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Citation: The Journal of Chemical Physics 143, 054504 (2015); doi: 10.1063/1.4927710
View online: http://dx.doi.org/10.1063/1.4927710
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Examination of the phase transition behavior of nano-confined fluids by statistical temperature molecular dynamics

Lili Gai,1,2 Christopher R. Iacovella,1,2 Li Wan,1,2 Clare McCabe,1,2,3 and Peter T. Cummings1,2

1Department of Chemical and Biomolecular Engineering, Vanderbilt University, Nashville, Tennessee 37235, USA
2Multiscale Modeling and Simulation (MuMS), Vanderbilt University, Nashville, Tennessee 37235, USA
3Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235, USA

(Received 4 April 2015; accepted 22 July 2015; published online 4 August 2015)

The fluid-solid phase transition behavior of nano-confined Lennard-Jones fluids as a function of temperature and degree of nanoconfinement has been studied via statistical temperature molecular dynamics (STMD). The STMD method allows the direct calculation of the density of states and thus the heat capacity with high efficiency. The fluids are simulated between parallel solid surfaces with varying pore sizes, wall-fluid interaction energies, and registry of the walls. The fluid-solid phase transition behavior has been characterized through determination of the heat capacity. The results show that for pores of ideal-spacing, the order-disorder transition temperature ($T_{ODT}$) is reduced as the pore size increases until values consistent with that seen in a bulk system. Also, as the interaction between the wall and fluid is reduced, $T_{ODT}$ is reduced due to weak constraints from the wall. However, for non-ideal spacing pores, quite different behavior is obtained, e.g., generally $T_{ODT}$ are largely reduced, and $T_{ODT}$ is decreased as the wall constraint becomes larger. For unaligned walls (i.e., whose lattices are not in registry), the fluid-solid transition is also detected as $T$ is reduced, indicating non-ideality in orientation of the walls does not impact the formation of a solid, but results in a small change in $T_{ODT}$ compared to the perfectly aligned systems. The STMD method is demonstrated to be a robust way for probing the phase transitions of nanoconfined fluids systematically, enabling the future examination of the phase transition behavior of more complex fluids. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4927710]

I. INTRODUCTION

Fluids confined by solid surfaces with separation distances on the order of a few molecular diameters are of great importance in industrial applications, including lubrication and separation processes, as well as emerging areas such as ionic liquid-based supercapacitors.1–4 When molecules are confined within such narrow pores, their phase behavior can be dramatically different from that of the bulk fluid.5,6 Such confinement-driven phase changes can be attributed to a combination of the effects of the fluid–wall interaction2,6 and spatial constraint of the pores.7 This phenomena has been widely examined experimentally,8–15 with strong evidence of confinement induced solidification, e.g., the observation of a several orders of magnitude increase in viscosity as a function of reduced pore separation.9,12,13,15 However, other studies have posited that systems undergo a constant vitrification as separation is reduced,10,16,17 resulting in a long standing debate within the community.2 Currently, there is no agreement as to the nature of the transition, in large part due to the intrinsic difficulties faced in experiment, i.e., it has not yet been possible to directly observe the structure within the pores. Such ambiguities and debate are only likely to increase as more complex fluids, such as ionic liquids,6,18–22 are now routinely being studied under nanoscale confinement and whose properties are strongly influenced by the size and nature of said confinement.

Molecular simulations, which allow structure to be clearly resolved within the pore, have been performed to study the behavior of fluids under nanoconfinement,2,6,19,23–12 with both coarse-grained and atomistically detailed models of the fluids and surfaces used. These studies have led to an important understanding of fluid behavior under confinement, and specifically the importance of the wall-fluid interactions,23 as dictated by the partial charges on the atoms when considering atomistically detailed models.2,29 However, most simulation studies have focused on highly idealized systems which may not be typical of experiment, e.g., ideal pore spacing and pore wall registry, and thus it is unclear as to what role non-ideality plays in the phase transitions. Furthermore, much like the experimental studies, there is some debate as to the nature of the simulated transition.25,33,34

