

Using swapping layers in molecular dynamics simulations to drive structural equilibration far below T_g

Richard B. Stephens ^{*}Department of Physics and Astronomy, *University of Pennsylvania*, Pennsylvania 19104, USA

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The anomalous surface mobility exhibited by many slowly vapor-deposited molecular solids, and their simulated counterparts, allows annealing their structure and increasing their density down to $T_{\text{dep}} \approx 0.85T_g$. This work describes the design and characteristics of a simulation that uses a “swept swapping” technique designed to extend structural annealing to lower temperatures. Films are grown using size-dispersed attractive Lennard-Jones (L-J) potential spheres deposited onto their free surface and then equilibrated with a surface-following Monte Carlo swap region. The motion of that region combined with sphere size dispersion speeds structural relaxation by orders of magnitude compared to bulk swapping. Sphere size span and size step (25% and $\sim 2.5\%$, respectively) are sufficient to completely suppress crystallization and maintain a high swap acceptance rate. The regime revealed by this technique attains a high packing fraction, which is near that of an hexagonal-close-packed L-J crystal with no size-dispersion. Additional swapping refines its structure, at near constant density, maximizing short-range icosahedral order to levels higher than seen previously; the levels apparently limited only by the computing budget.

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I. INTRODUCTION

Ultrastable, ultradense, disordered films can be made by vapor deposition of irregular molecules onto substrates held below a material’s glass transition temperature T_g [1–13]. It is generally understood that these film properties are achieved because of high structural mobility near the surface that, for sufficiently slow deposition, allows incoming molecules to settle into low-energy niches before being immobilized by subsequent incoming molecules [4,7,14]. The effectiveness of this relaxation mechanism decreases with temperature as the surface region thins and the mobility within it slows [15].

The freezing out of this mechanism limits relaxation of the film’s structural (e.g., fictive) temperature to $T_f \gtrsim 0.85T_g$ [4,16] (a value that depends only slightly on deposition rate [17]). This prevents experimental examination of improvement in the packing fraction φ and kinetic stability of the looked-for lowest entropy ideal glass structure that might appear at the Kauzmann temperature [18]. Replacing the thermally driven surface equilibration *in silico* with a user-controlled swap-induced mobility layer would allow one to sidestep this limit. This has been done in a number of cases, using mobility-inducing swaps dispersed throughout a simulation volume [19,20]. Such simulations have created films considerably more relaxed (e.g., higher φ and kinetic

stability, and lower potential energy E_p) than their corresponding liquid-cooled configurations [15,21].

Unlike previous investigations of densification and equilibration, which added mobility throughout a completely filled simulation space [15,20,21], or which slowly cooled individual incident particles [22], the simulations presented here equilibrate primarily within a surface-following layer with fixed thickness and user-controlled swap-induced mobility [Fig. 1(a)]. The mobility is created by swapping the sizes of randomly chosen pairs in that region. The resulting churn in particle positions has proved very efficient at structural equilibration, and effective to the lowest temperatures studied ($T_{\text{dep}} \sim 0.4T_g$).

II. SIMULATION

A. Parameters

The key features needed for exploring equilibration in these simulations are (i) size dispersion to prevent crystallization and phase separation, (ii) small steps between particle sizes to allow large acceptance fraction in particle swaps [20], (iii) sufficient cohesion to allow growth at a free surface, and (iv) sufficiently fast dynamics to structurally equilibrate in a reasonable computation time. The films presented here are built in dimensionless units using spheres uniformly distributed among 12 sizes spanning 25%. Those spheres interact *via* the Lennard-Jones (L-J) 12-6 potential [23]. The size span was large enough to prevent crystallization or phase separation and the size increments small enough ($\sim 15\%$) for usable swap acceptance rate. The attractive part of the L-J potential gives the film sufficient cohesive force to allow construction of a film with a free surface. The potential is cut off at about

^{*}Contact author: richst@sas.upenn.edu

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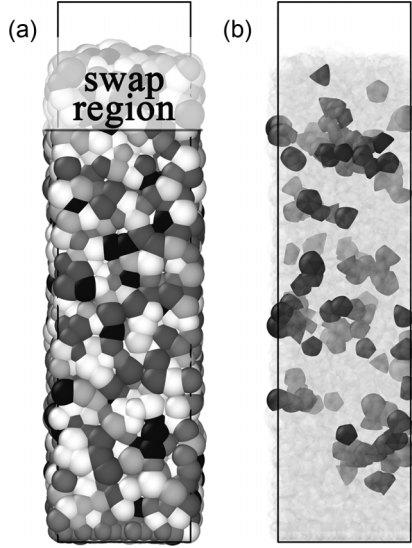


FIG. 1. Rendering of a completed film of $\sim 3 \times 10^3$ spherical Lennard-Jones spheres deposited at $T_{\text{dep}} = 0.42 T_g$ in a $10 \times 10 \times 40$ box on a rigid base of smaller spheres. (a) Shows the size-dispersed spheres (size-dispersion indicated by the different gray tones) and (b) In the same film those spheres at the core of icosahedral regions in dark gray, amid their translucent surroundings. The icosahedral regions are created as the film grows by swapping (7.5×10^3 swaps per atom in this case) in the surface-following swap area. For this film 4.5% of the atoms are at the core of icosahedral regions. The renderings were made using the OVITO program [24].

$2.5\times$ the largest sphere diameter (e.g., the attraction extends to second neighbors) resulting in pair-separation compression of $\approx 3.5\%$. This system structurally equilibrates extremely rapidly; it is analogous to metallic glasses, which are notorious for their rapid structural equilibration and subsequent crystallization; the first experimental success (Au-Si) [25] had an atom size spread of 23% and required cooling rates $\sim 10^6$ K/s, near the size spread and cooling rate used in this work: 25% and 4×10^5 K/s, the latter if one equates the parameters used here with those of argon atoms (see details in the Appendix).

Films were grown in a computation space $d \times w \times h = 10 \times 10 \times 40$ (in dimensionless units, which are used throughout), with periodic boundary conditions on the side and an L-J 12-6 bottom [Fig. 1(a)]. The bottom surface was roughened by adding a rigid bilayer of somewhat smaller spheres. Film construction alternated between (i) deposition of ≈ 0.1 monolayer onto the surface and (ii) swapping in the mobility layer; each event is separated by 100 molecular dynamics time steps to relax the new configuration.

