Specifics of freezing of Lennard-Jones fluid confined to molecularly thin layers

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Freezing of a Lennard-Jones fluid between solid surfaces was studied using grand canonical Monte Carlo and molecular dynamics simulations. We explored the formation of frozen phases of hexagonal and orthorhombic symmetry in mono-, bi-, and tri-layer structures. The freezing transition, the type of lattice, and translational and orientational ordering were identified on the basis of orientational order parameters, in-plane two-body and three-body translational correlation functions, orientational correlation functions, and analysis of molecular mobilities. We have found that the freezing temperature is a nonmonotonous function of the pore width: orthorhombic bi-layer freezes at lower temperatures than hexagonal monolayer and hexagonal bi-layer. As the pore width increases, the transition from a hexagonal monolayer to an orthorhombic bi-layer occurred via disordered liquidlike and quasi-long-range four-fold ordered bi-layers. The latter, “quadratic” structure is characterized by an algebraically decaying four-fold orientational correlation function. The transition from crystalline hexagonal bi-layer to orthorhombic tri-layer occurs through a bi-layer structure with two uncoupled hexagonal monolayers. The quadratic phase was observed also as an intermediate structure during freezing of a liquidlike bi-layer into an orthorhombic quasi-crystal. The formation of the quadratic phase was associated with step-wise densification of fluid, a sharp increase of the local orientational order parameter, and a significant reduction of fluid mobility. In the process of solidification, the system passed through a sequence of high-density jammed structures, in which the four-fold symmetry developed progressively, as the temperature decreased. © 2003 American Institute of Physics. [DOI: 10.1063/1.1560938]

I. INTRODUCTION

The freezing of fluids and colloids confined by solid surfaces to mono- and multilayers has been attracting considerable interest, particularly with respect to adsorption in microporous solids\(^1\) adhesion and lubrication,\(^2\) the behavior of fluids in the surface force apparatus,\(^3\) nanostructure synthesis, etc. Experimental studies of colloidal suspensions and different theoretical models of hard and soft spheres revealed that confined mono- and multilayers may exhibit different ordered morphologies.\(^4\) Phase transformations in two-dimensional (2D) monolayers have received special attention starting from the classical works of Landau\(^5\) and Peierls\(^6\) who argued that a two-dimensional crystal with long-range positional order cannot exist. This implies that the most ordered 2D structure is a quasi-crystal with an algebraically decaying (quasi-long-range) translational order and a truly long-range orientational order. Kosterlitz and Thouless\(^7\) proposed that melting of a 2D quasi-crystal is a continuous dislocation–unbinding transition. Nelson and Halperin\(^8\) found that the Kosterlitz–Thouless (KT) transition leads to a hexatic phase characterized by translational disorder and quasi-long-range orientational order. A second KT type disclination–unbinding transition is required for transformation of the orientationally ordered hexatic phase into a disordered liquid. This two-stage scheme of freezing and melting in 2D systems is known as the Kosterlitz–Thouless–Nelson–Halperin–Young (KTHNY) transition. The KT transition from a 2D quasi-crystal to a hexatic phase was demonstrated in Monte Carlo (MC) simulations by Bladon and Frenkel.\(^9\)

In transition from mono- to multilayers, transformations between phases of distinct symmetry are induced by variations of the size of confinement, pressure, or solvation force. It was found experimentally that colloidal particles confined between two parallel glass plates undergo a series of consecutive structural transitions from a hexagonal symmetry in 2D monolayers to orthorhombic (also known as “square”) and hexagonal (also known as “triangular”) multilayer crystalline phases as the separation between the plates increases.\(^10\)

\[
1H\rightarrow 2O\rightarrow 2H\rightarrow 3O\rightarrow 3H\rightarrow \cdots,
\]

where O and H denote orthorhombic and hexagonal symmetry. Transitions between these structures are governed by spatial factors, primarily, by the ratio of the molecule diameter to the pore width and the ratio of solid–fluid to fluid–fluid attractive energies.

Transitions between the phases of different symmetry were confirmed by MC simulations of hard spheres confined in slit pores with repulsive walls.\(^11–14\) Thorough MC simulations of hard sphere crystalline structures between repulsive walls revealed, in addition to hexagonal and orthorhombic, two-layer rhombic (triclinic) and buckling phases, which are stable at certain pore widths and lateral pressures. Zangi and Rice\(^13,14\) studied the transitions between different phases in a
system of colloidal particles interacting through the Marcus–Rice potential which has attractive and soft repulsive terms. They found prominent distinctions with a similar system which had no attractive interactions, and concluded that freezing transitions are governed by both repulsive and attractive forces.

Simulations of systems with strong attractive fluid–fluid interactions were focused mostly on the dependence of freezing temperature on solid–fluid interactions and pore size. Miyahara and Gubbins studied freezing of a Lennard-Jones (LJ) fluid in slit-shaped micropores using grand canonical Monte Carlo (GCMC) simulations. They found that the freezing temperature depends on the strength of the solid–fluid potential. In pores with strongly attractive walls, the freezing temperature is higher than the bulk freezing temperature, while in pores with repulsive walls, it is lower. Similar effects were observed in slit-shaped pores with heterogeneous walls. Later, Miyahara et al. employed molecular dynamics (MD) technique with an imaginary gas phase to modeling freezing and melting transitions in micropores induced by variations of temperature or pressure. Dominguez et al. also studied the freezing of a LJ fluid in pores by MC simulation with a fixed normal component of the pressure tensor. They developed a technique for determining the liquid–solid equilibrium via thermodynamic integration. Radhakrishnan and Gubbins used a Landau–Ginzburg approach based on calculations of the free energy as a function of an effective orientational order parameter. The authors found that freezing/melting of a LJ fluid in pores of simple geometries (such as a slit or a cylindrical channel) is mostly determined by the pore width and the ratio of the fluid–solid to fluid–fluid attractive potentials. In pores, which accommodate three or more adsorbed layers, the contact layer was found to freeze/melt at different conditions than the inner layers. The authors also found evidence of a liquid-to-hexatic transition that occurs prior to freezing, in accordance with the KTHNY theory. Qualitative agreement between the freezing temperatures of CCl\textsubscript{4} in graphite pores and the experimental data for microporous activated carbon fibers was presented in Ref. 1. An interesting approach to the characterization of ordering of complex liquids in pores was demonstrated in Ref. 24.

