Removal of cooperativity in glass-forming materials to reveal the primitive α-relaxation of the coupling model

Removal of cooperativity in glass-forming materials to reveal the primitive α-relaxation of the coupling model

K L Ngai

Naval Research Laboratory, Washington, DC 20375-5320, USA

Abstract. The microscopic short time dynamics of glass-forming materials seen by quasielastic neutron scattering, dynamic light scattering, high frequency dielectric relaxation and molecular dynamics simulation in the picosecond region show the existence of the primitive relaxation, $\exp(-t/\tau_0)$, for $t < t_c$, where $t_c \approx 2$ ps is the cross-over time of the coupling model. However, such an interpretation is not unique because the same data have also been considered to be evidence of the fast β-relaxation of the model coupling theory. An apparently unique test of the coupling model is via the macroscopic long time relaxation data of *ortho*-terphenyl confined in nanometre glass pores with a size that is smaller than the length-scale of cooperative motions of the molecules. Under this condition, motions of the majority of the molecules cease to be cooperative and the experimentally observed relaxation time is the primitive relaxation time, τ_0, of the coupling model. On the other hand, τ_0 can also be obtained from relaxation data of *bulk ortho*-terphenyl fitted to a stretched exponential correlation function, $\exp[-(t/\tau)^{1-n}]$, by the relation $\tau = [t_c^{-n}\tau_0]^{1/(1-n)}$ of the coupling model. Good agreement found between these two independently determined values of τ_0 provides strong support of the coupling model. A similar test of the coupling model is to compare the Johari–Goldstein β-relaxation time, τ_β, with the calculated τ_0 at temperatures above the glass transition temperature. Both the β-relaxation and the primitive relaxation time being non-cooperative in nature implies that τ_β is comparable in order of magnitude to that of the calculated τ_0, which is shown to be true for the fragile glass-former *ortho*-terphenyl as well as a non-fragile glass-former, cyclo-octanol.

1. Introduction

The coupling model (CM) [1, 2] is a general approach to relaxation and diffusion in systems wherein the basic units are constrained by mutual interactions. Its predictions have been shown to be applicable in depth to many problems of relaxation in different materials [3, 4]. Interaction between relaxing units implies some degree of 'cooperativity' between their movements is necessary in order for the entire system to relax. 'Cooperativity' is a vague concept used by different people in not necessarily exactly the same way. In the context of the CM, it is used to convey all the effects that the many-body interactions have on relaxation. Recent versions of the coupling theory are based on classical mechanics for systems that exhibit chaos caused by the anharmonic (nonlinear) nature of the interactions between the basic molecular units [2]. Examples include (i) intermolecular interaction between monomer units in polymers and small molecules in a glass-forming van der Waals liquid customarily modelled by the Lennard-Jones potential; (ii) the entanglement interaction between polymer chains; (iii) Coulomb interaction between ions in glass-forming electrolytes including the much studied $0.4\text{Ca(NO}_3)_2 \cdot 0.6\text{KNO}_3$ (CKN) and (iv) hard-sphere-like interaction between colloidal particles [1]. The interactions in these examples are all highly anharmonic and they give rise to chaos in the Hamiltonian

dynamics of the systems [5]. If one is looking for a fundamental approach to relaxation in these interacting Hamiltonian systems, the effects of chaos should not be overlooked. Although a rigorous theory based on first principles is still missing, there are theoretical results supporting the basic results of the CM proposed nearly two decades ago [1]. The results were obtained so far by simple models [2], but the fact that manifestation of the effect of chaos is usually general leads us to expect that the behaviour found in simple systems does carry over to real materials. The fundamental results of the coupling theory, which have remained unchanged since its inception 15 years ago, are restated here as follows. There exists a temperature insensitive cross-over time, t_c, before which ($t < t_c$) the basic units relax independently with correlation function,

$$\phi(t) = \exp\left(-\frac{t}{\tau_0}\right) \tag{1}$$

characterized by the independent (primitive or non-cooperative) relaxation time, τ_0, and afterwards ($t > t_c$) with a slowed-down non-exponential correlation function. A particularly convenient function, which is compatible with both computer simulations and experimental data, is the Kohlrausch–Williams–Watts (KWW) function [6, 7],

$$\phi(t) = \exp\left[-\left(\frac{t}{\tau}\right)^{1-n}\right] \tag{2}$$

where n is the coupling parameter whose value lies within the range $0 \leqslant n < 1$ and depends on the intermolecular interaction. What distinguish the CM from other models that may also have the simple exponential decay at short times and later a slowed-down decay is that in the other models the cross-over time t_c is strongly dependent on temperature. On the other hand, t_c of the CM is the onset of chaos, which is determined by the interactions and its magnitude is insensitive to change in temperature. The existence of a rather sharp cross-over from equation (1) to equation (2) has been shown for simple Hamiltonian models that exhibit chaos [2]. Realistically the cross-over occurs over a small neighbourhood about t_c, where the actual relaxation function $\phi(t)$ changes from the exponential function smoothly over to the KWW function, preserving continuity of the function and its derivatives. When the width of the neighbourhood is small as suggested by results of simple models, the approximate continuity of the two pieces of the correlation function at $t = t_c$ leads to the important relation

$$\tau = [t_c^{-n}\tau_0]^{1/(1-n)} \tag{3}$$

which links the effective (i.e. after cooperative dynamical constraints between the relaxing molecular units have been taken into account) relaxation time, τ, to the primitive (i.e. without taking into account of the cooperative dynamical constraints) relaxation time, τ_0.

