# Confinement Induced Topological Fluctuations in a System with Internal Surfaces

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The lamellar phase between two parallel walls, in the water, oil, surfactant system, exhibits strong topological fluctuations. As we change the distance between the walls we observe the formation of two layers, then the microemulsion between two layers, and finally four layers. The transition is marked by the peaks in the average Euler characteristics and in its variance. The topological fluctuations may be responsible for attractive background force found in force apparatus measurements of the system. [S0031-9007(97)03851-9]

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When the lamellar system (periodic stack of parallel layers) is confined between two parallel walls the solvation force acting between them oscillates as a function of the distance between the walls [1–3]. The same oscillations are found in simple fluids which also marks the layering of molecules parallel to the walls [4]. The oscillations in the lamellar phase are additionally superimposed on the background attractive force [1]. Although in simple fluids much of the effort has been devoted to the study of the structure of the confined fluids [5–8] there are no works indicating how the structure of the lamellar phase changes as we change the distance between the walls. So far it has been established that when the distance between the walls increases new layers are inserted between them. The transition is marked by the abrupt change of the solvation force [9]. Here we pose the following question: *How does confinement change the structure of the lamellar phase?*

The more general aspect of this work concerns the topological fluctuations. They should accompany the phase transitions between the surfaces of different topology. The passages [10–12] between the layers, which are the realization of topological fluctuations studied here, are also called, in soft matter, wormholes [12], because they have the similar geometry as wormholes studied in the theory of gravity [13]. In the process of fluctuations two adjacent layers may hit each other and fuse, creating a single passage between them. Since the fusion of surfaces changes their topology, as described below, we will call such fluctuations the topological fluctuations.

A flat surface, in the box, with periodic boundary conditions has the topology of the tori, i.e., its genus, $g$ (number of holes in the closed surface) is 1 and its Euler characteristics $\chi = 2(1 - g)$ is 0. A parallel stack of such surfaces is equivalent to the same number of disconnected tori, and therefore the Euler characteristics is 0 for the whole lamellar phase. Two layers with a passage between them are topologically equivalent to two tori with a handle joining them, and therefore their genus is now $g = 2$ (two holes) and consequently $\chi = -2$. This means that each passage changes the Euler characteristics in the system by $-2$ and the lamellar phase with many passages has large and negative Euler characteristics. The Euler characteristics is the direct measure of the number of passages in the system.

We show that confinement of the lamellar phase induces topological fluctuations in the system. We also show that transition between two and four layers involves the formation of the microemulsion for system size intermediate between the ones containing two and four layers. Finally, we observe in accordance with experimental results that in thin samples the distance between the layers is nonuniform and smaller than the lamellar bulk period [1]. In the mixtures of surfactants with oil and water the passages have been observed in experiments [14,15] and computer simulations of bulk systems [16–18]. They have been known to exist in large multilamellar vesicles of the egg-lecithin system [19] and studied in various models [10–12]. In our opinion the passages of energy comparable to the thermal energy should accompany all phase transitions in soft matter systems with internal surfaces. Such passages will be called fluctuations, as they can spontaneously form and disappear. Finally, we think that the attractive background force between the walls found in force apparatus measurements [1] can be related to the topological fluctuations (passages) since they induce attraction between surfaces as recently proposed by Golubović [11].

In order to illustrate the general concepts presented above, we have performed the Monte Carlo study of the Landau-Ginzburg model of microemulsions [20–22]. The Landau-Ginzburg free energy functional has the following form:

$$F[\phi] = \int d^3r[|\Delta\phi|^2 + g(\phi)|\nabla\phi|^2 + f(\phi)], \quad (1)$$

where

$$g(\phi) = g_2\phi^2 - g_0, \quad (2)$$

$$f(\phi) = (\phi^2 - 1)^2\phi^2. \quad (3)$$

Here $\phi$, the scalar order parameter, has the interpretation of the normalized difference between oil and water concentrations; $g_2 = g_0 + 4.01$ and $g_0$ is the strength

  

of surfactant. The latter constant is solely responsible for the creation of internal surfaces in the model. The function $f(\phi)$ is the bulk free energy and describes the coexistence of the pure water phase ($\phi = -1$), pure oil phase ($\phi = 1$), and microemulsion ($\phi = 0$).