Simulations of freezing in cylindrical pores using a combined MC/MD technique were performed by Maddox et al. The shifts in freezing temperature they obtained were qualitatively similar to those for slit pores, but the freezing temperatures were lower in cylindrical confinements. Koga et al. carried out MD simulations of water and amorphous ice in slit hydrophobic pores and observed the formation of an amorphous bi-layer with a network of hydrogen-bonded polygons without any long-range order. They also studied freezing of water in carbon nanotubes.

The structural transitions between the triclinic and bcc lattices were observed by Bordarier et al. in a slit pore with structured walls. Recently, Ghatak and Ayappa studied orthorhombic and hexagonal geometries in a LJ fluid confined to structureless slit pores. They observed transformations between the hexagonal and orthorhombic lattices according to scheme (1) in pores that are able to accommodate one, two and three adsorbed layers, and obtained an isotherm of the solvation force for this system. In the intermediate regime between 1H and 2O phases, the authors found a “buckled” hexagonal structure, where the atoms may move out-of-plane in the direction normal to the pore walls, while maintaining hexagonal in-plane order. The analysis of the phase symmetries was based on calculations of the orientational order parameters and the translational correlation function.

In this paper, we explore various structures and transitions between the phases of distinct symmetry in an LJ fluid confined between crystalline graphite walls. The LJ fluid parameters, molecular diameter \( \sigma_f \) and attraction energy \( \epsilon_{ff} \), were chosen to model nitrogen which is a standard adsorbate for adsorption studies. Varying the pore width (which is defined as the separation between the centers of outer carbon atoms in the opposite graphite walls and thus exceeds the thickness of the confined layer by roughly one molecular diameter) from 2 to 4.4 \( \sigma_{ff} \) and the temperature from 1.2 to 0.07 \( kT/\epsilon_{ff} \), we study fluid–solid and solid–solid transitions and demonstrate the existence of a variety of hexagonal and orthorhombic frozen phases characterized by different combinations of long-range, quasi-long-range, and short-range orientational, and translational orderings. The phase morphologies are comprehensively characterized by the whole arsenal of correlation functions, including orientational local order parameters, intra-layer and inter-layer translational and orientational correlation functions, solid–fluid correlation functions, and also three-body correlation functions. In so doing, we have found some interesting mechanisms of freezing/melting, which have not been reported earlier.

The paper is structured as follows: In Sec. II, we describe the system under consideration, a LJ model nitrogen condensed in slit-shaped graphite pores, and the methods employed for simulations and statistical analyses. In Sec. III A, we demonstrate “ideal” frozen phases obtained by quenching condensed fluid down to a very low temperature \( (kT/\epsilon_{ff}) = 0.16, 16 \text{ K} \) and consecutive MD equilibration for 5 ns. These structures, which comply with the scheme (1) of the sequence of hexatic–orthorhombic transitions, serve as references for further analysis. In Sec. III B we present and analyze the results of MC and MD simulations at the normal boiling temperature of nitrogen \( (kT/\epsilon_{ff}) = 0.762, 77.4 \text{ K} \) in 17 pores ranging from 2 to 4.4 \( \sigma_{ff} \). We show that the freezing temperature has a nonmonotonous dependence on the pore width. As the pore size increased, we found, along with frozen 1H, 2O, 2H, 3O, and 3H crystalline structures, a disordered liquidlike bi-layer and, most intriguingly, a frozen bi-layer with an algebraically decaying four-fold orientational correlation function. The latter structure was named a quadratic phase, in analogy with the definition of the hexatic phase. In Sec. III D, we study the freezing of liquidlike bi-layers into 2O and 2H solids employing a large simulation cell with 30\( \sigma_{ff} \times 30\sigma_{ff} \) base with structureless walls. The temperature was varied along the bulk vapor–liquid coexistence line. We show that freezing of bi-layers into orthorhombic quasi-crystals occurred continuously through an intermediate quadratic phase. The transition from the liquid to the quadratic phase was associated with a step-wise densification.
II. SIMULATION DETAILS

A. Potential models

We performed GCMC and NVT MD simulations of freezing of a Lennard-Jones fluid in slit-shaped pores. The parameters of fluid–fluid and solid–fluid interactions were chosen to model sorption of nitrogen in carbon nanopores, which is a typical and experimentally well-studied system. LJ parameters \( \sigma_{eff} = 3.6154 \text{ Å} \), \( \epsilon_{eff}/k = 101.5 \text{ K} \) were used for the fluid.\(^{29}\) The potential was cut off at \( 5\sigma_{eff} \) and not shifted. These parameters provide the best fit to the table data on the vapor–liquid equilibrium of bulk nitrogen, as calculated with the equation of Johnson et al.\(^{30}\) The nitrogen boiling temperature at the atmospheric pressure 77.4 K corresponds to \( 0.762 \epsilon_{eff}/k \).

