PHYSICAL REVIEW A VOLUME 40, NUMBER 2 JULY 15, 1989

Scaling concepts for the dynamics of viscous liquids near an ideal glassy state

T. R. Kirkpatrick and D. Thirumalai
Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742

P. G. Wolynes
Noyes Laboratory, University of Illinois at Urbana–Champaign, Urbana, Illinois 61801

(Received 23 December 1988; revised manuscript received 22 February 1989)

Motivated by recent mean-field theories of the structural glass transition and of the Potts glass model we formulate a scaling and droplet picture of an assumed ideal structural glass transition. The phase transition is a random first-order phase transition where the supercooled-liquid phase is composed of glassy clusters separated by interfaces or domain walls. Because of entropic driving forces the glassy clusters are continually being created and destroyed. As the ideal transition temperature is approached the entropic driving force vanishes and the size of the glassy clusters diverges with an exponent of $\nu=2/d$. All long-time dynamical processes are activated and the Vogel-Fulcher law is obtained for the liquid-state relaxation time.

I. INTRODUCTION

It is exceedingly tempting to try to relate the dramatic changes in various properties of a liquid undergoing a glass transition in the laboratory at finite cooling rates to an underlying ideal structural glass (STG) transition which would occur (at least in good glass formers) at a finite temperature upon infinitely slow cooling.[1] Many scenarios of this kind have been constructed over the years.[1–7] Recently, we have developed a picture of an ideal STG transition based on mean-field theories of the STG transition[8–10] and on the mean-field theory of the random Potts glass[11,12] (PG) and related p-spin models.[13] Having given in to the temptation of assuming an ideal STG transition, one is forced to consider what the scaling arguments used for equilibrium phase transitions might say about such an ideal glass transition and, *perhaps,* about laboratory glass transitions. In this paper we will further explore the concept of an ideal STG transition using scaling notions together with concepts arising from our earlier investigations of mean-field theories of structural glasses and of mean-field spin-glass models without reflection symmetry.

Due to the heuristic nature of our arguments, their range of validity and to what glass forming systems they apply is not clear. Our arguments always assume the liquid state is close to (metastable) equilibrium and consequently our ideas most naturally apply to generic-glass-forming materials and not to, say, metallic glasses which are formed by very rapid quenching from the melt and hence are systems far from equilibrium.[14] In addition, some of our arguments are based on large-scale droplet (or glassy clusters) ideas. Near the laboratory glass-transition temperature, T_g (which depends on the cooling rate), this is problematic because the size of these droplets (if they exist) is not very large. One of the main problems in constructing a theory for the glass transition is that if the laboratory glass transition is controlled by an ideal glass transition then one must come to grips with the fact that T_g is never asymptotically close to the ideal transition temperature which we call T_K. The main point is that because dynamics is controlled by activated processes even small correlation lengths lead to relaxation times that exceed typical experimental times. Even in the most favorable cases (say, *o*-terphenyl) the distance from an assumed ideal glass transition can be estimated to be $t=(T_g-T_K)/T_K>0.1$.[15] Nevertheless, we take the point of view here that the observed glassy phenomenology is controlled by an ideal transition, with, possibly, crossover effects playing a major role. We also point out that with minor modifications, our scenario is also valid if it turns out that the ideal glass transition is rounded by, for example, frustration effects. This is discussed further below.

The organization of this paper is as follows. In Sec. II we present the phenomenology relevant for our purposes. To motivate the scaling theory we also review our previous mean-field results. These considerations lead us to argue that an ideal glass transition would be a random first-order phase transition. In Sec. III we discuss the nature of the driving force for activated transport in viscous liquids. In Sec. IV we discuss the (finite-size) scaling exponents for a random first-order phase transition. In Sec. V we combine the ideas presented in Secs. II–IV with scaling ideas and derive the Vogel-Fulcher (VF) law for transport in a viscous liquid. In Sec. VI we discuss some of the other experimental consequences of our picture and conclude with some additional remarks.

II. REVIEW OF RELEVANT PHENOMENOLOGY AND MEAN-FIELD THEORY

The most obvious mystery of glassy behavior is the strongly non-Arrhenius slowing down of transport properties as the temperature is lowered. In the usual liquid regime above the melting point the isochoric activation energies are very small but the apparent activation energies grow dramatically in the supercooled regime. The viscosity for at least fragile glasses is often fit by the Vogel-Fulcher equation:[1,16]

$$\eta=\eta_0\exp[A/(T-T_0)] \ . \tag{2.1}$$

At the lowest temperatures a weaker divergence is often (but not always) reported.[17] This may be due in some cases to nonequilibrium effects but a true equilibrium crossover may sometimes be valid.

In general, at T_g there is no observed latent heat or change in volume. On the other hand the heat capacity and other susceptibilities change very rapidly in a nearly discontinuous manner.[1,16] The laboratory transition is a dynamic phenomenona dependent on the time scale of measurement and on the cooling rates. If the VF equation were to remain valid at low temperature the motions responsible for transport must freeze out at T_0 and the glass transition would be independent of the experimental time scale. Naively, we might expect this ideal glass transition to have the limiting characteristics of the laboratory transition—no latent heat but discontinuous susceptibilities. Generally the larger the discontinuities in heat capacity, etc., the more dramatic is the deviation from Arrhenius behavior.

Another mystery of the glass transition crucial to our picture is the behavior of the configurational entropy of the supercooled liquid.[3] It is important to note that, in general, the configurational entropy of a liquid is not a well-defined theoretical concept that different researchers mean different things by it (cf. Secs. III and VI). As pointed out by Simon[18] and Kauzmann[19] the extrapolation of heat-capacity data for supercooled liquids suggests that if a glass transition did not intervene the entropy of a supercooled liquid would be less than that of the corresponding crystal, at a temperature T_K less than the laboratory T_g. Since the vibrational entropies should be comparable for a crystal and a glass at these temperatures, this suggests a vanishing of a configurational contribution to the entropy at T_K. This temperature T_K is generally believed to be close to the T_0 in the Vogel-Fulcher equation and, as already remarked, we denote the ideal glass-transition temperature in this paper by T_K.