The model given by Eqs. (1)–(3) was discretized (three point formula for the Laplacian and two point symmetric formula for the gradient term [23]) and Monte Carlo (MC) simulations were performed on the $N_x \times N_y \times (N_z + 1)$ lattice with the lattice spacing $h = 0.8$. We set $N_x = N_y = 27$, and $N_z$ was changed between 4 and 14. The results were checked for the large lattice of size $N_x = N_y = 50$. We set $\phi(i, j, 1) = \phi(i, j, N_z + 1) = -1$ at the confining walls, making them strongly hydrophilic. In the perpendicular directions the periodic boundary conditions were used: $\phi_{1,j,k} = \phi_{N_x,j,k}$, $\phi_{0,j,k} = \phi_{N_x-1,j,k}$ and similarly in $y$ directions. The lattice points were chosen randomly and the field $\phi$ was changed by the random increment chosen from the interval $[-s, s]$. For $s = 0.3$ we had an almost 50% acceptance ratio for the bulk simulations. Typical runs consisted of 100 000 up to 300 000 MC moves per lattice site.

The surface between the oil-rich and water-rich domain is given by the equation $\phi(\mathbf{r}) = 0$. In order to locate the surface we make the linear interpolation between lattice sites, where field $\phi$ has a different sign. Next we specify the connections between the points of the surface, and in this way we cover the surface with triangles. The triangulation of the surface allows the study of topological fluctuations, since according to Euler formula $\chi = F + V - E$, where $F$ is the number of triangles, $V$ the number of their vertices, and $E$ the number of the edges. The averages of the Euler characteristics were taken over 500 configurations separated by thousands of MC steps. The average value of $\chi$ divided by $-2$ gives the average number of passages in the system.

From the Monte Carlo simulation [18] of the bulk system ($27 \times 27 \times 27$ lattice with periodic boundary conditions in all directions) we find that at $g_0 \approx 3.065$ there is a transition from the disordered microemulsion to the ordered lamellar phase, accompanied by large and negative Euler characteristics—indication of topological fluctuations. We have checked that for $g_0 = 4$ the average Euler characteristics is zero, indicating the absence of topological fluctuations in the bulk system. For the simulation in the restricted geometry we have chosen $g_0 = 4$ in order to be far away from the bulk phase boundaries.

Figure 1 shows the results for the internal energy $\langle F \rangle$ per lattice site, the heat capacity $\langle F^2 \rangle - \langle F \rangle^2$ per lattice site, the average Euler characteristics $\langle \chi \rangle$, and its variance $\langle \chi^2 \rangle - \langle \chi \rangle^2$, both divided by the size of the box $N_z$ along the direction perpendicular to the walls. The first two layers form when $N_z = 4$. Their distance from the walls is $d_0 = 0.75h$ and their mutual distance is $d_1 = 2.5h$ ($h$ is the lattice spacing). The bulk period of the lamellar phase is $d = 4h$, thus we conclude that the layers are squeezed

