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Liquid-glass transition, a free-volume approach

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The free-volume model, which has been useful for describing the behavior of the viscosity η of dense liquids and glasses, is extended to account for their thermodynamic behavior as well. Experimental results for the heat capacity C_p and the volume $\bar{v}$ show that the system falls out of complete, metastable thermodynamic equilibrium at the glass transition temperature T_g. As a first step in understanding these universal phenomena, a theory of the underlying metastable phase, the amorphous phase, is developed. Recent molecular-dynamic calculations demonstrating the existence of a cellular structure in liquids and the properties of the local free energy of the molecular cells permit us to formulate more precisely and justify in more detail the standard free-volume model. In particular, it is possible to define the free volume and distinguish solidlike and liquidlike cells. This leads to the introduction of percolation theory, which is used to describe the gradual development of the communal entropy of the amorphous phase. We then determine the probability distribution of the cellular volume as a function of the fraction of liquidlike cells, p. The equilibrium liquid-glass transition is associated with the increase of p with temperature. This occurs via a phase transition which is most probably first order. The results of our theory give a generalized equation for the viscosity which agrees accurately with experimental results at all temperatures. Results for C_p and $\bar{v}$ are also obtained. This equilibrium theory can provide the basis for a relaxation theory of the kinetic effects observed around and below T_g. The relationship between the entropy theory and the free-volume model is also clarified.

I. INTRODUCTION

The liquid-glass transition has been intensively studied for many years.[1-3] Nevertheless, there are no rigorous theoretical results known. There is one simple picture, the free-volume model,[4-13] which is useful in describing the behavior of the viscosity in the vicinity of the transition. This model has been applied to interpret transport and relaxation phenomena in a variety of molecular systems. One central result obtained is a simple justification of the Doolittle equation[14] for the fluidity

$$\phi = \phi_0 \exp(-\gamma v_m / v_f) \quad . \tag{1}$$

Here γ is a constant of order unity, v_m is the volume of the molecule or molecular segment, and v_f is the free volume of the liquid (defined below). This picture of the glass transition, while physically appealing, is incomplete in that it does not account for the behavior of the specific-heat or thermal expansion. It is the purpose of this paper to remove that incompleteness in the earlier work.

We begin by noting the two important differences between liquids and solids. First, a liquid flows while a solid does not. Second, a liquid is translationally invariant while a solid is not. There are of course two different kinds of bulk solids, crystals and glasses. Crystals are translationally ordered and stable. Glasses are amorphous, i.e., disordered, and metastable. To form a glass, the melt is usually cooled very quickly (sometimes as fast as 10^5 °K/sec) to avoid crystallization. It is now commonly believed that glass formation is in fact just a failure of crystallization.[15,16] Put most simply, the glassy state is an extension of the liquid state in which the viscosity $\eta = \phi^{-1}$ increases above $\sim 10^{13}$ poise (a quantification of what is meant that a solid does not flow) and relaxation rates become on the order of days or more. The transition by which this occurs could be a true thermodynamic phase transition, given that in the glass the translational symmetry of the liquid is broken. However, there is no experimental evidence for a sharp phase transition. There could still be an underlying phase transition obscured by kinetic effects, or there could be no phase transition at all. The glass transition would then be kinetic in nature, a gradual freezing out of equivalent configurations. In the latter case, the glass and the liquid form a single, metastable thermodynamic phase we shall refer to as the amorphous phase. Indeed, it is convenient to use that phrase even if the glass transition is a true phase transition in the limit of slow temperature variation.

Solids can be classified according to bonding type and by their constituents. Glasses[17-56] occur among all such classes of solids. The simplest ones have spherical or nearly spherical constituents and include

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the metallic glasses[17–23] and some molecular substances. In this group one also includes the dense random packing (DRP) of hard spheres[57–60] and a system of Lennard-Jones particles[61,62] studied by molecular dynamics (MD).[63] The more complex glasses include ionic,[24–28] polymeric,[2,29–32] and organic materials.[33–41] There are also the network glasses[42–56] which include systems covalently bonded in two or three dimensions, both insulators and semiconductors. These distinctions are not sharp, and the groupings overlap.

There are classes of universal behavior through the glass transition which overlap the above categories of bonding and structure type for each of the properties fluidity, specific heat, and volume. The fluidity ϕ, as shown in Fig. 1(a) is well described by a Doolittle equation with $v_f \propto T - T_0$ only for a limited temperature range for most materials. A few simple organic glasses,[34] and some network glasses[43–45] including SiO_2 and GeO_2 follow an Arrhenius behavior ($T_0 \rightarrow 0$) over almost the entire temperature range studied, as shown in curve *a* of Fig. 1(a). Most glasses, including the ionic,[24–27] polymeric,[2,32] and organic[33–36,38–41] materials are described in the high-temperature region ($\eta \leq 10^4 \rightarrow 10^6$ poise) by curve *b* or *c* of Fig. 1(a) with $T_\eta = T_{0H} \neq 0$. In Table I we present a partial list of glass formers and their characteristic temperatures T_η and T_g (defined below). Most of these results do not extend to lower temperatures near T where η becomes $\gtrsim 10^8$ poise. In those systems which have been measured at higher values ($10^8 < \eta < 10^{14}$) it is found that some become Arrhenius, T_0 changing from T_{0H} to $T_{0L} \rightarrow 0$, curve *b* of Fig. 1(a), while others are described by a finite value of $T_{0L} < T_{0H}$, curve *c* of Fig. 1(a). Examples of the former include the organic liquids salol,[40] α-phenyl-*o*-cresol,[40] *n*-butylbenzene,[34] and di-*n*-butyl phthalate[34] and the ionic glass 0.60 KNO_3-0.40 $Ca(NO_3)_2$.[28] The organic liquids *o*-terphenyl[36–46] and tri-α-naphthylbenzene[39,40] are examples of the latter. The organic glasses studied in Ref. 34 and listed above as having Arrhenius behavior could as well have a finite T_η because η was not measured below 10^3–10^4 poise. We have found only one system,[17,18] the metallic glass $Au_{0.77}Ge_{0.136}Si_{0.094}$ which can be fitted in both regimes with a value of $T_\eta \approx T_{0L}$, curve *c* of Fig. 1(a). Tweer *et al.*[64] have shown that many of these systems, which cannot be fitted by the three-parameter Doolittle equation over the entire range ($10^0 < \eta < 10^3$ poise) with a single value of T_0, can be fitted with a more general five-parameter equation for η which diverges only as $T \rightarrow 0$. Included in this fit is the organic liquid tri-α-naphthylbenzene which has a finite T_{0L} when fitted to the usual equation for η. This leaves open the possibility that T_{0L} always $\rightarrow 0$.

This deviation of η from its high temperature dependence with $v_f \propto T - T_0$ could be regarded as a

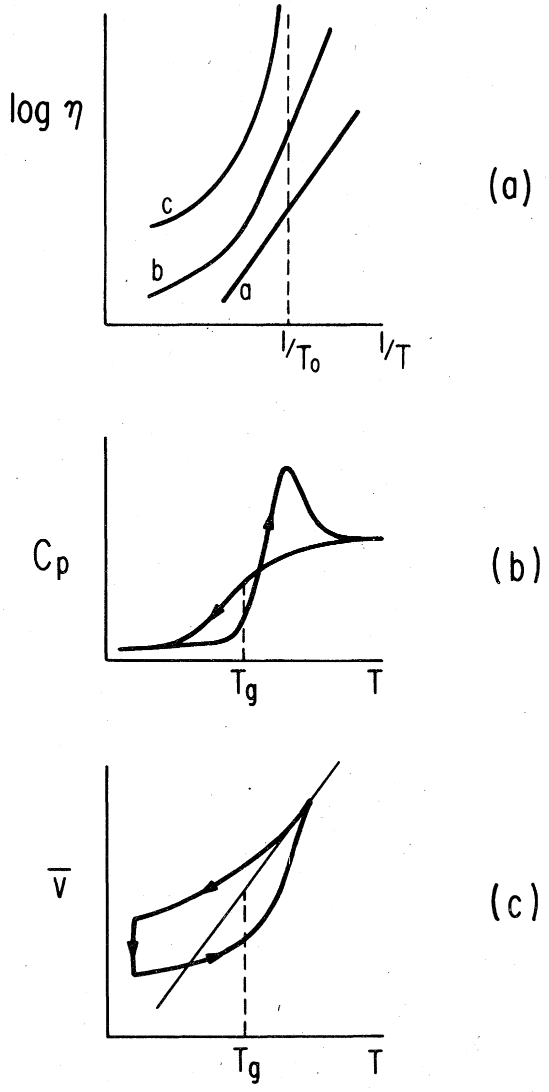

FIG. 1. (a) Logarithm of viscosity η vs reciprocal temperatures. Curve *a* corresponds to Arrhenius behavior, $T \rightarrow 0$. Curves *b* and *c* correspond to the Doolittle equation where the free volume $\bar{v}_f \propto T - T_{0H}$, $T_{0H} \neq 0$ at the high temperature and $\bar{v}_f \propto T - T_{0L}$ at low temperatures. In curve *b*, $T_{0L} \rightarrow 0$ while in curve *c*, $T_{0L} \neq 0$. (b) Heat capacity C_p at constant pressure vs temperature for a glass cooled and then reheated through the transition. The position of the glass transition temperature T_g depends on the cooling and heating rates employed. (c) Isobaric volume $\bar{v}$ vs T illustrating volume hysteresis effect. The equilibrium curve in the liquid well above T_g is unique. At a constant cooling rate q, the volume $\bar{v}$ falls out of equilibrium below T_g. When the sample is then annealed at constant T, the volume becomes densified and may reach a relaxed glass state, depending on the temperature. The lower portion of the solid curves represents the behavior after heating at a constant q. Note $\bar{v}$ remains under its liquid value to a $T > T_g$. This plot is similar to that found for *a*-Se in Ref. 56 and for a polymeric system in Ref. 67.

TABLE I. Characteristic temperatures for glass formers.

Glass Former	T_g (°K)	T_η (°K)	T_s (°K)
$Au_{0.77}Ge_{0.136}Si_{0.094}$[a]	295	241	...
tri-α-naphthylbenzene[b]	342	342	...
o-terphenyl[c]	240	248 231	200
salol[d]	230	226	...
α-phenyl-*o*-cresol[d]	230	210	...
2-methylpentane[e]	79.5	59	58
glycerol[e]	180	132	134
B_2O_3[e]	539	402	335
$ZnCl_2$[e]	375	260	250
$Ca(NO_3)_2$-$4H_2O$[e]	217	205	202
$0.62KNO_3$-$0.38Ca(NO_3)_2$[f]	328	320	...

[a] Reference 17.
[b] References 39 and 40.
[c] References 36, 37, 40, and 68.
[d] Reference 40.
[e] Reference 26.
[f] Reference 25.

nonequilibrium phenomenon. However v_f usually begins to deviate from this form at a temperature which is greater than the temperature at which the system is considered to fall out of thermal equilibrium, i.e., the temperature at which the anomaly in C_p occurs. For the organic glasses,[40] this deviation occurs at a viscosity $\eta \sim 10^4$ poise, while $\eta \geqslant 10^8$ poise at the glass transition. In the measurements for these organic glasses,[40] care was taken to assure that the equilibrium value of the viscosity was obtained. For the metallic glass[17] Au-Ge-Si, the viscosity when measured at its highest accessible values begins to deviate sharply from the simple exponential behavior, presumably from nonequilibrium effects. We expect that nonequilibrium phenomena will lead to a quite different pattern of temperature variation for η than occurs when Eq. (1) with $v_f \propto T - T_\eta$ no longer holds. In this work, we consider the deviation of η from its high-temperature behavior to represent equilibrium behavior and derive a more general equation for the free-volume which has the same high-temperature form that becomes Arrhenius at low temperatures.

There can also exist marked changes in the specific heat C_p within a narrow temperature range around a temperature T_g conventionally referred to as the glass transition temperature. The value of T_g and the shape of C_p are very dependent on the heating and cooling rates of the measurement and on the thermal history of the sample.[65–67] It is believed that the *observed* changes in heat capacity are the consequences of the falling out of complete thermodynamic equilibrium[68] of the system under observation as the time of measurement becomes comparable to the relaxation times of the system. Experimentally, it is found that T_g is higher for faster heating or cooling rates. It is also found that the anomaly in C_p depends on the sign of $q = dT/dt$. The majority of the measurements are done at a constant heating rate, starting from the glassy state, and the observed anomaly is shown in Fig. 1(b). When measured at a constant cooling rate[66] in materials which do not crystallize, C_p is a monotonic, decreasing function as also shown in Fig. 1(b). It is found experimentally that $T_g \gtrsim T_\eta$. On the other hand, in the two network glasses SiO_2 and GeO_2 having vanishing T_0, there is little evidence for anomalies in C_p and therefore for a T_g.[1] However, the organic classes having $T_0 \rightarrow 0$ for $\eta > 10^3$–10^4 poise[34] show well-defined values of T_g (Refs. 26 and 38); we suspect therefore that a finite T_{0H} may be needed to describe the region $\eta \lesssim 10^3$ poise. It is important to note that the viscosity varies smoothly through T_g, showing no sign of anomalies like those observed in C_p.