There are also experimental data that support this basic premise of the CM. Experimental evidence for the existence of such a cross-over at a time $t_c \approx 2$ ps, for molecular systems comes from quasi-elastic neutron scattering measurements in poly(vinylchloride) (PVC) [8], poly(isoprene) (PI) and polybutadiene (PB) [9] performed at temperatures high above T_g where τ_0 becomes short and of the order of 10 ps or less. Under this condition, the primitive α-relaxation decaying linearly exponentially is directly evident from the relaxational part of the experimental data. There are also evidences for the cross-over at $t_c \approx 2$ ps from (a) analysis of molecular dynamics data of ortho-terphenyl (OTP) [10], (b) high frequency dielectric measurement of a molten salt such as CKN [11], (c) molecular dynamics simulations [12, 13] and neutron scattering experiments [13] performed in polyethylene, (d) molecular dynamics simulation data of polystyrene [14], (e) high frequency dielectric measurements for glassy and non-glassy ionic conductors [15, 16] and (f) d.c. conductivity measurements of glassy and crystalline ionic conductors up to high temperatures where the conductivity relaxation time

is of the order of a picosecond or less [17]. For motion of small molecules in van der Waals liquids [10] and diffusion of ions in ionic glasses and melts [11, 15–17], such a cross-over has been observed by various experimental techniques to occur at $t_c \cong O(1\ ps)$. In all these high temperature, short time relaxation data, the observed primitive relaxation time, τ_0, has the characteristics of independent motion. These characteristics include the Q^{-2}-dependence found in neutron scattering, where Q is the momentum transfer, and the size of the activation enthalpy, which corresponds to the conformation energy barrier of a single chain for a polymer.

In this work I look into the long time dynamics of glass-formers and find from them other evidence for the primitive relaxation process and the veracity of $t_c \simeq O(1\ ps)$ in the CM. However, when considering relaxation phenomena of molecular systems occurring at macroscopically long times (i.e. when $(\tau/t_c) \gg 1$), the condition $\tau_0/t_c \gg 1$ holds by virtue of equation (3). As a result, the linear exponential $\exp(-t/\tau_0)$ has decayed by an insignificant amount at $t = t_c$, and the correlation function $\phi(t)$ is practically given at all times by $\exp[-(t/\tau)^{1-n}]$ which can be obtained experimentally. There is no opportunity of observing $\exp(-t/\tau_0)$. Consequently one cannot locate τ_0 and verify whether the basic equation (3) holds or not for a $t_c \cong O(1\ ps)$ previously deduced from short time dynamics data, even though τ and n have been obtained from the experimental data. The purpose of this work is to show that there are ways to remove the cooperativity in the long time dynamics of glass-forming materials, either partly or entirely. Removal of cooperativity corresponds to a reduction of n in the CM. When cooperativity is totally removed, n is exactly zero, equations (1) and (2) become one and the same and equation (3) collapses to become

$$\tau = \tau_0. \tag{4}$$

Thus the primitive relaxation is revealed directly by the experimental data. This direct determination of τ_0 can be compared with its value deduced indirectly from the basic equation (3) of the CM with a $t_c \cong O(1\ ps)$ for the normal situation of a bulk glass-forming material in which n is non-zero. In this manner, the key prediction, equation (3), of the CM can be either falsified or verified.

2. Removal of cooperativity in *nano*-pores

2.1. Interpretation of experimental data

By confining a small molecule glass-forming liquid in nanometre size pores to reduce its dimension [18–26], it is possible to remove partly or totally the intermolecular constraints or cooperativity of structural relaxation in the bulk materials. There are complications encountered sometimes in these studies caused by the modification of the surface layers of the liquid near the substrate or the confining material by chemical bonding. However, when this complication is either eliminated or taken into consideration, the dynamics of the liquid with reduced dimension are found to speed up compared with the bulk material at the same temperature [18–26]. A consequence of this change is that the glass transition temperature falls with reduced dimension. The experimental study by Jackson and McKenna on *ortho*-terphenyl has concluded that a reduction in density or a negative pressure effect is not the cause of the observed change. Several workers [19, 22, 25–27] have proposed that the principal cause of this effect is the reduced size d of the confined glass-former which limits the growth of the temperature dependent cooperative length-scale [28–31], $L(T)$, and thereby suppresses the cooperativity of the molecular motions. Some estimates of the size of $L(T)$ has been given by several authors [29, 30]. A recent determination of $L(T)$ at temperatures near T_g of a small molecule glass-former has located it to be in the range of 15–20 Å [31], comparable to

the smallest pore size. Although this way of interpreting the effect may be correct, it must be pointed out that cooperative length-scale is only one consequence among many of the molecular dynamics of glass-forming liquids. Thus, it would be more basic and more profitable, as we shall see, to address the problem from some theory or model of the molecular dynamics instead of just invoking the argument that $L(T)$ becomes limited by the pore size, d. The latter can only predict a shift of the glass transition to lower temperatures but not the magnitude of the shift.

