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Kauzmann's paradox and the glass transition

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Abstract

Kauzmann showed that the entropy of a liquid decreases rapidly on cooling towards the kinetic glass transition temperature and extrapolates to unreasonable values at lower temperature. The temperature where the extrapolated liquid entropy meets the crystal entropy is now called the Kauzmann temperature. Thermodynamics, with Planck's statement of the third law, shows that the entropy of a liquid cannot be less than the entropy of a glass with the same enthalpy. This is the thermodynamic condition violated by the Kauzmann extrapolation and it suggests a thermodynamic glass transition. Simulations show that, for the simple models studied and regardless of how the liquid entropy is extrapolated, the Kauzmann temperature cannot be reached because the entropy of glasses with the same enthalpy as the liquid is greater than that of the crystal.

Keywords: Glass transition; Kauzmann paradox

1. Introduction

Kauzmann [1] pointed out that the entropy of a supercooled liquid decreases rapidly on cooling towards the kinetic glass transition temperature, T_g, and usually extrapolates to the entropy of the more stable crystal not far below T_g. To illustrate the apparent paradox that intrigued Kauzmann in 1948, and still intrigues us today, Figs. 1 and 2 show the heat capacity and entropy of liquid, crystalline and glassy ethylbenzene; one of the simpler substances for which state of the art calorimetric measurements [2] are available. The heat capacity of the liquid is twice that of the crystal near 120 K and it drops sharply as the liquid becomes glassy on cooling below T_g. Within a transition range, $106<T<118$ K, where the measured heat capacity changes sharply, the measurement time (≈ 1 min [2]) is shorter than the time needed to equilibrate the liquid but still long enough to allow slow relaxation of glasses. The kinetic nature of the experimental glass transition is confirmed by observations that the drop in heat capacity occurs at a higher temperature when the liquid is cooled faster [3].

It is natural to ask how the amorphous phase might behave below T_g if it could be studied at equilibrium without freezing. Two conditions on the behavior below T_g, for real materials, are that the entropy cannot be negative and that the heat capacity must go to zero in the low temperature limit [5].

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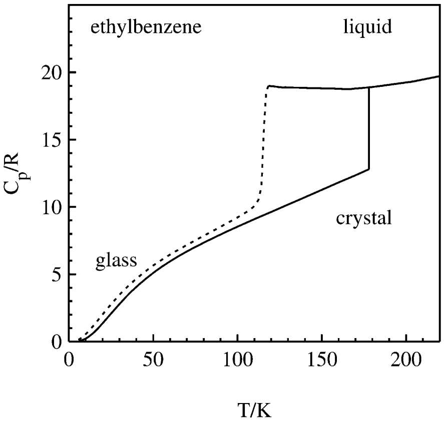

Fig. 1. The isobaric heat capacity of ethylbenzene vs. temperature at atmospheric pressure. The measured values from table 2 of Yamamuro et al. [2] are joined by straight lines except near the melting temperature, $T_m = 178$ K, where a short extrapolation [4] of the stable crystal measurements is used to smooth pre-melting effects. The glass was made by cooling the liquid quickly to approximately 5 K and its heat capacity was measured by adiabatic calorimetry while warming [2].

The slopes of the lines in Fig. 2 are related to the heat capacities shown in Fig. 1 by

$$(\partial S/\partial T)_P = C_P/T \qquad (1)$$

where S is the entropy and C_P is the isobaric heat capacity. Fig. 2 shows that if the heat capacity of the equilibrated amorphous phase did not drop sharply below T_g the entropy would become less than that of the experimental glass below 100 K, less than the crystal entropy below the 'Kauzmann temperature' $T_K \approx 88$ K and less than zero below 60 K. It is 'unthinkable' [1] that the entropy of a liquid can ever be much less than that of a solid, so if the idea of an equilibrated amorphous phase has meaning between T_g and absolute zero its heat capacity and entropy must follow paths quite similar to those shown by the dotted lines in Figs. 1 and 2.

Kauzmann [1] considered a thermodynamic glass transition but noted the unexplained coincidence between the kinetic and thermodynamic transitions. His preferred resolution of the apparent paradox was that spontaneous freezing prevents equilibration of the liquid near T_K, so that the concept of an equilibrated amorphous phase loses meaning.

Subsequently, Gibbs and DiMarzio [6] presented a lattice model for polymers with an ideal thermodynamic glass transition, where the entropy of a liquid tends to that of an essentially unique ideal glass. Adam and Gibbs [7] provided a plausible explanation for the near coincidence of the kinetic and thermodynamic glass transitions. DiMarzio [8] noted that glass forming atactic polymers do not have a crystalline phase so that freezing cannot always be invoked as a resolution. Angell et al. [9] showed that spontaneous freezing of an aqueous solution is orders of magnitude slower than the equilibration time within the liquid near T_g.

