Nondispersive relaxation in supercooled liquids and glasses

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We show that dispersive relaxation in supercooled liquids and glasses described in our earlier paper is not always inevitable. Here we discuss two circumstances where the relaxation is purely exponential.

We have recently developed a theory of relaxation processes in supercooled liquids and glasses[1,2] based on the free-volume model.[3-5] Our results are in good qualitative and quantitative agreement with experiment for both the relaxation of thermodynamic properties and for dissipative processes such as dielectric relaxation via ionic motion. We can account for the temperature dependences,[1] the magnitudes,[2] and the dispersion[2] of the observed relaxation times.[6,7]

The essence of the argument[2] is that there are two classes of configurations of the environment of each microscopic unit of the material: liquidlike and solidlike. These liquidlike cells cluster and diffusive motion is possible within large enough clusters of liquidlike cells. In thermodynamic relaxation the controlling variable is the fraction of liquidlike cells, which relaxes by diffusion at the cluster surface. The relaxation rate associated with a finite cluster or a piece of the infinite cluster is proportional to its surface to volume ratio. If $W(\nu)$ is the relaxation rate for clusters of size ν, the relaxation function $R(t)$ is given by

$$R(t) = \int P(\nu) e^{-W(\nu)t} d\nu ,$$
(1)

where $P(\nu)$ is the cluster size distribution function. For small times, we have shown that[2]

$$R(t) \sim e^{-\langle W \rangle t} ,$$
(2)

and for large times that

$$R(t) \sim e^{(t/\tau)^z} .$$
(3)

In (3),

$$z = \frac{y}{x+y} .$$
(4)

Here y is the power of ν in the argument of the exponential[2] in $P(\nu) \sim \exp(-c\nu^y)$, where c is a constant and x is the power of ν in cluster surface to volume ratio, $0 < x < \frac{1}{3}$. For dielectric relaxation by ionic motion, the polarization relaxation time is the time to diffuse across a liquid cluster, $L^2/4D \propto \nu^{-2x}$. Equations formally identical to (2) and (3) hold for $R(t)$ in this case also, but with different average re-

laxation rate $\langle W \rangle$ and characteristic time τ and with z replaced by

$$z' = \frac{y}{2x+y} .$$
(5)

Shear stress relaxation similarly requires diffusive motion to the interfaces so that its long-time behavior is given by (3) and (5).

In this Brief Report we point out that the dispersive relaxation described by (3) and (4) or (5) at long times is not inevitable. There are two specific sets of circumstances in which the relaxation function either is, or appears to be, purely exponential. We discuss the latter case first. Rewrite (1) as a cumulant expansion,

$$\ln R(t) = \sum_{n=1}^{\infty} C_n(W) t^n/n! ,$$
(6)

$$C_1 = \langle W \rangle .$$
(7)

$$C_2 = \langle W^2 \rangle - \langle W \rangle^2 , \text{etc.}$$
(8)

Exponential behavior ceases when the quadratic term in t in (6) becomes comparable to the linear term. Denoting that time as t_c, we see that relaxation will appear purely exponential if

$$\langle W \rangle t_c \gg 1 .$$
(9)

where $t_c \simeq 2C_1/C_2$. Thus the condition for apparent exponential behavior is

$$\tfrac{1}{2}(\langle W^2 \rangle / \langle W \rangle^2 - 1) \ll 1 .$$
(10)

Equation (10) can be examined only if $P(\nu)$ is explicitly known. We therefore augment the exponential form previously used for $P(\nu)$ to establish the asymptotic behavior (3) and take

$$P(\nu) = B y e^{-B\nu^y} \nu^{y-1} .$$
(11)

This choice of preexponential has no effect on the asymptotic behavior, but greatly facilitates the analysis. We obtain that

$$\frac{\langle W^2 \rangle}{\langle W \rangle^2} - 1 = \frac{\pi^2}{6} \left[\frac{1}{z} - 1 \right]^2$$
(12)

when z approaches its upper limit of unity. Inserting (12) into (10) gives us

$$\frac{\pi^2}{12}\left[\frac{1}{z}-1\right]^2 \ll 1 \qquad (13)$$

as the condition for the relaxation to appear exponential. The largest values of z observed are typically around 0.8.[6,7] Equation (13) predicts that relaxation would then be exponential over 100 factors of e. More generally, as z approaches its upper limit unity, it takes longer and longer for the asymptotic, nonexponential behavior to manifest itself. The smaller the dispersion of relaxation rates, the longer it takes to appear. Small dispersion corresponds to small x, that is to ramified clusters which result in turn from low cluster interfacial energy. Small x means that the cluster is practically all surface so that the surface-to-volume ratio and the distance to the surface are very weakly dependent on the cluster size.

