

## Relations between a Liquid and Its Glasses

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Ideas developed to describe the simulated glass transition in simple models, like hard spheres, are applied to real materials in which temperature, rather than density, is the important variable. The free energy of a liquid is expressed in terms of the free energy of all the glasses that it samples. The assumption that all glasses of the same substance have the same heat capacity allows an estimate of the number of glasses that it can form and the distribution of their enthalpies, from heat capacity measurements on the liquid and an experimental glass. The results suggest a thermodynamic glass transition underlying the experimental kinetic transition. The same ideas explain the relation between thermodynamic and kinetic measures of fragility in liquids, and they show that the fragility of a liquid is directly related to the total number of glasses that the material can form.

### 1. Introduction

Simulation studies of the glass transition in simple models,<sup>1–3</sup> like hard spheres,<sup>2</sup> show that the properties of a liquid can be expressed in terms of the properties of the glasses that it samples and that this leads to a simple description of the glass transition. The same idea is developed here for real materials in which temperature, rather than density,<sup>1–3</sup> is the important independent variable. The assumption that all glasses of the same substance have the same heat capacity allows an estimate of the number of glasses that it can form and the distribution of their enthalpies, from heat capacity measurements on the liquid and a single experimental glass. A short extrapolation of the distribution function suggests a thermodynamic glass transition<sup>4–7</sup> underlying the experimental kinetic glass transition. The same ideas explain the relation between thermodynamic and kinetic measures of the fragility of liquids in Angell's strong and fragile scheme,<sup>8,9</sup> and they show that the fragility of a liquid is determined by the total number of glasses<sup>9,10</sup> that the material can form.

An old idea,<sup>11</sup> central to discussions of liquids and glasses, is that the motion of the molecules in a cold liquid can be viewed as solidlike vibrations about local equilibrium positions within a basin in configuration space. In contrast to a crystal, the number of structurally distinct amorphous basins that a liquid can sample is enormous,<sup>1,2,10</sup> and this allows it to flow, by crossing the barriers between basins. At low temperatures the rate of barrier crossing slows dramatically, and when it stops altogether, the liquid is a nonergodic glass, stuck in one basin. These notions, developed precisely by Stillinger<sup>10</sup> and Weber,<sup>12</sup> can be traced back to Goldstein,<sup>13</sup> Adam and Gibbs,<sup>14</sup> Gibbs and DiMarzio,<sup>5</sup> Davies and Jones,<sup>15</sup> and Frenkel<sup>11</sup> and Simon.<sup>16,17</sup> They provide a natural way of dividing contributions to the properties of a liquid into those due to the vibrational motions within each glass that the liquid samples and those due to jumps between different glasses.

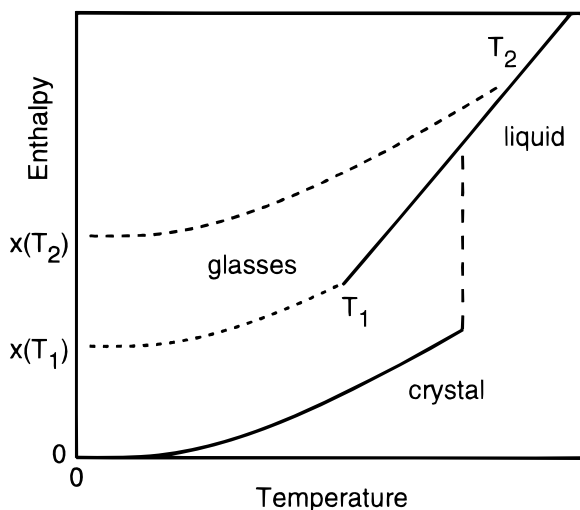
Glasses that are formed by cooling a liquid at different rates, or at different pressures, generally have different bulk properties,

while glasses with the same history have the same bulk properties.<sup>1,15,16</sup> The concept of an "order parameter",  $x$ , that distinguishes glasses with different bulk properties was introduced by Simon<sup>16</sup> and developed by Frenkel,<sup>11</sup> Davies and Jones,<sup>15</sup> and DiMarzio.<sup>18</sup> It allows us to group together all of the structurally distinct glasses of the same kind,  $x$ , and to count their number,  $N_g(x)$ .

