A molecular dynamics study of freezing in a confined geometry

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The dynamics of freezing of a Lennard-Jones liquid in narrow channels bounded by molecular walls is studied by computer simulation. We quantify the time development of ordering and observe a novel freezing mechanism. The liquid forms layers and subsequent in-plane ordering within a layer is accompanied by a sharpening of the layer in the transverse direction. The effects of channel size, the methods of quench, the liquid-wall interaction and the roughness of walls on the freezing mechanism are elucidated. Comparison with recent experiments on freezing in confined geometries is presented.

I. INTRODUCTION

The properties of liquids and solids confined in very small pores are highly interesting both from the basic and applied points of view. On a fundamental level, the interactions between molecules and surfaces and the effects of small size on thermodynamic behavior can be explored. At the practical level, these systems are of great importance in areas such as interfacial adhesion, lubrication, rheology, and tribology. The novel properties of confined liquids and solids have been studied using many experimental techniques. The confining geometries in these experiments are porous media such as glasses, rocks, and ceramics, which are hard to characterize and may have a complex and tortuous pore geometry. On the theoretical side, there have been no studies of freezing in restricted geometries. The primary difficulty in analytic studies is that freezing is a complex many body problem that is not easily tractable. Molecular dynamics (MD) simulations are ideally suited for an attack of this problem. In this paper, we describe the result of detailed studies of the dynamics of freezing of Lennard-Jones liquids in narrow channels.

Recently, several experimental studies of the freezing of geometrically confined fluids have been carried out. One category of experiments involves colloids confined in a flat channel. The results show that the system crosses over from three-dimensional (3D) to two-dimensional (2D) behavior on narrowing the channel size. Indeed, the monolayer colloidal system displays a continuous melting transition which can be understood in terms of a 2D melting theory proposed earlier. While the dynamics of a colloidal system is governed by Langevin's equation rather than Newton's equation, its long time dynamics is close to that of a hard sphere atomic system. The other category of experiments involves freezing of fluids of diatomic molecules confined in porous glasses where interesting observations on the dynamics and structure of the undercooled liquids have been reported.Awschalom et al. proposed a nucleation picture in which the restricted geometry results in a competition between a lowering of the free energy, proportional to the volume of the nucleus, and an increase of the interfacial free energy, because a wall-solid interface is less favorable than a wall-liquid interface. The model predicts a freezing point depression which has a magnitude inversely proportional to pore size, and is consistent with experimental data. One important assumption in the model is that the nucleation is not initiated by the wall. Further, the nucleation is assumed to occur in a reduced dimensionality due to the geometry of the pores. On the other hand, detailed structural studies, using elastic scattering of neutrons, of the freezing of oxygen, deuterium, and nitrogen in sol gel and vycor glasses have shown a variety of behaviors induced by the wall-liquid interaction. On freezing, the confined solids were found to have either an amorphous structure or an ordered structure that was similar to or different from the long range order in a bulk crystal of the same material. In this study, we investigate the microscopic freezing dynamics of fluids confined in simple geometries.

The liquid-solid transition remains a challenge to the theorist. The transition is a complicated many-body phenomenon in which information about short range structure near individual molecules cannot be neglected if an understanding of the symmetry change is desired. Thus, in contrast to the liquid–vapor phase transition, even a qualitative understanding of the structure change based on a simple discrete model does not yet exist. A rigorous formulation based on hierarchical equations, on the other hand, cannot be solved without making further assumptions to simplify the equations. Recent advances in the density functional methods applied to the freezing problem provide a systematic approach to determine the equilibrium state near a phase transition. The method is formulated in the form of a variational principle. Near a transition point, the free energies of various candidate states are treated as functional perturbations from that of a reference liquid state. The structural information of the liquid is included in the perturbed
terms in the form of direct correlation functions. The deviation of the density of a candidate state from the reference state is expressed as a Fourier series whose specific set of \(k\)-vectors are the reciprocal vectors of that candidate state. The coefficients in the expansion are used as variational parameters to minimize the free energy. The structural information that is an input in the formulation can be obtained from real experiments or computer simulations.