Section 2 shows that the entropy of a liquid cannot be less than the entropy of a glass with the same enthalpy. This is the thermodynamic condition likely to be violated when the liquid entropy is extrapolated below T_g and it suggests a thermodynamic glass transition. Section 3 reviews

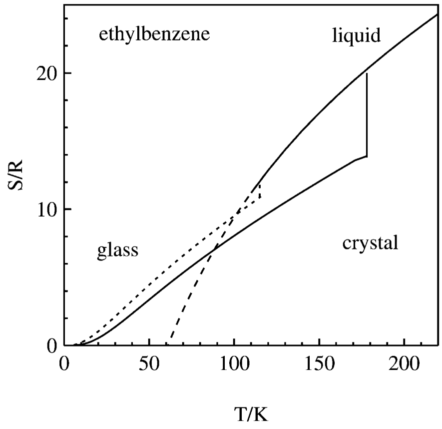

Fig. 2. The entropy of ethylbenzene obtained by integrating the heat capacities shown in Fig. 1, and using the measured entropy of melting from Yamamuro et al. [2]. In the transition range $106 < T < 118$ K, where irreversible relaxations occur, the heat capacities were extrapolated [4] from above and below to estimate the entropy of the equilibrated fluid or the stable glass. The vertical dotted line locates $T_q \approx 115$ K, where the liquid and glass have the same enthalpy, and its length shows the configurational entropy $S_c(T_q) \approx 1.1R$. If the liquid heat capacity stayed close to the value near 120 K, the liquid entropy would vary as $S_l(T) = S_l(120\text{ K}) - C_{P,l}(120\text{ K})\ln(120\text{ K}/T)$ and this is illustrated by the dashed extrapolation of the liquid entropy to temperatures below T_q.

some evidence from simulation studies to show that, for the models studied, and regardless of how the liquid entropy extrapolates, the Kauzmann temperature cannot be reached because the entropy of glasses with the same enthalpy as the liquid is greater than that of the crystal.

2. Entropy of a glass

The entropy of a glass is an ambiguous concept and it can be argued that it has no meaning [10–12]. The calorimetric entropy of a real glass, calculated by integrating Eq. (1) through T_g, is invariably greater than the crystal entropy in the low temperature limit [10–12]. But quantum mechanics requires that the entropy of any body vanishes in the low temperature limit [5], in accord with Planck's 1909 statement of the third law [13]. The apparent conflict arises because the kinetic glass transition is not a reversible process in the thermodynamic sense, and the entropy changes without an associated latent heat [14–16]. Section 3 summarizes some computer simulation studies that measure the irreversible entropy change at the transition.

The discussion is simplified by taking the pressure, P, to be constant and the temperature T to be the only external variable. The properties of an equilibrated, stable or metastable, liquid or crystal are determined by its composition and the temperature. The properties of a glass also depend on its history [17] and it is necessary to distinguish between glasses with different properties by specifying additional internal parameters. Davies and Jones [18] show that at least two internal parameters are needed when both P and T variations are considered but it is assumed here that one internal parameter is sufficient when only one external variable is considered. If structurally distinct glasses with the same history have significantly different bulk properties then more internal parameters are required to distinguish between them, but simulations support the view that the bulk properties of glasses formed with the same history are reproducible [17].

It is usually assumed [10,11] that a glass behaves reversibly at sufficiently low temperature. At higher temperatures, where irreversible relaxation is evident, the properties of a glass may be defined by extrapolation from temperatures where it behaves reversibly [2]. At some temperature $T=T_q$, a glass has the same volume and enthalpy, or heat content q, as the equilibrated liquid. T_q serves here as the internal parameter to distinguish between glasses with different properties. This choice is convenient but any other property that varies with T_q could serve as well [18]. For instance, in the inherent structures approach [19,20] an equilibrated liquid is instantaneously quenched to a glass in the low temperature limit and the enthalpy, $H_g(T_q, T=0)$ [20], of the glass is used as the internal parameter. By construction [20], the liquid configuration that quenched to that glass has the same enthalpy as the liquid at the temperature, T_q, from which the liquid was quenched. The definition of T_q as a thermodynamic parameter characterizing a glass allows us to consider the entropy difference between a glass and the equilibrated liquid at $T=T_q$.