For many purposes<sup>15,18</sup>  $x$  can remain an unspecified parameter, but it is helpful to have something concrete in mind. In the inherent structures approach,<sup>10,12</sup> an equilibrated liquid is "instantaneously" cooled to its inherent structure at absolute zero, and the order parameter is taken to be the energy or enthalpy per particle in the inherent structure. To take advantage of the familiarity of this concept,  $x$  is identified here as the enthalpy of a glass at absolute zero. However, if all bulk properties of glasses of the same kind are the same, then any other property that varies with  $x$  could serve as the order parameter. Figure 1 sketches the relation between the enthalpy of a crystal, a liquid, and two glasses. The volume and enthalpy of a liquid usually fluctuate negligibly, which means that the vast majority of the glasses that it samples have the same volume and enthalpy and hence that the liquid, at a given  $P$  and  $T$ , samples glasses of the same kind  $x(P, T)$ .

Glasses are unstable and they can relax irreversibly such that  $x$  changes with time. However, it is possible to study a glass at low temperature, under reversible conditions<sup>16,17</sup> in which  $x$  does not change, over a range of temperatures sufficient to permit extrapolation to the transition. As a device, to avoid introducing kinetics into the thermodynamic picture, the properties of a glass can be defined<sup>15</sup> by such extrapolation. The glass transition is located where the extrapolated volume and enthalpy of the glass are the same as those of the equilibrated liquid. An alternative device that might be implemented in simulation experiments is to apply constraints<sup>1–3,7,19</sup> that prevent a glass from relaxing. With suitable constraints,<sup>19</sup> a liquid could be trapped at any instant in one of the glasses that it samples and the properties of the constrained glass could be measured over a range of temperatures and pressures where a real glass would relax irreversibly. Kivelson<sup>20</sup> has pointed out that the work that must be performed to constrain a liquid to one of the  $N_g(x)$  glasses

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**Figure 1.** Schematic variation of the enthalpy with temperature for a fragile liquid, its crystal, and two glasses. The slopes of the crystal and glass lines are from an Einstein expression for the heat capacity  $C_p = (\theta/T)\exp(-\theta/T)/(1 - \exp(-\theta/T))$ , where  $\theta$  is the Einstein temperature. The liquid is assigned a constant<sup>21</sup> heat capacity, about twice that of the lower glass. The high-temperature glass would relax quickly near  $T_2$ , but we may imagine the application of constraints, or develop constrained simulation techniques,<sup>7</sup> that prevent such relaxation. The liquid at  $T_2$  can then be constrained to one of the glasses that it samples, and the constrained glass may be studied over the temperature range shown and cooled to absolute zero, where its enthalpy is  $x(T_2)$ .

that it samples reduces the entropy by  $k \ln\{N_g(x)\}$ , where  $k$  is the Boltzmann constant, and this is the residual calorimetric entropy of the glass at absolute zero.

The obvious questions are: what is the number  $N_g(x)$  of distinct glasses of kind  $x$ , and how do the thermodynamic properties of a glass of kind  $x$  vary with temperature and pressure? With answers to these questions we could describe the thermodynamics of the liquid, its glasses, and the glass transition. This paper attempts to get some insight by developing a simple model and testing it against the properties of a real liquid, ethylbenzene, and one of its many glasses, to build up a picture of the distribution of all its glasses. Ethylbenzene was chosen because it is one of the simpler substances for which the state of the art calorimetric data required for the analysis are conveniently tabulated in one paper.<sup>21</sup>

## 2. Basic Relations

We assume that all  $N_g(x)$  structurally distinct glasses of the same kind  $x$  have the same thermodynamic properties.<sup>1-3,15-17</sup> Several different order parameters may be needed in general,<sup>15,18</sup> but one is probably sufficient when attention is confined to a single isobar. The pressure  $P$  is therefore taken to be constant and is not specified.

An individual glass of kind  $x$  at temperature  $T$  has enthalpy

$$H_g(x, T) = x + \int_0^T C_{p,g}(x, T) dT \quad (1)$$

where  $x = H_g(x, 0)$  is the enthalpy at absolute zero and  $C_{p,g}(x, T)$  is the isobaric heat capacity. The entropy of an individual glass is

$$S_g(x, T) = \int_0^T C_{p,g}(x, T) d \ln\{T\} \quad (2)$$

The entropy defined this way is zero at absolute zero. It is the statistical entropy corresponding to the phase space that the particular glass can access, and it is not the same as the usual

calorimetric entropy, which is evaluated by integrating from the ideal gas limit. The latter is higher by the residual entropy at absolute zero, which depends on the history of the glass. Equations 1 and 2 also apply to the crystal, and the enthalpy of the crystal at absolute zero is taken as the reference point for enthalpy so that  $x = 0$  for the crystal.