In order to better appreciate our arguments leading to Eq. (2.1) we give a qualitative description of the crucial features of the free-energy surface in a viscous liquid. Formally, the concept of a free-energy surface is not well defined because it involves unjustified analytic continuations. The surface we discuss can be viewed as the energy surface of a coarse-grained Hamiltonian in terms of order parameters. Because such a Hamiltonian contains entropic contributions we refer to the energy surface as a free-energy surface. Our picture is motivated by recent mean-field theories of the STG transition and spin-glass models without reflection symmetry.[9-13]

As a liquid is cooled (quenched) to low temperatures, say, below its equilibrium crystallization temperature, T_{cry}, one intuitively expects a rough free-energy landscape in a very high-dimensional order-parameter space. The characterization of this high-dimensional free-energy surface is difficult. We begin by describing what some of the valleys on this surface are. By a state, s, we mean that set of configurations for the system as a whole which connects to s. Note that implicit in this definition of a state is a time scale argument. For infinite times, there is probably only the crystal state. We believe that this global thermodynamically stable phase is irrelevant to the glass-transition problem. It has been shown that mean-field theory leads to a multivalley structure in which an infinite number of aperiodic crystal phases can coexist, giving a finite "configuration" entropy above the ideal glass-transition temperature. For models with finite-ranged interactions this entropy will lead to an instability of the global mean-field states.[11] A state will break up into droplets. The resulting set of mosaic structures describes the liquid.

The main problem in glass formation is to understand how and why the relaxation time, τ, in the supercooled-liquid state grows so rapidly. As already mentioned, experiments indicate that for certain glass-forming materials τ appears to diverge at a temperature T_0 ($T_0 < T_g$) and the divergence is exponential. Exponentially large relaxation times are most naturally obtained by considering activated transitions between different mosaic states. Just as in ordinary nucleation theory, glass dynamics can be understood by using restricted statistical mechanics for metastable states.

This can be done by introducing restricted phase-space average: In statistical mechanical averages replace the trace Tr by Tr→Tr′ where Tr′ means including only those configurations belonging to the metastable glassy state.[9-13] The global metastable glassy states are essentially frozen liquid states with nonzero Debye-Waller factors which indicates they have elastic properties. To describe them we introduce two related key ideas.[10] First we imagine an order-parameter description in terms of frozen-density fluctuations, $\delta n = n - n_l$. Here n is the number density and n_l is the liquid-state number density. Other order parameters can be used but frozen-density fluctuations are the simplest and most directly related to the most trivial characterization of a solid: a nonzero Debye-Waller factor. Since the glassy state is amorphous or aperiodic the frozen-density order parameter is most naturally specified by a (functional) probability measure $DP[\delta n]$. Within a mean-field approach the glassy states are characterized by the first and second moments of this measure,[10]

$$\overline{\delta n(\mathbf{x})}=\int DP[\delta n]\delta n(\mathbf{x})=\frac{1}{V}\int d\mathbf{x}\,\delta n(\mathbf{x})=0 \ , \tag{2.2a}$$

$$\begin{aligned} q\equiv\overline{[\delta n(\mathbf{x})]^2}&=\int DP[\delta n][\delta n(\mathbf{x})]^2\\ &=\frac{1}{V}\int d\mathbf{x}[\delta n(\mathbf{x})]^2 \ . \end{aligned} \tag{2.2b}$$

The final equalities in Eqs. (2.2) assumes self-averaging and from Eq. (2.2b) it follows that the zero in Eq. (2.2a) is really a term of $O(V^{-1/2})$ with V the volume and the bulk limit is always taken. The Edwards-Anderson order parameter[20] q in Eq. (2.2b) is zero in the metastable liquid phase and is nonzero in metastable glassy states. Some features of this order parameter will be discussed below. The second key notion we introduce is that, in general, one expects a large number of distinct glassy metastable states. We denote a particular glassy state by the label s, with the frozen-density field in that state given by $n_s = n_l + \delta n_s$ and the free energy equal to F_s [the density fields in Eq. (2.1) should also be labeled by the index s]. Calculations indicate[10,11] that below a temperature we will call T_A, there are an extensive number (the number of states scales like $\exp[\alpha N]$ for an N-particle system) of global statistically similar incongruent metastable glassy states. Statistically similar states have the same spatially averaged correlation functions and incongruent states have zero overlap:[10,21]

$$q_{ss'} = \delta_{ss'} q = \frac{1}{V} \int d\mathbf{x}\, \delta n_s(\mathbf{x}) \delta n_{s'}(\mathbf{x}) \ . \tag{2.3}$$

Note that because these states are statistically similar, one cannot use an external field to pick out a particular state. Consequently, the partition for the global metastable states is given by a sum over all s:[21,22]

$$Z = \mathrm{Tr} \exp(-\beta H) = \sum_s \exp(-\beta F_s) \ . \tag{2.4}$$

Technically Eq. (2.4) is correct (in the restricted ensemble Tr′) if the barriers between states diverge in the bulk limit. Physically it is a reasonable equation for a restricted time interval if the barriers are large but finite. We argue below that even in this doubly restricted ensemble, entropic driving forces always lead to nucleation processes which in turn lead to mosaic states rather than global metastable glassy states. Nevertheless, the phase-space decomposition given by Eq. (2.4) is a useful intermediate step.

With Eq. (2.4) one can define a canonical free energy,[21,22]

$$F_c = -\frac{1}{\beta} \ln Z \tag{2.5a}$$

and a component averaged free energy for the global metastable states,

$$\bar{F} = \sum_s P_s F_s \tag{2.5b}$$

with P_s the probability of being in the s component,

$$P_s = \frac{1}{Z} \exp(-\beta F_s) \ . \tag{2.5c}$$

F_c'' and $\bar{F}$ are related by[21]

$$F_c = \bar{F} + k_B T \sum_s P_s \ln P_s \equiv \bar{F} - TI \ . \tag{2.6}$$

Here I is usually called the complexity, but we will argue it can also be interpreted as a state entropy which is bounded from above by a configurational entropy in non-mean-field models. In general I is related to the solution degeneracy and it is extensive (and $F_c \neq \bar{F}$) if there are an exponentially large number of states. Note that the physical free energy, if the barriers are infinite, is $\bar{F}$ because the term, $-TI$ in Eq. (2.6) is a entropy term which is a measure of parts of state space not probed in a finite amount of time. Since a physical entropy should only be associated with accessible configurations it follows that F_c is not the physically meaningful free energy of the global glassy metastable states.

