Comparing dynamic correlation lengths from an approximation to the four-point dynamic susceptibility and from the picosecond vibrational dynamics

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Recently an alternative approach to the determination of dynamic correlation lengths ξ for supercooled liquids, based on the properties of the slow (picosecond) vibrational dynamics, was carried out [Hong, Novikov, and Sokolov, Phys. Rev. E **83**, 061508 (2011)]. Although these vibrational measurements are typically conducted well below the glass transition temperature, the liquid is frozen at T_g, whereby structural correlations, density variations, etc., manifested at low temperatures as spatial fluctuations of local elastic constants, can be related to a dynamic heterogeneity length scale for the liquid state. We compare ξ from this method to values calculated using an approximation to the four-point dynamic susceptibility. For 26 different materials we find good correlation between the two measures; moreover, the pressure dependences are consistent within the large experimental error. However, ξ from Boson peak measurements above T_g have a different, and unrealistic, temperature dependence.

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A universal feature of liquids approaching their glass transition is an increasing length scale for the correlations between molecular rearrangements. This property, and the associated spatial heterogeneity of the motions, are inherent to the many-body dynamics and must be accounted for by theories of the glass transition [1]. This requires reliable data quantifying the dynamic correlation length ξ. An immediate difficulty is unambiguously defining the distance over which motions are correlated, given the fractal nature of the heterogeneous dynamics. Various approaches have been applied to the determination of ξ [2,3]. The maximum value of the dynamic susceptibility χ_4 yields the number of dynamically correlated molecules N_c [4]; however, since χ_4 involves both spatial and temporal correlations, it cannot be obtained from linear relaxation measurements without assumptions. Berthier *et al.* [5,6] proposed an approximation in terms of the temperature derivative of the experimentally accessible, two-point dynamic correlation function $\chi_T(t)$:

$$\chi_T(t) = \frac{\partial C(t)}{\partial T} \leqslant T^{-1} \left[\frac{\Delta c_P}{k} \chi_4(t) \right]^{1/2}, \qquad (1)$$

where Δc_P is the isobaric heat capacity change at T_g, and k is the Boltzmann constant. The lower bound on the number of dynamically correlated molecules is

$$N_c \geqslant \frac{k}{\Delta c_P} T^2 [\max \chi_T(t)]^2, \qquad (2)$$

$\max \chi_T(t)$ representing the maximum value of $\chi_T(t)$ for any state point. If the dielectric loss has the Kohlrausch form with a stretch exponent β that varies only weakly with temperature (which is true around T_g), Eq. (2) can be written as [7]

$$N_c \geqslant \frac{k}{\Delta c_P} \left(\frac{\beta}{e} \right)^2 \left(\frac{d \ln \tau_\alpha}{d \ln T} \right)^2, \qquad (3)$$

where e is Euler's number.

Confidence in the validity of χ_T as an approximation to χ_4 draws from several observations:

(i) The number of particles involved in dynamic heterogeneities near T_g has a reasonable magnitude ($\sim$100) [6–10] and agrees with more direct determinations based on the nonlinear susceptibility [11].

(ii) The increase in N_c is strongest at temperatures approaching T_g, in accord with the divergence of the relaxation time near T_g.

(iii) Although the χ_T approximation becomes less accurate at temperatures well above T_g, due to an increasing contribution from (neglected) density fluctuations, N_c from χ_T decreases to negligible values at sufficiently high temperature, consistent with molecular motions becoming noncooperative [8].

(iv) Molecular dynamics simulations (MDS) comparing the approximate N_c from χ_T and exact values from χ_4 agree over most of the supercooled regime [9,12]. And close to the glass transition, experimental N_c from χ_T are in agreement with the correlation length determined by multidimensional NMR [5].