The Gibbs free energy of an individual glass is

$$G_g(x, T) = H_g(x, T) - TS_g(x, T) \quad (3)$$

The entropy of the liquid is higher than that of one glass because the liquid samples  $N_g(x)$  glasses of kind  $x$ . The extra entropy of the liquid is  $k \ln\{N_g(x)\}$ , and the Gibbs free energy of the liquid is therefore

$$G_l(x, T) = G_g(x, T) - kT \ln\{N_g(x)\} \quad (4)$$

The first term,  $G_g(x, T)$ , gives the contribution from the vibrations in an individual glass, and the second is the contribution from the  $N_g(x)$  glasses that the liquid samples. The vast majority of the glasses sampled by the liquid, at a given  $P$  and  $T$ , are of the kind  $x(P, T)$  that minimize the free energy of the liquid, so  $x$  is determined by the condition<sup>15</sup>

$$(\partial G_l(x, T)/\partial x)_{T,P} = 0 \quad (5)$$

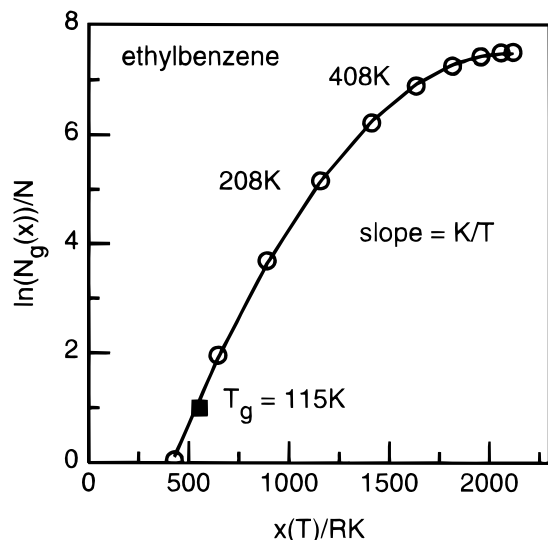
## 3. Simple Model

Little is known about how  $C_{p,g}(x, T)$  varies with  $x$ , so an assumption is necessary. The enthalpy of the experimental glass of ethylbenzene<sup>21</sup> is higher than that of the crystal by  $x = 4.5$  kJ/mol near absolute zero, and the heat capacity of the glass is only 8% greater than that of the crystal at 100 K. So the heat capacity does not vary strongly with  $x$ . Takeda et al.<sup>22</sup> show that a glass formed by vapor-depositing pentane has a much higher enthalpy than one formed by cooling the liquid but that their heat capacities are almost the same. We examine here the approximation that  $C_{p,g}(x, T)$  is independent of  $x$ . Stillinger<sup>23</sup> has recently estimated the distribution of inherent structures of *o*-terphenyl with the approximation that they all have the same heat capacity as the crystal. The approximation greatly simplifies the development because when  $C_{p,g}(x, T)$  is independent of  $x$ , eqs 1–5 yield

$$(\partial \ln\{N_g(x)\}/\partial x)_{T,P} = 1/(kT) \quad (6)$$

The calculation of  $\ln\{N_g(x)\}$  and  $x(T)$  from the heat capacity data for ethylbenzene is described in the appendix section, and the results are shown in Figure 2. The form of Figure 2 is determined by eq 6 and the fact that  $x(T)$  increases with  $T$ . Equation 6 requires that the curve has a maximum in the high-temperature limit, where the slope is zero, and it requires that the slope increases as  $T$ , and hence,  $x(T)$  values are reduced. The number of glasses  $N_g(x)$  cannot be less than 1, so eq 6 and Figure 2 suggest a Kauzmann<sup>24</sup> temperature,  $T_0$ , below which  $\ln\{N_g(x)\}/N$  is zero and the system is stuck in an essentially unique ideal glass.