Ultimately, most simulations still suffer from the fact that only short time scales, relative to experiment, can be captured; thus to offer a robust understanding of the nature of the phase transition, detailed and explicit calculations based on the underlying free energies are necessary.3 In early work, Gubbins and coworkers35 performed grand-canonical Monte Carlo simulations with umbrella sampling on the Lennard-Jones (LJ) fluid confined between structure-less walls. They calculated the relative free energy differences between the liquid and solid phases under fixed confinement for systems with both weak and strong attractive wall-fluid interactions. Two
transitions were observed corresponding to pre-crystallization (the layers near the walls freeze first while the rest of the system remains fluid-like) and another transition associated with full solid formation (all the layers are frozen). However, we note this approach relies on the definition of a suitable order parameter for umbrella sampling, which may be non-trivial for complex systems and the wrong choice of order parameter could result in failure to capture important behaviors in the system. In another early work, Dominguez et al. examined the free energy of the solid and fluid phases of confined LJ particles by thermodynamic integration in purely repulsive and weakly attractive pores, and provided the phase transition point accordingly. However, the method is not extensible to other cases of moderately or strongly attractive wall-fluid interactions, since it is difficult to find a suitable path of integration that is thermodynamically reversible at these conditions. Additionally, the calculations did not take into account the heterogeneous nature of the systems in cases where the wall-fluid interaction greatly exceeds the fluid-fluid interactions. Recently, Wan et al. examined the phase behavior of a LJ fluid confined by attractive walls modeled by explicit LJ particles using a combination of grand-canonical molecular dynamics (GCMD) simulations and absolute Helmholtz free energy calculations using a modification of the Einstein crystal method, which explicitly takes into account the heterogeneous nature of strongly interacting systems. This work specifically focused on the behavior of systems at both ideal and non-ideal pore separations. It was shown that the general trend was a reduction in the absolute free energy as the pore size was decreased when considering pore sizes that can accommodate an integer number of molecular layers; however, when considering non-integer pore spacings, higher free energies and oscillatory behavior in the free energy was observed. We note that the Einstein crystal method, while providing absolute free energies that allow direct comparison of the free energy of different pore sizes, is only applicable to stable solid states, and cannot be extended for determining the free energy of fluid-like confined states, and thus phase transitions cannot be directly probed.

Statistical temperature molecular dynamics (STMD) is an alternate approach allowing the determination of the density of states, from which the thermodynamic quantities can be calculated, specifically, relative free energy and heat capacity. STMD has been successfully used to study the phase transition behavior of a variety of different systems, including protein folding and the self-assembly of lipids. Unlike umbrella sampling, STMD does not require the definition of an order parameter and unlike the Einstein crystal method, can be used to study both crystalline and non-crystalline states (i.e., it can capture the phase transition). Here, STMD is used to calculate the density of states of nano-confined fluids in order to capture the phase transition from liquid to solid. A simplified Lennard-Jones system was chosen to model the fluid and pore walls, as this allows efficient examination of the various state parameters, including the effects of non-ideality on pore size and registry on the phase transition, which have not been previously examined in detail; this system also serves as a good surrogate for simple fluids such as octamethycyclootetrasiloxane or cyclohexane and also enables direct comparison of the STMD results with the behavior found in prior work using the Einstein crystal method. Here, we examine the temperature-dependent phase transition behavior directly via the calculation of the heat capacity and determine the effect of pore size, pore registry, and the fluid-wall interaction on nature of this phase transition. Although the system studied here is very simple, the results provide considerable insight into phase transition behavior of nano-confined systems under both ideal and non-ideal conditions and provide a framework for implementing the STMD methodology with more complex fluids and surfaces.

II. SIMULATION DETAILS
A. Model
The model nano-confined system employed in this work is similar to that used in Wan et al., where the system is composed of static wall particles arranged in a pore, in contact with a bulk phase of mobile fluid particles. All particles are modeled as LJ spherical particles (see Eq. (1)) of identical size (i.e., \( \sigma = 1 \)), with interactions between mobile fluid particles set as \( \epsilon_{\text{mm}} = 1.0 \) in all simulations,

\[
U(r) = \begin{cases} 
4\varepsilon \left( \frac{\sigma^{12}}{r^{12}} - \frac{\sigma^6}{r^6} \right), & r \leq r_{\text{cut}}, \\
0, & r > r_{\text{cut}}. 
\end{cases}
\]  

