Observation of Scaling Behavior in the Liquid-Glass Transition Range from Dynamic Light Scattering in Poly(Propylene Glycol)

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(Received 10 December 1991)

We have performed wide-time-range photon correlation spectroscopy (PCS) on poly(propylene glycol) to probe the dynamics in the glass transition range. In addition to the primary (a) relaxation which shows stretched-exponential behavior, we observe two relaxation processes not witnessed in PCS before. They are assigned to a' and β processes and exhibit similar power-law decays. All three relaxations are analyzed in terms of recent mode-coupling theories and the inherent scaling relations are verified by independent determinations of the relevant exponents from the spectra.

At present much attention is focused on the dynamics involved in the liquid-glass transition which to some extent is due to recent progress of the mode-coupling theories (MCT) [1-4]. In experiments, the most prominent feature of the transition is displayed by the relaxation behavior just above the calorimetric glass transition temperature T_g, commonly referred to as the a process. It exhibits a time scale that increases with temperature in a fashion corresponding to that of the viscosity and becomes immeasurably long as T_g is approached. Another characteristic is its nonexponential time decay which generally obeys the Kohlrausch-Williams-Watts (KWW) relaxation function [5]

$$\phi_K(t) = A\exp\{-(t/\tau)^{\beta_K}\}, \quad 0 < \beta_K \le 1, \tag{1}$$

where the degree of nonexponentiality is expressed by the stretching parameter β_K. Of lesser prominence is the β relaxation which has been observed in several glass-forming liquids [6] and is suggested to accompany the a process in general. Its time scale is considerably shorter, does not diverge near T_g, and the β process can therefore also be observed in the glassy state. Two types of relaxation dynamics are indeed revealed by MCT, which furthermore suggests that they are strongly correlated [1-4]. Some of the specific MCT predictions have recently been verified in real glasses (for a review, see Ref. [4]). However, since the relaxation dynamics for glass formation spans the enormous time range of some thirteen decades, a major problem of the tests is the limited time window generally available in experiments. In this Letter we present observations of the structural relaxation in glass-forming poly(propylene glycol) (PPG) obtained over the wide time range of eight decades by using photon correlation spectroscopy (PCS) techniques. We demonstrate that, having available such a broad time window for the experimental relaxation function, a severe test of the scaling relations predicted in MCT can be performed.

MCT describes the coupling between the decay of density fluctuations and the viscosity by a feedback mechanism, which causes a progressive enhancement of the macroscopic viscosity η as density increases. Ultimately this leads to a critical divergence of the viscosity when the system achieves a critical density or equivalently a critical temperature T_c, described by $\eta = \eta_0(T-T_c)^{-\gamma}$. Taborek *et al.* [7] showed that a variety of liquids display such a power law and corresponding T_c values were estimated. However, it fails below some temperature, typically $T_c + 20$ K, where the viscosity increases less rapidly [7,8]. This has in more recent versions of MCT qualitatively been accounted for by including activated jump processes through the introduction of a current correlator [3].

The fastest of the two relaxation processes in MCT is identified with localized motions beyond molecular time scales and is referred to as the β relaxation [1-4]. Computer simulations suggest that it represents cooperative localized motions of a small number of molecules within a cage formed by neighboring molecules [9]. On the time scale of the β relaxation, these cages appear frozen. Therefore, instead of relaxing towards the ergodic state of the whole system, the β process relaxes to some intermediate level f^c following a power law [1-4]

$$\phi_\beta(t) = f^c + h_\beta(t/t_0)^{-a}, \quad 0 < a < \tfrac{1}{2}. \tag{2}$$

Here t_0 is a transient microscopic time and h_β is the relaxation strength. Above T_c, collective rearrangements continue to occur allowing for the eventual relaxation of the cages, i.e., the a process, by which the medium reaches the full ergodic limit. MCT predicts that the initial part of the a process obeys von Schweidler time decay, i.e.,

$$\phi_a(t) = f^c - h_a(t/\tau_a)^b, \quad 0 < b < 1, \tag{3}$$

which in this regime is essentially a first-order expansion of Eq. (1). Numerical simulations [9] indicate that von Schweidler behavior is valid for about $t \le 100\tau_a$. In MCT the β process is regarded as the precursor of the a process and the exponents a and b are closely linked. Two relations arise from scaling arguments:

$$\lambda = \frac{\Gamma(1-a)^2}{\Gamma(1-2a)} = \frac{\Gamma(1+b)^2}{\Gamma(1+2b)}, \tag{4}$$

$$\gamma = \frac{1}{2a} + \frac{1}{2b}. \tag{5}$$

Here λ is the coupling parameter which quantifies the strength of the feedback mechanism, $\Gamma(x)$ is the gamma function, and γ is given by the viscosity power law predicted in MCT.

