1}{2} \phi_i (\mathbf{x}) + h_i (\mathbf{x}) - \mu (\delta_{ii} + \delta_{i2}) \right)$$

where $\tau = k_B T / b$ is the temperature in the energy unit, $\mu = \bar{\mu} / b$, and $\Omega$ is also measured in units of $b$.

Important feature of the CHS model is the fact that no assumptions concerning the geometry and topology of the surfactant monolayers are necessary. The Boltzmann factor (12) automatically discriminates between the relevant and irrelevant states.

The hydrophilic surface breaks symmetry, and we can distinguish two different classes of orientations of amphiphiles, corresponding to the positive or the negative sign of the scalar product $\mathbf{u} \cdot \mathbf{n}$, where $\mathbf{n}$ is the vector normal to
the surface. In the first class of orientations the head, and in the second class the tail of the amphiphile is oriented towards the wall. Also, the one dimensional description can be applied as in standard wetting theories, if one assumes that the average densities in the surfaces parallel to the external surface are constant.

In order to test the predictions, concerning the wetting and capillary condensation phase transitions in self-assembling systems, we have to find global minima of $\Omega$ for different values of $\mu$ and $L$. Moreover, the value of $\mu$ at the bulk phase transition has to be found with a very high precision. In the case of wetting we cannot directly consider the semiinfinite system. Instead, we consider $L = L_N$ with $N = 10^3$, so that there is no stress in the system. For small $L$ the capillary condensation occurs before the wetting layers are formed, and we need very large $L$ to verify Eq.(1). Local minima of $\Omega$ can be determined by solving numerically the equation

$$\rho_1(x) = \langle \hat{\rho}_1(x) \rangle_{MF}$$

(14)

where the probability distribution is given by the Boltzmann factor (12). Self-consistent solutions of (14) can be found by means of iterations with different initial configurations. The structure corresponding to the lowest value of $\Omega$ is identified with the stable phase. In Figures 1-3 we show density profiles far and close to the phase coexistence.

We have compared the numerically obtained coverage (3) as a function of $\Delta \mu$ with the form (1). The numerical results (Figure 4) show perfect agreement with the prediction (1), and hence the same behavior as in simple fluids is confirmed.

The excess grand potential is shown in Figure 5 and the deformations of the lamellar structure corresponding to compression and expansion of the slit are shown in Figure 6. In order to find the analog of capillary condensation, we have determined for what values of $L$ and $\Delta \mu$ the grand-potential values corresponding to the lamellar and the water-rich phases are equal. The obtained dependence between $\Delta \mu$ and $L$ agrees quite well with the simple prediction (10), provided that $L$ is sufficiently large, $L > 4 \lambda$, and is replaced by $L - 2l$ in (10), where $l$ is the thickness of the lamellar film adsorbed at the hydrophilic surface, when the water-rich phase is stable in the slit (see Figures 7 and 8). Indeed, in the presence of lamellar films at the walls the slit which can be filled with water is effectively thinner.
Fig. 1. The thermodynamic variables $k_BT/b$, $\mu/b$ correspond to stability of the microemulsion ($k_BT/b = 2.8$, $\mu/b = 4.4214$, $c/b = 4$, $g = 0$). The distance from the first-order transition between the microemulsion and the lamellar phase is $|\mu - \mu_{\text{mm}}|/b = 0.1$. Walls are covered by water. a: the density of surfactant as a function of a distance from the wall in units of the lattice constant. b: lamellar OP $\eta$ as a function of a distance from the wall measured in units of the period of the lamellar structure. Dashed lines are to guide the eye.
Fig. 2. The vicinity of the first-order transition from the microemulsion to the lamellar phase ($k_bT/b = 2.8, \mu/b = 4.3214, c/b = 4, g = 0, |\mu - \mu_{\text{cex}}|/b = 0.0003$). Walls are covered by water. a: the density of surfactant as a function of a distance from the wall in units of the lattice constant. b: lamellar OP $\eta$ as a function of a distance from the wall measured in units of the period of the lamellar structure. Dashed lines are to guide the eye.
Fig. 3. The vicinity of the first-order transition from the lamellar phase to the microemulsion \((k, T/b = 2.8, \mu/b = 4.3203, c/b = 4, g = 0, |\mu - \mu_{coex}| / b = 0.0008)\). Walls are not preferential for any state \(i\), i.e. \(h_i = -1\) for \(i = 1, 2, 3, 4\). a: the density of the surfactant as a function of a distance from the wall in units of the lattice constant. b: lamellar OP \(\eta\) as a function of a distance from the wall measured in units of the period of the lamellar structure.
Fig. 4. Excess lamellar OP $\Gamma_l$ at constant temperature $k_B T / b = 2.8$, $c / b = 4$, $g = 0$ in the case of water-covered walls. (a) as a function of the dimensionless difference between $\mu$ and its value at the bulk phase transition $\Delta \mu$; capillary condensations for different $L$ are indicated by the dashed lines. b: as a function of $\log(\Delta \mu)$. 
Fig. 5. Thermodynamic variables $k_bT/b$, $\mu$ and the material constant $c$ correspond to stability of the swollen lamellar phase with $\lambda = 13$, $k_bT/b = 0.84$, $\mu/b = 0.774$, $c/b = 1$, $g = 0$. The distance from the first-order transition between the water-rich and the lamellar phases is $|\mu - \mu_{\text{ex}}|/b = 0.003$. Walls are covered by water. a: excess thermodynamic potential $\Omega_{\text{ex}}$ (in units of $b/a^3$), as a function of the wall separation measured in units of the lattice constant $a$. b: solvation force $f$ (in units of $b/a^3$) as a function of the wall separation. Dashed lines are to guide the eye.
Fig. 6. The thermodynamic variables $k_b T / b$, $\mu$ and the material constant $c$ are $k_b T / b = 0.84$, $\mu / b = 0.774$, $c / b = 1$). Walls are water-covered. top: the density distribution of water between the walls for the separation $L = 54$. The period of the density oscillations is 11. bottom: the density distribution of water for the wall separation $L = 65$. The lamellar phase is stretched with the period of the oscillations equal to 13.75.
Fig. 7. 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 (10) with $L$ replaced by $L-2l$. The optimal value of the fitting parameter $l$ is 6.205. $\Delta\sigma = 0.000527 b/a^2$, $\Delta\rho = 0.003124$ 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 $k_B T/b = 2.7$ and the material constants are $c/b = 2$, $g/b = 0.15$. The bulk first-order transition is at $\mu_{coex}/b = 4.1541978$. 
Fig. 8. The density distribution of surfactant (top) and water (bottom) between the walls for the separation \( L = 83 \). The thermodynamic variables \( kT/b \), \( \mu/b \) and the material constants \( c/b \), \( g/b \) of the system correspond to stability of the water-rich phase \( kT/b = 2.7 \), \( \mu/b = 4.1566 \), \( c/b = 2.4 \), \( g/b = 0.15 \). The distance from the first-order transition between the water-rich and the lamellar phases is \( (\mu - \mu_{\text{coex}})/b = 0.0024 \). Walls are covered by water.