Experimental investigation of molecular dynamics of *ortho*-terphenyl (OTP) confined in nano-pores of porous glass with pore sizes of 2.5, 5.0 and 7.5 nm and a narrow pore size distribution was carried out by Ruths *et al* [32, 33]. The α-relaxation of OTP in the nanopores was probed in the time range of $10^{-6} \leqslant t \leqslant 10^{2.5}$ s by photon correlation spectroscopy (PCS) and the frequency range of 10^4 GHz $> f > 10^{-1}$ GHz by Fabry–Pérot interferometry (FPI). Details were given in the PhD Thesis of Ruths [32] and will be reported in the open literature by Ruths *et al* [33]. In this work, we are interested only in their results of OTP in nano-pores with inner surfaces that have been chemically treated to replace the –OH groups on the glass surface with trimethylsilyl groups. The coupling model will be used to interpret the data as well as to provide an estimate of the maximum reduction in the relaxation time possible when cooperativity is totally suppressed in the smallest pores.

Measurements in bulk OTP were made also using the same techniques [32, 33] and they are in good agreement with the more extensive results obtained previously by Steffen *et al* [34, 35] in the same laboratory. The published α-relaxation data of bulk OTP by Steffen *et al* have been fitted by the Kohlrausch–Williams–Watts (KWW) function,

$$\phi_b(t) = \exp\{-(t/\tau_b)^{\beta_b}\} \tag{5}$$

where the suffix b is used to indicate the bulk OTP quantity. The bulk OTP data used later on in this work, i.e. the values of τ_b and β_b at different temperatures, can be found in [34] and [35]. The dependence of τ_b on temperature is depicted as filled circles in the Arrhenius plot of $\log(\tau_b)$ against reciprocal temperature in figure 1.

Ruths *et al* found that the PCS data of the α-relaxation of OTP in nanometre pores with pore size equal to d (= 7.5, 5.0 and 2.5 nm) can also be fitted by the KWW functions,

$$\phi_d(t) = \exp\{-(t/\tau_d)^{\beta_d}\} \tag{6}$$

where the suffix d indicates quantities of OTP in pores of size d. The FPI susceptibility $\chi''(\omega)$ data of the α-relaxation of OTP in nanopores taken at higher temperatures and frequencies were fitted to the Cole–Davidson form [36] and then the KWW function whose Fourier transform approximates also the data well is obtained from the result given by Lindsay and Patterson [37]. The values of $\tau_d(T)$ obtained at a number of temperatures over a broad temperature range and for the three different pore sizes are shown in figure 1. Bulk OTP may be considered as being confined in a pore with exceedingly large d, and its relaxation data are now discussed altogether with the rest. At the same temperature, $\tau_d(T)$ decreases with the confining pore size d. The decrease is more dramatic at lower temperatures. A change of six orders of magnitude from the bulk relaxation time can be seen in figure 1 for OTP confined in 2.5 nm pores at the lowest temperature of measurement. The value of $\beta_d(T)$ is slightly smaller than $\beta_b(T)$, reflecting that the dispersion of the α-relaxation of OTP in nanopores is a little broader than bulk OTP. These changes of relaxation time and dispersion with d are consistent with dielectric data of other small molecule glass-forming liquids confined in pores [21, 22, 25, 26]. The dynamic light scattering by Ruths *et al* reveals a very different temperature dependence of $\beta_d(T)$ compared with that of $\beta_b(T)$. In contrast with the trend $\beta_b(T) \rightarrow 1$ at higher temperatures when $(2\pi\tau_b)^{-1}$ is in the GHz range (see [34] and [35]), $\beta_d(T)$ remains significantly smaller than 1 [32, 33]. In fact, for $d = 2.5$ nm, $\beta_d(T)$ has the value of about 0.50 and is almost temperature
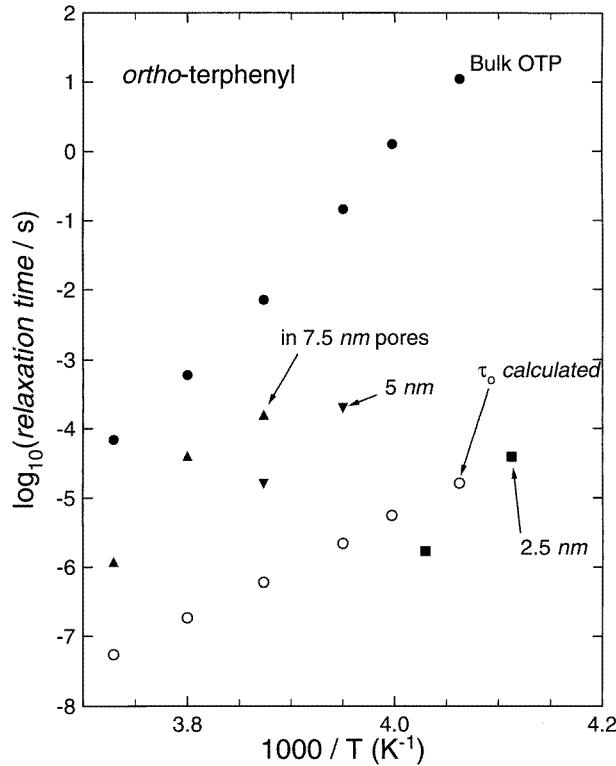
Figure 1. Temperature dependencies of the various relaxation times of OTP. Filled circles are τ_b for bulk OTP from photon correlation spectroscopy data of Steffen *et al*; open circles are the primitive relaxation times τ_0 of bulk OTP calculated by equation (8). The photon correlation spectroscopy relaxation times measured by Ruths *et al* on OTP confined in 7.5 nm pores (▲); 5.0 nm pores (▼); 2.5 nm pores (■).