Kauzmann<sup>24</sup> showed that the entropy of a supercooled liquid usually extrapolates toward that of its crystal at a temperature  $T_0$  not far below the experimental glass transition temperature,  $T_g$ , and he argued that spontaneous freezing would always intervene to keep  $T_0$  inaccessible. Di Marzio<sup>25</sup> pointed out that glass-forming atactic polymers do not have a crystalline phase so that spontaneous freezing cannot always be invoked to avoid the implications of Kauzmann's extrapolation. Angell and Donnelly<sup>26</sup> showed that the Kauzmann temperature seems to



**Figure 2.** Distribution of the glasses of ethylbenzene,  $\ln\{N_g(x)\}/N$  vs  $x(T)$ . The circles show values calculated from the measured heat capacities,<sup>21</sup> as described in the appendix. The line shows the Gaussian distribution, eq 7 with the fitted constants  $\alpha = 7.54$ ,  $\gamma = 2.677 \times 10^{-6} (\text{RK})^{-2}$  and  $x_m = 2094 \text{ RK}$ . The energy unit is  $\text{RK} = 8.314 \text{ J/mol}$ , and the crystal at absolute zero is the energy zero. The solid square locates the experimental glass transition at 115 K. The slope of the line is  $K/T$  if all glasses have the same heat capacity, so the peak of the distribution corresponds to the high-temperature limit where  $1/T \rightarrow 0$ .

lie above the temperature at which some solutions would freeze. Gibbs and DiMarzio,<sup>5</sup> Angell and Tucker,<sup>4</sup> and DiMarzio and Yang<sup>6</sup> identify  $T_0$  as the temperature of a thermodynamic glass transition, which is kept inaccessible by the intervention of the real kinetic glass transition. Stillinger<sup>27</sup> has argued that the extrapolation used to locate  $T_0$  is flawed, and the concept of a thermodynamic transition at  $T_0 > 0$  is not valid.

If each glass is viewed as a sum of many independent parts whose properties are uncorrelated, then the central limit theorem suggests a Gaussian distribution for  $N_g(x)$ . A Gaussian has been used to describe the distribution of the limiting densities of glasses obtained in simulation studies of a tetravalent network model,<sup>1</sup> hard spheres,<sup>2</sup> and hard disk mixtures.<sup>3</sup> Bowles<sup>28</sup> has recently analyzed the exact distribution of the glasses of a model mixture of hard rods, with nonadditive diameters, on a line, and he shows that the density distribution of the glasses is approximately Gaussian. A random energy model<sup>29</sup> for spin glasses naturally has ground states with Gaussian distribution of energies. The solid line in Figure 2 shows that the distribution of limiting enthalpies of the glasses of ethylbenzene is also accurately described by the Gaussian form

$$N_g(x) = \exp\{N[\alpha - \gamma(x - x_m)^2]\} \quad (7)$$

The material specific constants  $\alpha$ ,  $\gamma$ , and  $x_m$  are listed in the legend of Figure 2. The number of glasses must increase exponentially with the number of molecules,  $N$ , as shown in eq 7 so that its contribution to the entropy of the liquid,  $k \ln\{N_g(x)\}$ , is extensive. The slope of the line shown in Figure 2 is determined by eq 6, which suggests that eq 7 may represent  $N_g(x)$  equally well for any material for which  $C_{p,g}(x, T)$  is independent of  $x$ . Stillinger<sup>23</sup> has analyzed the heat capacity data for *o*-terphenyl to construct a picture similar to Figure 2. He extrapolates the curve into the region beyond the maximum, where the slope and temperature are negative, and he emphasizes that the resulting curve is not symmetrical about the maximum.

**TABLE 1: Comparison of the Measured Change in Heat Capacity at the Experimental Glass Transition,  $\Delta C_p(T_g)$ , with the Prediction of Eq 10<sup>a</sup>**

substance	$\alpha$	$T_0/\text{K}$	$T_g/\text{K}$	$\Delta C_p(T_g)/R$	$2\alpha(T_0/T_g)^2$
toluene	4.9	105	117	7.7	7.9
ethylbenzene	7.5	101	115	9.1	11.3
1 butene	7.7	50	60	8.0	10.4
<i>o</i> -terphenyl	11.3	205	240	13.1	16.5

<sup>a</sup> Values of  $\alpha$  are from Yamamuro et al.<sup>21</sup> In their paper  $\alpha = s_c N_A / R$ , and it is obtained by extrapolation of the configurational entropy to the high-temperature limit, using eq A2. They estimate an uncertainty of about 10% in  $\alpha$  for the first three substances and 20–40% for *o*-terphenyl. Other data are from Yamamuro et al.<sup>21</sup> (toluene, ethylbenzene), Takeda et al.<sup>34</sup> (1-butene), and Chang and Bestul<sup>35</sup> (*o*-terphenyl).

