

# Factors Contributing to the Glass-Forming Ability of a Simulated Molecular Liquid

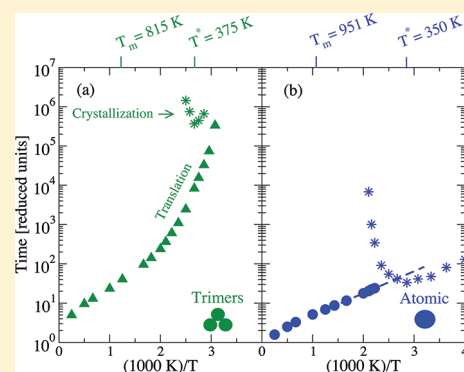
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**ABSTRACT:** The time scales of crystallization of two model liquids, an atomic liquid and a molecular liquid of bent trimers originally introduced as a model of the glass former *o*-terphenyl, are determined using molecular dynamics simulations. The molecular liquid is found to have a minimum crystallization time, on supercooling, that is  $10^4$  times larger than that of the atomic liquid. We present evidence that this enhanced glass-forming ability is due, in equal parts, to the slower dynamics and the larger crystal–liquid interfacial free energy in the molecular liquid.



The glass-forming ability of a liquid is measured by the minimum time for crystallization exhibited by the liquid over all values of the undercooling. This minimum time (or, equivalently, maximum crystallization rate) sets the slowest cooling rate required to bypass crystallization and achieve the glass state. That a maximum rate exists is ensured by the fact that the crystallization rate vanishes both at the melting point and at absolute zero. If  $T^*$  is the temperature at which the minimum crystallization time  $t_{\min}^*$  occurs, then the minimum cooling rate necessary to avoid crystallization is given by  $(T_M - T^*)/t_{\min}^*$ , where  $T_M$  is the melting point. This is a quantity of considerable practical significance. The smaller the minimum cooling, the thicker the ingots of the amorphous material that can be produced and, therefore, the broader the range of applications for the glass. The identification of the optimal glass formers is thus a dominating interest in the field of metallic glasses,<sup>1</sup> a growing interest in pharmacology,<sup>2</sup> and a necessary (if implicit) aspect in the development of computer models for the study of the character of the glass transition itself.<sup>3</sup> There is also considerable interest in avoiding the glass transition. What constitutes a good self-assembler, that is, a material that can avoid the amorphous state, is of increasing interest in material science, crystal engineering, and nanotechnology.<sup>4</sup>

Perhaps the most common strategy for optimizing glass-forming ability is to look to increasing the thermodynamic stability of the liquid with respect to the crystal phase. In mixtures, this means working at or close to a eutectic point, if present. In simulations of single-component liquids, features of the Hamiltonian can be varied to achieve an analogous effect.

Sastry and Angell<sup>3</sup> have, for example, described how the variation of a bond force constant in a model of silicon leads to the depression of the freezing temperature and an associated improvement of glass-forming ability.

With a few noteworthy exceptions, pure liquids with high glass-forming ability are molecular. Molecules offer considerable variability in structure and properties, available through chemical modification, so that understanding the relationship between molecular structure and glass-forming ability represents an important outstanding problem. In this paper, we address this question in the context of the glass-forming ability of a liquid composed of bent trimers, inspired by the organic glass former *o*-terphenyl (OTP).

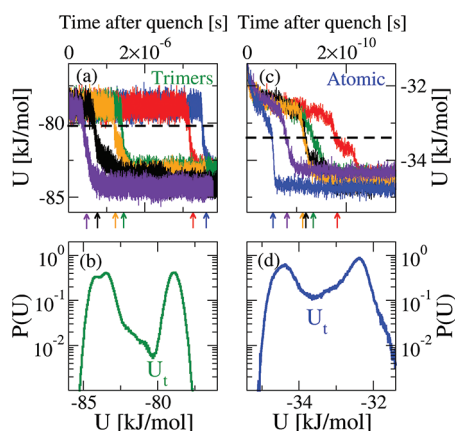
There have been a number of experimental studies describing how the glass transition temperature  $T_g$  varies across a homologous series of molecules.<sup>5,6</sup> Analogous studies of the glass-forming ability are rarer and limited in extent. Alba et al.<sup>7</sup> made use of the superior glass-forming ability of the low melting point *m*-xylene to study the glass transition in mixtures of *m*-xylene and either *o*- or *p*-xylene. Whitaker and McMahon<sup>8</sup> have reported on the glass-forming abilities of the four isomers of trisnaphthylbenzene; isomers 1–3 are good glass formers, while isomer 4 is described as not forming a glass. The poor glass-forming ability of