B. Dynamics

The swapping region, moving up with the rising surface (region thickness six, staying one below the surface; the results were not sensitive to these parameters; see Appendix), engulfs a recently incident sphere and includes it in the swapping action until the swap region's base rises above it. The average number of possible swaps for that (and every) sphere is given by the swap intensity s . Possible swaps are

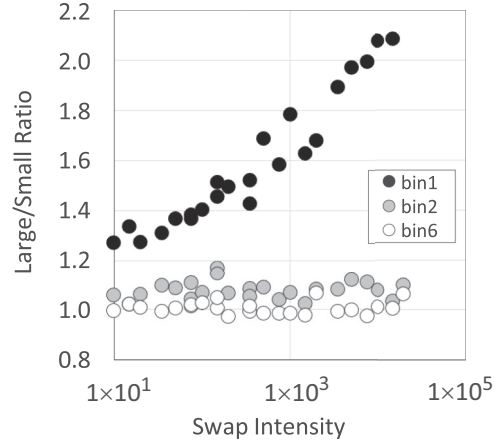


FIG. 2. Ratio vs swap intensity of the number of four largest to smallest particle types in top ($\bullet$), next ($\circ$), and bottom bins ($\circ$) within the swap region. All films were deposited at $T = 0.67 T_g$.

accepted on the basis of system energy change relative to temperature (the Metropolis rule [26]). They are less likely to be accepted (by a factor of 0.4) for each step in diameter difference ($\approx 2.5\%$); e.g., the majority of accepted swaps are of neighboring sizes. Since the swap region moves up on each cycle, it continually adds not-swapped (less dense) material at the top and leaves maximally swapped (more dense) material at the bottom. This motion-induced ϕ gradient causes a size-selective churning within the layer (larger particles are pushed to the top), creating a steady-state size disproportion at the top of the swap region that increases with swap intensity (Fig. 2). The disproportion created at the leading edge of the swap region, and its destruction by two layers down, completely erases all preexisting configurations, resulting in the structural equilibration about $10\times$ faster than the purely thermal equilibration of a growing film without added swaps (at $T \sim 0.7 T_g$) (Fig. 3) and $\sim 10^3\times$ faster than that of a static swap region without such churning (Fig. 4).

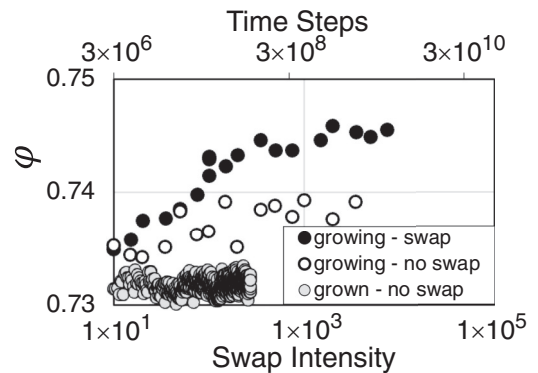


FIG. 3. Film ϕ vs s or the equivalent time steps for films that had swapping during growth ($\bullet$), grown at the same rate r_{dep} but without swapping ($\circ$) (for a swapped film the deposition rate is $\propto s^{-1}$), or grown rapidly then aged ($\circ$). Data for the first two averaged over three runs from 0.68 to $0.71 T_g$, the last at a higher temperature ($T = 0.78 T_g$) giving a lower ϕ that does not obscure the other data.

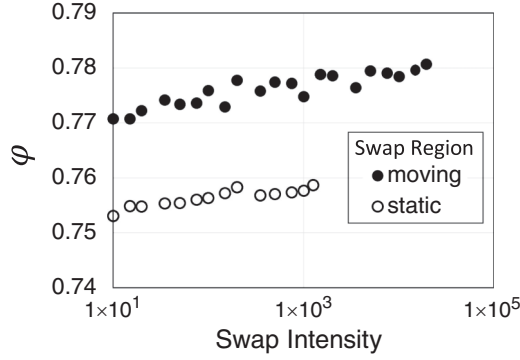


FIG. 4. ϕ at $T \approx 0$ of films created at $T = 0.67T_g$ for a moving (●) or static (○) swap region. The former had a thickness of 6 and rose with the surface. The latter region encompassed the whole predeposited film. The latter's lower density may reflect the presence of density defects that bulk swapping had no ability to remove. In any case, bulk swapping was not able to achieve a density at $s \sim 10^3$ that the moving swap region reached with $s \sim 10$.

The relatively low-density top edge, which causes disproportion, also causes it to contain one partner in most of the accepted swap pairs. And that tendency should increase with s (e.g., as ϕ in the lower part of that region increases), so that at the highest s very few of the swaps will occur away from the top.

The steady-state disproportion in the swap region necessarily carries some large spheres along with it. The final film should have a large-sphere deficit (excess) in the bottom (top) few layers, and be homogeneous in the middle, where the film properties are analyzed.

C. Analysis

The properties of the resulting films were characterized using observables common to physical films: their packing fraction ϕ at T_{dep} and $T \approx 0$, and the transition temperatures T_g and T_{rel} (respectively, the structural freezing temperature on cooling from the liquid state, and the structural relaxation temperature on first heating). $\phi|_{T=0}$ is calculated using as sphere diameters the zero-force separation of isolated pair of each size ($r_i = 2^{1/6}\sigma_{ii}$). As noted in the Appendix, all $\bar{r}_i$ pair separations in a condensed film (random or crystalline) are compressed 3.5% relative to their isolated value. The mobility d is the average displacement of spheres in a fixed number of time steps. In both cases the calculations are carried out for sphere z positions $10 < z < 25$ (e.g., ~ 10 sphere diameters away from either the top or bottom surface). T_{rel} is located by the abrupt changes in the slope of $\phi(T)$ and mobility $d(T)$ when films are thermally cycled between 0.6 and $1.4\text{--}1.7 T_g$ (Fig. 5). T_g of liquid-cooled films was determined by the second thermal cycle of these films¹ (Fig. 6) is $T_g \approx 0.2965$ at a standard heating or cooling rate $\mathbf{r}_0 = 1.53 \times 10^{-8}$ per time