However, a symmetrical Gaussian distribution is automatically obtained for *o*-terphenyl if the extrapolation to high (and negative) temperatures is consistent with eq 5 of Yamamuro et al.,<sup>21</sup> which is eq A2 of this paper.

Substituting eq 7 into eq 6 gives an explicit expression for the limiting enthalpy,  $x(T)$ , of glasses sampled by a liquid at temperature  $T$

$$x(T) = x_m - 1/(2\gamma RT) \quad (8)$$

In equations where  $x(T)$  is specified the meaning is that, in the equilibrium liquid,  $x$  is a variable related to  $T$  by eq 8. In a glass,  $x$  is fixed and  $T$  can be varied, so  $x$  may be indicated without the  $T$  in parentheses. However, we may wish to specify that a glass, at temperature  $T$ , is of the kind  $x(T')$  that is sampled by the equilibrium liquid at temperature  $T'$ , and in this case  $T'$  is the fictive temperature introduced by Tool and Eichlin.<sup>30</sup>

The entropy difference between the liquid and one of the glasses that it samples is, from eqs 7 and 8,

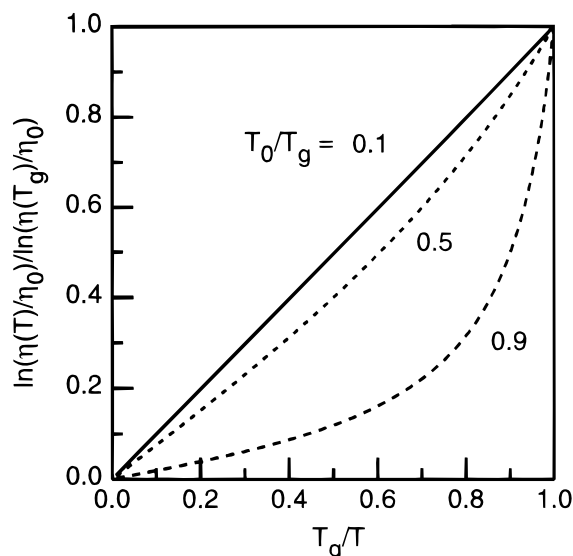
$$\begin{aligned} \Delta_g^1 S(x(T), T)/R &= \ln\{N_g(x)\}/N \\ &= \alpha - \gamma(x(T) - x_m)^2 \\ &= \alpha - \gamma/(2\gamma RT)^2 \\ &= \alpha\{1 - (T_0/T)^2\}, \quad T > T_0 \end{aligned} \quad (9)$$

The last line of eq 9 eliminates  $\gamma$  in favor of the Kauzmann temperature,  $T_0 = 1/[2R(\alpha\gamma)^{1/2}]$ , where the excess entropy vanishes. Since the number of glasses cannot be less than one, eq 9 implies that the most stable amorphous state at temperatures below  $T_0$  is a rare glass of kind  $x(T_0)$ . Because the excess entropy in eq 9 is defined relative to the glasses that the liquid samples,  $T_0$  is generally higher than the temperature where the entropy of the liquid extrapolates to that of the crystal, and the meaning of  $T_0$  does not depend<sup>25</sup> on the existence of a crystal.

The difference between the heat capacities of the liquid and one of the glasses that it samples is obtained by differentiating eq 9

$$\begin{aligned} \Delta_g^1 C_p(x(T), T) &= 2\alpha R(T_0/T)^2, \quad T > T_0 \\ &= 0, \quad T < T_0 \end{aligned} \quad (10)$$

The excess heat capacity drops suddenly to zero when  $T = T_0$ , according to the model, because  $x$  cannot vary at lower temperatures. Table 1 shows that eq 10 provides semiquantitative agreement between  $\alpha$  and the change in heat capacity at the glass transition temperature for several simple glass formers.



