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Connection between the high-frequency crossover of the temperature dependence of the relaxation time and the change of intermolecular coupling in glass-forming liquids

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In this paper, an interpretation of the high-frequency crossover, observed for glass formers at temperature far above the glass transition, is described in terms of the large change in the heterogeneous character of the dynamics. For five prototypical glass formers, dielectric relaxation data spanning many decades were analyzed. Unlike the temperature behavior of the dielectric (structural) relaxation times τ_α, which deviate from a Vogel-Fulcher-Tamman (VFT) relationship, the non-cooperative relaxation times, τ_0, calculated using the coupling model, are well described by a single VFT over the entire temperature range. Thus, the dynamic crossover evident in τ_α and other relaxation properties is suppressed for τ_0. This result suggests that the crossover is a direct consequence of the strong increase in intermolecular cooperativity (many-body effects), which also causes the dynamics of the system to become heterogeneous and non-exponential. This interpretation is consistent with recent findings concerning the pressure and temperature dependence of the dynamic crossover. Finally, a possible relationship of τ_0 to thermodynamic properties of the glass former is discussed.

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INTRODUCTION

The glass transition and the glassy state, found in materials of diverse chemical composition, have been a subject of research for many years.[1] A goal of these studies is to understand the underlying dynamics, which range from the microscopic regime on the order of picoseconds to the macroscopic regime on the order of days or longer. There are many factors governing the dynamics of the glass transition, including the specific volume,[2] configurational entropy,[3] and intermolecular coupling. The last factor encompasses many body effects such as caging, cooperativity, nonexponentiality, and dynamic heterogeneity. In addition, these factors can change with both temperature and pressure. Understandably, it is by no means an easy feat to achieve a satisfactory understanding of the glass transition phenomenon. Presently, most approaches focus on just one of these factors in making comparisons to experimental results, with the broader intent of constructing a more complicated theory by incorporating other factors.

The coupling model (CM),[4–6] when applied to the dynamics of glass-forming materials, is an example of such an approach. The CM tries to account for the effects of intermolecular coupling, such as the many-body cooperative dynamics and dynamic heterogeneity, while being at least mindful of the contributions from the other factors such as caging[7] and configurational entropy.[8] The basis of the CM is the putative existence of a temperature-insensitive crossover time, t_c, equal to about 2 ps for molecular liquids.[9] At times shorter than t_c, the basic molecular units relax independently of each other, yielding an exponential form for the normalized correlation function

$$\phi(t)=\exp[-(t/\tau_0)], \quad t<t_c, \tag{1}$$

where τ_0 is the primitive (non-cooperative) α-relaxation time. At times longer than t_c, the intermolecular interactions (i.e., cooperativity, which is inherently dynamic heterogeneous[10,11]) slow the relaxation, whereby the averaged correlation function assumes the Kohlrausch-Williams-Watts (KWW) form[12,13]

$$\phi(t)=\exp[-(t/\tau_{\mathrm{KWW}})^{\beta_{\mathrm{KWW}}}], \quad t>t_c, \tag{2}$$

where τ_{KWW} is an α-relaxation time, and β_{KWW} ($0<\beta_{\mathrm{KWW}}\leqslant 1$) is the stretch exponent. Continuity of $\phi(t)$ at t_c leads to the relation

$$\tau_{\mathrm{KWW}}=[t_c^{\beta_{\mathrm{KWW}}-1}\tau_0]^{1/\beta_{\mathrm{KWW}}} \tag{3}$$

between the two relaxation times. When relaxation time, designated herein as τ_α, is obtained experimentally from the frequency of the maximum of the α dispersion, the corresponding equation applies. In so far as $\tau_0(T)$ is not given by the CM, it is not a complete theory of the glass transition. Thermodynamics enter into the determination of the temperature dependence of $\tau_0(T)$, and this must be treated separately by other theories, such as that due to Adam and Gibbs[14] (also see Ref. 8) and/or free volume theories.

In this paper the CM is used to account for the change of the temperature dependence of τ_α as observed in many liquids at a characteristic temperature T_B.[15–18] On lowering of temperature, $\tau_\alpha(T)$ changes from one Vogel-Fulcher-Tamman (VFT) dependence

$$\log \tau_\alpha(T)=\log \tau_\infty + B/(T-T_0) \tag{4}$$

for $T>T_B$ to another VFT dependence for $T<T_B$. In Eq. (4), τ_∞, B, and T_0 are temperature-independent constants.