The specific volume $\bar{v}$ also shows an anomalous temperature dependence near T_g. The behavior of $\bar{v}$ is universal among all systems having a T_g. When measured at a constant cooling rate q, $\bar{v}$ as shown in Fig. 1(c) decreases linearly with T and changes slope at a temperature dependent on q but close to the T_g observed for the heat capacity. Below this breakaway temperature, the system is not in equilibrium. When the system is annealed, $\bar{v}$ decays towards a lower asymptotic value, $\bar{v}_0$, which can either lie on the extrapolated volume temperature curve for the liquid or above it if the annealing temperature is low enough.[56] This suggests the existence of a $\bar{v}$ vs T curve for metastable equilibrium which breaks away from the extrapolated liquid curve, but as yet no information is available on where or how it breaks away. There is hysteresis upon heating at a constant rate q. $\bar{v}$ remains under the extrapolated liquid volume, then rises rapidly to a final equilibrium liquid value at a $T > T_g$. The amount of hysteresis is dependent on the value of q.

These experimental results indicate, that as studied in the laboratory, the glass transition is a kinetic phenomenon which depends on the time scale of the measurements. The question still remains whether, as suggested by the volume annealing data, there exists a real thermodynamic glass transition in the limit of infinitely slow heating or cooling. That some such limiting behavior should exist has been demonstrated by extrapolations of heat capacity versus temperature for liquid.[26,28] These extrapolations suggest that at a temperature T_s from 20 to 200 °K below the observed value of T_g, depending on the material, the difference in entropy between the liquid and crystalline phases would vanish and then become negative. A partial list of values of T_s compiled by Angell and co-workers[25] is included in Table I. The existence of an amorphous phase with total entropy lower than the stable crystal phase at the same temperature is unreasonable. Moreover, the heat capacity of the glass is known to be higher than that of the crystal at low temperatures. To avoid this apparent paradox, C_p has to decrease precipitously at a temperature not far below the observed T_g. As pointed out by Angell and Sichina,[68] the most gradual possible decrease of C_p below T_g that remains consistent with the requirement that $S(\text{liquid}) > S(\text{crystal})$ still amounts to a very sharp change in C_p, comparable to the high-temperature end of a common λ transition. The existence of the vanishing excess entropy was first recognized by Kauzmann[69]; it points to the possible existence of an "ideal" glass transition T_p at a temperature $T_s \lesssim T_p < T_g$. In the limit of slow heating and cooling T_g would approach T_p. It is interesting to note that $T_\eta \simeq T_s$, as recognized by Angell and coworkers.[26]

The idea of a vanishing-excess-entropy temperature T_s suggests the notion that a real phase transition, either second or first order, may occur at T_g in the limit of slow heating or cooling. There exists only one detailed thermodynamic theory, the entropy theory developed by Gibbs and DiMarzio[70] and by Adams and Gibbs[71] to describe polymeric systems. In their theory, they place the polymer links on a lattice and introduce holes for the missing lattice sites. They then compute the entropy of mixing and the configurational entropy of the polymer and find a second-order transition at a temperature $T_2 \neq 0$. They point out that this temperature would correspond to T_g if the experiments could be done in the limit of infinitely slow warming, so that the system were always in equilibrium. For monatomic materials, the theory reduces to Frenkel's hole theory of liquids,[72] which is known not to be very accurate. Accordingly, we propose in the present paper an extension of the free-volume model for simple liquids which includes the thermodynamics. We find that the equilibrium glass transition is likely to be a first-order phase transition in the limit of slow cooling or heating. In the process, we develop a theory of the communal entropy[72] of liquids and glasses within the notion of the free-volume model, which we give a somewhat sounder basis. The entropy is evaluated by introducing results from the theory of percolation.[73,74] This allows us to calculate the heat capacity C_p and thermal expansion, and we find anomalies at a temperature we assimilate to T_p. A related study of the fluidity leads to the Doolittle equation with an appropriate temperature dependence of v_f.

The outline of the paper is as follows: In Sec. II, we elucidate and justify the basic assumptions which underlie the free-volume model. By consideration of the nature of the local free energy of the molecular cells, we are able to define the free volume and to distinguish solidlike and liquidlike cells. This leads naturally to the introduction of percolation theory in Sec. III, which we use to determine the communal entropy of the amorphous phase. In doing so, it is necessary to use a more general conception of communal entropy than is found in the literature on liquids. In Sec. IV, we find the probability distribution of the cellular and the free volumes as a function of the fraction of liquidlike cells, p. The liquid-glass transition, i.e., the softening of the glass, is associated with the increase of p with temperature. In the present theory this occurs via a phase transition, the order of which is shown in Sec. V to depend critically on the value of the exponent β which characterizes the growth with p of the percolation probability for liquidlike cells. The viscosity is derived in Sec. VI and successfully compared with experimental results. Corresponding results for the heat capacity and specific volume are obtained in Sec. VII. Finally, we summarize the important results, discuss the effects of eliminating the simplifications within our model on the proposed transitions, and discuss indicated further work in Sec. VIII.

II. FREE-VOLUME MODEL

Fox and Flory[4] first postulated that the liquid-glass transition resulted from the decrease of the free volume of the amorphous phase below some critical value. The subsequent derivation of Doolittle's fluidity equation[14] within the free-volume model is based on four simple assumptions[6–8] which can be worded as follows:

(i) It is possible to associate a local volume v of molecular scale with each molecule.

(ii) When v reaches some critical value v_c, the excess can be regarded as free.

(iii) Molecular transport occurs only when voids having a volume greater than some critical value v^* approximately equal to the molecular volume v_m form by the redistribution of the free volume.

(iv) No local free energy is required for free-volume redistribution.

The resulting equation for the diffusion constant[6-8] is of the form given by Eq. (1).

Assumption (i) is valid if each molecule is restricted to movement within a cell or cage defined by its nearest neighbors. Kirkwood proposed such cells to exist in a liquid, but for simplicity proposed further that the cells were all identical, forming a regular lattice.[72] He took for the free energy

$$F=\sum_i f_i - TS_c \ , \tag{2}$$

where f_i is the free energy of an atom or molecule moving within its cell in the mean potential of its neighbors, properly corrected for double counting of the interactions, and S_c is the communal entropy. f may be regarded as the local free energy referred to in assumption (iv). S_c arises in a liquid from the diffusion of molecules throughout the entire volume and may be written

$$S_c = k\ln[(N-1)v_s] \ ;$$
$$k\ln v_{s_i} = s_i = -\frac{\partial f_i}{\partial T} \ . \tag{3}$$

Clearly, the glass transition might profitably be examined within the framework of a thermodynamic theory such as this. Equally clearly, justification of assumptions (i)–(iv) would justify also such a thermodynamic theory.

Hsu and Rahman[75] have shown by MD calculations that the diffusion coefficient of a dense, supercooled Rubidium-like liquid at constant volume extrapolates to zero (but at a temperature which is essentially zero). Earlier a Lennard-Jones liquid had been quenched into what appeared to be a glassy state by rapid cooling to a temperature which turned out to be below T_{0H}.[61] Subsequent simulations showed, however, in a variety of systems the diffusion coefficient remained finite, though small, below T_{0H} and that crystallization ultimately occurred. Thus the crystal is the lowest energy state of the system, but there is a disordered state of low atomic mobility which is metastable, persisting for a time which is very long on the molecular scale. We identify this state as a glass, as did Rahman, Mandell, and McTague.[61] Rahman has not examined the thermodynamic properties for evidence of anomalies in C_p or $\bar{v}$ and therefore of a T_g. However, Wendt and Abraham[76] have found that the ratio of the values of the radial distribution function at the first peak and first valley shows behavior on cooling much like that observed for the volume of real glasses, Fig. 1(c), with a clearly defined T_g. Stillinger and Weber[77] have studied a Gaussian core model and find a self-diffusion constant which drops essentially to zero at a finite temperature. They also find that the ratio of the first peak to first valley in the radial distribution function showed behavior similar to that found by Wendt and Abraham[76] for Lennard-Jones liquids. However, the first such evidence for a nonequilibrium, i.e., kinetic, nature of the transition in a numerical simulation was obtained by Gordon *et al.*,[60] who observed breakaways in the equation of state and the entropy of a hard-sphere fluid similar to those in real materials.

The radial distribution function found for the putative Lennard-Jones glass at finite T was closely similar to that found for the DRP of hard spheres in a calculation effectively carried out at $T=0$.[78] The differences of detail suggest that the structure be considered the DRP of soft spheres. In the DRP of hard spheres, all spheres are completely constrained by their nearest neighbors.[57,79] It is thus possible to construct around each atom Voronoi polyhedra which differ in shape and volume and take these as the cells or cages in a cellular model. The results of Rahman *et al.* strongly suggest the same can be done for the Lennard-Jones glass and presumably all simple molecular glasses.

Jacucci[62] has examined the structure of a dense, argonlike, Lennard-Jones liquid in a novel and instructive way. MD calculations are typically done in about 10^4 times steps of 10^{-14} sec each. The positions are retained and the radial distribution function constructed from sets of position pairs taken at equal time. Jacucci first averaged the molecular positions over an intermediate time interval of 10^2 steps or 10^{-12} secs and then constructed the radial distribution function. He found a radial distribution function very close to that found by Rahman *et al.*[61] apart from an expansion of the distance scale. Thus, a well-defined cage or cellular structure persists in the liquid for a time scale longer than 10^{-12} sec. It would be of interest to determine on what time-scale and at what temperature this structure begins to break down.

Further MD calculations by Jacucci provide both detailed justification of assumption (iii) and additional support for the cage picture. Jacucci examined the separation of a pair as a function of time in his dense, supercooled, argonlike Lennard-Jones liquid. He found that the separation underwent occasional large changes of order the particle spacing. In between these, the separation showed rapid small fluctuations around a nearly constant value. In a cage picture, the former correspond to the diffusive steps of Cohen and Turnbull[6-8] which lead to an occasional reorganization of the cages, whereas the latter correspond to motion within a cage structure which remains roughly static in between diffusive steps. Their critical free-volume fluctuation picture of self-diffusion in dense liquids is similar to the vacancy model of self-diffusion in crystals. However, in crystals individual vacancies exist and retain their identity over long periods of time, whereas in liquids the corresponding voids are ephemeral. The free volume is distributed statistically so that at any given instance there is a certain concentration of molecule-sized voids in the liquid. However, each such void is short-lived, being created and dying in continual free-volume fluctuations. The Frenkel hole theory of liquids ignores this ephemeral, statistical character of the free volume.

These results of Rahman,[75] Rahman *et al.*,[61] and Jacucci[62] strongly suggest that there is a cage structure in a sufficiently dense liquid which, as the liquid is cooled, persists for longer and longer times until finally it is frozen. Assumption (i) is thus justified, and Eq. (2) can be made the basis for a simple theory of the glass transition. The computer quenching experiments and the structural results demonstrate as well the validity for the Lennard-Jones fluid of the concept of a single-condensed amorphous phase comprised of the vitreous and liquid states; the results of Wendt and Abraham[76] suggests that there can be a T_g below which the system goes out of equilibrium.

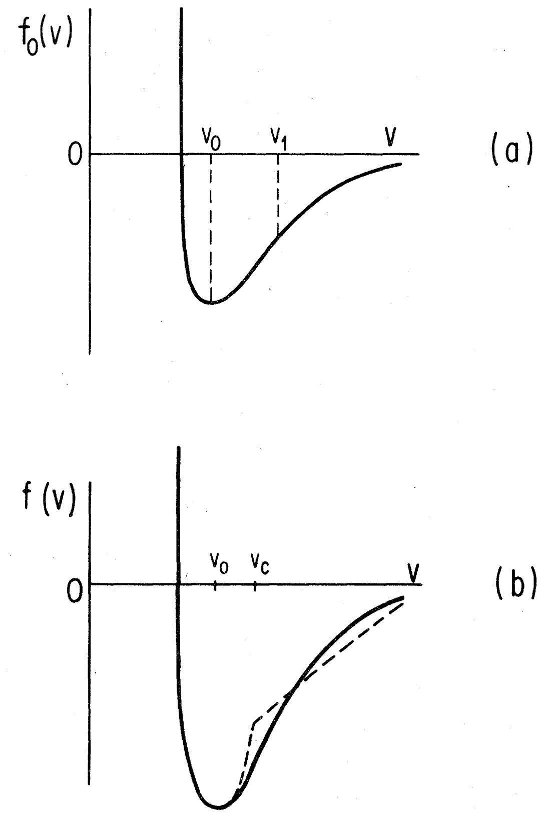

FIG. 2. (a) $f_0(v)$, the negative of the work to remove a molecule from the center of a cell vs cell volume v. v_0 marks the minimum and v_1 the point of inflection of $f_0(v)$. (b) Local free energy $f(v)=f_0(v)+f_1(v)$, where $f_1(v)$ is the work to expand the cage to the volume v from its average value. For $v > v_c$, $f(v)$ can be approximated as quadratic and for $v > v_c$, linear in its dependence on v as shown by the dashed curve.

