

# Supercooled liquids, glass transitions, and the Kauzmann paradox

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Many liquids have heat capacities that substantially exceed those of the corresponding crystal, and this discrepancy magnifies in the supercooled regime. Thus, liquid entropy declines more rapidly with temperature than does crystal entropy, and the former paradoxically seems to fall below the latter for temperatures below the Kauzmann point  $T_K$ . Although laboratory glass transitions inevitably intervene to prevent observation of this entropy crossing, it has often been argued that a second-order "ideal glass transition" in principle should occur at  $T_K$ . The inherent structure theory of condensed phases has been modified to describe supercooled liquids, and has been applied to this Kauzmann paradox. The conclusion is that an ideal glass transition of the type normally associated with the Kauzmann phenomenon cannot occur for substances of limited molecular weight and with conventional intermolecular interactions. This result also subverts theoretical expressions for shear viscosity (such as the Tamman-Vogel-Fulcher and the mode-coupling formulas) that diverge to infinity at an ideal glass transition temperature.

## I. INTRODUCTION

Glass-forming liquids possess wide technological significance, and their properties continue to draw basic research attention in chemistry, materials science, and condensed-matter physics.<sup>1-5</sup> This paper is devoted to developing and applying a statistical mechanical formalism for metastable states, specifically supercooled liquids, to clarify the molecular nature of several static and dynamic properties that arise in formation of the vitreous state. Some aspects of this formalism have been previously advanced in connection with the "inherent structure theory" for condensed phases.<sup>6-12</sup>

Although all glasses formed by supercooling through a glass transition region in temperature undergo dramatic changes in relaxation rates, the resulting kinetic arrest and the properties it affects do not appear to exhibit "universality," i.e., simple scaling laws generally do not apply. Instead such basic properties as density, heat capacity, and shear viscosity vary through the glass transition region in ways that are quite material specific. In this connection Angell and co-workers<sup>13-15</sup> have proposed a useful classification scheme for glass-forming liquids, placing them along a scale between "strong liquid" and "fragile liquid" extremes. The former displays Arrhenius behavior for shear viscosity, and relatively little change in heat capacity as the glass transition is traversed ( $\text{SiO}_2$  is prototypical). The latter exhibits strongly non-Arrhenius viscosity that can often be well represented by the Tamman-Vogel-Fulcher equation<sup>16-18</sup>

$$\eta(T) \cong \eta_0 \exp[A/(T - T_0)], \quad \eta_0, A, T_0 > 0, \quad (1.1)$$

and the heat capacity drops suddenly upon passing from supercooled liquid to the glass (*o*-terphenyl is a good example). In principle, the formalism developed below is equally applicable to all supercooled liquids whether strong or fragile.

Kauzmann pointed out in 1948 a peculiar thermodynamic circumstance presented by glass-forming liquids, that

achieves its most vivid form for the fragile liquids.<sup>19</sup> This peculiarity subsequently has been named the "Kauzmann paradox." Its genesis is illustrated by Figs. 1(a) and 1(b). Owing to the fact that the heat capacity of the supercooled

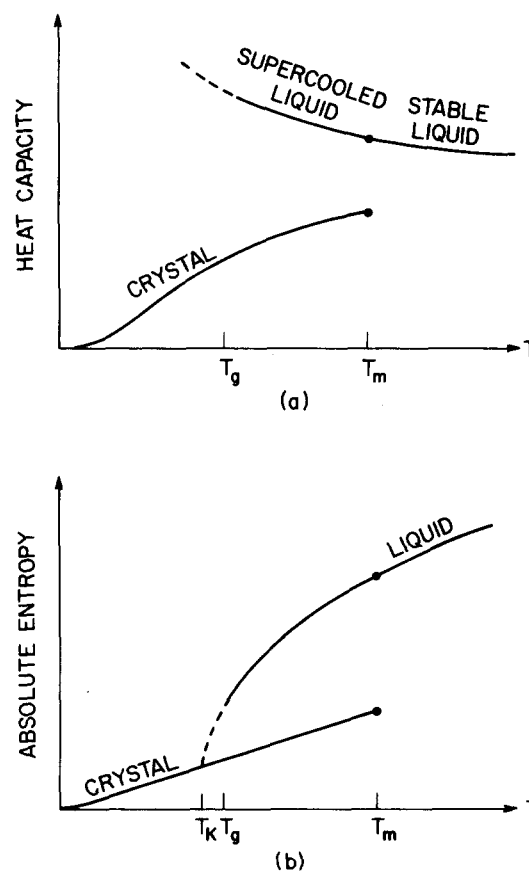


FIG. 1. Thermodynamic properties creating the Kauzmann paradox. (a) shows the heat capacities of the stable liquid, supercooled liquid, and crystal; (b) shows the corresponding absolute entropies. The Kauzmann temperature  $T_K$  is defined by intersection of the crystal entropy curve with that extrapolated for the supercooled liquid.

fragile liquid substantially exceeds that of the crystalline solid, the absolute entropy curves for these two phases appear to cross at a positive temperature  $T_K$ , the “Kauzmann temperature” that is close to  $T_0$  in the TVF equation (1.1). As Fig. 1 shows,  $T_K$  falls below the glass transition temperature  $T_g$  at which structural arrest occurs (for fragile liquids  $T_g/T_K = 1.05$  to  $1.10$ ), and for that reason the Kauzmann point is experimentally unachievable. But as a matter of principle one could conceive of a mechanism, or of a sufficiently slow experiment, which permits structural equilibration to obtain down to and below  $T_K$ . The resulting paradox is that the manifestly disordered metastable liquid below  $T_K$  would appear to have an entropy lower than that of the ordered crystal. Since vibrational entropies of crystal and amorphous forms at low temperature tend to be nearly equal for most substances,<sup>20</sup> this discrepancy concerns only configurational entropies of supercooled liquid and crystal, and thus appears to violate the inviolable third law of thermodynamics.