independent in the entire range $10^{-10} < \tau_d(T) < 8 \times 10^{-5}$ s of the measured $\tau_d(T)$. These contrasting temperature dependencies of β_d and β_b are interpreted here as consequence of the dispersion of the α-relaxation of OTP in 2.5 nm pores at all temperatures being caused by the spatial heterogeneity of the molecular dynamics of the confined liquid inside the pore. The measured dispersion of OTP in 2.5 nm pores is not contributed to any significant extent by the inherent cooperative or coupled molecular dynamics, which also gives rise to dynamic heterogeneity [38]. Spatial heterogeneity occurs naturally for a small 2.5 nm droplet because we are bound to have molecules closer to the surface that are freer to move than others. The reasoning behind this interpretation is as follows. In the bulk liquid, the sole contribution to the dispersion is from the inherent cooperative or coupled molecular dynamics. At high temperatures, cooperativity (i.e., coupling) tends to vanish in bulk OTP consistent with the observed dispersion narrowing to nearly a linear exponential (Debye) function of time at high temperatures (i.e., $\beta_b(T) \rightarrow 1$, see [34] and [35]). The same is expected for OTP confined in pores. Therefore, the fact that β_d is almost temperature independent and maintains the same value of about 0.50 at all temperatures indicates that the dispersion observed in OTP confined in 2.5 nm pores is entirely contributed by spatial heterogeneity. From this argument, we are led to the conclusion that, when OTP is confined in 2.5 nm pores, cooperativity or the coupled nature of the molecular dynamics becomes negligible (i.e., decoupled) at all

temperatures. This conclusion is applied in the following subsection. It must be pointed out that, unlike in photon correlation spectroscopy, the deduction of the α-relaxation time and dispersion from FPI data of OTP involves a more complicated procedure of removing other light scattering contributions to the spectrum [34, 35]. Therefore emphasis is placed on the photon correlation spectroscopic data at lower temperature of bulk OTP and OTP in pores which are relatively free of uncertainty in determining $\tau_0(T)$, and they exhibit the largest difference between the bulk OTP relaxation time, $\tau_b(T)$, and the relaxation time of OTP confined in pores, $\tau_d(T)$.

2.2. Decoupling of the molecular dynamics in nano-pores

We have seen in the previous subsection that one can rationalize the reduction of relaxation times and the downward shift of the glass transition temperature of OTP confined in nanopores by invoking the argument that the cooperativity length-scale, $L(T)$, becomes comparable with d, the size of the pore. However, as we have said, this argument alone cannot predict the magnitude of the shift. Also, there could be other factors contributing additionally or even completely to this effect observed. One possible factor is that the density of OTP in the pores may be less than the bulk. Thus, one can see the limitations of interpretation based on the length-scale argument alone without recruiting any model that can calculate the change independent of the cause of the effect.

The coupling model will now be used to estimate the maximum reduction in the relaxation time possible when cooperativity is totally suppressed in small pores. The advantage of the coupling model is that it is general and applicable in the present problem independent of how the degree of cooperativity of molecular dynamics is decreased when confined in nano-pores. The cause of the decrease can come from either the small pore size limiting the number of neighbouring molecules participating in the cooperative motions or by the increase in specific volume if the density of the liquid in the pore were indeed lower than the bulk. Regardless of how the reduction of intermolecular cooperativity comes about, in the context of the coupling model it is modelled by a decrease of the coupling parameter of the glass-former in the pore, $n_d(T)$, from the bulk value $n_b(T)$ at any temperature.

When applied to bulk OTP, the right-hand side of equation (2) of the CM is appropriately denoted by $\exp[-(t/\tau_b)^{1-n_b}]$. The parameters $\tau_b(T)$ and $n_b(T)$ can immediately be identified with the corresponding quantities in equation (5), which were obtained from the fits to the experimental data [34, 35]. Therefore,

$$1 - n_b = \beta_b \tag{7}$$

and applying equation (3),

$$\tau_b = [t_c^{-n_b}\tau_0]^{1/(1-n_b)}. \tag{8}$$

With the values of $\tau_b(T)$ and $\beta_b(T)$ known and $t_c \approx 2 \times 10^{-12}$ s, equations (6)–(8) enable the primitive (i.e. totally decoupled or without intermolecular cooperativity) relaxation time, $\tau_0(T)$, to be calculated from the relaxation data, $\tau_b(T)$ and $n_b(T)$, of the bulk material. The values of $\tau_0(T)$ are shown as open circles in figure 1. When totally devoid of intermolecular coupling or cooperativity, the coupling parameter n_b is exactly zero and the result, $\tau_b(T) = \tau_0(T)$, follows from equation (8). Thus, the values of $\tau_0(T)$ calculated would be the measured relaxation times of OTP at the respective temperatures, had there been a way to remove the intermolecular coupling totally in the measurement. They provide a theoretical upper bound of the maximal reduction of relaxation times of OTP possible by eliminating intermolecular cooperativity.

