Do liquids exhibit local fivefold symmetry at interfaces?

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We calculate the layer-resolved local fivefold symmetry of liquids near interfaces using computer simulation of hard sphere fluids on structured substrates. In the first few adjacent liquid layers, the presence of a surface suppresses local icosahedral packing while the magnitude of local fivefold symmetry in the next layers depends on details of the particle-substrate interaction. For a strong particle-substrate attraction, the local fivefold symmetry in these layers is higher than in the bulk liquid.

It is an old fascinating question whether a bulk liquid prefers configurations which favor a local surrounding with fivefold symmetry corresponding, e.g., to icosahedral or dodecahedral clusters; for a review, see Refs. [1,2]. The first clue for such a fivefold symmetry comes from the fact that simple liquids can be considerably supercooled such that the local liquid structure should be different from any bulk crystal structure. Computer simulations of hard spheres [3,4] and other simple one-component systems such as Lennard-Jones liquids [5,6] have revealed that a significant fivefold symmetry as manifested by a characteristic bond orientational correlation [5] is only present in strongly supercooled (i.e., metastable) liquids and glasses. These findings were confirmed by confocal microscopy studies on hard-sphere colloids [7]. This does not exclude, however, that for more realistic interactions stable liquids exhibit pronounced fivefold symmetry. A direct experimental detection of bulk liquid fivefold symmetry, however, is not straightforward as in typical scattering experiments an orientational average is performed. This problem has been revitalized in recent evanescent x-ray scattering experiments on liquid lead near a silicon surface by Reichert *et al.* [8]. A fivefold symmetry in the azimuthal distribution of the liquid scattering was detected indicative of fivefold symmetry. Though the experimental method of surface scattering is sensitive only for the first few adjacent liquid layers, the authors of Ref. [8] argue that this is a hint for bulk fivefold symmetry as the silicon-lead interaction is small as compared to the lead-lead interaction.

In the present paper, we address the general question of how liquid fivefold symmetry is affected by the presence of interfaces. In principle, a surface forces the liquid to inhomogeneous layering [9] and one may ask how this layering effect changes the fivefold symmetry with respect to the bulk liquid. In order to clarify this question, we use computer simulations of hard sphere systems near structured substrates. There are two main reasons to do so: first, in a simulation the particle configuration is available directly in real space so that one can directly probe distance resolved bond-orientational correlations near interfaces. Second, in computer simulation studies one can easily vary the substrate-particle interaction in order to explore the sensitivity of local fivefold symmetry with respect to details of this interaction. We have taken a hard sphere fluid since this is a relatively simple system whose bulk properties are characterized by a

single thermodynamic parameter (namely its bulk packing fraction η) and the bulk fivefold symmetry in hard sphere fluids and glasses is well understood from previous studies [3,4,7]. Furthermore, hard sphere interactions are realized in sterically stabilized colloidal suspensions [7,10].

Our target questions are as follows: How is the fivefold symmetry in bulk liquids changed near a surface? Is it possible by a tailored substrate-particle interaction to systematically increase or decrease the local fivefold symmetry? How can the threshold to surface-induced crystallization be avoided? In order to answer these questions, we have performed extensive Monte Carlo computer simulations for equilibrated hard sphere fluids near patterned substrates. The substrate-particle interaction is modeled to involve a hard structured surface (topographical part) and an additional attraction (energetical part). We have varied both the topographical part by considering different patterns and the energetical part by changing the strength of the attraction. Our simulation results give evidence for the following answers to the questions raised above: The substrate affects the local fivefold symmetry directly but it has a significant effect only in the first few layers. Although the next layers are structured perpendicular to the surface, their fivefold symmetry is similar to that of a bulk system provided the bulk density corresponds to the local density of the liquid layers. This finding supports the interpretation of the recent scattering experiments [8]. The topographical pattern strongly controls surface-induced crystallization. Only if the lattice mismatch with respect to a possible bulk crystal is large, is surface-induced crystallization is prevented [11,12]. The energetic part, on the other hand, controls the local density in the adjacent liquid layers and thus affects the magnitude of the fivefold symmetry directly. If there is a strong attraction the local density is enhanced such that the local fivefold symmetry can be much larger than that of the bulk liquid.

