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## A molecular view of vapor deposited glasses

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Recently, novel organic glassy materials that exhibit remarkable stability have been prepared by vapor deposition. The thermophysical properties of these new “stable” glasses are equivalent to those that common glasses would exhibit after aging over periods lasting thousands of years. The origin of such enhanced stability has been elusive; in the absence of detailed models, past studies have discussed the formation of new polyamorphs or that of nanocrystals to explain the observed behavior. In this work, an atomistic molecular model of trehalose, a disaccharide of glucose, is used to examine the properties of vapor-deposited stable glasses. Consistent with experiment, the model predicts the formation of stable glasses having a higher density, a lower enthalpy, and higher onset temperatures than those of the corresponding “ordinary” glass formed by quenching the bulk liquid. Simulations reveal that newly formed layers of the growing vapor-deposited film exhibit greater mobility than the remainder of the material, thereby enabling a reorganization of the film as it is grown. They also reveal that “stable” glasses exhibit a distinct layered structure in the direction normal to the substrate that is responsible for their unusual properties. © 2011 American Institute of Physics. [doi:10.1063/1.3586805]

### I. INTRODUCTION

Glasses are disordered materials that lack the long-range order of crystals but behave mechanically like solids.<sup>1–6</sup> Glasses are traditionally prepared by rapid cooling or quenching of a liquid below its melting point. In the absence of crystallization events, cooling of the liquid leads to slower dynamics, which eventually becomes so slow that the supercooled liquid is unable to remain in equilibrium.<sup>7</sup> The temperature at which the system falls out of equilibrium is the glass transition temperature ( $T_g$ ), and its precise value depends on a number of factors, including the cooling rate. If a liquid is cooled slowly, it has more time to sample a configuration space and it can reach lower temperatures before falling out of equilibrium and entering a glassy state. It is widely appreciated that the properties of a glass depend on the process by which it is formed,<sup>3</sup> and that  $T_g$  increases with cooling rate.<sup>1</sup> For many organic liquids,  $T_g$  decreases 3–4 K for every order-of-magnitude decrease in the cooling rate.

Theoretical research over the last few decades has established that a glassy state can be characterized in terms of a potential energy landscape, with thermodynamics and kinetics controlled by the minima and barriers on the landscape, respectively.<sup>8–10</sup> In terms of potential landscape theory, the supercooled liquid-to-glass transition is a kinetic event based on relaxation times growing rapidly as the temperature is decreased. Work to date has largely focused on understanding the nature of slow dynamics in supercooled liquids.<sup>11–20</sup>

Recently, a new experimental approach has been developed to prepare glasses that are considerably more stable than “ordinary” glasses.<sup>21–29</sup> In that approach, small organic molecules, such as 1,3,5-trinitrobenzene (TNB), indomethacin (IMC), or toluene are vapor deposited onto

a cold substrate.<sup>30</sup> The resulting materials, referred to as “stable” glasses, have a lower enthalpy (by as much as 10 J/g) and a higher density (by 0.5%–1.5%) than the corresponding “ordinary” glass.<sup>21–23, 28, 29, 31</sup> The experimental literature on “stable” glasses has also revealed the existence of an optimal substrate temperature for formation of the most stable glasses, which occurs at ~80%–85% of the ordinary glass transition temperature of the molecule under consideration.<sup>21–23, 28, 29, 31</sup> Leon *et al.*<sup>28</sup> reported that aging a thick vapor-deposited layer of toluene at 110 K for several hours did not modify the overshoot peak of the heat capacity nor the onset temperature; the absence of aging effects suggests that their vapor-deposited glasses did not progress further down into the potential energy landscape, implying that the molecular arrangement is already in a deep energy minimum. That is, the glass film is already in a dense state, free of voids, and aging does not lead to further densification. This is consistent with observations by Ishii *et al.* for ethylbenzene.<sup>31</sup>

