Enhanced cooperativity below the caging temperature of o-terphenyl

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(Dated: January 10, 2022)

The utility of a cooperative length scale for describing the dynamics of glass-forming liquids is shown using literature data on o-terphenyl. Molecular dynamics and Monte Carlo simulations reveal a distribution of cooperative fractal events below the caging temperature $T_A$. Guided by these results, we show how to extract the size of slow regions in any glass-forming liquid from probe rotation/diffusion measurements, which agrees quantitatively with 4-D NMR and grows steadily as temperature is lowered below $T_A$. We clarify why this length must also be the size of the largest cooperative events.

PACS numbers: 64.70.Pf; 61.43.Fs; 61.20.Lc

Many liquids either cannot crystallize or crystallize sufficiently slowly that they vitrify below their glass transition temperature $T_g$. A fundamental understanding of glass formation is still lacking because it has not been firmly established whether the pronounced slowing down is simply kinetic in origin or there is an underlying thermodynamic character [1, 2, 3, 4, 5, 6]. Building upon previous experimental results, this letter shows a natural length scale for cooperative motion in o-terphenyl that grows below a caging temperature, giving strong support to the thermodynamic viewpoint [1]. The caging temperature $T_A$, is seen in many dynamics experiments on glass-forming liquids [3, 4, 5]. Particularly lucid are experiments that measure translation and rotation of small probe molecules immersed in the liquid. Above $T_A$, these are coupled by the Stokes-Einstein relation and have the same temperature dependence. In contrast, below $T_A$ these measurements decouple, with translation having a weaker temperature dependence than rotation [5, 6, 10, 11]. A wide variety of ideas have been expounded to explain this observation [5, 6, 12, 13] and these ideas fall into two categories. One group of ideas suggest that translation is dominated by a different and faster moment of a distribution of relaxations than is measured by rotation [5, 6]. The second group of ideas consider both to be controlled by slow motions [12, 13], and in this paper we present compelling evidence that this is the correct picture.

The 1965 model of Adam and Gibbs [1] suggests that there should be cooperative motion in glass-forming liquids. The cooperative size $\xi$, is inversely related to the configurational entropy of the liquid $S_{\text{conf}}$. At temperatures sufficiently above $T_g$, all molecules undergo independent local
Brownian movements without signs of cooperativity, where the relaxation time $\tau_\alpha$, and the viscosity $\eta$, vary as

$$\tau_\alpha \sim \eta/T \sim \exp[E/k_BT] \quad T > T_A$$

(1)

where $E$ is the high-$T$ activation energy. As temperature is lowered, the density of the liquid gradually increases and Brownian motion becomes hindered, as neighboring molecules block each others attempts to move. This crowding leads to cooperative dynamics [2, 3, 14, 15, 16], active for all $T$ below the caging temperature $T_A$. The onset of cooperativity is also accompanied by the observed ‘caging effect’ in the mean-square displacement of a particle between the ballistic and diffusive regimes, and a reduction in $S_{conf}$, causing $\xi$ to grow. These changes result in a progressively stronger temperature dependence of $\eta$ and $\tau_\alpha$ at lower temperatures.

Since experimental attempts to identify the length scale for cooperative motion have met with limited success [4, 5, 6], the dominant evidence for this quantity is from computer simulations [15, 16, 17, 18, 19, 20, 21, 22, 23, 24]. Simulations have the profound advantages of direct observation of motion and straightforward identification of both the size and shape of cooperatively rearranged regions. Equilibrium simulations of liquids are not yet possible near $T_g$, but have been done down to 0.7$T_A$ [22]. In addition to confirming the essential aspects of the Adam and Gibbs model, simulations have provided two novel insights. Instead of a single size scale for cooperative motion, there is in fact a broad distribution of size scales below $T_A$ [15, 17, 18, 19, 20, 21, 24, 25, 26]. The largest size in this distribution $\xi$ grows rapidly as temperature is lowered, as expected by Adam and Gibbs [1]. The second important observation is that the cooperatively rearranging regions are not the three-dimensional volumes that were initially proposed, but instead are fractal [15, 18, 19, 21, 26]. The observed fractal dimension (of order 2) clearly shows that the majority of molecules within the volume $\xi^3$ have not participated in the cooperative event. Consequently, a new model for cooperative motion was proposed that accommodates these new insights [27]. All glass-forming liquids show a temperature dependence of cooperative size, with commensurate effects in viscosity and relaxation time, in reasonable accord with the expectations of dynamic scaling [27, 28].