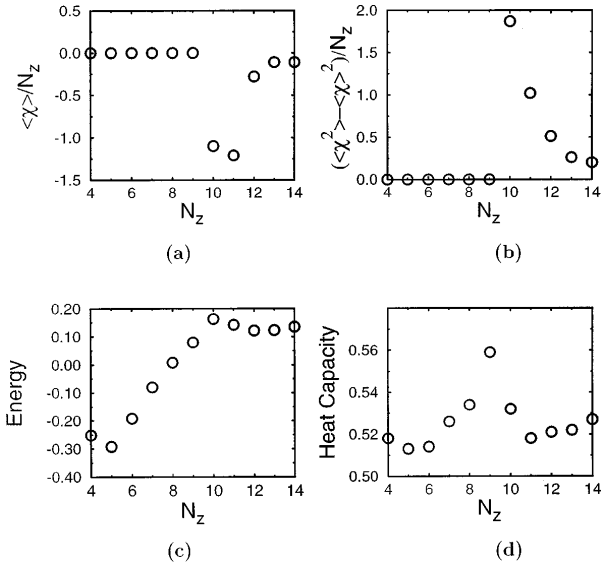


FIG. 1. The average Euler characteristics $\langle \chi \rangle$ (a), its variance $\langle \chi^2 \rangle - \langle \chi \rangle^2$ (b), the energy per lattice site (c), and heat capacity per lattice site (d) as a function of the size of the system perpendicular to the walls ($N_z h$) ($h = 0.8$ is the lattice spacing). The system size in the $x$-$y$ direction is $27 \times 27$. For $9 \geq N_z \geq 4$ the system contains two layers at a distance, roughly, $h$ from the wall. For $14 \geq N_z \geq 11$ there are four layers in the system. For $N_z = 10$ the system consists of two layers and a microemulsion between them.

in comparison to the bulk layers. As we change the system size we find for $N_z = 9$ that $d_0 = 1.25h$ and $d_1 = 6.5h$ so the layers are strongly swollen. For $N_z = 10$ we observe a jump in the average Euler characteristics and also a jump in its variance, which indicates the appearance of topological fluctuations. As we further enlarge the size of the system the number of passages decreases as indicated by $\langle \chi \rangle$. We also observe a peak in the heat capacity. All these changes are associated with the introduction of two new layers. For $N_z = 11$ we find four layers in the system. The two layers in the center are separated by the distance $2.5h$, the distance between the layers in the middle and the layers close to the walls is $3.25h$, while the distance between the walls and top layers is $1h$. We conclude the layers are not equally spaced at the moment of formation, and their mutual distance is much smaller than the bulk period ($d = 4h$). This effect has been also observed in mean-field calculations [24]. Although the internal energy exhibit minima as a function of the size of the system $N_z$, they do not appear exactly at distances for which the layers have the equal spacing, the same as the bulk period. We find that at $N_z = 6$ and at $N_z = 14$ the distance between the layers is equal to $4h$ and the distance between the first layer and the wall is equal to $1h$.

These results obtained for $N_x = N_y = 27$ were checked for the large system size, i.e., $N_x = N_y = 50$. We found that the energy per lattice site did not change

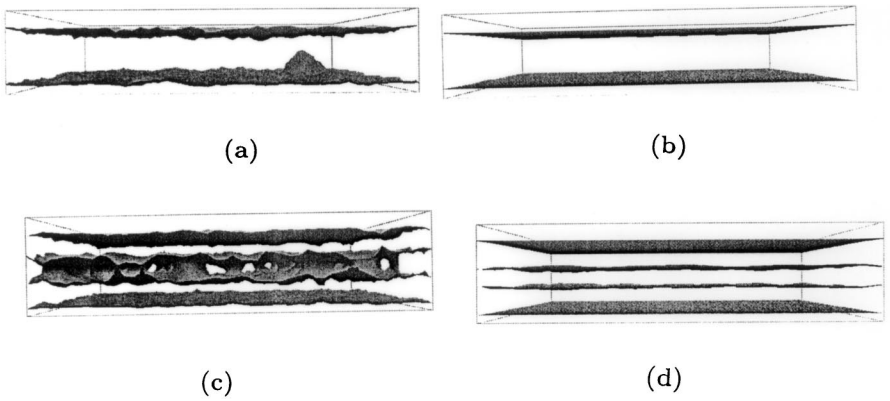


FIG. 2. The snapshot and the average configuration (perspective view) of the system for $N_z = 9$ [(a) and (b)] and $N_z = 11$ [(c) and (d)]. Please note the passages connecting two layers in the center of the system.

and the average Euler characteristics scaled as $N_x \times N_y$ as it should.