In our simulation [11,12] N hard spheres ($N \approx 8500$) with diameter σ at temperature T are in a rectangular box of size $V = L_x L_y L_z$ with periodic boundary conditions in x and y directions. Two patterned walls at distance L_z confine the system in the z direction. The number density of the spheres $\rho = N/V$ can conveniently be expressed in terms of the dimensionless packing fraction $\eta = \pi \rho \sigma^3/6$. For excluded volume interactions, temperature only sets the energy scale $k_B T$ (k_B denoting Boltzmann's constant) but does not affect phase transitions. The bulk hard sphere systems exhibits a freezing
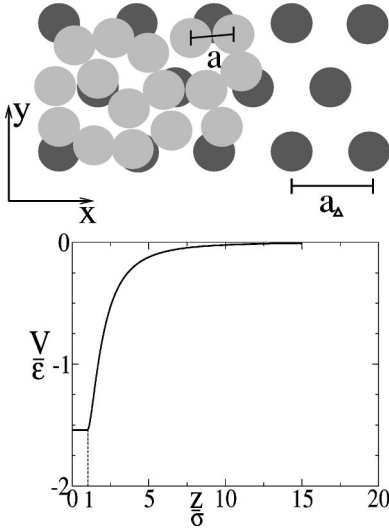
FIG. 1. Top: geometry of the system: A surface with a triangular surface pattern (dark gray spheres) with lattice spacing $a_\triangle \approx 1.37\sigma$ induces sixfold symmetry in the hard sphere fluid (light gray spheres) with mean particle distance $a = 1.07\sigma$. Bottom: the attractive potential of Eq. (1).

transition with volume fractions $\eta_f = 0.494$ and $\eta_s = 0.545$ of the coexisting fluid and solid [4].

The substrate pattern consists of hard spheres with the same diameter σ as the mobile ones. These spheres are fixed in a plane on a two-dimensional triangular lattice of lattice constant $a_\triangle$ at $z = 0$, see Fig. 1 (top). Additionally, we apply an attractive external potential

$$
V(z) =
\begin{cases}
-\dfrac{8}{3\sqrt{3}}\epsilon & \text{if} \quad z < \sigma \\[2ex]
4\epsilon\left[\left(\dfrac{l_0}{z - z_0}\right)^9 - \left(\dfrac{l_0}{z - z_0}\right)^3\right] & \text{otherwise}
\end{cases}
\tag{1}
$$

as shown in Fig. 1 (bottom). ϵ is the strength of the attraction and l_0 sets its range. We choose $l_0 = 2\sigma$. A virtual divergence is placed at $z = z_0 = -3^{1/6}l_0 + \sigma \approx -1.4\sigma$. Note that the external force $-dV/dz$ is continuous at $z = \sigma$.

Crystallization as well as formation of a fivefold symmetry are detected with bond orientational order parameters which are resolved in the z direction and are discretized into different layers. A particle belongs to the kth layer if its z coordinate is within $(k-1)a_z < z < ka_z$ where $a_z = 0.9\sigma$ is an average lattice spacing. The mean position of the kth layer is therefore located at $z_k = (k - 1/2)a_z$. Crystalline order is detected using the set of order parameters $\Psi^{(n)}(z_k)$ [12], which measure the bond orientational order in the kth layer. They are defined as

$$
\Psi^{(n)}(z_k) = \left\langle \left| \frac{1}{N_k} \sum_{l=1}^{N_k} \sum_{j=1}^{N_l} e^{ni\theta_{lj}} \right| \right\rangle
\tag{2}
$$

and probe n-fold symmetry. θ_{lj} is the angle between the separation vector of the particles l and j and the x axis. The sum over l includes all N_k particles of the kth layer. The sum