Simple temperature extrapolations of various properties indicate that in order to match the measured properties of “stable” vapor-deposited glasses, a supercooled liquid would have to be gradually cooled over a period of at least 1000 years.<sup>21–23</sup> It has been proposed that the formation of such stable glasses is enabled by the enhanced molecular mobility that arises at the surface of a growing vapor-deposited glass film; because every molecule in the glass was, at some point in time, part of a mobile surface layer, and because that surface region can explore phase space more efficiently, the entire sample is closer to equilibrium at the end of the deposition process than would otherwise be possible (e.g., in a traditional quenching process).<sup>21–23, 28, 29, 31</sup> A variety of arguments have been advanced to explain the properties of “stable” glasses. Chief amongst these are the existence of an underlying first order phase transition (and the formation of a distinct new polyamorph),<sup>32–43</sup> the formation of nanocrystals

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in the sample,<sup>26</sup> or the formation of a layered structure.<sup>26</sup> In the absence of a molecular level characterization of the glasses, it has been difficult to discuss the merit of each of these propositions.

In this work, we present a first detailed computational study of the structure and properties of a vapor-deposited glass of trehalose, a disaccharide of glucose. Its properties have been studied extensively as a part of efforts to develop excipients for long-term storage of pharmaceutical and biomedical products.<sup>44–49</sup> More importantly, available atomistic models have been shown to be capable of describing the properties of trehalose solutions and glasses quantitatively.<sup>48–51</sup>

By following a computational protocol that emulates the main features of laboratory vapor-deposited glass formation processes (see Methods section for details), we are able to prepare glasses that exhibit the key experimentally observed attributes of “stable” glasses. These include an enthalpy that is 9.5 J/g lower than that of glasses prepared by quenching the liquid, the existence of an optimal substrate temperature which is  $\sim 86\%$  of the glass transition temperature of an ordinary trehalose glass (388 K),<sup>49,52,53</sup> a significantly higher onset temperature during heating, and a density that is about 2% higher than that of the ordinary glass. Our structural analysis of our “stable” vapor deposited glasses reveals that their unusual properties are the result of a distinct layered structure, which is very different from that of the corresponding crystal and ordinary glass.

## II. METHODS

In the experiments of Refs. 21 and 27, glass-forming molecules were deposited from a vapor phase onto a substrate consisting of a  $\text{SiN}_x$  membrane suspended on a silicon frame. The deposition process was carried out in a vacuum chamber ( $P \approx 10^{-9}$  mbar). Hot molecules were evaporated from a crucible at  $T_h$ , onto a substrate whose temperature was kept constant (at  $T_s$ ). The deposition rate was adjusted by controlling the temperature of the crucible, and was monitored with a quartz crystal microbalance. In essence, the experimental process consists of depositing hot molecules onto a temperature controlled substrate at a controlled rate.

In our simulations, we used a substrate consisting of Lennard-Jones particles with characteristic size and energy chosen to correspond to those of silica ( $\sigma = 3$  Å,  $\epsilon = 5.2$  kJ/mol, mass = 60, and density = 2650 g/L). One layer of particles was organized in a fcc(111) planar arrangement, with atoms restrained to their positions by a harmonic potential with spring constant  $K = 10^3$  kJ/mol nm<sup>2</sup>. The simulation box was kept periodic only in the  $x$  and  $y$  directions (parallel to the silicon substrate). The volume of the system was kept constant, but the length of the simulation box in the  $z$  direction (perpendicular to the substrate) was sufficiently large to encompass a growing glass film and a vacuum region into which molecules were gradually introduced. Hot trehalose molecules ( $T_h = 500$  K) were brought into the vacuum region of the box, in batches of 1–5 molecules, and were placed at a random lateral location and with a random orientation at a distance 2 nm above the nearest molecule in

the film. After the addition of “hot” molecules, the energy of the entire system was minimized using a Polak-Ribier conjugate gradient scheme as implemented in the GROMACS simulation package.<sup>54</sup> The maximum force criterion on each particle was set to be less than 1 kJ/mol-nm to facilitate convergence of the energy minimization scheme.