MD simulations offer a promising source of detailed structural and dynamic information about liquid–solid transitions, not directly available from laboratory experiments. Unlike critical phenomena, there are no universal laws that describe the freezing phenomena and, indeed, the freezing properties are very sensitive to the details of a particular system.\(^8\) MD has the advantage that information about such details is readily available and the parameters of the systems are tunable. The disadvantage of the MD method is the limit in the amount of time and memory size available from current computers. A simulation may suffer from insufficient relaxation time if equilibrium properties are studied and the finite size of the system may affect the equilibrium structure and the dynamic process of growth.\(^11\) Since the discovery of freezing in a high density hard sphere system in 2D,\(^12\) MD studies of freezing have focused mainly on the dynamics of the early stage nucleation of the undercooled bulk liquid,\(^11\)–\(^14\) although there are simulations of the solid–liquid interface.\(^12\) Furthermore, recent MD simulations\(^16\) and experiments\(^17\) have shown the presence of liquid to solidlike transitions in molecularly thin films under shear. However, there have been no previous theoretical or computer simulation studies of freezing in confined geometries.

In this paper, we present the results of detailed constant density MD simulations of the freezing of a Lennard-Jones fluid in narrow channels (\(<\ 60\ \text{ Å}\)) confined by two molecular walls. The wall molecules interact with each other with a Lennard-Jones potential characterized by a larger interaction strength and a shorter range than the liquid–liquid interaction, thus allowing the solid walls to be in thermal equilibrium with the liquid. The length parameters have been chosen so as to eliminate any possible artifact arising from the coherence of any pair of length scales (see Sec. II). Our results indicate a novel freezing mechanism. The liquid forms layers and subsequent in-plane ordering is accompanied by a sharpening of the layer in the transverse direction (see Sec. III B). This freezing mechanism has been observed for a range of channel sizes, and independently of whether the liquid–wall interaction is Lennard-Jones (L-J wall) or purely repulsive. The attractive part of the liquid–wall interaction causes the layers to grow from the wall into the bulk while a repulsive wall leads to all layers forming more or less simultaneously. We have also studied the effects of rough walls on the freezing mechanism. On heating the systems from the frozen state, the melting occurs more or less simultaneously for all layers. However, in the case of repulsive confining walls, the heating does not bring the fluid to its original state but an intermediate metastable state with a layered structure persists till the end of the simulation. Our results suggest that the heterogeneity introduced by the attractive part of the wall–fluid interaction is the source of the difference in behavior between the two cases.

In Sec. II, we describe the details of the confined-fluid systems, their preparation, and the quenching methods. An analysis of the structure of the undercooled liquid is presented in the beginning of Sec. III, followed by the dynamics of freezing. The description of the melting process appears at the end of this section. Section IV presents a summary of our conclusions.

II. SYSTEM PREPARATION AND QUENCHING METHODS

All molecular interactions in the system are shifted Lennard-Jones 6-12 potentials,

\[
V(r) = V_{LJ}(r) = V_{LJ}(r_c) + V'(r_c)(r - r_c)
\]

for \(r < r_c\),

where

\[
V_{LJ}(r) = 4\epsilon \left[ \left( r / \sigma \right)^{12} - \left( r / \sigma \right)^{6} \right]
\]

and we chose \(r_c = 2.3\) times the \(\sigma\) of the fluid–fluid interaction.

Different sets of values were assigned to the energy parameter \(\epsilon\) and length parameter \(\sigma\), for fluid–fluid (f-f), wall–wall (ww), and wall–fluid (wf) interactions in such a way that the wall is a stable fcc crystal in equilibrium with the fluid (see Fig. 1).

The reduced density of the fluid \(\rho^* = \rho \sigma^3\) was chosen to be 0.95 (\(\rho\) is the number of molecules per unit volume). This value is within the range where previous MD studies of freezing of the bulk liquid have been carried out. (In evaluating the density of fluid, the volume of fluid molecules is the space in between the two surface wall molecule layers with a volume equivalent to a single layer of wall lattice excluded.) The density of the wall is chosen in such a way that it is incommensurate with the fluid density. The ratio between the average intermolecular-distance of wall molecules and of fluid molecules is 0.778, different from that between the interaction length parameters \(\sigma_w\) and \(\sigma_f\), which is 0.81. Finally, the wall–fluid interaction parameters were chosen to be different from those of the wall–wall interaction (see the caption of Fig. 1).