If we ignore the nonperturbative droplet (cf. below) fluctuations that lead to the mosaic states then a mean-field-like calculation gives the following.[10] (1) For $T < T_A$ there exist an extensive number of statistically similar incongruent global glassy metastable states. For $T = T_A^+$, q drops discontinuously to zero and the restricted ensemble Z' is no longer physical meaningful for higher temperatures. The only global state is the liquid state. (2) For $T < T_A$, F_c'' is identically equal to the liquid-state free energy, F_L, and $\bar{F} - F_L = TI \sim O(V)$, for all temperatures such that (defining T_K) $T_K < T < T_A$. This indicates that in this temperature range the glassy states are metastable with respect to the liquid phase. (3) At T_K, $\bar{F} = F_L$, and the complexity vanishes (or becomes nonextensive). The glassy states are then thermodynamically preferred to the liquid state. We identify T_K with an ideal STG transition temperature. It will be interpreted further below. (4) A mean-field dynamical theory leads to a glassy freezing for all $T < T_A$. Physically this is because the extensive solution degeneracy implies that with probability one the initial configuration of the system will be in a global glassy metastable state. Because nucleation out of a metastable state is a nonperturbative fluctuation effect that is ignored in a mean-field dynamical theory the system will stay in a particular metastable forever. Note that the equality of F_c'' and F_L is consistent with this result. The canonical free energy of all the glassy states is equal to the liquid-state free energy because of the entropy or complexity term in Eq. (2.6). Conceptually the existence of a temperature (region) T_A is important because it indicates (cf. Sec. III) that for all $T < T_A$, long-time dynamical processes are activated.

III. ENTROPIC DRIVING FORCES FOR ACTIVATED TRANSPORT

In this section we give a preliminary discussion of the expected nonperturbative droplet or domain-wall dynamics for $T_K < T < T_A$. The scenario given here will set the stage for the more refined arguments given in the subsequent sections of this paper. It should be pointed out that because the equation for the saddle point for the field theory we have proposed for the structural glass transition,[10] has multiple solutions, fluctuation effects cannot be accounted for by self-consistent variational (or perturbative) schemes. What is needed is to compute the instanton contributions and physically this corresponds to the large-scale droplets considered here. Crucial to our arguments is the nature of the entropic driving force for activated transport. We first discuss this driving force and then we will use it in a naive way to obtain some preliminary results.

The relevant entropy[11] for our scenario is associated with the multiplicity of disjoint ergodic states above T_K. In several exactly soluble models[11,13,23] this entropy does vanish at a temperature T_K, where a random first-order phase transition occurs. We assume a similar behavior for structural glasses. We shall refer to this entropy as the state entropy S_s since it is a measure of the number of disjoint (at least in mean-field theory) ergoidc states. A precise discussion about the meaning of S_s can be given by considering the model problem of the Potts glass in the mean-field limit.[11,12] For this model both the canonical free energy, F_c, and the component-averaged free energy, $\tilde{F}$, can be exactly computed and written as

$$F_c = -\frac{1}{\beta}\ln\left[\sum_s \exp(-\beta F_s)\right] = -\frac{1}{\beta}\ln N\int df\, e^{N[\alpha(f)-\beta f]} \tag{3.1a}$$

and

$$\tilde{F} = \sum_s P_s F_s = \frac{N}{Z''}\int df\, f e^{N[\alpha(f)-\beta f]} \,. \tag{3.1b}$$

Here $f = F/N$ is an intensive free-energy variable and $g(f) = \exp[N\alpha(f)]$ is the density of free-energy states. In the thermodynamic limit, the integrals in Eq. (3.1) can be evaluated by saddle-point methods and one gets

$$F_c = \tilde{F} - \frac{N}{\beta}\alpha(\bar{f}) \,, \tag{3.2a}$$

with $\alpha(\bar{f}) \neq 0$ for $T_K < T < T_A$. Here $\bar{f}$ satisfies the relation $\beta = \partial\alpha(\bar{f})/\partial\bar{f}$. Notice that the existence of $\bar{F}$ in non-mean-field theories is hard to justify in the region $T_K < T < T_A$ because the states being considered are metastable. We have assumed that the relaxation times are extremely long compared to the typical experimental time scales and that one can calculate F_s by considering those configurations belonging to s. From Eq. (2.6) and the discussion below it, the state entropy is

$$S_s = k_B N\alpha(\bar{f}) \,, \tag{3.2b}$$

i.e., S_s is related to the number of free-energy states. In the droplet arguments given below we shall assume that S_s is the important driving force for large-scale domain dynamics and when $S_s \neq 0$, there is liquid-like relaxation. Note that S_s is not precisely the configurational entropy, S_c, considered in the Adams-Gibbs[3] picture of the glass transition. The distinction between S_s and S_c can be seen in several ways. First, as already mentioned in Sec. II, S_s (there called the complexity) is not a physically meaningful entropy in mean-field theory. However, even in this case, in a given ergodic component one would imagine that both a vibrational and a configurational entropy exist. The configurational entropy would be associated with different defect arrangements in a particular ergodic state. In non-mean-field models S_s would become a physical entropy[11] because domains of a distinct glassy state inside an original glassy state are allowed if droplet fluctuations are taken into account. Within each droplet there will again be vibrational and configurational entropy. These arguments indicate that the total configurational entropy as is usually discussed is greater than or equal to the state entropy, S_s. Physically, we imagine that the distinction between the configurational entropy associated with defects and the "configurational" entropy associated with states is related to length scales. The configurational entropy associated with defects should lead to motion involving only a few particles because that is all it does in the crystal phase and consequently it does not lead to liquid-like relaxation. We argue below, on the other hand, that S_s leads to large-scale liquid-like transport involving many particles.