The minimization was followed by an equilibration run of 100 ps, maintaining the temperatures of “hot” molecules at  $T_h$  and the rest of the system at  $T_s$  through the use of two Nosé-Hoover thermostats. These steps cause the “hot” molecules to approach the already deposited molecules (the film) in an accessible amount of simulation time. The temperature of the “hot” molecules was then gradually brought down (at a rate of 0.1 K/ps) to the temperature of the substrate. During the cooling step the “hot” molecules adsorb on the surface of the film and have an opportunity to diffuse on that surface. The cooling step was followed by an equilibration, at  $T_s$ , for 200 ps. A final energy minimization step was then performed. The sequence of steps outlined above was repeated until a desired film thickness was attained (up to 14 nm). The rate of deposition was kept constant throughout a given simulation by controlling the cooling time and the number of “hot” molecules added per batch. The described step-by-step batch process leads to a close resemblance with the experimental procedure of Refs. 21 and 27. Molecular simulations were performed using a variant of the GROMACS simulation package.<sup>55–57</sup> The all-atom optimized potentials for liquid simulations (OPLS) force field optimized for carbohydrate simulations<sup>58</sup> was used for trehalose. To enhance the statistics and evaluate finite-size effects, the deposition was studied for 15 different box sizes (all possible combinations of  $x = y = 4, 5, 7, 12,$  and  $18$  nm and  $z = 5, 10,$  and  $18$  nm). Six independent runs were performed for each of the box sizes, using different initial velocities for newly added “hot” molecules in all batches. All simulation boxes with sizes of  $x = y = 5$  and  $12$  nm with different combinations of  $z$  box sizes, were studied for three different substrate temperatures ( $T_s = 300, 330, 350$  and  $380$  K). For all other box sizes only the optimal substrate temperature of 330 K was considered. The properties reported in this work therefore represent averages over more than 200 independent realizations of the thin films (see supplementary material).<sup>59</sup>

The “ordinary” glasses were prepared by cooling down the liquid at a rate of 1 K/ns. To that end, a procedure described in Ref. 51 was used. Ten independent runs with random initial configurations were performed to enhance the statistics. In addition to these ten independent runs, to evaluate the finite-size effects a single large configuration was produced by replicating the simulation box in all three directions. That structure was then equilibrated and cooled down using the same protocol.

Simulations of the crystal structure of trehalose were performed in order to compare the structure, energy, and density of the crystal to those of the stable glass. The initial structure for simulations of the crystal was taken from the Cambridge Crystallographic Data Center via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) (CCDC# 668079). The details of the structure can be found in Ref. 60. Six independent runs for each of the two different box sizes in

$x = y = z = 5$  nm and 12 nm were used for generating sufficient statistics.

In order to bring all samples to a common low temperature, all simulation boxes were brought to 200 K gradually at a rate of 1 K/ns.

### III. RESULTS AND DISCUSSION

#### A. Enhanced stability

Differential scanning calorimetry experiments<sup>27,28,61</sup> measure the specific heat by gradually heating a vapor-deposited glass film; the temperature at which a sudden overshoot of the specific heat is observed is referred to as the “onset” temperature. Past studies of TNB, IMC, toluene, and ethyl benzene<sup>21,22,28,29,31</sup> have shown that “stable” glasses have a higher “onset” temperature than ordinary glasses. Such an increased onset temperature is indicative of a higher stability of the material, as more energy is required to dislodge molecules from the glassy state. Our simulated vapor deposited trehalose glasses were heated from 200 K at a rate of 1 K/ns. The specific heat was determined from fluctuations of the energy; results are shown in Fig. 1. The most “stable” vapor deposited glass has an onset temperature about 80 K higher than the “ordinary” glass, consistent with experimental observations. Note that ordinary glasses are simulated by isobaric cooling at a rate of 1 K/ns to a temperature of 200 K, at a pressure of 1 bar.