Figure 2 shows the snapshots and the average configurations of the lamellar phase for $N_z = 9$ and $N_z = 11$. The snapshots clearly indicate the strong topological fluctuations for the four layer system. Interestingly, the two layers close to the wall are not involved, i.e., all the passages connect only the two layers in the center of the system. In the two layer system just before the transition there are some topological fluctuations, but $\langle \chi \rangle$ for $N_z = 9$ is more than three orders of magnitude smaller than the one for $N_z = 11$.

Figure 3 shows the typical Monte Carlo configuration for $N_z = 10$. In the perspective view of the structure [Fig. 3(a)] we observe extremely strong topological fluctuations, in which also the layers which are close to the wall are involved. The center of the film contains the structure that resembles strongly the microemulsion (disordered phase) [Fig. 3(b)]. In this figure we have shown the top view of the center of the system ($x$-$y$ plane) (i.e., the surface layers were removed in order to make the center of the system visible). A word of caution is needed at this point. When we simulated the system of small sizes $N_x = N_y = 27$, periodic boundary conditions promoted the appearance of the ordered array of cylinders instead of the microemulsion, and only for the large system of $N_x = N_y = 50$ did the truly disordered structure emerge.

The microemulsion forms in the system despite the fact that we are away from the bulk phase boundaries. The reason for this behavior is the stress imposed by confinement. One way to relieve the stress is to change the structure from the ordered to the disordered as we observe in the simulations.

Our results combined with theoretical analysis of Golubović [11] suggest that passages between the surfaces can induce significant intermembrane attractive interactions in the confined lamellar phases. Golubović [11] demonstrated that passage-induced attraction can be stronger than Helfrich's entropic repulsion [25] at large enough intermembrane distances in the lamellar phase. In the force apparatus experiments it has been observed that the overall force between the walls is attractive [1]. The appearance of topological fluctuations and the fact that they induce attraction may be a very good explanation for the attractive background force found in real experiments [1,26].

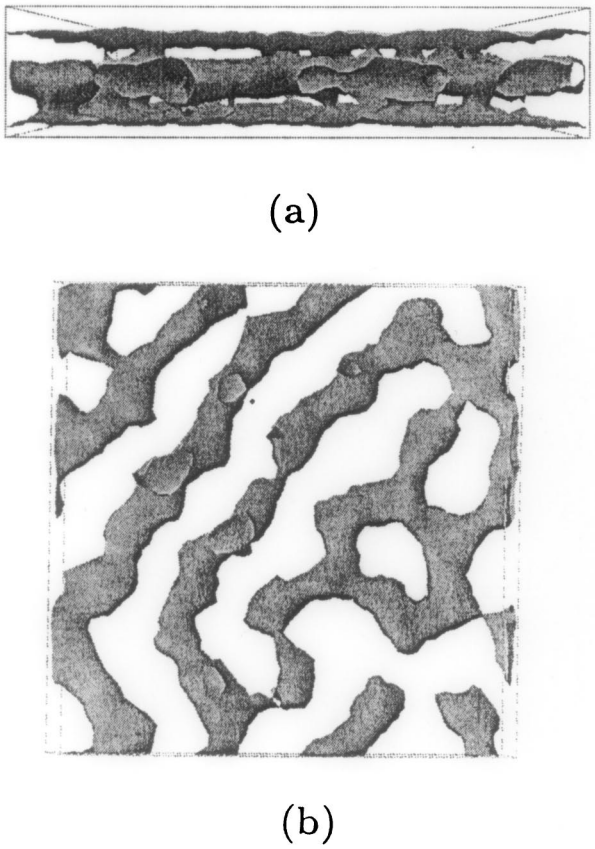


FIG. 3. The snapshot of the system configuration for $N_z = 10$ (a) and the top view of the inside structure formed in the middle of the system (b). The system consists of two layers attached to the walls (a) and the disordered network of channels lying in the $x$-$y$ plane (b) ($z$ axis is perpendicular to the walls).

In summary, we have shown that confinement induces topological fluctuations in a system with internal surfaces. We have also discussed in detail the type of structural changes which can be expected in the lamellar phase between two walls. The formation of new layers in the system is preceded by the formation of the intermediate disordered phase.

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