Interactions between the walls and mobile particles are varied with values of \( \varepsilon_{\text{wm}} = (1.0,2.0,4.0) \) \( \epsilon_{\text{mm}} \) to probe the impact of wall fluid interaction strength. XPLOR style interaction shifting in HOOMD-Blue is used, which applies a cubic spline to smoothly bring interactions to zero at the cutoff; this ensures that the well depth of the interaction is unchanged regardless of cutoff used. Due to the heterogeneous nature of the system we employ a cutoff of 3.0σ between mobile particles, where XPLOR shifting starts at 2.75σ, and a longer cutoff of 5.0σ between wall-mobile interactions, with XPLOR shifting starting at 4.75σ.

For each system, two identically sized pores are constructed and placed in contact with a bulk system of fluid particles, as shown in Fig. 1. Two pores are used as this provides a means to adjust pore size while keeping the box dimensions consistent between all systems when dealing with non-ideal pore sizes; this also provides a convenient way to alter the registry of the surfaces, by displacing the central region between the pores. System sizes are fixed at 7680 particles, with roughly 25% of the particles existing as part of the pore walls; the number of mobile particles varies slightly as pore size is varied. Wall particles are set in a face-centered cubic (fcc) structure with number density \( \rho_{\text{wall}} = 1.0 \), corresponding to the condition where nearest neighbors sit at the minimum of the LJ well (i.e., nearest neighbor spacing is \( 2^{1/6}/\sigma \)). Walls are oriented to make the “ABC” stacking planes parallel to the pore interface. In all cases, the box size is set at (11.225σ, 33.852σ, 21.996σ), which for an ideal state results in a bulk fluid with number density of 0.85 and confined fluids with number density of 1.0. While anisotropic NPT simulations are typically employed in
GCMD simulations, where the long dimension of the box can fluctuate, this approach cannot be used with STMD as the method is only defined for NVT simulations. However, the system size used is sufficiently large such that the bulk density is not strongly influenced by small fluctuations in pore density. For ideal pore separation, the distance is set to integer multiples of the fcc layer spacing (i.e., one layer $= 2^{1/6} \sqrt{6/9} \sigma$). All simulations were run using the HOOMD-Blue package, extended to include the STMD algorithm, allowing for highly efficient MD simulations on graphical processing units (GPU). For the STMD runs presented in this work, an energy bin size of $\Delta E = 32$ was used with an initial modification factor of $\ln f = 0.00025$. An overview of the STMD method is included in the Appendix.

III. RESULTS AND DISCUSSION

A. Ideal systems with varied fluid-wall interaction strength

The phase transition of nanoconfined fluids is first examined for nanopores that can accommodate integer numbers of fluid layers (i.e., ideal), both to validate the trends observed via STMD and examine the phase transition via heat capacity. Table I lists the temperature range used for various nanopore sizes and wall-fluid interaction strengths; these ranges were chosen such that the phase transition temperature is appropriately captured, as determined by performing preliminary STMD runs and from knowledge of prior simulations. To accelerate the simulations, the entire temperature range was split into two or three separate temperature windows which were merged in postprocessing, as has been done in other work. For example, for the 4 layer systems with $\varepsilon_{wm} = 1.0$, two windows of $T \in [0.65, 1.05]$ and $T \in [0.85, 2.0]$ were used, where the total simulation times for STMD were $8.3 \times 10^5$ and $5 \times 10^8$ MD steps, respectively, for each window to reach a modification factor of $\ln f < 5 \times 10^{-7}$. Examination of the simulation configurations within the overlapping temperature region(s) shows negligible differences when considering the density of confined fluids and the 2D global hexagonal order parameter.

1. Heat capacity analysis

Upon convergence of the STMD simulations, heat capacity, $C_v$, is calculated to provide a robust measure of the phase transitions. First, $C_v$ is compared for varied pore separations with $\varepsilon_{wm} = 4.0$, as shown in Fig. 2. As the size of the confined region is increased, a decrease in the fluid-solid phase transition temperature, $T_{ODT}$, is observed, as indicated by the shift

TABLE I. Overall temperature range for ideal systems studied, with separate temperature windows annotated in brackets when multiple windows are used.