Laboratory “stable” glasses have been observed to have a specific heat that is about 5% lower than that of “ordinary” glasses.<sup>29,31</sup> Our simulated stable glasses also exhibit such a lowering of the specific heat at low temperatures (below 300 K). At higher temperatures, the error bars become comparable to the actual values and we cannot draw definite conclusions regarding the lowering of the heat capacity.

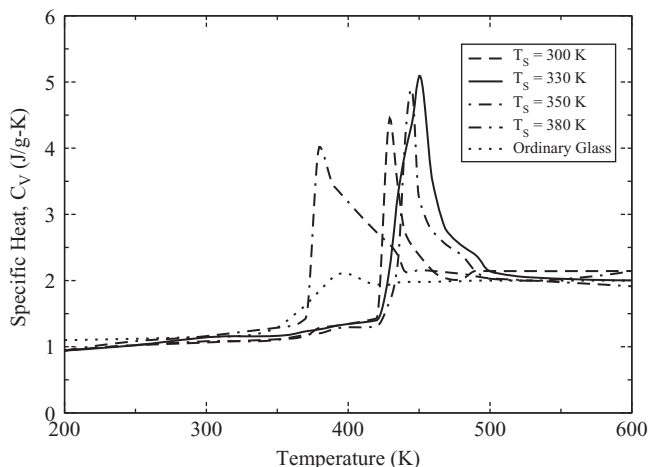


FIG. 1. Specific heat of trehalose glasses at various temperatures. The thin dotted line corresponds to an “ordinary” glass prepared by slow cooling of the liquid at a rate of 0.001 K/ps and a pressure of 1 bar. Dark lines represent “stable” glasses prepared by vapor deposition with a substrate of 300, 330, 350, and 380 K. The dark solid line represents the most “stable” glass prepared with a substrate temperature of 330 K. The specific heat has been measured from the fluctuations of the energy measured during heating of the glass samples at a rate of 1 K/ns. Results reported have been averaged over 6 independent trajectories for each substrate temperature simulation performed with a box size of  $x = y = 12$  nm and  $z = 18$  nm.

TABLE I. Difference in energy, density, and  $Q_6$  order parameters (See Refs. 66–68) for glasses prepared by different methods. A positive value for the difference in energy indicates that the energy is higher than that of the reference system. The energies are within  $\pm 0.14$  J/g of the corresponding values for the “ordinary” glass, while densities are within  $\pm 19$  g/L. Results reported have been averaged over 90 independent trajectories for the “stable” glasses prepared at the substrate temperatures of 330 K and over 36 independent trajectories for all other cases of “stable” glasses. The results for the “ordinary” glasses and the “crystal” structure have been averaged over 11 and 12 independent trajectories, respectively.

Process	Physical Conditions	Energy Difference <sup>a</sup> (J/g)	Density (g/L)	$Q_6$ Parameter
Vapor deposition	$T_S = 300$ K	+4.1	1467	0.0029
	$T_S = 330$ K	−9.5	1511	0.0105
	$T_S = 350$ K	−7.5	1509	0.0098
	$T_S = 380$ K	−2.9	1482	0.0057
Ordinary glass	$P = 1$ bar	...	1480	0.0021
	$P = 5$ K bars	−1.5	1505	0.0016
	$P = 20$ K bars	+1.2	1682	0.0011
	$P = 50$ K bars	+7.3	1798	0.0004
Crystal	$\rho = 1480$ g/L	+1.3	1480	0.0019
	$P = 1$ bar	−10.8	1528	0.57

<sup>a</sup>The energy difference has been calculated with respect to a reference system consisting of the “ordinary” glass prepared by gradual cooling of the liquid at 1 bar. All properties are reported here at 200 K. The energy represents only the potential energy of trehalose molecules in the system.