Three systems (I–III) having channel sizes, 11.3\(\sigma_f\), 12.92\(\sigma_f\), and 17.76\(\sigma_f\), containing 1372, 1568, and 2156 molecules, respectively, were prepared. In all cases, the interfacial area was \((11.30\sigma_f)^2\) and the \((100)\) wall surface was in contact with the fluid. Periodic boundary conditions were employed in the direction transverse to the walls. The center-of-mass velocities of the walls were kept at zero. To enable the use of the same integration time step for both the fluid and the wall molecules, the mass of the wall molecule was chosen to be five times that of the fluid molecule. The MD simulations were carried out with Gear's fifth order predictor-corrector scheme with the integration time step equal to 0.005\(\tau\), where \(\tau = \left( m \sigma^2 / \epsilon \right)^{1/2}\), and \(m\) is the mass of fluid molecule. The layered-linked cell algorithm\(^18\) was implemented in order to facilitate vectorization.

Two methods were used to prepare the system at a reduced temperature \(T^* = k_B T / \epsilon_f = 1.2\), prior to quench-
and there are 500 bins in a region 35 a, in width. (The horizontal lines above and below the density profile indicate the positions of the walls.) The origin of z differs in (a) and (c).

(a) x-z projection of the whole system, where a * represents the center of a wall molecule and a circle a fluid molecule. (b) The transverse (x-y) projection averaged over a period of 107. N is the number of molecules per bin and fluid placement of molecules and equilibrating at $T^* = 1.2$ for more than 40τ.

The liquid has reduced density $\rho^* = 0.95$, prepared by compressing a dilute random placement of molecules and equilibrating at $T^* = 2.8$ for more than 40τ. (a) x-z projection of the whole system, where a * represents the center of a wall molecule and a circle a fluid molecule. (b) The transverse (x-y) projection of the surface layer near the wall, close to $z = 0$. (c) The density profile averaged over a period of 10τ. $N$ is the number of molecules per bin and there are 500 bins in a region 35 $a_0$ in width. (The horizontal lines above and below the density profile indicate the positions of the walls.) The origin of z differs in (a) and (c).

FIG. 1. A snapshot picture of system II before quenching. The system has 1568 fluid molecules in the channel and 648 molecules on each wall. The relative position of the two walls is 0.54a in the x direction and 0.20a in the y direction from out-of-registry, where $a$ is the lattice constant of the fcc lattice. The ratio of wall and fluid densities is $\rho_w/\rho_f = 2.1:1$. The length parameters of wall-wall, wall-fluid, and fluid-fluid interactions have ratios $\sigma_{ww}/\sigma_{wf}/\sigma_{ff} = 0.811:0.1:0.1$. The energy parameters of wall-wall, wall-fluid, and fluid-fluid interactions are in the ratios $\epsilon_{ww}/\epsilon_{wf}/\epsilon_{ff} = 64:10:1:0$. The liquid has reduced density $\rho^* = 0.95$, prepared by compressing a dilute random placement of molecules and equilibrating at $T^* = 1.2$ for more than 40τ.

(b) The transverse (x-y) projection of the surface layer near the wall, close to $z = 0$. (c) The density profile averaged over a period of 10τ. $N$ is the number of molecules per bin and there are 500 bins in a region 35 $a_0$ in width. (The horizontal lines above and below the density profile indicate the positions of the walls.) The origin of z differs in (a) and (c).

Three methods of quenching were used. In the first method, the velocities of all molecules were scaled instantaneously to reduce the temperature to $T^* = 0.4$. The second case corresponded to a finite quench rate. The velocities of the fluid molecules were rescaled each time step by a constant factor of 0.9997 until the fluid temperature reached 0.4. The velocities of the wall molecules were rescaled by a variable factor chosen so as to keep the wall temperature at all times equal to the fluid temperature. The third method of quenching involved cooling the outer parts of the walls (not in contact with the fluid), thus removing heat from the fluid through the walls as in a laboratory thermostat. All three methods applied to system II with L-J walls showed the same layer-by-layer growth of order from the wall towards the center of the channel. The third method did not lead to a completion of solidification of all the layers before the end of the simulation (more than 40τ) due to the smaller heat conductivity at lower temperatures. At the later stages of the simulation, the evolution of the system is very slow. The details of the freezing dynamics of the finite-rate-quenching will be presented in Sec. III B.