In previous works,[19,20] it was shown that dielectric relaxation of small molecular glass formers can be described by a β_{KWW} close to unity and slowly varying for $T>T_B$, but more rapidly decreasing as temperature is decreased past $T \sim T_B$. The magnitude of the decrease of β_{KWW}, proportional to the value of β_{KWW} at the glass temperature T_g, correlates with the extent of the difference between the high and low temperature VFT functions at T_g. For example, "stronger" glass formers with larger $\beta_{\mathrm{KWW}}(T_g)$ show a weaker decrease

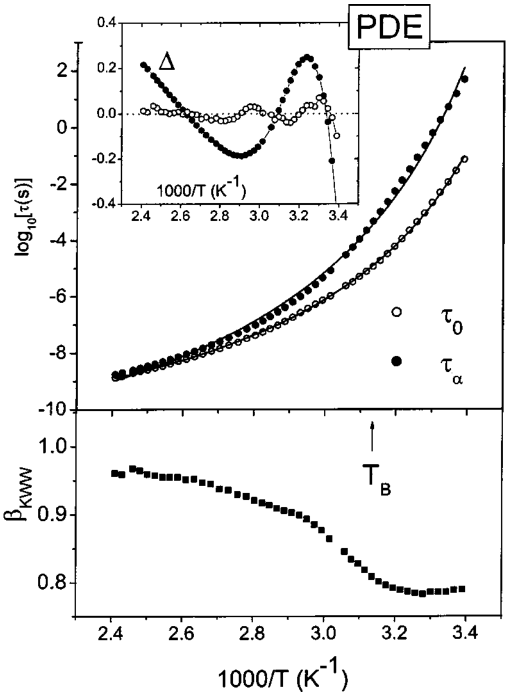

FIG. 1. τ_α and τ_0 (upper panels), together with the β_{KWW} (lower panels), are plotted as a function of inverse temperature for PDE. The lines in the upper panel are the best fit to VFT. The inset shows the differences between the experimental points and the best fit to VFT.

of β_{KWW} across T_B, and exhibit less of a difference between the two VFTs. In the framework of the CM, $(1-\beta_{\mathrm{KWW}})$ is a measure of the strength of the intermolecular coupling, and these experimental observations are interpreted to originate from the more rapid increase of intermolecular cooperativity with decreasing temperature below T_B. The correlation is consistent also with the well-established correlation between "fragility" and β_{KWW} found to be valid for many materials.[21–24]

If the crossover from one VFT dependence to another at T_B is caused by a change in intermolecular coupling, then τ_0, which is devoid of many-body effects, should not show any change in temperature dependence. Herein we assess this prediction, by using Eq. (3) to calculate τ_0 from experimentally-determined τ_α. The temperature dependence of τ_0 is expected to vary smoothly, in accord with a single VFT dependence, due only to changes of configurational entropy and/or specific volume with temperature.[2] This follows from the fact that the temperature dependence of τ_α for $T>T_B$ can be described by a VFT behavior.[25] Since β_{KWW} is close to unity throughout this regime, $\tau_0\sim\tau_\alpha$, and thus $\tau_0(T)$ should also follow a VFT behavior. If τ_0 has no crossover at T_B, this same VFT dependence should continue for $T<T_B$. This scenario could be used to also discuss recent evidences of a dynamics crossover under high pressure.[26–28]

RESULTS AND DISCUSSION

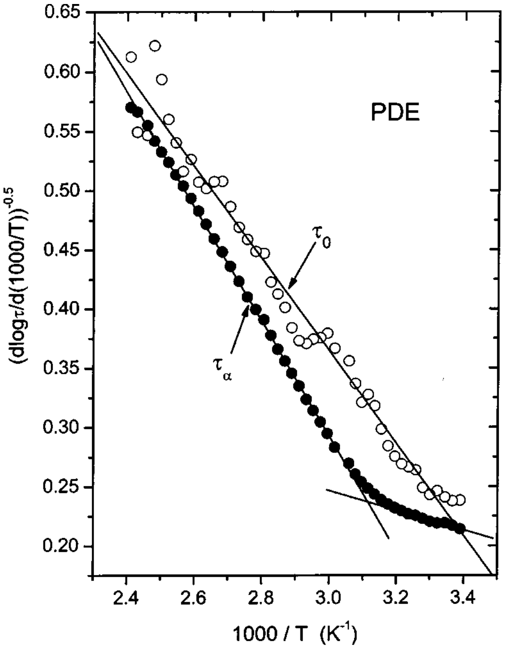

FIG. 2. Derivative ("Stickel") plots of τ_α and τ_0 for PDE. A break at T_B, evident in the former, is missing in the latter.