An alternative means to quantify ξ recently developed by Hong *et al.* [13–15] is based on the fact that dynamic heterogeneities are manifested in the fast (picosecond) dynamics [16,17]. Dynamic heterogeneity in the glassy state has been observed by MDS: Mobile particles, defined as those having large vibrational amplitudes, have a propensity to be surrounded by mobile particles, and less mobile particles tend to have a disproportionate number of immobile neighbors [18]. Although these clusters are more compact than those observed above T_g [18], the cessation of relaxation below the glass transition freezes in structural inhomogeneities, resulting in an excess density of states and the Boson peak in the inelastic scattering of amorphous solids. Spatial fluctuations of the local elastic constants induce corresponding fluctuations in the vibrational amplitudes (mean squared displacements), with the length scale of the fluctuations ξ_{BP} inversely proportional to the frequency of the Boson peak, ν_B [19]:

$$\xi_{BP} = Sc/\nu_B, \qquad (4)$$

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where c is the transverse sound speed and S is taken to be constant and about equal to unity. The implication is that structural heterogeneities intrinsic to the glassy state can be identified with the dynamic heterogeneities detected in the supercooled liquid by relaxation measurements [13–15].

Experimental confirmation that ξ_{BP} is indeed a measure of the correlation length relevant to the dynamics of supercooled liquids has thus far been limited to comparisons involving four materials (glycerol, sorbitol, o-terphenyl [OTP], and polyvinylacetate) [14] that had previously been studied by multidimensional NMR. The NMR method enables an exact determination of χ_4, but only in the vicinity of T_g [20]. In this report we compare ξ_{BP} to dynamic correlation lengths determined from $\chi_T(t)$ for 26 materials, including inorganic glass formers and molecular and polymeric organic liquids [21]. To do this we convert the number of correlating molecules calculated from Eq. (3) to a length scale using [10,22]

$$\xi_\chi = (N_c v_m)^{1/3}, \qquad (5)$$

where v_m is the molecular volume. Equation (5) ignores any stringlike character [4] of the cooperative volume, and if this assumption of a compact geometry is correct, the ξ_χ is an upper bound for the correlation length.

In Fig. 1 we plot the ξ_{BP} reported in Refs. [13,14] versus ξ_χ, using for the latter literature results [21] for the quantities in Eq. (3) and for the equations of state used to calculate v_m. All the correlation lengths in Fig. 1 correspond to T_g: ξ_χ was determined from quantities measured at T_g, and although the Boson peak was measured for the glass, the structure is assumed to have become fixed at the glass transition, so that the ξ_{BP} correspond to the values at T_g. The two measures of the dynamic correlation length are seen to be in good agreement, Pearson's correlation coefficient equal to 0.84. Even though the N_c from Eq. (3) is a lower bound, the ξ_χ in Fig. 1 are

FIG. 2. (Color online) Dynamic correlation length calculated from Eq. (3) (open symbols) and Eq. (4) (filled symbols) and normalized by the value at ambient pressure, as a function of pressure for o-terphenyl (circles), 1,4-polyisoprene (squares), and polymethylphenylsiloxane (diamonds). The ξ_χ data are at the pressure-dependent T_g, while for ξ_{BP} the samples were pressurized at room temperature and then quenched to 140 K, which is below the glass transition temperature in each case.

typically ∼40% larger than the ξ_{BP}; however, this is in part an artifact of using Eq. (5) to convert the number of correlating molecules to a length scale. Assuming a spherical volume [23], ξ_χ and ξ_{BP} would be more nearly equal.

Another comparison of the two measures of correlation lengths is their change for a given material with temperature and pressure. Hong et al. [13] reported ξ_{BP} versus pressure for seven compounds; these results, normalized by the ambient pressure values, are reproduced in Fig. 2 for the three materials (OTP, polyisoprene, and polymethylphenylsiloxane) for which ξ_χ could be calculated. For pressures up to 1.4 GPa, the changes in ξ_{BP} do not exceed 30%; however, as noted by Hong et al. [13], the data are ambiguous concerning whether the correlation length increases or decreases with pressure.