Originally it seemed that the way to avoid the paradox was to claim that nucleation of the crystal phase from the supercooled liquid became overwhelmingly probable as  $T_K$  was approached from above.<sup>19</sup> However, accumulating experimental evidence on the homogeneous nucleation behavior of glass-forming substances apparently contradicts this view.<sup>21</sup>

A popular alternative viewpoint is that  $T_K$  represents an ideal glass transition temperature. In this scenario, supported by the Gibbs–DiMarzio approximate lattice theory for polymer melts,<sup>22,23</sup> the supercooled liquid does indeed attain a vanishing configurational entropy at  $T_K > 0$ , and this point is a mathematically precise second-order phase transition point. Below  $T_K$  the ideal glass would retain its essentially unique configuration.

The analytical framework presented below for description of supercooled liquids permits a penetrating critique of the Kauzmann paradox. The conclusion is that for substances with molecules of bounded size interacting with physically reasonable potentials, an ideal glass transition in the strict sense is not possible. The simple and seemingly reasonable extrapolation of the metastable liquid entropy to temperatures below  $T_g$  is misleading. By implication this calls into question claims of strictly diverging viscosities and mean relaxation times at a positive temperature.<sup>24–29</sup>

## II. ISOTHERMAL–ISOBARIC PARTITION FUNCTION

Consider a many-body system composed of  $N_j$  particles of species  $j$  ( $1 \leq j \leq n$ ) with masses  $m_j$ , and denote the total particle number by

$$N = \sum_{j=1}^n N_j. \quad (2.1)$$

Measurements on glass formers typically occur at constant pressure  $p$ . Consequently we will assume that the  $N$  particles reside in a vessel that includes a movable piston with constant inward force. The interior volume  $V$  of the vessel can vary as the balance shifts between this inward force and the forces of collision of particles with the piston.

The total potential energy  $\Phi$  for this mechanical system includes three parts:

$$\Phi(\mathbf{r}_1 \cdots \mathbf{r}_N, u) = \Phi_0(\mathbf{r}_1 \cdots \mathbf{r}_N) + \Phi_1(\mathbf{r}_1 \cdots \mathbf{r}_N, u) + pAu. \quad (2.2)$$

The first,  $\Phi_0$ , is the interaction among the particles themselves, and depends only on their coordinates  $\mathbf{r}_1 \cdots \mathbf{r}_N$  (if the particles have structure these will specify internal coordinates as well as positions). The second,  $\Phi_1$ , comprises interactions of particles with vessel walls, one of which is the piston of area  $A$  whose position is described by coordinate  $u$ . Finally, the third term represents the work done to displace the piston. We have adopted the simple convention that the instantaneous volume is given by

$$V(u) \equiv Au. \quad (2.3)$$

Classical statistical mechanics should be adequate to describe the supercooling and glass transition phenomena of interest. Hence, effort will be directed toward developing a partition function to describe the supercooling extension of the equilibrium liquid. It is natural to start with the closed-system isothermal–isobaric partition function<sup>30</sup>

$$Y_N(\beta, p) = \left[ \prod_{j=1}^n \lambda_j^{3N_j} N_j! \right]^{-1} \times \int_0^\infty du \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_N \exp(-\beta\Phi). \quad (2.4)$$

Here  $\beta = (k_B T)^{-1}$ , the  $\lambda_j$  are mean thermal deBroglie wavelengths, and for notational simplicity we have assumed only point particles. The effective limits on the  $\mathbf{r}_1 \cdots \mathbf{r}_N$  integrals in Eq. (2.4) are set by the interactions comprised in  $\Phi_1$  of Eq. (2.2). Our principal interest lies in behavior of the large system limit, for which connection to thermodynamics is established by the identification

$$\ln Y_N(\beta, p) = -\beta G, \quad (2.5)$$

where  $G$  is the Gibbs free energy, an extensive quantity in that limit.

Equation (2.4) can be transformed into a simple quadrature by a minor generalization of the constant-volume inherent structure theory approach.<sup>6</sup> The configuration coordinates  $\mathbf{r}_1 \cdots \mathbf{r}_N, u$  generate a  $(3N + 1)$ -dimensional space within which  $\Phi$  has a set of discrete minima. These minima represent mechanically stable arrangements of the  $N$  particles and the piston subject to the given compressive force  $pA$  exerted on the latter from outside. Using arguments analogous to those for the constant-volume case, the number of  $\Phi$  minima in the large system limit will have the following asymptotic form:

$$\exp(\nu N) \prod_{j=1}^n N_j!, \quad \nu > 0. \quad (2.6)$$

The product of factorials is a trivial permutational factor that is present because any mechanically stable particle packing can be converted into an entirely equivalent one by interchanging the coordinates of identical particles. The nontrivial exponential factor enumerates inequivalent packings, and its exponent parameter  $\nu$  depends on interactions,

mole fractions, and pressure, and is of order unity.

