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DECOUPLED MOLECULAR DYNAMICS OF GLASS-FORMING LIQUIDS CONFINED IN NANO-METER PORES

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Abstract

Calorimetry is the method first used by Jackson and McKenna to study the effect of finite-size on the molecular dynamics of glass-formers confined in nano-meter scale pores. It was found that the glass transition is shifted to lower temperature as pore size decreases. Since then, other spectroscopic techniques have corroborated this finding and given more information on the molecular dynamics. These results are used to compare with the predictions of several theories of glass transition, and in particular the coupling model of the author.

Keywords: confinement effects, DSC, dynamic light scattering, finite-size effects, glass transition, *o*-terphenyl

Introduction

The study of the molecular dynamics of glass-forming substances in confined space is of both fundamental importance and practical interest. From the basic research standpoint, the finite-size effect can be used to test theories of glass transition. On the other hand, the finite-size effect will have important implications on materials engineering and technical applications. The investigation of the effect of finite-size on the dynamics of two glass-forming liquids, ortho-terphenyl (OTP) and benzyl alcohol (BA), imposed by a matrix with nanometer scale pores was first carried out by Jackson and McKenna using differential scanning calorimetry (DSC) [1, 2]. They examined the dependence on the system size of the glass transition temperature, T_g, and the change in the heat capacity, ΔC_p, at T_g. They found that T_g decreases as the pore size decreases, but ΔC_p is independent of pore size. Later, more work showed that the decrease of T_g and the nearly constancy of ΔC_p are independent of the degree of pore filling for both OTP and BA, indicating that a reduction in bulk density or a negative pressure effect is not the cause of the observed results. In fact, from their calculations any reduction in bulk density or negative pressure effect is not large enough to cause the observed changes in T_g.

The observed decrease in T_g of the confined liquids without a reduction in bulk density or a negative pressure effect immediately poses difficulty for the two classical approaches to glass transition, namely the configuration entropy model [3] and the various free volume models. For example, on the basis of the configurational en-

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tropy theory, the decrease in entropy due to confinement leads one to expect an increase in T_g. At best, the configurational entropy model predicts no change of T_g, if confinement does not cause a significant decrease in entropy.

Subsequent to the discovery of the finite-size effect on glass transition by calorimetry, other workers [4–9] have used other experimental techniques to give further insight into the modification of the molecular dynamics. The most commonly used technique is dielectric relaxation, but recently solvation dynamics and photon correlation spectroscopy [9] have also been employed to study small molecule glass-forming liquids confined in glass pores. The benefit these non-calorimetric techniques bring is more direct information on the dispersion of the relaxation over a wider frequency range than calorimetry has offered. For example, dielectric measurement can probe the α-relaxation of the glass-former in the bulk as well as in the confined geometry routinely from 10^{-2} to 10^{9} Hz. Photon correlation spectroscopy can do the same in the time domain from a microsecond up to a hundred seconds. These data will be cited in the following sections and from them some general properties and trends of the change in molecular dynamics of glass-formers confined in nanometer pores will emerge. These features are then compared with the predictions of current theoretical models of glass transition. More attention is given to the coupling model of the author [10–12] because it can predict the change of the α-relaxation time of the glass-former when confined in pores with size less than the cooperative length scale.

Molecular dynamics of OTP in pores

Photon correlation spectroscopy data of OTP (Ruths et al.)

Experimental investigation of molecular dynamics of ortho-terphenyl (OTP) confined in porous glass, with inner surfaces that have been chemically treated to replace the –OH groups on the glass surface with trimethylsilyl groups, was carried out by Ruths *et al.* [9]. The pore sizes are 2.5, 5.0 and 7.5 nm and each has a narrow distribution. The α-relaxation of OTP in the nanopores was probed in the time range of $10^{-6} \leq t \leq 10^{2.5}$ s by photon correlation spectroscopy (PCS). Measurements in bulk OTP were made also using the same techniques previously by Steffen *et al.* [13] 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 [14, 15],

$$\Phi_b(t) = \exp[-(t/\tau_b)^{\beta_b}] \tag{1}$$

where the suffix *b* is used to indicate 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 [13]. The dependence of τ_b on temperature is depicted as filled circles in the Arrhenius plot of $\log(\tau_b)$ against reciprocal temperature in Fig. 1.

