Correlation of nonexponentiality with dynamic heterogeneity from four-point dynamic susceptibility $\chi_4(t)$ and its approximation $\chi_T(t)$

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Various properties of vitrifying liquids are correlated with the dispersity of the dynamics, the latter reflected in the magnitude of the nonexponentiality parameter, β_K, describing the distribution of relaxation times. These properties include the mean relaxation time, τ_α, the fragility, and the dynamic crossover. The correlations with β_K are observed in both experimental data and the results from molecular dynamics simulations on Lennard-Jones (LJ) type systems. Another, rather obvious property to correlate with β_K is the dynamic heterogeneity, which can be quantified from the number of molecules, N_c, dynamically correlated over a time span τ_α. For a given LJ system, N_c can be rigorously calculated and we find that it does indeed correlate with β_K over a range of thermodynamic conditions. However, the analysis of experimental data for a broad range of real materials, wherein an approximation is required to obtain N_c, reveals the absence of any relationship between N_c and β_K among different materials. © *2010 American Institute of Physics.* [doi:10.1063/1.3481355]

I. INTRODUCTION

Viscous liquids are sufficiently dense for molecules to exert a reciprocal influence, and these correlated, many-body interactions distinguish the supercooled regime from the much simpler dynamics at high temperature. The degree of intermolecular cooperativity varies spatially, with the dynamic correlations persisting over time scales on the order of the relaxation time. Since dynamic heterogeneity is intrinsic to the supercooled liquid state, it is an obvious quantity to characterize dynamic properties.[1–4] One consequence of dynamic heterogeneity is deviation of the linear susceptibility from the Debye or exponential behavior, with the relaxation function becoming more dispersive to reflect the heterogeneity of the local dynamic environments. A variety of experimental methods have been employed to demonstrate that nonexponential relaxation results from a superposition of dynamically distinguishable contributions.[5] This nonexponentiality, commonly assessed from the magnitude of the Kohlrausch stretch exponent, β_K, is known to correlate with relaxation properties such as fragility[6] and the dynamic crossover (change in dynamics above T_g).[7] Additionally, β_K is related to phenomena such as rotational-translational decoupling[8–11] and the confinement-induced enhancement of molecular mobilities.[12–14] Thus, quantifying the dynamic heterogeneity and nonexponentiality of liquids can provide insight into the fundamental variables governing the dynamics near T_g. Indeed, models of the glass transition generally posit a growing dynamic correlation length as causing the marked increase of τ_α in vitrifying liquids[15–19] (although recent simulation results suggest an alternative viewpoint[20]).

Since the conventional description of the dynamics involves the correlation of a variable at two times (for example, $\langle \rho(\widetilde{k},0)\rho(\widetilde{k},t)\rangle$, where ρ is the density and $\widetilde{k}$ is the wave-vector), it follows that a four-point, time-dependent correlation function is required to describe dynamic heterogeneities.[21,22] Thus, the susceptibility defined in terms of spatial and temporal correlations,

$$\chi_4(t) = \int \langle \rho(r_1,0)\rho(r_1+r_2,0)\rho(r_1,t)\rho(r_1+r_2,t)\rangle_{r_1} dr_2,$$

(1)

has a maximum at $t \sim \tau_\alpha$ that is proportional to N_c, the number of correlating molecules[22–24]

$$N_c = \max\{\chi_4(t)\} \equiv \chi_4^{\max}.$$

(2)

Efforts to study dynamic heterogeneities have been stymied by the difficulty of determining $\chi_4(t)$ since conventional relaxation spectroscopies yield the linear susceptibility. However, molecular dynamics simulations[20,25–28] and multidimensional NMR[29–32] have been employed to obtain $\chi_4(t)$ respectively for model particle systems and a few real materials (data for the latter limited to low temperatures).

A development in quantifying dynamic heterogeneities in real materials was the derivation by Berthier *et al.*[21] of $\chi_4(t)$ in terms of the temperature derivative of two-point linear susceptibilities, $\Phi(t)$,

$$\chi_4(t) \geq \frac{k_B}{\Delta c_P} T^2 \chi_T^2(t) = \frac{k_B}{\Delta c_P} T^2 \left(\frac{\partial \Phi(t)}{\partial T} \right)^2,$$

(3)

where Δc_P is the isobaric heat capacity change at T_g and k_B is the Boltzmann constant. This offers the possibility of ob-

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taining the number of molecules with correlated dynamics in terms of readily accessible experimental quantities,

$$N_c(T,P) \approx \frac{k_B}{\Delta c_P(P)} T^2 \{ \max_t \chi_T(t,T,P) \}^2. \qquad (4)$$