Assuming that S_s is an entropic driving force for activated transport we next give a preliminary argument on the expected behavior of the liquid-state relaxation time as S_s decreases.[11] Consider a region of size L^d in a single glassy state and estimate the probability of a different glassy state forming inside this region. Because the different glassy states have roughly the same free energy the driving force for droplet formation is entropic: Nucleation of a new state occurs because there are so many states to escape to. The effective free-energy driving force for this process is of magnitude Ts_sL^d. Here s_s is the state entropy per unit volume. Opposing the droplet formation is a surface free energy cost, F_{surface}. For large L, F_{surface} can scale at most as σL^{d-1}, with σ the surface tension between two different glassy states. Comparing these two forces one sees that at large enough L a droplet will always form. Repeating this argument for every fluid region leads to the mosaic state already discussed. With this argument the typical size of a glassy cluster will be of order $L^* \sim \sigma T/s_s$ and the free-energy barriers for activated transport are of order $\Delta F^* \sim (\sigma T/s_s)^{d-1}$. Note that this picture predicts a divergent length scale, L^*, and a divergent relaxation time, $\tau \sim \exp(\beta\Delta F^*)$, as the ideal STG transition at T_K $[s_s(T=T_K)=0]$ is approached. Also note that if we consider transitions into the liquid state then the picture is unchanged because the free-energy driving force for this process is also $\bar{F} - F_L = \bar{F} - F_c'' = TI = TS_s$. In fact, because the formation and destruction of the glassy clusters will continuously occur, the mosaic state for $T_K < T < T_A$ is also a liquid state.

These considerations lead to the following picture of a viscous liquid at low temperatures (well below T_A). First the liquid consists of glassy clusters or amorphons separated by interfaces or domain walls. As the temperature is decreased the size of the glassy clusters, $L^* = \xi$, increases and the coherence length of the clusters, ξ, diverges st an ideal STG transition. Secondly, the long-time dynamics is controlled by activated processes where the glassy clusters are destroyed and created. The time scale for these processes diverges exponentially as the ideal STG transition is approached. Motivated by the appearance of the divergent coherence length, ξ, we use scaling ideas in the following sections to refine these ideas.

We stress the dynamical picture given above is very different than the nucleation and growth picture near a usual first-order phase transition.[24] The glassy clusters we consider remain small (on a scale given below) because once a droplet nucleates, another droplet can nucleate inside the previous one (because of the entropic driving force) and consequently the system will consist of many percolating domains. Thus the kinetics is both controlled and limited by fluctuation effects. In usual nucleation theory the growth is exponentially fast immediately subsequent to nucleation and it is not controlled by fluctuations. These arguments also suggest that unlike usual first-order phase transitions, fluctuations are very important in the droplet picture of the glass transition and the physics should be controlled by a single divergent length scale $\xi \sim t^{-\nu}$, with ν a correlation or coherence length exponent. Because a domain within domain picture makes sense only on scales greater than or equal to ξ, we expect ξ is the typical size of a glassy cluster. In general we can also argue that because the driving forces for activated transport scale as

$$F_{\text{driving}} \sim -Ts_s L^d \sim -tL^d \sim -t\xi^d \sim -t^{1-\nu d} ,$$

the activation barriers for critical transport near T_K must scale as

$$\Delta F^* \sim t^{1-\nu d} . \tag{3.3}$$

Here $t=(T-T_K)/T_K$ and we assume s_s vanishes linearly at T_K. If one prefers throughout this paper one could write s_s where $t=(T-T_K)/T_K$ occurs. This may be preferable if one looks at variations with other parameters other than the temperature such as pressure or if the transition really eventually becomes rounded. If the transition is rounded, our physical picture still makes sense, as long as large (but finite in this case) amorphous clusters determine transport in the glass-transition region and these clusters increase in size as temperature is decreased.

IV. SCALING EXPONENTS NEAR RANDOM FIRST-ORDER PHASE TRANSITIONS

As already mentioned we imagine an ideal STG transition that is in part characterized by glassy clusters whose typical size ξ is assumed to diverge as the ideal transition temperature is approached. The following arguments, as well as earlier ones by others, give estimates of the correlated volumes as containing 50–500 particles at the laboratory glass transition. In general, this indicates that T_g is a considerable distance from a possible ideal STG transition. In fact, $(T_g-T_K)/T_K$ is typically estimated to be ≥ 0.1. All of this implies that droplet arguments based on large length scales are somewhat problematic near the experimental T_g. With this caveat in mind, we now proceed to investigate the supposed ideal STG transition.

In this section we provide two different arguments for the value of the exponent ν which characterizes the divergence of ξ near T_K. The first argument is heuristic and is based on an approximate use of the fluctuation formula. The argument was originally hinted at by Donth.[25] We assume that the correlated volumes are large enough that they can be treated as independent thermodynamic systems. Because of our belief that an ideal glass transition exists, the correlation length becomes anamolously large near T_K and hence for $t \ll 1$, such an assumption is valid. The temperature fluctuation in a correlated volume is given by[26]

$$\delta T^2 = k_B T^2/NC , \tag{4.1a}$$

where N is the number of particles in a correlated volume of dimension ξ, C is the specific heat per particle, and the difference between constant volume and constant pressure density is ignored. Let the mean temperature of a correlated volume be $T=T_K(1+t)$ with $t \ll 1$. We now assume that mean-temperature fluctuation δT is less than the deviation of T from T_K, i.e., $\delta T \leq tT_K$. The rationale for this is that the temperature fluctuation is related to entropy fluctuation and this implies that if δT is large then there is sufficient entropic driving force at $T=T_K(1+t)$ for relaxation. Since, $t \ll 1$ this is not very probable. This assumption allows us to write Eq. (4.1a) as

$$k_B/NC \leq t^2 . \tag{4.1b}$$

The number of particles N scales like $\xi^d \sim t^{\nu d}$ and using this in Eq. (3.1b) we get the inequality,

$$\nu d + \alpha \geq 2 , \tag{4.2a}$$

or

$$\nu \geq 2/d . \tag{4.2b}$$

In obtaining Eq. (4.2b) we have assumed that the specific-heat exponent $\alpha=0$. The specific heat at $T=T_g$ for most glass-forming materials is discontinuous at $T=T_g$ and presumably it is also discontinuous at $T=T_K$. This allows one to estimate $\alpha=0$. Note that the equality form of Eq. (4.2) is just a hyperscaling law.[27] This connection justifies our assumption that $\delta T \leq tT_K$ for T near T_K. Notice that Donth applied the fluctuation formula at $T=T_g$. His expression for the mean size of the domain ξ involves the experimental decrease in specific heat at constant pressure and T_g.