In the following it is implicit that the liquid and glass heat capacities are extrapolated to T_q from temperatures where they behave reversibly and that in Fig. 1, for instance, the steep dotted line near T_g is replaced by a vertical line at T_q. The subscripts cr, l and g denote crystal, liquid and glass, respectively.

The enthalpy of a glass is

$$H_g(T_q,T)=H_g(T_q,0)+\int_0^T C_{P,g}(T_q,T)\mathrm{d}T \tag{2}$$

where $H_g(T_q, 0)$ is the enthalpy at absolute zero. The enthalpy of the liquid at T is the same as that of a glass with $T_q=T$ by definition

$$H_l(T)=H_g(T_q,T), \quad T_q=T. \tag{3}$$

Fluctuations in the enthalpy of a liquid are negligible, in the thermodynamic limit, so the liquid samples only those glasses with $T_q \approx T$ which satisfy Eq. (3). The thermodynamic difference between a liquid and a glass is that $T_q=T$ in the liquid but for a glass T_q is fixed and T can be varied. This explains [18] the jump in heat capacity at T_q because differentiating Eq. (3) gives

$$C_{P,\mathrm{l}}(T)=\left(\partial H_\mathrm{l}/\partial T\right)_P=C_{P,\mathrm{g}}(T_q,T)+\left(\partial H_\mathrm{g}(T_q,T)/\partial T_q\right)_{P,\mathrm{T}} \tag{4}$$

where $C_{P,\mathrm{g}}(T_q,\ T)=(\partial H_\mathrm{g}(T_q,\ T)/\partial T)_{P,Tq}$.

The residual calorimetric entropy of a glass, $S_0(T_q)$, relative to the crystal, in the low temperature limit [10–12], is calculated by integrating the heat capacity around the loop shown in Fig. 1, starting with the crystal at low temperature, adding the entropy of melting and integrating back towards the low temperature limit along the liquid and glass lines.

$$S_0(T_q)=\int_0^{T_\mathrm{m}}\frac{C_{P,\mathrm{cr}}(T)}{T}\mathrm{d}T+\Delta_\mathrm{cr}^\mathrm{l}S(T_\mathrm{m})+\int_{T_\mathrm{m}}^{T_q}\frac{C_{P,\mathrm{l}}(T)}{T}\mathrm{d}T+\int_{T_q}^{0}\frac{C_{P,\mathrm{g}}(T_q,T)}{T}\mathrm{d}T \tag{5}$$

where T_m is the equilibrium melting temperature. That calculation views the transition at T_q as a thermodynamically reversible process, with no entropy change because there is no heat change.

The dotted line in Fig. 2 shows the vibrational entropy of the glass, defined by

$$S_\mathrm{g}(T_q,T)=\int_0^{T}\frac{C_{P,\mathrm{g}}(T_q,T)}{T}\mathrm{d}T \tag{6}$$

which tends to zero in the low temperature limit [5,13]. The difference between the liquid and glass entropies at T_q, shown in Fig. 2, is the configurational entropy [6,7], $S_\mathrm{c}(T_q)$, defined by

$$S_\mathrm{c}(T_q)=S_\mathrm{l}(T)-S_\mathrm{g}(T_q,T),\quad T=T_q. \tag{7}$$

Summing the entropy changes around the loop shown in Fig. 2 gives the vibrational entropy of the glass, relative to the crystal, in the low temperature limit,

$$S_\mathrm{g}(T_q,0)=\int_0^{T_\mathrm{m}}\frac{C_{P,\mathrm{cr}}(T)}{T}\mathrm{d}T+\Delta_\mathrm{cr}^\mathrm{l}S(T_\mathrm{m})+\int_{T_\mathrm{m}}^{T_q}\frac{C_{P,\mathrm{l}}(T)}{T}\mathrm{d}T-S_\mathrm{c}(T_q)+\int_{T_q}^{0}\frac{C_{P,\mathrm{g}}(T_q,T)}{T}\mathrm{d}T. \tag{8}$$

The entropy of a real substance cannot be negative [5] so $S_0(T_q)\geqslant 0$, and the vibrational entropy $S_\mathrm{g}(T_q,\ 0)=0$ from Eq. (6), so Eqs. (5)–(8) imply that

$$S_\mathrm{c}(T_q)=S_0(T_q)\geqslant 0 \tag{9}$$

and

$$S_\mathrm{l}(T)\geqslant S_\mathrm{g}(T_q,T),\quad T_q=T. \tag{10}$$

Eq. (9) expresses the familiar notion [7,10–12] that the residual calorimetric entropy is the entropy that was 'frozen in' at some higher temperature. Adam and Gibbs [7] used Eq. (9) (equation 34 of [7]) to estimate S_c.