<table>
<thead>
<tr>
<th>Confined layers</th>
<th>Separation (\sigma)</th>
<th>$\varepsilon_{wm} = 1.0$</th>
<th>$\varepsilon_{wm} = 2.0$</th>
<th>$\varepsilon_{wm} = 4.0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>3.67</td>
<td>0.65-2.0 [0.65, 1.05] [0.85, 2.0]</td>
<td>0.65-2.2 [0.65, 1.05] [0.85, 2.2]</td>
<td>0.65-2.8 [0.65, 1.05] [0.85, 2.0] [1.8, 2.8]</td>
</tr>
<tr>
<td>5</td>
<td>4.58</td>
<td>0.65-1.8 [0.65, 1.05] [0.8, 1.8]</td>
<td>0.65-1.85 [0.65, 1.05] [0.85, 1.85]</td>
<td>0.65-2.3 [0.65, 1.05] [0.85, 1.5] [1.3, 2.3]</td>
</tr>
<tr>
<td>6</td>
<td>5.50</td>
<td>0.65-1.65 [0.65,1.65]</td>
<td>0.65-1.65 [0.65,1.65]</td>
<td>0.65-1.8 [0.65,1.8]</td>
</tr>
<tr>
<td>7</td>
<td>6.42</td>
<td>0.65-1.5 [0.65,1.5]</td>
<td>0.65-1.5 [0.65,1.5]</td>
<td>0.65-1.5 [0.65,1.5]</td>
</tr>
<tr>
<td>4.5</td>
<td>4.13</td>
<td>0.6-1.2</td>
<td>0.75-1.35</td>
<td>0.7-1.3</td>
</tr>
<tr>
<td>5.5</td>
<td>5.04</td>
<td>0.75-1.35</td>
<td>0.6-1.2</td>
<td>0.7-1.3</td>
</tr>
<tr>
<td>6.5</td>
<td>5.96</td>
<td>0.6-1.2</td>
<td>0.6-1.2</td>
<td>0.7-1.3</td>
</tr>
<tr>
<td>4, unregistered</td>
<td>3.67</td>
<td>0.85-2.0</td>
<td>0.85-1.85</td>
<td>1.8-2.8</td>
</tr>
</tbody>
</table>
in the peak of the $C_v$ curve; this trend matches that of prior work.\textsuperscript{23,30} It can also be seen that as pore size is increased, $C_v$ attains a sharper and higher peak, more closely resembling the behavior seen for a bulk LJ fluid. This change in the $C_v$ curve shape is related to several factors. First, the interaction between the central-most layer(s) of the pore and wall is reduced as the size of the pore walls is increased. Second, as the pore size increases, the number of particles in the confined region increases, contributing to a larger total change in energy upon crystallization and thus sharper changes in the heat capacity.

For a fixed pore size, the heat capacity at different interactions, $\varepsilon_{wm}$, is compared in Fig. 3. For all the systems, as $\varepsilon_{wm}$ is reduced, a lower $T_{ODT}$ is observed, where the peak(s) in $C_v$ also become sharper and higher. This is in agreement with the above discussion that suggests that the reduced interaction between mobile particles and walls requires a lower temperature to crystallize, and that the overall system behavior becomes more bulk like, as expected,\textsuperscript{23,30,48} validating the use of STMD for nanoconfined fluids.\textsuperscript{23,48} Note that for weaker wall-fluid interactions and larger pores, two peaks are observed, which will be discussed separately below.

Table II provides a summary of the $T_{ODT}$ for all the systems studied, where, in all cases, $T_{ODT}$ is reported as the peak(s) in the $C_v$ curve (if multiple peaks are observed, both values are reported in Table II for consistency). Similar trends are observed as compared to Wan \textit{et al.}\textsuperscript{30} and as predicted by the unifying theory of Gubbins and coworkers,\textsuperscript{27,28,49} in that $T_{ODT}$ increases as pore size is reduced, and large pores demonstrate more bulk like transition temperatures. However, $T_{ODT}$ as determined from STMD using the maximum of the
peaks of the \( C_\nu \) curve, tends to be slightly higher than seen in the simulations performed by Wan et al.,\(^{30}\) with this deviation increasing as pore size increases and wall-fluid strength decreases. This may be related to the use of a smaller system size in this study, but we also note that the values in Wan et al.\(^{30}\) were estimated from order parameters that identified when a crystalline state was achieved in the pore (with resolution of \( \Delta T = 0.1 \)).