over j is taken over the N_l neighbors of particle l which are also in the kth layer. For simulation purposes particles are defined as neighbors if the distance between particle l and j is less than $1.35\cdots1.40\sigma$. This somewhat arbitrary definition for neighbors can be used as the resulting $\Psi^{(n)}$ only weakly depend on the exact definition of a neighbor distance. For a crystalline layer the order parameters $\Psi^{(n)} \to 1$ and for a fluid layer we obtain $\Psi^{(n)} \to 0$. Finally, in Eq. (2), $\langle \cdots \rangle$ denotes a canonical average.

Fivefold symmetry in a layer parallel to the surface is detected using the layer resolved $\hat{W}_6$ order parameter [1]. According to Refs. [5,13–15] we can define this order parameter by assigning a set of numbers $Q_{\ell m}(lj) = Y_{\ell m}t(\theta_{lj}, \varphi_{lj})$ to every bond between neighboring particles l and j, where neighboring particles are defined as described above. Here, $Y_{\ell m}(\theta, \varphi)$ are the spherical harmonics and θ_{lj} and φ_{lj} are the polar angles of the bond between particles l and j with respect to an arbitrary reference axis. $Q_{\ell m}(lj)$ defines a local order parameter which has to be averaged in the kth layer to obtain the global order parameter as

$$
\bar{Q}_{\ell m}(z_k) = \frac{1}{N_k} \sum_{l=1}^{N_k} \sum_{j=1}^{N_l} Q_{\ell m}(lj),
\tag{3}
$$

where the sum over l is defined as in Eq. (2). However, the sum over j now includes all neighbors even those of neighboring layers. We note that we do not count the fixed surface particles. Therefore the first layer obviously has a smaller average number of neighbors.

The order parameter $\bar{Q}_{\ell m}(z_k)$ is still dependent on the choice of the reference axis but we can obtain an invariant by considering the second order combination

$$
Q_\ell(z_k) = \left(\frac{4\pi}{2\ell + 1} \sum_{m=-\ell}^{\ell} |\bar{Q}_{\ell m}(z_k)|^2 \right)^{1/2}
\tag{4}
$$

and the third order invariant

$$
W_\ell(z_k) = \sum \begin{pmatrix} \ell & \ell & \ell \\ m_1 & m_2 & m_3 \end{pmatrix} \bar{Q}_{\ell m_1} \bar{Q}_{\ell m_2} \bar{Q}_{\ell m_3},
\tag{5}
$$

where the sum goes over all m_1, m_2, and m_3 with $m_1 + m_2 + m_3 = 0$ and

$$
\begin{pmatrix} \ell & \ell & \ell \\ m_1 & m_2 & m_3 \end{pmatrix}
\tag{6}
$$

are the Wigner $3j$ symbols [16]. A particularly good measure [5] for different orientational symmetries can be obtained by the further invariant

$$
\hat{W}_\ell(z_k) = \frac{W_\ell(z_k)}{\left(\sum_{(m=-\ell)}^{\ell} |\bar{Q}_{\ell m}(z_k)|^2\right)^{3/2}}.
\tag{7}
$$

The order parameters from Eqs. (4) and (7) detect various three-dimensional (3D) crystalline symmetries [5]. Fivefold
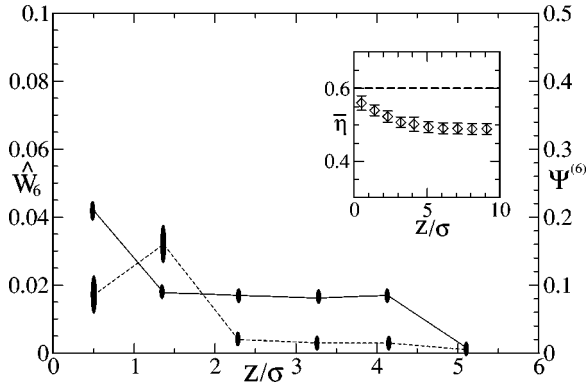
FIG. 2. The order parameter $\hat{W}_6$ (dashed line) and $\Psi^{(6)}$ (solid line) are shown vs the separation z from the surface for a nonattractive structured surface ($\epsilon = 0$). The symbols are simulation data with their size indicating the statistical error. The inset shows the layer-resolved mean local density $\bar{\eta}(z_k)$.