If we suppose in Eq. (2) that the local free energy f_i of a cell depends only on its volume v_i, $f=f(v)$, the free energy becomes

$$F=N\int P(v)[f(v)+kT\ln P(v)]dv-TS_c \tag{4}$$

where we have added the entropy of $P(v)$, the probability that a cell has a volume v, to Eq. (2). The local-free-energy function $f(v)$ contains two contributions, the negative of the work to remove a molecule from the interior of a cage of volume v, $f_0(v)$, and the work to expand the cage to the volume v from some suitable average value, $f_1(v)$. The work to remove a molecule from the center of a cage at $T=0\,^\circ\mathrm{K}$ has the same general shape as a function of cage volume that the intermolecular pair potential has as a function of pair separation.[7] Thermal effects will not modify this, and we use for $f_0(v)$ the shape shown in Fig. 2(a). The essential features of $f_0(v)$ are a minimum at v_0 and a point of inflection at v_1. The discussion of $f_1(v)$ is more intricate because it depends on the state of the neighborhood of the particular cell in question. One can, however, argue that for smaller v, the total $f(v)$ must be quadratic in v. Moreover, as v increases beyond the minimum in $f_1(v)$, $f_1'(v)$ decreases because of the reduced effect of interaction across the void. The asymptotic behavior of $f_1(v)$, however, depends on whether v is in a liquidlike or solidlike environment. In the latter case one has both a surface energy and an elastic component, in the former case only surface energy. We are not interested in such wide variation of v, and for us the significant thing in both $f_0(v)$ and $f_1(v)$ is the decrease in slope below that of quadratic dependence on v as v increases away from the minimum. Thus a shape for $f(v)$ like that of $f_0(v)$ is good enough for our purpose. Accordingly, we suppose $f(v)$ to have the model form shown in Fig. 2(b). To simplify the system to the point where quantitative analysis becomes possible, we approximate the continuous curve of Fig. 2(b) by the model free energy

$$f(v)=\begin{cases} f_0+\frac{1}{2}\kappa(v-v_0)^2, & v<v_c \\ f_0+\frac{1}{2}\kappa(v_c-v_0)^2+\zeta(v-v_c), & v>v_c\ . \end{cases} \tag{5}$$

The parameters f_0, v_0, κ, $v_0<v_c<v_1$, and ζ can be determined on a best-fit basis. All are functions of T

and particle density. f_0 and v_0 turn out to be irrelevant. Thermal smearing effects and thermal expansion at constant pressure give $\partial v_c/\partial T$, $\partial\kappa/\partial T < 0$.

The segmenting of $f(v)$ in Eq. (5) enables us to divide the cells into two classes. Those with $v > v_c$ we call liquidlike, and those with $v < v_c$ we call solidlike. Following Turnbull and Cohen,[7] we say that only liquidlike cells with $v > v_c$ have a free volume, which we take as

$$v_f = v - v_c\ , \quad v > v_c\ . \tag{6}$$

It immediately follows that the part of the sum of local free energy $\sum_i f_i(v)$ contributed by liquidlike cells, $v_i > v_c$, depends only on the average value of v_i among the liquidlike cells. That is, according to Eq. (6) it depends only on their average free volume, v_f, and is unchanged by any repartition of the free volume among the liquidlike cells. It is in this sense that a free volume can be defined, as in assumption (ii), and can be redistributed without change of free energy, as in assumption (iv). This is as far as Turnbull and Cohen got in formulating their version of the free-volume model; they were unable to proceed to a thermodynamic calculation.

As stated above, $f(v)$ has two contributions $f_0(v)$ and $f_1(v)$, the latter of which depends sensitively on the nature of the cell's immediate environment. This dependence is not so crucial for smaller expansions, $v < v_c$, in the quadratic range, but in the linear range, $v > v_c$, it must be taken into account. We therefore, decompose ζ into two corresponding parts ζ_0 and ζ_1, leave ζ_0 as a constant, and introduce the environment dependence into ζ_1. The system clearly becomes more rigid as the volume decreases; ζ_1 is maximal when the system is entirely solidlike. We can characterize the deviation from solidlike behavior through the mean free volume within the liquidlike fraction of the material,

$$\bar{v}_f = \int_{v_c}^{\infty} (v - v_c)\, P(v)\, dv \Big/ \int_{v_c}^{\infty} P(v)\, dv\ . \tag{7}$$

As will emerge in Sec. III, we are primarily interested in liquidlike cells with a substantial number of liquidlike neighbors. Accordingly as $\bar{v}_f$ increases, the environment becomes progressively less rigid and ζ_1 decreases monotonically. A very simple function of $\bar{v}_f$ which has that monotonic behavior over a large range of $\bar{v}_f$ and approaches a finite limit when $\bar{v}_f \rightarrow 0$ (solidlike) is

$$\zeta_1 = \frac{kT_1}{v_a + \bar{v}_f}\ , \tag{8}$$

where v_a and T_1 are constants of the dimension of volume and temperature, respectively. This form for ζ_1 will have important implications for the final forms of the average free volume $\bar{v}_f$ and viscosity η. We show below that this term is not an entropic contribution to the free energy but must come from effects of environment on the free energy of each cell. We arrive therefore at

$$\zeta = \zeta_0 + \frac{kT_1}{v_a + \bar{v}_f} \tag{9}$$

for ζ in Eq. (5).

The entire cage picture on which the free-volume model and the mobility theory are based is valid only for a sufficiently dense material. As the material expands, the time scale over which the cage structure persists becomes comparable to the time scale of motion within the cages, and the picture loses its meaning. We emphasize that it should be used primarily for discussion of supercooled liquids where the Doolittle equation holds, of the glass transition, and of certain aspects of the glassy state. Our model excludes the possibility of a channel to crystallization. Since most glasses are stable for periods greater than years, this does not pose a problem.

III. PERCOLATION THEORY AND THE COMMUNAL ENTROPY

The essence of the free-volume theory of Sec. II is that the only change in free energy associated with a redistribution of free volume is in the entropy of the probability distribution of the free volume. This arises from the decomposition of the free energy into a sum of terms depending only on the volume of a single cell, the local free energy $f(v_i)$, and from the linearity of $f(v_i)$ in v_i. Of the two, the former is the more serious approximation. Consider two liquidlike cells which are not nearest neighbors and are individually surrounded by solidlike cells. From the construction of the Voronoi polyhedra defining the cell volume, it is clear that the cell volumes are not all independent variables. It is not possible to change the volume of an isolated liquidlike cell without also changing the volumes of the neighboring solidlike cells. Thus, a change in the local free energy of an isolated liquidlike cell which is linear entails quadratic changes in those of the neighboring solidlike cells. An exchange of free volume between isolated liquidlike cells therefore entails a change in the sum of the local free energies of all of the cells and will be an activated process. A free exchange of free volume can take place only between liquidlike cells which are nearest neighbors and which have a sufficiently large number of other liquidlike nearest-neighbor cells $\geqslant z$ that the volumes of any neighboring solidlike cells are not constrained to change simultaneously. This defines a type of percolation problem.[73–74]

The fraction of liquidlike cells is

$$p = \int_{v_c}^{\infty} P(v)\, dv\ . \tag{10}$$

When p is nonzero, there are clusters of liquidlike cells each one of which has at least z liquidlike neighbors. It is well known that in such situations there is a critical concentration p_c above which there exists an infinite cluster. Thus, for $p > p_c$ there is an infinite, connected liquidlike cluster, and we can consider the material within it to be liquid. For $p < p_c$, only finite liquidlike clusters exist, which might imply a glass phase because the fluidity would be reduced. However, percolation theory tells us that just above p_c the infinite cluster is very stringy or ramified[80–83] so that bulk glass properties are not fully developed.

We have defined a liquidlike cell to be in a cluster if it has at least z neighbors which are also liquidlike. Within such a liquidlike cluster cells can exchange their free volume freely without restriction by neighboring solidlike cells. The usual percolation problem has $z=1$ so that all isolated liquidlike cells would be clusters of size one. Thus, we have introduced a new percolation problem, one to our knowledge not previously discussed in the literature.[84] We do know that a system with $z=2$ has the same value of p_c and is essentially the same as the $z=1$ case, with only a few dangling cells excluded from the clusters. For $z > 2$, the percolation threshold p_{cz} becomes z dependent. The various critical exponents associated with the percolation problem are z dependent as well, and we have no knowledge of their values. The general structure of the theory must remain unchanged, and it is only this which we use in the following. The value of z appropriate to this free-volume theory is uncertain; a reasonable estimate is $z \simeq \frac{1}{2}n$, where n is the average number of nearest neighbors.

At this point one is tempted to anticipate the results of the quantitative analysis and suppose that the liquid phase has $p > p_{cz}$, the glass phase has $p < p_{cz}$, and $p = p_{cz}$ at the glass-transition temperature. If so, the transition would be second order because the infinite cluster is formed sharply.[73,74] Calculations based on the model show that it can be second order in some circumstances, but in most circumstances it is first order with a range of values of p around p_c included. Elimination of the simplifications we have introduced wipes out the second-order phase transition, but the first-order phase transition persists in the circumstances we believe hold experimentally, as we shall discuss after presenting the calculations.

We note also that atomic mobility occurs within finite liquidlike clusters which exist below the transition. Thus, the fluidity of the system would in principle persist below T_p as is observed.

Let us now proceed via the relevant quantitative features of percolation theory to a theory of the communal entropy.

In the usual percolation problem with $z=1$, if one counts all isolated liquidlike cells as clusters of size one, then all pN liquidlike cells are in clusters. That is no longer true when $z \neq 1$. Only a fraction $a_z(p)$ of the pN liquidlike cells are now in the cluster $[a_1(p) \equiv 1]$. The cluster distribution $C_{\nu z}(p)$, $\nu = 1, 2, \ldots,$ is normalized so that

$$\sum_{\nu=1} \nu C_{\nu z}(p) = \begin{cases} 1, & p \leq p_{cz} \\ 1 - P_z(p), & p > p_{cz} \end{cases} , \tag{11}$$

where $P_z(p)$ is the percolation probability, the probability of being in the infinite cluster $(P_z(p) = 0, p < p_{cz})$. Thus, the number of cells in finite clusters is $Npa_z(p) \sum_\nu C_{\nu z}(p)$, that in the infinite cluster is $Npa_z(p) P_z(p)$, and the total in clusters is $Npa_z(p)$.

According to Turnbull and Cohen,[6–8] atoms can diffuse when a fluctuation in cellular volume of atomic size v_m or greater occurs. This arises from redistribution of the free volume (free exchange of free volume) only within a given cluster in the present picture; otherwise an activation free energy is required. The total free volume within a cluster of size ν must therefore be greater than v_m for diffusion to occur,

$$\sum_{i=1}^{\nu} (v_i - v_c) > v_m , \quad v_i > v_c \ . \tag{12}$$

The average free volume within a liquidlike cluster is $\bar{v}_f$, given by Eq. (7). Thus, for diffusive motion to take place within a given cluster, its size ν must be at least $v_m / \bar{v}_f$,

$$\nu \geq \nu_m = v_m / \bar{v}_f \ . \tag{13}$$

We have called all clusters liquidlike. However, a cluster for which Eq. (13) holds is liquid, rather than liquidlike, in the sense that each atom or molecule within it moves in time through the entire cluster. That is, each molecule finds accessible the configuration space of every other molecule in the cluster. We now suppose that exchange of free volume between solidlike and liquidlike cells is sufficiently slow compared to exchange between liquidlike cells that it can be ignored in the computation of equilibrium properties. We return to this point later.