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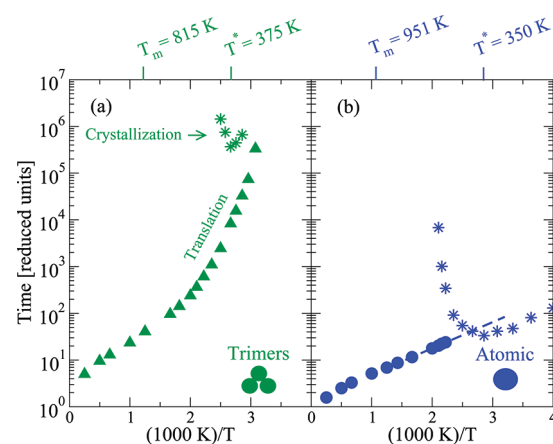
**Figure 1.** Drop in potential energy  $U$  due to crystallization in individual runs of the trimer at  $T^* = 375$  K (a) and atomic liquid at  $T^* = 350$  K (c), and histograms of the potential energies for the trimer (b) and atomic liquid (d) sampled during runs at the conditions in top panel. From this, we estimate  $t^* = 1.7 \times 10^{-6}$  s for the trimers and  $t^* = 1.3 \times 10^{-10}$  s for the atomic liquid as described in the text. For clarity, only six out of 100 runs are shown for the atomic liquid in panel (c).

the isomer 4 was correlated with its higher melting point. Mandanici et al.<sup>9</sup> have looked at a series of alkylcyclohexanes. They report that propylcyclohexane exhibits a significantly better glass-forming ability than the ethyl- or the butyl-substituted compounds. Ping et al.<sup>10</sup> compared the glass-forming abilities of a series of cyclic stilbenes, reporting a nonmonotonic variation with respect to ring size.

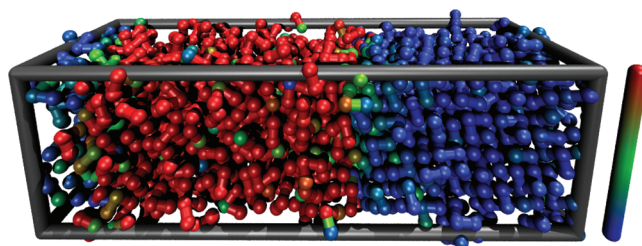
Our strategy to understand the origin of stability against crystallization of a molecular glass former is to compare the minimum crystallization time of the trimer liquid with that of a simple atomic liquid. Establishing which liquid has the higher glass-forming ability is straightforward, a simple matter of deciding which liquid has the largest value of  $t_{\min}^*$ . Establishing *why* the better glass former is better is more subtle. The minimum crystallization time is a complex property that depends on the kinetics of particles in the liquid, the chemical potential difference between the bulk phases of crystal and supercooled liquid, and effects, both thermodynamic and kinetic, arising from the heterogeneous environments associated with the interface between crystal and liquid. The physical properties of the particles (i.e., shape, mass, and interaction potential) will influence all of these contributing phenomena. In this paper, we shall first quantify the difference in glass-forming ability between our two liquids and then sort out how this difference should be attributed to the different contributing phenomena.