Given the gradual nature of the transition indicated by the width of the \( C_\nu \) peaks, the maximum of the peak, while a convenient and consistent way to compare systems, is likely an overestimate of the transition temperature. To better demonstrate the gradual phase transition process, a layer-by-layer global two-dimensional order parameter is calculated and analyzed in conjunction with \( C_\nu \) curves, as discussed below.

### 2. Order parameter (OP) analysis

The 2D global hexagonal OP\(^{46,47}\) is examined as a function of \( T \) for different spatial regions in the pore (i.e., layers parallel to the pore surfaces), and simultaneously compared to the heat capacity. Fig. 4 plots the OP for each specified layer (shown in Fig. 4(a)) for a pore that can hold six ideal layers, as a function of \( T \) at varied \( \varepsilon_{wm} \) (Figs. 4(b)-4(d)). For all interaction strengths, particles in layer 1 (i.e., those particles in contact with the walls) demonstrate a high value of the OP over the entire \( T \) range considered; the changes in the OP are relatively minimal as \( T \) is increased beyond \( T_{ODT} \) (as predicted by the peak(s) in \( C_\nu \) curves), suggesting a highly ordered state persists at the walls even at high \( T \), and as seen in other works (i.e., the pre-crystallization transition seen by Gubbins and coworkers\(^{23}\)). For all systems, layers 2 and 3 demonstrate a more significant drop in the OP value as \( T \) is increased, where the reduction in OP value roughly coincides with the peak(s) in the \( C_\nu \) curves. In all three cases, the OP of layer 3 is reduced to values of \( \sim 0.2 \), while the change in the OP for layer 2 becomes smaller in magnitude as \( \varepsilon_{wm} \) is increased.

Specifically, in Fig. 4(b) for \( \varepsilon_{wm} = 1.0 \), the OP of layer 2 drops to \( \sim 0.2 \), and in Fig. 4(d) for \( \varepsilon_{wm} = 4.0 \) the OP of layer 2 is still large (\( \sim 0.5 \)) at the right end of the \( C_\nu \) peak. That is, layer 2 becomes increasingly ordered as \( \varepsilon_{wm} \) is increased, while layer 3 appears to be mostly independent of \( \varepsilon_{wm} \). As such, the ordering of the central most layer(s), in this case layer 3, is ultimately indicative of the formation of a solid phase in the pore.

The difference in structural ordering between layers 2 and 3 as a function of \( T \) appears to manifest itself in the number of peaks seen in the \( C_\nu \) curves. Specifically, for the system with 6 total layers, systems with weak \( \varepsilon_{wm} \) demonstrate two distinct peaks (Fig. 4(b)), where the peaks steadily reduce in magnitude until only a single peak is seen for the strongest interaction with \( \varepsilon_{wm} = 4.0 \) (Fig. 4(d)). The increased ordering

### Table II. Summary of \( T_{ODT} \) from STMD in this paper with resolution of \( T = 0.001 \), compared to the one from Ref. 30.

<table>
<thead>
<tr>
<th>No. of layers</th>
<th>( \varepsilon_{wm} = 1.0 )</th>
<th>( \varepsilon_{wm} = 2.0 )</th>
<th>( \varepsilon_{wm} = 4.0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( T_{ODT} ) STMD</td>
<td>( T_{ODT} ) STMD</td>
<td>( T_{ODT} ) STMD</td>
</tr>
<tr>
<td>4</td>
<td>1.598</td>
<td>1.4</td>
<td>1.920</td>
</tr>
<tr>
<td>5</td>
<td>1.371</td>
<td>1.1</td>
<td>1.614</td>
</tr>
<tr>
<td>6</td>
<td>1.234/1.302</td>
<td>0.9</td>
<td>1.385/1.429</td>
</tr>
<tr>
<td>7</td>
<td>1.145/1.224</td>
<td>0.8</td>
<td>1.242/1.298</td>
</tr>
</tbody>
</table>