4. DISCUSSION

Based on the structure factor of microemulsions, we have realized the analogy between simple fluids on a microscopic length scale and self-assembling systems on the mesoscopic length scale. We have also noticed the difference between these systems on the respective length scales -- namely, the molecules are 'hard', whereas the water- or oil-rich domains are 'soft', i.e. the domains can change their shape under external stress, since they contain many molecules and are surrounded by surfactant monolayers, which behave as elastic membranes.
The similarities between simple and self-assembling fluids are clearly seen in semiinfinite geometry - the wetting behavior is described by the same law (1) in the simple and the complex fluids. The domains behave like molecules in the absence of external stress. This observation has been confirmed by explicit calculations in the CHS model.

In contrast, when the external stress is applied and the self-assembling system is confined between parallel walls separated by a distance incompatible with the period of the structure, then the lamellar phase exhibits a solid-like behavior, and responds elastically to the stress. The elastic contribution to the grand-potential leads to a delayed condensation of the lamellar phase when the width of the slit is incompatible with the period of the lamellar phase in the bulk. The solid-like response to compression or expansion leads to a modification of the Kelvin equation (10). Note, however that the periodic structure, and the associated nonuniform density distributions on the nanometer length scale, have no effect on the Kelvin equation for $L = L_N$, once the space-averaged densities are taken into account. The modification of the Kelvin equation, Eq.(10), has been confirmed in the CHS model, with the modulus of elasticity, surface tensions and the solute densities all determined by independent calculations.

There is another, solid-like feature of the lamellar phases, namely their anisotropy. This property leads to a new phase transition, absent in simple fluids. This transition takes place between very weakly hydrophilic surfaces. When the wall separation corresponds to strong deformations of the lamellar structure, then a switch to a perpendicular orientation of the lamellae takes place. In the perpendicular orientation the period of the lamellar phase can be the same as in the bulk, but the surface tension is somewhat higher. When the slit is expanded, a sequence of switches between parallel and perpendicular orientation of lamellae takes place. We have found such a transition in the case of small-period lamellar phases (surfactant-concentrated systems) in the CHS model in Ref. [18].

We stress that despite the complex structure on the nanometer length scale, the equations describing the analogs of wetting and capillary condensation in self-assembling systems are remarkably simple.

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Alina Ciach was born in 1955 in Łęczyca. She graduated from Theoretical Physics Department, Warsaw University, in 1979. She received Ph.D. degree in physics at the Institute of Physical Chemistry, Polish Academy of Sciences in 1986. The next two years she spent as a postdoctoral fellow at the Trondheim University (1987) and, as a Humboldt fellow, at the University of Essen (1988). In 1994 she received habilitation (D.Sc.) in chemistry at the Institute of Physical Chemistry, where she is still employed. In 2002 she became a professor. She is interested in statistical mechanics of complex systems – in particular self-assembling systems and ionic fluids. Recently she focuses on effects of boundaries and confinement on structure and thermodynamic properties of simple and complex fluids.