Thermodynamics does not require the liquid entropy to be greater than the crystal entropy, and rare cases are known where a crystal melts on cooling [21,22], which implies that the liquid entropy is less than the crystal entropy at equilibrium. But Eqs. (3) and (10) require that the liquid entropy cannot be less than the vibrational entropy of a glass with the same enthalpy, and this is the thermodynamic condition likely to be violated first when the liquid entropy is extrapolated below the kinetic glass transition temperature.

The vibrational entropy of a real glass [2] is typically 5–10% greater than the crystal entropy near T_g. Fig. 2 shows that $S_\mathrm{l}(T)-S_\mathrm{g}(T_q\approx 115\ \mathrm{K},\ T)$ extrapolates to zero at $T\approx 100$ K, but this does not violate Eq. (10) if a glass with the same enthalpy as the liquid at $T=T_q=100$ K has a lower entropy than the experimental glass with $T_q\approx 115$ K. The unknown factor is the way that $S_\mathrm{g}(T_q,\ T)$ changes with T_q. For instance, if all glasses of ethylbenzene have about the same heat capacity [4], independent of T_q, Eq. (6) implies that $S_\mathrm{g}(T_q=100\ \mathrm{K},\ T)=S_\mathrm{g}(T_q=115\ \mathrm{K},\ T)$ and the extrapolation of the liquid entropy shown in Fig. 2 does violate Eq. (10) below $T=T_q=100$ K. But a more plausible [23] estimate of the way $C_{P,\mathrm{g}}(T_q,\ T)$, and hence $S_\mathrm{g}(T_q,\ T)$, vary with T_q, shifts the violation to lower T. The sign and magnitude of $[\partial S_\mathrm{g}(T_q,\ T)/\partial T_q]_T$ is examined in Section 3.

The significance of the configurational entropy owes much to Frenkel's [24] insight that the vibrational motions of the molecules in a liquid are like those in a solid. In a solid the molecules vibrate about the sites of a fixed configuration. A liquid samples many structurally distinct configurations, or glasses, each with vibrational entropy $S_g(T_q, T)$, $T_q = T$, but the entropy of the liquid is higher than that of one glass because the liquid samples an extensive number, $N_g(T_q)$, of structurally distinct glasses. If the vibrational entropy of the liquid is $S_g(T_q, T)$, $T_q = T$, the configurational entropy $S_c(T_q) = k_B \ln(N_g(T_q))$ counts the number of structurally distinct glasses that the liquid samples. k_B is the Boltzmann constant.

The structure of a glass is fixed, except for vibrations, so structural relaxation and flow depends on transitions between glasses. Adam and Gibbs [7] identify the rapid decrease in $S_c(T_q)$ with decreasing $T_q = T$ as the main cause of the rapid increase in viscosity as a liquid is cooled near T_g. If $S_c(T_q) \to 0$, as many extrapolations suggest, the number of glasses $N_g(T_q)$ becomes sub-extensive and transitions between them become improbable. Adam and Gibbs argue that this causes a thermodynamic glass transition where structural relaxation times diverge.

3. Simulations

Simulation studies of model glasses compliment studies of real systems and this section shows that simulations can give evidence for an ideal glass transition that is not available from studies of real systems. One reason is that $S_c(T_q)$ can be calculated directly in simulations [14,15,17,25–31] whereas estimates of $S_c(T_q)$ for real liquids depend on assumptions and extrapolations [23]. A second reason is that some simulated models evidently [14,15,17,25] approach closer to the ideal glass transition temperature where $S_c(T_q) \to 0$. This is puzzling because molecular dynamics simulations are currently limited to time scales of microseconds while real materials are studied for 10^8 times longer [3]. The kinetic glass transition temperature decreases with slower cooling rates [3] so a natural expectation is that the much slower cooling rates possible in real experiments should allow closer approach to the ideal glass. A third reason is that simulations permit the quantitative study of glasses with a range histories and properties [17,26–31] so that the variation of $S_g(T_q, T)$ with T_q can be measured. A fourth reason is that a fluid can be made glassy in simulations by applying constraints [30,31] and the entropy of a constrained glass can be measured at temperatures where an unconstrained glass is unstable. These points are illustrated by the simulation studies described below.