We have also applied the reverse process of each of the latter two quenching methods to melt the frozen solids. We present the results in Sec. III C.

III. RESULTS

A. Structure of the frozen solid

For the three systems studied, there were 12, 14 (Fig. 2), and 19 (Fig. 3) layers formed, respectively, in the final structure. In each layer, a distorted triangular lattice was formed with defects and disclinations. A detailed check of the sequences of layers indicated that they were not periodic stacks of triangular lattices, as would be expected in a three-dimensional crystalline structure. The in-plane ordering was measured by a normalized peak value of the $xy$ structure factor (excluding the peak at $k_x = k_y = 0$),

$$S_m = \frac{\max S(k_x, k_y)}{S(0,0)},$$

where

$$S(k_x, k_y) = \frac{1}{N} \left| \sum_{j=1}^{N} e^{i (k_x x_j + k_y y_j)} \right|^2,$$

$N$ is the number of molecules in the layer, and $x_j$ and $y_j$ are the $x$ and $y$ coordinates of the $j$th molecule. It is found that the peak location in $k$-space always occurs roughly in the (11) or (17) direction of the (00) surface. The closer a layer is to a wall the more the peak vector is in the (11) or (17) direction. These results indicate that the undercooled fluid in the vicinity of the wall was affected by the wall periodicity, while layers in the center of channel were less in-
fluenced by the molecular corrugation on wall surfaces. For system I the two walls were exactly out of registry, whereas in system II, the two walls were neither in registry nor out of registry. In system I, we found that five layers near one wall were predominately in the $(11)$ direction, whereas the other seven layers were in the $(11)$ direction. No such domain structure was found in system II.

We calculated the “powder-averaged” structure factor by Fourier transforming the radial distribution function for system II,

$$ S(Q) = 1 + 4\pi/Q \int_0^\infty r [g(r) - 1] \sin(Qr) dr. $$

The result is shown in Fig. 4 along with $g(r)$ in the inset. The first peak of the $S(Q)$ of the channel liquid has a value very close to that of bulk liquid at the same temperature and density. Note that the $S(Q)$ in the frozen state has two contributions, peaks corresponding to the ordering developed in the system and amorphous components characteristic of the liquid state. Similar structure factors have been observed in scattering experiments on the frozen state both in the colloidal system and in the fluids confined in the porous media.
B. Dynamics of freezing

We now present the detailed dynamics of freezing in system II confined by the L-J walls (Figs. 1 and 2), prepared by compressing a dilute random initial configuration followed by a finite-rate quench (see Sec. II). The quenching from 1.2 down to 0.4 took 20τ after which the fluid temperature evolved freely. (The wall temperature was always rescaled to be the same as the fluid temperature.) The formation of layers was monitored by calculating the spread in the z direction (normal to the walls), defined as the standard deviation of the average z coordinates of all molecules within a zone during time interval 0.2τ. The in-plane ordering was monitored by recording the time evolution of $S_m$ defined in Sec. III A [see Fig. 5(a)].

Even before the quench, the distribution of fluid molecules along the z direction is not uniform at $T^* = 1.2$. The 1st and the 14th layer are clearly discernible in a snapshot of the molecules; the 2nd and 13th layers are also identifiable [see Fig. 1(a)]. A density profile averaged over 10τ shows oscillations with 14 peaks, the amplitude of the peak normalized to that of the boundary layer (1 or 14) decreasing to 6% at the center of the channel [see Fig. 1(c)]. A similar behav-

FIG. 5. Time evolution during cooling of the two systems described in Sec. III B. (a) Temperature, spread, and $S_m$ of system II with L-J walls. (b) Temperature, spread, and $S_m$ for system I with repulsive walls. The curves shown correspond to the first, second, third, fifth, and seventh layers, as indicated in the figure. Note that the $S_m$ of a surface layer near a L-J wall has nonzero value at zero time, in contrast to the repulsive wall case, where $S_m \approx 0$. 
behavior is observed in the spread. There is some degree of in-plane ordering in the 1st and 2nd layers from wall, with $S_m = 0.7$ and 0.2, respectively [Fig. 5(a)]. Studies of in-plane diffusion show that layers 1 and 14 are solid like with a diffusion coefficient $\sim 40$ times smaller than in the middle of the channel (Fig. 6). Our results are qualitatively consistent with previous studies$^{21}$ that have shown the role played by the molecular nature of the wall on the in-plane diffusion coefficient.