Conceptually, from the argument based on the comparison between pore size and cooperative length-scale, one is led to expect that the intermolecular coupling will be mitigated as the pore size is decreased. From the discussion of the dispersion of the dynamic light scattering spectra of Ruths *et al* in the previous section, we are even more assured that cooperativity of the molecular dynamics of OTP indeed becomes negligible when confined in 2.5 nm pores. This conclusion is further supported by the good approximate agreement at two temperatures, 248.15 and 243.15 K, between the calculated relaxation time $\tau_0(T)$ and the relaxation times $\tau_d(T)$ measured by photon correlation spectroscopy in 2.5 nm pores (see figure 1). Ruths [32] did not give any estimate of error in the values of $\tau_d(T)$ that he obtained from photon correlation spectroscopy. At $T = 248.15$ K, $\langle\tau_d\rangle$ is equal to 3.4×10^{-6} s, which is close to the shortest time limit of his correlator of about 8×10^{-7} s. Thus one can expect significant error can be involved in the determination of τ_d at $T = 248.15$ K, and the departure of τ_d from τ_0 by roughly a factor of three in figure 1 could well be within the experimental error. Also, one has also to bear in mind that there is also some uncertainty, ± 0.02, in the value of β_b of bulk OTP obtained by Steffen *et al* [34, 35] that I use to calculate $\tau_0(T)$. Within experimental error, we may conclude that there is good agreement between the calculated $\tau_0(T)$ and the experimental $\tau_d(T)$ for OTP confined in 2.5 nm pores. At $T = 243.15$ K, the ratios $\tau_0(T)/\tau_b(T)$ and $\tau_d(T)/\tau_b(T)$ have about the same value of approximately 10^{-6}. There is a six orders of magnitude reduction of the bulk OTP relaxation time at 243.15 K caused by decoupling of the molecular dynamics of OTP when it is confined in 2.5 nm pores, and this change is correctly predicted by the primitive relaxation time of the coupling model. In other words, the measurable decoupled relaxation of OTP confined in 2.5 nm pores is almost a realization of the primitive relaxation process in bulk OTP of the coupling model.

3. Reduction of cooperativity by confining high molecular weight polymer in ultra-thin film

A possible mechanism of reduction of cooperativity in polymeric glass-formers, with a high molecular weight and a large end-to-end $\langle r \rangle$, is the induced orientations of the polymer chains when confined in an ultra-thin film of thickness h less than $\langle r \rangle$. The polymer chains that have acquired some orientations in the plane of the film are forced toward a nematic parallel chain structure and motion of parallel chain segments in the chain backbone direction see a smaller occupied volume. Oriented chains compared with Gaussian chains in the bulk therefore have reduced intermolecular constraints imposed on the local segmental motion [39]. The reduction of intermolecular constraints increases with decreasing film thickness and is expected to be dependent on the location of the chain segments. Polymer chain segments located at distances closer to the surfaces than the cooperative length-scale, $L(T)$, will have fewer other chain segments with which to cooperate, resulting in a reduction of intermolecular constraints. The removal of cooperativity in thin free-standing polystyrene films [40, 41] has been modelled in the coupling model by a reduction of the coupling parameter from the bulk value, as in the case of confinement of OTP in nano-pores. Although the coupling parameter of the 23.4 nm thin PS film is not reduced to zero value, the primitive relaxation time, τ_0, the cross-over time, t_c, and equation (8) play their roles in determining the resultant faster dynamics of the thin film. Details of the analysis of the experimental data of the polymer thin film using the coupling model that reveals τ_0 can be found in a recent published work [42]. An exponential decrease of the relaxation time with decreasing film thickness has been observed in thin films (30–80 Å) of a glass-forming liquid crystal by Jérôme *et al* [43]. The time dependence of the relaxation of the molecules in the thin films has been found to be a linear exponential function of time, which indicates that the coupling parameter is effectively reduced to zero and is possibly responsible for the effect observed.

4. Use of the β-relaxation to reflect the primitive relaxation

The β-relaxation having characteristics such as an Arrhenius temperature dependence of its relaxation time has been considered to be simple molecular motion that is not cooperative in nature [44–47]. Thus in this respect the β-relaxation bears some resemblance to the primitive α-relaxation. However, they *cannot be exactly the same* otherwise the former like the latter will be slowed down by intermolecular interactions to become the cooperative α-relaxation observed at longer times. From this similarity it is expected that $\tau_\beta(T)$ and $\tau_0(T)$ may be comparable in order of magnitude. But they are not necessarily exactly equal because the β-relaxation and the primitive α-relaxation are merely closely related but definitely not identical motions. To compare the experimental values of $\tau_\beta(T)$ with $\tau_0(T)$, the latter is calculated as a function of temperature from the experimental values of $\tau_\alpha(T)$ and $(1 - n(T))$ by solving the equation

$$\tau_0(T) = t_c^n [\tau_\alpha(T)]^{1-n} \tag{9}$$

where $t_c = 2$ ps. It is worth emphasizing once more that the value of $t_c = 2$ ps used in the calculation is not arbitrary and had been predetermined by experiment. In fact in a recent work [48] experimental data of many glass-formers were used to show that, at the glass transition temperature T_g, the β-relaxation time, $\tau_\beta(T_g)$, and the primitive α-relaxation time, $\tau_0(T_g)$, are close to each other in order of magnitude. The latter can be calculated from the measured α-relaxation time, τ_α, according to equation (9) at $T = T_g$.

In some glass-formers both $\tau_\alpha(T)$ and $(1 - n(T))$ have been measured, and hence $\tau_0(T)$ can be calculated, as a function of temperature above T_g. These glass-formers provide the opportunity of comparing $\tau_\beta(T)$ with $\tau_0(T)$ for a range of temperature in between T_g and T_β, the temperature at which β-relaxation is expected to merge into the α-relaxation.