The trimer model, introduced by Lewis and Wahnström (LW),<sup>11,12</sup> consists of a rigid three-particle complex, each particle interacting with particles in another molecules' spherically symmetric Lennard-Jones (LJ) potential<sup>13</sup>  $u(r)$ , where  $u(r) = 4\epsilon((\sigma/r)^{12} - (\sigma/r)^6)$  with  $\epsilon = k_B \times 600$  K  $\approx 4.988$  kJ/mol and  $\sigma = 0.483$  nm. The two trimer bonds are of length  $\sigma$ , and the fixed bond angle was chosen to be  $75^\circ$ . Each of the three atoms is given a mass of  $m_{\text{atom}} = 76.768$  au. A number of papers have been published<sup>14</sup> investigating the properties of the supercooled liquid. The crystallization of the LW trimer has been described in detail recently.<sup>15</sup>

We implemented the LW trimers and the atomic LJ liquid into the LAMMPS<sup>16</sup> software packages. The trimers were held rigid using the SHAKE algorithm,<sup>17</sup> forces were truncated at  $2.5\sigma$ , and



**Figure 2.** Characteristic times in reduced units for translational motion  $\tilde{t}_D$  (filled symbols) and crystallization  $\tilde{t}^*$  (stars) plotted against inverse temperature for the trimers (a) and the Lennard-Jones liquid (b). Dashed line in panel (b):  $1.35\exp((1290 \text{ K})/T)$ .



**Figure 3.** Simulation to determine the melting line of the trimers. Configuration after 200 ns at 625 K and 3600 atm contains crystal (left) and liquid (right). Molecules are colored according to mobility to highlight phases. Blue corresponds to stationary particles and red to  $\geq 0.5$  nm displacements after  $\Delta t = 0.2$  ns.

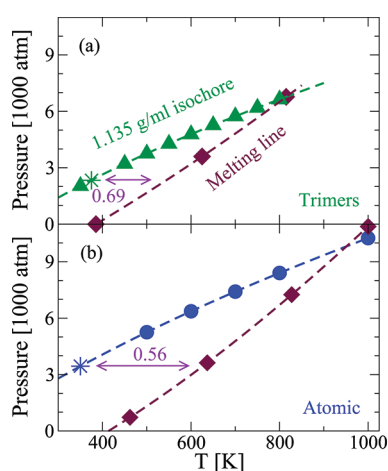
pair energies were accordingly shifted by  $-u(2.5\sigma) \approx 0.08$  kJ/mol. Liquid dynamics and crystallization were investigated in a periodic cubic box with fixed volume  $V$  and temperature  $T$  using the Nosé-Hoover thermostat<sup>18</sup> (the canonical ensemble). We consider a system of  $N = 324$  trimer molecules and  $N = 3 \times 324 = 972$  for the LJ liquid. For both liquids, we restrict ourselves to the  $\rho = 1.135$  g/mL isochore corresponding to a box length of  $L = 4.78$  nm.

The time  $t^*$  marking the onset of crystallization was determined over a range of supercoolings as follows. First, liquids were equilibrated at a high temperature,  $T = 800$  K. The equilibrated liquids were then subjected to an instantaneous drop in the thermostatted temperature to the final supercooled value, and the potential energy was monitored as a function of time elapsed from the quench. Examples of energy trajectories for the trimer and the LJ liquid are shown in Figure 1a,c, respectively. We define a waiting time of a given run, marked with arrows in Figure 1, as the time interval between the quench and the drop in the potential energy to a value  $U_t$  marking the exit of the liquid state. We determine  $U_t$  as the local minimum in the energy distribution over the duration of the nonstationary run, shown in panels b and d of Figure 1. From a series of independent runs, we calculate  $t^*$  as the average of these waiting times. Using this protocol, we estimate  $t^* = 1.7 \times 10^{-6}$  s for the trimers at 375 K and  $t^* = 1.3 \times 10^{-10}$  s for the LJ liquid at 350 K. Figure 2 (stars) shows  $t^*$  for a range of temperatures along 1.135 g/mL isochore.