It is natural to divide the  $(3N + 1)$ -dimensional configuration space into basins, each one of which contains precisely one minimum of  $\Phi$ . The basin  $B_\alpha$  surrounding minimum  $\alpha$  is defined to be that set of configurations for the system as a whole which connect to the minimum by means of the mass-weighted descent equations:

$$m_j \frac{dr_j}{ds} = -\nabla_j \Phi, \\ M \frac{du}{ds} = \frac{-\partial\Phi}{\partial u}, \quad s \geq 0, \quad (2.7)$$

where  $M$  is the macroscopic piston mass. The inclusion of masses as shown is important to make the boundaries between contiguous basins normal to the conventionally defined reaction paths connecting the respective minima.<sup>31</sup>

The partition function  $Y_N$  can be written as a sum over distinguishable basins

$$Y_N = \left[ \prod_{j=1}^n \lambda_j^{-3N_j} \right] \sum'_\alpha \\ \times \exp(-\beta\Phi_\alpha) \int_{B_\alpha} d\mathbf{R} \exp[-\beta\Delta_\alpha\Phi(\mathbf{R})],$$

$$\Delta_\alpha\Phi = \Phi - \Phi_\alpha. \quad (2.8)$$

Here we have let  $\Phi_\alpha$  stand for the value of  $\Phi$  at the local minimum  $\alpha$ , and the primed summation includes only one of each of the permutation-equivalent basins. The vector  $\mathbf{R}$  is shorthand notation for the collection of  $3N + 1$  configurational coordinates. All basins  $B_\alpha$  are connected, but may not be simply connected.

When the system size and particle number have macroscopic magnitudes the number  $\exp(\nu N)$  of distinguishable minima is enormous. Consequently a statistical representation of those minima and their associated basins becomes appropriate. Thus, it is useful to classify minima by  $\phi$ , their depths on a per particle basis:

$$\phi = \Phi_\alpha/N, \quad (2.9)$$

and in terms of this parameter we expect to have a continuous distribution of minima. To be consistent with Eq. (2.6) we write

$$\exp[\sigma(\phi)N]d\phi \quad (2.10)$$

for the number of minima whose depths per particle lie in the range  $\phi \pm d\phi/2$ . Clearly we must have

$$\exp(\nu N) = \int \exp[\sigma(\phi)N]d\phi, \quad (2.11)$$

and since these expressions are intended to apply only to the large-system limit ( $N \rightarrow \infty$ ,  $\beta$  and  $p$  fixed) where the integral in Eq. (2.11) is dominated by the neighborhood of the integrand maximum,

$$\nu = \max_{(\phi)} \sigma(\phi). \quad (2.12)$$

The basin integrals appearing in the  $Y_N$  expression (2.8) may be identified as classical vibrational partition functions. While these quantities certainly can be expected

to vary from basin to basin, it makes sense to introduce a suitable average for those basins whose depths are given essentially by  $\phi$ . For these we can define a mean vibrational free energy per particle as follows:

$$f_v(\beta, \phi) = -\lim_{\epsilon \rightarrow 0} \lim_{N \rightarrow \infty} (N\beta)^{-1} \ln \langle I_\alpha(\beta) \rangle_{\phi \pm \epsilon}, \\ I_\alpha(\beta) = \int_{B_\alpha} d\mathbf{R} \exp[-\beta\Delta_\alpha\Phi(\mathbf{R})], \quad (2.13)$$

where the angular brackets denote an *a priori* average over all basins whose minima lie between the subscripted limits.

Having introduced the packing enumeration function  $\sigma(\phi)$  and the vibrational free energy  $f_v(\beta, \phi)$ , we can now write  $Y_N$  as a simple quadrature over  $\phi$ :

$$Y_N(\beta, p) = \left[ \prod_{j=1}^n \lambda_j^{-3N_j} \right] \\ \times \int d\phi \exp\{N[\sigma(\phi) - \beta\phi - \beta f_v(\beta, \phi)]\}. \quad (2.14)$$

Both  $\sigma$  and  $f_v$  depend on  $p$ . The  $\phi$  integral will have finite lower and upper limits that are determined respectively by the best possible crystalline packing of the particles, and the worst (highest energy) mechanically stable packing.

An asymptotically correct evaluation of  $\ln Y_N$  only requires evaluating the integrand in Eq. (2.14) at its maximum. Let  $\phi_m(\beta, p)$  be that value of  $\phi$  which produces the integrand maximum at the prevailing  $\beta$  and  $p$ :

$$\sigma(\phi_m) - \beta\phi_m - \beta f_v(\beta, \phi_m) = \text{maximum}. \quad (2.15)$$

Then we have [as required by Eq. (2.5)]

$$N^{-1} \ln Y_N \sim -\sum_{j=1}^n (N_j/N) \ln \lambda_j^3 \\ + \sigma(\phi_m) - \beta\phi_m - \beta f_v(\beta, \phi_m). \quad (2.16)$$

The quantity  $\phi_m$  identifies the subset of basins within which the system will be found with overwhelming probability at the given  $\beta$  and  $p$ . Equation (2.16) in principle gives the equilibrium properties at any  $\beta$  and  $p$ , and in particular properly represents the first-order phase transition between equilibrium liquid and crystal.