**Figure 3.** Ratio of the logarithm of the viscosity to its value at the glass transition, from eq 13, plotted against  $T_g/T$ . Values of  $T_0/T_g$  are shown.

The enthalpy of a liquid is the same as that of the glasses that it samples, as shown in Figure 1, so  $\Delta_g^1 H(x(T), T) = 0$ . The excess enthalpy of the liquid can be defined relative to the enthalpy of an experimental glass, which has the same enthalpy as the liquid at its glass transition temperature  $T_g$ . Because the heat capacity is assumed to be the same for all glasses, the excess enthalpy is due solely to the difference between  $x(T)$  and  $x(T_g)$  so that

$$\Delta_g^1 H(x(T_g), T) = x(T) - x(T_g) \quad (11)$$

Equations 4–11 relate a liquid to its glasses, for a substance in which  $C_{p,g}(x, T)$  is independent of  $x$ , in terms of the material-specific parameters  $\alpha$  and  $T_0$  or in terms of the constants in eq 7. It is clear that the model oversimplifies the behavior of real substances. For instance, the excess heat capacity varies as  $T^{-2}$  according to eq 10, but it is known from experiment<sup>31</sup> that near  $T_g$  it varies as  $\sim T^{-1}$ . At temperatures well above  $T_g$  the predicted  $T^{-2}$  dependence is a good approximation for several substances.<sup>21</sup> The  $T^{-1}$  form is unsuitable at high temperatures because it implies that the excess enthalpy diverges in the high-temperature limit.

#### 4. Strong and Fragile Liquids

Glassblowers speak of quick and slow glasses according to the rate at which the melt solidifies on cooling. If the viscosity of the melt is very sensitive to temperature, then it solidifies quickly within a small temperature range near  $T_g$ . Angell<sup>8,9</sup> introduced the terms “fragile” to describe liquids whose viscosity varies strongly with temperature near  $T_g$  and “strong” for those, like silica, that have a gentler Arrhenius temperature dependence. He points out a striking correlation<sup>8,9</sup> between the thermodynamics and kinetics of strong and fragile liquids. For the most fragile materials the heat capacity of the liquid near  $T_g$  is about twice that of its glass, implying that the structure of the liquid changes rapidly with temperature and hence is “fragile”. The structure of a strong liquid resists thermal change, and the change in heat capacity at the glass transition is much smaller.<sup>8,9</sup>

These general patterns have a simple explanation in terms of the Adam and Gibbs<sup>14</sup> expression for the shear viscosity

$$\eta(T) = \eta_0 \exp\left(\frac{C}{TS_c}\right) \quad (12)$$

where  $\eta_0$  and  $C$  are constants. The configurational entropy of Adam and Gibbs,  $S_c$ , can be identified with the excess entropy given by eq 9. Expressing the logarithm of the viscosity relative to its value at the glass transition temperature and using eq 9 for  $S_c$  yields

$$\frac{\ln\{\eta(T)/\eta_0\}}{\ln\{\eta(T_g)/\eta_0\}} = \frac{T_g\{1 - (T_0/T_g)^2\}}{T\{1 - (T_0/T_g)^2(T_g/T)^2\}} \quad (13)$$

Figure 3 shows that when  $(T_0/T_g)$  is small, the viscosity has the Arrhenius temperature dependence of a strong liquid and the behavior is fragile when  $(T_0/T_g)$  is larger.

To quantify the relationship between kinetic and thermodynamic measures of fragility and to relate them to Figure 2, we need a quantitative measure of the kinetic fragility. The slope,  $f$ , of the line shown in Figure 3, as  $T_g/T$  tends to 1, is a suitable measure. For a strong liquid  $f = 1$  and  $f$  is larger for more fragile liquids. With the help of eq 9  $f$  can be expressed as

$$f = \frac{2\alpha R}{\Delta_g^1 S(T_g)} - 1 \quad (14)$$

and this shows that  $f$  is determined by the ratio of the height,  $\alpha$ , of the peak in Figure 2 to the excess entropy,  $\Delta_g^1 S(T_g)$ , at the kinetic glass transition. The kinetic fragility is therefore related to the total number of glasses that the substance can form  $\exp(\alpha N)$ , and this quantifies Angell's observation<sup>9</sup> that fragile liquids sample more basins in configuration space than strong liquids. The same conclusion was reached for hard particle models in which density, rather than temperature, is the independent variable. The number of glasses that the fragile hard sphere fluid<sup>2</sup> can form is about  $\exp(2N)$  while for a stronger tetraivalent network model<sup>1</sup> it is about  $\exp(1.2N)$ .