We can now write down the communal entropy. Let $\bar{v}_s$ be the average configuration volume of a liquidlike cell:

$$\bar{v}_s = p^{-1} \int_{v_c}^{\infty} v_s(v) P(v) \, dv \ , \tag{14a}$$

where

$$s(v) = -\frac{\partial f(v)}{\partial T} = k \ln v_s(v) \ . \tag{14b}$$

The communal entropy is that entropy associated with the accessibility of all of the configurational volume within the finite liquid clusters and within the infinite cluster *when present.* That is,

$$S_c = Nkpa_z(p)\left\{ \sum_{\nu=\nu_m}^{\infty} \nu C_{\nu z}(p)\ln[(\nu-1)\bar{v}_s] + P_z(p)\ln[Npa_z(p)P_z(p)\bar{v}_s] \right\} , \qquad (15)$$

where Np is the total number of liquidlike cells, $Npa_z(p)$ is the number of liquidlike cells in clusters, and k is the Boltzmann constant. The first term in Eq. (15) arises from finite clusters and the second from the infinite cluster. Note the extra $N\ln N$ in Eq. (15) arising from our classical treatment. It could be eliminated by treating the molecules as indistinguishable; it is very convenient, however, to keep it and simply regard the $N\ln N$ correction as understood. Using Eq. (11) we can bring Eq. (15) into a more convenient form,

$$S_c = Nkpa_z(p)\left\{ A_z(p)\ln\bar{v}_s + \sum_{\nu=\nu_m}^{\infty} \nu C_{\nu z}(p)\ln(\nu-1) + P_z(p)\ln[Npa_z(p)P_z(p)] \right\} , \qquad (16)$$

where

$$A_z(p) = 1 - \sum_{\nu=1}^{\nu_m} \nu C_{\nu z}(p) . \qquad (17)$$

We have thus expressed S_c in terms of p, $\bar{v}_s$, ν_m, $a_z(p)$, $C_{\nu z}(p)$, and $P_z(p)$. The first two of these quantities depend only on $P(v)$; and in Sec. IV we develop a method of determining $P(v)$. $a_z(p)$ and $P_z(p)$ depend on $C_{\nu z}(p)$. Because $C_{\nu z}(p)$ enters the free energy through S_c, Eq. (15), it should be determined by minimization of the free energy. As we shall see below, the results are the same as those of a percolation problem somewhat different from the environmental percolation problem described above. The essential point is that clusters with $\nu \geq \nu_m$ are favored because they contribute to the communal entropy, while the formal structure of the problem remains that of a percolation problem. Here we summarize important results from percolation theory which we expect to carry over to the new percolation problem.

We first ignore the effects of the communal entropy on the character of the percolation problem. For $p > p_{cz}$ and $|p - p_{cz}| << 1$,

$$P_z(p) = B_z|p - p_{cz}|^{\beta_z} . \qquad (18)$$

Numerical results are not available for the z-environment percolation problem we introduced above, the problem not having been discussed, but we expect a larger value of p_{cz} for $z > 2$ and a slower growth of the infinite cluster, i.e., a larger value of β_z, for $z > 1$. Below p_{cz}, we expect the sum in Eq. (16) also to scale with the power β_z.[81] In the absence of theoretical results, we turn to some experiments on magnetic alloys for useful information. There are several systems, e.g., NiCu, in which a magnetic atom (Ni) must have a minimum number of like neighbors before it can have a magnetic moment.[85–87] For NiCu, $n = 12$ and $z = 8$. The percolation threshold appears at $p_{c8} = 0.44$ and our estimates give $0.5 < \beta_8 < 0.7$ for β_8 (note $p_{c1} = 0.19$ and $\beta_1 = 0.39$). These estimates were made by analyzing the p dependence of the low-temperature magnetization above but near p_{c8}. They are necessarily very crude because of the limited accuracy of the data, contributions to the magnetization from finite clusters (superparamagnetism plus weak ferromagnetic coupling of the finite clusters), and a probable dependence of the Ni moment on the number of Ni neighbors above the critical value of $z = 8$. A more refined description must await further investigation, e.g., by Monte Carlo techniques. The essential point is that there exists a well defined p_{cz} and a characteristic exponent β_z whose values we do not yet know.

We now consider the effects of the communal entropy on the features of the percolation problem. Clusters of sizes less than ν_m tend to be suppressed. $a_z(p)$ and $A_z(p)$ move towards unity. The problem moves away from environmental percolation based on an uncorrelated distribution of cells towards the continuum percolation problem studied by Scher and Zallen,[88] and Webman, Jortner, and Cohen.[89] For the latter $p_c = 0.15$ and $\beta = 0.39$. These together with the considerations of the last paragraph give us very rough bounds on the values of p_c and β appropriate to the present percolation problem

$$0.15 \leq p_{cz} \leq 0.45,\quad 0.4 \leq \beta_z \leq 0.7 . \qquad (19)$$

Qualitatively speaking, as p increases towards p_{cz}, the mean cluster size grows, i.e., the scale of the ν's is important in Eq. (16), until at p_{cz} an infinite cluster emerges. Above p_{cz}, the percolation probability increases. Thus, S_c shows a monotonic increase with p with maximum and possibly divergent slope as $p \rightarrow p_{cz} \pm 0^+$.

We can go no further towards the explicit evaluation of S_c without introducing more information about $C_{\nu z}(p)$. The latter can be obtained in a mean-field approximation simply by maximizing the communal entropy with $P(v)$ and therefore p fixed, as $C_{\nu z}(p)$ does not enter elsewhere. The procedure developed by Fisher[90] in his study of the droplet model can be followed with only slight modification. The entropy now contains an additional $\ln\nu$ contribution for $\nu > \nu_m$. The result in mean-field theory,[91] dropping the subscript z for convenience, for $\nu > \nu_m$

and $p > p_c$ is

$$C_\nu(p) = q_0\nu^{-\tau}\exp(\epsilon\nu^\sigma) \ , \tag{20a}$$

$$\epsilon = q_1(p_c - p) \ , \tag{20b}$$

$$\sigma = \beta^{-1}\delta^{-1} = (\gamma+\beta)^{-1}; \ \ \tau = 2+\delta^{-1} \ . \tag{20c}$$

The quantities q_0 and q_1 are positive quantities which may depend analytically on p and which depend on the specific percolation problem. For $\nu < \nu_m$, τ in Eq. (20a) is replaced by $\tilde{\tau} > \tau$. This occurs because only clusters with $\nu > \nu_m$ contribute to the communal entropy and are therefore favored. These results differ from those of a typical percolation problem only through the discontinuity at $\nu = \nu_m$. They can be generalized beyond the mean-field approximation for $\nu > \nu_m$ to[80]

$$C_\nu(p) = q_0\nu^{-\tau}g(\epsilon\nu^\sigma) \ , \tag{21}$$

where g is a universal function of its argument, depending only on dimension and z. A simple form of $g(x)$ is sketched in Fig. 3.

We can now evaluate S_c near p_c. Inserting Eq. (21) into Eq. (16) and replacing the sum over ν by an integral leads for p near p_c and $\beta < 1$ to

$$\begin{aligned} S_c = Nkpa_z(p)\{&A_z(p)\ln\bar{v}_s + B_1^{\pm}|p-p_c|^\beta \\ &+ B|p-p_c|^\beta u(p-p_c) \\ &\times \ln[Npa_z(p)B|p-p_c|^\beta] + S_c'\} \end{aligned} \tag{22}$$

for the communal entropy, where $u(x)$ is the unit step function, S_c' stands for analytic contributions to S_c and

$$B_1^{\pm} = (\beta\delta)^2 q_0 q_1 \int_0^\infty dx\, x^{-1-\beta}[g(\pm x) - g(0)]\ln\left|\frac{x}{|\epsilon|}\right| \ , \tag{23}$$

the (+) corresponding to $p < p_c$ and (−) to $p > p_c$.

We know that as $p \to 0$, $S_c \to 0$ while as $p \to 1$, $S_c \to Nk\ln(N\bar{v}_s)$. From Eq. (22), S_c is a monotonic function of p and is sketched in Fig. 4. The slope of S_c,

$$\frac{\partial S_c}{\partial p} \underset{p\to p_c}{\longrightarrow} A_{\pm}|p-p_c|^{\beta-1} \ , \tag{24}$$

diverges as $p \to p_c$ for $\beta < 1$. The behavior of the slope of S_c and, therefore, the value of β turns out to be critical in determining the order of the phase transition at T_p, as discussed in Sec. V.

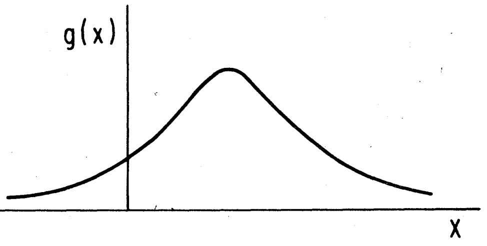

FIG. 3. Sketch of one possible form for the cluster distribution function $g(x)$.

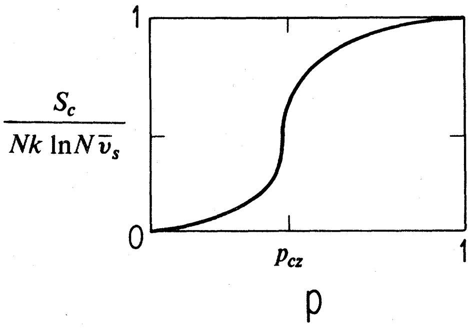

FIG. 4. Sketch of the communal entropy S_c as a function of the fraction of liquidlike cells, p.

We wish to hold open the possibility that β equal or exceed unity. Such a situation may occur in more complex glasses, e.g., polymer glasses. In such systems, the moving units are molecular segments constrained by their connections to the rest of the molecule. Such constraints imposed by the complexity of the material increase z and otherwise decrease the growth rate of the clusters with increasing p, increasing the value of β. In that case, the sum over ν can be approximated by an integral as above,

$$\sum_{\nu=\nu_m}^{\infty} \nu[C_\nu(p) - C_\nu(p_c)] = q_0\epsilon^\beta \int_{\epsilon\nu_m^\sigma}^{\infty} dx\, x^{-1-\beta}\,[g(\pm x) - g(0)] \tag{25}$$

but now the leading correction is analytic and scales with the first power of ϵ. The leading nonanalytic correction scales as ϵ^β. Using these results in Eq. (16), we find that the leading corrections to S_c for p near p_c scale with the powers $|p-p_c|$ and $|p-p_c|^\beta$. The slope of S_c at p_c arises from the analytic dependence on p and

$$\frac{\partial S_c}{\partial p} \underset{p\to p_c}{\longrightarrow} A_0 \ , \tag{26}$$

where A_0 is a constant. Thus the slope of S_c is constant as $p \to p_c$ for $\beta \geq 1$. We show below how this dependence of the slope of S_c is critical to the determination of the order of the transition.

IV. STATISTICAL MECHANICS

Now that we have an expression for the communal entropy, we can derive the probability distribution $P(v)$. We start from the configurational free energy $\mathcal{F}$ given by

$$e^{-\beta\mathcal{F}}=\int D[N]e^{-\beta\mathcal{V}[N]} \quad . \tag{27}$$

Here $D[N]$ is the volume element in the N-particle configuration space, and $\mathcal{V}[N]$ is the sum of the pairwise interaction potentials among the N molecules. We deal with the case of spherical molecules for simplicity; the results are general. We must convert Eq. (27) into an integral over a set of N independent dynamical variables which have a monotomic relationship to the cell volume variable v we have used thus far. Consider the configurations $[N-i]$ of the $N-1$ molecules other than the ith which contribute significantly to Eq. (27). These produce an interaction potential with the ith molecule,

$$\mathcal{V}[\vec{r}_i|N-i]={\sum_j}' V(|\vec{r}_i-\vec{r}_j|) \quad , \tag{28}$$

where $V(|\vec{r}_i-\vec{r}_j|)$ is the pairwise interaction, which for the densities we are dealing with has closed contours (defining a cell for the ith molecule) up to values of $\mathcal{V}$ so large that they are unimportant in Eq. (27), a consequence of the steepness of the repulsive part of V. For fixed $[N-i]$, the volume τ_i accessible to the center of the ith molecule is the volume inside the contour of constant $\mathcal{V}[\vec{r}_i|N-i]$ corresponding to the largest value of $\mathcal{V}$ of significant probability, $\mathcal{V}^*$. Fortunately, we do not need to know $\mathcal{V}^*$ because of the steepness of the repulsive part V; using the contour $\mathcal{V}[\vec{r}_i|N-i]=0$ gives us adequate accuracy. We therefore define, formally,

$$\tau_i=\int d^3x\, u(\mathcal{V}[\vec{x}|N-i]) \quad , \tag{29}$$

where $u=1$ for $\mathcal{V}<0$, i.e., for x inside the contour $\mathcal{V}=0$ and zero otherwise; τ_i is the volume inside this contour.

