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Dispersion of relaxation rates in dense liquids and glasses

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The structural relaxation rates, which are crucial in understanding the liquid ⟷ glass transition, are investigated within the free-volume theory. We discuss the origin of the observed dispersion of relaxation times and show that it is simply related to the dispersion of the total surface-to-volume ratio of the liquid clusters.

It is now well known that the observed changes in the heat capacity and molecular volume at the liquid ⟷ glass transition is the result of the system falling out of complete metastable thermodynamic equilibrium. This occurs when the time of the measurement becomes comparable to the structural relaxation times near the glass transition temperature T_g and the system cannot reach equilibrium during the cooling or heating process.

The changes in volume $\bar{v}$ and enthalpy H consequent to a stepwise or continuous change in temperature has been investigated by a number of workers[1–7] and has been extensively reviewed.[4,5,8] The salient features of all these theories are very similar. They all stress the importance of including a distribution of relaxation times and keeping track of the thermal history of the sample. However, all of these have been largely phenomenological in nature and make no microscopic specification of the structural relaxation modes which are important. Here we discuss how these strongly temperature-dependent structural relaxation rates near T_g can be described within the free-volume model.[9–11] The analysis differs significantly from the previous work because we have at our disposal an equilibrium theory[9] of the liquid ⟷ glass transition from which to begin our discussion. By starting from a concrete model of a glass, we can identify the dominant structural modes and establish their relaxation mechanism.

The three key quantities in our equilibrium free-volume theory[9–11] are $P(v)$, p, and $C_{\nu z}(p)$. $P(v)$ is the probability that a cell has a volume v, p is the fraction of liquidlike cells, and $C_{\nu z}(p)$ is the cluster distribution function. The reader is referred to Refs. 9 and 11 for a complete review of our equilibrium theory. Consider now the effect of a stepwise or continuous change in the temperature. Equilibrium with regard to $P(v)$ can be established for a given value of p simply by phononlike density fluctuations, which are very fast. The quantity $C_{\nu z}(p)$ depends entirely on p and presumably relaxes with it. However, p can change only if there is an exchange of volume between liquidlike and solidlike cells, which is not a free exchange.[9,10] To change p requires the diffusion of a molecule across the interface between a liquid cluster and its solid surroundings. Accordingly, if we make a single relaxation-time approximation for p, the temperature dependence of the relaxation time should be the same as the viscosity η and therefore be given by[10]

$$\tau = \tau_0 e^{v_m/\bar{v}_f} , \tag{1}$$

where v_m is a molecular volume and $\bar{v}_f$ is the average free volume. The value of the preexponential τ_0 will be determined below. The properties of the system depend on p, as in the equilibrium theory, since the system remains in secular equilibrium with respect to p. However, when τ is large compared to the measurement time, p itself may no longer have its metastable equilibrium value p_{eq}. In fact, for $T \lesssim T_g$, p can no longer follow its equilibrium value but freezes out at a value $p_{\text{froz}} \neq 0$, which depends on the cooling rate q. In a previous paper,[10] we have calculated the effect p falling out of equilibrium has on the heat capacity. We find that T_g depends linearly on $\log_{10} q\tau_0$ with a slope in excellent agreement with experimental observations. These results lead us to conclude that all the important relaxation times are proportional to the viscosity η and that the temperature dependence of the free energy and entropy are smooth through the region of T_g.

We found that preexponential τ_0 (the only additional free parameter beyond those of our equilibrium theory) was about 10^{-10} sec from our studies of the time-dependent heat capacity. To test the simple diffusion picture for τ outlined above, it is important to calculate τ_0 directly. This can be done by considering the time rate of change of p, which can be written as

$$\frac{dp}{dt} = -\frac{1}{\tau}(p - p_{\text{eq}}) \ . \tag{2}$$

The two terms in Eq. (2) can be thought of as (i) the forward or the liquid-to-solid transition and (ii) reverse or solid-to-liquid transition. The first term corresponds to the generation of solid regions from liquid ones and depends on the state of the liquid through p. The second term, however, corresponds to the generation of free volume from the solid which is governed only by the equilibrium value of p. To find τ, consider the forward process in more detail,

$$\frac{dp}{dt} = \frac{1}{N}\frac{dN_l}{dt} \ , \tag{3}$$

where N_l is the number of molecules in liquid clusters of the N molecules. The change in N_l depends on the surface area of the liquid cluster approximately as

