

Surface-induced ordering of a molecular fluid of flat hexagonal structure in a narrow graphite slit

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We systematically investigate by Monte Carlo simulations the role of the wall structure on a fluid of flat hexagonal molecules confined between two graphite walls. Our simulations show that the centers of mass of the molecules in different layers undergo an *order-disorder* transition as the wall separation increases, irrespective of the details of the wall structure. The wall structure thus becomes insignificant for the intervening fluid even down to a surprisingly low wall separation. [S1063-651X(99)10106-5]

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INTRODUCTION

The molecular structure at the interface between a solid substrate and a complex fluid is of profound academic interest as well as technological importance [1]. The behavior of benzene molecules on a graphite substrate has drawn considerable attention because of the symmetry of the molecules: the carbon-carbon distances of the flat benzene ring are in registry with the carbon hexagons of the graphite surface. Physisorbed layers of benzene on a graphite surface have been studied extensively [2–4]. These studies seem to indicate that the corrugation of the graphite wall, resulting from its hexagonal structure, has only a weak contribution to the physisorption process. Hence, most of these works (see Ref. [2], for instance) ignore the local substrate feature. Nevertheless, one should note that the role of lateral wall structure is not obvious for a strongly confined benzene. Here we consider a pair of confining graphite walls at a separation H , comparable to the range over which the surface influence extends within the pore in a direction normal to the wall [4]. Highly confined fluids are in general known to have layered structures, along with precrystallization of the substrate layer into a triangular lattice [5]. This emerging long-range structure in turn would provide a modulation for the inner layers, if the confinement is strong enough. The substrate benzene layers adjacent to the graphite walls will experience a modulation due to the hexagonal lateral structure of the walls. The questions naturally arise: would the commensuration of the symmetries, namely, that between the wall structure, the molecular structure, and the emerging long-range translational order, enhance the emergence of the long-range order in these layers? If so, what will be the manifestation in the dynamics of the fluid? These considerations lead us, for the first time to the best of our knowledge, to systematically investigate the effect of the graphite wall structure, namely, hexagonally ordered carbon atoms (structured) in relation to randomly distributed carbon atoms on the (smeared) wall [6] for a given areal density of the wall atoms, on a strongly confined fluid of molecules with the same structural symme-

try as benzene. Our Monte Carlo (MC) simulations show that the effect of wall structure is qualitatively insignificant to determine the structural and the dynamic properties of the confined molecular fluid even down to strong confinement conditions.

Since we are mainly interested in the symmetry aspects, we take the benzene molecule in our study to be a flat hexagonal object, with the corners being occupied by Lennard-Jones atoms connected by rigid bonds. The Lennard-Jones (LJ) atoms interact via a spherically symmetric potential, $v(r) = 4\epsilon_{CC}[(\sigma_{CC}/r)^{12} - (\sigma_{CC}/r)^6]$, ϵ_{CC} being the depth of the interaction and σ_{CC} the hard core diameter (the range over which the potential is repulsive). We consider the Coulomb interaction between the atoms by associating a charge at each site of LJ atom whose magnitude is determined so that the quadrupolar tensor component along the normal to the molecular plane corresponds to the experimentally known value for benzene [7]. The bond vibrations are ignored, since typically these excitations are much more costly at a given T than the energy associated with the LJ depth parameter [7]. The length scale in the simulations is set by the bond length in the molecules and the energy is scaled according to $k_B T$. Graphite walls in reality consist of several layers of hexagonally arranged carbon planes. But the effect of the wall corrugation falls off exponentially with the distance from the wall [7,8]. So the predominant wall effect would come from the layer adjacent to the intervening fluid. Hence, we consider a single graphite plane. The wall atoms interact with the atoms in the molecule via LJ potential, characterized by ϵ_{CG} and σ_{CG} .