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

$$\Phi_d(t) = \exp[-(t/\tau_d)^{\beta_d}] \tag{2}$$

where the suffix d indicates quantities of OTP in pores of size d. The values of $\tau_d(T)$ obtained at a number of temperatures over a broad temperature range and for the three different pore sizes (7.5, 5.0 and 2.5 nm) are shown in Fig. 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 Fig. 1 for OTP confined in 2.5 nm pores at the lowest temperature of measurement. The values of $\beta_d(T)$ is slightly smaller than $\beta_b(T)$, reflecting that the dispersion of the α-relaxation of OTP in nanopores is broader than bulk OTP. This difference is consistent with the observation by calorimetry on OTP by Jackson and McKenna [1, 2] and is interpreted here as a consequence of an additional contribution to the dispersion of the α-relaxation of OTP in pores coming from the spatial heterogeneity of the molecular dynamics of the confined liquid.

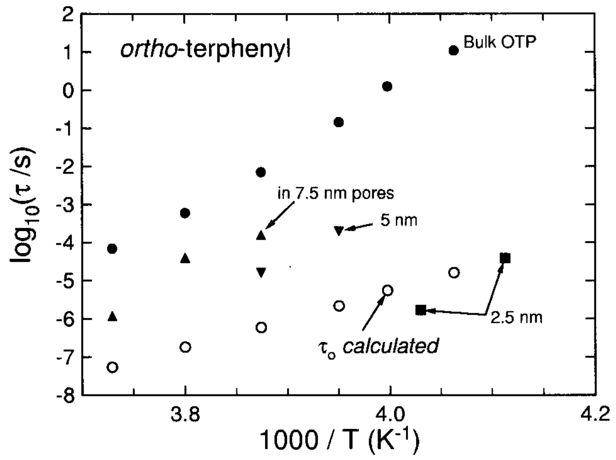

Fig. 1 Temperature dependencies of the various relaxation times of OTP. Filled circles are τ_b for bulk OTP from photon correlation spectroscopy data of Steffen *et al.*; open circles are the primitive relaxation times τ_o of bulk OTP calculated from bulk OTP data by Eq. (2). The photon correlation spectroscopy relaxation times measured by Ruths *et al.* on OTP confined in 7.5 nm pores (▲); 5.0 nm pores (▼); 2.5 nm pores (■)

Correlation between the magnitude of the shift and the KWW exponent

The changes of relaxation time and dispersion with d found by photon correlation spectroscopy are consistent with dielectric data of other small molecule glass-forming liquids, *N*-methyl-ε-caprolactam (NMEC), propylene glycol and salol, confined in pores [4–9]. Although the size of the change measured by the ratio, $\tau_d(T_{gb})/\tau_b(T_{gb})$, varies. Here T_{gb} denotes the glass transition temperature of the bulk liquid. Comparing the results in Fig. 1 with the dielectric relaxation data of salol, propylene glycol and NMEC one observes that $\tau_d(T_{gb})/\tau_b(T_{gb})$ is largest for OTP, which has the smallest $\beta_b(T_{gb})$, and the ratio decreases with increasing $\beta_b(T_{gb})$. Dielectrically, $\beta_b(T_{gb})$ is equal to 0.48 for OTP, 0.56 for salol, 0.70 for propylene glycol and about 0.75 for NMEC. Another way to compare the finite-size effect on different glass-formers is by their shifts in glass transition temperature, ΔT_g, measured by calorimetry. In 5 nm glass pores, ΔT_g is equal to 12.6 K [9], 11.0 K [8], 8 K [6b] and 6 K [6b] respectively for OTP, salol, propylene glycol and NMEC. Again, ΔT_g decreases with increasing $\beta_b(T_{gb})$ as depicted in Fig. 2.