The energy and the density of glasses prepared by different methods are listed in Table I. Energy differences are reported with respect to the ordinary glass at 200 K. The most “stable” vapor-deposited simulated glass has 9.5 J/g less energy than the “ordinary” glass. These results are well within the experimental values reported for vapor-deposited “stable” glasses.<sup>21–23,28,29,31</sup> The density of the most stable glass produced here is higher than that of the ordinary glass by about  $1.9\% \pm 0.92\%$ , consistent with experiments. In order to establish whether such an energy increase is directly caused by the change in the density or not, we also compare results for glasses prepared by cooling supercooled trehalose at higher pressures, ranging from 5 to 50 000 bar. While the densities of such glasses are also found to be considerably higher than that of the “ordinary” ambient-pressure glass, their energies (with the exception of glasses formed at 5000 bar pressure) are found to be actually higher. These results indicate that “stable” glasses are energetically different from merely pressurized, high-density glasses, and suggest that the origin of stability is structural (see below). Future references to the “stable” vapor deposited glass refer to the one formed with an optimal substrate temperature of 330 K, unless otherwise specified.

#### B. Enhanced mobility of particles at the surface

The molecular mobility of vapor-deposited glasses is determined by measuring the Debye-Waller factor, denoted by  $\langle u^2(z) \rangle$ , as a function of the distance from the substrate layer  $z$ . The analysis of Debye-Waller factors is common in the glass literature<sup>51,62–64</sup> because it can be extracted from both simulations and neutron scattering experiments. Furthermore, it is often interpreted as a measure of the free volume

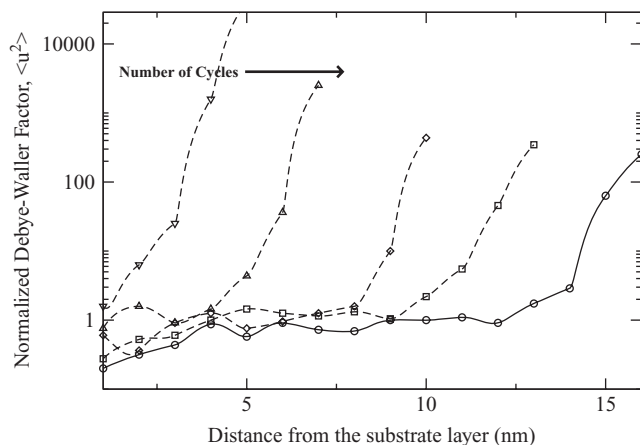


FIG. 2. Normalized Debye-Waller factor  $\langle u^2(z) \rangle$  for the “stable” glass as a function of the distance from the substrate layer. Different symbols represent different simulation time;  $\langle u^2 \rangle$  is represented on a logarithmic scale. Results are shown in increasing order of the number of growth cycles, as indicated by the arrow in the figure. The results correspond to the most “stable” glass prepared at a substrate temperature of 330 K, and have been averaged over 90 independent trajectories of different system size (as described in the Methods section).

surrounding a given particle<sup>64</sup> or, within the framework of the harmonic model, as a measure of the stiffness of a glassy matrix.<sup>62,63</sup> Various approaches have been adopted to calculate this parameter,<sup>62,64,65</sup> the most common of which is to take  $\langle u^2(z) \rangle$  as the mean-squared displacement after a specific amount of time, which can be chosen depending upon the physical phenomena of interest.<sup>64,65</sup> Choosing a short time near the beginning of the caging regime provides a reasonable measure of the free volume in the system.<sup>51,64</sup> Figure 2 shows  $\langle u^2(z) \rangle$  for a time window of 10 ps, normalized with the mean value observed in the bulk of the “stable” glass film, at various times during the vapor deposition process. The Debye-Waller factors were calculated by averaging particle displacements in a slab of thickness 1.1 nm over a time frame of 10 ps. A slab thickness of 1.1 nm was chosen based on the thickness of a layer, as deduced from the center of mass distribution shown in Fig. 6. We find that after the deposition of five to six layers, the normalized value of  $\langle u^2(z) \rangle$  becomes independent of the film thickness in the bulk of the film, but it exhibits significantly higher values near the free surface. These results confirm that molecular mobility at the surface of “stable” glasses is indeed more pronounced than in the bulk of the vapor-deposited material.