We now transform Eq. (27) into an integral over the τ's

$$e^{-\beta\mathcal{F}}=\int D[\tau]\, e^{-\beta F'[\tau]} \quad , \tag{30a}$$

where

$$e^{-\beta F'[\tau]}=\int D[N]\prod_i \delta\left(\tau_i-\int d^3x \times u(\mathcal{V}[\vec{x}|N-i])\right)e^{-\beta\mathcal{V}[N]} \quad . \tag{30b}$$

There is a monotonic relationship between τ_i, the volume accessible to the center of the molecule within its cell, and v_i the volume of the cell. We can thus transform Eq. (30) into an integral over the v_i, exponentiating the Jacobian and absorbing it into the free energy $\bar{F}[v]$,

$$e^{-\beta\mathcal{F}}=\int D[v]\, e^{-\beta\bar{F}[v]} \quad . \tag{31}$$

The results embodied in Eqs. (30) and (31) are obviously too formal to be directly useful, so we assume further that the probability $P[v]=\prod_i P(v_i)$. We can therefore take for $\bar{F}[v]$ the simple cell model form (4), which depends only on the probability distribution $P(v)$. Thus Eq. (31) can be converted into a functional integral over $P(v)$, and $\bar{F}$ is replaced by $F[P]$, a Landau-Ginzburg free-energy functional

$$e^{-\beta\mathcal{F}}=\int D[P]\, e^{-\beta F[P]} \quad . \tag{32}$$

The transformation from $[N]$ to $[\tau]$ has not been shown to exist. One requirement for its existence is that τ_i be finite for any configuration $[N-i]$ of significant probability. Assign each molecule $j\neq i$ a diameter equal to the separation at which $V(|\vec{r}_i-\vec{r}_j|)$ goes through zero. Define a continuous percolation problem with p' the fraction of the space outside the molecules. As long as p' is below a percolation threshold p_c', all the τ_i will be finite. We can expect p_c' to be substantially larger than the value for the purely random case, 0.15, because large voids are suppressed by the large free energy they require and because the minimum dimension of a continuous void must exceed a molecular diameter. For hard spheres, the density of melting is $\frac{2}{3}$ of the density of the ideally close-packed crystal.[1] The density for dense random packing (the glass form) is 15% larger than that of the crystal. Thus the thermal expansion on melting is about 18%, close to the random percolation threshold and presumably much less than p_c'. We expect therefore that the τ_i are finite and that the transformation $[N]\rightarrow[\tau]$ exists.

To find $P(v)$, we do a mean-field calculation. We choose $F[P]$ to be of the form given by Eq. (4), insert $f(v)$ from Eqs. (5) and (9), and S_c from Eq. (16). We require that $\delta F[P]/\delta P=0$, with the constraint $\int_0^\infty P(v)dv=1$. $P(v)$ enters both explicitly in $F[P]$, cf. Eq. (4), and implicitly through the presence of $\bar{v}_s$, v_m, and p in S_c, cf. Eqs. (14), (17), and (13), and (10). A convenient simplification of Eq. (14) is

$$\bar{v}_s=v_s(v_c)+v_s'(v_c)\bar{v}_f \quad . \tag{33}$$

We note that $f(v)$ in Eq. (4) is regarded as independent of $P(v)$ and yet that in Eqs. (5) and (9) $f(v)$ has in it an implicit dependence on $P(v)$ through the presence of $\bar{v}_f$. The most convenient way to resolve this inconsistency is to treat $f(v)$ as though it were a self-consistent field, itself the result of a first functional derivative of the total local free energy with respect to $P(v)$, and not differentiate it further in the variation of $F[P]$. Otherwise we should have to deal more explicitly with a complex nonlinear function of $P(v)$ with no direct physical interpretation, in order to avoid multiple counting. Moreover, the introduction of $\bar{v}_f$ into $f(v)$ forces it into the role of a self-consistent field.

We now write the communal entropy in the form

$$S_c = Nk\mathcal{S}(p, \nu_m, \bar{v}_s) \ . \tag{34}$$

Its variation is, from Eqs. (33), (7), (13), and (10),

$$\delta S_c = Nk \int_0^\infty [R_1(v-v_c) - R_2] \times u(v-v_c)\,\delta P(v)\,dv \ , \tag{35a}$$

$$R_1 = \frac{1}{p}\left(\frac{-\nu_m}{\bar{v}_f}\frac{\partial \mathcal{S}}{\partial \nu_m} + v_s{}'\frac{\partial \mathcal{S}}{\partial \bar{v}_s}\right) \ , \tag{35b}$$

$$R_1 = a_z(p)\left(\frac{\nu_m^2}{\bar{v}_f}C_{\nu_m}(p)\ln(\nu_m - 1) + A_z(p)\frac{v_s{}'}{\bar{v}_s}\right) \ , \tag{35c}$$

$$R_2 = R_1\bar{v}_f - \frac{\partial \mathcal{S}}{\partial p} \ , \tag{35d}$$

where Eq. (35c) is obtained from Eqs. (35b) and (16). Inserting this into the variation of $F[P]$ gives us the desired expression for $P(v)$,

$$P(v) = (1-p)v_g^{-1}e^{-\kappa(v-v_0)^2/2kT} \ , \quad v < v_c \ , \tag{36a}$$

$$P(v) = p\bar{v}_f^{-1}e^{-(v-v_c)/\bar{v}_f} \ , \quad v > v_c \ , \tag{36b}$$

where

$$v_g = \int_0^{v_c} e^{-\kappa(v-v_c)^2/2kT}\,dv \ , \tag{37}$$

$$\bar{v}_f^{-1} = \Gamma = \zeta/kT - R_1 \ , \tag{38}$$

$$\begin{aligned} p &= \bar{v}_f(\bar{v}_f + v_g Q)^{-1} \\ &= (1 + v_g\Gamma Q)^{-1} \ , \end{aligned} \tag{39}$$

$$Q = e^{\mu_c/kT} \ ; \ \ \mu_c = \tfrac{1}{2}\kappa(v_c - v_0)^2 + kTR_2 \ . \tag{40}$$

Our result for $v > v_c$ is essentially identical to that derived earlier by Cohen and Turnbull[6] for the most probable distribution of free volume x, $P(x) = \gamma/v_f \exp(-\gamma x/v_f)$, where v_f is the free volume averaged over all cells, $v_f = p\bar{v}_f$, and γ is a numerical factor between $\frac{1}{2}$ and 1 introduced to correct for overlap of the volume between neighboring cells. Comparing the exponent $\gamma x/v_f = (\gamma/p)(x/\bar{v}_f)$ with the exponent in Eq. (36b), $(v - v_c)/v_f$, we see that the two distributions are identical if x is taken as $(v - v_c)$ and γ is taken as p, which would be close to $\frac{1}{2}$ in the temperature region considered in Ref. 7.

Equation (39) is a self-consistency condition for p since its right-hand side contains p through the presence of R_1 in Γ, Eq. (38), and R_2 in Q, Eq. (40). We must therefore, solve Eq. (39) before we can calculate the heat capacity or thermal expansion and characterize the glass transition. We do so in Sec. V.

V. p AND THE ORDER OF THE TRANSITION

A. General considerations

The self-consistency condition (39) is the key to the glass transition. To make its content and meaning clearer, we derive it by an alternative procedure. Instead of considering all possible variations of $P(v)$ which leave it normalized, we consider only those which leave p invariant. Variation of $F[P]$ subject to these two constraints leads again to Eq. (36) for $P(v)$ but with p unspecified, i.e., without Eq. (39). Insertion of $P(v)$ in the form (36) back into Eq. (4) gives

$$\begin{aligned} F[P] &= N[f_0 + \tfrac{1}{2}p\kappa(v_c - v_0)^2] \\ &\quad + NkT\{(1-p)\ln[(1-p)/v_g] \\ &\qquad + p\ln(p/\bar{v}_f) + pR_1\bar{v}_f - \mathcal{S}\} \\ &= \mathcal{F}(p) + Nf_0 \ , \end{aligned} \tag{41}$$

for the free energy as a function of p. In Eq. (41), $-NkT(1-p)\ln v_g$ is the part of the free energy $\mathcal{F}(p)$ associated with the solidlike cells,

$$Np[\tfrac{1}{2}\kappa(v_c - v_0)^2 + kTR_1\bar{v}_f - kT\ln\bar{v}_f]$$

that associated with the liquidlike cells,

$$Nk[(1-p)\ln(1-p) + p\ln p]$$

the entropy of mixing of solidlike and liquidlike cells, and $Nk\mathcal{S}$ the communal entropy.

The values of p which make $F[P]$ in Eq. (36) stationary are obtained by differentiating Eq. (41) with respect to p and setting the result equal to zero. Carrying out the differentiation and simplifying the result by using the stationarity of $F[P]$ with respect to $P(v)$ at constant p gives Eq. (39) as the condition of stationarity of the free energy with respect to p. We now study its solution for the cases $\beta < 1$ and $\beta \geq 1$.

B. $\beta < 1$

Returning then to Eq. (39), we see that it has the form $p = h(p) = (1 + Qv_g\Gamma)^{-1}$. v_g is independent of p. Γ is a smoothly decreasing function of p. R_1 and $\bar{v}_f$ are essentially independent of p as shown below, but R_2 is nonmonotonic, going to $-\infty$ at p_c because of the divergence to $+\infty$ of $\partial\mathcal{S}/\partial p$ for $\beta < 1$. Thus, μ_c goes to $-\infty$ at p_c, Q to zero, $h(p)$ to unity. Equation (39) therefore, does not possess a solution for p

in the vicinity of p_c, and p cannot increase continuously through p_c with increasing temperature. The graphical solution of Eq. (39) is sketched in Fig. 5 for several temperatures. There is a bifurcation from one solution $p_1 > p_c$ at high temperatures to three solutions $p_1 > p_c$, $p_2 < p_c$, $p_3 < p_c$ at low temperatures.

Recall that these p_i are stationary points for the free energy $\mathcal{F}(p)$. We therefore pass from a single minimum in $\mathcal{F}(p)$ at high temperatures with $p > p_c$, corresponding to the liquid, to three extrema in $\mathcal{F}(p)$ at lower temperatures. Fig. 6 shows a sketch of these features of $\mathcal{F}(p)$. There are two minima at $p_1 > p_c$ and $p_3 < p_c$ separated by a maximum at p_2 at lower temperatures. At some temperature T_p, $\mathcal{F}(p_1) = \mathcal{F}(p_3)$, and there is a first-order phase transition. Below T_p, $\mathcal{F}(p_1) > \mathcal{F}(p_3)$, and the minimum-free-energy state has $p = p_3 < p_c$ corresponding to a solid, the glass. Above T_p, $\mathcal{F}(p_1) < \mathcal{F}(p_3)$, and the minimum-free-energy state has $p = p_1 > p_c$, corresponding to the liquid. At a temperature $T_3 > T_p$, curves b in Figs. 5 and 6, the minimum at p_3 disappears, and the glassy state is no longer locally stable. The minimum at p_1 persists down to $T = 0$, so that there is no critical endpoint for the liquid state. This results only because $(\partial \mathcal{S}/\partial p)_{p_c} = \infty$. The expected dependence of p on T in the vicinity of T_p is shown in Fig. 7. The persistence of the minimum at p_1 down below T_p can give rise to hysteresis and relaxation effects associated with cooling, and the persistence of the minimum at p_3 up to T_3 can give rise to similar effects on heating. These are not the relaxation effects commonly observed at $T_g \geq T_p$ which are associated with nonequilibrium liquid states.

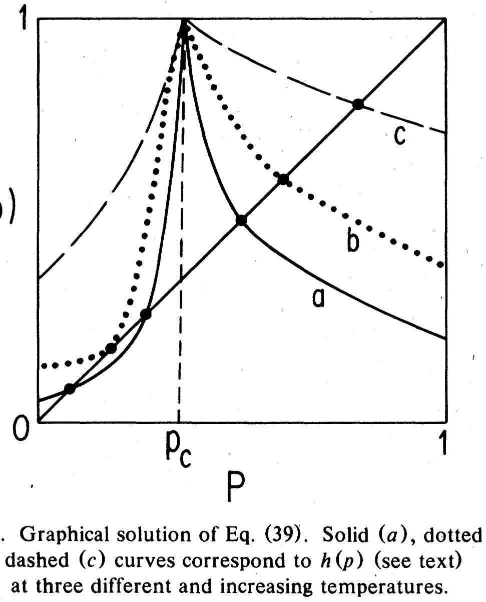

FIG. 5. Graphical solution of Eq. (39). Solid (a), dotted (b), and dashed (c) curves correspond to $h(p)$ (see text) for $\beta < 1$ at three different and increasing temperatures. The circles give the values of p which satisfy Eq. (39). Case (a) has three solutions, and case (c) has one. Case (b) corresponds to the bifurcation point between (a) and (c).