On quenching, a rapid decrease of the spread is found to take place at a certain time (which is different for different layers), which we identify with initiation of the layer formation. The completion of the layering phenomenon is signalled by the final leveling off in Fig. 5(a). The major growth in $S_m$ occurs during the layering process. Figure 5(a) shows that the formation of layers and the in-plane ordering proceed from the walls towards the center. Further, the system sometimes adjusts the structure of well-formed layers (e.g., layers 2 and 3) to the subsequent ordering of other layers (e.g., layer 5 and 7) [see Fig. 5(a) around $31\pi$]. We have also studied systems I and III, they show qualitatively the same freezing mechanism. Figure 3(a) shows the density profile of system III before quenching. Its frozen state has a layered structure as shown in Fig. 3(b).

We have studied system I with repulsive walls, prepared and quenched in the same way as in the previous case. Our results are summarized in Fig. 5(b). Before quenching, the transverse diffusion of molecules in the surface layers is approximately the same as those of other layers, even though their perpendicular diffusion is significantly smaller (Fig. 7). This indicates that the surface layer near a repulsive wall is liquidlike, in contrast to those near a L-J wall. The most striking difference in this case is that the layers form more or less simultaneously. The ordering within each of the layers except those well-formed ones near the walls also occurs around the same time. Unlike the L-J case, the onset of the structure factor growth takes place at a later time than the beginning of the layer formation. Indeed, the formation of layers and their subsequent ordering has been observed directly in a colloidal system confined in a channel bounded by flat repulsive walls without any corrugation on the scale of the size of the colloidal particles. At $30\pi$, the temperature, spread, and $S_m$ level off abruptly [Fig. 5(b)], signaling the completion of layering and in-plane ordering, while in the L-J case, all three quantities change smoothly approaching their final stable values. These results indicate that the layer-by-layer growth is due to the attractive part of the wall-fluid interaction.

We have carried out a few runs to estimate the position of the solid--liquid interface as a function of temperature in system II with L-J walls. We found no solidification had taken place in the center of the channel over a time scale of $30\pi$, when $T^* = 0.8$. This suggests a depressed freezing temperature (the transition temperature for bulk liquid $\approx 1.1$) due to the presence of the walls, in agreement with experiment.

We have also studied a system of 1176 molecules (Fig. 8) in a channel characterized by two widths. For this case,
the nucleation occurs first in the constricted regions and then proceeds to the entire channel, in contrast to the picture proposed by Awschalom et al. Four and 13 layers form in the narrow and wide regions, respectively. This even-odd effect causes frustration at the junction of the regions resulting in a tilted layer structure in the middle of the channel. We have also considered systems with bumps and holes of thickness $1.25\sigma_0$ and area $24.0\sigma_0^2$ placed randomly on both walls (Fig. 9). Layering is found to occur locally, but the frustration at the junction causes the coherence in the layering to be less pronounced.

C. Melting of the frozen solid

On heating system II with L-J walls from $T^* = 0.4$ to $T^* = 1.2$ at a rate equal in magnitude to that of the cooling, the layered structure along with the in-plane-ordering disappeared more or less simultaneously for all layers [Fig. 10(a)]. We monitored the number of molecules within each layer as a function of time (Fig. 11), and found that transitions of molecules between layers occasionally occurred even in the frozen state. These transitions correspond to the hopping of crystal defects. The presence of these defects initiates the global melting of the solid within the channel and prevents the system from staying in a superheated state. However, for system I with repulsive walls (Sec. III B), while the spreads for all the layers increased with a simultaneous decrease in the in-plane ordering, the system did not go back to the original state. It reached a metastable state with layered structure and stayed in that state till the end of the simulation, $40\tau$ after the temperature was raised to 1.2 [see Fig. 10(b)]. We have also studied the melting process for the L-J wall case by heating the walls to $T^* = 1.2$. In this case, there is a competing effect of the walls attempting to melt the layer adjacent to it along with the tendency of the

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FIG. 9. Snapshot projection of the frozen state of the fluid in a channel with bumps and holes on walls.