The slit pores were formed by two base graphite planes parallel to the \( xy \) plane. We employed two models of graphite with atomically structured and structureless walls. The basic cell of structured graphite was rectangular, with lateral dimensions of \( 13.60\sigma_{eff} \times 14.15\sigma_{eff} \) (49.20 Å \( \times \) 51.15 Å), in accordance with the lattice periodicity of graphite. The solid–fluid interactions were also described by the LJ potential with \( \sigma_{eff} = 3.494 \text{ Å} \), \( \epsilon_{eff}/k = 53.22 \text{ K} \). These parameters were found to provide good agreement between the experimental and simulated nitrogen adsorption isotherms on nonporous graphite at the normal boiling temperature.\(^{29}\) The carbon atoms were immobile. A cutoff of \( 5\sigma_{eff} \) in the lateral direction was introduced for the solid–fluid LJ interactions. Beyond the cutoff, the graphite surface was treated as a structureless uniform plane, and its interaction with a fluid molecule was described by a fluid–fluid potential: \( U_{10.4}(z) = 2\pi \rho_{s} \epsilon_{s} \sigma_{eff}^{2} (0.4\sigma_{eff}^{10}/(z^{2} + \alpha_{1}^{2})^{5} - \sigma_{eff}^{10}/(z^{2} + \alpha_{1}^{2})^{10}) \); also see Eq. (2). Only the outer, surface layers of the carbon atoms were structured. The second and further layers were structureless and uniform and thus interacted with the fluid via 10-4-3 potential of Steele:\(^{31}\)

\[
U_{sd}(z) = 2\pi \rho_{s} \epsilon_{s} \sigma_{eff}^{2} \Delta \frac{2}{5} \left( \frac{\sigma_{sd}}{z} \right)^{10} \left( \frac{\sigma_{sd}}{z} \right)^{4} - \frac{\sigma_{sd}^{4}}{3\Delta(0.61\Delta + z)^{7}},
\]

where \( z \) is the distance between the molecule and the solid surface, \( \rho_{s} \) is the surface density of sites, \( \Delta \) is the separation between the graphite layers. For graphite \( \Delta = 3.35 \text{ Å} \), the length of the C–C bond is 1.42 Å.

The structureless graphite model was employed to perform simulations in a larger \( 30\sigma_{eff} \times 30\sigma_{eff} \) basic cell. The solid–fluid interactions in this case were described by the 10-4-3 potential (2).

B. Simulations

The MC simulations were carried out in the grand canonical ensemble. In each GCMC simulation, the chemical potential of the fluid corresponded to the vapor–liquid equilibrium in the bulk at a given temperature \( T \). That is, the fluid in the pore was kept in a virtual thermal and chemical equilibrium with the saturated bulk vapor, similarly to earlier simulation works on freezing.\(^{16}\) The equation of Johnson et al.\(^{30}\) was employed as an equation of state for the bulk LJ fluid. The temperature–saturation pressure relationship for the LJ parameters used in this work was computed earlier.\(^{29}\)

The MC runs consisted usually of 250 000 steps per molecule, the properties were averaged over the last 100 000 steps per molecule (each step included one attempt of particle displacement, insertion and removal). Up to 600 000 steps per molecule were done in selected systems, as described below.

In order to obtain lateral diffusion coefficient \( D_{l} \) in selected systems, molecular dynamics (MD) simulations were performed in the canonical (NVT) ensemble. The initial configurations for MD were obtained from GCMC simulations. Equilibration and temperature scaling were carried out over 1 ns. Then, statistics were collected over 5 ns. The time step was 2 fs. The diffusion coefficients were calculated from mean-square displacements.

C. Order parameters and correlation functions

Translational and orientational ordering in confined layers was quantified by local order parameter and correlation functions. The longitudinal variations of fluid structure are traditionally characterized in terms of the local density profile. In narrow pores like the ones considered here, the condensed fluid always forms distinct adsorbed layers. Thus, the in-plane structure (i.e., the structure in the lateral directions, parallel to the \( xy \) plane) is considered layer by layer. Translational order is characterized in terms of layer-to-layer in-plane radial distribution functions (RDF):

\[
g_{ij}(r) = \langle l_{i}l_{j} \rangle = \frac{dN_{ij}}{2\pi N_{i}r \, dr},
\]

where \( dN_{ij} \) is the number of particles of the \( i \)th layer at an in-plane distance ranging between \( r \) and \( r + dr \) from a reference molecule located in the \( j \)th layer, \( N_{i} \) is the average number of molecules in the \( i \)th layer, and \( l_{x} \) and \( l_{y} \)—lateral dimensions of the basic cell. In-layer RDF \( g_{ii}(r) \) characterizes translational order within a given layer. Layer-to-layer RDFs \( g_{ij}(r) \), \( i \neq j \) characterize inter-layer correlations and longitudinal ordering. In liquidlike layers with a short-range order, \( g_{ij}(r) \) oscillates with exponentially decreasing magnitudes and relaxes to 1 at several \( \sigma_{eff} \). In crystalline layers with long-range translational order, oscillations of \( g(r) \) span over the whole sample. An algebraic decay of \( g(r) \) oscillations is a fingerprint of a frozen layer with a quasi-long-range translational order.

Orientational order is quantified by the local orientational order parameters and the orientational correlation
functions. The local bond-orientation order parameter is calculated for each layer:

\[ \psi_B = \left( \frac{1}{n_b} \sum_{k=1}^{n_b} \exp(iB \theta) \right) = \langle |\Psi_B| \rangle. \]  
\( \text{(4)} \)

Here, \( B \) is the coordination number (\( B = 4 \) corresponds to an orthorhombic structure, and \( B = 6 \) corresponds to a hexagonal structure). \( \theta \) is the angle between the projection of the vector connecting a pair of two nearest neighbors to the \( xy \) plane and a fixed reference axis. The real number of nearest neighbors of each molecule is denoted as \( n_b \); the nearest neighbors are identified as the particles that belong to the same layer as the given molecule, and are within the in-plane cutoff distance from the latter. The in-plane cutoff is defined as the location of the first minimum at the pair correlation function \( g_{ii}(r) \) for the given layer. For a perfect 2D square lattice, \( \psi_4 = 1 \) and \( \psi_6 = 0 \). For a perfect 2D hexagonal lattice, \( \psi_6 = 1 \) and \( \psi_4 = 0 \).