The second argument that leads to $\nu=2/d$ is more formal. Mean-field calculations based on a model Hamiltonian written in terms of density fields, indicate that at the ideal STG transition temperature, T_K, the Edwards-Anderson order parameter [Eq. (2.2)] is discontinuous. Because q is a second moment of a probability measure we call such a transition a random first-order phase transition. We also expect that, in general, there is a discontinuity in q at T_K. As a liquid is cooled above T_K (and above T_g) it is well documented that at finite time or frequency scales there exist solidlike behavior, e.g., shear waves. This effectively implies the presence of finite-frequency elastic coefficients, or a finite-frequency Debye-Waller factor. It would seem that any reasonable dynamical scaling law which contains solid behavior at *short times* and liquid behavior at *long times* will imply a discontinuous Debye-Waller factor as the relaxation time diverges. This, in turn, implies a discontinuous q at T_K.

Scaling exponents for regular first-order phase transitions and their interpretation have been discussed before by many authors. Here we generalize the finite-size-scaling arguments of Fisher and Berker[28] to random first-order phase transitions. We first give the argument and then interpret the results.

In a finite system of size $L^d=V$ there can be no sharp phase transition. To describe the growth of a sharp random first-order phase transition as $L \rightarrow \infty$, we assume a finite-size-scaling hypothesis. We again use a density order parameter. For the conjugate field we use a chemical potential $h=\mu(T,p)-\mu(T_K,p_K)$. Here we allow for the fact that, in general, an ideal STG transition will depend on both the temperature T and the pressure p. We postulate that the scaling part of the free-energy density behaves as

$$f(h,L)\sim L^{-\zeta}Z(L/\tilde{\xi})\equiv L^{-\zeta}Y(hL^{\theta})\ , \tag{4.3}$$

where $\tilde{\xi}$ (the finite-size correlation or coherence length) is the length scale where finite-size rounding takes place. The last equality in Eq. (3.1) follows from the definition $\tilde{\xi}\sim|h|^{-\tilde{\nu}}$ (where $\tilde{\nu}$ is the finite-size-coherence-length exponent) and $\theta\equiv1/\tilde{\nu}$. The exponents $\tilde{\nu}$ and ζ can be determined from the scaling ansatz given by Eq. (3.3) and Eqs. (2.2) with q discontinuous at T_K. We first consider

$$\left[\frac{\partial f}{\partial h}\right]^2=\frac{1}{L^{2d}}\left[\int d\mathbf{x}\,\delta n(\mathbf{x})\right]^2$$
$$\sim L^{-d}q\sim L^{-2\zeta+2\theta}[Y'(hL^{\theta})]^2\ . \tag{4.4a}$$

Using the discontinuity of q at T_K^- this implies the equality

$$\theta-\zeta=-\frac{d}{2}\ . \tag{4.4b}$$

Another equality can be obtained by considering the susceptibility squared. Following Fisher and Berker[28] we obtain the equality

$$2\theta-\zeta=0\ . \tag{4.4c}$$

Combining these equations yields

$$\tilde{\nu}=1/\theta=\frac{2}{d},\ \ \zeta=d\ . \tag{4.5}$$

The corresponding result for a regular first-order phase transition is $\tilde{\nu}=1/d$. The difference arises because the conjugate field for the Edwards-Anderson order parameter is effectively $\sim h^2$. If we identify $\tilde{\nu}=2/d$ with the correlation-length exponent ν and use hyperscaling $\alpha=2-\nu d$, then we conclude that at T_K there is no latent heat and the specific heat is discontinuous (or perhaps logarithmically divergent). We remark the first-order-like phase transitions with these properties are somewhat unusual. However, there are several exactly soluble random-spin models with precisely these properties: the random-energy model,[23] mean-field p-spin-interaction spin-glass models,[13] and mean-field Potts glass models.[11]

There is another way of looking at this scaling physically.[11] Above T_K, the state entropy per particle is finite and the number of thermally accessible states grows linearly with the volume of the region. Below T_K the state entropy per particle vanishes yet the number of thermally accessible state is not *one* for a macroscopic sample. Rather it is a large but finite number diverging at T_K from below. There will be a characteristic size $V^*\sim\xi^d$ where we will be able to distinguish these two behaviors, that is, below T_K the number of states will increase exponentially with size until V^* is reached and saturation observed. Using the scaling ansatz above and below the transition then gives $\xi^d\sim(T-T_K)^{-2}$ and hence leads to the exponent $\nu=2/d$. In obtaining this result we have assumed that for $T>T_K$, $S_s\sim Vt$, and that for $T<T_K$, $S_s\sim V^0|t|^{-1}$. The exponent for the divergence of S_s below T_K has been taken from a mean-field calculation.[11] Above the transition, V^* will be the size after which exponential growth of the number of states clearly applies.

We also note that these exponents are consistent with the observed phenomenology at the laboratory glass transition where a latent heat is not found but there is fairly sharp (at least in fragile glass formers) discontinuity in the specific heat.[1] In fact the scaling exponent $\alpha=0$ (and by hyperscaling $\nu=2/d$) follows phenomenologically if we naively assume that the ideal STG transition has the limiting characteristics of the laboratory glass transition. This assumption is actually more reasonable than it probably appears at first glance. In both the ideal and laboratory transitions the crucial physical picture is the (effective) vanishing of the configurational entropy: The system gets trapped in a region of phase space. In the ideal transition there is a real phase transition because the number of liquid states becomes nonextensive and because the global glassy state is free energetically preferred to the liquid state. In the laboratory transition the effective number of liquid states become nonextensive because other states are not accessible on the experimental time scale. The similarity of these transitions is also indicated by the fact that glass transitions observed in computer simulations are similar to laboratory glass transitions.

Finally, we note that if the starting STG Hamiltonian has a random part in it and if the STG transition was due to this randomness then the rigorous inequality $\nu\geq2/d$ must be obeyed.[29(a)] The equality $\nu=2/d$ is most naturally associated with a random first-order phase transition.[29(b)] It is not clear, however, whether these arguments are relevant for the STG transition where the randomness is self-generated. Within our picture, however, the equality, $\nu=2/d$, is however necessary to give relaxation times in accord with the Vogel-Fulcher law. Thus, insofar as the experimental fits to viscosity data obeys the VF equation, it seems that the STG transition mimics the behavior seen in systems where the transition is random first order.