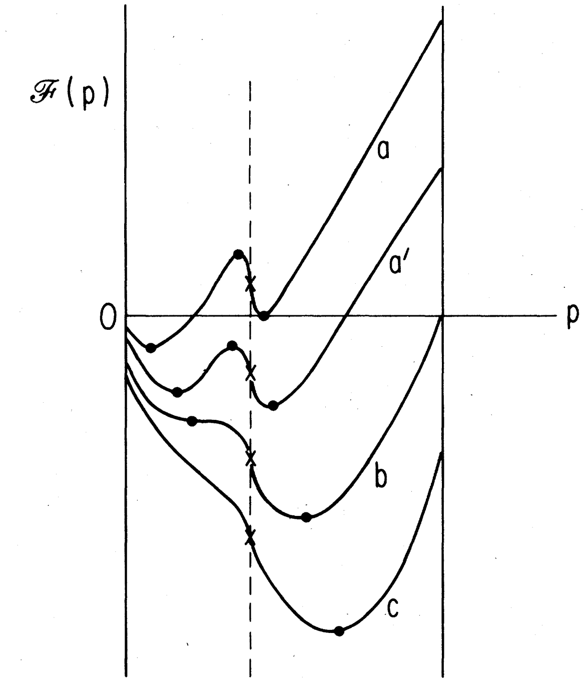

FIG. 6. Sketches of the free energy $\mathcal{F}(p)$ as a function of the liquidlike cell fraction p. Curves a, b, and c correspond to those so labeled in Fig. 5. The positions of the solutions of Fig. 5 are indicated by dots. Crosses emphasize the infinite negative slope of $\mathcal{F}$ at p_c, the percolation threshold.

The first order transition is a direct result of the divergence of $\partial \mathcal{S}/\partial p$ as $p \rightarrow p_c$ for $\beta < 1$. The latter is caused by the rigid and arbitrary manner in which the cells were divided into liquidlike and solidlike cells. In Sec. VII, we discuss the consequences of eliminating this unphysical feature of the model.

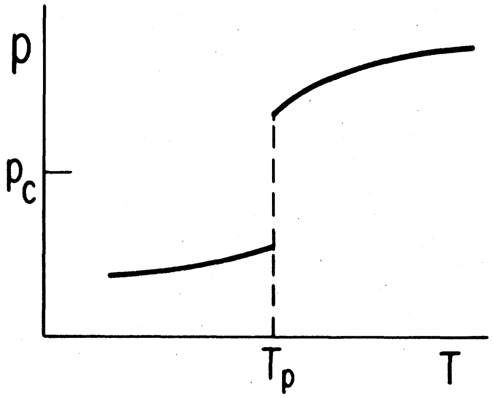

FIG. 7. Sketch of the probability of liquidlike cells p vs T near T_p for $\beta < 1$.

C. $\beta \geqslant 1$

For $\beta \geqslant 1$, $\partial \mathcal{S}/\partial p$ is finite at p_c, though nonanalytic, and therefore R_2 is always finite. The order of the transition now depends critically on the value of $(\partial \mathcal{S}/\partial p)_{p_c}$. For $(\partial \mathcal{S}/\partial p)_{p_c}$ large, the function $h(p)$ is similar to that found for $\beta < 1$. That is, $h(p_c)$ approaches 1 and there are three solutions for p for some range of temperatures. In our search of the parameter space, as discussed below, this occurred most of the time. For smaller values of $(\partial \mathcal{S}/\partial p)_{p_c}$ coupled with a slow variation in $\partial \mathcal{S}/\partial p$ vs p, $h(p)$ will vary more slowly as a function of p and can give rise to only one solution p for each T which satisfies Eq. (39). Nevertheless, $\mathcal{S}$ changes its functional dependence on p at p_c, and there is a phase transition. Since p is a continuous function of T, the transition is second order, with T_p corresponding to $p = p_c$. Thus the transition for $\beta \geqslant 1$ may be either first or second order depending on the value of $(\partial \mathcal{S}/\partial p)_{p_c}$ and the magnitude of the variation in $\partial \mathcal{S}/\partial p$ vs p. We find, as discussed in Sec. VII, that the former is most often the case. This situation with $\beta \geqslant 1$ may correspond to the complex organic and polymeric glasses where the infinite cluster has difficulty developing because of the additional constraints. β, therefore, increases and may become $\geqslant 1$. Even if β remained less than unity in the complex glasses, the interplay between the configurational entropy (present in them but not in the simple glasses) and the communal entropy could lead to a variation in the total entropy with p characterized by an exponent $\tilde\beta$ near p_c, with $\tilde\beta = \beta + x > 1$. Thus, x describes the retardation in the growth of the configurational entropy imposed by the constraints on the free volume. If either β or $\tilde\beta \geqslant 1$, our thermodynamic results for some values of the parameters may be compared to those of Gibbs and Di Marzio[70] for polymers, who predict the glass transition is a second-order phase transition in the limit of slow cooling.

VI. FREE VOLUME AND VISCOSITY

In Sec. V, we found that p is usually a discontinuous function of T. Here, we show that both the free volume $\bar v_f$ and the viscosity η are only weakly dependent on p and therefore do not reflect strongly the existence of the transition.

The free volume $\bar v_f$ is given by the self-consistency condition, Eq. (38). The contribution to R_1 from $\partial \mathcal{S}/\partial v_m$ can be neglected since from Eqs. (20a) and (20c) we note that the function $C_{v_m}(p)$, the number of clusters of size v_m, is exponentially small compared to the total number of clusters present. We have after combining Eqs. (9), (35c), and (38), a simple equation for $\bar v_f$,

$$\frac{\bar v_f a_z(p) A_z(p)}{\bar v_f + v_s(v_c)/v_s'(v_c)} = \frac{\zeta_0 \bar v_f}{kT} + \frac{T_1 \bar v_f}{T(\bar v_f + v_a)} - 1 \;. \tag{42}$$

Here $A_z(p)$ measures the number of clusters which are larger than some minimum value v_m and $a_z(p)$ measures the number of liquidlike cells which belong to liquid clusters. As we found in Sec. III, clusters of size $v < v_m$ are less favored since they do not contribute to S_c. We expect the number of these clusters to be reduced compared to an ordinary percolation problem and therefore $a_z(p)$ and $A_z(p)$ to be close to unity for p and p_c and nearly independent of p. In the extreme limit that no clusters of size $v < v_m$ are allowed, $a_z(p)$ and $A_z(p)$ would be identically equal to one. Thus Eq. (42) gives a cubic equation for $\bar v_f$ which depends on T and only very weakly on the probability p. Neglecting this dependence on p by setting $a_z(p)$ and $A_z(p) = 1$, we see $\bar v_f$ is a smooth function of T near T_g. The contribution on the left-hand side of Eq. (42) arises from the communal entropy and would be absent if we had neglected the communal entropy in our derivation of the free energy. The first two terms on the right-hand side follow from our choice of ζ, Eq. (9). The second term, which depends on ζ_1 is similar to the entropic contribution R_1, except for the temperature dependence. The latter is important at low temperature where one can neglect the contribution on the left-hand side. This important difference in the temperature coefficients arises because S_c only enters the free energy as TS_c. Thus the dependence of ζ_1 on $\bar v_f$, Eq. (8), cannot be an entropic effect, since it has both the wrong T dependence and sign. For higher temperatures, $R_1 \bar v_f$ is constant and including it in Eq. (43) does not effect the general form of $\bar v_f$. Thus including R_1 in the expression for $\bar v_f$ will make only a quantitative, not qualitative modification at high T and no change at low T, and we can absorb its effect in the remaining three parameters. This helps to reduce the proliferation of free parameters and gives a simple result for the free volume which is valid at all temperatures,

$$\bar v_f = \frac{k}{2\zeta_0}\{T - T_0 + [(T - T_0)^2 + 4 v_a \zeta_0 T/k]^{1/2}\} \;, \tag{43}$$

where $kT_0 = kT_1 + v_a \zeta_0$. This result is noteworthy since $\bar v_f$ vanishes only as $T \to 0$. This limiting behavior is independent of the exact form of R_1 or ζ and follows from Eq. (38) since R_1 is finite as $T \to 0$. Because of the explicit free-volume dependence in ζ, Eq. (9), $\bar v_f$ has its characteristic dependence $\propto T - T_0$ at high temperatures.

The original work on the free-volume model by Cohen and Turnbull[6-8] showed that the fluidity obeyed the Doolittle equation (1). We show that the percolation ideas developed in this paper give rise to the same equation for the fluidity.

Let D_ν be the diffusion coefficient for a particle moving in a cluster of size ν. The total diffusion coefficient D is then given by

$$D=\sum_{\nu=\nu_m} D_\nu \nu C_\nu(p) \quad . \tag{44}$$

From Ref. 8, we have that

$$D_\nu=\tfrac{1}{3}\bar{u}\int_0^\infty P_\nu(v)\tilde{f}(v)a(v)\,dv \quad , \tag{45}$$

where $\bar{u}$ is the average gas kinetic velocity, $\tilde{f}(v)$ is a correlation factor which may be associated with the magnitude of each displacement within the cluster and $a(v)$ is some function which depends on the immediate neighborhood of the moving particles and incorporates cooperative effects. $\tilde{f}(v)$ must go from 0 to $v=0$ to 1 at $v=\infty$. The basic assumption[8] is that $\tilde{f}(v)$ is a step function such that it is zero for $v<v^*$ and unity for $v>v^*$. Here $v^*=v_c+v_m-b\bar{v}_f$, where b is a constant. v^* is the minimum size of the cell necessary to accomodate two atoms. The correction $b\bar{v}_f$ in v^* is present because the second atom does not have to fit entirely into the cell but can use some of the free volume of the neighboring cells. In Ref. 8, $a(v)$ was chosen to be proportional to v. Then since $P_\nu(v)=p\Gamma e^{-\Gamma(v-v_c)}$ we have

$$D=D_0 p a_z(p) A_z(p) e^{-v_m/\bar{v}_f} \quad , \tag{46}$$

where we have added the contribution from the infinite cluster for $p>p_c$ and D_0 is a constant. We have included in D only the contributions from the liquid clusters. This can be rewritten in the form

$$D=D_0 p e^{-v_m/\bar{v}_f} \tag{47}$$

when $\bar{v}_m/v_f \ll \bar{\nu}$, the average cluster size; then

$$\sum_{\nu=1}^{\nu_m} \nu C_\nu(p) \ll 1$$

and one obtains the Doolittle equation. This is valid for p near and greater than p_c. For $p \ll p_c$, this expression is no longer valid because $a_z(p)$ and especially $A_z(p)<1$. However, this probably occurs at lower temperatures in the region which is not experimentally accessible. Since D depends on p, we may expect a discontinuity at T_p. This is not seen experimentally because the material goes out of equilibrium at T_g and $T_p<T_g$. The value of the viscosity at T_g is usually between 10^8–10^{11} poise. Thus a value of T_p only 20–30° below T_g would usually give a value of η too large to measure, even if an equilibrium measurement could be made. In any event, the jump in η would be difficult to detect.

In fitting the experimental data for η by the Doolittle equation, $\bar{v}_f$ is successfully approximated as $\propto T-T_{0H}$ for the high-temperature, low-viscosity regime, and as $\propto T-T_{0L}$ for the low-temperature regime, where T_{0L} may vanish. A viscosity in the range $10^4 \rightarrow 10^6$ poise is typical of the crossover region separating these two regimes. Our theory gives a formula for $\bar{v}_f$, Eq. (43), which is more general and which we expect to fit in both regimes. We have fitted the viscosity of several organic glasses, B_2O_3 and KNO_3-$Ca(NO_3)_2$ for which data are available over a large range to

$$\log_{10}\eta=A+2B/\{T-T_0+[(T-T_0)^2+4v_a\zeta_0 T]^{1/2}\} \quad , \tag{48}$$

where $B=v_m\zeta_0\log_{10}e$. The fit was excellent for all available data and the parameters of best fit are shown in Table II. The goodness of fit parameter

$$\chi^2=(\log_{10}\eta^{\mathrm{cal}}-\log_{10}\eta^{\mathrm{exp}})^2/(N-4) \quad ,$$

where N is the number of data points, was typically between 0.001 and 0.007 for the glasses considered. The error in the fit is comparable to the experimental error. For all the glasses in Table II η was measured over at least 12 orders of magnitude. We find from the fits that $T_0>T_\eta$ for each of these glasses. Included in the fit were two glasses, *o*-terphenyl and

TABLE II. Parameters used in the fit for the viscosity η, Eq. (48).

Glass Former	A	$2B$ (° K)	$4v_a\zeta_0$ (° K)	T_0 (° K)
tri-α-naphthylbenzene[a]	−2.44	345.3	10.6	401.8
o-terphenyl[b]	−2.65	253.0	6.4	278.7
phenyl-*o*-cresol[c]	−1.11	92.4	2.9	252.8
salol[c]	−0.52	25.3	0.94	264.6
B_2O_3[d]	0.63	1825.4	72.6	609.5
$0.60KNO_3$-$0.40Ca(NO_3)_2$[e]	−1.79	362.0	6.4	365.4

[a] Reference 39.
[b] References 40 and 41.
[c] Reference 40.
[d] Reference 46.
[e] Reference 27.

tri-α-naphthylbenzene for which $T_{0L} \neq 0$, while the other four showed Arrhenius behavior at low temperature, $T_{0L} \to 0$. The fit for tri-α-naphthylbenzene is shown in Fig. 8. The best fit[39] to the Doolittle equation with $\bar{v}_f \propto T - T_{0H}$, $T_{0H} = 342$ K is shown by the dashed curve. We also tried fits where the preexponential A was temperature dependent, since $\eta \sim T^{1/2} D^{-1}$. However this dependence is so weak compared to the exponential dependence on $v_m/\bar{v}_f$ that the fits are comparable to those with A constant.