### III. MODIFICATION FOR SUPERCOOLED LIQUIDS

In the event that the  $N$  particles constitute a pure substance or a congruently melting mixture,  $\phi_m(\beta, p)$  defined by Eq. (2.15) above will have a simple discontinuity at the melting temperature  $T_m$ . When  $T > T_m$  the relevant particle packings are amorphous and relatively high in potential energy, while for  $T < T_m$  they correspond to the (nearly) perfect crystal and have low potential energy. For simple substances at low pressure the discontinuity seems to be roughly 0.8 of the heat of fusion.<sup>7,8</sup>

Successful supercooling of a liquid requires that its configuration remain within basins whose stable packings (potential minima) are devoid of substantial crystallites. If they were present these crystallites could act as nucleation centers and would lead to subsequent crystal growth that eventually would consume the entire system. In order to extend the partition function  $Y_N$  from the strict equilibrium

regime to the supercooled liquid regime it suffices to project out of consideration that portion of the  $(3N + 1)$ -dimensional configuration space covered by basins whose packings contain crystallites beyond some critical lower size limit.<sup>8,9,12</sup> Furthermore, this projection must eliminate crystallites not only of the stable crystal form, but also of qualifying metastable allomorphs.

For present purposes it is not necessary to display all numerical details of a packing projection algorithm. It suffices to state that any packing and its basin should be eliminated if it contains a recognizable compact crystallite with, say,  $2^3 = 8$  unit cells of any "dangerous" crystal structure. In any case, application of the required pattern recognition is likely to be an NP-complete task<sup>12</sup> if implemented by computer.

After projection we are left with a reduced set of amorphous minima and their basins, the enumeration of which can be expressed in terms of  $\sigma_a(\phi)$ , the direct analog of the full-configuration-space function  $\sigma(\phi)$ . Obviously we have

$$\sigma_a(\phi) \leq \sigma(\phi), \quad (3.1)$$

and these two functions should differ most for the lowest values of the depth per particle  $\phi$ .

A depth-dependent vibrational free energy  $f_{va}$  can immediately be defined for the amorphous subspace using the same format (2.13) as before, but where the averaging operation includes only those basins remaining after projection. Just as before, both  $\sigma_a$  and  $f_{va}$  depend implicitly on pressure.

An amorphous region analog  $Y_{Na}$  for the partition function  $Y_N$  shown in Eq. (2.14) as a simple quadrature can now be written down:

$$\begin{aligned} Y_{Na}(\beta, p) &= \left[ \prod_{j=1}^n \lambda_j^{-3N_j} \right] \\ &\times \int d\phi \exp\{N[\sigma_a(\phi) - \beta\phi - \beta f_{va}(\beta, \phi)]\} \\ &\equiv \exp(-\beta G_a). \end{aligned} \quad (3.2)$$

The corresponding Gibbs free energy has been denoted by  $G_a$ . The  $\beta$  and  $p$  dependent depth  $\phi_{ma}$  of the dominating amorphous region basins is determined by the obvious modification of the earlier variational equation (2.15):

$$\sigma_a(\phi_{ma}) - \beta\phi_{ma} - \beta f_{va}(\beta, \phi_{ma}) = \text{maximum}, \quad (3.3)$$

whereupon we have

$$\begin{aligned} N^{-1} \beta G_a &\sim \sum_{j=1}^n (N_j/N) \ln \lambda_j^3 \\ &+ \sigma_a(\phi_{ma}) - \beta\phi_{ma} - \beta f_{va}(\beta, \phi_{ma}). \end{aligned} \quad (3.4)$$

Above the melting temperature  $Y_{Na}$  should be virtually identical to  $Y_N$  since the system containing thermodynamically stable liquid will be found with almost unit probability in amorphous basins. The assumption that  $Y_{Na}$  is the correct extension for the supercooled liquid presumes that below the melting point the system can continue to explore the amorphous region of configuration space in an adequately ergodic fashion on a time scale less than or equal to laboratory measurement times. The ability to carry out reproducible experiments on real supercooled liquids above their glass transition temperature justifies this presumption. On the other hand,

$Y_{Na}$  ceases to have direct experimental significance below the glass transition, but even then it remains important to understand how low temperature nonergodic dynamics evolves on the  $\Phi$  hypersurface in the amorphous region of configuration space, to understand relaxation phenomena.

One can imagine erecting an impenetrable barrier in the  $(3N + 1)$ -dimensional configuration space between the retained amorphous region and the rejected crystallite-containing portion. With such a barrier in place to reflect dynamical orbits specularly, the concept of an equilibrium partition function for just one side of that barrier is obviously legitimate.  $Y_{Na}$  is precisely the partition function for the amorphous side of the barrier.

The two Gibbs free energy functions  $G$  and  $G_a$ , in principle, should differ slightly for the equilibrium liquid. The former is believed to include a weak essential singularity at the melting point whose origin concerns the so-called "heterophase fluctuations."<sup>32-36</sup> The pattern recognition capacity embedded in the projection operation places an upper limit on the size of such fluctuations and thereby annihilates the essential singularity. The characteristic properties of good glass formers suggest that they are especially immune to heterophase fluctuations (since nucleation is improbable). Consequently the essential singularity in their  $G$  functions would be exceptionally weak, and  $G_a$  would be nearly invariant to changes in placement of the impenetrable barrier, i.e., to the specific limits on admissible crystallite sizes and shapes.

It should be noted in passing that Goldstein has also discussed the properties of glasses in terms of the multidimensional geometry of the potential energy function.<sup>37</sup> However, his analysis was offered without benefit of the formal and detailed theoretical superstructure upon which the present work has been based.

#### IV. LOW TEMPERATURE EQUILIBRATION

To set the stage for analysis of the putative Kauzmann point in glass formers, it will be instructive to trace operation of the formalism first for the equilibrium crystal phase below its melting temperature. Hence we first refer to the unprojected partition function  $Y_N$  in Eq. (2.14) and the associated variational criterion (2.15).