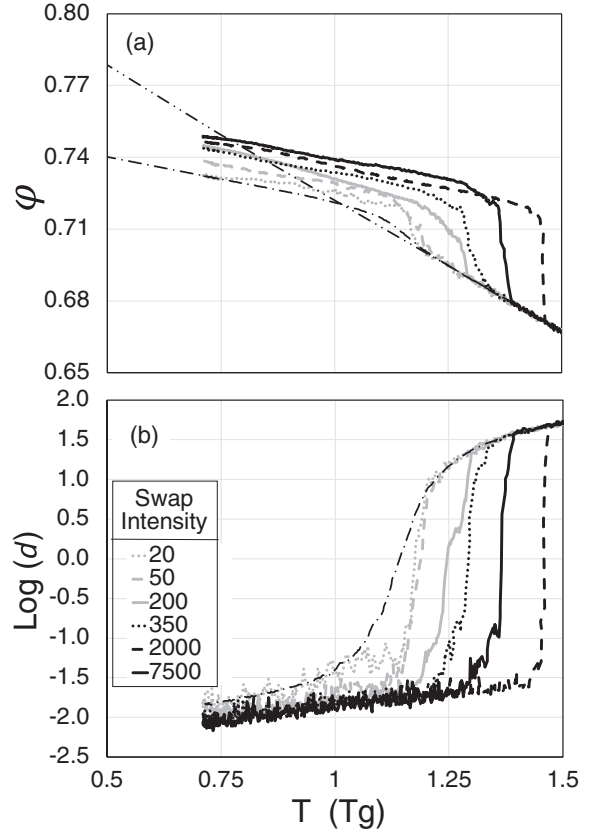


FIG. 5. (a) ϕ and (b) $\log(d)$ vs T/T_g during first heating of films deposited at $T = 0.74 T_g$ with selected swap intensities. The average curve heating for the second thermal cycle is shown by dash-dot lines and the extrapolated liquid ϕ line is shown in with dash-double-dot. T_g is determined by the intersection of these two lines. T_{rel} is determined in both (a) and (b) by the temperature at which warming curve joins the liquid line.

step ($= 4 \times 10^5$ K/s in real units assuming the properties of argon atoms).

Like their physical cousins, these *in silico* films show an anomalously high surface mobility that spreads into the bulk on the approach to T_g [Figs. 7(a) and 7(b)]. And like physical films, such surface melting can be eliminated by capping the film with a stable layer [27–29]. In this case it proved sufficient to freeze the surface, creating a rigid, floating cap, to obtain a film whose top-to-bottom properties were uniform [Figs. 7(c) and 7(d)].

That the swapping increases the kinetic stability of these films can be qualitatively seen in the very large increase in T_{rel} ($T_{\text{rel}}/T_g \sim 1.4$; Fig. 5), which is much larger than the ~ 1.1 seen for films of the molecular glass indomethacin [30], a difference partly due to the lower fragility of these size-dispersed spheres ($m \sim 40$, see Appendix) compared to more typical molecular glasses, like indomethacin ($m \sim 90$) [31,32]² A quantitative measure of kinetic stabilization, obtained by directly measuring the relaxation time of a swapped

¹The first cycle apparently completely eliminated the initial structure; in test runs the second and third cycles were identical.

²The very high effective speed of temperature scans in these simulation do not change that statement. Increasing the experimental scan

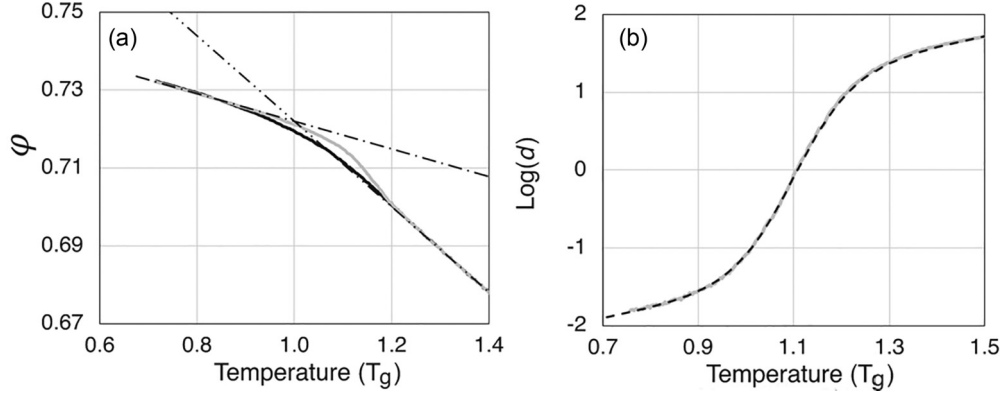


FIG. 6. (a) ϕ and (b) $\log(d)$ vs reduced temperature of the average of several hundred simulated films on their second heat and cool cycle. In (a) the dash-double-dot and the dash-dot lines are fit to the liquid and glass curves respectively and T_g is defined as the intersection of those lines. $T_g = 0.2965$. The mobility data is well fit by $d_{\text{fit}}(T) = a * \tanh(T) + b * T$. The ϕ -determined T_g corresponds in our mobility measure to $\tanh = -1.09$.

film at T_{rel} compared to its equilibrated liquid (see Appendix), shows that at high s the structure's kinetic stability is enhanced $s_{\text{liq}}|_{T=T_{\text{rel}}} \approx 6 \times 10^3$.

D. Structure

The packing of these films—their density, structure and strain, is examined after cooling them from T_{dep} to $T \approx 0$ ($E_K < 10^{-4} E_P$) (where E_K , E_P are, respectively, the kinetic and potential energies of the system), using a barostat to maintain zero external pressure on the side walls (because of the free surface the pressure is zero in the z direction).

The local structure has been examined using tools found in OVITO [24]: coordination analysis for partial radial distribution

functions to detect size segregation (none) and internal compression (3.5%); Voronoi tessellation to detect the prevalence of environments with fourfold, fivefold, and sixfold symmetry [$C(V_4)$, $C(V_5)$, $C(V_6)$, respectively] [34]; common neighbor analysis [35] to find icosahedrally configured neighborhoods (IN's); and cluster analysis to characterize the IN spatial distribution. See Appendix for detailed discussion of all these analyses.

A crystalline analog to these films was created by depositing monosized spheres. The pair interaction potentials ($\epsilon = 1.0$, $\sigma = 0.833$, and σ cutoff = 2.857) were chosen to approximate the average interaction potential of the size-dispersed system. With slight adjustment of the computation box dimensions ($d_{x,y} \approx 20$) a defect-free crystal could be obtained. It had $\phi_{\text{xtal}}|_{T=0} = 0.777$.

III. RESULTS

Swapping during deposition increases both the ϕ and the kinetic stability of the resulting film (Fig. 5), but details are

rate to $\sim 10^4$ K/s changes $m \lesssim 2$ for indomethacin and much less for an Au-based metallic glass [33].