$$\xi \sim [(T - T_C)/T_C]^{-3/2} \quad T_C < T < T_B$$

(2)

$$\tau_\alpha \sim \xi^6 \exp(E_\alpha/k_BT) \sim (T - T_C)^{-9} \exp(E_\alpha/k_BT)$$

(3)
FIG. 1: Simulation results for the length scale of cooperative motion as a function of reduced temperature. From molecular dynamics simulations of Lennard-Jones sphere mixtures (▲[23]) and from Monte Carlo simulations of the bond fluctuation model at density 0.8 for chains of 10 monomers (●[26]). Inset is the temperature dependence of the configurational entropy (◇[22]) and the product of cooperative length and configurational entropy (□[26]) for chains of 10 monomers.

\[ \eta \sim \xi^6 \exp(E_\eta/k_BT) \sim (T - T_C)^{-9} \exp(E_\eta/k_BT) \]  

(4)

The critical temperature \( T_C \), is below \( T_g \) and is the temperature at which the equilibrium extrapolated values of \( \xi, \tau_\alpha \) and \( \eta \) all diverge. The material-specific activation energy apparently depends on whether segmental relaxation \( (E_\alpha) \) or viscosity \( (E_\eta) \) is measured, with \( E_\eta/E_\alpha \simeq 1.2 \) for non-polymeric organic glasses [29]. \( T_B \) is the crossover temperature [6, 30] below which all molecules are caged by their neighbors \( (T_B < T_B < T_A) \). \( T_B \) is typically about 20 K below \( T_A \) and corresponds to the upper temperature limit where dynamic scaling (and Vogel-Fulcher) quantitatively describe the temperature dependence of relaxation.

Figure II shows data for \( \xi \) as obtained from molecular dynamics simulations [23] and new results from Monte Carlo (MC) simulations on the bond fluctuation model [22, 26]. In the MC simulations the mobile particles are identified as those that move over a time scale of interest. We then look for clusters of these mobile particles and find that their sizes are a function of time for short times, but quickly become time independent up to \( \tau_\alpha \). We only consider cluster sizes in this intermediate time range. Figure II shows the sizes of the largest mobile particle clusters as a function of \( T \). Both sets of simulations show that \( \xi \) is sensibly independent of temperature above \( T_A \), but then grows...
rapidly when temperature is lowered below $T_A$. The very different nature of the simulations used for the data in Fig. 1 suggests there may be universal aspects to the growing length scale below $T_A$. The inset of Fig. 1 shows that $S_{\text{conf}}$ as defined by Adam and Gibbs also changes character at $T_A$ with a broad crossover between $T_B$ [31] (below which Eqs. 3 and 4 or Vogel-Fulcher should describe dynamics) and a much higher temperature above which dynamics obey Eq. 1 [31]. The inset also shows that the product of $\xi S_{\text{conf}}$ is essentially temperature independent. Hence, the growing length scale is reciprocally related to the vanishing configurational entropy, in qualitative agreement with Adam and Gibbs [1].

Guided by simulations, and owing to the abrupt change in the very nature of relaxation at $T_A$ [16, 22, 32, 33, 34], the caging temperature is easily identified by a variety of experiments probing liquid dynamics. We demonstrate this point with o-terphenyl using rotation and translational diffusion of molecular probes, dielectric spectroscopy, viscosity and Fabry-Perot interferometry. Molecular probe techniques provide a *model independent* measure of $T_A$. The length scales extracted from these experiments, which are in *quantitative* agreement with existing $\xi(T)$ data from 4-D NMR [35, 36], show a strong temperature dependence only below $T_A$. 4-D NMR [36, 37, 38, 39, 40, 41] provides the benchmark length scale of the slow regions, but unfortunately this method can only be used over a very limited temperature range [41].