SIMULATION DETAILS

The simulations are carried out on N molecules in a parallelepiped box whose center defines the origin of the space-fixed frame. Periodic boundary conditions (PBC's) are employed in the x and y directions with the dimensions $L_x/L_y = \sqrt{3}/2$ and there are no PBC's in the z direction with the walls $z = \pm H/2$. Note that a molecule, being a flat rigid hexagon in our studies, is described relative to the space-fixed frame by the coordinates of its center of mass (c.m.) and the orientations of the long molecular axis (the diagonal joining one of the corners of the hexagon to the c.m.) and an axis, normal to the molecular plane. We define a local body-fixed

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TABLE I. Different parameters used in the simulations.

Parameter	Value
ϵ_{CC}	0.12 kcal/mol
σ_{CC}	3.64Å
Molecular bond length	1.4Å
ϵ_{CG}	0.06 kcal/mol
σ_{CG}	3.82Å
Graphite areal density	0.382Å ⁻²

frame at the center of the ring with the z' axis being parallel to the normal to the molecular plane, the y' axis parallel to the long molecular axis, and the x' axis defined by the cross-product of these two vectors, so that x' and y' describe the plane of the hexagon. The six atoms in the molecule have coordinates $\{(\sin[n2\pi/6], \cos[n2\pi/6]), n=0, \dots, 5\}$ in the body-fixed frame. The coordinates of the atoms in the space-fixed frame are related to those in the body-fixed frame by a combination of a translation and a rigid rotation. One MC move is comprised of constructing the translation vectors and the rotation matrices by performing the following operations on a randomly chosen molecule: (1) The c.m. is given a random translation. (2) The normal to the molecular plane is rotated randomly over a unit sphere. (3) The direction cosines of the molecular axis in the plane are chosen at random subject to the constraints that it remain perpendicular to the normal obtained from step (2) and that of unit magnitude. Note that these moves take care of the six degrees of freedom needed to describe a rigid body: three associated with the location of the c.m., two polar angles to describe the normal to the molecular plane, and one component of the direction cosines of the long molecular axis, the other two components being fixed by the constraints. Two neighbor lists, one of all the molecules and the other of all the wall atoms lying within an annulus bounded by two cylinders of radii $r_{low}(=2)$ and $r_{up}(=3)$ about the c.m. of a molecule, are employed to calculate the energy cost of a MC move. The acceptance of a MC move is determined according to the standard METROPOLIS algorithm. The step sizes are adjusted so as to achieve 40% acceptance. For the bulk cases we employ the PBC's for all three directions, turn the wall potential off and use a spherical cutoff for calculating the energy of interactions. Typically starting from an initial configuration, we allow the system to evolve first 25 000 steps to equilibrate, after which we carry out a further 25 000 steps to calculate different quantities of interest.

The system parameters, shown in Table I, are chosen from Ref. [7] for the sake of illustration. The choice of H can be motivated from geometrical constraints as follows. Since earlier simulations [2] seem to indicate that the benzene molecules in the substrate layer prefer to lie with their planes parallel to the walls and under a strong confinement condition the inner layers are likely to follow the substrate layers, we consider the case where the molecules lie with their planes parallel to the plane of the wall in every layer. First, a given n number of such molecular layers can be fitted in, if the wall separation is $H' \approx m\sigma_{CC} + 2\sigma_{CG}$, with $m=n-1$ for an odd n and $m=n$ for an even n . Second, anticipating that a precrystallization into a triangular lattice could take place, we take the number of molecules consistent with the forma-

tion of triangular lattice in the layers. The lowest N thus chosen is 108, consistent with the formation of $n=3$ layers of triangular lattice in the manner described above and the corresponding H ($=9.71$), approximately [9] equal to the wall separation required to fit in $n=3$ layers, to achieve ρ_o ($=N/V$, V being the volume of the box) $=0.019$ [2]. We do the calculations with the cross-sectional area of the walls and ρ_0 held fixed for other higher H , namely, for $H=16.19$ and 19.43 with $N=180$ and 216 , respectively. Note that the intermediate value of H is approximately equal to the fitting of $N=4$ layers and the highest one equal to that of $n=6$ layers, as already explained.