3.1. Hard spheres

The measured pressure of the stable [32] and metastable [33] hard sphere fluid is represented by an empirical equation [33]

$$PV/RT = 1 + \frac{4y + 1.2162y^2 + 1.2467y^3}{1 - 2.1959y + 1.21035y^2} + D(y),$$
$$y < 0.56 \tag{11}$$

where y is the fraction of the space occupied by the spheres. For N spheres of diameter σ in a volume V, $y = (\pi/6)(N\sigma^3/V)$. The small term $D(y) = 0$ when $y < y_f$, where $y_f = 0.491$ is the equilibrium freezing density [33,34], and $D(y) = 985(y - y_f)^3$ when $y_f < y < 0.56$.

Accurate empirical equations are available [35] for the pressure [35,36] and entropy [34,35] of the face centered cubic hard sphere crystal.

Many glasses [25,37] were made by compressing the hard sphere fluid to $y \geqslant 0.58$ fast enough to avoid the formation of crystallites [15,25,37]. The direct test [15] for the absence crystallites in a glass is to decompress the glass instantaneously to the density $y = 0.54$, where the supercooled fluid freezes quickly [15,33] if a crystal nucleus is present. After the glasses are annealed near $y = 0.58$, which is just above the kinetic glass transition density, they behave reversibly when the density is cycled up and down and they are remarkably reproducible [15,25,37]. The glass pressures fit the empirical equation of state [17,25]

$$PV/RT = 1 + Cy/(y_0 - y), \quad y_0 > y \geqslant 0.58 \tag{12}$$

with $C = 2.8$ and $y_0 = 0.648 \pm 0.001$. The uncertainty quoted is the standard deviation in the best fit value of y_0 for 11 independently formed glasses of $N = 1372$ spheres. The limiting density y_0 is not sensitive to N but the variance is larger when N is smaller [25].

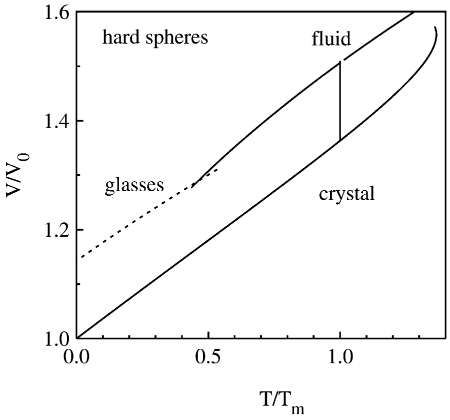

Fig. 3. The volume of the hard sphere fluid (Eq. (11)), crystal [35] and glasses (Eq. (12)) vs. temperature on an isobar. V/V_0 is the volume relative to the close packed crystal and T/T_m is the temperature relative to the equilibrium melting temperature. The glass volumes are reproducible to within the line width when the glasses are formed fast enough to avoid crystallites and subsequently annealed at $T/T_m \approx 0.44$ [15,25,37]. The fluid and glass lines are extrapolated (Eqs. (11) and (12)) when $0.52 > T/T_m > 0.44$ $(0.56 < y < 0.58)$, to show the change in slope at $T_q/T_m \approx 0.466$, where the density $y_q \approx 0.574$, and where the fluid and glasses have the same volume and enthalpy at the same temperature and pressure. The crystal line extrapolates to a spinodal instability above the melting temperature [35]. A plot of enthalpy against temperature has the same form because the enthalpy is $3RT/2+PV$ and the pressure is constant.

The isobaric temperature dependence of the volume of the hard sphere fluid, crystal and glasses is shown in Fig. 3. On an isobar PV_0 is constant and the temperature varies as RT/PV_0. The volume of the perfect crystal at close packing, $V_0 = N\sigma^3/\sqrt{2}$, is the volume unit. For hard spheres $PV_0/RT = 8.17$ at the equilibrium melting point [33,34] so the temperature relative to the melting temperature is $T/T_m = 8.17/(PV_0/RT)$ on an isobar. Short extrapolations of Eqs. (11) and (12) imply that the fluid and glasses have the same volume and enthalpy at the same pressure and temperature when $T_q/T_m \approx 0.466$ and $y_q \approx 0.574$.

The change in entropy due to a change in density is calculated by integrating the thermodynamic relation $P/T = (\partial S/\partial V)_U$. The entropy, relative to an ideal gas at the same N, V and T, is

$$\Delta_{ig}S(y) = \Delta_{ig}S(y_r) - R\int_{y_r}^{y} \frac{PV/RT-1}{y}\,dy \qquad (13)$$

where y_r is a reference density where the entropy is known. For the fluid $\Delta_{ig}^{f}S(y_r) = 0$ when $y_r = 0$ provides the reference state.