A number of works have appeared in which the $\chi_T(t)$ approximation was used to evaluate N_c for different materials[33,34] and different thermodynamic conditions.[35] A comparison of simulation results for χ_4 and χ_T indicated reasonable correspondence between the two methods for longer τ_α.[27]

Conceptually the spatial extent and amplitude of the dynamic correlations are expected to have a connection to the dispersion in the relaxation times since dynamic heterogeneity is defined by molecular mobilities. By the same token properties that correlate with β_K should also correlate with N_c and vice versa. Up until now, any relation between β_K and N_c has not been evaluated. In this paper, we provide the test, using simulations of the Kob–Andersen Lennard-Jones (LJ) mixture[36] as a function of temperature T and density ρ. The nonexponentiality parameter β_K is obtained from the self-intermediate scattering function and N_c from the four-point dynamic susceptibility, $\chi_4(t)$. Correlation between β_K and N_c is assessed by comparing the changes of these two quantities on varying the thermodynamic conditions, i.e., at different combinations of T and ρ. To test the correlation between β_K and N_c obtained from χ_T via Eq. (4), we use experimental data of 45 glass-formers including polymers, oxide glass-formers, selenium, hydrogen bonded materials, and van der Waals glass-formers.

II. RESULTS

A. Correlation between stretching parameter β_K and N_c from $\chi_4^{\max}$

Previously it was shown[28] from molecular dynamics simulation of the Kob–Andersen binary mixture with particles interacting according to a 12-6 LJ potential that the full t-dependence, and thus the maximum in $\chi_4(t)(=N_c)$, were invariant over a relevant range of T and ρ for state points for which the scaling variable ρ^γ/T is constant with $\gamma=5.07$. Moreover, the reduced relaxation time τ^*, defined as the Kohlrausch decay time for the self-intermediate scattering function $F_s(k,t)$ multiplied by $\rho^{1/3}T^{1/2}$,[37] is also invariant for state points for which ρ^γ/T is constant. Thus, the same value of the material constant $\gamma=5.07$ superposes both $\chi_4^{\max}$ and τ^* of the system versus ρ^γ/T, which means that the number of dynamically correlated particles is a unique function of τ^*, at least in the regime where density scaling holds.

Values of β_K were obtained by nonlinear fitting of the stretched exponential function $\Phi(t)=\Phi_0 \exp(-(t/\tau)^{\beta_K})$ to the long-time portion of $F_s(k,t)$ at a reduced wave-vector $k\rho^{1/3}=7.44$ over the same range of T and ρ as in Ref. 28. The fit was cut off at short times where the contribution of the fast initial decay of $F_s(k,t)$ became significant; that is, where the shape of the curve begins to deviate from a stretched exponential.[38] Representative fits are shown in the inset of Fig. 1. This figure shows β_K plotted as a function of ρ^γ/T using $\gamma=5.07$, the same exponent superposing $\chi_4^{\max}$ versus
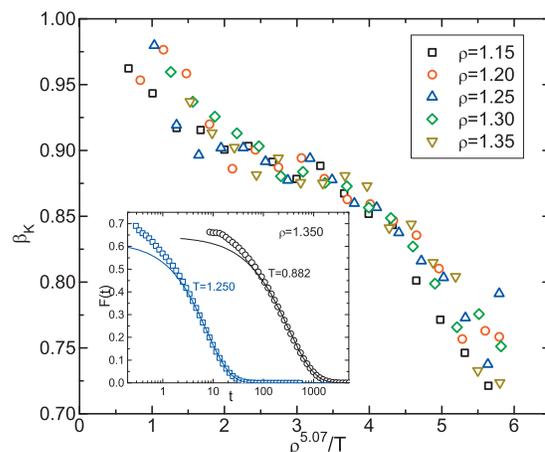

FIG. 1. Kohlrausch exponent as a function of the product variable $\rho^{5.07}/T$ for simulated LJ particles. Each symbol represents a distinct state point. Fits to the self-intermediate scattering function at longer time are shown for two temperatures in the inset. Simulation data are from Ref. 28.

ρ^γ/T in Ref. 28. Within the experimental error, β_K is invariant for state points for which the scaling variable ρ^γ/T is constant. In Fig. 2 these same β_K are plotted as a function of τ^*, and the results indicate that β_K is a unique function of τ^* for any thermodynamic condition in the regime where density scaling holds. This constancy of β_K for all state points at any fixed τ_α has been shown from experimental data on many glass-formers.[39,40]