More complicated relaxation behavior including multiple relaxation processes has also been treated by MCT [10]. PPG was then chosen for a detailed analysis and it can be used for a direct comparison with present results. We obtain three relaxation processes and assign them to α', β, and α processes, respectively, from comparisons with dielectric relaxation data of PPG [11]. We show that the MCT relations given above prove to be valid for the PPG system.

Poly(propylene glycol) of molecular weight 4000 (Polysciences) was dried, filtered (Millipore, 0.22 μm), and loaded into an optical cuvette. The temperature was controlled with an accuracy of ± 0.3 K. The 488-nm line of an argon-ion laser was used for excitation. The correlator (ALV 3000) employs a pseudologarithmic time base to achieve a wide time range (10^{-6} to 10^2 s) of the autocorrelation function in a single run. This improves enormously upon linear correlators which are limited to about two decades. The symmetrical normalization procedure described in Ref. [12] has been used. Experimental details are given elsewhere [13].

The intensity autocorrelation function was measured at temperatures ranging from 132 to 263 K ($T_g = 200$ K). It is related to the relaxation function $\phi(t)$ by $\sigma\phi^2(t) = \langle I(0)I(t)\rangle/\langle I\rangle^2 - 1$, where σ represents the spatial coherence factor. $\langle I\rangle^2$ is taken as the constant background level obtained in the long-time limit of the spectrum. Results for $\sigma\phi^2(t)$ obtained above T_g are summarized in Fig. 1(a). It is evident that upon increasing temperature the relaxation decreases in strength and shifts towards shorter times. For $T > 260$ K it is no longer detectable. In the range 208–215 K, the spectra are highly nonexponential and well fitted by Eq. (1) using a stretching parameter β_K of 0.39 ± 0.03; see Fig. 1(b). This is in agreement with reported β_K data for the α process in PPG [14–16] as is also the obtained relaxation times and their temperature dependence [11,14–16]. As temperature increases the form of the relaxation curve is changed and a long-time tail is revealed; see Fig. 1(a). This is even more obvious in Fig. 1(b) which displays two distinctly different stretching parameters, $\beta_K \approx 0.39$ and $\beta_K \approx 0.20$ for the short respectively long-time regime. Moreover the figure shows that the crossover in the dynamics is shifted with temperature; $\beta_K \approx 0.39$ is dominating the probe window at lower temperatures and $\beta_K \approx 0.20$ at higher temperatures. Such a drastic change in β_K can hardly be attributed to the α process, as present views favor either a temperature-independent β_K or else $\beta_K \rightarrow 1$ upon heating [17–20]. For PPG the stretching parameter of the α process is reported to be constant [14–16,18]. We therefore conclude that the long-time tail is not a feature of the α relaxation but is of different
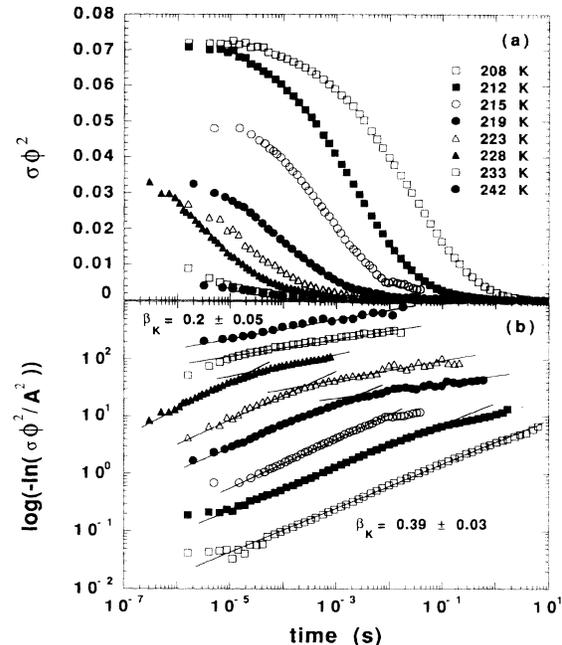

FIG. 1. (a) Autocorrelation function $\sigma\phi^2(t)$ of PPG 4000 from 208 to 242 K; (b) normalized autocorrelation function ($\sigma\phi^2/A^2$) in a Kohlrausch representation (double log vs log) displaying crossover in β_K. Beginning with 212 K, the spectra are shifted for clarity by consecutive factors of 2.

origin.