Dielectric relaxation times are known to exhibit a crossover at T_B from one to a second VFT dependence, with results published for, among various glass formers, phenolphthalein-dimethyl-ether (PDE), phenyl salicylate (salol), propylene carbonate (PC), ortho-terphenyl (OTP),[15,29] and 54% chlorinated biphenyl (PCB54).[30] We now reanalyze the same data, but for each case employ only a single VFT dependence to fit the experimental τ_α and the calculated τ_0. In Refs. 15 and 30, values for w, the full-width at half maximum of the dielectric loss peak normalized to that of an ideal Debye loss peak, are given for PDE, salol, PC, and PCB54. From these, we can calculate the value of the β_{KWW} using the relation of Dixon:[31]

$$\beta_{\mathrm{KWW}}=1-1.047(1-w^{-1}). \tag{5}$$

Since the dielectric loss of OTP is weak and hence the shape factor more uncertain, we use the β_{KWW} determined from light scattering.[32] From the values of τ_α and β_{KWW}, we in turn calculate τ_0 using the Eq. (3) and $t_c=2$ ps.

TABLE I. VFT parameters and deviation from the least squares fits for τ_α and τ_0.

Liquid		B (K)	T_0 (K)	log τ_∞ (s)	χ^2
PDE	τ_α	1350	255	-12.7	3×10^{-2}
	τ_0	1010	253	-11.6	9×10^{-4}
Salol	τ_α	839	195	-12.6	0.1
	τ_0	570	190	-11.7	8×10^{-3}
PC	τ_α	612	139	-12.3	1×10^{-2}
	τ_0	576	134	-12.0	3×10^{-3}
PCB 54	τ_α	2110	194	-15.0	6×10^{-2}
	τ_0	1220	196	-12.6	2×10^{-3}
OTP	τ_α	1510	205	-15.0	0.2
	τ_0	1190	189	-13.7	8×10^{-3}

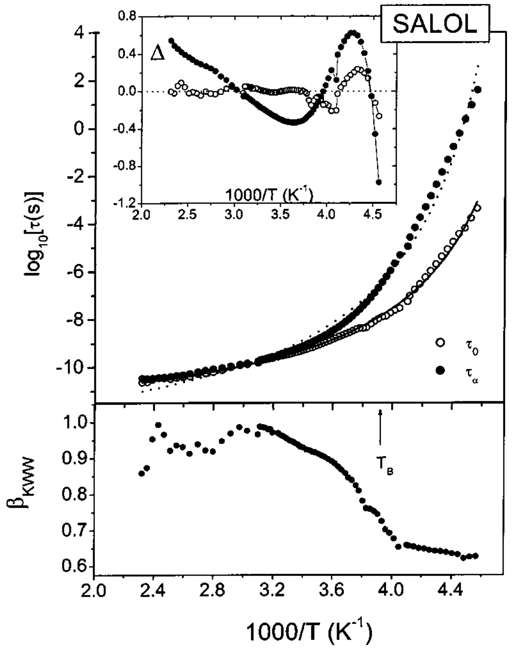

FIG. 3. τ_α and τ_0 (upper panels), together with the $\beta_{\rm KWW}$ (lower panels), are plotted as a function of inverse temperature for salol. The lines in the upper panel are the best fit to VFT. The inset shows the differences between the experimental points and the best fit to VFT.

τ_α and τ_0 (upper panels), together with the $\beta_{\rm KWW}$ (lower panels), for PDE are plotted as a function of inverse temperature in Fig. 1. The dynamic crossover temperature T_B is obtained using the derivative method (Fig. 2), as proposed by Stickel *et al.*[33] The least squares fits to a single VFT equation, using equal weighting of the data, are shown for both τ_0 and τ_α, with the fitting parameters listed in Table I. It is evident that, while a single VFT equation cannot describe the temperature behavior of τ_α, the fits of the τ_0 show much smaller deviations. The χ^2 for the least squares fits are given in Table I. As seen in Fig. 2, the change in dynamics seen as a break in the derivative plot of τ_α is absent in the corresponding plot of τ_0.