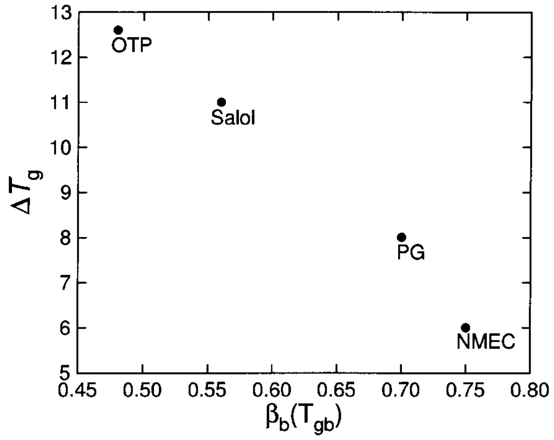

Fig. 2 Experimentally observed decrease of glass transition temperature by calorimetry of four glass-formers, OTP, salol, propylene glycol (PG) and NMEC confined in 5 nm pores from their bulk values, T_{gb}, plotted *vs.* the Kohlrausch exponent, $\beta_b(T_{gb})$. Data taken from [5–9]

By calorimetry, Jackson and McKenna observed that the shift of the glass transition temperature in the pores of the same size is much larger for OTP than butyl alcohol. Also broadening of T_g is measured in OTP confined in 8.5 nm pores, but not observed in the case of BA confined in the same size pores. These observations are in accord with the correlation shown in Fig. 2 because it is expected that $\beta_b(T_{gb})$ of OTP is smaller than that of butyl alcohol.

Decoupling of the molecular dynamics in nano-pores

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 [16]. 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, coupled or dynamically heterogeneous 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., $\beta_b(T)\to 1$, [13]). The same is expected for OTP confined in pores. Therefore, the fact that β_d is almost temperature independent and maintains to have the same value of about 0.50 at all temperature [9] indicates that the dispersion observed in OTP confined in 2.5 nm pore 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.

Calculation of the shift using the coupling model

The coupling model [10–12] shall now be used to estimate the maximum reduction in the relaxation time possible when cooperativity is totally suppressed in small pores. Briefly summarized, the coupling model starts by considering the independent and exponential (primitive) relaxation of the molecules, $\exp(-t/\tau_o)$. The molecules relax independently till a microscopic time, $t_c\approx 2\cdot 10^{-12}$ s is reached. After t_c intermolecular interaction slows down and broadens the independent relaxation of the molecule to become the α-relaxation having the KWW form, $\exp[-(t/\tau_b)^{1-n_b}]$, where n_b is the coupling parameter. There exists an important relation,

$$\tau_b = [t_c^{-n_b}\tau_o]^{1/(1-n_b)} \tag{3}$$

between $\tau_o(T)$ and $\tau_b(T)$. The parameters $\tau_b(T)$ and $[1-n_b(T)]$ can immediately be identified with the corresponding quantities in Eq. (1), which were obtained from the fits to the experimental data of bulk OTP [13]. 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 neighboring 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 modeled 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.

With the values of $\tau_b(T)$ and $\beta_b(T)$ known and $t_c\approx 2\cdot 10^{-12}$ s, Eq. (3) enables the primitive (i.e. totally decoupled or without intermolecular cooperativity) relaxation time, $\tau_o(T)$, to be calculated from the relaxation data, $\tau_b(T)$ and $n_b(T)$, of the bulk material. The values of $\tau_o(T)$ are shown as open circles in Fig.1. When totally devoid of intermolecular coupling or cooperativity, the coupling parameter n_b is exactly zero and the result, $\tau_b(T)=\tau_o(T)$, follows from Eq. (3). Thus, the values of $\tau_o(T)$ 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.