symmetry is most clearly indicated by the $\hat{W}_6$ parameter from Eq. (7); see Ref. [5]. The authors of Ref. [1] have defined that values of $|\hat{W}_6| > 0.045$ show fivefold symmetry and values $|\hat{W}_6| < 0.02$ are an indication for crystalline order if other crystalline order parameters pick up a crystalline structure. $|\hat{W}_6| \rightarrow 0$ is characteristic for a fluid system without preferred symmetry. In the following, we will use $\hat{W}_6$ from Eq. (7) to analyze the inhomogeneous fluid for fivefold order near the surface.

It is important that the geometry of the surface pattern is chosen such that prefreezing is prevented [12,17]. Therefore we choose an extremely unfavorable surface pattern for the system. Using $a_\triangle \approx 1.37\sigma$ makes it entropically very unfavorable to adapt the surface structure. The system can then react in two ways: It either adapts the bulk crystalline structure and reacts with lattice defects to compensate the mismatch between bulk and surface lattice or it stays in the inhomogeneous fluid state. In fact, by varying the wall-particle interaction, we found that both possibilities are realized. In contrast, for the parameter range investigated and at high fluid densities, we never observed an adsorbed solid layer which picks up the substrate lattice.

First, we analyzed a system without attractive surface ($\epsilon = 0$). Results are depicted in Fig. 2. The fluid bulk density is $\eta = 0.49$. Close to the surface the sixfold symmetry $\Psi^{(6)}$ is slightly increased due to the influence of the surface. This low sixfold symmetry comprises the first four layers. $\hat{W}_6$, on the other hand, increases from the first to the second layer and reaches a value which does not exceed 0.03 and is therefore not indicative of fivefold symmetry. For large z, $\hat{W}_6$ decays to the bulk fluid value close to zero. The inset of Fig. 2 shows the layer averaged mean local density $\bar{\eta}(z_k)$. Close to the surface it is raised but it decays away from the surface in strong correlation with the $\Psi^{(6)}$ order parameter. Hence for the nonattractive surface no significant fivefold symmetry can be found. The increase of $\hat{W}_6$ from the first to the second layer may have important consequences for heterogeneous crystal nucleation: One can expect that crystal nucleation
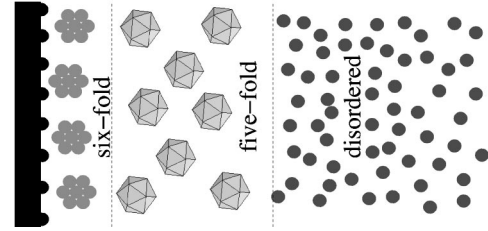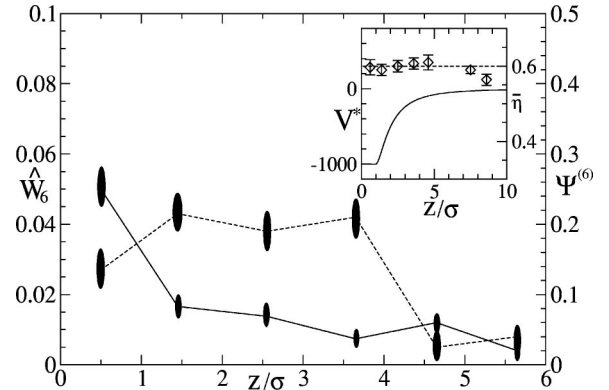

FIG. 3. Top: same as Fig. 2 but for $\epsilon = 650 k_B T$. The inset shows the external potential $V^*(z) = V(z)/k_B T$ and the symbols represent the mean local density $\bar{\eta}(z_k)$. Bottom: sketch of the transition from sixfold symmetry to fivefold symmetry to the disordered bulk fluid.

starts where $\hat{W}_6$ is small and $\Psi^{(6)}$ is large which is realized close to the surface. The surface may thus serve as a heterogeneous nucleation center.