The orientational pair correlation function, calculated for each layer, is given by

\[ G_B(r) = \langle \Psi_B(r) \Psi_B(r_0 + r) \rangle_{r_0}. \]  
\( \text{(5)} \)

Here, \( \Psi_B = (1/n_B) \sum_{k=1}^{n_B} \exp(iB \theta) \), as defined in Eq. (4). \( G_B(r) \) measures correlations of the nearest neighbor vectors of two molecules of the same layer separated by in-plane distance \( r \). In a two-dimensional liquid, \( G_B(r) \) decays exponentially to zero within several molecular diameters. In a 2D quasi-crystal with a long-range orientational order, \( G_B(r) \) asymptotically flattens to a nonzero constant;\( ^{32} \) in a system with a quasi-long-range orientational order, e.g., hexatic phase, \( G_B(r) \) decays algebraically.\( ^{32} \)

To analyze the evolution of orientational order in the process of freezing and during the transitions between the phases of distinct symmetry, we also employed the three-body correlation function. Let \( \vec{r}_1, \vec{r}_2 \) be two vectors that connect a reference molecule with two of its nearest neighbors. The three-body correlation function is expressed as \( C_3(r, \alpha) = P(r, \alpha) / r \, d\alpha \), where \( P(r, \alpha) \) is the probability of \( \vec{r}_1 \) and \( \vec{r}_2 \) to form angle \( \alpha \in [0, \pi] \), provided that \( |\vec{r}_2| = r \). Correspondingly, the three-body correlation function may be depicted as \( C_3(x, y) = C_3(\sqrt{x^2 + y^2}, \arcsin x) \).

**III. RESULTS AND DISCUSSION**

**A. Reference structures quenched to low temperature**

To generate almost ideal frozen phases, we performed canonical ensemble MD simulations at a very low temperature \( kT/\epsilon_{ff} = 0.16 \) (16 K for the LJ model of nitrogen) in a series of pores with structured graphite walls. These simulations revealed the evolution of crystalline structures observed in layers of different thickness, from 1 to 3 molecular diameters. The initial configuration for MD simulation was generated by GCMC simulation at the condition of bulk vapor–liquid equilibrium \( kT/\epsilon_{ff} = 0.762 \) (normal boiling temperature 77 K for the LJ model of nitrogen). Then, the temperature was gradually decreased within 200 ps to \( kT/\epsilon_{ff} = 0.16 \). Within the range of pore widths from 2.0 to 4.0, we observed frozen phases with periodic variation of density and symmetry in accord with the scheme (1).

The densities and the local order parameters \( \psi_4 \) and \( \psi_6 \) obtained from the GCMC and MD simulations are presented in Fig. 1. The density profiles, correlation functions, and selected snapshots are shown in Figs. 2 and 3. The low-temperature structures are not ideal, since local defects such as vacancies and dislocations are still present, possibly due to the limited size of the simulation cell. At such low temperature and limited system size, the translational correlation function exhibits a series of distinct peaks (Fig. 2), similarly to 3D solids, which can be used as a fingerprint of the given morphology.
In 2.0σ_fl pore, the solid density is ρσ^3 = 0.875, and the six-fold orientational order parameter is ψ_6 = 0.95. As the pore widens, a single layer splits into two sub-layers and the six-fold symmetry gives place to the four-fold orthorhombic symmetry. The transition is clearly indicated by the changes in the local order parameters, as ψ_6 falls from 1 to 0, while ψ_4 almost reaches 1 [Fig. 1(b)]. The locations of the peaks of the translation correlation functions change abruptly (Fig. 2). Snapshots also indicate the transition to the orthorhombic geometry (Fig. 3). Pronounced orthorhombic bi-layer phases are characteristic to pore widths of 2.4–2.6σ_fl. As the pore widens further, the four-fold symmetry transforms back into the six-fold symmetry. In 2.8–3.2σ_fl pores, we find pronounced hexagonal bi-layer phases with ψ_6 ≈ 1 [Fig. 1(b)]. g_{11}(r) clearly indicates the hexagonal symmetry of the individual layers (Fig. 2). The bi-layer in 2.8σ_fl and 3.0σ_fl pores has an almost ideal hexagonal packing. The distance between the layers gradually increases with the pore width. In 3.2σ_fl pore, each layer splits into two sublayers demonstrated by four peaks on the local density profile (Fig. 2). While a near to perfect six-fold symmetry is observed in both layers [ψ_6 = 0.97, Fig. 1(b)], the atoms of one layer are shifted from the ideal locations between the atoms of the other layer (snapshot, Fig. 3). The formation of the third layer in 3.4σ_fl – 3.5σ_fl pores is associated with the development of tri-layer orthorhombic packings. The subsequent transition to hexagonal tri-layer phases occurs in 3.6σ_fl pore, where we observe ABA stacking, i.e., the projections of atoms of the outer layers coincide. In the widest pore of 4.0σ_fl modeled at the low temperature, a hexagonal tri-layer phase is well defined (Fig. 2).

The periodic variation of the solid state symmetry is clearly indicated by the coupled change of the ψ_6 and ψ_4 orientational order parameters depicted in Fig. 1(b). The transitions between the layers of different symmetry imply a characteristic nonmonotonous dependence of the layer density [Fig. 1(a)]. The properties of solid layers at the low temperature summarized in Figs. 1, 2 serve as references in the following analysis of the process of freezing.