The generalization of these results to include the effects of the pressure P is straightforward. The free energy $f(v)$ then contains an additional term Pv. The effect of the term on $P(v)$, $v > v_c$, is simply to change $\zeta_0 \to \zeta_0 + P$. Thus the free volume has the same form as in Eq. (43) with $\zeta_0 \to \zeta_0 + P$. The characteristic temperature T_0 then has the form

$$T_0(P) = T_0 + v_a P \quad . \tag{49}$$

High-temperature viscosity measurements[25] at elevated pressure for 0.62 KNO_3-0.38 $Ca(NO_3)_2$ were fitted to the usual three-parameter Doolittle equation with a T_0 which had a linear dependence on pressure as in Eq. (49). The fit gave a value of $v_a = 1.1$ Å^3. Unfortunately, we know of no high-pressure, low-temperature studies of η which can be used to check fully the temperature and pressure dependence of Eqs. (43) and (47).

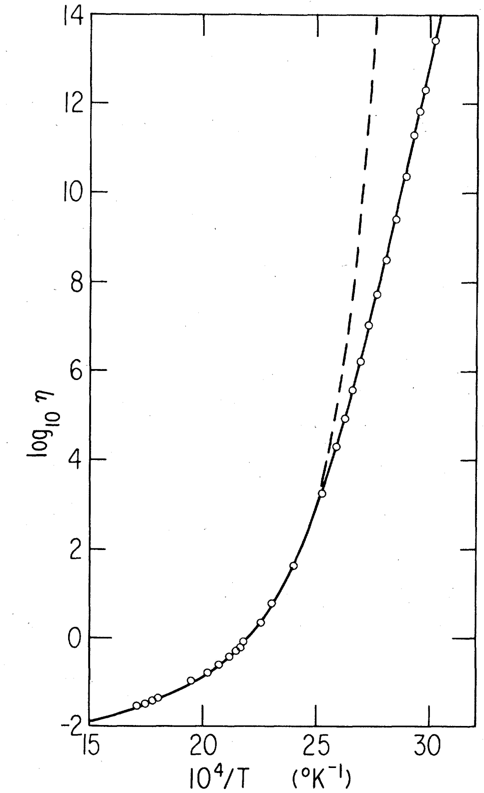

FIG. 8. Viscosity vs temperature for tri-α-naphthylbenzene, based on data of Ref. 39. The solid curve is the best fit to Eqs. (43) and (47), for the parameters given in Table II. The dashed curve is the best fit (Ref. 39) with $\bar{v}_f \propto T - T_{0H}$, $T_{0H} = 342$ K.

From Table II and Eq. (48), we obtain the value of 260.5 for v_m/v_a in 0.60 KNO_3-0.40 $Ca(NO_3)_2$. The two compositions, 0.62-0.38 and 0.60-0.40, are close enough for the difference to be ignored. These values of v_m/v_a and v_a lead to a value of v_m of 237 Å^3. This corresponds to a radius r_m of 3.8 Å which is to be compared to the ionic radii of 1.33 Å for K^+, 0.99 Å for Ca, and approximately 3.0 Å for NO_3^-. The comparison shows clearly that the diffusive units are most probably not the individual ionic species but complexes instead.

Angell and co-workers[26] have pointed out that $T_\eta = T_{0H}$ and T_s are nearly equal in many materials. This can be understood in our model as follows. If $\bar{v}_f \propto T - T_\eta$, then $\bar{v}_f$ extrapolates to zero from the range of observation of η at T_η. If $\bar{v}_f \to 0$, then $p \to 0$ from Eq. (39), so that the communal entropy and entropy of mixing also vanish. The only nonvanishing contribution to S is the entropy of the solidlike cells which is essentially the same as the entropy of the crystal. This is true since no liquidlike cells remain when $p \to 0$. Thus extrapolating the entropy to the crystal values using C_p data from essentially the same range of temperature as that from which the extrapolation of η to ∞ was made must yield, according to our theory,

$$T_s \cong T_\eta \tag{50}$$

because $p = 0$ both at T_η and at T_s and p is a single-valued function of T.

VII. THERMODYNAMIC PROPERTIES

A. Specific heat

The specific heat can be calculated in the vicinity of T_g from $C_p = T \partial S / \partial T$, where from Eq. (41),

$$S = Nk \{ -(1-p) \ln[(1-p)/v_g] - p \ln(p/\bar{v}_f) - pR_1 \bar{v}_f + \mathfrak{s} \} \quad . \tag{51}$$

The heat capacity is the sum of contributions from the configuration and communal entropy,

$$C_p = C_p^{\text{conf}} + C_p^{\text{comm}} \quad , \tag{52}$$

$$C_p^{\text{conf}} = T \left\{ \frac{p}{\bar{v}_f} (1 - R_1 \bar{v}_f) \frac{\partial \bar{v}_f}{\partial T} + \frac{(1-p)}{v_g} \frac{\partial v_g}{\partial T} + \ln \left[\frac{\bar{v}_f (1-p)}{v_g p} \right] \frac{\partial p}{\partial T} - \bar{v}_f \frac{\partial (pR_1)}{\partial T} \right\} \quad , \tag{53}$$

and

$$C_p^{\text{comm}} = T\frac{\partial \mathcal{S}}{\partial p}\frac{\partial p}{\partial T} , \tag{54}$$

where we assume p is a smooth function of T away from T_p so that we can use the chain rule. We know little about $\tilde{C}_p = \partial \mathcal{S}/\partial p$ except its scaling form near p_c. From Eq. (15), we know that $\tilde{C}_p \propto |p - p_c|^{-\alpha}$ where $\alpha = 1 - \beta$. With our earlier estimates of β we crudely estimate α to be positive and in the range 0.3 → 0.6. Note that the usual exponent α for the percolation problem is negative since the entropy is related to the configuration probability of being in a cluster. Here the communal entropy is present and results in a different expression for α, dependent only on β. For the critical contribution to $\tilde{C}_p$, which is dominant in the vicinity of p_c, we take

$$\tilde{C}_p = A\left|\frac{p - p_c}{p_c}\right|^{-\alpha} - D + \frac{E(p_c - p)}{p_c} , \tag{55}$$

for $p < p_c$ and the same function with primed parameters for $p > p_c$. We set $D = D'$ and $E = E'$ because these contributions arise from analytic terms in S_c which are continuous through p_c. We also take $A' > A$, because the presence of the infinite cluster makes a large additional contribution to S_c and therefore $\tilde{C}_p$ above p_c.

In order to complete the calculation of C_p we must know the temperature dependence of $\bar{v}_f$, v_a and most importantly p. This can only be done by solving the self-consistency condition $p = h(p)$, Eq. (39), in more detail. To reduce the number of free parameters, we use the viscosity data for tri-α-naphthylbenzene fitted by the parameters in Table II for the temperature dependence of $\bar{v}_f$. The remaining parameters are then v_0, v_c, and κ to describe $f(v)$ and p_c, α, A, A', D, and E in $\tilde{C}_p$. If we scale all volumes by v_0 taken equal to v_m that leaves only v_c/v_0 and $\tilde{\kappa} = \kappa v_0^2$ as unknowns in $f(v)$. The latter is constrained, since we know

$$[df(v)/dT]_{v_c^-} > [df(v)/dT]_{v_c^+} ,$$

that is the derivative of the free energy is rising more rapidly in the solidlike than in the liquidlike regimes. This gives

$$\kappa(v_c - v_0) \gtrsim \zeta_0 + T_1/(\bar{v}_f + v_a) ,$$

where we can take $\bar{v}_f$ equal to its value at T_p. The value of v_c/v_0 is taken to be between 1.05 and 1.15. This leaves only the parameters in $\tilde{C}_p$ to be determined. However, these are constrained by the requirement that there must be three solutions of p in the vicinity of T_g and $\mathcal{F}(p_1) = \mathcal{F}(p_3)$ at T_p, which should satisfy the condition $T_s \leqslant T_p \leqslant T_g$. Here T_g is the temperature at which the system falls out of thermodynamic equilibrium for the experimental heat-capacity measurements. For tri-α-naphthylbenzene $T_g = 342\,^{\circ}\mathrm{K}$. We also require that

$$\Delta C_p = C_p(\text{liquid}) - C_p(\text{glass}) > 0 .$$

This reduces the range of parameter space that is allowed. In practice, choosing values for p_c, α, κ and v_c/v_0 effectively reduces the freedom in choosing the remaining parameters in $\tilde{C}_p$. We have not tried to span the complete parameter space but show here typical results for C_p vs T. In the example below, we choose $\alpha = 0.3$. The results are not critically dependent on α as we have found similar results for both larger and smaller values of α. The important effect of the parameter α is on the size of the latent heat at T_p. In general, the larger the value of α, the larger the latent heat.

In Fig. 9, we show the result for the probability distribution function $P(v)$ vs v for tri-α-naphthylbenzene for the parameters given in the figure caption. Note the bimodal distribution of $P(v)$, which is discontinuous at $v = v_c$. In Fig. 10, we show a result for C_p vs T near T_p for a set of parameters given in the figure caption. Since T_s is unknown for this system, we have chosen parameters to give $T_p = 335\,^{\circ}$. The rise in C_p in the equilibrium liquid phase is characteristic of several of the organic glasses.[37] Since the transition is first order, there is a latent heat at T_p, denoted by a δ function spike. There may also be other contributions to C_p which we have not included, but they should be smooth near T_p.

This result cannot be compared directly to the experimentally measured C_p since that is greatly affected by kinetic phenomena occuring around T_g. These

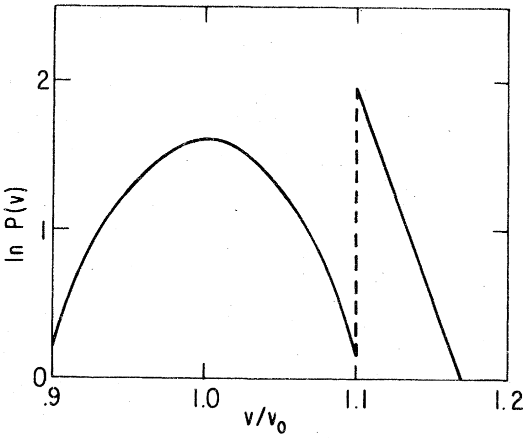

FIG. 9. Plot of the ln of the probability distribution function $P(v)$ vs v for tri-α-naphthylbenzene at $T = 350\,^{\circ}\mathrm{K}$ and $p = 0.25$. The free-volume parameters from Table II are used for $\bar{v}_f$ and we have chosen $\tilde{\kappa} = \kappa v_0^2 = 10^5\,^{\circ}\mathrm{K}$, and $v_c/v_0 = 1.1$.

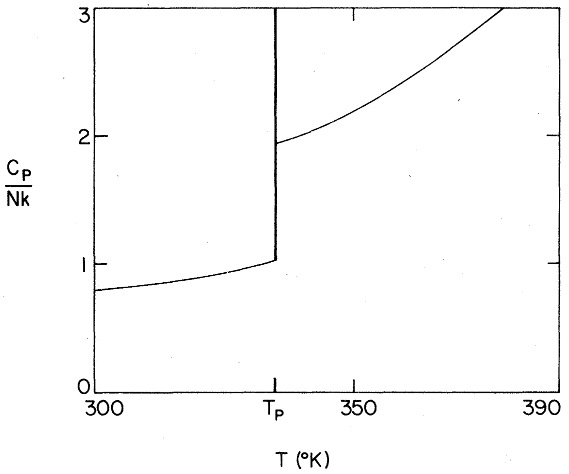

FIG. 10. Equilibrium heat capacity C_p vs T near T_p. The transition is first order and the latent heat is represented by a spike at T_p in C_p. We have used the free-volume parameters from Table II for tri-α-naphthylbenzene, $T_0 = 401.7\,°\mathrm{K}$, $v_m \zeta_0 = 397.2\,°\mathrm{K}$, and $v_a / v_m = 0.00664$. The other parameters chosen are $\tilde{\kappa} = 10^5\,°\mathrm{K}$, $v_c / v_0 = 1.1$, $R_1 = 0$, $p_c = 0.2$, $\alpha = 0.3$, $A = 1.0$, $A' = 2.0$, $D = 1.0$ and $E = 0.0$, which give $T_p = 335\,°\mathrm{K}$.

