

The anomalous Debye–Waller factor and the fragility of glasses

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The correlation between the magnitude of the Debye–Waller anomaly and the temperature dependence of the relaxation time and viscosity of glass-forming liquids (i.e., their fragility) is investigated using the coupling model of relaxation. The correlation is shown to be a natural consequence of the relationship between the noncooperative and intermolecularly cooperative relaxation times of the model. Specifically, the deviation of the mean squared displacement from a linear temperature dependency increases as the fragility (in the Angell sense) of the glass-forming liquid increases because more fragile glasses exhibit substantially more short-time, noncooperative relaxation. This latter fact arises from their shorter noncooperative relaxation times, as deduced from the coupling model. © 1996 American Institute of Physics. [S0021-9606(96)50108-8]

INTRODUCTION

A comprehensive interpretation of the myriad properties associated with glass-forming liquids remains an unattained goal. The diffusion of supercooled small molecules, proteins, and polymers is frequently observed.¹ A notable feature of this diffusion is the departure of the mean square displacement, $\langle r^2 \rangle$, from a linear dependence on temperature. The onset of supralinearity, referred to as the anomalous Debye–Waller factor, has been viewed as the onset of inelastic effects^{2–4} or anharmonic vibrational motion,^{1,5,6} or the result of “soft phonons.”⁷ On the other hand, we have recently demonstrated^{8–10} that anomalous Debye–Waller factors can be associated with the appearance of relaxation processes, with the vibrations remaining strictly harmonic. Experimentally this is found to occur at temperatures for which relaxation becomes significant over the experimental time scale; this, of course, is in the vicinity of the glass transition temperature.

It has been pointed out by Angell^{5,6} that the fragility of the liquid (i.e., the degree to which the normalized temperature dependence of viscosity or relaxation time, τ , departs from Arrhenius behavior) correlates with the temperature associated with observation of an anomalous Debye–Waller factor; “stronger” liquids exhibit the supralinearity in $\langle r^2 \rangle$ at higher temperatures than found for fragile liquids.^{5,6} It is also apparent^{5,6} that more fragile liquids exhibit steeper rises in $\langle r^2 \rangle$ at high temperature. Fragility, and the associated connection to the shape of the relaxation function, can be directly accounted for by the coupling model of relaxation.^{11–14} We have previously demonstrated that the short time ($\sim 10^{-12}$ s) relaxation of amorphous glasses can be well-described by the coupling model.^{8–10} It is of interest to consider the properties of $\langle r^2 \rangle$, with the intent to examine any correlation between the temperature dependencies of τ and $\langle r^2 \rangle$.

ANALYSIS

We are interested in the diffusion of particles in the glassy state. Provided the Gaussian approximation holds, the mean squared displacement, $\langle r^2 \rangle$, is related to the density–density self-correlation function, $C(t)$, as¹⁵

$$\langle r^2 \rangle = -\frac{6}{Q^2} \ln C(t), \quad (1)$$

where Q is the wave vector (Q th mode of the density fluctuations). Note that the essential conclusions of the present work will be valid even when the Gaussian approximation breaks down. In general, density fluctuations arise from translational, rotational, and vibrational degrees of freedom. If the former (the relaxation part) and the vibrations are independent, the correlation function can be expressed as a product

$$C(t) = C_{\text{pho}}(t) \times C_{\text{rel}}(t) \quad (2)$$

with the phonon contribution $C_{\text{pho}}(t; Q, T)$ given by¹⁵

$$C_{\text{pho}}(t; Q, T) = \exp[-Q^2 W(t, T)]. \quad (3)$$

Although Eq. (2) is assumed for convenience, again the results presented herein should remain qualitatively the same regardless. For harmonic phonons

$$W(t, T) = K \int g(\omega) [1 - \cos(\omega t)] \omega^{-1} \times \left[\frac{2}{\exp(\hbar \omega / kT) + 1} \right] d\omega, \quad (4)$$

where K is a temperature-independent constant. The vibrational density of states, $g(\omega)$, can be represented by¹⁰

$$g_D(\omega) = \omega^2 \exp\left(-\frac{\omega}{\omega_D}\right), \quad (5)$$

where ω_D is the Debye frequency. The exact vibrational density of states could be used in place of the assumed $g_D(\omega)$ in Eq. (4). We are also neglecting the boson peak herein. Using Eqs. (3)–(5), $C(t)_{\text{pho}}$ can be obtained by fitting low temperature experimental data, for which $C_{\text{rel}}(t)$ remains equal to unity over the time range of interest.