FIG. 4. (a) Simulation snapshot for a system of six ideal layers and order parameter analysis for (b) \( \varepsilon_{wm} = 1.0 \), (c) \( \varepsilon_{wm} = 2.0 \), and (d) \( \varepsilon_{wm} = 4.0 \). Note, OP values are calculated with a resolution of \( T = 0.01 \) to capture the curve of change, but for clarity symbols are shown at only every third value.
in layer 2 at this larger $\varepsilon_{wm}$ results in a less significant change in structure as the system is cooled down, which manifests itself in a more gradual, less sharply peaked $C_v$ behavior. Systems with weaker $\varepsilon_{wm}$ have more significant structural changes, as seen in Fig. 4(b), where both layers 2 and 3 change from mostly disordered to ordered states. Conversely, systems with larger $\varepsilon_{wm}$ demonstrate wider peaks of lower magnitude, since the structural transition primarily occurs on a smaller subset of particles, and most of the particles transitioning are in layer 3, as seen in Fig. 4(d).

As shown previously in Fig. 3, the appearance of one or two peaks is also dependent on pore separation, where larger pores tend to demonstrate two peaks in heat capacity, corresponding with the different ordering behavior in the central most layers (i.e., those layers not in contact with the walls). For example, in Fig. 3(a), $C_v$ is plotted for a system that can contain 7 ideal layers; even $\varepsilon_{wm} = 2.0$ appears to have two peaks, albeit less well defined than for $\varepsilon_{wm} = 1.0$. Comparing to a pore size of 5 ideal layers, only two peaks are observed for $\varepsilon_{wm} = 1.0$, although weakly differentiated; only a single, wide peak is seen for $\varepsilon_{wm} = 2.0$. Further considering an even smaller pore, e.g., 4 ideal layers, only one peak in $C_v$ is seen for all $\varepsilon_{wm}$, due to the fact that there are no particles that would exist in layer 3 (i.e., no particles separated from both walls by two layers of particles) and thus, the system is unable to introduce different ordering behaviors as a function of $T$. Hence, the nature of the phase transition, and whether there are one or two identifiable transitions within the main phase transition (not considering the high temperature pre-crystallization transition), appears to be strongly linked to both the size of the pore and strength of the wall-fluid interaction.

B. Non-ideal pore size

STMD was used to examine systems with non-ideal pore spacing, specifically, those that correspond to 4.5, 5.5, and 6.5 layers, via calculation of the heat capacity, as shown in Fig. 5. Only a single temperature window was used in these STMD calculations (see Table I). Overall, we observe that $T_{ODT}$ is shifted to smaller values than seen for the ideal systems, with the largest shift occurring for systems with strong wall-fluid interaction. This shift appears related to the density within the pore. Specifically, the density of particles within the pores was found to be lower than that for the ideal pores, as shown in Fig. 6(a) as a function of pore size for $\varepsilon_{wm} = 1.0$. As compared to the ideal-pore systems, the particles tend to be more disordered resulting from the lower density and thus require a lower temperature to obtain well-ordered structures.

An even more significant difference is found when examining trends in $T_{ODT}$ with respect to the wall-fluid strength. As seen in Table II, $T_{ODT}$ increases with increasing $\varepsilon_{wm}$ in ideal systems, for the pore sizes considered. However, for the non-ideal pore sizes, $T_{ODT}$ shows little dependence on wall-fluid interaction strength for $\varepsilon_{wm} = 1.0$ and 2.0, while $T_{ODT}$
TABLE III. Snapshot for the confined system with non-ideal separation at different $\varepsilon_{wm}$; note, the bulk region is omitted and only the confined region is shown.

<table>
<thead>
<tr>
<th></th>
<th>4.5L</th>
<th>4.5L</th>
<th>6.5L</th>
<th>6.5L</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_{wm} = 2.0$</td>
<td><img src="image1.png" alt="Snapshot" /></td>
<td><img src="image2.png" alt="Snapshot" /></td>
<td><img src="image3.png" alt="Snapshot" /></td>
<td><img src="image4.png" alt="Snapshot" /></td>
</tr>
<tr>
<td>$\varepsilon_{wm} = 4.0$</td>
<td><img src="image5.png" alt="Snapshot" /></td>
<td><img src="image6.png" alt="Snapshot" /></td>
<td><img src="image7.png" alt="Snapshot" /></td>
<td><img src="image8.png" alt="Snapshot" /></td>
</tr>
</tbody>
</table>