The entropy of a glass, relative to an ideal gas, from Eqs. (12) and (13), is

$$\Delta_{ig}^{g}S(y)/R = C\ln(y_0 - y) + S_0 \qquad (14)$$

where S_0 is a constant of integration [34] that must be measured independently.

The vibrational entropy of a real glass (Eq. (6)) is calculated by integrating the heat capacity from the low temperature limit, where $S_g(T_q, 0) = 0$, but that method cannot be used for the classical models studied in simulations because the heat capacity stays finite and the entropy diverges to minus infinity in the low temperature limit [34,36]. The tether method was developed [14] to measure the entropy of classical model glasses and it was used to measure the crystal and the glass entropies shown in this section. For the hard sphere crystal the method agrees [35] well with the original method of Hoover and Ree [34]. The entropy measurements confirm that the glasses behave reversibly and they determine the constant of integration in Eq. (14): $S_0 = -0.25 \pm 0.01$ [25].

Fig. 4 shows the entropy of the hard sphere fluid and glasses, minus the entropy of the crystal at the same pressure and temperature. Eqs. (11)–(14) yield $S_c(T_q) \approx 0.22R$, which is much smaller than the value $S_c(T_q) \approx 1.1R$ for ethylbenzene in Fig. 2. This result is striking because the effective cooling rate used to make hard sphere glasses is approximately 10^{15} times [37] the cooling rate used to make real glasses. Another significant result [25] is that the difference between fluid and crystal entropy is four times larger than $S_c(T_q)$ at $T = T_q$.

Long extrapolations of the fluid entropy [14,38,39] locate the Kauzmann temperature at $T_K/T_m \approx 0.3$ (where the fluid $y_K \approx 0.62$). If T_K is the low temperature limit for the fluid [39] then Eq. (9) implies the existence of an extensive number of glasses, with the same density and enthalpy as the fluid but with lower entropy than

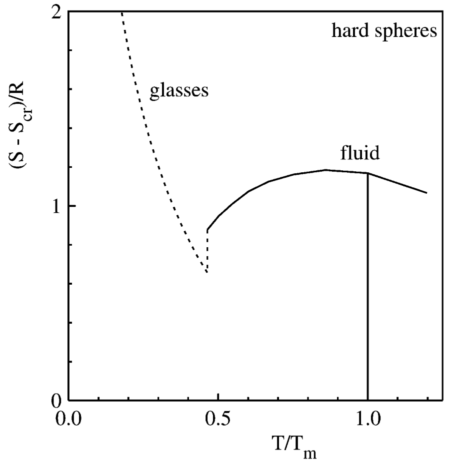

Fig. 4. The entropy of the hard sphere fluid (Eqs. (11) and (13)) and glasses (Eq. (14)) relative to the crystal [35] at the same temperature and pressure, vs. T/T_m on an isobar. The vertical solid line shows the entropy of melting [33,34]. The vertical dotted line locates $T_q/T_m \approx 0.466$ (Fig. 3) shows the configurational entropy $S_c(T_q) \approx 0.22R$. The glass line has a negative slope because the crystal entropy diverges to minus infinity faster than the glass entropy [15] as $T \rightarrow 0$ K.

the crystal at T_K, which is possible only if $[\partial S_g(T_q, T)/\partial T_q]_T$ is large and positive. However, much shorter extrapolations, with plausible assumptions [25] that allow for the variation of $S_g(T_q, T)$ with T_q, suggest that $[\partial S_g(T_q, T)/\partial T_q]_T$ is negative, and that Eq. (10) is violated at the higher 'ideal glass transition temperature' $T^0_{gt}/T_m \approx 0.428$ (where the density is $y^0_{gt} \approx 0.586$ [25]).

The reproducibility of hard sphere glasses has the drawback that it is difficult to make and characterize glasses with different T_q, and $[\partial S_g(T_q, T)/\partial T_q]_T$ has not been measured directly. Lower density glasses can be made, by compressing the fluid quickly to high density without annealing, but it is difficult to measure their properties because they relax quickly to more stable glasses when they are decompressed [25].

3.2. Tetravalent saturated square well model

A tetravalent saturated square well model, SSW, was developed to mimic tetravalent network glasses [17]. The results are relevant here because stable glasses with a range of properties can be made by compressing the SSW fluid at different rates. Glasses formed by compressing the fluid at the same rate are reproducible [17] but varying the compression rate by 10^5 changes the volume and enthalpy of the glasses by 6%, as shown in Fig. 5.

