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The aperiodic crystal picture associates the glass transition with freezing into a nonperiodic structure. Dynamics in the glassy state involves activated jumps between different aperiodic free energy minima. Activation barriers may be estimated through the use of freezing theory and the theory of dense solids. The results resemble, but are distinct from, free volume theory. Reasonable fits to experimental data are obtained.

The glass transition is most clearly manifested in the strong dependence of rate processes such as diffusion on thermodynamic state. Some theories of glasses such as those based on dense fluid kinetic theory or mode coupling theories make this observation the touchstone of their approach to the problem.[1,2] Other theories are based on equilibrium considerations and thus the observed dynamic phenomena are derived properties.[3,4] The two styles of approach are not necessarily orthogonal[5] and a complete theory will probably give equal weight to both views, at least near the glass transition itself. In this paper we will explore some dynamical consequences of the quasiequilibrium aperiodic crystal picture of the glass transition.[3,4] In particular we will derive approximate expressions for the free energy barriers between different structures of a glass. The theory thus deals with some of the local features of the dynamics of glasses while, at the same time, skirting some of the global questions of complicated sequential or hierarchical dynamics.[6,7]

The aperiodic crystal picture that we employ can be understood in terms of either a liquid based theory such as the density functional theory of freezing[8,9] or a solid based, cell-type theory such as the self-consistent phonon theory of Fixman.[10] The density functional theory starts with the free energy of the system expressed as a functional of the spatially varying number density of the fluid. Freezing is understood to arise from the existence of minima of the free energy corresponding with periodically varying densities. Starting with Ramakrishnan and Yusouff[8] this approach has led to a quantitatively successful theory of freezing in a variety of simple systems.[9] It is far from clear that the space of free energy minima is exhausted by those periodic solutions. The self-consistent phonon theory[3,10] assumes that each atom vibrates about its lattice site with some nonzero frequency. In this theory both the centers-of-vibration and the vibrational frequencies are determined by minimizing the appropriate free energy functional. As in the density functional approach, both periodic and aperiodic solutions are possible. The aperiodic crystal picture of the glass transition connects the broken ergodicity of glasses with the system being trapped in a free energy minimum with an inhomogeneous but aperiodic density. Without symmetry, however, the complete search for free energy minima is made difficult.

At zero temperature minimum energy structures which lack periodicity have been generated on computers by a variety of methods.[11,12] Once these zero temperature minima are located they can be used to generate an inhomogeneous spatial density that would be smeared by thermally excited vibrations about the minimum energy structure. In the simplest version[3,4] a single variational parameter analogous to a Debye–Waller factor can be introduced to search for free energy minima using the energy minima as starting points. When the thermal motions are too large the inhomogeneous density no longer corresponds with a minimum of the free energy—signaling the restoration of ergodicity in the system. In passing we note there are many points of contact of the aperiodic crystal picture with the density functional theory of quasicrystals.[13] Quasicrystals correspond with quasiperiodic densities that minimize the free energy. It may turn out that the aperiodic minima we discuss can be thought of as defected quasicrystals or other structures connected with crystals in curved space.[14] We feel it is useful to discuss the glass problem without making this identification because many of the formal relationships that arise in the aperiodic crystal picture may be carried over to more complex molecular systems where quasiperiodicity or curved space considerations may be difficult to apply in the classification of the aperiodic states.

Since there are many minimum energy structures there are likely to be many minimum free energy structures. For these to correspond with thermodynamic pure states the free energy barrier between these minima should not be microscopic. That is they should scale with a positive power of the size of the system. The purely thermodynamic analyses of the glass transition essentially made this assumption. In this sense the theories were like early treatments of spin glasses[15] that ignored the effects now associated with replica symmetry breaking. Many of the observations made in experiments and simulations of glasses can be rationalized on the basis that some of the free energy barriers are large but still microscopic. Thus transitions between these states gives rise to the slow relaxation processes in glasses. Thus the consideration of free energy barriers is important in addressing both questions of principle and practice.