FIG. 10. Time evolution during heating of the frozen liquids of the systems whose freezing is shown in Fig. 5 (see Sec. II C). (a) Temperature, spread, and $S_m$ of system II with L-J walls. (b) Temperature, spread, and $S_m$ of system I with repulsive walls. Note that there is a transition occurring between $4\tau$ and $20\tau$. The new metastable phase has z-spread $=0.17\sigma_0$ and $S_m=0.45$ for all layers. Both are significantly different from those of the liquid before quenching [see Fig. 5(b)].
The numbers of molecules as functions of time within frozen layers 1, 2, 3, 5, and 7 in system II with L-J walls at $T^* = 0.4$.

wall to retain some ordering. Our data suggest that the melting process is qualitatively as before with no clear evidence that proceeds from the wall into the center of the channel. The behavior of the frozen solid confined by repulsive walls is qualitatively similar.

IV. DISCUSSION

Layering phenomena have been studied widely by experimentalists and theorists, in problems related to physisorption and freezing/melting of multilayer films on a substrate.\textsuperscript{22} The major difference between the adsorption case and our studies is that we treat a closed system with two walls. Nevertheless, our results suggest that the new layer-by-layer freezing mechanism ought to be operative in cases where a solidlike layer is adjacent to the wall in the liquid state.

The attractive part of the fluid–wall interaction introduces an inhomogeneity into the fluid system—the fluid near the wall is distinct from the fluid in the center of the channel. Before cooling, in either the repulsive-wall-confined system or the L-J-wall-confined fluid system, there is one clearly identifiable surface layer near each wall, indicated by the $z$-spread at time zero. However the $S_m$ values of these layers are quite different in the two cases. The surface layer near a repulsive wall is liquidlike and is essentially produced by the geometry of the wall, while that near a L-J wall has some degree of ordering indicating that the molecules are more localized by the attractive interaction from the wall (see Fig. 5). During the cooling process, the surface layers near the L-J walls become more ordered and induce the formation and ordering of subsequent layers.

On heating up the systems, the presence of the walls inhibits any surface-initiated melting. Thus, all the layers are involved in the transition simultaneously. In the repulsive-wall system, the transition leads to a metastable state with a layered-structure, whereas in the L-J-wall system, the system reverts back to the original liquid state. One feature of the metastable state is that all layers have the same $S_m$ and $z$-spread values [Fig. 10(b)]. Note the dual role played by the confining walls; they introduce heterogeneity into the system facilitating the layer-by-layer nucleation in freezing; they also allow for global melting by eliminating free surfaces and surface melting.

The individual molecules acquire a two-dimensional character as reflected in the oscillating density profile [see Figs. 1(c), 2, and 3(a)], due to the planar walls of our systems. While there is a conflict between preferred short range order and simple global packing in bulk three-dimensional systems, no such conflict exists in two dimensions.\textsuperscript{23} Indeed, this may explain why the system solidifies so readily on quenching. We have calculated the normal stress in the frozen states for both the L-J and repulsive wall cases and find that in the former it is almost a decade lower than in the latter case. Indeed, it is this squeezed effect that may be responsible for the long-lived metastable state for the repulsive wall case.

Our system has an idealized geometry and simple interactions. Thus our simulation results may not be directly applicable to experiments on freezing of diatomic molecules in complex porous media. Indeed, the planar geometry of the walls in our simulations leads to the system having a greater tendency to form a quasi-two-dimensional layered structure since the energy of such a state is lower than other competing states. This may be why the nucleation mechanism postulated by Awschalom et al.,\textsuperscript{2} is not observed in our simulations. Nevertheless, our simulation results are in qualitative agreement with the neutron scattering experiments of Sokol et al.\textsuperscript{6,7} In the experiment, as in our simulations, there are several incommensurate length parameters including pore size, intermolecular distances and the characteristic length of the wall–fluid interaction. Experimentally, the frozen liquid has a structure factor characterized by a crystalline component plus a liquidlike amorphous component in qualitative accord with Fig. 4. Moreover, the effect of the attractive part of the wall–fluid interaction can be related to a length parameter ("elastic healing length") that characterizes the range of the inhomogeneity caused by the wall. The ratio between the pore size and the elastic healing length may determine whether the frozen state is ordered, and if so whether its structure is the same as in the bulk.\textsuperscript{7}

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