To compare dynamic correlation to nonexponentiality, in Fig. 3 $\chi_4^{\max}$ is plotted versus β_K. The correspondence is good and in accord with the usual interpretation of dynamic heterogeneity—an increasing correlation (larger N_c) associated with an increasing breadth of the relaxation function (smaller β_K). Also shown in Fig. 3 are the values of N_c calculated from $\chi_T(t)$ [Eq. (4)]. The agreement is good at low temperatures and higher densities, but otherwise the approximation underestimates the number of dynamically correlated particles. This agrees with previous simulation results comparing $\chi_4(t)$ and $\chi_T(t)$ as a function of temperature at zero pressure.[27]
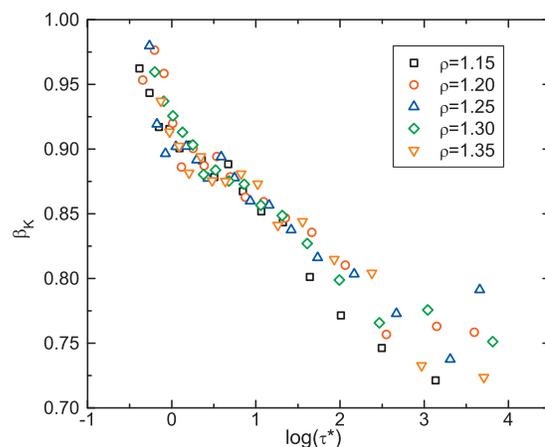

FIG. 2. Kohlrausch exponent as a function of the relaxation time determined from fits of $F_s(k,t)$ at longer time. Each symbol represents a distinct state point. Simulation data are from Ref. 28.
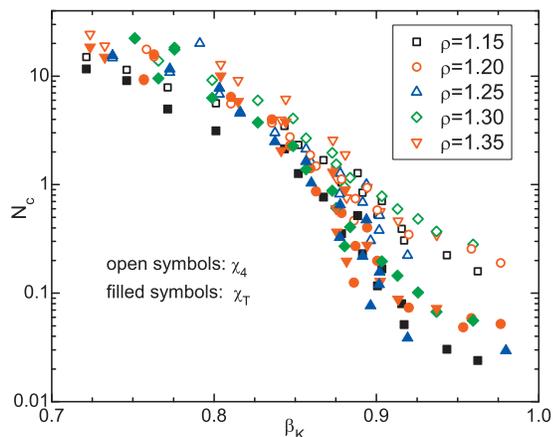
FIG. 3. N_c from χ_4 [Eq. (2)—open symbols] and from χ_T [Eq. (4)—filled symbols] vs the Kohlrausch exponent for LJ particles. Each symbol represents a distinct state point. Increasing dynamic heterogeneity is associated with a broader dispersion of relaxation times. The χ_T approximation departs from the rigorous calculation at higher temperatures and lower densities. Simulation data are from Ref. 28.

B. Lack of correlation between β_K and N_c from $\chi_T(t)$ approximation

In Fig. 4 plotted versus β_K is N_c calculated at T_g from Eq. (4) using experimental measurements for 45 materials. The N_c data were taken from Ref. 34 and β_K are as reported in the original papers (references in Ref. 34). Since a larger number of dynamically correlated molecules should coincide with a greater dispersity of relaxation times, we expect these quantities to be inversely related. However, a linear correlation of the data in Fig. 4 yields a Pearson correlation coefficient $R = -0.22$, indicating an absence of dependence. If we replace N_c by the corresponding molar volume or the number of chemical groups (e.g., "beads" as defined by Stevenson and Wolynes[41]), the correlation deteriorates further, with the absolute value of R becoming smaller.

If $\Phi(t)$ has the Kohlrausch form, to a very good approximation Eq. (4) can be rewritten so that β_K appears explicitly,[34]
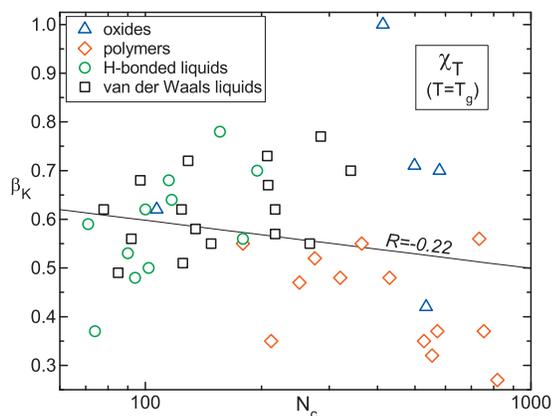