### C. Structural details

We now examine the structure of the “stable” glass, and compare it to that of crystalline trehalose and that of the “ordinary” glass. Note that the energy of the crystal structure is found to be within 2 J/g of that of the “stable” glass, and its density is higher than that of both the “ordinary” and the “stable” glasses. The local order in the material can be assessed by measuring the order parameter  $Q_6$  (Refs. 66–68) (see supplementary material for a definition of  $Q_6$ ).<sup>59</sup> Our analysis reveals that while the “stable” glass is significantly more ordered than the “ordinary” glass, it exhibits significantly less order than the crystal (see Table I).

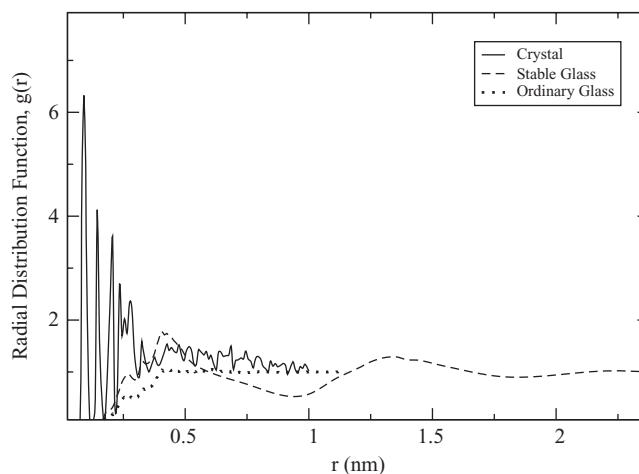


FIG. 3. All-atom radial distribution function (rdf),  $g(r)$ , for different systems. The solid curve represents the rdf of the crystal. The dashed and the dotted lines represent the rdf of the “stable” and the “ordinary” glass, respectively. The results shown have been taken from one of the trajectories of the most stable glass prepared at a substrate temperature of 330 K and a system size of  $x = y = z = 18$  nm.

The structure of the “ordinary” glass, the “stable” glass, and the crystal can also be compared by inspecting the corresponding all-atom radial distribution functions (rdf). These functions are plotted in Fig. 3. The differences are significant, and demonstrate that the packing arrangement in these three materials is not the same. These functions also serve to discard the possibility that “stable” glasses consist of small nanocrystals embedded in an ordinary glass matrix.

### D. Anisotropy

It is of interest to consider the structural details of the “stable” and the “ordinary” glasses in different directions; Fig. 4(a) shows the all-atom radial distribution functions of the two systems that arise when only the  $x - y$  directions parallel to the substrate are considered. The structure in these directions is remarkably similar, indicating that both the “stable” and the “ordinary” glasses exhibit similar packing arrangements along the plane of the substrate. In contrast, when a similar radial distribution function is calculated by only taking into account the  $z$  direction, normal to the substrate (see supplemental material for a definition of directional radial distribution functions),<sup>59</sup> a very different profile emerges for the “stable” glass [see Fig. 4(b)]. By construction, it remains unchanged from that in the  $x - y$  directions for the “ordinary” glass [Fig. 4(b)]. There is a pronounced anisotropic order in the “stable” glasses. The structural similarity of the “stable” and “ordinary” glasses in the  $x - y$  directions parallel to the substrate is evidenced by the  $Q_{6,\parallel}$  order parameter, calculated along the directions parallel to the substrate. (See Fig. S3 of the supplemental material).<sup>59</sup>