B. Freezing in pores at the normal boiling temperature

1. Sequence of hexagonal and orthorhombic frozen structures

It is well understood that, at the conditions of bulk vapor–liquid equilibrium, fluid in wetting pores condenses into a liquidlike state. Due to the fluid–solid interactions, the contact liquid layers may exhibit 2D hexatic order with algebraically decaying in-plane orientational correlation function.21,22 In slit ultramicropores of few molecular diameters in width, the condensed phase may be frozen into a crystalline structure of either hexagonal or orthorhombic symmetry.13 We have performed GCMC simulations of a LJ model of nitrogen at its boiling temperature T = 77.4 K (kT/ε_fl = 0.762) in the gaps between structured graphite walls. Within the range of pore widths from 2 to 4.4
we observed frozen phases with a periodic variation of density and symmetry in accord with the scheme $\sim 1$. These phases are in general similar to their quenched counterparts presented in Figs. 1–3, however, they are more defective. The formation of new layers is well seen on the local density profiles given in Fig. 4 $\sim 2.2s_{ff}$, Fig. 4(a), $3.2s_{ff} - 3.6s_{ff}$, Fig. 4(b), $3.8s_{ff} - 4.4s_{ff}$, Fig. 4(c)]. As expected, in the pores, which can accommodate just one layer of molecules, a 2D solid is characterized by an algebraically decaying quasi-long-range translational order and a long-range hexagonal orientational order, as demonstrated by the translational and orientational correlation functions for $2.0s_{ff}$ pore (Fig. 5). $g_{11}(r)$ exhibits pronounced peaks at the same positions as the low-temperature structure (see Fig. 1) and visibly decays to 1. $G_{\theta}(r)$ asymptotically approaches a constant of about 0.7 (Fig. 5).

Studying the transitions between different morphologies shown in Fig. 6, we have found several interesting features, which have not been observed before.

2. Nonmonotonous dependence of the freezing temperature on the pore size

The transition from the 1H phase in $2.0s_{ff}$ pore to 2O phase in $2.6s_{ff}$ pore proceeds through a disordered liquidlike phase in $2.4s_{ff}$ pore (the snapshot in Fig. 6) to a phase with a short-range translational order and a quasi-long-range fourfold orientational order in $2.5s_{ff}$ pore. This is demonstrated by the structural characteristics shown in Fig. 5. In a liquid-

![FIG. 3. (Color) Configuration snapshots of selected systems at the low temperature $kT/\epsilon_{ff}=0.16$. The contact layer in blue and the underlying second layer in yellow. In three-layer configurations the third, i.e., the opposite contact layer in pink.](image-url)
like phase in $2.4\sigma_{ff}$ pore, $g_{11}(r)$ decays swiftly to 1, while both $G_6(r)$ and $G_4(r)$ decay exponentially. The liquidlike state of the condensed fluid in $2.4\sigma_{ff}$ pore was also confirmed in a MD simulation, which showed a relatively high lateral diffusion coefficient of $D_i = 7.8 \times 10^{-3} \sigma_{ff}^2 \epsilon_{ff}^{0.5}/M_{N2}^{0.5} (4.9 \times 10^{-10} \text{ m}^2/\text{s})$. This value is in line with diffusion coefficients for liquids in narrow pores previously obtained by different authors. On the contrary, lateral diffusion in $2.0\sigma_{ff}$ and $2.6\sigma_{ff}$ pores was found to be negligible. Therefore, we conclude that the dependence of the freezing temperature on the pore width is nonmonotonic.

3. Quadratic phase

The structure observed in $2.5\sigma_{ff}$ pore has a four-fold quasi-long-range order as indicated by an algebraically decaying $G_6(r)$ (Fig. 5). In analogy to a hexatic phase, which is characterized by an algebraically decaying $G_6(r)$, this structure can be named a “quadratic” phase. The size of the simulations cell employed in these simulations is not sufficient.
enough to make a well-founded conclusion about the discovery of a quadratic phase with a quasi-long-range four-fold orientationally ordered structure. However, more precise simulations performed in a larger cell in Sec. III D also confirm this finding.

4. 2X1H structure

The use of layer-to-layer correlation functions allowed us to make another interesting observation. The transition from 2H phase in $2.8\sigma_H$ pore to 3O phase in a $3.4\sigma_H$ pore proceeds through a 2H phase with two uncoupled 2D hex-

FIG. 6. (Color) Configuration snapshots of selected systems at the normal boiling temperature $kT/\epsilon_{ff}=0.762$. The contact layer in blue; the underlying second layer in yellow. In three-layer configurations the third, opposite contact layer in pink.
agonal solid layers found in $3.2\sigma_{ff}$ pore (see the density profile in Fig. 4 and the snapshot in Fig. 6). In each of the two layers, $\psi_b=0.85$ [Fig. 1(e)], $g_{11}(r)$ and $G_\delta(r)$ (Fig. 5) confirm a 2D solid structure. However, the interlayer correlation function $g_{12}(r)$ (Fig. 5) does not show any correlation between the layers. This structure can be named $2 \times 1H$.

5. Hexagonal symmetry in polymolecular layers

A tri-layer hexagonal structure forms in $3.6\sigma_{ff}$ pore (Figs. 4–6). Unlike the low temperature lattices, the ABA stacking is observed in $3.6\sigma_{ff}$ pore, while in $3.8\sigma_{ff}$ and $4.0\sigma_{ff}$ pores the stacking is ABC. The tri-layer hexagonal symmetry remains until the pore width reaches $4.2\sigma_{ff}$ (Fig. 4), where the inner layer swells and melts to a 2D liquid with no long-range orientational order (Figs. 4, 5). In $4.4\sigma_{ff}$ pore, a four-layer structure forms (see the density profiles in Fig. 4) with two liquidlike central layers. Larger pores also contain hexatic or solid 1H contact layers and liquidlike inner layers as shown in Ref. 20.

C. Freezing of bi-layers

We reported above that at $kT/\epsilon_{ff}=0.762$, the transition from 1H to 20 frozen phases occurred through a liquidlike bi-layer observed in $2.4\sigma_{ff}$ pore and a peculiar “quadratic” bi-layer phase in $2.5\sigma_{ff}$ pore. To study the structure of condensed bi-layers in more details, we performed MC and MD simulations in a larger $30\sigma_{ff} \times 30\sigma_{ff}$ basic cell. In order to speed up calculations, we compromised on the pore wall structure and considered structureless, uniform walls with 10–4–3 potential (2) for solid–fluid interactions. A comparison of the simulation results with crystalline and structureless walls is given in the Appendix.