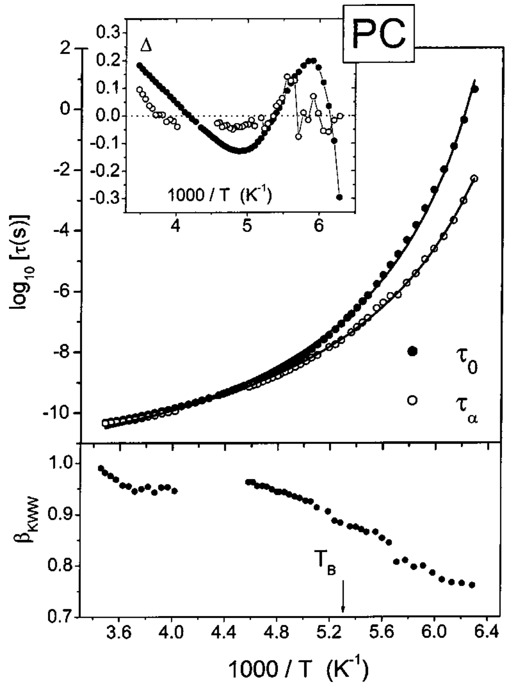

FIG. 4. τ_α and τ_0 (upper panels), together with the $\beta_{\rm KWW}$ (lower panels), are plotted as a function of inverse temperature for PC. The lines in the upper panel are the best fit to VFT. The inset shows the differences between the experimental points and the best fit to VFT.

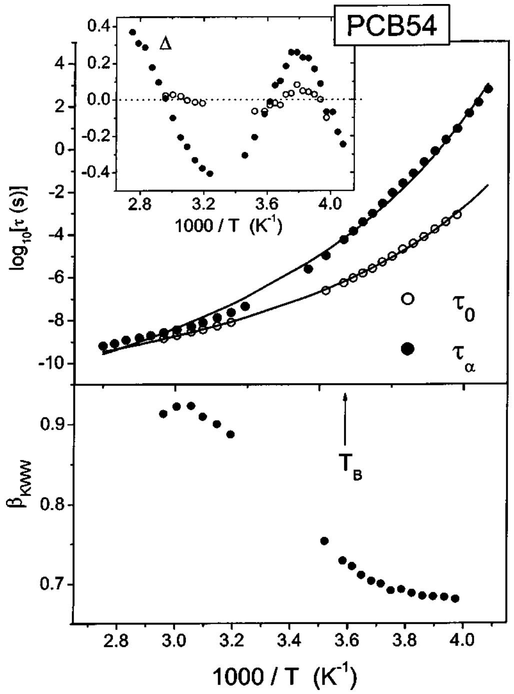

FIG. 5. τ_α and τ_0 (upper panels), together with the $\beta_{\rm KWW}$ (lower panels), are plotted as a function of inverse temperature for PCB54. The lines in the upper panel are the best fit to VFT. In the inset shows the differences between the experimental points and the best fit to VFT.

In Figs. 3–6, we show results for τ_α and τ_0 (upper panels), and $\beta_{\rm KWW}$ (lower panels), for salol, PC, PCB54, and OTP, respectively. All fitting parameters, along with the errors, are listed in Table I. Similar to the results for PDE, the τ_α exhibit a break at T_B, while the τ_0 conform to a single VFT equation over the entire temperature range.

Some reduction in deviation from the fitted VFT curve will result solely from the smaller span of the τ_0 data. However, as seen in the insets to Figs. 1 and 2–5, showing the differences between the experimental points and the best-fit VFT curve, for τ_0 these differences are random, unlike the systematic deviations for τ_α. Since $\beta_{\rm KWW}$ is an exponent in Eq. 3, any uncertainties are magnified in the determination of τ_0, and this engenders some error. This is especially the case for salol (Fig. 3) and PC (Fig. 4). The uncertainty in $\beta_{\rm KWW}$ gives rise to random scatter in the error curves; however, the systematic deviation of the fitted VFT equation from τ_α is absent for τ_0.

In recent dielectric relaxation measurements on PDE and PCB54 (Refs. 26–28) under varying pressure and temperature, it was shown that for a given material, the crossover in