Additional evidence for the layered structure of “stable” glass films can be gleaned by direct observation of the material when molecules deposited at different time intervals of the growth process are represented by different colors. Figure 5 shows a representative configuration of the system extracted

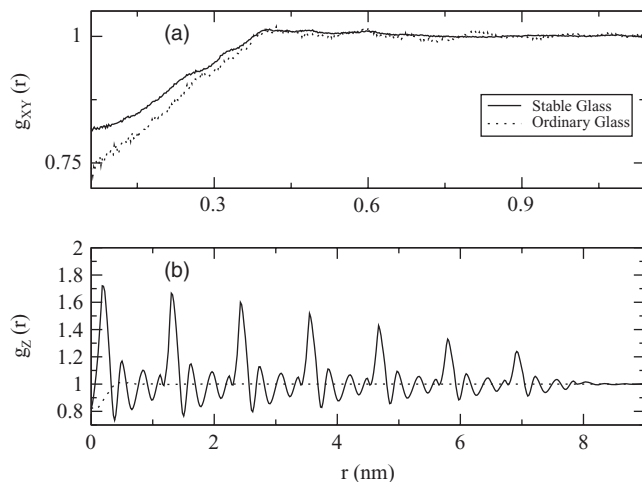


FIG. 4. Radial distribution function of the “stable” and the “ordinary” glasses measured in different directions. Plot (a) represents the rdf calculated by taking distances only in the  $x - y$  directions, along the plane of the substrate. Plot (b) represents the rdf calculated by taking distances only in the  $z$ -direction, normal to the substrate. The solid curve represents the rdf for the “stable” glass, and the dotted curve corresponds to the “ordinary” glass. The results shown have been taken from one of the trajectories of the most stable glass prepared at a substrate temperature of 330 K and a system size of  $x = y = z = 18$  nm.

from our simulations; the formation of layers is apparent. Figure 6(a) shows the local density of the center of mass of trehalose molecules as a function of the distance from the substrate layer. The periodicity of the density is consistent with the periodic layered structure shown in Fig. 5. The Fourier transform of the local density profile, shown in Fig. 6(b), exhibits a pronounced peak that is reminiscent of the additional scattering peak reported by Dawson *et al.* for

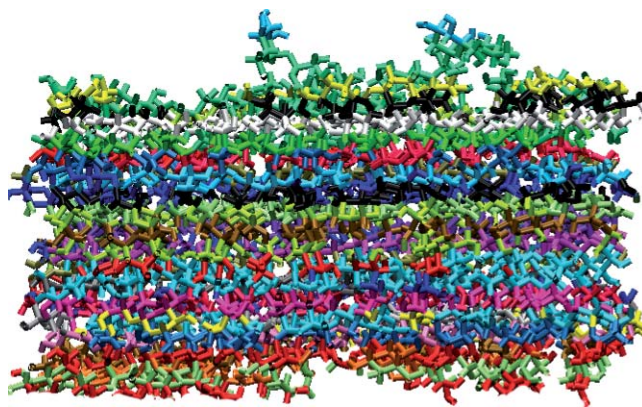


FIG. 5. Layered structures of the vapor-deposited “stable” glass (taken from an arbitrarily chosen trajectory). Representative configuration of a vapor-deposited “stable” glass system. Different colors represent molecules deposited during different time intervals throughout the deposition process.