Simulations in the larger cell were performed in $2.4\sigma_{ff}$, $2.5\sigma_{ff}$, $2.6\sigma_{ff}$, and $2.8\sigma_{ff}$ pores. We gradually cooled down the fluid from a liquidlike state equilibrated at the temperature $kT/\epsilon_{ff}=1.3$. The chemical potential was changed along the line of vapor–liquid coexistence in the bulk LJ fluid (see Sec. II). The final configuration at a given temperature served as the starting configuration for the next simulation at a lower temperature. Similarly to the simulations in smaller cells with structured walls, fluid in wider pores of $2.6\sigma_{ff}$ and $2.8\sigma_{ff}$ in width froze to well-pronounced 2O and 2H structures, respectively. As shown in the Appendix, the structure of pore walls did not affect the fluid structure appreciably. In pores of $2.4\sigma_{ff}$ and $2.5\sigma_{ff}$, we found that freezing into a 2O quasi-crystal proceeds through a sequence of quadratic structures with an algebraic decay of the four-fold orientational ordering. Below, we demonstrate some specifics of this transition.

1. Liquid-to-quadratic transition

The temperature dependences of the density and the local orientational order parameter for $2.4\sigma_{ff}$ and $2.5\sigma_{ff}$ pores are shown in Fig. 7. As the temperature decreases, a notable step-wise densification is observed for $2.4\sigma_{ff}$ and $2.5\sigma_{ff}$ pores at $kT/\epsilon=0.75$ and $kT/\epsilon=1.18$, respectively [Fig. 7(a)]. The densification is accompanied by sharp alterations of the local orientational order parameters: $\psi_4$ increases, while $\psi_6$ decreases [Fig. 7(b)]. In $2.4\sigma_{ff}$ pore, the density changes from $0.48\sigma_{ff}^{-3}$ at $kT/\epsilon=0.762$ to 0.51 $\sigma_{ff}^{-3}$ at $kT/\epsilon=0.73$; the local orientational order parameter $\psi_4$ changes from 0.72 to 0.85, respectively. In $2.5\sigma_{ff}$ pore, the density changes from $0.5\sigma_{ff}^{-3}$ at $kT/\epsilon=1.2$ to 0.53 $\sigma_{ff}^{-3}$ at $kT/\epsilon=1.15$; the local orientational order parameter $\psi_4$ changes from 0.71 to 0.78, respectively.

We argue that the coupled densification and ordering displayed in Fig. 7 indicate a “liquid-to-quadratic transition.” Indeed, let us analyze the changes in the bi-layer structure in the vicinity of the transition temperature. The snapshot of a configuration in $2.4\sigma_{ff}$ pore at a slightly higher temperature, $kT/\epsilon_{ff}=0.762$ [Fig. 8(a)], resembles a liquidlike structure. The local orientational order parameter for this state, $\psi_4 = 0.72$, equals that in a liquidlike state simulated in the smaller pore [Fig. 1(e)]. The lateral diffusion coefficient of $7.8 \times 10^{-3} \sigma_0^2 / \epsilon M^{1.5} (4.9 \times 10^{-10} \text{m}^2/\text{s})$, estimated in a MD simulation, is characteristic to a liquid. In liquidlike states, both the orientational correlation function $G_4(r)$ (Fig. 9) and the translational correlation function $g(r)$ (Fig. 10) decay exponentially. An exponential decay of $G_4(r)$ is clearly seen for liquidlike states at $kT/\epsilon_{ff}=0.8$ in $2.4\sigma_{ff}$ pore [Fig. 9(a)] and at $kT/\epsilon_{ff}=1.25$ in $2.5\sigma_{ff}$ pore [Fig. 9(b)].

As the temperature decreases, the asymptotic behavior of the orientational correlation function $G_4(r)$ changes drastically. The development of the quasi-long-range orientational order occurs within a narrow range of temperatures: from $kT/\epsilon=0.80$ to $kT/\epsilon=0.73$ in $2.4\sigma_{ff}$ pore and from $kT/\epsilon=1.2$ to $kT/\epsilon=1.15$ in $2.5\sigma_{ff}$ pore. A transition from exponential to algebraic decay is clearly seen for $2.5\sigma_{ff}$ pore [Fig. 9(b)]. The translational correlation function $g(r)$ does not show any translational ordering [Fig. 10(a)]. The orientational ordering is accompanied by a sharp decrease of fluid mobility. At $kT/\epsilon_{ff}=0.73$, the lateral diffusion coefficient in a $2.4\sigma_{ff}$ pore was estimated as $4.5 \times 10^{-4} \sigma_0^2 / \epsilon M^{0.5} (2.9 \times 10^{-11} \text{m}^2/\text{s})$, which is by an order of magnitude lower than that at $kT/\epsilon_{ff}=0.762$.

Thus, we conclude that we observe the formation of a quadratic phase with an algebraic decay of the four-fold orientational ordering. However, a notable fluid mobility prevents us from considering the phase state as a solid. Solidification of the quadratic phase occurs at lower temperatures. Although the steps on the temperature dependences of the density and the local orientational order parameter are quite pronounced, we cannot make a definitive conclusion about the type of the liquid-to-quadratic transition we observed.

We should emphasize the drastic difference at the temperature of the liquid-to-quadratic transition in two pores, caused by a little change in pore width. The fact that the liquid-to-quadratic transition occurred at a lower temperature in a narrower pore also confirms a nonmonotonic dependence of the freezing temperature on the pore width.

2. Formation of a quasi-crystalline phase

After the liquid-to-quadratic transition, we observed a continuous freezing transition without any appreciable stepwise alteration of density. The densities and the four-fold local orientational order parameters increase gradually (Fig.
The progressive development of the long-range orientational order is seen on the orientational correlation function $G_4(r)$ (Fig. 9). In 2.4$\sigma_g$ pore, $G_4(r)$ exhibits a prominent algebraic decay at $kT/\epsilon_{hi}=0.55$. The fluid mobility in this state is not notable within 1 ns MD simulation runs. At $kT/\epsilon_{hi}=0.5$, the type of the orientation correlation function changes. $G_4(r)$ asymptotically approaches a nonzero constant of about 0.45 showing the development of the long-range orientational order (Fig. 9). At the same time, the inlayer RDF demonstrates the development of a quasi-long-range translational order [Fig. 10(a)]. The RDF oscillations span over the whole system. The snapshot at $kT/\epsilon_{hi}=0.5$ resembles an orthorhombic solid that consists of two “patches” with different orientations of the symmetry axis.