V. SCALING AND ACTIVATED TRANSPORT

In this section we combine the physical picture set up in Sec. II with the scaling ideas given in Sec. III, to obtain an expression for the relaxation time in the liquid state. The fundamental assumption is that there are glassy domains that are metastable, and consequently they continuously undergo transitions with a characteristic relaxation time which determines transport in the viscous liquid. For large scale domains, we first argue that this notion automatically implies that the free energy opposing the transition must scale as

$$F_{\text{opposing}}\simeq\gamma L^{\theta} \tag{5.1a}$$

with

$$\theta \le \frac{1}{\nu}(\nu d-1) , \tag{5.1b}$$

or $\theta \le d/2$ if $\nu=2/d$. In Eq. (5.1a), γ is a positive constant. The inequality given by Eq. (5.1b) can be rationalized by the following argument. In general, for $T_K < T \ll T_A$, we expect the driving force of activated transport in a volume of size L^d to be entropic and of order

$$F_{\text{driving}} \simeq -Ts_s L^d \simeq -tAL^d . \tag{5.2a}$$

Here $t=(T-T_K)/T_K$ and we have assumed that s_s vanishes linearly at T_K and A is a positive constant. If the typical size of a glassy cluster scales like $L \sim \xi \sim t^{-\nu}$ then Eq. (5.2a) becomes

$$F_{\text{driving}} \sim -At^{-(\nu d-1)} . \tag{5.2b}$$

Similarly, Eq. (5.1a) scales as $F_{\text{opposing}} \sim \gamma t^{-\nu\theta}$. Therefore, in order for the droplets to be unstable at large enough scales, the inequality given by Eq. (5.1b) must be satisfied.

We next give two arguments for the expected behavior of the liquid-state relaxation time near T_K. The most naive argument is as follows. If the typical size of a glassy cluster behaves like $L \sim \xi \sim t^{-\nu} \sim t^{-2/d}$ then Eq. (3.3) implies that the free-energy barriers for activated transport must behave like

$$\Delta F^* \sim t^{-(\nu d-1)} \sim t^{-1} . \tag{5.3a}$$

This immediately leads to a relaxation time of order,

$$\tau \simeq \tau_0 \exp[DT/(T-T_K)] . \tag{5.3b}$$

Here τ_0 is a microscopic relaxation time, D is a positive constant and we note that Eq. (5.3) is just the Vogel-Fulcher law. Also note that this is a consistent result only if the free-energy force opposing activated transport scales as

$$F_{\text{opposing}} \simeq \gamma L^{d/2} , \tag{5.4}$$

with γ a positive constant. This should be contrasted with the ansatz $F_{\text{surface}} = F_{\text{opposing}} \sim L^{d-1}$ used in Sec. III.

We next give a more careful discussion of the free-energy forces which oppose activated transport. We generalize an argument due to Villian[30] for the random-field Ising model (RFIM) to the structural glass problem. Our main conclusion will be that the surface forces which oppose activated transport do scale as Eq. (5.4) for the length scales of interest. Equations (5.1a) and (5.4) then independently of Sec. IV lead to Eq. (5.3) and all of our arguments are consistent with each other. Our arguments also lead to other features which are of experimental consequence which we discuss in Sec. VI and elsewhere.

In general in disordered phases one does not expect a finite macroscopic surface energy. This implies that the force opposing activated transport should be written $F_{\text{opposing}} \sim \sigma(L)L^{d-1}$ with $\sigma(L)$ meaningless beyond a length scale related to ξ. To understand the vanishing surface tension we start with a small droplet with a finite surface tension and then use renormalization-group-like ideas to determine the larger-scale behavior of $\sigma(L)$. The basic idea is to note that a smooth domain wall can decrease its free energy, $F_{\text{DW}} = F_{\text{surface}}$, by forming bumps of a third glassy state (say 3) if the original smooth domain wall separates two other glassy states (say, 1 and 2). Because there are an extensive number of different glassy states they have a free-energy distribution that is Gaussian and the typical free-energy difference between any two states in a volume of size L^d is of order $\pm L^{d/2}$. Thus the typical free-energy gain for a bump of radius r and height ξ is

$$\delta F_1 \sim -Hr^{d/2} \left[\frac{\xi}{r} \right]^{1/2} \tag{5.5a}$$

with H a positive constant. The free-energy loss due to the additional surface tension σ is (here ξ is assumed to be less than r and that the bump is not very rough)

$$\delta F_2 \sim \sigma r^{d-1} \left[\frac{\xi}{r} \right]^2 . \tag{5.5b}$$

Finally, as for the bulk processes, there is also an entropic driving force

$$\delta F_3 \sim -tAr^{d-1}\xi . \tag{5.5c}$$

We avoid explicitly including δF_3 by considering the surface free energy at T_K where δF_3 vanishes. If we assume scaling, then these results will be shown to lead to Eq. (5.3a). Minimizing $\delta F_{\text{DW}} = \delta F_1 + \delta F_2$ with respect to ξ yields

$$\xi \sim \left[\frac{H}{\sigma} \right]^{2/3} r^{(5-d)/3} , \tag{5.6a}$$

and the resulting free-energy gain per unit area is

$$\frac{\delta F_{\text{DW}}}{r^{d-1}} \sim -H \left[\frac{H}{\sigma} \right]^{1/3} r^{-2(d-2)/3} . \tag{5.6b}$$

Equation (5.6b) can be interpreted as a modification of σ due to the elimination of degrees of freedom of wavelength of order r. In a renormalization-group spirit we write Eq. (5.6b) in differential form as

$$d\sigma(r) = -K^{4/3}H \left[\frac{H}{\sigma} \right]^{1/3} r^{-2(d-2)/3} \frac{1}{r} dr , \tag{5.7}$$

with K a constant. Integrating Eq. (5.7) yields

$$\sigma(r) \sim KH/r^{(d-2)/2} . \tag{5.8}$$

In obtaining Eq. (5.8) we have imposed the boundary condition $\sigma(r \to \infty) \to 0$. At $T=T_K$ this is required to obtain a scale-invariant surface tension. With Eq. (5.8) and using that r scales with L, the surface-free-energy opposing activated transport at T_K is

$$F_{\text{opposing}} \sim \sigma(L)L^{d-1} \sim KHL^{d/2} , \tag{5.9}$$

which is just Eq. (5.4). Note that Eq. (5.8) in Eq. (5.6a) yields $\xi \sim r$.