$$\frac{dN_l}{dt} = -\frac{1}{2}\frac{S}{A}\nu_J \ , \tag{4}$$

where S is the surface area of the liquid cluster, A is the surface area per cell, and ν_J is the jump frequency. From our previous calculation[9] of the diffusion rate, we have that

$$\nu_J = \frac{\bar{v}}{3a} e^{-v_m/\bar{v}_f} \ , \tag{5}$$

where $\bar{v}$ is the average velocity and a is the cell diameter. Substituting Eqs. (4) and (5) into Eq. (3), gives, for the forward process,

$$\frac{dp}{dt} = -\frac{p}{16}\frac{S}{V}\left(\frac{3kT}{M}\right)^{1/2} e^{-v_m/\bar{v}_f} \ , \tag{6}$$

where (S/V) is the total surface-to-volume ratio of the liquid clusters plus the percolation channel. To obtain this result, we have used $NAa = \frac{8}{3} V_{\text{tot}}$ and $pV_{\text{tot}} = V_{\text{liq}}$. Therefore, we find that the preexponential τ_0 is given by

$$\tau_0^{-1} = \frac{1}{16}\frac{S}{V}\left(\frac{3kT}{M}\right)^{1/2} \ . \tag{7}$$

We can approximate τ_0 near the percolation threshold where the minimum-sized liquid cluster contains $v_m/\bar{v}_f$ molecules and S/V is well approximated by $5(v_m^2/\bar{v}_f)^{-1/3}$. For $T = 300$ K, $M = 60$, and $v_m/\bar{v}_f \simeq 30$, we find $\tau_0 \approx 10^{-10}$ sec, in excellent agreement with the value found in our studies of the heat capacity.[10]

The results discussed so far have been based on a single relaxation-time approximation. However, it should not be surprising that a dispersion of relaxation times is crucial in understanding all of the experimental results. Indeed, there has been substantial evidence presented in the literature which suggests a relaxation function of the form[3,4,8]

$$R(t) = e^{-(t/\tau)^z} \ , \tag{8}$$

instead of a simple exponential. In the present theory, such a dispersion of relaxation times would be due to a dispersion of the S/V values for finite clusters and for the infinite cluster broken into finite clusters at the weak links. One can write for $R(t)$,

$$R(t) = \int P(W) e^{-Wt} dW \ , \tag{9}$$

where W is a relaxation time and $P(W)$ its probability distribution. Percolation theory strongly[12–15] suggests a power-law dependence of S/V on cluster size for finite clusters,

$$S/V = \sigma\nu^{-x} \ , \tag{10}$$

where σ is a constant. We propose that a similar dependence on fragment size, also designated by ν, holds for disjoint pieces of the infinite cluster broken at the weak links. Then Eq. (7) yields

$$W = W_0\nu^{-x} \ , \tag{11}$$

where

$$W_0 = \frac{1}{16}\sigma\left(\frac{3kT}{M}\right)^{1/2} e^{-v_m/\bar{v}_f} \ . \tag{12}$$

Equation (9) becomes

$$R(t) = \int P(\nu) e^{-W_0 t\nu^{-x}} d\nu \ , \tag{13}$$

after change of variables of integration. Here $P(\nu)$ is the probability distribution for ν for fragments of the infinite cluster and for finite clusters. We assume that $P(\nu)$ has the same form as that given by percolation theory[15–18] for finite clusters alone

$$P(\nu) = Ae^{-c\nu^y} \ , \tag{14}$$

where c is a constant and A a slowly varying function of ν. We now substitute Eq. (14) into Eq. (13) and evaluate the result for asymptotically long times

$$R(t) = Be^{-c'(W_0 t)^z} \ , \tag{15}$$

$$z = y/(x + y) \ , \tag{16}$$

where B is a slowly varying function of t and c' a constant. The forms of Eqs. (8) and (15) are identical apart from normalization with $\tau^{-1} = c'^{1/z} W_0$.