Increasing the attractive potential of the surface enhances the local density of the fluid at the surface. The system was observed to stay in the inhomogeneous fluid state. We note, however, that it is very difficult to decide when equilibration of a system at these high densities is achieved. Figure 3 depicts results for a system with a strong attractive potential of $\epsilon = 650 k_B T$ which raised the local density close to the surface up to $\eta = 0.6$, see the inset of Fig. 3 [17]. Close to the surface the attractive wall enforces a sixfold surface symmetry in the fluid as can be seen by a raised $\Psi^{(6)}$ order parameter. However, a few layers away from the surface a clearly visible increase in the $\hat{W}_6$ order parameter indicating a certain degree of fivefold symmetry in the system shows up. For larger z the density gets lower and the fivefold symmetry is lost in favor of the completely unordered bulk fluid.

For a hard sphere *bulk* system the authors of Ref. [7] reported similar findings: A fluid hard sphere system of bulk density less than $\eta \approx 0.6$ does not exhibit fivefold symmetry. On approaching the density of $\eta = 0.6$ the system begins to exhibit an increased order parameter $\hat{W}_6$ indicative of fivefold symmetry. For the bulk system, however, a fluid at this high density is not thermodynamically stable and these studies are done, e.g., at snapshots of random-closed-packed models. Our findings correspond to them in a way that fivefold symmetry occurs when the *local* density is high enough and the system is still in a noncrystalline state. We achieved the increased density by an attractive surface but kept the bulk density always at fluid densities, i.e., $\eta < \eta_f = 0.494$.
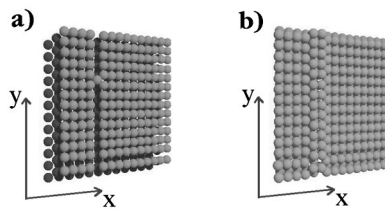
FIG. 4. First and second layer of a crystalline sheet adjacent to a square surface pattern incommensurate with the bulk crystal. The formation of line defects can be seen in these simulation snapshots ($\epsilon > 1000 k_B T$, $\eta = 0.49$).

The mean density shown in inset of Fig. 3 exhibits clearly a correlation to the actual data of $\hat{W}_6$. The qualitative behavior of the fluid symmetry as a function of z is also sketched in the bottom part of Fig. 3: Near the wall there is sixfold symmetry which is then changed to fivefold symmetry as indicated by the icosahedra until the disordered bulk fluid with practically no symmetry is reached.

For a square surface pattern [12] with a lattice constant $a_\square = 1.37\sigma$ and an increased attraction of $\epsilon > 1000 k_B T$, we observed prefreezing into several layers of a square lattice on top of the substrate pattern together with line defects which compensate a mismatch of the bulk and substrate lattice constants. For a snapshot of the computer simulation, see Fig. 4. These lattice defects are reminiscent of commensurate/incommensurate transitions as found, e.g., in Ref. [18].

In conclusion, a hard sphere system does not exhibit fivefold symmetry at local densities which are smaller than the freezing packing fraction η_f. However, raising the fluid density locally increases the bond orientational order parameters to values indicating fivefold symmetry. One way to achieve this is by offering an attractive surface to the system. Strong enough attraction increases the local density and fivefold symmetry emerges. This local density enhancement, however, is in thermodynamic competition with surface freezing. Details of the crossover to surface freezing should be investigated more systematically by theory, computer simulation, and experiment. For outlook we remark that it would be very useful to classify the classes of clusters occurring in the fivefold symmetric fluid. Also an investigation of lattice defects which are induced by the incommensurate surface would be of great interest.

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