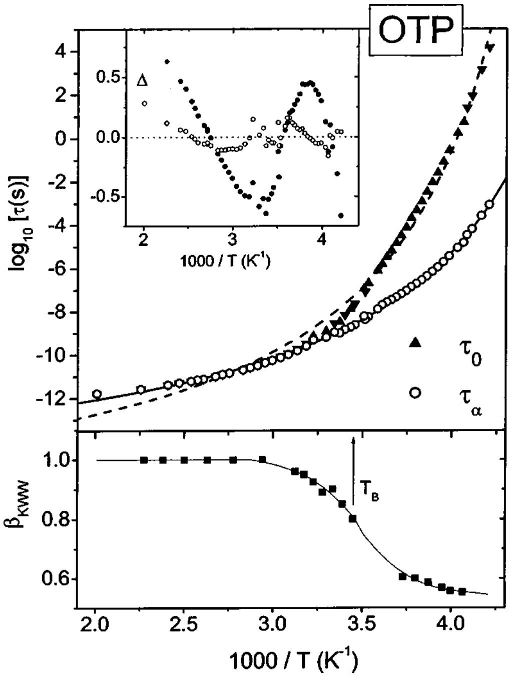

FIG. 6. τ_α and τ_0 (upper panels), together with β_{KWW} (lower panels), plotted as a function of inverse temperature for OTP. The lines in the upper panel are the best fit to VFT. The inset shows the differences between the experimental points and the best fit to VFT.

dynamics occurs at the same characteristic relaxation time, independent of whether temperature or pressure is being varied. This result is consistent with the interpretation of the crossover as a consequence of the development of stronger cooperativity. For the present materials, *w* depends only on τ_α, and not on the particular value of temperature and pressure.[26] According to the CM, *w* (or β_{KWW}) reflects the strength of the intermolecular cooperativity.

The change of dynamics reflected in the temperature dependence of the relaxation times is manifested in other properties, such as the decoupling of translational and rotational motions[34–39] and the splitting off from the structural relaxation of a faster, secondary process,[16,40,41] which in fact can be identified with the noncooperative relaxation of the CM.[7,42–44] Another characteristic of T_B is departure of $\tau_\alpha(T)$ from the predictions of the Adam-Gibbs (AG) model.[8,17,18,26,44] According to this model, the loss of degrees of freedom as T_g is approached from above forces molecular reorientations to transpire collectively, within a subvolume referred to as the cooperatively rearranging region. The AG model makes no explicit consideration of the many-body interactions at least that part giving rise to the dynamic heterogeneity and non-exponentially inherent to the supercooled state of glass formers. The proportionality between τ_α and the product TS_c predicted by the Adam-Gibbs model breaks down with two separate dependences above and below T_B.[8,17,18,44] The thermodynamic considerations underlying the Adam-Gibbs model do not account for the change in dynamics, since the latter is a consequence of many-body interactions.

The apparent agreement with the AG theory of τ_α data for $T < T_B$ reported previously[17] can qualitatively be explained in terms of the near steplike behavior of β_{KWW} such that for $T < T_B$, β_{KWW} is approximately constant. In fact, from Eq. (3) it can be easily shown that for constant β_{KWW},

$$\log(\tau_\alpha) = \kappa + \frac{1}{\beta_{\mathrm{KWW}}} \log(\tau_0), \tag{6}$$

where κ is a constant. Thus, if the AG equation is satisfied for τ_0, then it also has to be satisfied for τ_α (for approximately constant β_{KWW}).

It should be noted also that the fit of data for $T < T_B$ for very fragile liquids often yields a value of τ_∞ that is far too small[17,26,45,46] to be reconciled with any actual physical quantity like a vibrational time; however, while using the approach presented herein the values obtained for τ_∞ are physically reasonable.

CONCLUSIONS

In the supercooled regime of glass-forming liquids, starting from high temperatures, certain properties of the α relaxation exhibit a crossover as temperature is reduced (or pressure increased). If this change in dynamics is a consequence of the development of stronger intermolecular cooperatively, then removal of the effects of the latter should likewise remove the crossover. One manifestation of the change in dynamics is a change of the temperature dependence of τ_α from one VFT form to another. By using a relation from the CM, we calculate the non-cooperative (intermolecularly uncoupled) relaxation times τ_0 for various molecular glass formers, and show that the temperature dependence of τ_0 over a range encompassing T_B down to T_g can be well described by a single VFT equation. Thus, we conclude that intermolecular cooperativity (many-body effects) underlies the crossover phenomenon. At the same time, beneficially other problems of τ_α caused by intermolecular coupling are removed.

The implication of such behavior is that the combined effects of configurational entropy changes and intermolecular coupling govern structural relaxation. Any theoretical model must include both thermodynamics and many-body dynamics in order to accurate describe the general properties of the glass transition. This result suggests that the departure of experimental data from the predictions of the Adam-Gibbs equation could be due to the absence in the model of consideration of the effects of intermolecular cooperativity and the related dynamic heterogeneity. The CM addresses these effects directly, and thus can account for many of the dynamic properties of glass formers.[6] A complete theory of the glass transition would have to provide a first-principle account of the non-cooperative dynamics together with a treatment of intermolecular coupling. Such a complete satisfactory theory is still not yet at hand.

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