We showed previously that when isochronal superpositioning [1] is valid, the change in N_c with pressure is given by [8]

$$N_c \approx (1 + \gamma \alpha_P T)^2 / \Delta c_p, \qquad (6)$$

in which α_P is the isobaric thermal expansion coefficient, and γ is the scaling exponent in the equation relating the structural relaxation time τ_α to temperature and density ρ [1,24]:

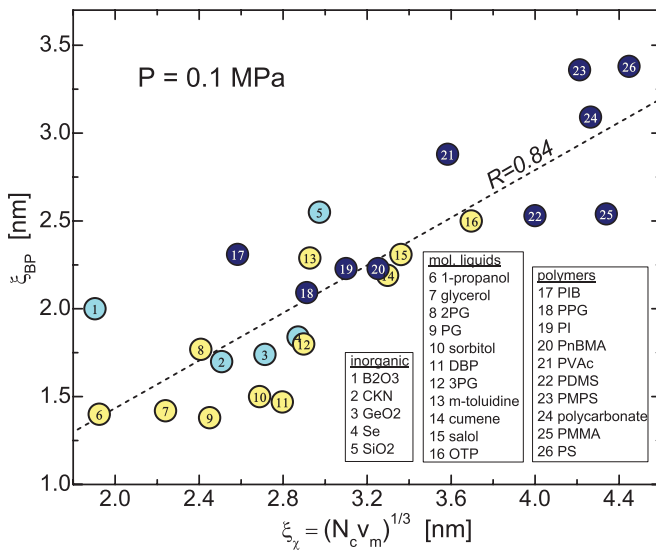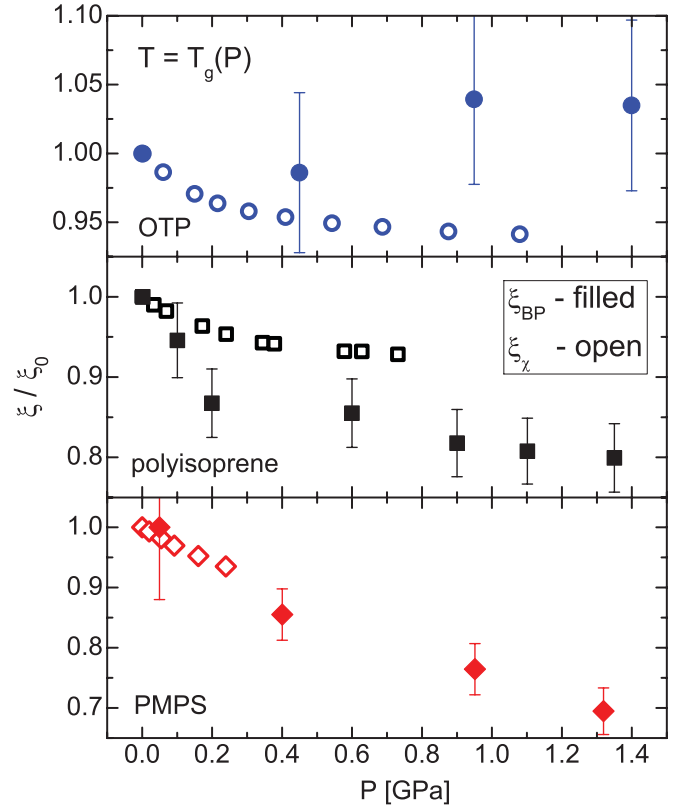$$\tau_\alpha = f(T \rho^{-\gamma}); \qquad (7)$$

FIG. 1. (Color online) Dynamic correlation length defined as the ratio of the transverse sound speed to the Boson peak frequency measured at 140 K versus the same quantity at T_g calculated from the approximation to the four-point dynamic susceptibility. The fitted line has a slope = 0.68, with a Pearson correlation coefficient as indicated.

γ is a material constant, and since the change with pressure of the heat capacity difference at T_g between the liquid and glassy states is negligible [25,26], the variation of $N_c(T_g)$ in Eq. (6) with pressure is governed by changes in the quantity $(1 + \gamma \alpha_P T_g)$. At ambient pressure the product $\alpha_P T_g$ is a near-universal constant (the Boyer-Spencer rule [27]), but this quantity decreases for a given material with pressure. This change can be assessed from the pressure dependence of the isobaric fragility [8]:

$$m_p = m_V(1 + \gamma \alpha_P T_g), \qquad (8)$$

where m_V is the (pressure-independent [28]) isochoric fragility. [Note from Eqs. (6) and (8) that the dynamic correlation length cannot correlate with the fragility.] Experimentally for van der Waals liquids, m_p has been found to decrease $\sim 10\%$ over the range from ambient to 0.5 GPa [28], implying about the same variation in ξ_{BP} over the larger pressure range in Fig. 2. This variation is within the scatter of the data, although the correlation length for normal liquids is unambiguously a decreasing function of pressure, notwithstanding the behavior of ξ_{BP} for OTP.