At higher temperatures relaxation contributes to the decay of the correlation function, with the coupling model of relaxation used to describe this contribution. Discussed in detail elsewhere,^{16,17} the important feature of the model is the assumption that in densely packed, interacting systems

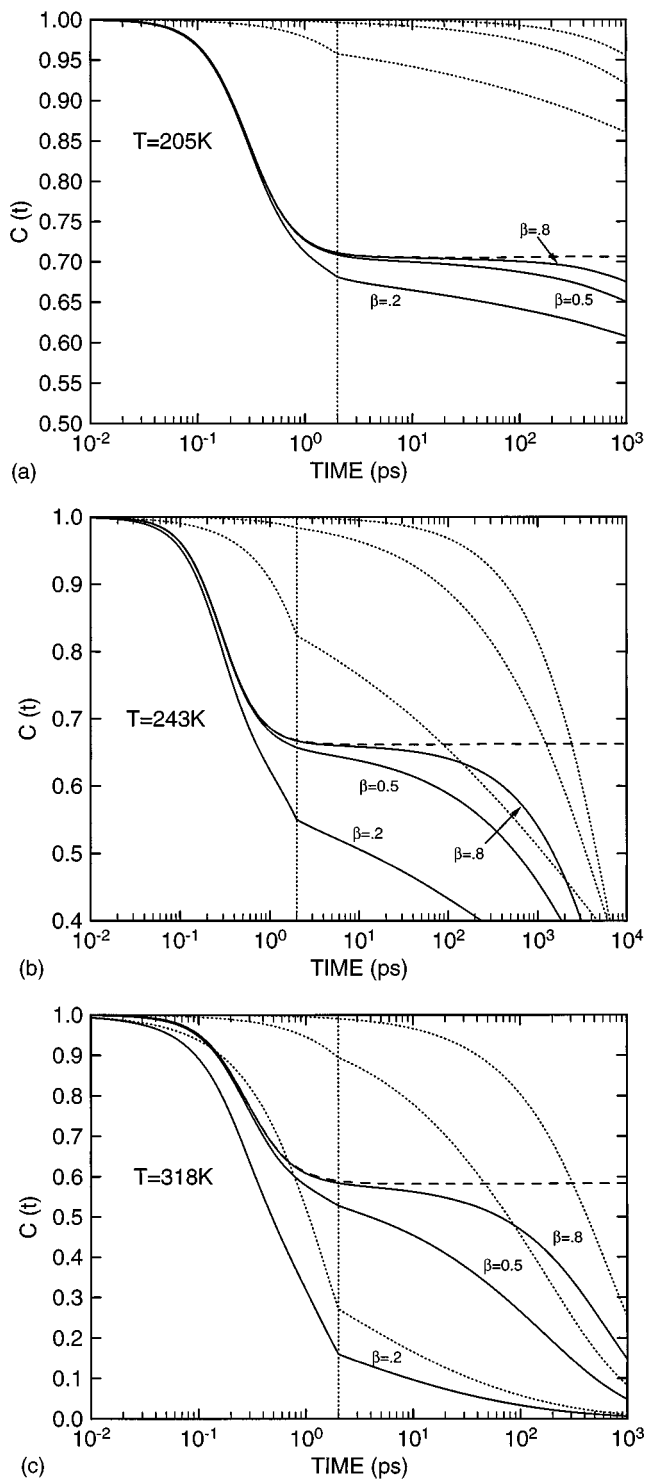


FIG. 1. Density–density self-correlation function (solid lines) for $Q = 1.94 \text{ \AA}^{-1}$ calculated using the indicated values of the stretch exponent for temperatures (a) below, (b) at, and (c) above the glass transition temperature. The relaxation time was determined using a (constant) value of the activation energy necessary to yield $\tau^* = 7.3 \times 10^{-9} \text{ s}$ at $T = 243 \text{ K}$ for all β . The phonon, $C_{\text{pho}}(t)$, and relaxation, $C_{\text{rel}}(t)$, components [Eq. (2)] are represented by the respective dotted and dashed lines. The crossover time of the coupling model, $t_c = 2.0 \times 10^{-12} \text{ s}$, is indicated by the vertical dotted line. Note that, as a consequence of Eqs. (6) and (8) the broader relaxation function ($\beta=0.2$) decays much faster at short times ($t < t_c$), particularly at higher temperatures.

there exists a temperature independent crossover time, t_c , separating two regimes. At short times, $t < t_c$, the correlation function has the Debye form

$$C(t) = \exp\left(-\frac{t}{\tau_0}\right) \quad (6)$$

and often an Arrhenius temperature dependence, whereas for $t > t_c$,

$$C(t) = \exp\left(-\left(\frac{t}{\tau^*}\right)^\beta\right) \quad (7)$$