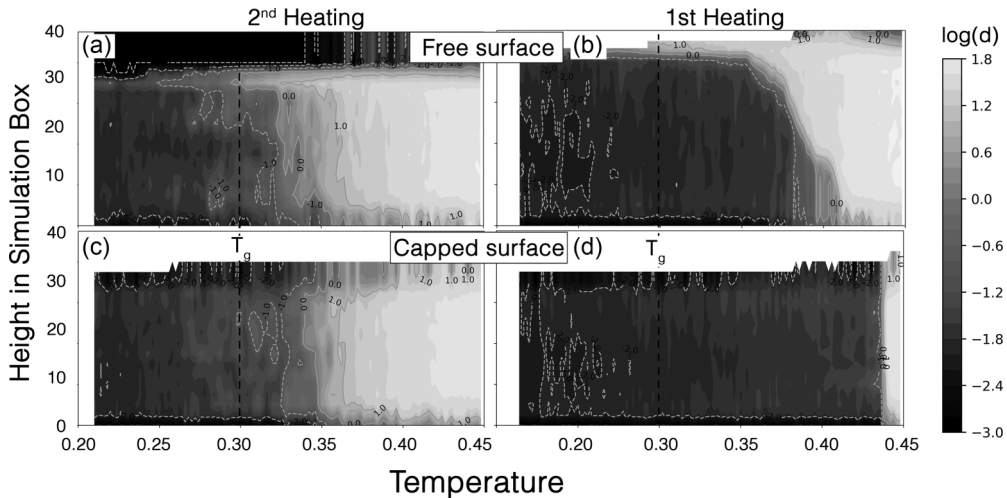


FIG. 7. Sphere mobility maps vs height in the simulation box and temperature in films deposited at $T_{\text{dep}} = 0.71 T_g$ with $s = 1 \times 10^4$ on first (b), (d) or second (a), (c) heating, without (a), (b) or with (c), (d) a floating rigid cap. $\log(d)$ calculated at each height is indicated by the grayscale, where solid is dark, liquid is light.

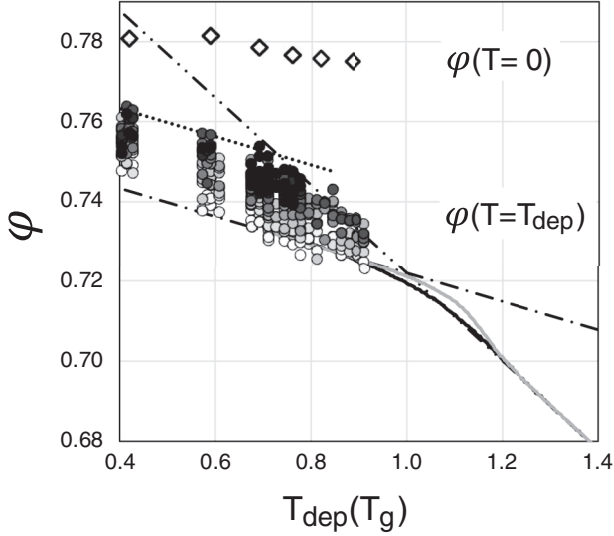


FIG. 8. The gray-filled circles show ϕ achieved for simulation runs deposited and measured at various T_{dep} for s up to 2×10^4 , with the darkness of the fill increasing with s . Those ϕ 's approximately fill the space between the extrapolated glass (dash-dot) and supercooled liquid ϕ (dash-double-dot) lines for temperatures down to $\approx 0.75 T_g$. It appears that the slope of the line connecting the maximum achieved ϕ below $0.75 T_g$ (dotted) and that of the lower frozen-structure glass line is the same. The diamonds at the top show ϕ for the high s runs of those films when cooled to $T \sim 0$. Each of those points were averaged over many (12–16) runs of similar temperature.

complicated. ϕ increases to that of the extrapolated liquid ϕ , as one would expect, only for $T_{\text{dep}} \gtrsim 0.7 T_g$. For $T_{\text{dep}} \lesssim 0.7 T_g$ ϕ stalls at lower values whose variation with deposition temperature matches that of the liquid-cooled glass (Fig. 8). Cooling those films, to $T = 0$ removes most of the variation; $\phi|_{T=0}$ is nearly independent of T_{dep} for low T_{dep} . Figure 9(a), which plots $\phi|_{T=0}$ vs s shows that that limit occurs because densification effectively stops for swapping intensity $s \gtrsim 500$, as does the reduction in E_P .

The kinetic stability of a highly swapped film (measured by relaxation time, see Appendix), is much improved for a swapped film over a liquid equilibrated at T_{rel} ($s_{\text{liq}} \simeq 6 \times 10^3$). That is low compared to the experimentally determined 10^4 – 10^5 reported for molecular glasses [36]. But the stability is more properly compared to those of metallic glasses whose bonding and fragility ($m \sim 20$ – 40 [37]) are similar to these L-J spheres whose fragility $m \sim 40$. There exists a limited set of m and s_{liq} available suggest the stability is lower for low- m materials [12].

Measures of local structure continue to evolve with increasing $s > 500$. The concentration of crystalline symmetries [$C(V_4)$, $C(V_6)$] were at the 10–15 % level and decrease with increasing s while $C(V_5)$ (indicating nontiling symmetries) dominates and continues to increase [Figs. 9(c) and 9(d)]. On a slightly larger scale, the concentration of sphere clusters forming icosahedral neighborhoods (IN's) more than triples on going to high s ; it continues to increase to the limit of this study [Fig. 9(e)]. The IN's are distributed randomly in the film [Fig. 1(b)]; there is little indication of clustering or of avoidance in their distribution for small clusters (Fig. 12); large clusters seem overrepresented at large s but the numbers