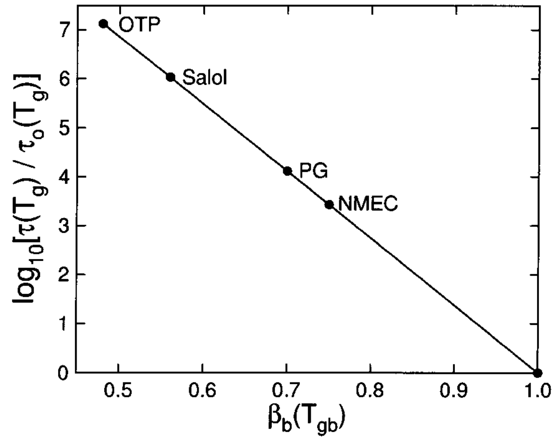

Fig. 3 A plot of the calculated difference, $\log\tau_b(T_{gb})-\log\tau_o(T_{gb})$, for four glass-formers, OTP, salol, propylene glycol and NMEC *vs.* the Kohlrausch exponent, $\beta_b(T_{gb})$

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 approximately good agreement at two temperatures, 248.15 and 243.15 K, between the calculated relaxation time $\tau_o(T)$ and the relaxation times $\tau_d(T)$ measured by photon correlation spectroscopy in 2.5 nm pores (Fig. 1). Ruths [9] 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, $<\tau_d>$ is equal to $3.4\cdot10^{-6}$ s, which is close to the shortest time limit of his correlator (about $8\cdot10^{-7}$ s). Thus, one can expect significant error can be involved in the determination of τ_d at T=248.15 K, and the discrepancy between τ_d and τ_o, by roughly a factor of three in Fig. 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.* [13] that is used to calculate $\tau_o(T)$. Within experimental error, we may conclude that there is good agreement between the calculated $\tau_o(T)$ and the experimental $\tau_d(T)$ for OTP confined in 2.5 nm pores. At T=243.15 K, the ratios $\tau_o(T)/\tau_b(T)$ and $\tau_d(T)/\tau_b(T)$ have about the same value of approximately 10^{-6}. There is 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, $\tau_o(T)$, 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.

Defining T_{gb} as the temperature at which $\tau_b(T_{gb})=10^2$ s, the values of $\tau_o(T_{gb})$ of OTP, salol, propylene glycol and NMEC can be calculated by Eq. (3) from the known values of $(1-n(T_{gb}))\equiv \beta_b(T_{gb})$ and $t_c=2$ ps. Figure 3 shows the difference, $\log\tau_b(T_{gb})-\log\tau_o(T_{gb})$, for these glass-formers as a function of $\beta_b(T_{gb})$. From the example of OTP discussed above, we can expect $\tau_o(T_{gb})$ to be a good estimate of $\tau_d(T_{gb})$ also for other glass-forming liquids confined in 2.5 nm pores. Thus, one can conclude from Fig. 3 that the change in relaxation time, $\log\tau_b(T_{gb})-\log\tau_d(T_{gb})$, when the liquid is confined in 2.5 nm pores is correlated with $\beta_b(T_{gb})$. This predicted correlation of the effect with $\beta_b(T_{gb})$ from the coupling model is consistent with experimentally observed correlation of the decrease of the glass transition temperature with $\beta_b(T_{gb})$ shown before in Fig. 2.

Conclusions

Molecular dynamics of glass-forming liquids speeds up dramatically resulting in a decrease in the glass transition temperature, T_g, when the material is confined in pores of nanometer scale. If the configuration entropy model of Adam and Gibbs is considered, the entropy is expected to either decrease or remain unchanged by confinement. Consequently T_g either increases or is unchanged, which contradicts the observed large decrease. The magnitude of the finite size effect seems to increase with increasing nonexponentiality (i.e. decreasing value of the KWW exponent, $\beta_b(T_{gb})$ or increasing value of the coupling parameter, $n(T_{gb})$) of the bulk α-relaxation at its glass transition temperature. This finite-size effect can be understood as the removal of cooperativity in the molecular dynamics and can be accounted for quantitatively by the coupling model. The effect, first discovered by calorimetry, has serious implications on fundamental theory of the glass transition and on technical applications in materials engineering, biochemistry and medicine. However, at present there are only a few studies of the finite-size effects. It seems there are ample opportunities in the study of finite-size effects in various glass-forming materials waiting exploration by researchers, including those who use principally calorimetry as a tool.

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