We will use the density functional theory itself to estimate the free energy barriers between any two aperiodic minima. From the pristine thermodynamic derivations of free energy functionals it may seem odd to investigate this nonequilibrium question. Nevertheless, there is ample precedent for using free energy functions outside of strict equilibrium. Near to equilibrium such functionals determine the dynamics of small amplitude motions as in Landau–Ginz-
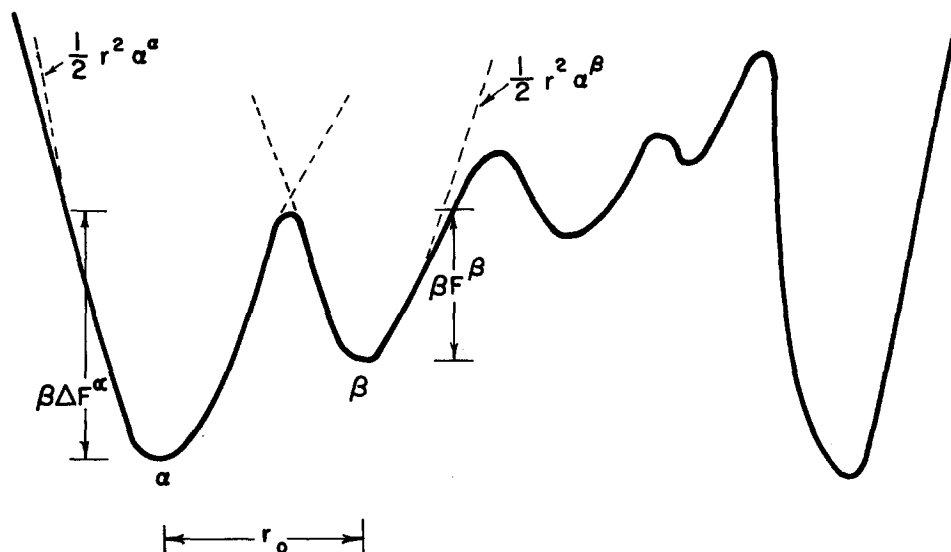
FIG. 1. A schematic cross section of the free energy surface for various aperiodic packings. The local harmonic approximations are indicated with dashed lines.

characteristic of the dynamics of a glass. We also note that S and $\mathbf{m}$ are $O(N_m)$, the number of particles that move. As a result, the activation free energy will not necessarily be macroscopic but can lead to long relaxation times.

As an example of our scheme, we study the interaction free energy functional arising from Stoessel and Wolynes's[3] modification of Fixman's[10] self-consistent phonon theory. In this theory

$$\beta F^{int} = - \sum_{j \neq k} \ln\left\{1 + \int d\mathbf{r}\, \rho_j(\mathbf{r}) \int d\mathbf{r}' f(\mathbf{r}' - \mathbf{R}_j)\rho_k(\mathbf{r}')\right\},$$

where $f(\mathbf{r}) = \exp[-\beta V(\mathbf{r})]$, $\rho(\mathbf{r}) = \Sigma_j \rho_j(\mathbf{r})$, $\rho_j(\mathbf{r}) = (\alpha_j/\pi)^{3/2} \exp[-\alpha_j(\mathbf{r} - \mathbf{R}_j^2)]$, $V(\mathbf{r})$ is the pair potential energy, and $\mathbf{R}_j$ is the center of vibration for the jth atom. Notice that the atoms interact only with the fiducial sites of the other atoms. This feature results from the fact that this is essentially a cell theory,[22] where atoms are assumed to be restricted to cells. For simplicity, we further assume that $S_j = 0$ and $\mathbf{m}_{jk} = \Delta^2 \delta_{j,k} \mathbf{l}$ and $\alpha_j = \alpha$ for all j. We refer to this as an Einstein approximation since it assumes that all the vibrational frequencies are the same. The result of these approximations is

$$\beta \Delta F^\dagger = \frac{\delta^2}{6} N_m \Delta^2 \operatorname{Tr}(\nabla^2 \beta F^\alpha_{int})$$

$$= \frac{1}{2} r_0^2 \alpha,$$

where $r_0^2 = (\delta\Delta)^2 N_m$ is the "distance" moved to the transition state and α is an effective force constant and we assume $\delta = 1/2$ at the transition state. We expect r_0 to be only weakly dependent on density (since it has to do with alternative geometrical packings) and hence expect most of the density dependence to be manifested in α. For the Stoessel–Wolynes functional, it is possible to show that

$$\lim_{\rho \to \rho_0} \alpha(\rho) = \frac{A}{[1 - (V_0/V)^{1/3}]^2},$$

where ρ_0 is the close packed density (usually taken to be

$\rho_0 \sigma^3 \cong 1.22$) and

$$A = \frac{9\pi}{\sigma^2 z^2}$$

and z is the number of nearest neighbors. This result is more general than might be expected from our derivation. Since α has units of inverse length squared, it must depend on the length scales involved in the problem. For the hard sphere system studied here, the only relevant length scales are the hard sphere diameter σ (which is related to the random close packed density and, hence V_0) and the nearest neighbor distance d (which is related to the density and, therefore, V). We can quantify the expected relationship by calculating the mean square average displacement of an atom from its fiducial site, holding all other atoms fixed. We find