The model and its properties [17] are described briefly because the analysis is very similar to that given for spheres in Section 3.1. The particles have a hard sphere core of diameter σ and a square well of diameter $\lambda\sigma$. A pair whose centers are within $\lambda\sigma$ are bonded. When a particle has four bonds it is saturated and other particles bounce off it as though they are hard spheres of diameter $\lambda\sigma$. To mimic the angle dependence of real molecular interactions, triangles of bonds are prohibited and $\lambda = \surd(8/3)$ is chosen so that the model forms a close packed diamond crystal in which the four bonded neighbors of each particle are tetrahedrally disposed with their centers separated by $\lambda\sigma$.

The results shown in Figs. 5 and 6 are for the special case where the bonds have zero energy so that the potential energy of the system is zero and the temperature varies as RT/PV_0 on an isobar. The volume of the perfect diamond crystal at close

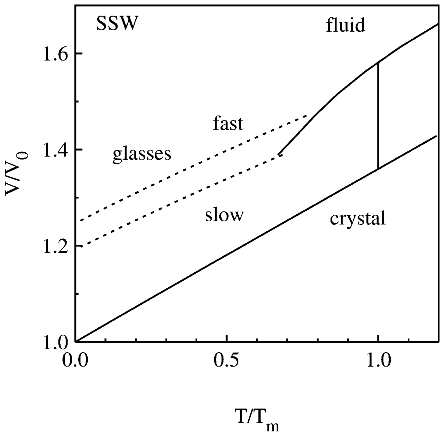

Fig. 5. The volume of the SSW fluid, crystal and glasses vs. temperature on an isobar. V/V_0 is the volume relative to the close packed diamond crystal and T/T_m is the temperature relative to the equilibrium melting temperature. The 'fast' glasses (data from row 2 of table 4, of Ref. [17]) were formed by compressing the fluid 10^5 times faster than the 'slow' glasses (data from row 13 of table 4, of Ref. [17]). The fluid and crystal data are from empirical equations [17].

packing is $V_0 = N\sigma^3(8/\sqrt{27})$ and $PV_0/RT = 8.15$ at the equilibrium melting temperature [17] so the temperature relative to the melting temperature is $T/T_m = 8.15/(PV_0/RT)$.

Fig. 5 shows the volume of the fluid, crystal and two glasses [17]. The 'slow' glass was formed by compressing the fluid at slowest practical rate and the 'fast' glass was formed by compressing 10^5 times faster. After the glasses are annealed at density $V_0/V = 0.73$ they behave reversibly and conform to Eqs. (12) and (13). The properties of many other glasses formed with intermediate compression rates [17] interpolate smoothly with the compression rate and are not shown.

The volume and enthalpy of the two glasses shown in Fig. 5 differ by 6% and their T_q values differ by 25%, so if $S_g(T_q, T)$ varies significantly with T_q the difference would be evident. Fig. 6 shows that the two glasses have essentially the same entropy when they are compared at the same T and P. For the SSW model then, there is no indication that a large positive value of $[\partial S_g(T_q, T)/\partial T_q]_T$ can be invoked to prevent the impending violation of Eq. (10) well above the Kauzmann temperature.

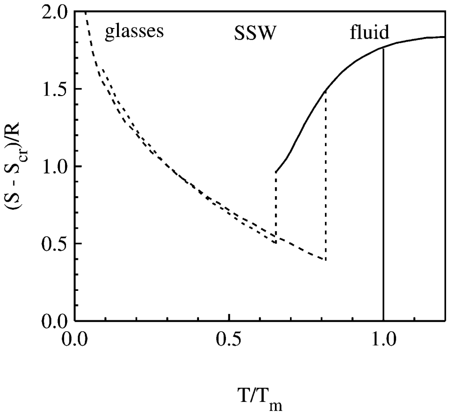

Fig. 6. The entropy of the SSW fluid and glasses [17] relative to the crystal at the same temperature and pressure, vs. T/T_m on an isobar. The vertical solid line shows the entropy of melting. The vertical dotted lines locate $T_q/T_m = 0.652$ (from Fig. 5) for the 'slow' glasses and $T_q/T_m = 0.813$ for the 'fast' glasses, where $S_c(T_q) \approx 0.46R$ and $S_c(T_q) \approx 1.09R$, respectively.