If the temperature is not too large the relevant particle packings are those for the perfect crystal (for which we write  $\phi = \phi_c$ ), and for slightly imperfect crystals ( $\phi > \phi_c$ ) containing low concentrations of point defects such as vacancies and interstitials. The immediate objective is to see how Eq. (2.15) is related to (and determines) the equilibrium concentration of those point defects.

We initially restrict attention just to simple vacancies as the possible point defects. Let their number be denoted by  $n_v$ . Under the assumption that the vacancies are sufficiently dilute to be treated as noninteracting, the number of defective crystalline packings containing the  $n_v$  vacancies is given by the elementary combinatorial quantity

$$(N + n_v)! / N! n_v! \quad (n_v \ll N). \quad (4.1)$$

The corresponding value of  $\phi$  may be taken to be linear in  $n_v$ ,

$$\begin{aligned}\phi &= \phi_c + \Delta\phi, \\ \Delta\phi &= \epsilon_v (n_v/N),\end{aligned}\quad (4.2)$$

where  $\epsilon_v > 0$  expresses vacancy creation enthalpy. Using Stirling's factorial formula in Eq. (4.1) and eliminating  $n_v$  in favor of  $\Delta\phi$ , we obtain the following expression for  $\sigma(\phi)$  for  $\phi$  just above its lower limit  $\phi_c$ :

$$\sigma(\phi) = -\epsilon_v^{-1} \Delta\phi \ln \Delta\phi + O(\Delta\phi). \quad (4.3)$$

The basic conclusion to be drawn is that  $\sigma$  increases from zero at  $\phi_c$  initially with infinite slope. Inclusion of other types of point defects, and of a finite number of defect configurations at any location within the crystalline matrix would not alter the basic functional form shown in Eq. (4.3) (though the numerical multiplier would be affected).

In contrast to the infinite-slope singularity displayed by  $\sigma(\phi)$ , one expects the vibrational free energy to have a nonsingular dependence:

$$f_v(\beta, \phi) = f_v(\beta, \phi_c) + b(\beta)\Delta\phi + O[(\Delta\phi)^2]. \quad (4.4)$$

The presence of point defects certainly will influence vibrational normal mode frequencies, but any reasonable model shows that the influence is additive over the defects while they are still dilute and widely separated. As a result of Eq. (4.4) we have

$$\begin{aligned}\beta\phi + \beta f_v(\beta, \phi) &= \beta[\phi_c + f_v(\beta, \phi_c)] \\ &+ \beta[1 + b(\beta)]\Delta\phi + O[(\Delta\phi)^2].\end{aligned}\quad (4.5)$$

The combination  $1 + b(\beta)$  can be expected to be positive since the per particle influence of isolated point defects is a modest perturbation overall.

We now return to the variational criterion in Eq. (2.15). It is satisfied when the slopes with respect to  $\phi$  of the  $\beta$ -independent enumeration function  $\sigma$  and of the combination  $\beta(\phi + f_v)$  are exactly equal. Figure 2 illustrates how this comes to pass. As temperature declines ( $\beta$  increasing to infinity) the latter combination produces a family of curves with increasing inclination. Slope matching then occurs at lower and lower  $\phi$ , but  $\phi_m$  only equals  $\phi_c$  at absolute zero because of the diverging slope of  $\sigma(\phi)$ . Referring to Eqs. (4.3) and (4.4) we have ( $A > 0$ ):

$$\phi_m(\beta) \cong \phi_c + A \exp[-\beta(1+b)\epsilon_v], \quad (4.6)$$

which explicitly shows how strongly the defect concentration vanishes as absolute zero is approached.

Next consider the supercooled liquid with the modified functions  $\sigma_a$  and  $f_{va}$  introduced in Sec. III. We need to identify mathematical circumstances for these modified functions which conceivably could produce a Kauzmann phenomenon at a positive temperature. Such an occurrence requires that the corresponding  $\phi_{ma}(\beta)$  become equal to  $\phi_L$ , the lowest value possible for the amorphous packings, at that positive Kauzmann temperature:

$$\lim_{\beta \rightarrow \beta_K - 0} \phi_{ma}(\beta) = \phi_L \quad (\beta_K < \infty), \quad (4.7)$$

and furthermore that  $\phi_{ma}(\beta)$  "stick" at this lower limit for all lower temperatures:

$$\phi_{ma}(\beta) \cong \phi_L \quad (\beta > \beta_K). \quad (4.8)$$

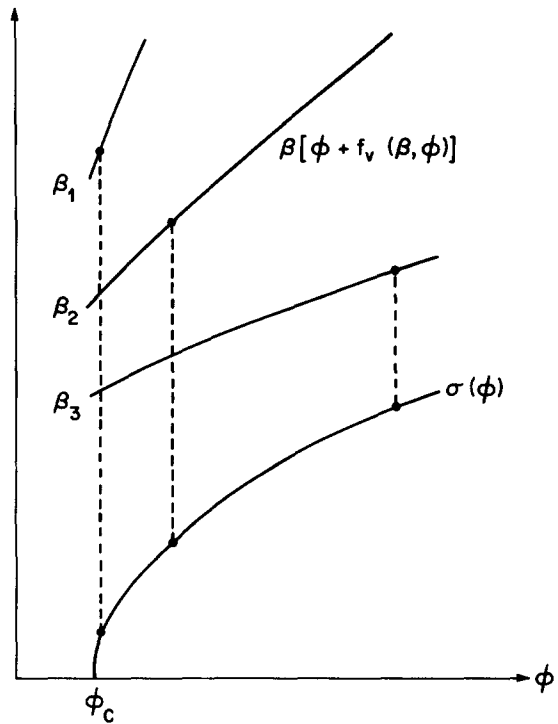


FIG. 2. Slope-matching construction to determine  $\phi_m(\beta)$  for the low temperature crystalline phase. Three members of the  $\beta(\phi + f_v)$  family of curves are shown, with  $\beta_1 > \beta_2 > \beta_3$ .