$$\langle (r - R)^2 \rangle = \int d\mathbf{r}^3\, r^2 \theta(d - \sigma - r) / \int d\mathbf{r}^3\, \theta(d - \sigma - r)$$

$$\sim (d - \sigma)^2 \sim [1 - (V_0/V)^{1/3}],$$

and since α is the spring constant for atomic motion,

$$\alpha \sim \frac{1}{\langle (r - R)^2 \rangle}$$

and, hence,

$$\alpha \sim \frac{1}{[1 - (V_0/V)^{1/3}]^2}.$$

Thus, although we have derived the high density expression for α from a particular expression for βF^α, we can see that from purely dimensional arguments that α must have the above behavior. If viscous relaxation proceeds via transitions between different packings we would predict that the viscosity should go as

$$\ln \eta = \ln \eta_0 + \beta \Delta F^\dagger,$$

$$\ln \eta = \ln \eta_0 + \frac{c}{[1 - (V_0/V)^{1/3}]^2}, \tag{1}$$

where $c = \frac{1}{2} r_0^2 A$. For $V - V_0 \ll V$, we find

$$\ln \eta = \ln \eta_0 + \frac{c'}{(V - V_0)^2}.$$

TABLE I. Parameters for the fits of viscosity to both the free volume and aperiodic crystal theories. The IPB are the results of the isopropyl benzene of Jonas *et al.* (Ref. 24) at the indicated temperatures, TNB are the results for tri-napthyl benzene (Ref. 26) with fits to the low temperature (LT), high temperature (HT), and entire (full) temperature range, NPB is the result for n-propyl benzene (Ref. 25) and NBB is the result for n-butylbenzene (Ref. 25). The parameters are for both Doolittle (D) and aperiodic (HW) equations, with meanings of the parameters indicated in the text. ρ_L^* and ρ_H^* are calculated using σ_{HW} ($\rho^* = \rho\sigma^3$) and the lowest and highest densities studied experimentally.

| Compound | | $\ln \eta$ | | c | | $\sigma(\text{Å})$ | | r_0^2/σ^2 | ρ_L^* | ρ_H^* |
		D	HW	D	HW	D	W			
IPB	253 K	− 4.0	− 3.3	1.33	0.064	5.75	5.54	0.29	0.80	0.90
IPB	228 K	− 2.1	− 1.3	0.58	0.017	5.93	5.80	0.08	0.93	1.03
IPB	203 K	− 2.8	− 1.7	0.90	0.030	5.89	5.74	0.14	0.93	1.00
TNB	LT	− 41.0	− 28.7	4.58	0.088	9.04	8.92	0.40	1.06	1.09
TNB	HT	− 6.4	− 5.1	0.33	0.004 2	9.29	9.21	0.02	1.04	1.15
TNB	Full	− 12.6	− 8.4	1.14	0.015 5	9.18	9.09	0.07	1.00	1.15
NPB		− 10.5	− 7.3	0.547	0.005 6	6.20	6.16	0.03	1.13	1.15
NBB		− 10.8	− 7.4	0.599	0.006 38	6.45	6.40	0.03	1.13	1.14

This form is different from the traditional Doolittle equation, which stems from free volume theory. Nevertheless, it shows a divergence of the activation free energy as close packing is approached.

The actual calculation of βF^{int} involves averaging over a distribution of fiducial sites $\{\mathbf{R}\}$; we have used the $g(r)$ tabulated by Bennett[11] in his studies of the random close packing of spheres. This calculation combined with the known limiting form of $\alpha(\rho)$ allows the determination of z, which we find to be $z = 8$, in accordance with the number of nearest neighbors in Bennett's study. Thus, by fitting our form for $\ln \eta$ to experiment, we can determine both $\ln \eta_0$ and r_0^2 and compare with the simulation studies. In a series of papers, Stillinger and Weber[19] have looked at potential energy minima (as opposed to our course here) and has calculated r_0^2 for two systems (in their terminology $\langle |u_i|^2 \rangle N = 4r_0^2$): a system of pseudo-Lennard-Jones atoms, for which $r_0^2 = 0.095\sigma^2$, and for a Ni–P mixture, for which $0.01\sigma^2 < r_0^2 < 0.25\sigma^2$. We expect $\ln \eta_0$ to be a typical liquid value and, hence, estimate the range to be expected from Lennard-Jones simulation studies.[23] The values obtained are $-1.2 \lesssim \log(\eta_0\sigma^2\sqrt{mkT}) \lesssim -0.5$. Experimentally, there are usually two regions to be found in the viscosity data, one from $\eta \sim 0.01$ P to $\eta \sim 10^3$P and the other from $\eta \sim 10^3$ P to $\eta \sim 10^{13}$ P. We expect our theory to be physically most reasonable in the latter region (which we call the low temperature region). We have fit some of the available experimental data[24–26] with both the Doolittle equation and Eq. (1) and found that, within each region, both equations fit equally well. The fit parameters are tabulated in Table I.