4.1. β-relaxation of a fragile glass-former, OTP

First we consider again the fragile liquid OTP in which a β-relaxation in the glassy state has been observed. In figure 2, dielectric relaxation [49–51] (solid circles) and light scattering [34, 35] (solid triangles) data of $f_\alpha(T) = [2\pi\tau_\alpha(T)]^{-1}$, the dielectric relaxation data of $f_\beta(T) = [2\pi\tau_\beta(T)]^{-1}$ in the glassy state, together with $f_0(T) = [2\pi\tau_0(T)]^{-1}$, where $\tau_0(T)$ is calculated by equation (9), are shown. There is good agreement between the $f_\alpha(T)$ from both experimental techniques, but $(1-n(T))$ from dielectric data [52] in the temperature range spanned by the stars in figure 2 is slightly smaller than the corresponding $(1 - n(T))$ from light scattering. Values of $(1 - n(T))$ from dielectric measurement at temperatures higher than those shown by the stars in figure 2 are unavailable. The open triangles are the $f_0(T)$ calculated by using both $\tau_\alpha(T)$ and $(1 - n(T))$ from dynamic light scattering data. The open circles are the $f_0(T)$ calculated by using $\tau_\alpha(T)$ from dielectric data and $(1 - n(T))$ from dynamic light scattering data. The stars are the $f_0(T)$ calculated by using $(1 - n(T)) = 0.50$ and $\tau_\alpha(T)$, both from dielectric relaxation data. On comparing $f_0(T)$ with values of $f_\beta(T)$ obtained by extrapolating the Arrhenius temperature dependence of the β-relaxation data to higher temperatures, one can conclude the two relaxation frequencies are close (within less than approximately one order of magnitude) for all temperatures above T_g. This remarkable closeness in values of $f_0(T)$ and $f_\beta(T)$, or of $\tau_0(T)$ and $\tau_\beta(T)$, for $T \geqslant T_g$ is anticipated by the resemblance between the two processes. Again it is worth reiterating that we do not expect $f_0(T)$ and $f_\beta(T)$ to be equal or even have exactly the temperature dependence because the two relaxation processes, though closely related, are not identical.

The vertical line in figure 2 indicates the value of $1000/T_B$ at which Stickel *et al* [49–51] found that the temperature dependence of the dielectric relaxation time and the viscosity
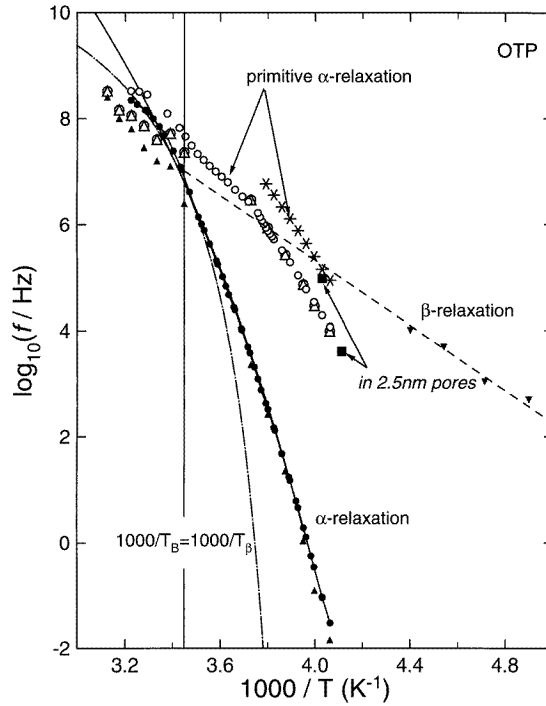
Figure 2. The α-relaxation frequencies ($\bullet$ from dielectric relaxation, $\blacktriangle$ from light scattering), β-relaxation frequencies ($\blacktriangledown$ from dielectric relaxation) and the calculated primitive α-relaxation frequencies ($*$, $\bigcirc$, $\triangle$) plotted against $1000/T$ for OTP. The full and the dashed–dotted curves are the two VFT dependencies of the α-relaxation frequency obtained by Stickel *et al*. The dashed line is an Arrhenius extrapolation of the β-relaxation frequencies determined below T_g. The α-relaxation frequencies of OTP in 2.5 nm pores obtained by Ruth *et al* ($\blacksquare$) are also included.

relaxation time (not shown here in figure 2) changes from one Vogel–Fulcher–Tammann (VFT) form to another. These two VFT forms are shown in figure 2 by the two curves intersecting at $1000/T_B$ with $T_B = 290$ K. The interesting fact that $T_B \approx T_\beta$ first pointed out by Stickel *et al* [49, 50] is evident from figure 2.