is significantly reduced for $\varepsilon_{wm} = 4.0$. This appears related to the increased density within the non-ideal sized pores for $\varepsilon_{wm} = 4.0$ compared to the weaker interaction strength, as seen in Fig. 6(b); however, this density is still slightly lower than that of the ideal systems that attain a value of $\sim 1$. Examining simulation snapshots for each pore (Table III), we find that for weak interactions such as $\varepsilon_{wm} = 1.0$ and 2.0, the number of layers of particles that appear corresponds to rounding down the size (e.g., for a pore size of 4.5 layers, there are only four layers of particles in each pore), thus introducing a lower density in the pore. For $\varepsilon_{wm} = 4.0$, we see a mixture of behaviors, for example, for a system with spacing 4.5, we see five layers in the top pore and four in the lower pore; for 6.5, we found the upper pore shows seven layers and bottom pore shows six layers. These results support the behavior seen previously\(^{30}\) that showed an oscillatory behavior in free energy as a function of nanopore diameter. Specifically, non-ideal spacings had higher free energy than ideal spacings for constant $T$; when considering only the central most layers of the system, the free energy of confined solids at non-ideal separations was, in some cases, higher than that of an equivalent density bulk phase, suggesting that a lower $T$ is need for crystallization, as is seen in the $C_v$ curves here. Hence, a state that would normally crystallize at a given temperature may instead remain fluid like or adopt a glass-like structure if pore spacing is not an integer multiple.

C. Registry of the surface

In all of the systems studied thus far in this work, the confining walls represent perfectly aligned ideal fcc structures. However, registry between the top and bottom surfaces may not be guaranteed in experiment, and surface structure has been shown to influence the nature of the phase transition.\(^{26,29,31,34}\) To examine this, the middle wall separating the two pores was shifted to the right by the characteristic distance between two particles in this direction (i.e., $\sqrt{3} \times 2^{1/6} \times 0.5$), and thus a perfect fcc crystal would not be able to form without a defect. Note, only a single temperature window was used in these STMD calculations (see Table I). Again, a fluid-solid transition is observed as $T$ is reduced, indicating non-ideality in the orientation of the confining walls does not impact the ability to form a solid phase. However, examining the $C_v$ curve in Fig. 7(b) reveals a slight change in the $T_{ODT}$ compared to the perfectly aligned systems, in all cases, shifting this to lower values of $T$. Thus, defects in the registry of solid walls slightly affect the overall solidification behavior, specifically by shifting the transition to lower temperatures. Hence, a pore size and temperature combination that would crystallize for an ideally registered system may instead remain fluid or adopt a glass-like configuration for a system lacking registry, as was also seen when pore spacing deviated from the ideal.

FIG. 7. (a) Simulation snapshot of a system with unregistered walls, and (b) the calculated heat capacity. The dashed lines represent results for the unregistered systems studied and the solid lines for the perfect fcc systems.
IV. CONCLUSIONS

We have examined the nature of the fluid-solid phase transition in nano-confined regions directly by performing STMD simulations and determining the heat capacity. For systems in which the pore separation is ideal (the distance is set to integer multiples of the fcc layer spacing), the $T_{ODT}$ decreases to lower values when either the pore separation is increased or the wall–mobile fluid strength $\varepsilon_{wm}$ is reduced. Both of these observations agree with the idea that a reduced interaction between mobile particles and the walls requires a lower temperature to crystallize and the behavior becomes more bulk like. For the systems with non-ideal spacing separation, quite different results are obtained with much lower $T_{ODT}$. The density profile indicates more disordered states obtained for non-ideal pore size, showing an obvious oscillatory behavior (with lower density in non-ideal pores than the ideal ones). For systems that lack registry between the surfaces, the $T_{ODT}$ is universally shifted to lower values, as compared to ideal states, although well ordered systems still form. While the LJ fluids investigated in this work are simple, they allow a large variety of important parameters to be investigated and clearly demonstrate that the STMD method provides a robust way to probe the phase transitions of nanoconfined fluids for both ideal and non-ideal systems, enabling future examination of the phase transitions of more complex fluids, which may be challenging to explore with other free energy approaches.