Several points can be made by examining the data in Table I. First of all, the fitting parameters are not monotonic functions of density. However, we found it possible to degrade the fits somewhat and obtain monotonic behavior. This suggests that the experimental data have not been accumulated over a wide enough density range to adequately test the two theories. This is quite clear when we examine ρ_L^* and ρ_H^*, the density regime over which our fitted σ value suggests the experimental data were obtained. Further examination shows that only the tri-napthyl benzene has really been studied at a high enough density and over a large enough density

range to really test our theory. We have fit each region separately and the full data. The values of ρ_L^* and ρ_H^* obtained from the separate fits indicate that, once again, the fit is not over a large enough range (particularly for the low temperature region). Thus we expect good fits in the two regions, but simply because we have three fitting parameters at our disposal. Thus, at the moment we feel the best test of the two theories is the fit to the full data, shown in Fig. 2. We notice that, while the fit is not as good, the values of r_0^2 are indeed reasonable. In addition, the value for the reduced viscosity $\log(\eta_0\sigma^2/\sqrt{mkT})$ is − 0.58 reasonably close to the range expected (by contrast, the values for the low and high temperature fits are − 9.3 and + 0.90, respectively, both outside the expected range). While the free volume fit is as good as our theory, the value of η_0 is about 100 times smaller than we should expect.

As previously mentioned, the α values correspond to vibrations of the atoms about their fiducial site ($\alpha = 3/2\langle r^2 \rangle$). If our theory is correct, then we have a definite prediction of how the viscosity should vary with the mean square displacement,

$$\ln \eta = \ln \eta_0 + \frac{3}{4} r_0^2/\langle r^2 \rangle. \tag{2}$$

The mean square displacement can be measured in Mössbauer scattering experiments and, hence, we should be able to predict the variation in viscosity with density. Unfortunately, there exist very few overlaps between studies of viscosity in the glass region and Mössbauer studies. We have found, however, some data due to Champeney and Sedgwick[28] on n-propyl benzene and n-butyl benzene that have corresponding viscosity data. The recoilless fraction determined in a Mössbauer experiment is given by

$$\ln f = \ln \gamma - Q^2 \langle r^2 \rangle/3, \tag{3}$$

where $\ln \gamma$ is determined by extrapolation to low temperature and Q is the wavelength of the radiation. Combining Eqs. (2) and (3), we find

$$\ln \eta = \ln \eta_0 - \frac{Q^2 r_0^2}{4 \ln(f/\gamma)}.$$

Thus, by fitting $\ln \eta$ vs $1/\ln(f/\gamma)$, we can see if this form is correct. This will also allow us an independent determina-
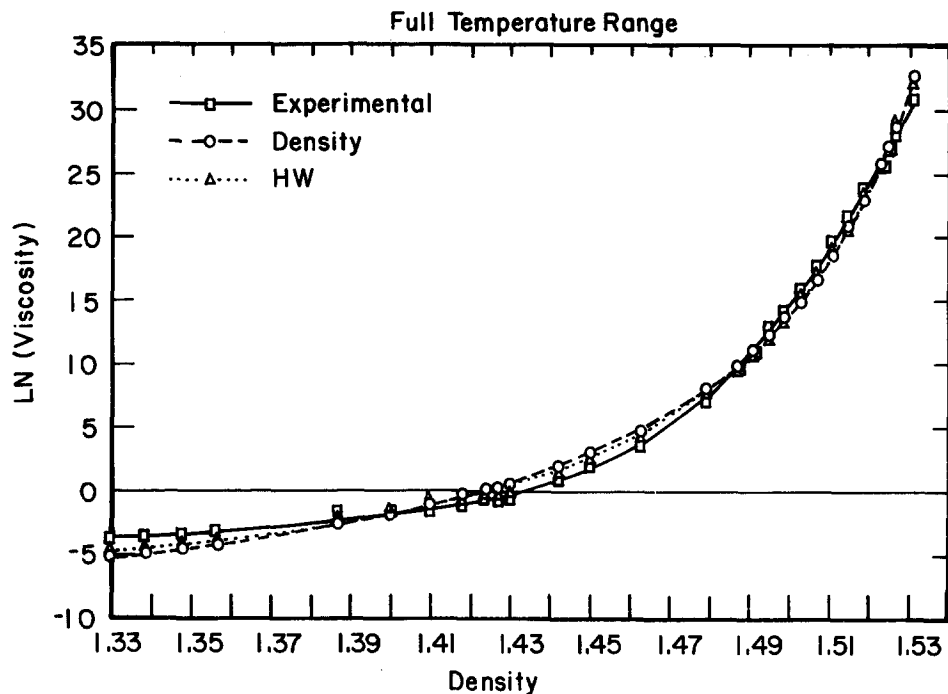
Full Temperature Range