For compact clusters $x = \frac{1}{3}$, which is also its maximum value. For stringy or ramified clusters x is smaller. Therefore, the full range of x over all possible cluster shapes is

$$0 < x \leq \tfrac{1}{3} \ . \tag{17}$$

Percolation theory also yields stringent limits on y,

$$\tfrac{2}{3} < y \leq 1 \quad . \tag{18}$$

In the asymptotic limit of very large clusters, Kunz and Souillard[17] have shown that

$$y = \begin{cases} 1, & p < p_c \\ \tfrac{2}{3}, & p > p_c, \end{cases} \tag{19}$$

in three dimensions. Here p_c is the percolation threshold. However, in two dimensions for $p < p_c$, Leath and Reich[18] have shown that $y = 2\phi \approx 0.80$ for clusters of size $\nu \lesssim 85$ but crosses over to $y = 1$ for larger values of ν. Since 2ϕ increases with dimensionality and is unity for dimensions of 6 or greater[18] we expect a reasonable estimate of y might be 0.90. We thus find the limits of z to be

$$\tfrac{2}{3} < z < 1 \quad , \tag{20}$$

with the value more likely to be in the range 0.70–0.85. This is in excellent agreement with the values obtained from experiments on the isothermal relaxation to a single-temperature step as well as relaxation during continuous heating and cooling. Moynihan *et al.*[4] found that for B_2O_3 $z = 0.83$, for As_2Se_3 $z = 0.67$, and for 5-phenyl-4-ether $z = 0.70$. The one known material which gives a value of z far outside of our predicted range ($z \approx 0.50$) is a polymer material,[19] for which we do not expect the free-volume theory to be appropriate. It is important to note that the exponent x is not a critical exponent and is therefore not universal, thus explaining the observed variability in z.

In addition to the response of the system to a stepwise or continuous change in temperature, stress relaxation and dielectric relaxation have also been studied in many glass formers.[8] From these measurements, the value of z is often found to be lower than observed in relaxation after a temperature step. For dielectric relaxation in ionic glasses, the proper mechanism for the response is conduction across the liquid cluster, for which

$$\tau \simeq L^2/4D \quad . \tag{21}$$

Here L is the cluster dimension in the direction of the field and will scale as $L \simeq a\nu^x$ and D is the diffusion constant. Consequently, we have that

$$z = \frac{y}{2x + y} \quad . \tag{22}$$

Using our results for x and y from Eqs. (17) and (18), we find

$$\tfrac{1}{2} < z < 1 \tag{23}$$

for relaxation across the liquid cluster. The value of z is most likely to be in the range 0.50–0.60 for compact clusters, $x \simeq \frac{1}{3}$. Typical values for z observed[8] from dielectric relaxation experiments are 0.74 for $3KNO_3 \cdot 2Ca(NO_3)_2$, 0.56 for polyvinyl acetate, 0.55 for anthrone, and 0.47 for $HZnCl_3 \cdot 4H_2O$, which agrees well with our estimates. Thus the value of z depends on the specific relaxation process involved; one must make a separate calculation of z for each one.

The relaxation function $R(t)$ given by Eq. (8) is the correct form in the asymptotic, long-time limit, when the dispersion of S/V values dominate. However, at very short times, $R(t)$ should be a simple exponential, i.e., $z = 1$, with the average value of S/V determining the average value of the relaxation rate as in Eq. (7) of our L^{-2} as in Eq. (21). This can be seen most easily from a semi-invariant expansion of the exponent in the relaxation function. Only at longer times does the dispersion in S/V or L^{-2} begin to play a role.

In summary, we have demonstrated that the free-volume model[9–11] correctly predicts the size of the preexponential factor τ_0 and the asymptotic form for the relaxation function $R(t)$. These two predictions should be taken as strong evidence in favor of our picture of dense liquids and glasses. One of the important predictions of this model is that the system breaks up into solidlike and liquidlike regions. From only this simple assumption and known results of percolation theory, we can explain the observed form for the relaxation function $R(t)$. In a previous paper,[10] we correctly predicted the dependence of the heat capacity on heating and cooling rates. However, this cannot be taken as strong evidence for the free-volume model. It only showed that the relaxation time τ, Eq. (1), should have the same form as the viscosity and should be smooth in the region of T_g. The prediction of the correct order of magnitude for τ_0, however, is significant, since it gives strong justification for the picture of diffusion between liquid and solidlike cells.

We should emphasize that the above results do not depend on the literal applicability of the free-volume model. They require only that there be a local configuration coordinate analogous to the cell volume with respect to which the free energy is nearly flat in certain localized regions of the corresponding configuration space.[11]

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