Temperature Dependence of Characteristic Length for Glass Transition

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The temperature dependence of the characteristic length for the dynamic glass transition in ortho-terphenyl is determined, for the first time, from combined results of depolarized dynamic light scattering, photon correlation spectroscopy, and viscosity experiments. The length is found to vary according to $\xi_a \sim (T-T_\infty)^{-\nu}$, where T_∞ is the Vogel temperature, with an exponent $\nu = 0.69 \pm 0.06$ in the temperature region from T_g up to T_g+80 K.

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The glass transition is at present a central problem of condensed-matter physics [1,2]. There is no generally accepted theory of it, and computer simulation cannot as yet overcome the time gap between the integration step of Newton's equation (10^{-14} s) and the scale of a real glass transition ($\tau \gtrsim 10^{-6}$ s). Three theoretical approaches can be distinguished. (i) A dynamic singularity at a critical temperature T_c far above the conventional glass temperature T_g is supposed by mode coupling theory [3]. (ii) Following prior work [4–6] there is a search for an underlying phase transition at the Vogel temperature T_∞ [7], far below T_g. (iii) A fluctuation theory directly referring to cooperativity and Williams-Landel-Ferry (WLF) scaling covers the whole region between T_g and the breakdown of cooperativity at a temperature T_s ($\approx T_c$) [8].

The cooperativity concept, generally accepted to be essential, requires a characteristic length ξ_a. Both the phase-transition and the fluctuation approach predict a length according to

$$\xi_a \sim (T-T_\infty)^{-\nu} \tag{1}$$

with $\nu = 2/d$ ($=2/3$ in $d=3$ dimensions). Using fluctuation theory formulas the characteristic length at T_g was estimated from calorimetric data of the transformation interval to be $\xi_a = 1$–2 nm [9]. There are also other indications for this order of magnitude: sensitivity of the glass transition to the thickness of the amorphous layers in semicrystalline polyethyleneterephtalate [10], and a sharp increase of viscosity and shear modulus of liquids in thin layers [11].

The size of a cooperative region, $V_a \approx \xi_a^3$, affects the viscosity η of a glass-forming liquid. Therefore in the following a method is proposed to determine ξ_a from a comparison of η with reorientational relaxation times τ_{DLS} (from depolarized light scattering, DLS).

There is a well-known relation, originally suggested for dilute solutions, between τ_{DLS} and η, the Stokes-Einstein-Debye formula [12]

$$\tau_{\mathrm{DLS}} = V_h \eta / kT + \tau_0 , \tag{2}$$

with k the Boltzmann constant, τ_0 a time constant of the order of picoseconds, and V_h the so-called hydrodynamic volume of the order of the volume of one molecule. Rössler [13] pointed out that Eq. (2) is not valid for the dynamic glass transition. A significant deviation from Eq. (2) in a $\ln(\tau/\eta)$ vs T^{-1} plot below T_s is also observed [14] in ortho-terphenyl (OTP).

In Eq. (2) the relaxation time is caused by the viscosity of the liquid surrounding a given molecule. With regard to cooperativity we should leave this local picture and switch to a more thermodynamic or continuum approach. Starting from a Kubo formula, the viscosity is determined by the time correlation of shear stress [15], which implies a correlation time τ_K [see Eq. (6) below] and a correlation length ξ_K,

$$\eta = (kTV)^{-1} \lim_{q\to 0} \int \langle \sigma_q^{xz}(t) \sigma_q^{xz}(0) \rangle dt , \tag{3}$$

where σ_q^{xz} is the spatial Fourier component of the shear stress fluctuation. The aim of this paper is to explain the experimental results with the postulate that this correlation length determines the characteristic length of the dynamic glass transition, $\xi_K = \xi_a$.

For this purpose we must connect τ_K with the light scattering experiment [16,17]. The xz dielectric tensor fluctuation $\epsilon^{xz}(t)$ important for DLS can be related [18] to the shear angle fluctuation $\Delta\gamma(t)$. In such a continuum approach the contrast factor is given by a Pockels constant, symbolically described by $A = (\partial\epsilon/\partial\gamma)^{xz}$. The shear stress σ^{ij} in Eq. (3) is related to the shear angle γ_{ij} by a constitutive equation. For the simplest case, a Maxwell element, we have $\eta = G_0 \tau_K$, and the steady-state compliance J_e^0 is given [19] by $J_e^0 = \tau_K/\eta$. Generally, the relation between shear compliance J and $\Delta\gamma$ is given by the fluctuation dissipation theorem

$$V_a \Delta\gamma^2(\omega) = kTJ''(\omega)/\pi\omega , \tag{4}$$

where $\Delta\gamma^2(\omega)$ is the spectral density of $\Delta\gamma(t)$ in the volume V_a. Integration of Eq. (4) yields for the mean-square value of the shear angle fluctuation, $\overline{\Delta\gamma^2}$,

$$V_a \overline{\Delta\gamma^2} = kT(J_e^0 - J_g) \approx kTJ_e^0 , \tag{5}$$

with $J_g = \lim J(\tau)$ for $\tau \to 0$, and assuming $J_g \ll J_e^0$.