Heat capacity measurements on a given material at low (but not extremely low) temperature in both crystalline and in unrelaxing glassy states show that vibrational properties change relatively little upon amorphization.<sup>20</sup> Therefore, it is physically reasonable to suppose that the amorphous state combination  $\beta(\phi + f_{va})$  produces a family of curves vs  $\phi$  that are nonsingular in  $\Delta_a\phi = \phi - \phi_L$  just as shown in Eq. (4.5) for the crystalline case. Specifically,

$$\begin{aligned}\beta\phi + \beta f_{va}(\beta, \phi) &= \beta[\phi_L + f_{va}(\beta, \phi_L)] \\ &+ \beta[1 + b_a(\beta)]\Delta_a\phi + O[(\Delta_a\phi)^2].\end{aligned}\quad (4.9)$$

Existence of the novel Kauzmann point behavior consequently must require a qualitative change in the enumeration function  $\sigma_a$  compared to  $\sigma$ . Figure 3 illustrates what must happen, namely that  $\sigma_a$  retains finite slope for  $\phi$  near  $\phi_L$ :

$$\begin{aligned}\sigma_a(\phi) &= c\Delta_a\phi + O[(\Delta_a\phi)^2], \\ \Delta_a\phi &= \phi - \phi_L, \quad c > 0.\end{aligned}\quad (4.10)$$

Matching of slopes above the Kauzmann temperature locates  $\phi_{ma}(\beta)$  which declines monotonically to  $\phi_L$ . Exactly at  $\beta_K$  slopes match at the left ends of the curves, and are equal to  $c$  in Eq. (4.10). For lower temperatures,  $\beta > \beta_K$ , slope matching is no longer possible. However the condition that variational criterion (3.3) continue to be satisfied demands that  $\phi_{ma}$  stick at the lower limit  $\phi_L$ . This is precisely what would be required by an ideal glass transition.

We should remark in passing that the amorphous state of minimum potential energy per particle  $\phi_L$ , to be relevant

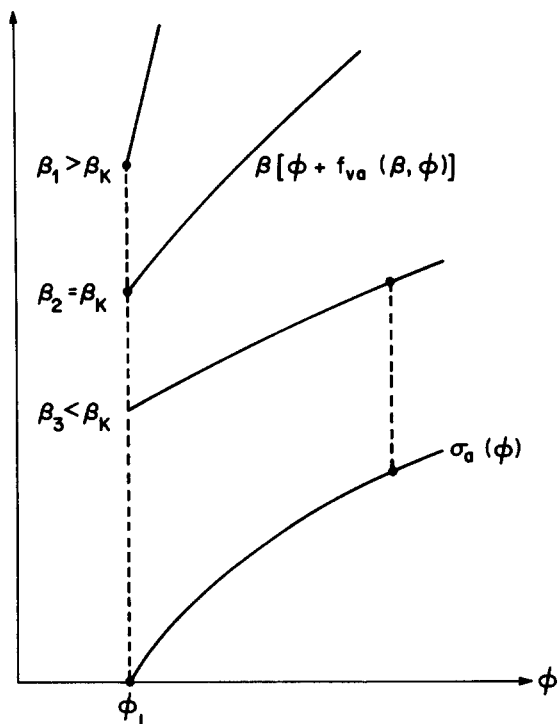


FIG. 3. Hypothetical circumstance required for existence of a positive temperature Kauzmann point. The decisive feature is the finite initial slope of the amorphous basin enumeration function  $\sigma_a(\phi)$ .

to a legitimate Kauzmann point, would have to have vanishing packing entropy per particle, i.e.,

$$\sigma_a(\phi_L) = 0. \quad (4.11)$$

This is not quite equivalent to claiming that the lowest potential energy attainable with an amorphous packing is unique (apart from permutations of identical particles). If there remains any packing degeneracy at  $\phi = \phi_L$  it would have to be less than exponential in  $N$  because of the way  $\sigma_a$  enters into the theory. A degeneracy, say, of some positive power of  $N$  or of the exponential of a fractional power of  $N$  would not affect the large-system-limit thermodynamic behavior at a Kauzmann point.

The finite initial slope character, Eq. (4.10), apparently demanded for  $\sigma_a$  by the existence of a Kauzmann point has remarkable consequences. In particular the lowest-lying structural excitations out of the ideal-glass state could not be described as independent point defects. If they were, a minor variant of the arguments concerning point defects in the crystal, culminating in the infinite initial slope result (4.3), would be immediately applicable. The function  $\sigma_a$  then would also have the same logarithmic singularity and infinite initial slope as does  $\sigma$ . The alternative seems to be either that (a) the structural excitations are localized and require bounded enthalpy but have a very much restricted set of positions (i.e., not proportional to  $N$ ) compared to the case for independent excitations, or (b) that excitation enthalpy diverges as the concentration of excitations goes to zero.