Using Eq. (5.9) and assuming scaling we write the surface term opposing activated transport as $F_{\text{opposing}} = L^{d/2}h(L/\xi)$, where $h(x)$ is a scaling function with $h(0)$ a constant. Minimizing $F_{\text{opposing}} + F_{\text{driving}}$ then self-consistently gives $L^* \sim \xi \sim t^{-2/d}$. We conclude that the Vogel-Fulcher form, Eq. (5.3), is probably the asymptotic relaxation time near T_K and that the typical size of the cooperatively rearranging regions (CRR's) diverges as $\xi \sim t^{-2/d}$ as T_K is approached from above. Note that the typical cluster size, $\xi \sim t^{-2/d}$, is less than that indicated by the naive arguments of Sec. III for all $d > 2$.

Finally, it is easy to verify that if Eq. (5.5c) is retained then this picture is not changed. As already mentioned Eq. (5.8) in Eq. (5.6a) yields $\zeta \sim r$. As a consequence of this δF_3 can be interpreted as a renormalization of F_{driving}. We stress, that we have generalized only the simplest of Villian's arguments for the RFIM problem.[30] More sophisticated arguments could lead to a more complicated scaling behavior characterized by additional exponents. In particular, the bulk driving force could also be renormalized in a nontrivial way. Physically, the main conclusion we draw is that there are mechanisms that decrease the surface free energy from its naive behavior $\sim L^{d-1}$.

VI. DISCUSSION

The arguments we have put forward in this paper are speculative and in some respects similar to previous qualitative pictures of the liquid-glass transition. Our picture is, however, grounded in the study of some exactly solved, albeit, mean-field models of random-phase transitions which have transition characteristics bearing a strong resemblance to observations on the glass transition. In this section we would like to highlight the contrasts between our picture and previous ones and discuss experimental tests that might distinguish alternative hypotheses. There are several independent points that arise in this consideration and they are enumerated below.

(1) One of the hallmarks of our picture is the presence of a length scale diverging near T_K and that rearrangements of regions of this size have barriers dependent on that size. Such a divergent length connected with an impending entropy crisis also plays a role in the Adams-Gibbs-DiMarzio theory of the glass transition.[3] Divergent or nearly divergent lengths unconnected with an entropy crisis also enter into other theories of glass transitions such as those for metallic glasses[4] and, of course, continue to be invoked in entirely qualitative accounts of the glass transition. The divergence according to our analysis, $\xi \sim (T - T_K)^{-2/d}$ is stronger than the Adams-Gibbs-DiMarzio divergence $\xi \sim (T - T_K)^{-1/d}$. The $1/d$ exponent would ordinarily be associated with a traditional first-order transition rather than a random one. Thus, the Adams-Gibbs-DiMarzio exponent would give extremeley small connected clusters. On the other hand, the $2/d$ exponent would, in favorable cases, give lengths of several nanometers. Thus, experiments on glass formation in confined geometries may give some insight. Experiments along these lines are progress,[31] although it is clear that many complicating features can and do enter, such as surface effects and the difficulty of achieving a homogeneous distribution for confined systems. Other direct probes of such length scales are also conceivable. One important possibility is the use of the scanning tunnel microscope or various tribiological experiments[32] on friction in ultrathin films where nonlinear effects may be connected with phenomena at the correlation length scale.

(2) An issue we have not addressed in our scenario is the distribution of relaxation times. The problem of distributed relaxation times has attracted a great deal of attention lately in the study of many systems. The droplet scenario presented here puts great store in the random parts of the free energies of different droplets. It therefore suggests a rather wide distribution of activation energies and, therefore, relaxation times. Although there is a distribution of activation energies in glasses, others have emphasized the relative narrowness of this distribution in their speculations on the glass transition. A calculation of the width in our picture requires assessing the relative size of the renormalized surface energy and the randomness energies themselves. They are dimensionally the same but need not be numerically comparable. There is some evidence that the distribution gets broader in fragile glasses with decreasing temperature and this would be consistent with our picture.[33] Furthermore we have not dealt with droplet interaction effects and/or the question of the pinning of the walls in our so-called mosaic states. An *ad hoc* explanation of a narrow relaxation-time distribution would be a motional narrowing of the randomness due to fluctuations of other droplets because there is no quenched randomness in the glass Hamiltonian. Such a phenomenon would be however outside the scope of our single-droplet calculations and would require a complete dynamical analysis.

(3) It is worth emphasizing the distinction between configurational entropy S_c and the entropic driving force we have considered here. As stated before these differences become transparent by considering the mean-field spin-glass models without reflection symmetry. In these models, there is an Edwards-Anderson order parameter for $T < T_K$ even though the thermodynamics of this model is not frozen entirely below this transition temperature. Hence, there are still relaxing degrees of freedom, which can, for example, give a β relaxation. These can be further frozen out by the time the system reaches zero temperature. Any estimation of configurational entropy in real glasses is also complicated by the existence of additional relaxing degrees of freedom below the laboratory glass-transition temperature. We would agree with the recent observation[7] that as usually defined, the configurational entropy will not vanish in any realistic model with finite-ranged forces. This is because point defects are always present and they lead to a finite contribution to what is usually called configurational entropy.[34] Still, this in itself does not make a random first-order phase transition impossible. Even in the case of a crystalline solid, where we known there is a first-order phase transition from liquid to solid, there is a finite "configurational" entropy in the crystal phase associated with point defects.

(4) The remarks about the ambiguity of configurational entropy (see Sec. III) must translate into some ambiguity about the value of T_K or even its existence as a sharp point. Suffice it to say that our arguments correlate the impending vanishing of an entropy at T_K with the Vogel-Fulcher behavior of the activation barriers. Thus, even if some crossover to another type of phase transition or if rounding of the transition were to occur below the laboratory transition, we believe our arguments are relevant to the temperature range usually studied. We also point out, that for the exactly soluble spin models which we considered previously,[11-13] T_K is a temperature where both S_s vanishes and where the free energy of the high-temperature phase is equal to the free energy of the low-temperature glassy phase. Thus, within our picture, at T_K the liquid-state free energy is equal to the free energy of a global glassy state. This is another independent and less ambiguous condition for an ideal glass transition to occur.