**Table 1.** Melting Line of the Lewis–Wahnström Trimers and the Atomic LJ Liquid

|                              | trimers |         |         | atomic            |
|------------------------------|---------|---------|---------|-------------------|
| $p_m$ [atm]                  | 1       | 3600    | 6771    | 3627 <sup>a</sup> |
| $T_m$ [K]                    | 385     | 625     | 815     | 637 <sup>a</sup>  |
| $U_{liq}$ [kJ/mol]           | −72.123 | −70.177 | −66.277 | −27.695           |
| $U_{cry}$ [kJ/mol]           | −82.484 | −79.445 | −75.571 | −31.924           |
| $V_{liq}$ [mL/mol]           | 225.39  | 210.69  | 203.00  | 74.312            |
| $V_{cry}$ [mL/mol]           | 206.63  | 196.80  | 190.68  | 68.373            |
| $\Delta H_{fus}$ [kJ/mol]    | −10.363 | −14.335 | −17.746 | −6.412            |
| $\Delta S_{fus}$ [J/(mol K)] | −26.917 | −22.936 | −21.774 | −10.065           |
| $dp_m/dT_m$ [atm/K]          | 14.160  | 16.297  | 17.442  | 16.726            |
| $b$                          | 14.051  | 15.941  | 17.438  | 17.801            |

<sup>a</sup> From ref 22. <sup>b</sup>  $dp_m/dT_m$  of quadratic fit in Figure 4.



**Figure 4.** Phase diagram ( $pT$ ) of trimers (a) and the LJ liquid (b). The melting line of the LJ liquid is adapted from ref 22. The melting lines are interpolated with an quadratic polynomial;  $p_m/\text{atm} = -4824.6 + 11.018T_m/\text{K} + 3.9387 \times 10^{-3}(T_m/\text{K})^2$  for the trimers and  $p_m/\text{atm} = -5444.7 + 10.78T_m/\text{K} + 5.5107 \times 10^{-3}(T_m/\text{K})^2$  for the atomic liquid. The pressure at  $T^*$  for the LJ liquid is an extrapolation (we note, however, that since the liquid is not metastable at this state, there is no well-defined liquid pressure).

Each point is an estimate based on 4 to 6 crystallization events for the trimers and 100 for the atomic LJ liquid.

Next we must estimate the melting temperature. The melting line of the trimers was determined as follows. First, a crystal configuration, taken from spontaneously formed crystals at low temperature, was replicated three times along the  $z$  direction to generate a crystalline starting configuration in a  $L \times L \times 3L$  box. Next, half of the crystal was melted at high temperature, while the other half of the particles were pinned in their crystalline configuration. This protocol produced a two-phase configuration with the crystal–liquid interface perpendicular to  $\vec{z}$  (on average), as shown on Figure 3. After removing the pinning constraint, simulations were carried out in the  $NpT$  ensemble using an anisotropic barostat over a range of temperatures. The melting point was determined as the crossover between growth and melting. Melting points were determined this way for a number of values of the pressure shown in Table 1. As a consistency check, we note that  $dp_m/dT_m$  evaluated using the Clausius–Clapeyron relation,  $\Delta S_{fus}/\Delta V$ , agrees with the slope of the

quadratic fits (dashed line in Figure 4) to the melting points (see the last two rows of Table 1). For the atomic LJ liquid, we used the melting line reported in ref 22.

Our first task is to quantify the difference in glass-forming ability of the two liquids, in this case under the conditions of constant volume. In Figure 2, we plot the  $\log_{10}(t^*)$  as a function of inverse temperature for the two liquids. The temperatures of minimum crystallization times  $T^*$  for the trimer and atomic liquids are 375 and 350 K, respectively, and the trimer’s superiority as a glass former over the LJ liquid is a substantial 4 orders of magnitude.  $T^*$  corresponds to  $0.69T_m$  and  $0.56T_m$  for the trimer and atomic liquids, respectively (see Figure 4). This ratio  $T^*/T_m$  is lower than what is typically found experimentally. This difference may be a consequence of the fact that both liquids studied here are very poor glass formers as compared to those studied experimentally (i.e., the simulated values of  $t_{\min}^*$  are small).