Equations 9 and 10 show that, at the kinetic glass transition temperature,

$$\begin{aligned} \Delta_g^1 C_p(T_g) &= 2\{\alpha R - \Delta_g^1 S(T_g)\} \\ &= (f - 1)\Delta_g^1 S(T_g) \end{aligned} \quad (15)$$

$\Delta_g^1 S(T_g)$  is generally a small fraction of  $\alpha R$ , as shown in Figure 2, so the change in heat capacity at  $T_g$  is mainly determined by the total number of glasses,  $\exp(\alpha N)$ . The second line of eq 15 relates the thermodynamic and kinetic measures of fragility more directly and shows that for a strong liquid, with  $f = 1$ ,  $\Delta_g^1 C_p(T_g) = 0$ . A simple explanation of eq 15 is that the higher the peak in Figure 2 the steeper is the climb from  $T_g$  to the top.

#### 5. Conclusions

To describe the glass transition, it is necessary to start with a model that includes the liquid and its glasses within a unified formalism and eq 4 serves this purpose. Thermodynamically, the glass transition is purely entropic. The equilibrated liquid samples  $N_g(x)$  glasses of kind  $x$ , but if time, or some other constraint, does not allow transitions between glasses, the system is stuck in one glass. In a statistical sense, there is an entropy loss of  $k \ln\{N_g(x)\}$  at the glass transition, but there is no latent heat involved and the calorimetric entropy does not change, so the lost entropy turns up as the residual calorimetric entropy at absolute zero.



To develop eq 4, all the glasses were assumed to have the same heat capacity and the distribution of the glasses was assumed to be Gaussian. These are the simplest plausible approximations, and they are not likely to be accurate, but they identify relations between kinetic and thermodynamic measures of fragility, and the number of glasses that a liquid can form, that are likely to be qualitatively correct. The assumptions lead directly to a thermodynamic glass transition that, by the Adam and Gibbs<sup>14</sup> argument, is pre-empted by a real kinetic transition.

The assumption that all glasses of the same substance have the same heat capacity is the main quantitative weakness of the model. An implausible consequence of this assumption is eq 6, which implies that  $(\partial \ln\{N_g(x)\}/\partial x)_{T,P}$  is the same for all substances at the same temperature. Glasses with higher enthalpies are likely to have higher heat capacities (although there is some contrary evidence<sup>22</sup>) because the molecules are less strongly bound, and moderate variation of the heat capacity of the glasses with  $x$  can change the magnitude and temperature dependence of the excess heat capacity and entropy significantly. Estimates of the excess entropy of a liquid or the "configurational" entropy  $S_c$  in Adam and Gibbs<sup>14</sup> eq 12 invariably use the entropy of the liquid relative to an experimental glass<sup>21</sup> (eq A4) or relative to the crystal.<sup>23</sup> However, the excess entropy that Adam and Gibbs<sup>14</sup> had in mind is that defined by eq 9, and estimates of this quantity are sensitive to the generally unknown variation of the heat capacity of the glasses with  $x$ .

The temperature and pressure at which a glass is formed can be varied independently so that, in general, the energy and density of glasses can be varied independently.<sup>1</sup> To account for both temperature and pressure variations, a more general model should use at least two order parameters,<sup>15</sup> for instance, an energy and a density,<sup>2</sup> to characterize the glasses. The distribution of the glasses in eq 7 can then be expressed as a function of the two parameters, and eq 5 can be applied to each parameter.<sup>18</sup> This complication was not included because there are outstanding questions<sup>15,18</sup> about the validity of the order parameter description of the glass transition that need to be resolved.<sup>36</sup> Davies and Jones<sup>15</sup> showed that a single order parameter description predicts that the Prigogine Defay ratio<sup>32</sup> is unity, and this is contradicted by experiment<sup>9,15,33</sup> for real materials. Di Marzio<sup>18</sup> argued further that the contradiction cannot be resolved by introducing more order parameters, but there is a flaw<sup>36</sup> in his argument. The objection<sup>15,18</sup> to a single-order parameter description of the glass transition does not apply to hard spheres<sup>2</sup> or to other models in which the potential energy is constant because the Prigogine Defay ratio is unity for such models.<sup>36</sup> A single-order parameter description may also be valid when only one independent variable is considered.