and the temperature dependence of the relaxation time can be non-Arrhenius. The stretch exponent, β , is related to the coupling parameter $n = (1 - \beta)$, whose magnitude ($0 \leq n < 1$) reflects the degree of intermolecular cooperativity of the relaxation.

In reality the crossover from Debye behavior [Eq. (6)] to the stretched exponential form of Eq. (7) occurs over some range of times in the vicinity of t_c . Continuity of Eqs. (6) and (7) at $t = t_c$ gives the important relation

$$\tau^* = (t_c^{\beta-1} \tau_0)^{1/\beta}. \quad (8)$$

An Arrhenius temperature dependence of the noncooperative relaxation time

$$\tau_0 = A Q^{-2} \exp\left(\frac{E_a}{RT}\right), \quad (9)$$

where E_a is the activation energy and the prefactor A is temperature independent, together with Eq. (8) yields for the intermolecularly coupled relaxation time

$$\tau^* = (A Q^{-2} t_c^{\beta-1})^{1/\beta} \exp\left(\frac{E_a}{\beta RT}\right). \quad (10)$$

$C_{\text{pho}}(t)$ is thus determined from low temperature, short time data, while at higher temperatures Eqs. (6)–(8) are used

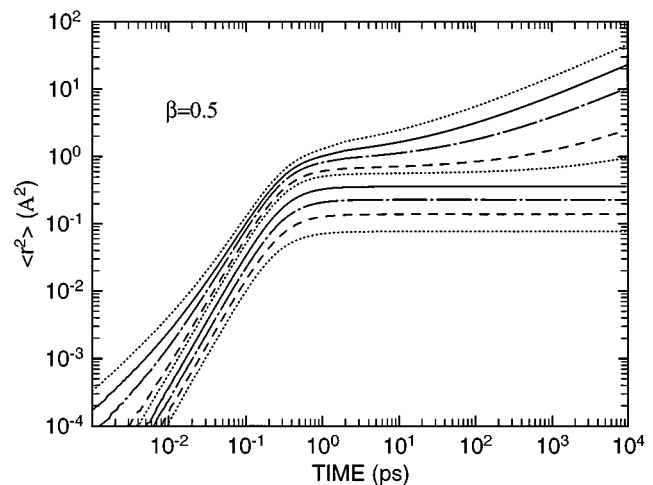


FIG. 2. Representative calculations of the mean square displacement for $\beta=0.5$ using $\omega_D = 3.2 \times 10^{12} \text{ rad/s}$, $K = 1.8 \times 10^{-27} \text{ s}^2$, $t_c = 2 \times 10^{-12} \text{ s}$, and $E_a = 3.9 \text{ kcal/mol}$. The curves correspond to $T = 25, 50, 84, 133, 205, 243, 305, 350,$ and 400 K (bottom to top). At longer times there is no diffusion at low temperature.