Neither of these alternatives seems reasonable for materials composed of limited size particles with interactions of a physically acceptable character. While it is possible that low-

lying two-level systems as point defects may be absent in the ideal glass state for such materials, there is no way to avoid the possibility of vacancy creation in any dense packing, simply by plucking out one or more particles from any location, placing them at the surface, and relaxing the result to reestablish mechanical equilibrium. The work that must be expended per vacancy in such a process is strictly bounded. Similar remarks may apply to other defects inserted in the ideal glass structure, such as interstitials, molecular conformational changes, etc. Consequently,  $\sigma_a$  inevitably must also have an infinite initial slope as described in Eq. (4.3). This in turn denies the possibility of a strict Kauzmann point for extrapolated entropy of supercooled liquids. Instead of the sharp bend indicated in Fig. 1(b), a rounding is in principle required. But since this occurs below the glass transition temperature it is not surprising that naive extrapolations from above  $T_g$  would fail to uncover it. Figure 4 illustrates how extrapolations for  $\phi_{ma}$  and configurational entropy for fragile liquids should appear.

We emphasize that our negative conclusion regarding an ideal glass transition of second order at a sharply defined Kauzmann point applies only to materials whose constituent molecules have upper bounds to their molecular weight. By contrast one can envision a polymeric system where the mean molecular weight is proportional to the system size. Then in the large system limit the molecular weight diverges

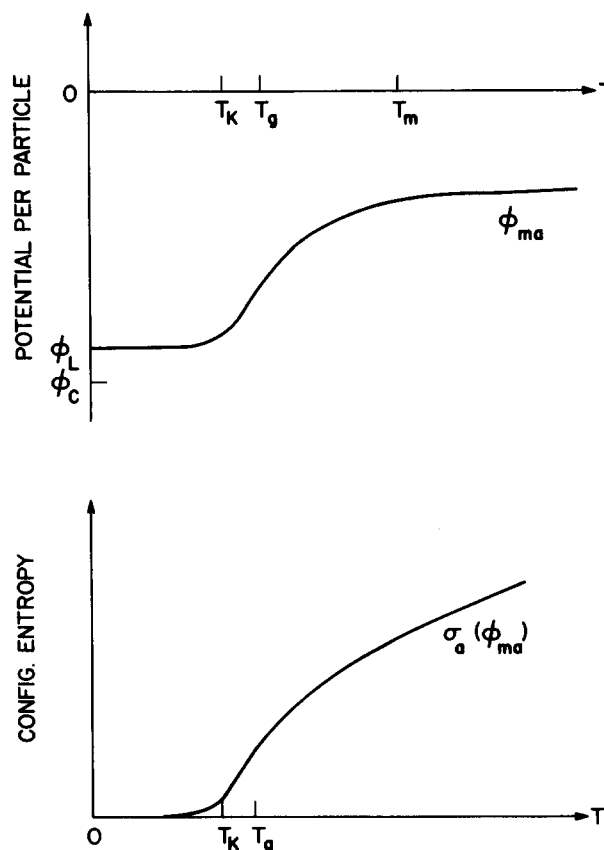


FIG. 4. Proper extrapolations below  $T_g$  of the predominant amorphous basin depth  $\phi_{ma}$ , and of the configurational (packing) entropy, for fragile liquids.

(i.e., the polymer chains become arbitrarily long). Under the assumption that polymer chemical bonds must always remain intact, it may indeed be impossible to create bound-enthalpy point defects (such as vacancies) at arbitrary locations in the optimally packed amorphous glass.

## V. DISCUSSION

The preceding considerations begin by supposing that if an ideal glass transition occurs within the amorphous manifold of basins that it is second order and is to be associated with the Kauzmann paradox. While this is the thermodynamic scenario most directly suggested by measurements on glass formers (notably the fragile liquids), alternatives cannot be entirely dismissed. It is conceivable that a transition of different order could be called for, requiring a modification of the analysis in Sec. IV. As an example, the tiling model for glass formation<sup>38–40</sup> is known to involve a first-order transition to an amorphous zero-entropy state with long-range coherence at positive temperature, but intrinsic kinetic bottlenecks render this state essentially unachievable. It is also possible that a strict transition, but to a nonideal glass, could exist wherein the low temperature phase still retained positive configurational entropy at positive temperatures.

The multidimensional configuration space description employed in this paper may have some advantages in explaining basic differences in behavior between the strong and fragile liquids. For any of these liquids,  $\phi_{ma}(\beta)$  identifies by depth the amorphous-region basins that predominate at any given temperature and pressure (assuming that equilibration in this region can be attained). Characteristic properties of the strong liquids imply that the  $\Phi$  hypersurface topography is rather uniform throughout the available configuration space, and that  $\phi_{ma}(\beta)$  only distinguishes basins by depths. The uniform roughness of strong-liquid topography is determined perhaps by the existence of relatively independent localized bonding defects in their networks, and by nearly fixed activation barriers for formation and exchange of those bonding defects.

By contrast, fragile liquids appear to possess nonuniform topographies for their  $\Phi$  hypersurfaces. At relatively high temperature  $\phi_{ma}(\beta)$  apparently identifies basins with rather low barriers. But as temperature declines the populated basins are to be found in regions of increasingly rugged topography, with greater elevation changes between minima and saddle points, and correspondingly more widely separated minima. This topographic variation may be associated with an increasing appearance of large well-packed regions of molecules in the lowest- $\phi$  packings, necessitating the un-bundling of larger and larger regions to get from one low-lying minimum to another.

Figures 5(a) and 5(b) schematically illustrate the topographic distinction offered as the underlying cause of observable differences between strong and fragile liquids.