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## Appendix: Ethylbenzene

This appendix details the calculation of the excess entropy and enthalpy of ethylbenzene from heat capacity data for the liquid, crystal, and an experimental glass.

For the crystal and glass the heat capacity data in Table 2 of ref 21 was integrated numerically to get the enthalpy and

**TABLE 2: Coefficients in the Equation  $C_p(T)/R = \sum_{n=0} C_n(100K/T)^n$  for Ethylbenzene<sup>a</sup>**

phase	crystal $T =$ 102–171 K	liquid $T =$ 118–300 K	glass $T =$ 62–106 K	glass $T =$ 90–300 K
$C_0$	32.23	54.65	30.40	51.91
$C_1$	−57.78	−186.93	−40.52	−157.59
$C_2$	50.42	364.30	24.91	236.67
$C_3$	−16.32	−317.15	−5.54	−164.44
$C_4$	0	104.93	0	42.69

<sup>a</sup> The first three columns are from regression fits to the data in Table 2 of ref 21 over the indicated temperature range. The last column fits data for the glass (90–106 K) together with values of  $C_{p,g}$  that are consistent with eq A2 in the range 250–300 K. The equations fit the data with a standard deviation of less than 0.02 in  $C_p/R$ .

entropy. A Debye  $T^3$  law was used for the lowest temperatures, and the heat capacities were fitted to polynomials in the inverse temperature at higher temperatures. Some of the polynomial coefficients are listed in Table 2.

A polynomial for the crystal (Table 2) was used to extrapolate the enthalpy and entropy from 171.11 K to the melting temperature<sup>21</sup>  $T_m = 178.08$  K. Adding the measured<sup>21</sup> enthalpy and entropy of fusion gives the enthalpy and entropy of the liquid at the melting temperature relative to the crystal at absolute zero. No other use was made of the crystal data.

The difference between the (extrapolated) glass and liquid polynomials was used to get values of

$$\Delta_g^1 C_p(x(T_g), T) = C_{p,l}(T) - C_{p,g}(x(T_g), T) \quad (\text{A1})$$

The experimental glass transition temperature is  $T_g = 115$  K.

Yamamuro et al.<sup>21</sup> fit the heat capacity of the glass using a combination of Debye and Einstein functions, and they suggest that their extrapolation of the glass heat capacity to 300 K, using the theoretical forms, is reliable to within 5%. They make the general observation<sup>21</sup> that for all the simple substances for which they calculate the excess entropy (toluene, ethylbenzene, 3-bromopentane, 1-butene, and *o*-terphenyl), the empirical form

$$\Delta_g^1 S(x(T_g), T) = a + C/T^2 \quad (\text{A2})$$

is accurate for the high-temperature data, and this form was used for ethylbenzene above 250 K. To match their extrapolation between  $T_g$  and 250 K, a polynomial was fitted to the values of  $C_{p,g}(x(T_g), T) = C_{p,l}(T) - 2C/T^2$  implied by eq A2 in the range 250–300 K and also to the measured values for the glass in the range 90–106 K, with the coefficients shown in the last column of Table 1. The results shown in Figure 2 derive from eq A1 with the coefficients listed in Table 1 under liquid or glass (90–300 K) and eq A2 ( $T > 300$  K).

The enthalpy of the liquid relative to that of the experimental glass is

$$\Delta_g^1 H(x(T_g), T) = \int_{T_g}^T \Delta_g^1 C_p(x(T_g), T) dT \quad (\text{A3})$$

The lower limit is the experimental<sup>21</sup> glass transition temperature where the experimental glass has the same enthalpy as the liquid. The excess entropy is

$$\Delta_g^1 S(x(T_g), T) = \int_{T_0}^T \Delta_g^1 C_p(x(T_g), T) d \ln\{T\} \quad (\text{A4})$$

The lower limit is the temperature  $T_0 = 101$  K where the entropy of the liquid extrapolates to that of the glass.<sup>21</sup> The excess entropy in eq A4 is relative to the entropy of the experimental

glass, whereas eq 9 refers to the entropy of the liquid to one of the glasses that it samples at temperature  $T$ . The two values are the same only if all the glasses have the same heat capacity.

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