FIG. 2. A fit of the density dependence of the viscosity of trinaphthylbenzene. Experimental results are indicated with squares. The free volume theory by circles and a dashed line and the current theory by triangles and dotted lines.

tion of r_0^2, which we can compare to the results in Table I. We have estimated the values of $\ln(f/\gamma)$ from the published graphs (see Fig. 3) and have determined $r_0^2 = 0.02\sigma^2$ for η-propyl benzene and $r_0^2 = 0.01\sigma^2$ for n-butyl benzene, in fair agreement with our other estimate. As can be seen from Table I, the regions on density spanned by most of the experimental studies is rather small, so it is (perhaps) not surpris-
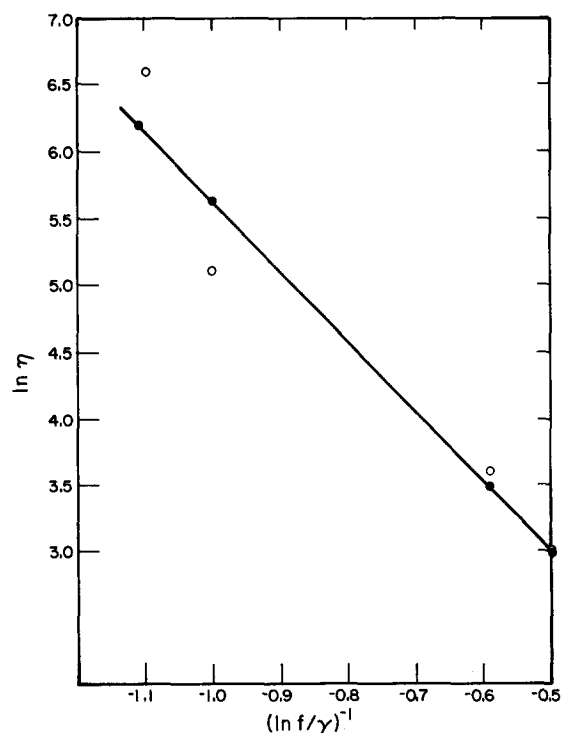

FIG. 3. Logarithmic plot of viscosity vs Mössbauer parameter $\ln(f/\gamma)^{-1}$ for n-propylbenzene.

ing that both our form and the Doolittle equation match experiment.

We have shown how to determine the free energy barriers in amorphous systems, using the stationary points of the free energy functional. Interestingly, the properties are dependent on overlap functions of the positions of nearby minima, similar to the order parameters in the replica symmetry breaking theories of spin glasses.[28] In a simple approximation, the theory replaces each minimum by a parabola and the transition state is determined by the crossing point, in a manner similar to theories of electron transfer reactions. The distance of least motion is analogous to the principle of minimum chemical distance (PMCD) common in organic chemistry.[29] In particular, our distance corresponds to the geometrical changes considered in the PMCD. The distribution of distances between minima leads to a distribution of free energy barriers and, hence, the nonexponential behavior seen in glasses. We have applied our theory to a series of experiments and fit the data as well as the previous free volume theory. While we have used the high density form in determining the density dependence of α, fits using the actual α values obtained using the Bennett $g(r)$ were not qualitatively different. At the same time, we have a microscopic justification for the density dependence, as opposed to the somewhat controversial mechanism involved in the free volume theory. The free volume theory assumes that when enough free volume accumulates, a particle can jump. It is also assumed that it requires no energy to redistribute the free volume. Our theory, on the other hand, depends on the underlying lattice to form the free energy surface on which particles diffuse. Thus, it is a much more reasonable mechanism than the seemingly empirical free volume theory. We have also shown that the parameters determined from fitting our functional to the data are not unreasonable numbers, particularly by comparing to Mössbauer data. It would be

very useful to have more experiments that probe the viscosity as a function of density in connection with Mössbauer experiments to rigorously test both theories. We have also assumed that there is only one free energy barrier at a given density, which we know to be incorrect. We should, therefore, average over a distribution of free energy barriers (corresponding to a distribution of r_0^2), which could very well lead to a fractal power of $V-V_0$ determining $\ln \eta$. We are in the process of determining these distributions.[30]

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