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 $\tau_a$, which deviate from a Vogel-Fulcher-Tamman (VFT) relationship, the non-cooperative relaxation times, $\tau_0$, calculated using the coupling model, are well described by a single VFT over the entire temperature range. Thus, the dynamic crossover evident in $\tau_a$ and other relaxation properties is suppressed for $\tau_0$. 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 $\tau_0$ 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, non-exponentiality, 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 caging7 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

$$\phi(t) = \exp\left[\frac{-t}{\tau_0}\right], \quad t < t_c,$$

where $\tau_0$ is the primitive (non-cooperative) $\alpha$-relaxation time. At times longer than $t_c$, the intermolecular interactions (i.e., cooperativity, which is inherently dynamic hetero-

geneous10,11) slow the relaxation, whereby the averaged correlation function assumes the Kohlrausch-Williams-Watts (KWW) form12,13

$$\phi(t) = \exp\left[\frac{-(t/\tau_{KWW})^{\beta_{KWW}}}{}, \quad t > t_c, \right.$$ (2)

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

$$\tau_{KWW} = \left[\frac{t_c^{\beta_{KWW}-1}}{\tau_0}\right]^{1/\beta_{KWW}}$$

(3)

between the two relaxation times. When relaxation time, designated herein as $\tau_a$, is obtained experimentally from the frequency of the maximum of the $\alpha$ 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 Gibbs14 (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 $\tau_a$ as observed in many liquids at a characteristic temperature $T_B$.15–18 On lowering of temperature, $\tau_a(T)$ changes from one Vogel-Fulcher-Tamman (VFT) dependence

$$\log \tau_a(T) = \log \tau_\infty + B/(T - T_0)$$

(4)

for $T > T_B$ to another VFT dependence for $T < T_B$. In Eq. (4), $\tau_\infty$, $B$, 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 $\beta_{KWW}$ 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 $\beta_{KWW}$, proportional to the value of $\beta_{KWW}$ at the glass temperature $T_{\infty}$, correlates with the extent of the difference between the high and low temperature VFT functions at $T_{\infty}$. For example, “stronger” glass formers with larger $\beta_{KWW}(T_{\infty})$ show a weaker decrease
of \( b_{KWW} \) across \( T_B \), and exhibit less of a difference between the two VFTs. In the framework of the CM, \( (1 - b_{KWW}) \) 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 \( b_{KWW} \) 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 \( \tau_0 \), 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 \( \tau_0 \) from experimentally-determined \( \tau_a \). The temperature dependence of \( \tau_0 \) 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 \( \tau_a \) for \( T > T_B \) can be described by a VFT behavior.\(^{25}\) Since \( b_{KWW} \) is close to unity throughout this regime, \( \tau_0 \sim \tau_a \), and thus \( \tau_0(T) \) should also follow a VFT behavior. If \( \tau_0 \) 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**

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 \( \tau_a \) and the calculated \( \tau_0 \). 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 \( b_{KWW} \) using the relation of Dixon:\(^{31}\)

\[
\beta_{KWW} = 1 - 1.047(1 - w^{-1}).
\]

Since the dielectric loss of OTP is weak and hence the shape factor more uncertain, we use the \( b_{KWW} \) determined from light scattering.\(^{32}\) From the values of \( \tau_a \) and \( b_{KWW} \), we in turn calculate \( \tau_0 \) using the Eq. (3) and \( t_c = 2 \) ps.

**TABLE I. VFT parameters and deviation from the least squares fits for \( \tau_a \) and \( \tau_0 \).**

<table>
<thead>
<tr>
<th>Liquid</th>
<th>( B ) (K)</th>
<th>( T_0 ) (K)</th>
<th>( \log \tau_a ) (s)</th>
<th>( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDE</td>
<td>( \tau_a )</td>
<td>1350</td>
<td>255</td>
<td>-12.7</td>
</tr>
<tr>
<td></td>
<td>( \tau_0 )</td>
<td>1010</td>
<td>253</td>
<td>-11.6</td>
</tr>
<tr>
<td>Salol</td>
<td>( \tau_a )</td>
<td>839</td>
<td>195</td>
<td>-12.6</td>
</tr>
<tr>
<td></td>
<td>( \tau_0 )</td>
<td>570</td>
<td>190</td>
<td>-11.7</td>
</tr>
<tr>
<td>PC</td>
<td>( \tau_a )</td>
<td>612</td>
<td>139</td>
<td>-12.3</td>
</tr>
<tr>
<td></td>
<td>( \tau_0 )</td>
<td>576</td>
<td>134</td>
<td>-12.0</td>
</tr>
<tr>
<td>PCB 54</td>
<td>( \tau_a )</td>
<td>2110</td>
<td>194</td>
<td>-15.0</td>
</tr>
<tr>
<td></td>
<td>( \tau_0 )</td>
<td>1220</td>
<td>196</td>
<td>-12.6</td>
</tr>
<tr>
<td>OTP</td>
<td>( \tau_a )</td>
<td>1510</td>
<td>205</td>
<td>-15.0</td>
</tr>
<tr>
<td></td>
<td>( \tau_0 )</td>
<td>1190</td>
<td>189</td>
<td>-13.7</td>
</tr>
</tbody>
</table>
\( \tau_0 \) and \( \tau_a \) (upper panels), together with the \( \beta_{KWW} \) (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 \( \tau_0 \) and \( \tau_a \), with the fitting parameters listed in Table I. It is evident that, while a single VFT equation cannot describe the temperature behavior of \( \tau_a \), the fits of the \( \tau_0 \) show much smaller deviations. The \( \chi^2 \) 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 \( \tau_a \) is absent in the corresponding plot of \( \tau_0 \).

In Figs. 3–6, we show results for \( \tau_a \) and \( \tau_0 \) (upper panels), and \( \beta_{KWW} \) (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 \( \tau_a \) exhibit a break at \( T_B \), while the \( \tau_0 \) 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 \( \tau_0 \) 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 \( \tau_0 \) these differences are random, unlike the systematic deviations for \( \tau_a \). Since \( \beta_{KWW} \) is an exponent in Eq. 3, any uncertainties are magnified in the determination of \( \tau_0 \), and this engenders some error. This is especially the case for salol (Fig. 3) and PC (Fig. 4). The uncertainty in \( \beta_{KWW} \) gives rise to random scatter in the error curves; however, the systematic deviation of the fitted VFT equation from \( \tau_a \) is absent for \( \tau_0 \).

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

$$\log(\tau_a) = \kappa + \frac{1}{\beta_{KWW}} \log(\tau_0),$$

where $\kappa$ is a constant. Thus, if the AG equation is satisfied for $\tau_0$, then it also has to be satisfied for $\tau_a$ (for approximately constant $\beta_{KWW}$).

It should be noted also that the fit of data for $T<T_B$ for very fragile liquids often yields a value of $\tau_a$ that is far too small\cite{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 $\tau_a$ are physically reasonable.

**CONCLUSIONS**

In the supercooled regime of glass-forming liquids, starting from high temperatures, certain properties of the $\alpha$ 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 cooperativity, 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 $\tau_a$ from one VFT form to another. By using a relation from the CM, we calculate the non-cooperative (intermolecularly uncoupled) relaxation times $\tau_0$ for various molecular glass formers, and show that the temperature dependence of $\tau_0$ 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 $\tau_a$ 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 accurately describe the general properties of the glass transition. This result suggests that a 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. 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.

**ACKNOWLEDGMENT**

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Here we do not consider the higher temperature regime, $T > T_A$, where an Arrhenius temperature dependence would be observed.