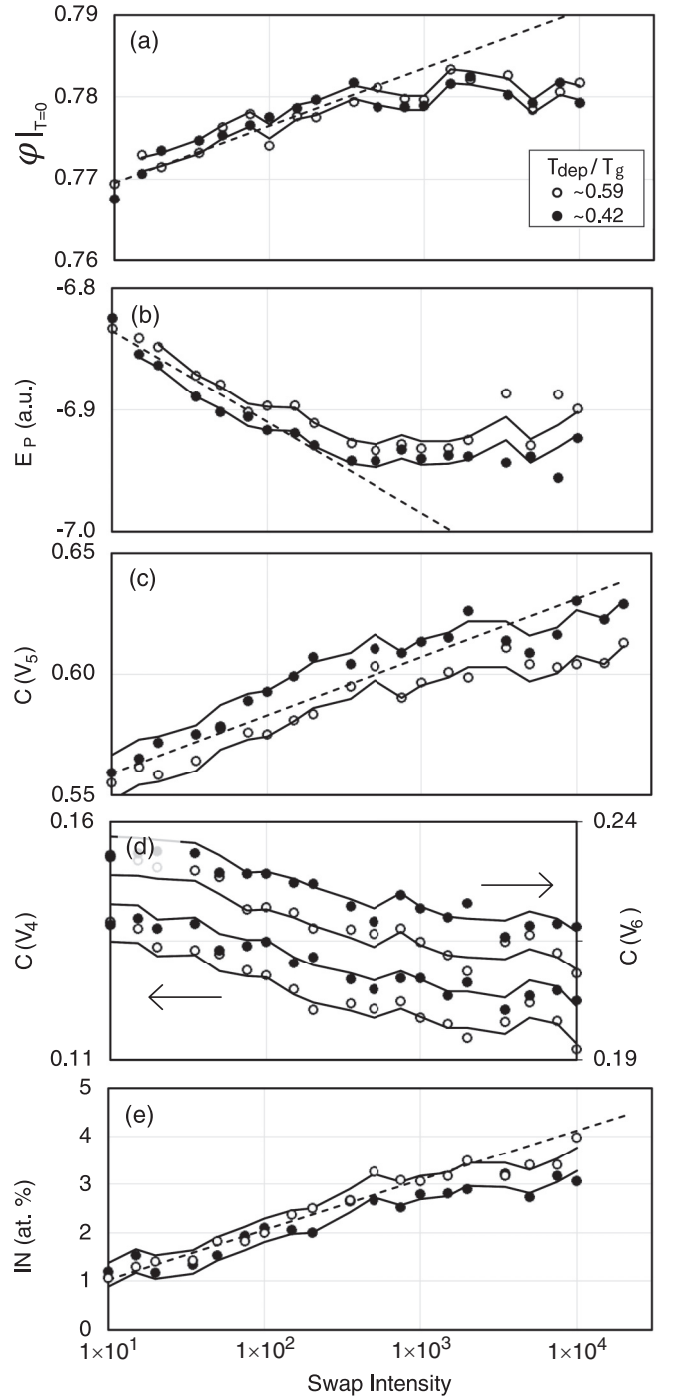


FIG. 9. (a) ϕ , (b) E_P , (c) $C(V_5)$, (d) $C(V_4)$ and $C(V_6)$, and (e) IN concentration vs s after cooling to $T \sim 0$ for films deposited at $T_{\text{dep}}/T_g \sim 0.42$ (●) and ~ 0.59 (○). The data points are averages of four simulation runs of similar temperature. The dashed lines have been added to suggest that each parameter, $X(s)$, initially varies linearly with log swap intensity. The pairs of solid lines mark the $X(s) \pm \sigma_{\text{av}}$ values, where σ_{av} is the average over all s of the standard deviation of X observations at each s .

are too small (cluster sizes $\gtrsim 10$ appeared in half of 13 cases) to say much quantitative about that. A quick study showed the IN concentration is unchanged in films grown with half the compression.

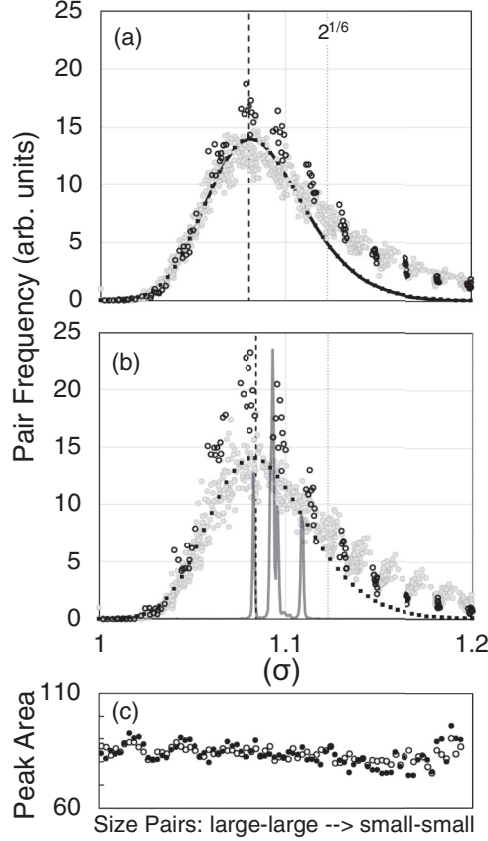


FIG. 10. The circles show the distribution of separations at $T = 0$ between every combination of sphere pair type for L-J 12-6 interaction cut off at 3.0σ and pair height ($5 < z < 30$). The separation is scaled by the σ for that pair. The data is shown for two swap intensities: (a) low ($10 < s < 35$) or (b) high ($5 \times 10^3 < s < 2 \times 10^4$). The thick dotted black lines show the distribution of separations expected for sphere pairs thermalized in a L-J 12-6 potential with the addition of an effective temperature and compressive force that were adjusted to match the peak in the observed distribution. That force reduced sphere pair separations by 3.5% compared to that expected for isolated pairs ($\sigma = 2^{1/6}$; dotted lines). The highly swapped films ($s = 5 \times 10^3 - 2 \times 10^4$) showed a marked narrowing of the distribution for the smallest spheres ($\sigma = 0.900, 0.927, 0.955, 0.982$). The gray line in (b) shows the pair separation distribution for monosized L-J spheres arranged in an hcp crystal; the distribution height scaled to fit on the graph. (c) shows the area under the peak in (b) for each combination of pair sizes for low- s ($\circ$) and high- s ($\bullet$) films. The values (in arbitrary units) are proportional to the average number of neighbors for each combination of pair sizes. The combinations are ordered from large-large on the left to small-small on the right.

IV. DISCUSSION

The saturation of $\phi|_{T=0}$ at ≈ 0.78 for large s almost independent of T_{dep} suggests the films reach some fundamental packing limit. That it is the same as its analog crystal, a hexagonal-close-packed crystal of monosized L-J spheres ($\phi_{\text{xtal}} = 0.777$) is surprising. The continuous decrease of the fourfold and sixfold symmetries with increasing s [Fig. 9(d)] and the unchanging breadth of the pair distribution [Figs. 10(a) and 10(b)] rule out local crystalline ordering [38], and the unchanging area under the pair frequencies

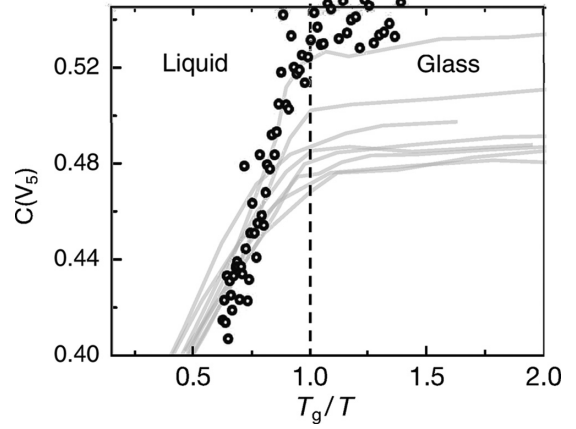


FIG. 11. The evolution of $C(V_5)$ for this system as it is cooled from the melt overlain on simulations by Hu *et al.* [39] of two- and three-element metallic glasses (the bottom cluster of lines and the top three, respectively).