To investigate this tail in detail the spectra recorded at the highest temperatures are plotted in the double logarithmic plot in Fig. 2(a). The adherence of the spectra to Eq. (2) suggests an interpretation in terms of the β relaxation. This is, however, in conflict with the MCT picture of β being assigned to the shorter-time dynamics within the molecular cages, noting that the process in Fig. 2(a) is observed at *longer* times than that of the α. A more probable explanation is that the long-time tail is the precursor of the α' process associated with the diffusional motion of single polymer chains [11]. The relaxation time range is indeed consistent with dielectric observations of the α' process.

As T_g is passed the measurements reveal the freezing out of the α relaxation and the appearance of a new relaxation process at short times. Close to T_g both processes were observed [see inset of Fig. 2(b)]. The short-time process was detected down to the lowest temperature measured, 135 K. For the measurements well below T_g the time averaged scattered intensity was observed to vary randomly, within $\pm 10\%$, with the position of the scattering volume in the sample, i.e., the time averaged and the ensemble averaged correlation function are different. Thus, the system is nonergodic at these temperatures. The shape of the relaxation function observed well below T_g was, within the experimental accuracy, in-
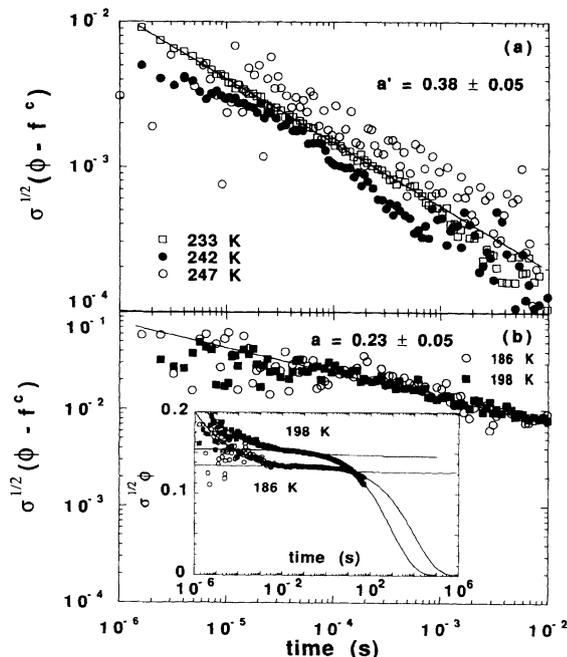
FIG. 2. Log-log plot of the autocorrelation function $\sigma^{1/2}\phi(t)$ of PPG with the nonergodic level f^c subtracted out as described in text; (a) data obtained at 233, 242, and 247 K; (b) data below T_g. Solid lines represent linear fits. Inset: $\sigma^{1/2}\phi(t)$ obtained at 198 and 186 K.
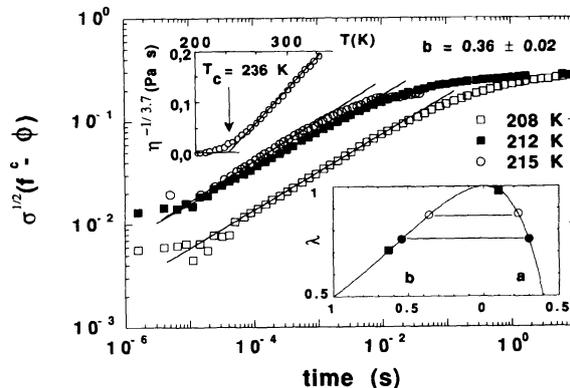

FIG. 3. Plot of $\sigma^{1/2}[f^c - \phi(t)]$ for spectra of PPG collected at 208, 212, and 215 K displaying the short-time von Schweidler decay, Eq. (3), with $b = 0.36 \pm 0.02$. Top inset: Viscosity data [21] in a power-law representation with $\gamma = 3.7$. Bottom inset: Graphical representation of the coupling parameter $\lambda(a,b)$. Present PPG data (O) and data from Lennard-Jones systems ($\bullet$,$\blacksquare$, Ref. [2]) are shown.

dependent of temperature and the detected scattered volume. (This is at present the subject of a detailed study.) Dielectric loss measurements [11] report a relaxation process present below T_g in this same time range and it is attributed to cooperative motions occurring on the local scale, i.e., to the β relaxation. It is found to be more distributed than α, having a FWHM of about four decades which corresponds to $\beta_K \sim 0.25$ in accordance with present observations. Thus we assign the dynamics below T_g to β relaxations.