Since [20]

$$J_e^0\eta=\int dt\,tG(t)\Big/\int dt\,G(t)=\tau_K\,, \tag{6}$$

from Eqs. (5) and (6) we obtain

$$V_a\overline{\Delta\gamma^2}\eta/kT=\tau_K\,. \tag{7}$$

Finally we have to connect $\overline{\Delta\gamma^2}$ with the total depolarized intensity I_{VH} of light scattering. The dependence of the DLS on the correlation volume V_a is expressed by

$$I_{VH}=KA^2\overline{\Delta\gamma^2}V_a^2\,, \tag{8}$$

where K is a constant. One of the factors of V_a results from the fact that I for $\mathbf{q}\cdot\mathbf{r}\ll 1$ is determined by an integral over the orientational correlation function $\varphi(r)$. Assuming scaling (also a property of the glass transition cooperativity [8]) this integral is proportional to $\xi_a^3 \sim V_a$. This can be seen from the simple example $\varphi \sim \exp(-r/\xi_a)$, $\int\varphi(r)d^3r=\text{const}\times\xi_a^3$. The other factor of V_a results from the fact that we consider the scattering from V_a as representative for the whole sample.

With these assumptions we find from Eqs. (7) and (8)

$$V_a^{-1}=KA^2kT\tau_K/\eta I_{VH}=K'T\tau/\eta\,, \tag{9}$$

where $\tau_K=\tau_{\text{DLS}}\equiv\tau$ is assumed, similarly as for the length $(\xi_K=\xi_a)$.

Experiments were carried out with ortho-terphenyl as a model substance. The details are described elsewhere [14,21]. Briefly, relaxation times are calculated either from Rayleigh depolarized scattering (0.5 ps-100 ns) measured by four Fabry-Pérot interferometers [14] or from photon correlation spectroscopy (PCS, 10 μs-100 s) [21]. The viscosity was taken from Refs. [22,23]. The total intensity I_{VH} was found to be constant ($\pm 10\%$) after density correction in the whole temperature range (250-430 K). Therefore K' in Eq. (9) can be regarded as a constant.

To determine the exponent ν in Eq. (1) we must have the Vogel temperature T_∞. The WLF fit to the PCS times (>10 μs) results in $T_\infty=186$ K, but including the suitable Fabry-Pérot data (>1.5 ns) gives $T_\infty=215$ K (Fig. 1, [14]). As the experimental exponent ν is heavily influenced by T_∞ we should try to narrow the T_∞ interval by comparison with other glass formers. The correlation is made in a X^a vs T plot with $X\equiv T\tau/\eta$ and the exponent $a=1/3\nu$, see Eq. (9) $(V_a\approx\xi_a^3)$. The X values calculated from the experiments vary from 6.4×10^{-7} K/Pa at $T_g=244$ K up to 48×10^{-7} K/Pa at $T_s=323$ K, i.e., by a factor of 7.5, large enough for a reasonable correlation. The small uncertainties of the τ determination from spectra with varying width and from the change from shear modulus G [Eq. (6)] to the longitudinal wave modulus M for DLS can surely be neglected.

The powers X^a with a series of exponents a are linearly correlated with temperature. The intersections obtained with the T axis are called $T_\infty(a)$ (see inset in Fig. 2). We obtain, for example, $T_\infty(0.6)=217$ K and $T_\infty(0.4)=186$ K. These $T_\infty(a)$ values are close to the T_∞'s from the WLF fits quoted above. The corresponding fragility parameters $F\equiv T_g/(T_g-T_\infty)$ are $F=4.2$ for $a=0.4$ and $F=9.0$ for $a=0.6$. Compared to good glass formers with high fragility [24] such as polyvinyl acetate ($F=7.5$) or 60/40 KCa nitrate ($F=7.0$), and to low fragility glass formers such as As_2Se_3 ($F=3.1$) or B_2O_3 ($F=2.7$), it seems that $F=4.2$ is too low and $F=9.0$ is too high for OTP. Supposing that F is in the range $F=5\text{-}7\equiv6\pm1$ for OTP we find that the exponent a is ranging from $a=0.44$ (for $F=5$) to $a=0.53$ for $F=7$. This corresponds to a ξ_a exponent $\nu=1/3a$ ranging from $\nu=0.63$