FIG. 7. Freezing in pores. (a) Temperature dependence of density in large simulation cells in 2.4$\sigma_g$, and 2.5$\sigma_g$ pores; (b) temperature dependence of the four-fold orientational and six-fold local order parameter in pores. The step-wise alteration of density indicates the liquid-to-hexatic transition.

FIG. 8. Freezing in 2.4$\sigma_g$ pore. Configuration snapshots of the liquidlike state at $kT/\epsilon_{hi}=0.762$ (a) and the patch-wise 2O solid at $kT/\epsilon_{hi}=0.5$ (b).
each of which looks like a 2D crystalline phase [Fig. 8(b)]. The longitudinal density profiles in a liquidlike state at $kT/\epsilon_{ff} = 0.762$ and in a solid state at $kT/\epsilon_{ff} = 0.5$ are given in Fig. 10(b). A similar development of the quasi-crystalline order is seen on a sequence of the orientational correlation functions $G_4(r)$ in 2.5$\sigma_{ff}$ pore [Fig. 9(b)].

3. Development of the orientational order in the course of freezing

It is difficult to quantify the structures observed at the intermediate temperatures between the liquid-to-quadratic transition and the formation of a quasi-crystal. It appears that in the course of freezing, after the liquid-to-quadratic transition has occurred, the fluid passes through high-density jammed structures with vanishing mobility. The progressive development of the orientational order is associated with the gradual densification and immobilization of particles. However, despite an abundance of structural information, we cannot quantify the phase state of these jammed structures.

Simulations in the larger cell revealed that upon cooling, liquidlike states exhibit a prominent orientational order resembling corresponding solid phases. In liquid bi-layers, which freeze into orthorhombic solids, the local four-fold ordering is pronounced even at high temperatures, $\phi_4$ is substantially larger than $\phi_6$ [Fig. 7(b)]. The progressive development of the four-fold orientational order is clearly seen with the three-body correlation functions (Fig. 11). The four peaks on the three-body correlation function depict the four neighbors of a given central molecule. The graphs in Fig. 11 show the evolutions of the local order in a bi-layer in 2.4$\sigma_{ff}$ pore starting from a liquidlike state at $kT/\epsilon_{ff} = 0.762$, to quadratic phases at $kT/\epsilon_{ff} = 0.7$ and 0.63 to a quasi-critical at at $kT/\epsilon_{ff} = 0.5$.

IV. CONCLUSIONS

We have explored confinement-induced transitions between liquid, hexagonal, and orthorhombic phases formed by LJ fluid condensed in narrow carbon pores, which accommodate from one to three layers of condensed fluid. The translational and orientational orders were characterized by the local orientational order parameters, in-plane layer-to-layer radial correlation functions, orientational correlation functions, and three-body correlation functions. Fluid mobility was estimated by up to 6 ns MD simulations. MC simulations were performed in the cells with two lateral dimensions, 14$\times$16$\sigma_{ff}$ and 30$\times$30$\sigma_{ff}$; the pore separation varied from 2 to 4.4$\sigma_{ff}$. The longest run involved ca. $9\times10^8$ MC steps. The largest system considered contained about 2500 fluid molecules. The use of a combination of order parameters and correlation functions allowed us to demonstrate several mechanisms of freezing/melting and structure formation in confined bi-layers, which have not been reported earlier.
MC and MD simulations of a model system mimicking nitrogen condensed in slit-shaped carbon pores confirmed a classical hierarchy of ordered frozen structures depending on the pore width: monolayer hexagonal 1H in 2.0–2.3σff pores, bi-layer orthorhombic 2O in 2.4–2.6σff pores, bi-layer hexagonal 2H in 2.8–3.3σff pores, tri-layer orthorhombic 3O in 3.4–3.6σff pores, tri-layer hexagonal 3H in 3.6–4.0σff pores. Almost ideally ordered structures were generated by quenching condensate to the low temperature of \( kT/\epsilon_{ff} = 0.16 \). At the normal boiling temperature (\( kT/\epsilon_{ff} = 0.762 \)), we found somewhat defective yet prominently ordered phases of the same type. In pores wider than 4.2σff, the condensate is liquidlike with 1H or hexatic contact layers. Interestingly enough, the transition from the 2H to the 3O phase occurs through a 2σ1H structure with two uncoupled 1H contact layers.

We have not obtained bi-layer rhombic and maze-type structures reported earlier for hard spheres and Marcus–Rice particles. It is possible that the strong attractive fluid–fluid and solid–fluid interactions prevented the condensate from forming those structures. We did not observe also a buckled phase in the intermediate regime between 1H and 2O recently reported by Ghatak and Ayappa. The buckled phase was found at the temperature of the bulk liquid–solid equilibrium. Our simulations were performed at the temperature of the bulk vapor–liquid equilibrium, which is significantly higher.

We found that the freezing temperature is a nonuniform function of the pore width. The 2O phase in 2.5–2.6σff pores freezes at lower temperatures than the 1H phase in 2.0–2.3σff pores and the 2H phase in 2.8–3.0σff. At the conditions of bulk vapor–liquid equilibrium, the transition from 1H to 2O occurs through the formation of disordered liquidlike and quasi-long-range four-fold ordered bi-layers. The latter structure with four-fold orientational order can be referred to as a “quadratic”, in analogy to the “hexatic” phase with quasi-long-range six-fold orientational order.