Having identified the three types of relaxation dynamics we proceed to compare with MCT predictions, starting with the shortest time process, the β process. The spectrum obtained at 198 K is analyzed since it represents the required ensemble averaged correlation function (the experimental time t_{exp} is $> 100\tau_a$). The data are shown in a log-log plot in Fig. 2(b) with the nonergodic level f^c, determined from a KWW fit of the α process [see inset of Fig. 2(b)] subtracted out. The data adhere to a power law [Eq. (2)] with $a = 0.23$ over approximately three decades of time. The 186-K spectrum is found to closely follow the same power law [see Fig. 2(b)] after subtraction of a nonergodic level. Note, however, that at 186 K the ensemble averaging is less complete ($t_{exp} \approx 4\tau_a$). Next we turn to the α relaxation and the range 208–215 K where it is dominating; see Fig. 1(a). We analyze its initial decay in terms of Eq. (3) assuming that

the top of the spectrum is a sufficient approximation of f^c. The exponent b is obtained from a plot of $\sigma^{1/2}[f^c - \phi(t)]$; see Fig. 3. von Schweidler relaxation is apparent over about the first three decades but fails at longer times as anticipated by MCT. The data correspond to an exponent $b = 0.36 \pm 0.02$. For the relaxation observed at high temperatures, attributed to the precursor of the α' process, the double log-log plot of Fig. 2(a) results in the exponent $a' = 0.38 \pm 0.03$ (the prime refers to the α' process), assuming the background level to be the f^c level. We conclude that the time decay of all processes —β, α, and α'—are well described by the functional forms of MCT.

Next, we turn to the conditions which the exponents a and b must satisfy, see Eqs. (4) and (5). The exponents are, within the experimental accuracy, temperature independent in accordance with MCT. In the inset of Fig. 3 we show a graphical representation of (a,b) solutions to Eq. (4) together with our results and data from Lennard-Jones and hard-sphere systems taken from the literature. It can be seen that the present values of a and b satisfy Eq. (4) remarkably well. Then we use our measured exponents to obtain $\gamma = 3.7 \pm 0.8$ from Eq. (5) and test this value as exponent in the power-law representation of viscosity data [21]. Figure 3 (inset) shows excellent agreement and gives $T_c \approx 236$ K. Finally we compare our findings with recent MCT analysis of the α, α' scenario for PPG. Using a three correlator model, Fuchs et al. [10] fitted dielectric data of Johari [11] and obtained $\lambda = 0.865 \pm 0.01$ and $b = 0.37 \pm 0.01$. Then from Eq. (4) they obtain $\gamma = 3.54$ and show that the time scale of the α relaxation exhibits the expected power-law behavior ($T_c = 236$ K) for temperatures above 255 K. Thus the exponents are in good accordance with the present re-

sults.

In summary, we have presented the first PCS observations of power-law relaxations in glassy dynamics. The results show that the relaxation behavior is well represented by the power-law forms suggested by MCT. Whereas in previous investigations [5,22,23] generally only one of the scaling exponents has been determined and one must rely on the MCT scaling relations to obtain the other, the strength of the present study is that both exponents are measured independently. Although all the exponents satisfy the specific conditions of the theory, it is remarkable that there is no sign of any anomalies as T_c is passed in the temperature dependence of the correlation function. Thus the significance of T_c remains unclear.

The success of MCT to describe the present system is based on the time-temperature superposition principle (i.e., constant exponents) holding for the relaxation dynamics of PPG. Dielectric relaxation measurements show that although this is the case for some polymers [18], for several glass-forming low-molecular-weight liquids β_K increases continuously with temperature [17,18] in the supercooled regime. Recent developments of MCT are introducing activated jump-diffusion processes to approach the region $T < T_c$. Then the formalism is changed such that for $\lambda > \pi/4$ exponent b takes a value of 0.5 below T_c, whereas exponent a changes according to γ. This is, however, not observed for PPG. To see whether such an approach can explain the more complicated relaxation behavior of the low-molecular-weight liquids, for which the dynamics in the supercooled regime may indeed be dominated by jump diffusion, remains to be answered. Noting the richness of relaxation behavior in experimental glass formers, we still believe that the present study show that new insights of glass formation in real systems can be gained using idealized mode-coupling theories.

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