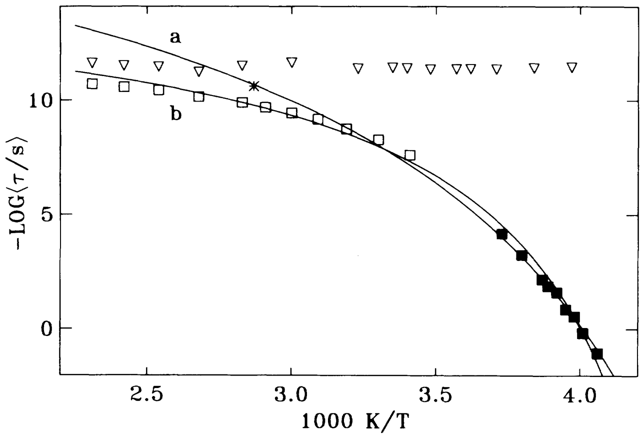

FIG. 1. WLF fits for the glass transition in OTP. All data are from light scattering. ▽, fast component; □, DLS; ■, PCS; ∗, from $\omega\tau=1$ for Rayleigh-Brillouin spectra. Curve a: Only PCS data, $T_\infty=186$ K. Curve b: Common fit for $\tau\geq1.5$ ns, $T_\infty=215$ K.

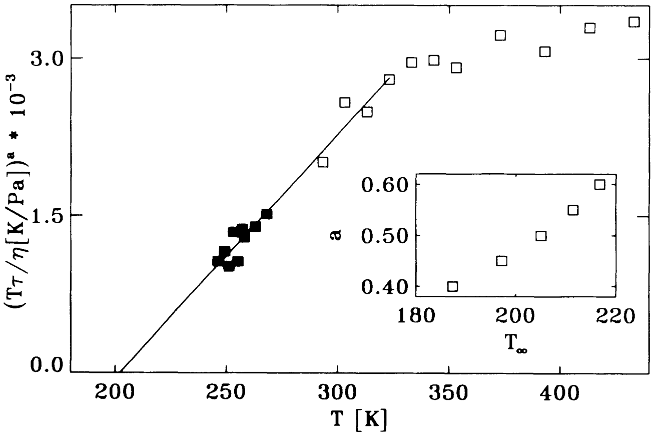

FIG. 2. Plot of X^a vs temperature T for $a=0.48$, $X=T\tau/\eta\sim V_a^{-1}$ according to Eq. (9). Above $T_s\approx325$ K the data reflect local motions. ■, from PCS; □, from DLS. Observe that the transition to cooperativity at $T_s\approx325$ K is not marked by a change of the experimental method. Inset: Extrapolated $T_\infty(a)$ as a function of the exponent a (see text).

($F=7$) to $\nu=0.76$ ($F=5$). Taking $a=0.48$, for $F=6$, we have $\nu=0.69\pm0.06$ corresponding to $T_\infty=203\pm6$ K. The X^a vs T correlation for this case is shown in Fig. 2.

An exponent $\nu=0.33$ that is sometimes connected to the Adam and Gibbs approach [25] (corresponding to $a=1$, i.e., to $V_a \sim T-T_\infty$) would imply $F\approx50$, beyond any experience.

The following are two implications of our result.

(i) Viscosity η and relaxation time τ cannot simultaneously fit the WLF equation because Eq. (9) defines a transmission function $V_aT \sim T(T-T_\infty)^{-2}$ between η and τ that will become singular at T_∞. This fact completely fits into the fluctuation theory where WLF scaling means that the relaxation modes probed by different susceptibilities or transport coefficients may be different but are nevertheless guided by a common set of $\ln(\tau)$ vs T curves (hyperbolas) with two common asymptotes, one being T_∞.

Viscosity can also be compared with the self-diffusion D [26]. The product ηD is not a constant; the function $\eta D(T)$ can also be interpreted in terms of the characteristic length [26].

(ii) The characteristic length decreases for increasing temperatures. Consequently, at some temperature T_s the cooperativity volume V_a will become too small to define cooperativity at all. Obviously this happens for OTP at about $T_s\approx325$ K in the GHz range which is in agreement with the characteristic length of a few nanometers at T_g [9]. The temperature T_s is therefore to be interpreted as the onset of cooperativity of the molecular motion; T_s is therefore the upper temperature limit of the WLF scaling.

In summary, the temperature dependence of the characteristic length for the dynamic glass transition in OTP was found from light scattering (DLS,PCS) and viscosity experiments to be in accordance with $\xi_a \sim (T-T_\infty)^{-\nu}$ with $\nu=0.69\pm0.06$ between $T_g=244$ K and $T_s=325$ K. This result corresponds to the prediction ($\nu=0.67$) of the fluctuation theory approach for the glass transition, connecting this ξ_a behavior directly with WLF scaling for $T_g<T<T_s$.

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