[Fig. 10(c)] rules out phase separation. These all suggest that the ϕ 's seen here are near the maximum random jamming value. The density deficit one might expect from the disorder in these films ($\approx 14\%$ for monosized arrangements)³ seems to have been offset by the size dispersion which give some freedom to arrange the local distribution of sizes for best fit. Such increasing of density with size dispersion is consistent with several recent studies in L-J packings [40,41] and with packing of hard ellipsoids where it is the freedom to choose local orientations that allows for denser packing [42].

It is evident that increasing s drives a continuing structural evolution away from crystal ordering and toward pentagonal symmetry. The idea of disordered films having local tetragonal symmetry and even icosahedral structure is not new. Their existence as isolated clusters was suggested by Frank about 70 years ago [43] to explain the ease of liquid metal supercooling. And their existence was shown recently by Hu *et al.*, [39] in simulations of multielement metallic glass. The values of $C(V_5)(T)$ become sensitive to simulation details for $T \sim T_g$, being smallest for binary, larger for ternary mixtures, and largest for the 12-component glass presented here (Fig. 11). This work takes their observations a step further, showing that $C(V_5)$ can increase substantially beyond what had previously been observed (from $\sim 52\%$ up to $\sim 63\%$). Moreover, with increasing concentration, the regions with five-fold symmetry expand their domains; they make local clusters that then extend to make icosahedral neighborhoods. And they, in turn, aggregate into larger groups (Fig. 12). At the limit reached by this study, one finds clusters of > 10 IN's and most of the spheres are either an IN core or part of its periphery (Fig. 13). The radius of an icosahedron is some 5% smaller than its edge, so it is natural that the cores tend to be in the lower half of the size distribution.

³The disordered maximally random-jammed (mrj) (Torquato *et al.*, [38]) and crystalline hexagonal-close-packed (hcp) limits are $\phi_{\text{mrj}} \approx 0.64$ and $\phi_{\text{hcp}} = 0.74$, respectively.

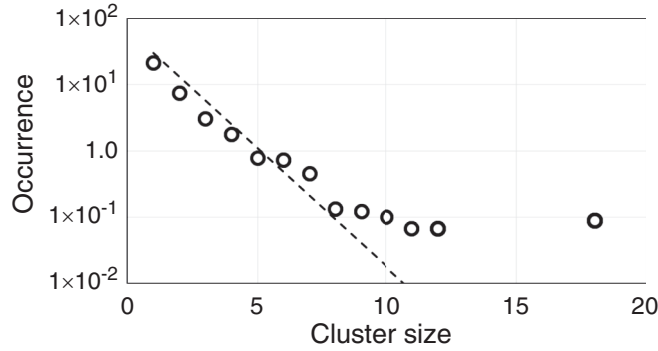


FIG. 12. Occurrence of clusters vs the number of icosahedral neighborhoods they contain. The data averaged over 13 highly swapped films, containing an average of 3.8% IN's. A prediction derived from simple expectations of cluster size assuming 12 neighbors for each sphere and random positioning is shown by the dashed line.

Apparently the freedom to adjust the local sphere size distribution enables this system to relax toward a dominantly icosahedral local structure. At longer distances those local symmetry axes are randomized by the local distortions necessary to allow pentagonal growth. The only limitation to such a final state would seem to be the availability of the necessary distribution of sphere sizes. It can be seen in Fig. 13 that the IN's require rather more of the smaller and the largest of the spheres than the middle of the range. A lack of the appropriate sizes might limit IN concentration for the uniform distribution used here. Possibly a broad bipeaked 1.25:1 size distribution would enable one to reach (in a very long time) a completely icosahedral local structure.

V. CONCLUSIONS

We have shown, combining Monte Carlo swapping of size-dispersed spheres to explore configuration space with a molecular dynamics simulation to settle into configurational minima, that a moving swap region speeds structural equilibrium, allowing it to proceed at temperatures $T_{\text{dep}} \ll T_g$. This approach led to the discovery of a maximally dense film and the further discovery that its ultimate disordered state is not completely defined by its packing fraction. Rather, it appears (i) that the degrees of freedom inherent in the spatial distribution of sphere sizes are exploited to continue structural

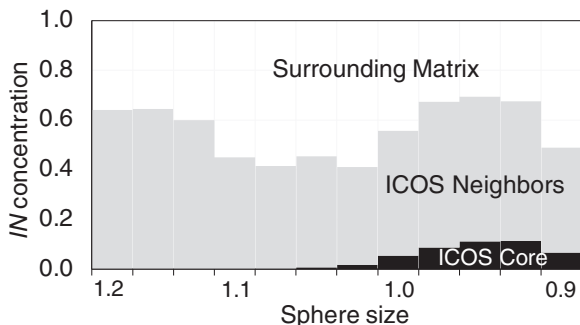


FIG. 13. Fraction of spheres of each size that are either IN cores or associated with IN's.

optimization, and (ii) that the variable geometric distortion of local clusters caused by that same size distribution allow a reduced-strain packing of local icosahedral order with minimal interstitial structures. The result being, in this case, that local pentagonal symmetries aggregate into larger and larger clusters to the limit of this work.

ACKNOWLEDGMENTS

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DATA AVAILABILITY

The data that support the findings of this article are openly available [44,45].

APPENDIX A: SIMULATION CODE

The molecular dynamics simulations described in this article used LAMMPS [45–47], with modifications to the modules `fix_atom_swap` that allow a user to optionally restrict max pair separation, to select swap pairs from a list of many atom types, and to return statistics on the fraction of accepted swaps as a function of separation and in `fix_deposit` to optionally allow random choice of deposit type from a list of many atom types. The simulations were run using dimensionless Lennard-Jones (L-J) units.

APPENDIX B: SYSTEM PARAMETERS

The size-dispersed spheres in these simulations interacted by a L-J 12-6 potential with 12 uniformly spaced parameters spanning 25% in size: $0.9 < \sigma_{ii} < 1.2$ (relative standard deviation $\sigma \approx 24\%$), and in interaction energy: $0.75 < \epsilon_{ii} < 1.0$; $m_i = 1$. The bottom spheres had $(\sigma_{ii} = 0.75, \epsilon_{ii} = 10.0)$ and were frozen to form a rigid layer. The effective size and interaction strength between unlike types $(\sigma_{ij}, \epsilon_{ij})$ were the geometric average of their respective parameters $(\sigma_{ij} = \sqrt{\sigma_{ii}\sigma_{jj}})$, which slightly disfavors unmixing.⁴ Little difference was found between films made using arithmetic vs geometric calculation of σ_{ij} , and ϵ_{ij} : ϕ increased at a similar rate, but was $\sim 1/2\%$ smaller using the linear scheme (consistent with the effective size increase) and had $\sim 1\%$ lower T_g . The first peak in the self-rdf of sphere pairs showed that all of their pair

⁴For the work presented here, the maximum nonadditivity (the difference between the geometric and arithmetic average) is $\Delta\sigma \approx 0.01$, about 1/3 the minimum value used by Ninarello *et al.* [20].