When Lewis and Wahnström proposed the bent trimer as a model glass former, they supposed that its shape was sufficiently low symmetry to preclude crystallization at all. Having recently demonstrated that the trimer can, indeed, crystallize, we have now established that it still is a much better glass former than the simpler liquid. Why? The molecule differs from the atom in a number of ways—mass, size, interaction strength, and shape. The contribution of particle mass and size can be accounted for by scaling the time scale as follows:

$$\tilde{t}^* = t^*(k_B T/m)^{1/2} (N/V)^{1/3} \quad (1)$$

where  $m = 3m_{\text{atom}}$  for the trimers and  $m = m_{\text{atom}}$  for the LJ liquid. We find that, on applying this scaling to the crystallization time, the difference in minimum crystallization times changes by only a factor of  $\sim 1.2$ . We note, in passing, that this is the proper reduced unit for “isomorphic scaling”,<sup>19</sup> that is, quantities in such reduced units are invariant along  $T \propto \rho^{n/3}$  lines in the phase diagram where  $n$  is an effective inverse power-law exponent. This scaling is exact for liquids with  $u \propto r^{-n}$  pair interactions and a good approximation for the liquids studied here.<sup>20</sup>

Next, to include the influence of collective dynamical behavior in the liquid, we shall scale the crystallization time by the characteristic time scale for translational diffusion  $t_D$  in the liquid, defined as

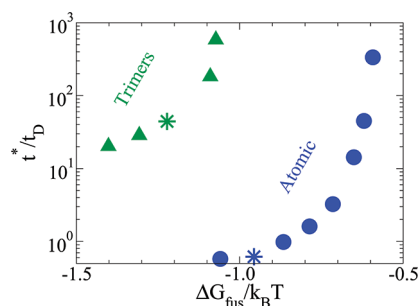
$$t_D = (6D)^{-1} (V/N)^{2/3} \quad (2)$$

The self-diffusion constant  $D$  is determined from the asymptotic time derivative of the mean squared displacement  $R^2(t) = \langle [\vec{r}(0) - \vec{r}(t)]^2 \rangle$  using

$$D = \lim_{t \rightarrow \infty} \frac{1}{6} \frac{dR^2}{dt} \quad (3)$$

We define a reduced translational diffusion time  $\tilde{t}_D$  by replacing  $t^*$  with  $t_D$  in eq 1. As can be seen in Figure 1, the LJ liquid does not achieve a stationary metastable state before the onset of crystallization over a significant range of supercoolings. As a result, the value of the LJ diffusion constant used here represents only an estimate of the characteristic time scale of atomic motions in the liquid and should not be taken as a (metastable) equilibrium transport coefficient.

The diffusion times  $\tilde{t}_D$  for the trimer and atomic liquids are plotted in Figure 2. It is clear that the mobility of the trimers is always less than that of the atoms and that  $\tilde{t}_D$  for the trimers increases more rapidly on cooling than does  $\tilde{t}_D$  for the atomic



**Figure 5.** Crystallization time relative to the translation time,  $t^*/t_D$ , plotted against thermodynamic drive,  $\Delta G_{\text{fus}}/k_B T = \Delta S_{\text{fus}}(T - T_m)/k_B T$  of the LW trimers (triangles) and the atomic LJ liquid (circles). Stars indicate the point of maximum crystallization rate.

liquid. This difference in mobility of the liquid will clearly be an important contributor to the superior glass-forming ability of the molecular liquid. It remains for us to establish whether the difference in liquid dynamics is the only contributor.