$T_B$ was found to be 286K from extrapolation of the $\beta$-relaxation time to the $\alpha$-relaxation (Fig. 2A), in agreement with the literature [30]. The temperature dependence of $\tau_\alpha$ and $\eta$ (Fig. 2A) were fit using Eqs. 3 and 4 and values for $T_C$, $E_\alpha$, and $E_\eta$ were determined to be 227 K, 120 kJ/mol and 140 kJ/mol respectively. In figure 2A, equation 1 was fit to $\eta$ using $E = 22$ kJ/mol. This activation energy was then used to fit $\tau$ (with a result that extrapolates to about $10^{-14}$ sec at an infinite temperature). A $T_A$ of 313 K was then defined by the crossover between Eq. 1 and Eqs. 2 and 4. The $T_A$ from this crossover between Eqs. 2 and 4 and Arrhenius behavior is also the temperature below which the Stokes-Einstein relation breaks down. This ‘breakdown’ below $T_A$ is apparent in figure 2B where both probe and self-diffusion show a temperature dependence below $T_A$ [47, 48]. The calorimetric $T_g$ of o-terphenyl was previously determined to be at 241 K [49].

The Stokes-Einstein relation expects the rotational relaxation time $\langle \tau_r \rangle$ and translational diffusion coefficient $D$ of probe molecules are coupled so that their product is independent of temperature. Above $T_A$ the probes diffuse a distance of order their own size in the time it takes for the probe to rotate. However, at $T_A$ these two dynamics *decouple*, a fact which can be used to establish the cooperative length scale. To understand this, consider a bimodal distribution with a small quantity (volume fraction $\phi_f << 1$) of fast and $\phi_s = 1 - \phi_f$ slow particles [50]. The average
FIG. 2: Dynamic data for o-terphenyl above and below $T_A$. Model dependent measures of $T_A$ (A): viscosity ($\eta$ [42, 43]), dielectric spectroscopy ($\alpha$-relaxation ($\Delta$ [44]) and $\beta$-relaxation ($\gamma$ [45])) and Fabry-Perot interferometry ($\nabla$ [46]). The dashed line is $T_A$. The dotted line is a fit to the $\beta$-relaxation data extrapolated to $T_B$. Solid curves are fits to $\tau_\alpha$ and $\eta$ using Eq. 1 for $T > T_A$ and Eqs. 3 and 4 for $T < T_B$. Model independent quantities affected by $T_A$ (B): self-diffusion ($\times$ [7]) and tetracene probe dynamics (+ [47, 48]). Solid curve is Eq. 7.

Rotational time is dominated by the slow molecules

$$\langle \tau_r \rangle = \phi_s \tau_s + \phi_f \tau_f \approx \phi_s \tau_s$$  \hspace{1cm} (5)

since $\phi_s \gg \phi_f$ and $\tau_s \gg \tau_f$. The diffusion coefficient is the sum of fast and slow contributions

$$D = \phi_s D_s + \phi_f D_f = \phi_s \xi_s^2 / 6 \tau_s + \phi_f \xi_f^2 / 6 \tau_f$$  \hspace{1cm} (6)

where $\xi_s^2 \equiv 6 D_s \tau_s$ and $\xi_f^2 \equiv 6 D_f \tau_f$. Since $\phi_s \approx 1$, the product $6D\langle \tau_r \rangle \approx \phi_s^2 \xi_s^2 + \phi_f \phi_s \xi_f^2 \tau_s / \tau_f$ can be used to define a length scale,

$$\xi \equiv \xi_s = \sqrt{6D\langle \tau_r \rangle}.$$  \hspace{1cm} (7)

Fig. 3A shows the temperature dependence of this length scale for two probe molecules in o-terphenyl. We find that the length scale defined by Eq. 7 quantitatively agrees with 4-D NMR, which is known to target the slow contribution $\xi_s$. This quantitative agreement requires $\phi_s^2 \xi_s^2 \gg \phi_f \phi_s \xi_f^2 \tau_s / \tau_f$, justifying Eq. 7.