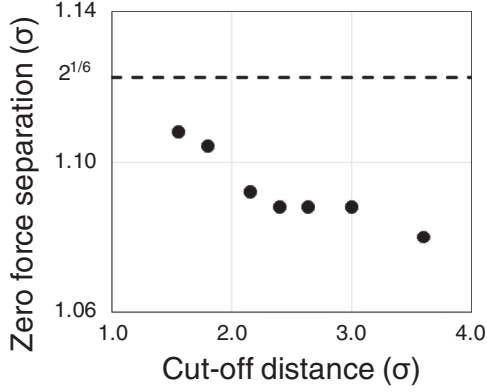


FIG. 14. Zero-force pair separation r_0 vs L-J potential cutoff distance. The dashed line indicates the separation expected for an isolated pair. The work presented here has cutoff distance = 2.5σ .

separations were reduced by 3.5% compared to isolated pairs (Fig. 10); the area under the peaks were the same for each size pair, and did not change at high ϕ , indicating no size-selective separation with swapping. Reducing the σ_{ii} cutoff from 2.5 to 1.8 [reducing sphere-sphere compression by about half (Fig. 14)] reduced T_g by 15% (to 0.256), but had no noticeable effect on rate of densification or the occurrence of IN's.

The metastability of the disordered film structure was tested by building films using size spans from 15%–35% [Fig. 15(a)]. Crystallites always formed in 15% films; their growth distorted the growth surface into a freestanding column. They appeared about 1/4 of the time in 18% films, generally as small clumps at the bottom of the film. They essentially never formed as more than a few isolated nuclei for spans of 20% or higher. The maximum IN growth was found in 25% films [Fig. 15(b)].

APPENDIX C: FILM GROWTH

The film construction process interleaves (i) a deposition and (ii) a mobility phase. The deposition phase adds ~ 0.1 atomic layer (randomly placing 12 spheres of randomly cho-

sen sizes for the smaller simulation, 48 for the larger) in 100 time steps (one step = 0.005τ).⁵ That is as fast as could be managed without creating a local pile on the surface. Inserted spheres started just above the existing surface with a small downward velocity. The mobility phase swapped randomly chosen atom pairs using the Metropolis rule [26] in a region six thick starting one below the top of the film. The film evolution was not sensitive to the region's thickness and position; quick tests when setting up this work showed <30% change in stabilization for thickness 2–8 and depths 0–5. The swaps occur at intervals of 100 time steps to allow local structures to equilibrate after each swap, and there are 6 s swaps ($s \equiv$ swap intensity) during this phase. Both deposition and swapping proceeded $5\times$ more slowly for the first 10–20 cycles because of the very slow energy thermalization of energy occurring with small atom numbers; three-body collisions, required to thermalize, are relatively rare at that point. The film was built to a height of 36 for the smaller simulation (about 3×10^3 spheres, filling 90% of the computation space) at a temperature controlled between $T = 0.12$ and 0.30 ($0.41 T_g$ – $1.0 T_g$, where $T_g = 0.2965$), and with swap intensities between 10 and 2×10^4 .

APPENDIX D: ANALYSIS

The resulting films were thermocycled from $T = 0.21$ to ~ 0.50 ($0.71 T_g$ – $1.7 T_g$) at a rate $\dot{r}_0 = 1.53 \times 10^{-8}$ per time step.

One can approximate these film properties in real units assuming the spheres have the property of argon atoms [48]: $\epsilon/k_B = 120$ K, $\sigma = 3.4 \times 10^{-10}$, and mass = 0.04 kg/mol. Those parameters result in $T_g = 40$ K, $\tau = 2$ ps, the standard heating rate 4.2×10^5 K/s, and the deposition rate from 3.4×10^8 to 3.4×10^5 nm/s for swap intensity 10 and 1×10^4 , respectively (taking 100 atoms/monolayer).

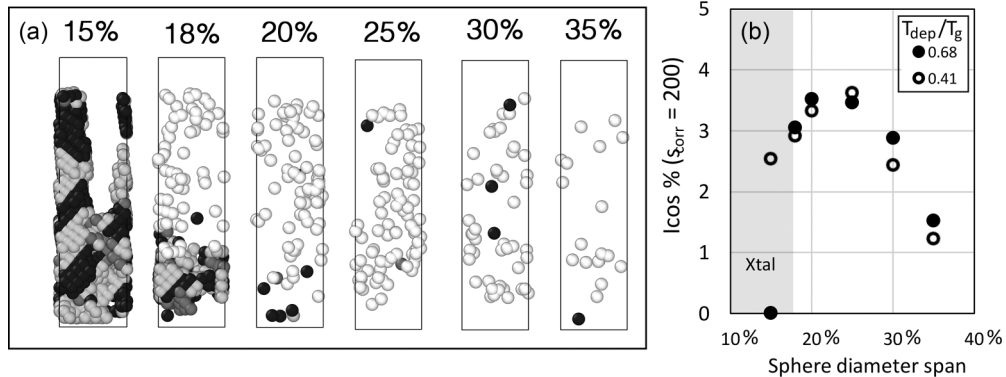


FIG. 15. (a) Rendering of films created with indicated sphere size span, all deposited at $0.41 T_g$ with swap intensity 350. Spheres in a face-centered cubic, hexagonal close-packed, body-centered cubic, or icosahedral environment are shown with $\bullet$, $\bullet$, $\bullet$, or $\circ$, respectively; all others have been erased. These images were created using OVITO [24]. (b) For each of the films in (a), the concentration of spheres in icosahedral environments vs the sphere size span. The environment determination was done using the common neighbor analysis function in OVITO.

⁵ $\tau \equiv \sqrt{m\sigma^2/\epsilon}$ is an approximation of the fastest oscillation frequency in the assembly.