Also plotted in Fig. 2 are ξ_χ calculated using Eqs. (5) and (6) for these three materials, at pressures for which the required data were available; again we normalize by the ambient pressure value for each. The magnitudes of the changes with pressure are similar to those for ξ_{BP}, but ξ_χ always has the expected inverse dependence on P. One significant difference between the determinations of ξ_{BP} and ξ_χ is that while data for the latter were obtained at $T_g(P)$, for ξ_{BP} the Boson peak was actually measured at 140 K, following application of pressure at room temperature and subsequent cooling to induce the transition to the glassy state. This method relies on the assumptions that the structure of the glass becomes fixed and there is no significant effect of temperature *per se*; therefore, the correlation length measured in the glassy state is taken to represent the value expected for the supercooled liquid at T_g. The fact that in glasses subnanometer density fluctuations [29] and the secondary relaxation dynamics [30] are both sensitive to thermal history indicates that this first assumption cannot be strictly correct.

In Fig. 3 the two correlation lengths for OTP and glycerol at ambient pressure are plotted as a function of temperature normalized by T_g. ξ_χ decreases with increasing temperature, with the steepest change being near the glass transition (and steeper for OTP than for glycerol, the former the more fragile liquid [31,32]). In contrast, ξ_{BP} shows negligible change with temperature, behavior that cannot be reconciled with our understanding of the glass transition. Indeed, the fact that
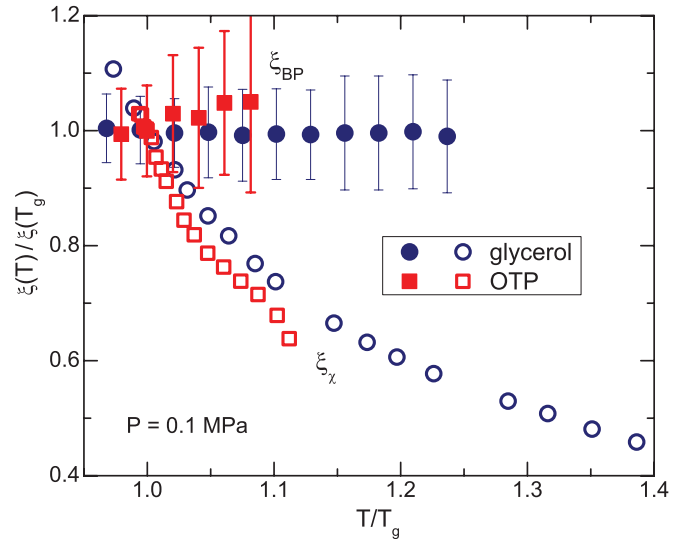

FIG. 3. (Color online) Dynamic correlation length normalized by the value at T_g calculated using Eq. (3) (open symbols) and Eq. (4) (filled symbols) plotted versus temperature over T_g, for glycerol (circles) and *o*-terphenyl (squares).

the dynamic correlation length depends primarily on τ_α [1,8] means that ξ must increase markedly in the vicinity of T_g. (This dependence on τ_α is at odds with the suggested correlation [13] of ξ with the activation volume $\Delta V^\# = RT \partial \ln(\tau) / \partial P |_T \tau_\alpha$.) Note that whereas the ξ_{BP} in Figs. 1 and 2 were measured below T_g, thus corresponding to values at the glass transition, the results in Fig. 3 are based on measurements of the liquids at various temperatures. As pointed out by Hong *et al.* [13], the possibility exists that the prefactor S in Eq. (4) may be temperature dependent.

In summary, correlation lengths calculated as the ratio of the transverse sound speed and the Boson peak frequency, both measured in the glassy state, correspond well to values of the dynamic correlation length at T_g determined using an approximation to the four-point dynamic susceptibility. However, ξ_{BP} measured above T_g has an unrealistic T dependence, suggesting its broad correlation with ξ_χ for different materials at T_g does not guarantee that terahertz vibrational measurements can provide accurate dynamic correlation lengths for a given liquid over a range of conditions.

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