4.2. β-relaxation of a non-fragile glass-former, cyclo-octanol

Next, we consider a non-fragile glass-former, cyclo-octanol. Although cyclo-octanol is a plastic crystal the dielectric relaxation data of cyclo-octanol [53, 54] resemble strongly that of glycerol, propylene carbonate and propylene glycol, and all of them can be scaled in the manner proposed by Dixon and Nagel [55] to the same master curve. By studying dielectric relaxation of cyclo-octanol in both the disordered and ordered states, Brand *et al* [54] were able to confidently resolve the β-relaxation peak from the dominant α-relaxation peak. The temperature dependencies of $\tau_\alpha(T)$ and $\tau_\beta(T)$ are depicted in figure 3. The KWW exponent, $\beta_{KWW} \equiv (1 - n(T))$, of cyclo-octanol was determined by Brand *et al* as a function of temperature and its values are used via equation (9) with $t_c = 2$ ps to calculate $\tau_0(T)$. The results of $\tau_0(T)$ compare well with $\tau_\beta(T)$ (see figure 3) and support again the expected result that $\tau_\beta(T)$ is a good approximant to $\tau_0(T)$ for temperatures above T_g.
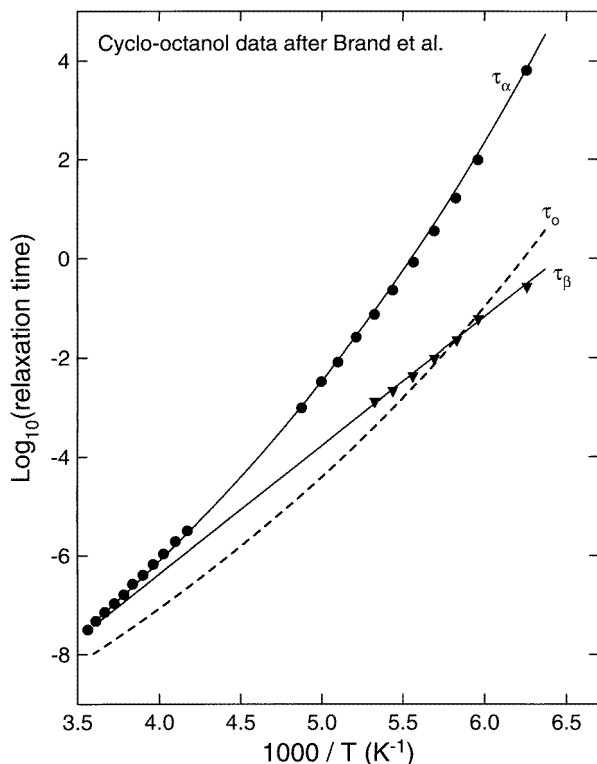
Figure 3. The α-relaxation frequencies ($\bullet$), β-relaxation frequencies ($\blacktriangledown$) and calculated primitive α-relaxation frequencies (- - - -) plotted against $1000/T$ for cyclo-octanol.

5. Conclusions

By confining OTP in the smallest nano-pores, the experimental data indicate that the molecules are almost totally decoupled from each other in motion and cooperativity is nearly completely suppressed. In this case, the coupling parameter at all temperatures is equal to zero. Thus, by confining OTP in small nanopores to totally decouple the molecules in motion, we can observe the primitive relaxation time, $\tau_0(T)$, of OTP directly by experiment. The good agreement between the observed photon correlation spectroscopy relaxation times of OTP in 2.5 nm pores and the calculated $\tau_0(T)$ from *bulk* OTP relaxation data has borne out the physical reality of the primitive relaxation of the bulk liquid in the coupling model even at lower temperatures where the observed relaxation time is long compared to $t_c \approx 2$ ps. Further support of the same comes from comparing the Johari–Goldstein β-relaxation time, τ_β, with the calculated τ_0 at temperatures above the glass transition temperature. Both the β-relaxation and the primitive relaxation time being non-cooperative in nature implies that τ_β is comparable with the calculated τ_0, which is shown to be true for the fragile glass-former *ortho*-terphenyl as well as a non-fragile glass-former, cyclo-octanol.