NUMERICAL RESULTS

We illustrate in detail the case of $T=300$ K. The bulk simulations ($N=108$) reveal a fluid phase with no predominant tendency of alignment of the long molecular axis of the molecules. The nematic order parameter S [defined by the largest eigenvalue of the nematic tensor $Q = \sum_i \frac{1}{2} (3\xi_\alpha^i \xi_\beta^i - \delta_{\alpha,\beta})$, $\{\xi_\alpha^i\}$ being the direction cosines of the long molecular axis in the space-fixed frame] ≈ 0.27 and decreases with increasing N . The mean-squared displacements (MSD's) of the c.m. in the x - y plane and z direction [defined by $S_{xy} = (1/N) \langle \sum_i \{ [x_i - x_i(0)]^2 + [y_i - y_i(0)]^2 \} \rangle$, and $S_z = (1/N) \langle \sum_i \{ [z_i - z_i(0)]^2 \} \rangle$, respectively, where (x_i, y_i, z_i) are the

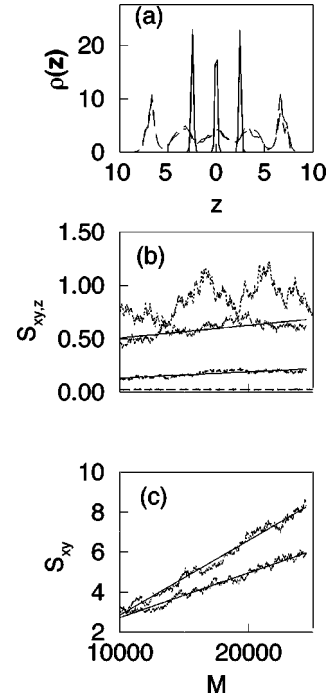


FIG. 1. (a) The density profile $\rho(z)$ as a function of z for $H=9.71$ (solid line) and $H=19.43$ (dashed line). The distinction between the structured and the smeared wall cases is insignificant. (b) S_{xy} (dotted line) and S_z (dashed line) as functions of MC step, M for $H=9.71$ with two types of walls. The solid lines are the linear fits to the data in the smeared wall case. The slopes are essentially negligible. (c) S_{xy} as functions of M for $H=19.43$. The upper curve is for the smeared wall and the lower one for the structured wall. The linear fits, shown by the solid lines, confirm diffusive behavior. Note the difference in the vertical scales in (b) and (c). The MSD data in all the cases are averaged over three independent runs.

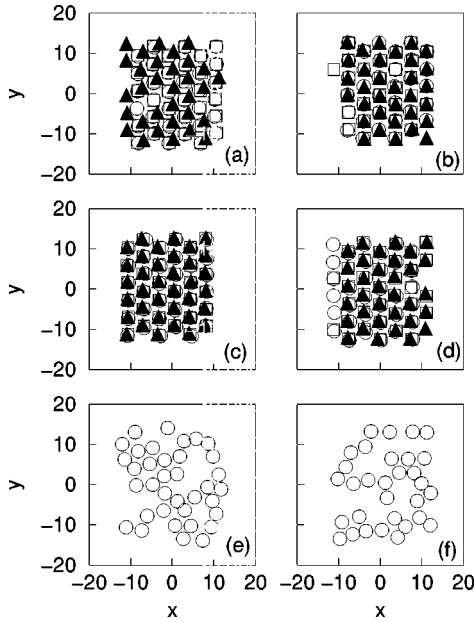


FIG. 2. The snapshots for different cases: (a) substrate layer, (b) central layer with smeared wall, (c) substrate layer, and (d) central layer with the structured wall; $H=9.71$ in all the cases. Three equilibrium configurations 5000 steps apart are superposed on each other. The solid triangles provide a quick glance at the translational order in the layer. Note the crystalline orders apart from vacancies [(a), (b), and (d)]. (e) and (f) are the snapshots at the substrate layer for the smeared and the structured wall cases, respectively, for $H=19.43$. The disordered phase is quite evident in these cases.