to describe the relaxation part of Eq. (2). This approach has previously been shown to describe molecular dynamics simulations and quasielastic neutron scattering results on several glass forming liquids and polymers.^{8–10,18,19}

Herein we use as our starting point earlier results used to fit molecular dynamics simulation data on *ortho*-terphenyl.¹⁰ It was shown therein that taking $t_c = 2 \times 10^{-12}$ s, $\omega_D = 3.2 \times 10^{12}$ rad/s, and $K = 1.8 \times 10^{-27}$ s², molecular dynamics simulation results on the high frequency relaxation of OTP at a fixed $Q = 1.94 \text{ \AA}^{-1}$ could be faithfully reproduced with $\beta=0.5$, $E_a = 3.9$ kcal/mol, and $A = 9.8 \times 10^{-15} \text{ s \AA}^{-2}$.¹⁰ Since our interest herein is investigating the manner in which fragility influences diffusion, we calculate the mean squared displacement [Eq. (1)] for various β . It is well-established, and follows directly from Eq. (10), that a smaller stretch exponent, signifying more intermolecular cooperativity,^{14,20,21} results in a stronger temperature dependence of the relaxation times^{11–14,22–25} (greater “fragility”). To execute a valid comparison of the effect of β on diffusion, we use a constant value of the cooperative relaxation time, $\tau^* = 7.3 \times 10^{-9}$ s, at the calorimetric glass transition temperature of OTP, for which $T_g = 243$ K. This value of τ^* then determines the value of τ_0 for any given β [Eq. (8)]. Note that this relaxation time for $\tau^*(243 \text{ K})$ is rather small in comparison to macroscopic values, which typically are on the order of 100 s, because of the small length scale ($Q^{-1} < 1 \text{ \AA}$) considered herein, and also accessed in the molecular dynamics simulation.¹⁰

We calculate $C(t)$ and $\langle r^2 \rangle$ by two procedures. (i) The activation energy for the noncooperative relaxation, E_a , is kept constant (=3.9 kcal/mol), with the prefactor A in Eq. (9) adjusted to give the same value for the cooperative relaxation time, $\tau^* = 7.3 \times 10^{-9}$ s, as determined for OTP at 243 K. Alternatively, (ii) the activation energy is adjusted to yield this value of $\tau^*(243 \text{ K})$, using the same prefactor ($A = 9.8 \times 10^{-15} \text{ s \AA}^{-2}$) as for OTP, independent of β . The results obtained using these two procedures are given in the next section.

RESULTS

In Fig. 1 we show representative results for the correlation function at three temperatures, as calculated using various values of the stretch exponent in Eq. (7). The phonon contribution is the same for all β , with the value of the prefactor A in Eq. (10) adjusted to give a fixed $\tau^*(243 \text{ K}) = 7.3 \times 10^{-9}$ s. The noteworthy feature of this data is that while smaller β gives a slower rate of relaxation at longer times, when $t < t_c$ the decay is actually *faster*. This is a consequence of the smaller value for the noncooperative relaxation, τ_0 , which follows from Eq. (8) of the coupling model. The temperatures in Fig. 1 correspond to $T < T_g$, $T = T_g$, and $T > T_g$. The steeper decay at short time is enhanced at higher temperatures, for which relaxation begins to dominate the $C(t)$ in Eq. (2).