3.3. Constrained glasses of a hard disc mixture

A fluid of pure hard discs freezes too quickly to allow study of its glass transition. An estimated phase diagram for mixtures [40] suggests that an equimolar mixture of small discs with diameter σ_s and big discs with diameter $\sigma_b = 1.4\sigma_s$ shows eutectic freezing [31,40]. Crystallites of the big discs form when $PV_0/RT \approx 21.6$ and crystallites of the small discs form when their mole fraction is increased [31]. The deep eutectic [40] allows the fluid mixture to be studied to high density without freezing. The volume unit $V_0 = N\sqrt{3}(\sigma_s^2 + \sigma_b^2)/4$ is the volume of two pure crystals of the components, which is probably the stable state of the system in the low temperature limit [40]. Empirical equations are used for the pressure and entropy of a pure hard disc crystal [34,36] and for the fluid and glasses of the mixture [31,40]. The equilibrium melting temperature of the mixture has not been determined precisely [31,40] but that is not impor-

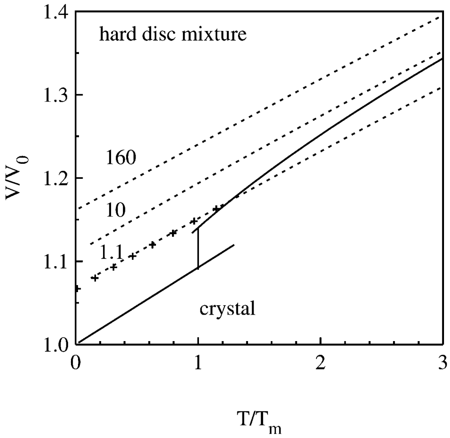

Fig. 7. The volume of the fluid, crystal and constrained glasses of a hard disc mixture vs. T/T_m on an isobar. The model [31,32,40] is an equimolar mixture of discs with diameters in the ratio 1.4:1. V/V_0 is the volume relative to the close packed volume of two pure crystals of the components and $T/T_m = 21.6RT/PV_0$ is the temperature relative to the estimated [31,40] eutectic freezing temperature. Numbers show the temperature, T_q/T_m, where the fluid was constrained to make the glass and where the glass has the same volume and enthalpy as the fluid at the same temperature and pressure. Crosses show the measured volumes kinetic glasses formed by compressing the fluid without constraints [40].

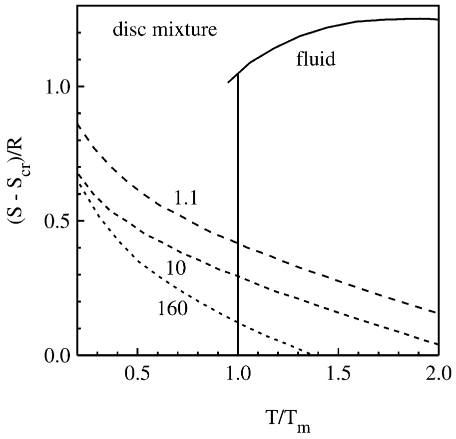

Fig. 8. The entropy of the fluid and constrained glasses [30,31] of the hard disc mixture relative to the entropy of two pure crystals of the components at the same temperature and pressure, vs. T/T_m on an isobar. The vertical solid line shows the entropy of melting. Numbers show the temperature, T_q/T_m for each glass. The fluid entropy includes the entropy of mixing $0.69R$. $S_c(T_q) \approx 0.8R$ when $T_q/T_m = 1.1$.

tant for the present purpose and $T/T_m = 21.6/(PV_0/RT)$ is used in Figs. 7 and 8.

Glasses can be made by constraining the fluid [30,31]. Starting with an equilibrated fluid configuration, each disc is permanently constrained to stay within the triangle of three close neighbors, by requiring the disc and any two of the discs that constrain it bounce off the line joining their centers whenever they become collinear in a molecular dynamics simulation [31]. Applying the constraints causes a thermodynamic glass transition where the heat capacity and entropy decrease but the volume and enthalpy are unchanged [30,31]. The value of PV_0/RT at the density where the constraints are applied determines T_q for the constrained glass. The constraints can be applied in the low density limit where $PV_0/RT \to 0$ and $T_q/T_m \to \infty$.

Fig. 7 shows that the volume and enthalpy of the constrained glasses vary by approximately 16% with T_q at the same T. Fig. 8 shows that entropy of the glasses increases as T_q decreases so the fluid entropy cannot approach the crystal entropy without violating Eq. (10) at a higher temperature.

4. Conclusion

Quantum mechanics [5] and Planck's statement of the third law [13] require that the entropy of a glass tend to the crystal entropy in the low temperature limit, which implies that entropy of a liquid cannot be less than the entropy of a glass with the same enthalpy. This is the thermodynamic condition violated by the Kauzmann extrapolation and it suggests a thermodynamic glass transition. Simulations show that, for the simple models studied, and regardless of how the liquid entropy extrapolates, the Kauzmann temperature cannot be reached because the entropy of glasses with the same enthalpy as the liquid is greater than that of the crystal.

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