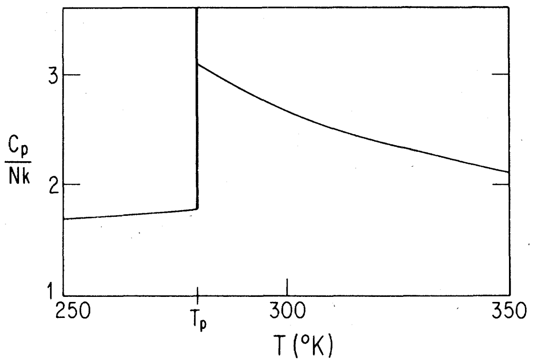

FIG. 11. Equilibrium heat capacity C_p vs T near T_p using the free-volume parameters for the metallic glass $Au_{0.77}Ge_{0.136}Si_{0.094}$: $T_0 = 241.3\,°\mathrm{K}$, $v_m \zeta_0 = 590.6\,°\mathrm{K}$, and $v_a = 0$. The latent heat is represented by a spike at T_p. The other parameters chosen which give $T_p = 280\,°\mathrm{K}$ are $\tilde{\kappa} = 10^5\,°\mathrm{K}$, $v_c / v_0 = 1.1$, $R_1 = 0$, $p_c = 0.2$, $\alpha = 0.3$, $A = 0.7$, $A' = 2.0$, $D = 0.5$, and $E = 0.30$.

measurements do not give an equilibrium result for C_p, which is what we have calculated.

As a second example, we have calculated the heat capacity for the metallic glass $Au_{0.77}Ge_{0.136}Si_{0.094}$. Using the viscosity and heat capacity measured by Chen and Turnbull,[17] we learn that $\bar{v}_f / v_m = (T - 241.3)/540.6$ and $T_g = 295\,°\mathrm{K}$. Results for C_p vs T are shown in Fig. 11 for parameters given in the caption. Here we have chosen parameters to give $T_p = 280\,°\mathrm{K}$, but the results are similar for other values of T_p. Note that the heat capacity decreases with increasing temperature above T_p, as observed experimentally. As discussed above, it is difficult to compare our results directly with the measurements, which are probably not for equilibrium.

For $\beta \geq 1$, the temperature dependence of p relates to the value of $(\partial \mathcal{S} / \partial p)_{p_c} = -D > 0$ in Eq. (55). For most values of D, the transition is similar to that found for $\beta < 1$. That is, Q is very small near p_c and $h(p_c) \lesssim 1$. This gives three solutions of the equation $p = h(p)$ for some range of temperatures. The only differences are a reduction in the latent heat and the introduction of a critical endpoint for the liquid. The latter is the temperature below which the liquid state does not exist. There is a much smaller range of parameter space for which p is a continuous function of T through T_g, and a second-order phase transition occurs at $T = T_p$ when $p = p_c$. This requires values of D, A, and A' in Eq. (55) so small that C_p becomes a very smooth function of T, with no anomalous rise. The decrease in C_p with decreasing T is then too gradual to avoid the entropy crisis. We therefore conclude that while a second-order transition is possible in our model, it is very improbable and does not correspond to the type previously proposed by Gibbs and Di Marzio.[70]

B. Thermal expansion

Experimentally, the volume depends on the cooling and heating rates of the measurement and shows hysteresis. Here we calculate the average volume $\bar{v}$ as a function of T; it is given by

$$\bar{v} = \int_0^\infty v P(v)\, dv \quad . \tag{56}$$

Inserting Eqs. (36a) and (36b) into Eq. (56), we have

$$\bar{v} = p(v_c + \bar{v}_f) + (1-p) v_0 + (1-p) \frac{kT}{\kappa v_g} \left[\exp\left(\frac{-\kappa v_0^2}{2kT} \right) - \exp\left(-\frac{\kappa (v_c - v_0)^2}{2kT} \right) \right] \quad . \tag{57}$$

Thus, with the exception of p, the parameters in Eq. (57) for $\bar{v}$ are smooth functions of temperature and show no anomaly at T_p. However, p is a discontinuous function of T at T_p and, as a result, this model predicts a jump discontinuity in $\bar{v}$ at T. The volume will show a change of slope near T_p, as the contributions from the infinite cluster dominate for $p > p_c$, while the solidlike and finite-size clusters dominate for $p < p_c$. In Fig. 12 we show the result for $\bar{v}$ vs T using the parameters for $\bar{v}_f / v_m$ for tri-α-naphthylbenzene and those in the caption of Fig. 10.

Above T_g, where the material is in equilibrium, a

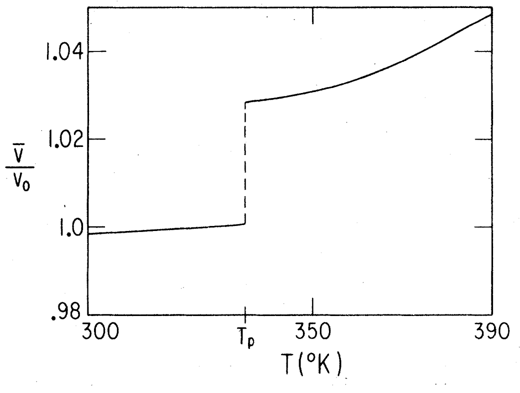

FIG. 12. Equilibrium volume $\bar{v}$ vs T near T_p for tri-α-naphthylbenzene. The parameters are the same as in Fig. 10.

direct comparison can be made between our theory and experiment. The observed value of $\alpha = d\ln v/dT$ is constant. Our theoretical values are not constant as α continues to increase with T. For tri-α-naphthylbenzene, the observed value of α is $5.2 \times 10^{-4}/°\text{K}$. This difference is probably related to our mean-field theory, which neglects interaction between neighboring cells. These interactions should retard the growth of $\bar{v}$ in the liquid. Note that we have left the temperature dependence of v_0 and v_c out of consideration. These would largely compensate for each other in the liquid domain. Below T_p, the calculated value of α for the solidlike domain is far smaller than the value observed below T_g. As the variation of p with T is largely frozen out below T_g, and the temperature dependence of $\bar{v}_f$ makes a small contribution below T_p, the value of α observed below T_g should in fact correspond to our calculated value below T_p. The discrepancy arises from our neglect of dv_0/dT and can yield an estimate of it. These results indicate that the volume $\bar{v}$ is very sensitive to the simplifications we have introduced in our model. However, we expect that η and C_p are not so sensitive and should be more characteristic of a dense liquid and glass.

VIII. SUMMARY AND CONCLUDING REMARKS

In this paper, we have extended the free-volume model to encompass the thermodynamic behavior of dense liquids and glasses in metastable equilibrium. The model had previously been useful in describing the behavior of the viscosity η. Until now, it had not been used to examine the heat capacity and volume, or to explore the possibility of an equilibrium liquid to glass phase transition. Experimental results for C_p and $\bar{v}$ show that the system falls out of complete, metastable equilibrium at the glass transition temperature T_g. Our calculation should be considered as a first step in understanding these universal phenomena, as it describes the underlying metastable phase, the amorphous phase, towards which the material relaxes. Further work is needed to extend our theory to include the relaxation phenomena.

The free-volume model is based on the four simple assumptions outlined in Sec. II. Recent molecular dynamic calculations demonstrate the persistence of a cellular structure in dense liquids for relatively long times and justify the basic assumptions of the free-volume model. With these assumptions as a basis, it is possible to define the free volume and distinguish solidlike and liquidlike cells. The local free energy of a cell, depending only on its volume v, contains two contributions: the negative of the work to remove a molecule from the interior of a cage and the work to expand the cage to the volume v. We have assumed $f(v)$ to have the simple form shown in Fig. 2. The slope ζ of $f(v)$ in the liquidlike region, $v > v_c$, is taken to have the form given by Eq. (9). The second contribution in ζ which depends on $\bar{v}_f$ accounts for the environmental dependence of the free energy on its neighbors. This term has important implications for the final form of η, and leads to the high-temperature form for $\bar{v}_f \propto T - T_0$.

The notion that cells are either solidlike or liquidlike leads directly to the introduction of percolation theory, which is used to describe the development of the communal entropy in Sec. III. When the fraction of liquidlike cells $p > p_c$, there is an infinite, connected liquidlike cluster and the material is liquid. For $p < p_c$, only finite liquidlike clusters are present and a glass phase exists. We find that in our model, the equilibrium transition from the liquid to glass phase is first order and a region of p near p_c is excluded. The probability distribution of the cellular volume as a function of p is obtained as well as a self-consistency condition for p, Eq. (39). After parametrizing these equations for two glass formers, an organic and a metallic glass, we solve for p vs T and calculate the thermodynamic properties of interest.

The average free volume and viscosity were determined in Sec. VI. We find that $\bar{v}_f$ and η are essentially unaffected by the phase transition and also by the presence of the communal entropy. That is, had one initially neglected S_c there would have been no phase transition, p would vary continuously with T, and the results for $\bar{v}_f$ and η would be largely unchanged. However, results for C_p and $\bar{v}$, obtained in Sec. VII, depend crucially on the presence of the communal entropy S_c.

These thermodynamic results are associated with an equilibrium phase transition at a temperature $T_p \geqslant T_s \cong T_\eta$. Values of the viscosity at T_s and therefore T_p are not known, but it is possible that some are within the liquid range of viscosities, i.e., $\leqslant 10^{13}$ poise. Candidates for the direct observation of

T_p are those materials for which the annealing times are manageable, i.e., those with the smallest values of η at T_s. There is in fact some evidence[56] for *a*-Se that annealing times of $\lesssim 100$ hours are sufficient to reach the equilibrium configuration just below T_p. This holds out the possibility of mapping out the entire equilibrium course of $\bar{v}$, or some functions such as the dielectric constant closely related to it, around T_p.

There are several important simplifications in our model which should be pointed out. They include the artificially sharp distinction between liquidlike and solidlike cells. The local free energy was approximated by a quadratic and linear region. This led us to allow only liquidlike cells to exchange volume. However, there surely exist activated processes by which solidlike and liquidlike cells can exchange volume. We have ignored all such thermally activated motion which should be important at low temperatures where the number and sizes of the liquidlike cells are reduced. There are also time-dependent effects, in which solidlike cells become liquidlike and vice versa. We have assumed that the time scale for this to occur is substantially longer than that for atomic motion within a liquid cluster. This effect will also become important at low temperatures, when the liquidlike clusters are small, but should not be important for T near and above T_p, when $p > p_c$. Finally, we have factored the joint probability distribution of cell volumes and treated the total free energy in a mean-field theory. We assumed that $f(v)$ and $P(v)$ depend only on the cellular volume v and neglected any interaction with neighboring atoms. The only local environmental effect we included was in the dependence of ζ_1 on $\bar{v}_f$, Eq. (8), and this we treated as a mean-field correction. However, we expect none of these effects to change the qualitative nature of the liquid-glass transition we have described. We expect that p can still be defined even though the loss of a sharp distinction between liquidlike and solidlike cells vitiates use of percolation theory. The nonanalyticity in $\mathcal{S}$ is lost, leading to a communal entropy for which $(\partial \mathcal{S}/\partial p)_{p_c} < \infty$. However, the first-order phase transition should be preserved, just as it was for most of the parameter space even when $\beta \geqslant 1$. We do expect the discontinuity in p and $\bar{v}$ to be reduced as would be the latent heat. One important effect of this smearing will be the appearance of a critical endpoint for the liquid, a temperature below which the liquid phase is no longer even metastable. The second-order transition, which is only a small region of parameter space for $\beta \geqslant 1$, is now wiped out completely by the restoration of analyticity. Our theory thus leads to a first-order phase transition or no transition at all. However, the entropy crisis can be resolved within our theory only if a transition occurs.

The free-volume theory as developed here has many features which are similar to the entropy theory developed by Gibbs and Di Marzio.[70] This entropy theory was developed to describe polymers. By mixing polymer links with holes on a lattice, they could determine the entropy of mixing and the configurational entropy. In the free-volume model, we have a distribution of free volumes in place of the sharply defined holes and both an entropy of mixing and a communal entropy. The free-volume model is realistic for monotonic or rigid molecules, while the entropy theory reduces to Frenkel's hole theory of liquids, which is known not to be very accurate because of the sharpness and permanence of the holes. However, when the free-volume model is used for the treatment of flexible molecules, it suffers from the confusion of the internal configurational entropy with the communal entropy because the internal constraints are not explicitly included. These constraints can be encompassed only in an approximate manner by adjusting the parameters of the theory to compensate for this weakness, in particular the value of β. The complementary weakness of the entropy theory for monotonic systems is not overcome as easily. The essential point to remember is that entropy is central to both theories. In this sense, the two theories are closely related. Both theories yield what is essentially a vacancy model for molecular motion, the free-volume theory giving the more realistic description by including the fluctuations of the voids. The free-volume theory, moreover, admits a description of the evolution of the communal entropy, perhaps the most fundamental aspect of the passage from the solid to the liquid state.

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