An important open question concerns the nature of the lowest- $\phi$  packings for any given potential function. From the mathematical point of view it is known that specific pair potentials exist for which the absolute  $\Phi$  minimum is highly degenerate, with configurations including crystalline structures but also a preponderance of amorphous structures.<sup>41</sup>

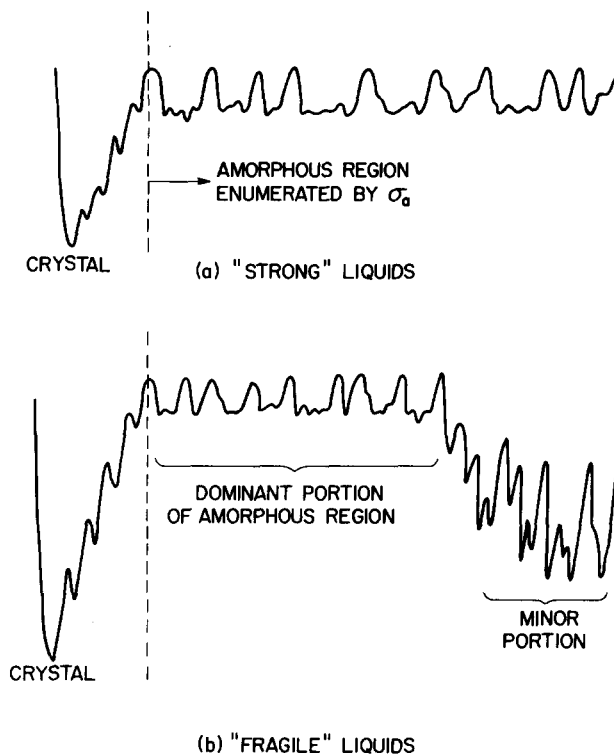


FIG. 5. Schematic view of potential energy hypersurface topographies. (a) illustrates the uniform roughness expected for the so-called “strong” liquids. (b) illustrates the nonuniform topography expected for “fragile” liquids.

The physical relevance of these special cases has not yet been fully assessed. It may turn out that for a substantial and physically applicable class of potentials (particularly for certain multicomponent substances) that the lowest- $\phi$  noncrystalline packings have quasicrystalline order.<sup>42</sup>

Understanding the nature of the multidimensional  $\Phi$  hypersurface at a deep level is a prerequisite for developing an accurate kinetic theory of supercooling, glass formation, and relaxation phenomena in vitreous solids. Such a kinetic theory would indicate circumstances whereby the amorphous state partition function  $Y_{Na}$ , Eq. (3.2), ceases to have relevance, and it should also be capable of explaining all time-dependent phenomena. It may be adequate in the low temperature regime to utilize a Master equation approach.<sup>9,43</sup>

Adam and Gibbs<sup>44</sup> have produced a theory for mean relaxation time  $\langle\tau\rangle$  near the measured glass transition. In the notation of the present paper their result is the following:

$$\langle\tau\rangle = \tau_0 \exp\{ +\beta C / \sigma_a [\phi_{ma}(\beta)] \}, \quad (5.1)$$

where  $\tau_0$  and  $C$  are appropriate positive constants. This states that relaxation processes are controlled by the availability of alternative configurational states at the given temperature, and so slowing of kinetics upon cooling is simply coupled to decline in configurational entropy ( $\sigma_a$ ). To the extent that comparisons are possible, the Adam–Gibbs relation appears approximately to describe the behavior of many real glass formers.<sup>45</sup> It is clear from Eq. (5.1) that if an ideal

glass transition point of the Kauzmann type were to exist,  $\langle \tau \rangle$  would pass continuously to infinity as the system were cooled to that point. The main conclusions of this paper, however, deny that possibility.

Theoretical models for glasses that are amenable to quantitative study seem to vary in the extent to which the Adam–Gibbs hypothesis is satisfied. Extensive Monte Carlo studies<sup>46</sup> of the Fredrickson–Andersen  $m$ -spin facilitated kinetic Ising model<sup>47,48</sup> show excellent agreement with Eq. (5.1). However, analogous studies for the tiling models of glasses<sup>39,40</sup> seem to show systematic deviations. One should expect that relaxation rates are inextricably connected to details of  $\Phi$  topographic roughness over a wide range of length and energy scales, with enough opportunity for variation from one case to the next to cause a logical decoupling of  $\langle \tau \rangle$  from configurational entropy. Therefore, it may eventually be possible (if only through artificial example) to display a dramatic violation of the Adam–Gibbs relation (5.1).

Both the TVF viscosity formula, Eq. (1.1), and the analogous algebraically divergent result from mode coupling theories<sup>27,29</sup>:

$$\eta(T) \cong \eta_1 (T - T_0)^{-\gamma}, \quad \eta_1, \gamma > 0, \quad (5.2)$$

imply that  $\eta$  becomes infinite at an ideal glass transition temperature  $T_0 > 0$ . The present paper's results imply that this cannot rigorously be true for limited size molecules with conventional interactions. Particle rearrangements of finite free energy cost are always available at any positive temperature to mediate flow at a finite rate under applied stress.

Finally, it should be emphasized that the general approach applied here to supercooled liquids can be adapted to other metastable states. One important case concerns liquids or solids under tension (i.e., negative pressure).<sup>49,50</sup> An isothermal–isobaric partition function can be derived for this circumstance as well. The required basin projection must remove all packings that contains voids larger than a prescribed critical size.

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