In addition to its important influence on the liquid state kinetics, the temperature determines the magnitude of the free energy difference  $\Delta G_{\text{fus}}$  between the crystal and liquid states and, hence, the thermodynamic driving force for crystallization. Relating  $\Delta G_{\text{fus}}$  to dynamics relies heavily on the assumptions employed in theories of nucleation and crystal growth.<sup>21</sup> In the classical theories of crystal nucleation and growth,<sup>21</sup> once the crystallization time has been scaled by  $t_D$ , the only significant dependence of temperature left in the expression for the crystallization time  $t^*$  occurs in the form of  $\Delta G_{\text{fus}}(T)/k_B T$ . Plotting the reduced crystallization time  $t^*/t_D$  against  $\Delta G_{\text{fus}}/k_B T$  will then “remove” both of these accountable influences and, thus, expose any remaining differences between the kinetics of the molecular and atomic liquids. We have estimated  $\Delta G_{\text{fus}}$  using the relation

$$\Delta G_{\text{fus}} = \Delta S_{\text{fus}}(T - T_m) \quad (4)$$

where  $\Delta S_{\text{fus}}$  is the entropy of fusion at  $T_m$  (see Table 1; for the trimers, we used an interpolated  $\Delta S_{\text{fus}} = 24 \text{ kJ}/(\text{mol K})$ ). Note that the entropy loss on freezing of the trimer liquid is almost twice that of the atomic liquid, in spite of the residual orientational disorder previously reported for the molecular crystal.<sup>15</sup> This means that  $\Delta G_{\text{fus}}/k_B T$  at  $T^*$  for the molecular liquid is almost twice that of the atomic liquid.

Considering Figure 5, we find that the scaling of the crystallization time has significantly reduced the difference between trimer and atomic liquid so that, at their respective values of  $T^*$ , the difference is down to a factor of  $\sim 10^2$ . When comparing liquids at the same value of  $\Delta G_{\text{fus}}/k_B T$ , however, we find that the crystallization time of the trimer liquid is substantially larger than that of the LJ liquid, even with the difference in liquid kinetics scaled out. For example, when  $\Delta G_{\text{fus}}/k_B T \sim -1.06$ ,  $t^*/t_D$  for the atomic liquid is just under 3 orders of magnitude smaller than that of the trimer liquid. To understand this persistent difference, we must turn to the classical theory of nucleation for some guidance. The remaining physical property that appears in the theory of nucleation rates that we have not accounted for is the crystal–liquid interfacial free energy. A small increase in this property can significantly increase the free energy of the critical nucleus and, in turn, drastically increase the crystallization time. We conclude that the surface free energy of the trimer crystallites exceeds that of the atomic liquid but that the full kinetic effect of

this is, to some extent, offset by the fact that the thermodynamic driving force for crystallization,  $\Delta G_{\text{fus}}/k_B T$ , increases more rapidly on cooling of the molecular liquid, thanks to its higher entropy of fusion.

In conclusion, we have demonstrated that the model trimer introduced as a glass former by Lewis and Wahnström has indeed a superior glass-forming ability as compared to a simple atomic liquid with a minimum crystallization time  $10^4$  times larger. This difference we attribute in roughly equal parts to slower diffusion dynamics in the molecular liquid and a higher crystal–liquid interfacial free energy of the trimers, noting that the latter effect is negated, to some extent, by the more rapid increase in the thermodynamic driving force to crystallize on cooling the molecular liquid.

It is not at all clear where that leaves the intuition that the superior glass-forming ability of the trimers depended on its low symmetry. If shape does matter, then the results of this paper make clear that the role of shape, at least with respect to the LW trimer, is *not* to produce a “bad” crystal, “bad” in the sense of a crystal with high enthalpy.<sup>15</sup> For the slow crystallization kinetics of the trimer to be attributed to the low symmetry of the molecule, it is necessary to link this shape with both the slower liquid state dynamics and the higher crystal–liquid interfacial energy. The role of shape on molecular diffusion is an intriguing question. The general observation of decoupling between rotational and translational diffusion in supercooled liquids<sup>23</sup> would suggest that molecular shape would exert a decreasing influence on translational motion as a liquid is cooled. Chong and Kob,<sup>24</sup> however, have demonstrated that the mechanical coupling between rotational and translational actually increases on supercooling, even as the respective diffusion constants exhibit increasingly different temperature dependence. The influence of shape in the crystal–liquid interface is an even more open question. While the computational tools now exist for accurate calculations of the interfacial free energy for molecules,<sup>25</sup> there have not, to our knowledge, been any systematic studies of the influence of shape.

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