coordinates of the c.m. of the i th molecule at a given MC step, $(x_i(0), y_i(0), z_i(0))$ are the initial positions, and angular brackets denote averaging over the initial configurations] show a linear dependence on the MC steps, M for large steps, characteristic of a fluid behavior.

Figure 1(a) shows the density profile $\rho(z)$ of the c.m. of the molecules calculated by binning their z coordinates, when such a system is confined between two graphite walls with $H=9.71$. For both the smeared wall and the structured wall cases, $\rho(z)$ has a pronounced peak structure that implies the formation of layers. We find that there are three layers: one at the center, the central layer, and two symmetrically situated close to the walls, the substrate layers. The position vectors of the c.m. of the molecules lying within the half-width of a peak are projected onto the constant $z=z_m$ plane, where z_m is the position of the peak, and this projected plane is identified as a layer located at $z=z_m$. We observe that the molecules orient with their plane parallel to that of the wall, even though the molecules in the central layer tend to be slightly more disordered than those in the substrate layer. We find that S is rather large (≈ 0.9) for all the layers, implying a very strong orientational order. The wall-induced orientational order does not find enough space to decay in such a strong confinement. S_{xy} and S_z , shown in Fig. 1(b), indicate negligible (almost zero) in-layer and interlayer transports. This makes it worthwhile to check the distribution of the c.m. of the molecules in the layers. The bond orientation order parameter $|\psi_6|^2$ (defined by $\psi_6 = \langle 1/N \sum_{\alpha=1, N} \frac{1}{6} \sum_{\beta} \exp(i6\Theta_{\alpha\beta}) \rangle$, the angular brackets indicating the configuration average, $\Theta_{\alpha\beta}$ being the angle be-

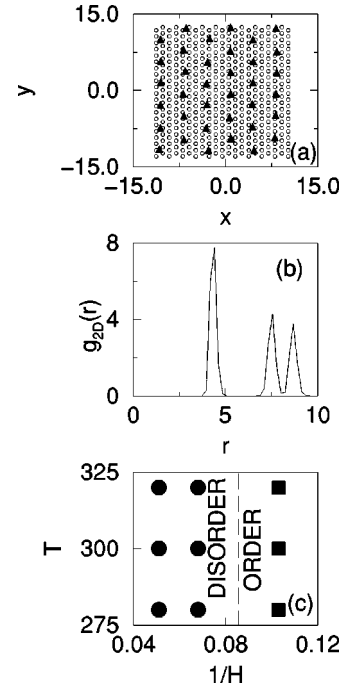


FIG. 3. (a) The commensurate ordered structure shown on the background of the graphite wall. (b) Pair correlation function $g_{2D}(r)$ for the commensurate phase as a function of the distance r in the plane. (c) The phase diagram in the $1/H$ - T plane: disordered (solid circles) and ordered (solid squares). The symbols represent actual simulated points. The dashed line is a guide to the eye.

tween a fixed axis (here x axis), and the bond joining a c.m. α with another c.m. β lying within a radius of $1/[\rho(z_m)]^{1/2}$ around α , $\rho(z_m)$ being the areal density at the peak), which is sensitive to local crystalline order [$|\psi_6|^2=0$ for a fluid (disordered) phase and $|\psi_6|^2 \neq 0$ for a crystal (ordered) phase of hexagonal order], shows strong crystal order in the layers, $|\psi_6|^2 \sim 0.36$. Note that due to the strong confinement situation, the layers in the system behave in a coherent manner. Hence, we denote the system to be in an ordered phase, despite its layered structure. The ordered structure is further confirmed from Figs. 2(a) and 2(b), where the snapshots of the c.m. in the substrate and the central layers with the smeared wall case are superposed on each other for three well (5000 steps) separated equilibrated configurations and show predominant translational order apart from vacancies. The snapshots for different layers in the structured wall case, shown in Figs. 2(c) and 2(d), exhibit essentially the same qualitative feature.