The other case, in which the relaxation function is strictly exponential, occurs when the relaxation process is local, taking place entirely within a liquidlike cluster. In the free-volume model, such a process requires only that there be enough free volume present in the cluster that the required local configuration for relaxation can be achieved by free-volume fluctuations. If the saddle configuration corresponds to an expansion volume of v_s, only clusters of size larger than $v_s = v_s/\bar{v}_f$, where $\bar{v}_f$ is the average free volume, admit the relaxation process. The relaxation rate then has the form

$$W = W_0 \exp(-v_s/\bar{v}_f) \ . \qquad (14)$$

A beautiful example of such a local relaxation process has recently been studied by Zeller.[8] In pure cyanobiphenyl CB5 and in solutions of the trinuclear compounds CT5 and CP4 in CB5, Zeller has found a single dielectric relaxation time in the nematic phase. Samples were supercooled below the melting point and studied below the glass transition temperature as well. In the supercooled liquid and the glass there is nearly complete orientational ordering but translational disorder. The dielectric relaxation studies were carried out in electric fields parallel to the directrix. Thus the elementary step in the dielectric relaxation was reorientation of the molecules by $180°$ along the directrix. Zeller gives cogent arguments that the reorientation is made possible by free-volume fluctuations. Such reorientation clearly corresponds to the local mechanism described above; it can take place anywhere within a cluster of size v_s or larger. The relaxation function is exponential, and its temperature dependence is given by (14). We have already shown[3-5] that $\bar{v}_f \propto T - T_0$ at sufficiently high temperatures so that W would obey the Vogel-Fulcher law as found explicitly by Zeller.[8] However, he finds that the Volgel-Fulcher law continues to hold through and below T_g, the glass transition temperature, whereas in most glasses the Vogel-Fulcher law greatly overestimates the viscosity or relaxation rates at T_g. Using the free-volume model, we have shown that $\bar{v}_f$ makes a transition from proportionality to $T - T_0$ to proportionality to T in a temperature range which has nothing to do intrinsically with T_g, the latter being set by kinetic considerations alone.

Zeller concludes that the absence of observed dispersion is the relaxation rates is evidence against the existence of percolation effects in the supercooled nematics and the nematic glasses. We propose instead that dielectric relaxation by orientation flipping is insensitive to the size and shape of clusters and that the existence of clusters has in fact not been tested in the nematics. We suggest that enthalpy relaxation in response to small temperature steps be studied with a view to establishing the presence or absence of dispersion such as implied by (3).

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[1] G. S. Grest and M. H. Cohen, Phys. Rev. B **21**, 4113 (1980).

[2] M. H. Cohen and G. S. Grest, Phys. Rev. B **24**, 4901 (1981).

[3] M. H. Cohen and D. Turnbull, J. Chem. Phys. **31**, 1164 (1959).

[4] M. H. Cohen and G. S. Grest, Phys. Rev. B **20**, 1077 (1979).

[5] G. S. Grest and M. H. Cohen, in *Advance in Chemical Physics,* edited by I. Prigogine and S. A. Rice (Wiley, New York, 1981), Vol. 48, p. 455.

[6] C. T. Moynihan *et al.,* Ann. N. Y. Acad. Sci. **279**, 15 (1976); C. T. Moynihan and A. V. Lesikan, *ibid.* **371**, 151 (1981).

[7] J. Wong and C. A. Angell, *Glass: Structure by Spectroscopy* (Dekker, New York, 1976).

[8] H. R. Zeller, Phys. Rev. Lett. **48**, 334 (1982).