Acknowledgments

References

[1] Ngai K L 1979 *Comments Solid State Phys.* **9** 121
     Ngai K L and Rendell R W 1997 *Supercooled Liquids, Advances and Novel Applications (ACS Symposium Series 676)* ed J T Fourkas *et al* (Washington, DC: American Chemical Society) p 45
[2] Tsang K Y and Ngai K L 1996 *Phys. Rev.* E **54** R3067
     Tsang K Y and Ngai K L 1997 *Phys. Rev.* E **56** R17
[3] Ngai K L 1994 *Disorder Effects on Relaxational Properties* ed R Richert and A Blumen (Berlin: Springer) pp 89–150
[4] Ngai K L and Plazek D J 1995 *Rubber Chem. Tech. Rubb. Rev.* **68** 376
[5] MacKay R S and Meiss J D 1987 *Hamiltonian Dynamical Systems* (Bristol: Hilger)
[6] Kohlrausch R 1847 *Pogg. Ann. Phys.* **12** 393
[7] Williams G and Watts D C 1970 *Trans. Faraday Soc.* **66** 80
[8] Colmenero J, Arbe A and Alegria A 1993 *Phys. Rev. Lett.* **71** 2603
     Ngai K L, Colmenero J, Arbe A and Alegria A 1992 *Macromolecules* **25** 6727
[9] Zorn R, Arbe A, Colmenero J, Frick B, Richter D and Buchenau U 1995 *Phys. Rev.* E **52** 781
[10] Roland C M, Ngai K L and Lewis L 1995 *J. Chem. Phys.* **103** 4632
[11] Ngai K L, Cramer C, Saatkamp T and Funke K 1996 *Non-Equilibrium Phenomena in Supercooled Fluids, Glasses and Amorphous Materials* ed M Giordano, D Leporini and M P Tosi (Singapore: World Scientific) p 3
[12] Roe R J 1994 *J. Chem. Phys.* **100** 1610
     Ngai K L 1993 *J. Chem. Phys.* **98** 7588
[13] Smith G D, Paul W, Yoon D Y, Zirkel A, Hendricks J, Richter D and Schober H *J. Chem. Phys.* **107** 4751
[14] Roe R J 1998 *J. Non-Cryst. Solids* **235–238** 308
[15] Cramer C, Funke K and Saatkamp T 1995 *Phil. Mag.* **71** 701
[16] Ngai K L 1996 *J. Non-Cryst. Solids* **203** 232
[17] Ngai K L, Greaves G N and Moynihan C T 1998 *Phys. Rev. Lett.* **80** 1018
[18] Jackson C L and McKenna G B 1991 *J. Non-Cryst. Solids* **131–133** 221
     Jackson C L and McKenna G B 1996 *Chem. Mater.* **8** 2128
[19] Schick C and Donth E 1991 *Phys. Scr.* **43** 423
[20] Liu G, Li Y and Jonas J 1991 *J. Chem. Phys.* **95** 6892
[21] Schüller J, Mel'nichenko Y, Richert R and Fischer E W 1994 *Phys. Rev. Lett.* **73** 2224
[22] Pissis P, Daoukaki-Diamanti D, Apekis L and Christodoulides C 1994 *J. Phys.: Condens. Matter* **6** L325
     Barut G, Pissis P, Pelster R and Nimitz G 1998 *Phys. Rev. Lett.* **80** 3543
[23] Stapf S, Kimmich R and Seitter O R 1995 *Phys. Rev. Lett.* **75** 2855
[24] Streck C, Mel'nichenko Yu and Richert R 1996 *Phys. Rev.* B **53** 5341
[25] Haralampus N, Argiriadi P, Gilchriest A, Ashmore E, Scordlakes C, Martin W, Kranbuehl D and Verdier P 1998 *J. Non-Cryst. Solids* **235–237** 428
[26] Arndt M, Stannarius R, Gorbatschow W and Kremer F 1996 *Phys. Rev.* E **54** 5377
     Arndt M, Stannarius R, Groothues H, Hempel E and Kremer K 1997 *Phys. Rev. Lett.* **79** 2077
[27] Ngai K L and Rizos A K 1997 *Structure and Dynamics of Glasses and Glass Formers (Mater. Res. Soc. Symp. Proc. 455)* ed C A Angell *et al* (Pittsburgh, PA: Materials Research Society) p 147
[28] Adam G and Gibbs J H 1965 *J. Chem. Phys.* **4** 139
[29] Donth E 1991 *Relaxation and Thermodynamics in Polymers, Glass Transition* (Berlin: Akademie Verlag)
     Donth E 1991 *J. Non-Cryst. Solids* **131–133** 204
[30] Fischer E W, Donth E and Steffen W 1992 *Phys. Rev. Lett.* **68** 2344
[31] Rizos A K and Ngai K L 1998 *Structure and Dynamics of Glasses and Glass Formers (Mater. Res. Soc. Symp. Proc. 455)* ed C A Angell *et al* (Pittsburgh, PA: Materials Research Society) p 141
     Rizos A K and Ngai K L 1999 *Phys. Rev.* E at press
[32] Ruths T 1997 *PhD Thesis* Johannes Gutenberg University, Mainz
[33] Ruths T, Patkowski A and Fischer E W to be published
[34] Steffen W, Patkowski A, Gläser H, Meier G and Fischer E W 1994 *Phys. Rev.* E **49** 2992
[35] Patkowski A, Steffen W, Meier G and Fischer E W 1994 *J. Non-Cryst. Solids* **172–174** 52
[36] Davidson D W and Cole R H 1951 *J. Phys. Chem.* **19** 1484
[37] Lindsay C P and Patterson G D 1980 *J. Chem. Phys.* **73** 3348
[38] Heuer A, Wilhelm M, Zimmerman H and Spiess H W 1995 *Phys. Rev. Lett.* **75** 2851
     Böhmer R, Schiener B, Hemberger J and Chamberlin R V 1995 *Z. Phys.* B **99** 91
[39] Ngai K L, Roland C M and Yee A F 1993 *Rubb. Chem. Tech.* **66** 817
[40] Forrest J A, Dalnoki-Veress K A, Stevens J R and Dutcher J R 1996 *Phys. Rev. Lett.* **77** 2002

[41] Forrest J A, Svanberg C, Revesz K, Rodahl M, Torell L M and Kasemo B 1998 *Phys. Rev.* E **58** R1226
[42] Ngai K L, Rizos A K and Plazek D J 1998 *J. Non-Cryst. Solids* **235–237** 435
[43] Jérôme B and Commandeur J 1997 *Nature* **386** 589
[44] Garwe F, Beiner M, Hempel E, Schawe J, Schröter K, Schönhals A and Donth E 1994 *J. Non-Cryst. Solids* **172–174** 191
[45] Johari G P and Goldstein M 1970 *J. Chem. Phys.* **53** 2372
[46] Perez J, Cavaille J Y, Etienne S, Fouquet F and Guyot F 1983 *Ann. Phys., Paris* **8** 417
[47] Fujimori H and Oguni M 1995 *Solid State Commun.* **94** 157
[48] Ngai K L 1998 *Phys. Rev.* E **57** 7346
[49] Stickel F, Fischer E W and Richert R 1996 *J. Chem. Phys.* **104** 2043
[50] Stickel F 1995 *PhD Thesis* Mainz University (Aachen: Shaker)
[51] Hansen C, Stickel F, Berger T, Richert R and Fischer E W 1997 *J. Chem. Phys.* **107** 1086
[52] Wagner H and Richert R 1998 unpublished
[53] Leslie-Pelecky D L and Birge N O 1994 *Phys. Rev. Lett.* **72** 1232
[54] Brand R, Lunkenheimer P and Loidl A 1997 *Phys. Rev.* B **56** R5713
[55] Dixon P K, Wu L, Nagel S, Williams B D and Carini J P 1990 *Phys. Rev. Lett.* **65** 1108