MC simulations performed in the range of temperatures from \( kT/\epsilon_{ff} = 1.3 \) to \( kT/\epsilon_{ff} = 0.5 \) show that freezing of liquid-like bi-layers may lead to high-density jammed structures in which a four-fold symmetry develops progressively. Therewith, orientational correlation functions evolve from exponentially decaying to algebraically decaying to asymptotically approaching a well-defined constant. This hierarchy of orientational correlation functions can be formally treated as a transition of the KTNHY type from a disordered liquidlike phase to a quadratic phase with a quasi-long-range orientational order followed by a continuous transformation to a 2O quasi-crystal. The development of the four-fold orientational ordering at decreasing temperatures was displayed also with three-body correlation functions. In simulations in 2.4 and 2.5σff pores, the liquid-to-quadratic transition was characterized by step-wise densification, a sharp increase of the local orientational order parameter, and a significant reduction of fluid mobility. However, more work is needed to make definitive conclusions about the nature of the liquid-to-quadratic transition and the phase state of the quadratic structures we have observed.

The conclusion that nitrogen at its normal boiling temperature may be frozen in some ultramicropores of less than 1 nm in diameter calls for reconsideration of conventional protocols of the pore size characterization routine based on nitrogen sorption. Indeed, it is well documented in adsorption literature that the smallest ultramicropores in carbons and carbon fibers of a low degree of activation are not accessible for nitrogen due to diffusion limitations. Freezing...
leads to the loss of mobility in two groups of pores, the most narrow slits of internal width around 0.4 nm, which can accommodate just a monolayer, and the pores of 0.6–0.8 nm, which accommodate bi- and tri-layers. Therewith, condensate in intermediate ultramicropores of ca. 0.5 nm and supermicropores wider than ca. 0.9–1.0 nm remains liquidlike. This implies that in an ultramicroporous carbon with a polydisperse pore size distribution, an effective diffusion coefficient must depend not only upon the pore size distribution but also on the spatial correlations between different groups of pores. The problem of fluid transport in such a system should be considered as a percolation problem in a system of permeable (liquidlike) and impermeable (frozen) regions.

Finally, it worth noting that from a methodological standpoint that a LJ fluid confined between solid surfaces represents a case study system for the investigation of a molecular structure of confined liquids and solids, freezing, structure formation and ordering in nanophases and colloids by using the machinery of translational, and orientational correlation functions and order parameters.

APPENDIX: INFLUENCE OF THE SUBSTRATE MORPHOLOGY ON THE LAYER STRUCTURE

1. Adsorbate–substrate correlations

Since the lattice parameter of graphite is substantially smaller than the diameter of the typical adsorbate molecule, such as nitrogen or methane, the influence of the graphite structure on the conditions of freezing and melting transitions and the crystalline lattice of the adsorbate is expected to be insufficient.\textsuperscript{16,17} Using in-plane solid–fluid RDF, we checked the possible correlations between the graphite and frozen fluid lattices. The solid–fluid RDFs are similar to the interlayer fluid–fluid RDF [Eq. (3)], if we treat the outer layer of carbon atoms in the same way as a layer of fluid molecules. Examples of the solid–fluid correlation functions obtained are presented in Fig. 12. As expected, for two infinite incommensurate 2D solid lattices, there is no correlation and $g_{sf}(r) = 1$. In this simulation, the size of the basic cell in any lateral direction imposed a common periodicity for both solid structures. This is a typical problem in simulations. The translational motion of the fluid layer over the substrate is alone sufficient to bring $g_{sf}(r)$ to 1, but in our simulations the adsorbate and graphite lattices are visibly correlated, as shown in Fig. 12. The most pronounced correlations were found in the pores with larger packing densities. For example, 2.8$\sigma_{fl}$ pore is the narrowest where 2H structure is formed from a 2O lattice; hence, the layers are tightly packed. This system has one of the strongest solid–fluid lateral correlations. On the contrary, the 1H structure in 2.0$\sigma_{fl}$ pore is “loose;” it has smaller correlations (Fig. 12). Thus, even an adsorbent with a smooth surface such as graphite may artificially influence the fluid structure and mobility in a small model system. This influence will become stronger, if the substrate is rougher or its lattice has irregularities or defects. For example, unexpectedly low diffusion coefficients observed in carbon pores with rough walls,\textsuperscript{34} where the adsorbed layers were tightly packed, is possibly an artifact of a small simulation cell, which induced a lateral periodicity in the fluid.

FIG. 12. Adsorbate–substrate correlations between the graphite atoms and the contact adsorbed layer for selected pores at $kT/\varepsilon_{fl} = 0.762$.

FIG. 13. The influence of the system size and the substrate structure on the adsorbate structure. Local density profile (a), radial distribution function (b), and orientation correlation function $G_4(r)$ in 2.6$\sigma_{fl}$ pore (c) obtained in the smaller cell with structured graphite walls and in the larger cell with uniform 10–4–3 walls.
2. Comparison of simulations with crystalline and structureless walls

In the smaller cell with crystalline walls, the fluid freezes into a 2H phase in the 2.8σ_hℓ phase, and into a 2O phase in 2.6σ_hℓ pore (Fig. 5). A comparison of the structural characteristics in the smaller and larger simulation cells at the same conditions shows that the crystalline structure in the larger cells is more pronounced (Fig. 13). The peaks on the density profiles in the larger cell are narrower and higher (because the crystalline structure of graphite implies some energetic heterogeneity), the RDF peaks are more distinctive [Fig. 13(b)], and the asymptote of the orientational correlation functions is higher, as the incommensurate structure of graphite and periodic boundary conditions caused some distortions in the fluid crystalline lattice [Fig. 13(c)].

For graphite pores, the surface crystalline structure has a minor effect on the structure of confined LJ fluid and the symmetry of frozen phases that agrees with earlier studies. However, for pores between crystalline walls of a square lattice symmetry, Patrykiejew et al. found that a strongly corrugated surface potential significantly affects the incommensurate (square) and incommensurate (triangular) layered structures. The authors employed canonical ensemble MC simulations with a given surface fluid density. Depending on the pore width, they identified seven different structures of alternating, commensurate and incommensurate symmetries.