The mean square displacement can be calculated from the correlation functions using Eq. (1). An illustrative result is shown in Fig. 2 (which is strikingly similar to the data of

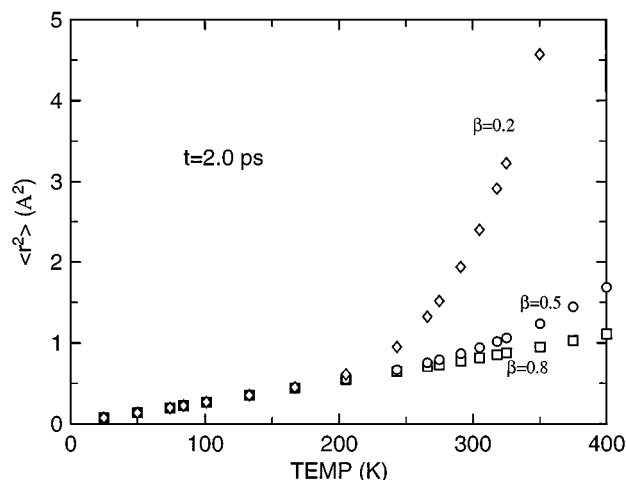


FIG. 3. The variation in the plateau value of the mean square displacement with temperature, evaluated at 2×10^{-12} s from data such as is shown in Fig. 2. The prefactor A [Eq. (10)] was adjusted to give a constant τ^* at 243 K. The change in slope, occurring near $T = T_g$, corresponds to the anomaly in the Debye–Waller factor.

Roe²⁶) for the case of $\beta=0.5$. Note that at low temperatures there is no diffusion at longer times; the molecules are bound within a volume governed by their liquid state neighbors. This long time limiting value is referred to as the Debye–Waller factor. As the temperature approaches the glass transition temperature, $\langle r^2 \rangle$ begins to rise above this long time plateau. This process has been described as the onset of anharmonicity,^{1,5,6} implying that vibrations propel the molecules over the potential barrier imposed by the surrounding atoms. However, it is clear from examination of the $C(t)$ synthesized using Eqs. (2)–(10) that the supralinear diffusion cannot be due to vibration, but rather is a direct consequence of relaxation. Specifically, the mean square displacement begins to rise at temperatures for which τ^* [Eq. (7)] assumes a value low enough that the contribution from $C_{rel}(t)$ in Eq. (2) becomes significant. This temperature is in the vicinity of T_g .

Following the suggestion of Angell,^{5,6} we choose a time in the range 0.5–2 ps, and plot the corresponding value of the mean square displacement as a function of temperature. Note that experimental data on selenium by Buchenau and Zorn⁷ were obtained by essentially the same procedure.²² Results are given in Fig. 3 for $\beta=0.2$, 0.5, and 0.8 evaluated at $t = 2$ ps. For each calculation $\tau^*(243 \text{ K})$ was set equal to 7.3×10^{-9} s, with the consequent values of the relaxation time at all other temperatures calculated assuming $E_a = 3.9$ kcal/mol, independent of β . As described above, the phonon contribution, calculated using Eqs. (3)–(6), was the same for all β . Figure 3 shows that smaller values of β give substantially more departure of $\langle r^2 \rangle$ from a linear temperature dependence. The anomaly in the Debye–Waller factor, at least in the present case, is a direct consequence of greater relaxation occasioned by the smaller τ_0 . A lower value for the noncooperative relaxation time is inevitable for smaller β whenever we have the condition $\tau_0 > t_c$ as seen from Eq. (8). Since smaller β means greater fragility,^{11–14,23–25} the corre-

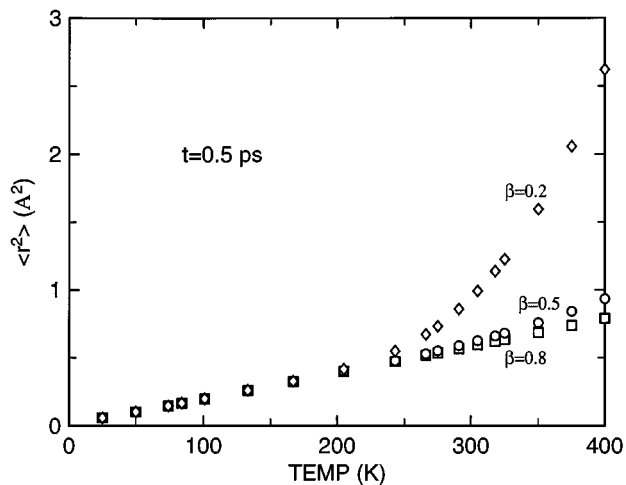


FIG. 4. As in Fig. 3, evaluated at 0.5×10^{-12} s.

lation of the magnitude of the anomalous Debye–Waller factor with fragility follows directly.