In the calculation of $\xi$ over a wide temperature range, $\langle \tau_r \rangle$ was interpolated using the noted relationship $\langle \tau_r \rangle \sim \eta / T$ along with the viscosity data of Fig. 2. $\xi$ from rotation/translation of anthracene (circles in Fig. 3) shows a strong temperature dependence over the entire experimental temperature range because all $T < T_A$, whereas the larger tetracene probe (triangles in Fig. 3) gives $\xi$ that is clearly temperature dependent below $T_A$ and independent of temperature above $T_A$. 
FIG. 3: The temperature dependence of the cooperative length scale in o-terphenyl ($T_C = 227$ K). From 4-D NMR (■ with error bars [35]) and calculations using probe dynamics (○ anthracene [47]; △ tetracene [47]). Dashed lines denote $T_g = 241$ K, $T_B = 286$ K and $T_A = 313$ K. The solid line is the slope of $-3/2$ expected by dynamic scaling (Eq. 2).

Ideally a probe molecule would have the same shape, size, polarity and properties as the liquid matrix in which it was inserted. $^1$H-NMR can provide measurements of translational and rotational self-diffusion coefficients [7]. This allows for direct measurement of $\xi$ using Eq. 7. Although measurements of $\langle \tau_r \rangle$ exist [7], they are rare. In the case where measurements of $\langle \tau_r \rangle$ are lacking, we assume that $\eta/T$ properly describes the temperature dependence of $\langle \tau_r \rangle$ [7, 48]. This assumption allows for measurements of $T_A$ that stand in agreement with the other measurements of $T_A$ (see × symbols in Fig. 2), but with the limitation of not being able to give an absolute measure of $\xi$.

In Fig. 3 measurements of $\xi$ are plotted along with the absolute measurements of $\xi$ provided by 4-D NMR ($\xi = 2.9 \pm 1$ nm at 252 K [36]). While each technique measures $\xi$ differently, they all stand in quantitative agreement. This result strongly suggests that the vast majority of the molecules are “slow”, $\phi_f \approx 10^{-5}$, which makes the slow term dominate even if $\tau_s/\tau_f = 10^3$. This concept of the slow molecules dominating near-$T_g$ dynamics has also been suggested by recent models [12, 13].

The cooperative length estimated from figure 3 is $5.2 \pm 1.0$ nm at $T_g$ and $0.33 \pm 0.06$ nm at $T_A$. The van der Waals sphere radii $r_{vdW}$ of o-terphenyl was calculated from atomic radii using the procedures of Edward [51]. A $r_{vdW} = 0.37$ nm for o-terphenyl is within the calculated range of $\xi(T_A)$, suggesting that the magnitude of cooperative size calculated herein is reasonable. This result $\xi(T_A) = r_{vdW}$ appears to be general [29].

The length scale for cooperative motion has been estimated from measurements of probe diffu-
sion and rotation. At $T_g + 10$ K this method agrees quantitatively with 4-D NMR and also provides a measure of the cooperative size at higher temperatures. This length decreases as temperature is raised and adopts the van der Waals radius of the glass-forming liquid above $T_A$. The size of the slow regions exhibits the temperature dependence expected by dynamic scaling for the largest cooperatively moving (fast) regions, suggesting that there is only one important length scale in this problem. This makes sense because cooperative sizes need not grow any larger than the size of the slow regions.

Despite the fact that the cooperative volume is fractal instead of space-filling, the essential features of the Adam-Gibbs model [1] are correct. The cooperative size does indeed grow rapidly as temperature is lowered below the caging temperature. Over a temperature range extending from $T_A$ to $T_g$, $\xi$ of o-terphenyl has been observed to increase by an order of magnitude from the van der Waals radius of each molecule, making the insight of Adam and Gibbs particularly noteworthy.

We thank the National Science Foundation (DMR-0422079) for funding and S.K. Kumar for discussions.

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