FIG. 4. Plot of Kohlrausch exponent vs N_c obtained from the $\chi_T(t)$ approximation for 45 glass-formers at T_g and atmospheric pressure (data are from Ref. 34): polymers (diamonds), oxide glass-formers and selenium (circles), hydrogen bonded materials (triangles), and van der Waals glass-formers (squares). The absence of correlation is indicated by the small value of the Pearson linear correlation coefficient.
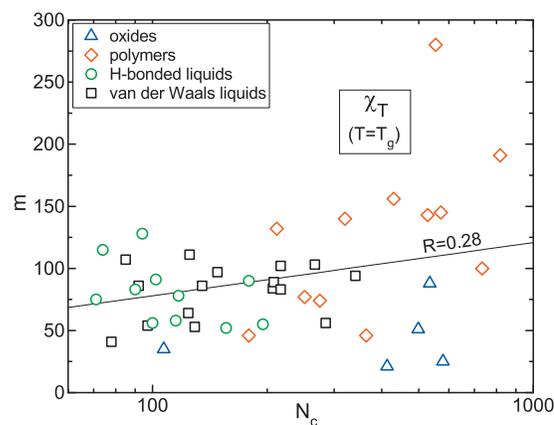

FIG. 5. Fragility corresponding to data in Fig. 4. Correlation coefficient is indicated.

$$N_c = \frac{k_B}{\Delta c_P} \left(\frac{\beta_K}{e} \right)^2 \left(\frac{d \ln \tau_\alpha}{d \ln T} \right)^2 , \qquad (5)$$

where e is Euler's number. One of the most common dynamic properties of supercooled liquids is their fragility, m, proportional to the apparent activation enthalpy at T_g normalized by $k_B T$; that is, m is proportional to the last factor in brackets in Eq. (5). It is well accepted that m correlates with the breadth of the relaxation time distribution; this has even been quantified as $m = 250(\pm 30) - 320\beta_K$ (Ref. 6) or $m \propto \beta_K^{-2}$ (Ref. 34). This implies that a smaller β_K in Eq. (5) is compensated by a larger fragility. The inference is that the variation of N_c among different materials is almost entirely a consequence of differences in Δc_P. Thus, both the form of Eq. (5) and the data in Fig. 4 indicate that there is essentially no relationship between the dispersion of relaxation times and the degree of correlation of the dynamics as quantified using $\chi_T(t)$.

Since β_K and m are correlated (inversely), it follows from the results in Fig. 4 that N_c and m would exhibit no mutual dependence. Previously Berthier et al.[21] examined data for 15 materials and concluded: "Dynamic correlations revealed by $\chi_T(t)$ increase weakly with fragility." Extending the data set threefold (Fig. 5) emphasizes the weakness of this putative correlation. Hong et al.[42] recently reported that the dynamic heterogeneity length scale deduced from the frequency of the Boson peak for various polymers and molecular liquids is not correlated with fragility. This is consistent with our results herein. Moreover, at T_g N_c from Eq. (5) shows an inverse proportionality to the configurational entropy (assuming the latter is related to the heat capacity change at T_g),[34] which implies no correlation with β_K.

III. CONCLUSIONS

We find that $\max\{\chi_4(t)\}$ correlates with β_K as T and ρ are varied for a given system, and although the χ_T approximation is inaccurate away from T_g, using the latter to obtain N_c this correlation with β_K is maintained *for a given material*. The problem arises when comparing different systems at their respective T_g. Different materials exhibit different N_c (from χ_T) for a given β_K because of differences in Δc_P. The form

of Eq. (4) obviates the possibility of a correlation of dynamic heterogeneity with either β_K or fragility.

Thus, it appears that short of abandoning the idea that a growing χ_4 susceptibility implies more dispersive dynamics, it may be necessary to re-examine the assumptions underlying χ_T. Its derivation assumes that the contribution to the nonlinear susceptibility from density fluctuations is significantly smaller than the effect of energy fluctuations.[21] However, for van der Waals molecular liquids, density and thermal energy exert about equal effects on the linear response, and even for polymers the contribution from density is not negligible.[43] Note that differences between the exact and approximation values for N_c are larger for an LJ system than for simulated silica (at least at higher T),[27] and indeed the density contribution is expected to be more important for the liquid than for the network glass-former.

Berthier *et al.*[27] pointed out that the susceptibility can change not only due to a growing length scale but also because of the growth in the magnitude of the local fluctuations. Whereas β_K depends on how much the individual (molecular) time varies within this volume, greater differences among reorientational rates do not necessarily imply a longer length scale for decay of mutual correlations. In other words, how different two quantities are is not equivalent to how fast their correlation decays. Nevertheless, it is not obvious how the amplitude of the fluctuations would not be manifested in the magnitude of β_K, although in the model of Wolynes,[18] different glass-formers are distinguished by the range of activation barriers within their correlation volume, rather than by the size of the latter. Clearly, further work on real materials measured by techniques such as multidimensional NMR is required in order to better assess the relationship between the relaxation time dispersion and N_c, and the utility of the $\chi_T(t)$ approximation in quantifying the latter.

ACKNOWLEDGMENTS

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