In Fig. 4 we show the same data as in Fig. 3, however, the $\langle r^2 \rangle$ is now evaluated at $t = 0.5$ ps. While the displacements are smaller, the general pattern remains. The increasing magnitude of the anomalous Debye–Waller factor with decreasing β is not sensitive to the particular time used for the assessment of $\langle r^2 \rangle$.

The data in Figs. 3 and 4 was generated assuming a constant activation energy. As an alternative, we can fix the pre-exponential factor A to be a constant ($= 9.8 \times 10^{-15}$ s). This means we let E_a vary in order to maintain $\tau^*(243\text{ K}) = 7.3 \times 10^{-9}$ s for all β . This method is no more to be recommended than the first; real materials differing in β can be expected to differ somewhat in both activation energy and A . The results of the two calculation methods are very similar. As illustrated in Fig. 5, the qualitative behavior is un-

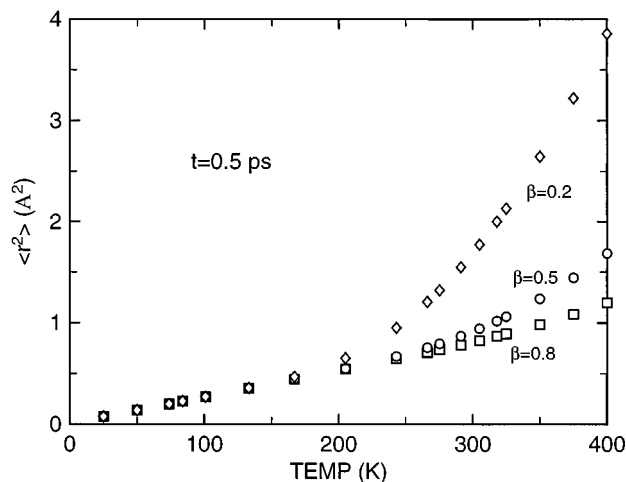


FIG. 5. The variation in the value of $\langle r^2 \rangle$ at 0.5×10^{-12} s, calculated for various β using $\omega_D = 3.2 \times 10^{12}$ rad/s, $K = 1.8 \times 10^{-27}$ s², $t_c = 2 \times 10^{-12}$ s, $A = 9.8 \times 10^{-15}$ s Å^{-2} . The activation energy was adjusted to give a fixed value for the relaxation times at $T = 243$ K.

changed; smaller β is associated with a more intense Debye–Waller anomaly.

CONCLUSIONS

The main conclusion of the present work is affirmation of previous indications^{9,10} that many features of the high frequency dynamics of glass-forming liquids can be rationalized in terms of the coupling model of relaxation. Implicit in this approach is the idea that many “anomalies” variously ascribed to anharmonic vibrations, soft phonons, or a fast beta process,^{9,10} may in fact be a direct consequence of the onset of relaxation processes. In particular, the unique aspects of relaxation captured by the coupling model — a fast Debye relaxation at short times transitioning to a slow Kohlrausch (stretched exponential) relaxation at longer times — are found to underlie the high frequency behavior of dense liquids. We also point out that while in the soft phonon model⁷ the pronounced softening of the boson peak modes above T_g is responsible for the fast relaxation, to make a connection to structural relaxation and viscous flow, this model has to assume a viscosity varying as $\exp(1/\langle r^2 \rangle)$. On the other hand, in the coupling model, $\langle r^2 \rangle$ is immediately related to structural relaxation and viscous flow.

ACKNOWLEDGMENT

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