“stable” glasses of IMC.<sup>26</sup> These results lead us to conclude that the scattering peak reported by Dawson *et al.* is due to the molecular anisotropy of “stable” glasses, and suggest that their unusual properties are the result of a layered structure induced by the formation process, as opposed to an underlying first order transition or the emergence of a new polymorph. It is worth noting that upon annealing, the scattering peak seen in IMC gradually disappears; the enhanced stability of the glass also disappears as the peak diminishes.<sup>69</sup>

#### IV. CONCLUSIONS

We have presented a molecular simulation study of vapor-deposited “stable” glasses of trehalose. While there is

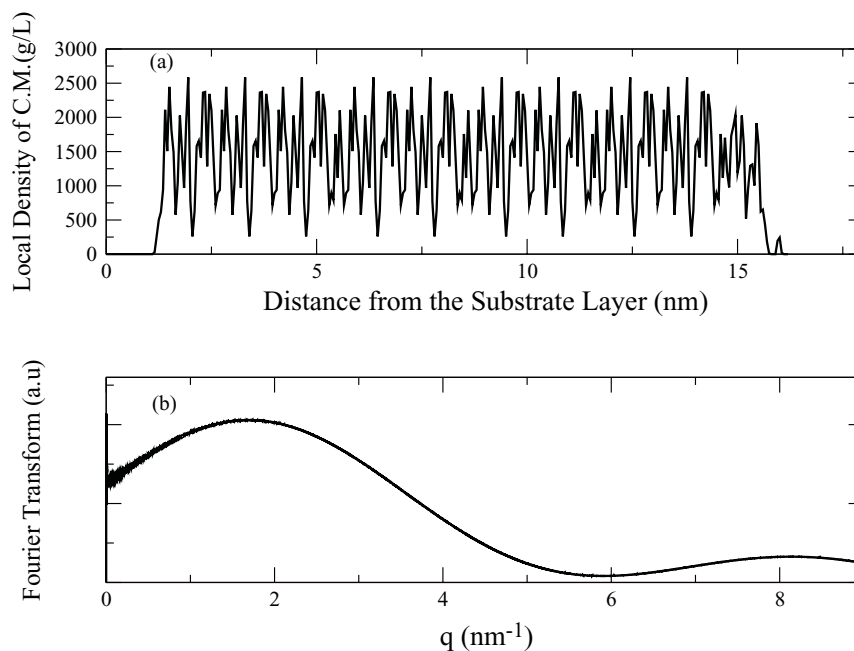


FIG. 6. (a) Local density profile of the center of mass of trehalose molecules as a function of the distance from the substrate layer. (b) Fourier transform of the local density profile for the “stable” glass. A large initial peak is consistent with the wide angle x-ray scattering (WAXS) pattern seen in experiments with “stable” glasses of IMC. (See Ref. 26) All results shown are from six independent runs of the vapor-deposited glass prepared at the substrate temperature of 330 K and a system size of  $x = y = z = 18$  nm.

no precedent for simulations of stable glasses, the results presented here are completely consistent with experimental observations for a variety of small organic molecules, including TNB, IMC, and toluene. These observations include a lower enthalpy, a higher density, a higher onset temperature, and a lower heat capacity than the corresponding “ordinary” glass. This agreement with experiment serves to validate the models and methods employed in our simulations.

Past experimental studies of “stable” glasses have focused on macroscopic observables; molecular-level information pertaining to the structure of “stable” glasses is limited. In the absence of that information, it has been difficult to determine the origin of the enhanced stability of vapor-deposited glasses. Our simulations reveal that computer-generated “stable” glasses of trehalose exhibit a distinct layered structure along the direction normal to the substrate. In contrast, the packing in the directions parallel to the substrate is the same as that observed in bulk “ordinary” glasses.

Dawson and co-workers<sup>26</sup> have recently reported that scattering experiments of IMC “stable” glasses exhibit an additional anisotropic peak whose origin has been elusive. Our simulated density profiles along the thickness of the “stable” trehalose glass films are completely consistent with such an anisotropic peak, and lend credence to the layered-structure predictions of our simulations. Interestingly, the observed anisotropy of the “stable” organic glasses created in our simulations is reminiscent of that observed in amorphous magnetic materials<sup>70,71</sup> and C-60 fullerenes<sup>72</sup> prepared using vapor deposition. This similarity will be examined in future work.

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