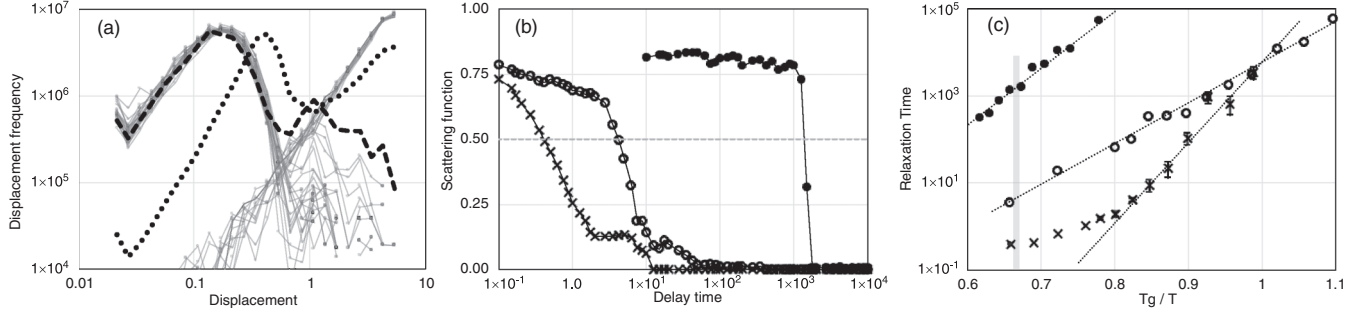


FIG. 16. (a) The displacement spectrum of a highly swapped film with $T_{\text{dep}} = 0.41T_g$ and $T_{\text{rel}} = 1.5T_g$ plotted after delays spaced by 25%. The heavy dashed and dotted lines, at delays of 1.25 and 1.5×10^3 time steps, respectively, mark the breakdown of the caged vibrations and correspond to the two points on the scattering function cliff in (b). (b) The self-intermediate scattering function at $T = 0.45$ for three cases: A highly swapped film ($\bullet$) with $T_{\text{dep}} = 0.12$ and $s = 2 \times 10^4$ whose $T_{\text{rel}} = 1.5T_g$; that film melted and cooled to a solid ($\circ$) then rapidly heated to T_g , and a liquid equilibrated for some time at $T_{\text{eq}} = 1.5T_g$ ($\times$). (c) shows the variation of structural relaxation times (T_{rel} defined to be $f = 0.5$) with anneal temperature for the three cases in (b). The data in (b) was taken at the temperature marked with the vertical bar. Multiple analyses of the equilibrated liquid were made using variable anneal times to ensure it had reached structural equilibrium; the bars show the uncertainty $\equiv \pm \sigma / \sqrt{n}$ from multiple measurements; the uncertainty becomes insignificant at higher temperatures, and was not significant for the other cases. The m -value is taken from the slope of t_{rel} on approaching T_g .

Data from the second melt and freeze cycle from many simulations⁶ was averaged to accurately determine $\varphi(T)$ for the liquid-cooled glass. That data was fit to straight lines whose intersection defines T_g ($T = 0.2965$) (Fig. 6). φ was calculated by taking the diameter of each particle equal to its L-J potential minimum, $r_i = 2^{1/6}\sigma_{ii}$. The mobility d is determined from those same runs by calculating the average sphere displacement for structures separated by 8×10^4 time steps (400τ). The mobility shown in Fig. 6(b) is the average of those values for all spheres between heights 10 and 25 (0.25 and 0.625 as a fraction of box height). The temperature dependence of that average is very well fit by $d_{\text{fit}}(T) = a * \tanh(T) + b * T$ [Fig. 5(b)]. Binning the mobility by height, as in Fig. 7, allows detection of internal flaws or surface melting, whose presence would invalidate a film run. s_{gl} , the factor by which the structural relaxation kinetics is slowed for a low-temperature, highly swapped film compared to a liquid-cooled film, can be determined using the self-intermediate scattering function $F_s(k, t) = \langle f_s(k, t) \rangle = \langle \frac{1}{N} \sum_j e^{i\mathbf{k} \cdot [\mathbf{r}_j(t) - \mathbf{r}_j(0)]} \rangle$ where the vertical expansion during relaxation is eliminated by ignoring any z displacement, which, with assumed isotropy, allows $\mathbf{k} \cdot \Delta \mathbf{r} \Rightarrow 2/3 k \Delta r$. $k = 7.2$, is a convenient value for displaying the breakdown of caging behavior [28,49] [Fig. 16(a)]. That breakdown is quite abrupt for the highly swapped films ($\bullet$), more gradually for the as-quenched ($\circ$) and the equilibrated liquid ($\times$) films [Fig. 16(b)]. For the liquid, the kinetics analysis was delayed after reaching the anneal temperature to ensure structural equilibrium. The structural relaxation time t_{rel} is taken here as $F_s(k, t|_{\text{relax}=0.5})$. One can plot $\ln t_{\text{rel}}$ as a function of the anneal temperature [Fig. 16(c)] to get the activation energy of the fixed-structure solid films, and for the structurally equilibrating liquid.

For structural analysis, the films were cooled to $T = 3 \times 10^{-4}$ ($E_K < 10^{-4} E_P$, where E_K and E_P are the film's kinetic and potential energy, respectively). A LAMMPS Nose-Hoover barostat function was used to maintain zero lateral pressure by appropriately shrinking the side wall dimensions. The hcp crystal was similarly cooled. The resulting pair distribution function [Fig. 10(b)] showed a nearest-neighbor peak compressed the same amount as the average for the disordered system. The structure was very ordered; common neighbor analysis showed no icosahedral neighborhoods; it almost completely hcp. Voronoi analysis gave $C(V_5) = 0.01$ while $C(V_4) = 0.30$ and $C(V_6) = 0.39$.

The partial static structure analysis was calculated for every combination of sphere sizes, and plotted vs the σ specific to their potential. Figure 10(a) shows the first peak for the as-made film and Fig. 10(b) that made with large s .

Voronoi tessellation [34], which divides the film into polyhedral cells centered on each atom with each face bisecting the distance to the next, can sensitively detect the presence of various symmetries around each individual atom. The Voronoi tessellations were analyzed for the concentration of four-, five-, and six-sided facets; $C(V_4)$ and $C(V_6)$ indicated a potential crystal environment and $C(V_5)$ disorder.

Common neighbor analysis examines the slightly larger scale of pairs of atoms [34,35]. It classifies the environment of each pair of neighboring particles using the first two peaks of the pair correlation function to determine (i) number of common neighbors of the pair, (ii) the number of nearest-neighbor bonds among these common neighbors, and (iii) the length of the longest chain which can be formed with these bonds. Fivefold symmetries are singled out with the (1,5,5) classification, which identifies a pentagonal bipyramid (half of an icosahedron) [35]. Other symmetries, such as hexagonal close-packed and body or face centered cubic have distinctly different signatures; they appear only rarely in the films made in this study [$\sim 0.1\%$; Fig. 15(a)]. That approach has proved useful in discriminating local structures in, e.g., clusters and nanoparticles [50].

⁶One melt cycle was sufficient to completely erase the structure of the previous glassy state; there were no differences found on subsequent cycles.

There was little evidence of anomalous clustering or avoidance of these icosahedral neighborhoods; they were distributed throughout the film [Fig. 1(b)] and the frequency of cluster sizes (for size <8) decreased geometrically with a

slope consistent with a random distribution model: the product of the concentration of such neighborhoods in the film times the number of atom contacts (assumed to be 12) (Fig. 12). Large clusters (size >10) were overrepresented.

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