ACKNOWLEDGMENTS

This work is supported by the National Science Foundation under Grant No. OCI-0904879. Supercomputer time was provided by the Advanced Computing Center for Research & Education (ACCRE) at Vanderbilt University.

APPENDIX: STATISTICAL TEMPERATURE MOLECULAR DYNAMICS ALGORITHM

In this section, a brief summary of the STMD method is presented. For a detailed formulation of the method, the reader is referred to original Ref. 40. Similar to the Wang–Landau method, 45 STMD allows the calculation of the density of states, but achieves a flat energy distribution by the systematic refinement of the statistical temperature $T(E)$ as

$$T_{j+1} = T_j \frac{T_{j+1}}{1 + T_j \left(\ln f / 2\Delta E\right)}, \quad (A1)$$

where $f$ is the modification factor, and $\Delta E = E_{j+1} - E_j$ ($E_j = \text{nint}[E / \Delta E\Delta E]$ (nint being a function returning the nearest integer value) is the energy bin size, i.e., the update changes temperature estimates only at the discrete values of $E_{j+1}$. The temperature is updated in a range $T_j < T_j < T_a$ and at the boundary or beyond set to $T_j = T_b$ or $T_a$ as appropriate, where $T_j$ and $T_a$ are the lower and upper boundaries, respectively. To implement STMD, all $T_j$ are set to a constant value at the start of the simulation (usually $T_a$). When the simulation terminates with convergent temperature, a linear interpolation scheme is used to connect successive bins. For a value of the potential energy $E$ between $E_j$ and $E_{j+1}$,

$$T(E) = T_j + \lambda_j (E - E_j), \quad (A2)$$

where $\lambda_j = (T_{j+1} - T_j) / \Delta E$ is the slope of the linear segment connecting the two neighboring bins. The continuum $g(E)$ estimate is then calculated by analytical integration at the end of MD simulations,

$$\ln[g(E)] = \int_{E_j}^{E} \frac{1}{T(E')} dE'$$

$$= \sum_{j'=1}^{i} \frac{1}{\lambda_{j'-1}} \ln \left[1 + \frac{\lambda_{j'-1}(E - E_{j'-1})}{T_{j'-1}}\right] + \frac{1}{\lambda_{i}} \ln \left[1 + \frac{\lambda_{i}(E - E_{i})}{T_{i}}\right], \quad (A3)$$

where $i = i - 1$ for $E_{i-1} \leq E \leq E_i (E_i = (E_j + E_{j+1})/2)$, and $i = i$ for $E_i \leq E \leq E$. By updating the intensive variables $T_j$ located at discrete points, a continuum description of $g(E)$ can be obtained through analytical integration of $T(E)$.

After obtaining $g(E)$, the partition function $Q$ can be calculated at any given temperature and other thermodynamic properties determined. For example, the average energy $\langle E \rangle$ and heat capacity $C_v$ can be calculated as

$$\langle E \rangle = \frac{\sum E_i g(E_i) e^{-E_i/T}}{Q}, \quad (A4)$$

$$C_v = \frac{1}{T^2} \left[\langle E^2 \rangle - \langle E \rangle^2\right], \quad (A5)$$

where $E$ is the system potential energy, and $\langle E^2 \rangle - \langle E \rangle^2$ is the fluctuation in the energy.

To implement the variable $T(E)$ into a MD simulation and realize a random walk in energy space, a generalized ensemble technique 50 is used based on the weight $\mu(E) = e^{-S(E)}$, leading to the effective potential in the canonical ensemble as $V_{eff} = T_0S(E)$. The force $\tilde{f}$ acting on each particle is scaled by an energy dependent term as

$$\tilde{f} = -\frac{\partial V_{eff}}{\partial q} = T_0 \frac{\partial E}{T(E)} f. \quad (A6)$$

Thus, the statistical sampling weight $e^{-S(E)}$ is realized in a MD simulation with the Nose–Hoover thermostat by maintaining the kinetic energy at the reference temperature $T_0 = T_u$ and constantly adapting the forces with the energy dependent scaling factor.


See http://codeblue.umich.edu/hoomd-blue for Hoomd installation and documentation.


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