In this regard, the connection of the glassy state and the random-field Ising model alluded to in Sec. V (as well as by others[6]) may conceal a deeper analogy. The renormalization-group analysis of nonrandom Potts systems proceeds more readily with the introduction of new Ising-like variables in addition to the original Potts variables.[35] If such an analysis is applied to a random Potts system with short-range interactions these Ising variables attain both random and regular fields upon renormalization.[36] Thus, on longer length scales there may be a natural connection of the Potts glass and the random-field Ising magnet. The presence of regular, as well as random fields in this analogy should remind us of another possibility. A random Ising model with an average field will probably only show a critical point when that field vanishes. In the glass analogy this is equivalent to having a vanishing configurational entropy not along a line in the temperature-pressure phase diagram but only at a point, where the critical behavior will occur. We point out that such a possibility allows one to accommodate in a simple way deviations of the Prigogine-deFay ratio from unity.[1] Such deviations, of course, can also be explained in a variety of dynamical fashions at the laboratory, as opposed to the ideal glass transition.

(5) The role of crystallization in any scenario needs to be addressed. First, macroscopic nucleation theory is applicable if the critical embryo for the periodic crystalline phase is larger than the correlation length ξ. In this case the growth of the critical nuclei is severely impeded by the large value of viscosity.[37] If the critical embryo is smaller than ξ then new considerations apply. In this case nucleation is not strongly impeded by slow transport but the thermodynamics of the transition is modified. The situation would be like solid-in-solid nucleation. The surface energies (barriers) for this situation are very large and consequently these processes are not very likely.

Finally we remark that the basic ideas of the droplet pictures require the existence of some sort of coherent structure on a moderate length scale. Once simulations on good glass formers are done on long length scales and rather long times this may become more apparent.

ACKNOWLEDGMENTS

This work was supported by National Science Foundation Grant Nos. DMR-86-07605, CHE-86-57356, and CHE-84-18619.

---

[1] For a recent review of structural glasses see, J. Jackle, Rep. Prog. Phys. **49**, 171 (1986).

[2] (a) D. Turnbull and M. H. Cohen, J. Chem. Phys. **29**, 1049 (1958); (b) G. S. Grest and M. H. Cohen, Adv. Chem. Phys. **48**, 454 (1981).

[3] (a) J. H. Gibbs and E. A. DiMarzio, J. Chem. Phys. **28**, 373 (1958); (b) G. Adam and J. H. Gibbs, J. Chem. Phys. **43**, 139 (1965).

[4] (a) D. R. Nelson, Phys. Rev. B **28**, 5515 (1983); (b) J. F. Sadoc, J. Non-Cryst. Solids **75**, 103 (1985), and references therein.

[5] R. G. Palmer and D. Stein, Phys. Rev. B **38**, 12035 (1988).

[6] J. Sethna, Europhys. Lett. **6**, 529 (1988).

[7] F. Stillinger, J. Chem. Phys. **89**, 6461 (1988); **88**, 7818 (1988).

[8] Y. Singh, J. P. Stoessel, and P. G. Wolynes, Phys. Rev. Lett. **54**, 1059 (1985).

[9] T. R. Kirkpartrick and P. G. Wolynes, Phys. Rev. A **35**, 3072 (1987).

[10] T. R. Kirkpartrick and D. Thirumalai, J. Phys. A **22**, L149 (1989).

[11] T. R. Kirkpartick and P. G. Wolynes, Phys. Rev. B **36**, 8552 (1987).

[12] (a) T. R. Kirkpatrick and D. Thirumalai, Phys. Rev. A **37**, 4439 (1988); (b) Phys. Rev. B **37**, 5342 (1988); (c) D. Thirumalai and T. R. Kirkpartrick, *ibid.* **38**, 4881 (1988).

[13] T. R. Kirkpartrick and D. Thirumalai Phys. Rev. Lett. **58**, 2091 (1987); Phys. Rev. B **36**, 5388 (1987).

[14] See, for example, the papers in *Proceedings of the Third International Conference on Rapidly Quenched Metals, Brighton 1978*, edited by B. Cantor (The Metals Society, London, 1978).

[15] S. S. Chang, J. A. Horman, and B. B. Bestul, J. Res. Natl. Bur. Stand. Sect. A **71**, 293 (1967).

[16] C. A. Angell and W. Sichina, Ann. N.Y. Acad. Sci. **279**, 53 (1976).

[17] W. T. Laughlin and D. R. Uhlmann, J. Phys. Chem. **76**, 2317 (1972).

[18] F. Simon and Z. Anorg, Algemine. Chem. **203**, 217 (1931).

[19] W. Kauzmann, Chem. Rev. **43**, 219 (1948).

[20] This terminology is taken from the spin-glass literature. See K. Binder and A. P. Young, Rev. Mod. Phys. **58**, 801 (1986).

[21] R. G. Palmer, Adv. Phys. **31**, 669 (1982).

[22] C. DeDominicis and A. P. Young, J. Phys. A **16**, 2063 (1983).

[23] B. Derrida, Phys. Rev. B **24**, 2613 (1981).

[24] J. D. Gunton, M. San Miguel, and P. S. Sahni, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, New York, 1983), Vol. 8, p. 269.

[25] E. Donth, J. Non-Cryst. Solids **53**, 325 (1982).

[26] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Per-

gamon, London, 1980).

[27] S. K. Ma, *Modern Theory of Critical Phenomena* (Benjamin, Reading, 1976).

[28] M. E. Fisher and A. N. Berker, Phys. Rev. B **26**, 2507 (1982).

[29] (a) J. T. Chayes, L. Chayes, D. S. Fisher, and T. Spencer, Phys. Rev. Lett. **57**, 2999 (1986); (b) D. Huse, Ref. 7 in Ref. 29(a).

[30] J. Villian, J. Phys. **46**, 1843 (1985).

[31] J. Jonas (unpublished).

[32] J. N. Israelachvilli, P. M. McGuiggon, and A. M. Hourola, Science **240**, 189 (1988).

[33] P. K. Dixon and S. Nagel (unpublished).

[34] C. P. Flynn, *Point Defects and Diffusion* (Clarendon Press, Oxford, 1972).

[35] B. Nienhuis, E. K. Riedel, and M. Schick, Phys. Rev. B **23**, 6055 (1981).

[36] P. G. Wolynes (unpublished).

[37] C. A. Angell, D. R. MacFarlane, and M. Oguim, Ann. N.Y. Acad. Sci. **484**, 241 (1986).