Figure 1 summarizes our observations also for a larger separation, $H=19.43$. Figure 1(a) shows $\rho(z)$ for the smeared and structured wall cases. For both situations, $\rho(z)$ indicates the presence of more layers than in the strong confinement case, but the peaks are now comparatively broader and reduced in height. It is interesting to note that the number of peaks obtained here is less than the number of layers that actually could be fitted in from the geometrical constant ($n=6$). This could be understood in terms of a larger freedom the molecules have to rotate here than in the $H=9.71$ case. In order to allow for different possible orientations of the hexagons, the layer separation must increase, and thereby the number of layers that can fit in must decrease. This is

further supported by a low $S(\approx 0.29)$ in the layers in contrast to the strong confinement case. This clearly demonstrates a nontrivial coupling between the orientational and translational degrees of freedom. The MSD's, shown in Fig. 1(b), reveal a fluid behavior in confirmation of observations on the structural properties. The difference in the slopes of the linear fits to these curves is only a qualitative one. We draw attention to the disordered snapshots of the c.m. in the substrate layer in Figs. 2(e) and 2(f). This observation suggests that the system undergoes an *order-disorder* transition as H increases. A snapshot of the ordered substrate layer, observed with the structured walls, superimposed on the underlying graphite wall in Fig. 3(a) and the pair-correlation function, $g_{2D}(r)$ [10] in Fig. 3(b) as a function of distance r in the plane show that the ordered phase is a commensurate $\sqrt{7} \times \sqrt{7}$ phase. The broadening and the reduction in the heights of the peaks at the substrate layers for larger H mean that the coverage at the substrate layer decreases as H increases. The decrease in the coverage helps the disordering effects that compete with the sixfold external modulating potential acting on the substrate layer, to outweigh the order above a critical $H=H_c$, when the substrate layer becomes disordered and the inner layers simply follow the substrate layers due to strong confinement condition. The transition seems to be analogous to experimentally observed order-disorder transition for physisorbed benzene [3] or alkanes [11] on graphite. It is interesting to note that the ordered phase in the smeared wall case shows similar $g_{2D}(r)$, indicating a $\sqrt{7} \times \sqrt{7}$ structure. But the transition here, observed around H_c , is simply driven by precrystallization due to the confinement effect. Our observations suggest that H_c should lie within the bound $16.19 < H_c < 19.43$ for both cases. We

show a phase diagram in Fig. 3(c) in the $1/H$ - T plane. The order-disorder transition point appears to be insensitive to temperature in the range we consider. The confinement effect clearly outweighs any effect caused by the details of wall structure.

CONCLUSION

To summarize, our studies indicate that the graphite wall structure gets outweighed by the confinement effect and does not crucially affect the structural and the dynamic properties of a strongly confined molecular fluid of hexagonal structure. Hence, ignoring the details of wall structure is a reasonable approximation down to an extreme confinement situation; namely, H is comparable to the typical length scale up to which surface effects extend in the pore. There is a critical wall separation H_c above which the confined fluid undergoes an order-disorder transition. We elucidate the connection between the dynamics and the structure of the confined fluid across this transition. These predictions can be verified by systematic experiments. While further studies addressing the issue of the existence of H_c would be worthwhile, the role of the wall structure in the kinetics of the transition observed here merits further investigation. The kinetics might show up as a difference between the two situations, due to the difference in diffusion in the two cases [Fig. 1(c)].

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particle potential [7]. We ignore the dynamics of the wall atoms in our studies.

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