Characterizing dynamic length scales in glass-forming liquids

**To the Editor** — Recently, Kob et al.\(^1\) reported non-monotonic temperature dependence of a dynamic length scale, \(\xi^{sm}\), in a model supercooled fluid. Specifically, they found that \(\xi^{sm}\) peaks around a temperature at which deviations from mode-coupling-like fits to the relaxation time become visible (\(T = 6.0\) for their model) and that there is a decrease of \(\xi^{sm}\) below the mode-coupling crossover temperature (\(T = 5.2\) for their model). According to Kob et al., the maximum of \(\xi^{sm}\) signals a profound change in particles’ motions. Its presence allows the mode-coupling crossover to be identified without relying on any fitting procedure. It is consistent with a non-monotonic temperature dependence of finite size effects\(^2\).

To determine \(\xi^{sm}\), Kob et al. froze all particles in a semi-infinite space in an equilibrium configuration and analysed the dynamics of the particles in the other half-space as a function of the distance from the boundary. This ‘point-to-set’ method to determine a dynamic length scale differs from earlier calculations\(^3-4\) where the spatial correlations of particles’ dynamics were analysed. By examining these correlations, we found that the more commonly used\(^5\) dynamic correlation length, \(\xi_\alpha\), increases monotonically with decreasing temperature in the range of temperatures investigated by Kob et al.

We simulated the binary harmonic sphere system of Kob et al. using system sizes ranging from \(N = 10,000\) to \(100,000\) particles with up to \(10^6\) time steps for the 100,000 particle system at \(T = 5\). To determine \(\xi^{sm}\), we followed the method of refs 4 and 5. We defined a microscopic overlap function \(w_n(t) = \Theta(a - \|r_n(t) - r_0(0)\|)\) where \(r_n(t)\) is the position of particle \(n\) at a time \(t\), \(\Theta(x)\) is the Heaviside step function, and \(a = 0.3\sigma\) (\(\sigma\) is the diameter of the smaller particle). We calculated

\[
S_n(q,t) = N^{-1} \left\langle \sum_{n,m} w_n(t) w_m(t) e^{i q (r_n(0) - r_m(0))} \right\rangle
\]

which is the structure factor at wavevector \(q\) calculated using the initial positions of the particles that have moved less than a distance \(a\) over a time \(t\). Long-range correlations of these particles are revealed by an increase of \(S_n(q,t)\) at small \(q\). To facilitate the fitting procedure used to determine \(\xi(t)\), we independently calculated the four-point susceptibility \(\chi(q) = \frac{1}{2} \langle \chi(q) \rangle\) using the method proposed by Berthier et al.\(^6\) and described in detail in ref. 5.

In Fig. 1a we compare \(\xi_\alpha(t)\) and \(\xi^{sm}\). The relaxation time \(\tau_\alpha\) is defined through \(N^{-1} \left\langle \sum_n w_n(t) \right\rangle = e^{-1}\). In contrast to \(\xi^{sm}\), \(\xi_\alpha(t)\) is monotonically increasing with decreasing temperature. This is also evident from a direct examination of \(S_n(q,t)\) (Fig. 1b): it is readily apparent that \(\xi_\alpha(t)\) at \(T = 5\) (circles) cannot be smaller than at \(T = 8\) (triangles), as was reported for \(\xi^{sm}\). We shall emphasize that the finite wavevector data in Fig. 1b are ensemble independent. As discussed in ref. 6, the integrals of the four-point correlation functions are ensemble-dependent and this dependence is removed by adding correction terms derived in ref. 5.

We do, however, find evidence for a change of the particles’ dynamics in the temperature range examined by Kob et al., albeit at a slightly higher temperature of \(T = 8\), rather than \(T = 6\). By examining the relationship between the self-diffusion coefficient, \(\tau_\alpha\), \(\xi_\alpha(t)\) and \(\chi(q)\), we conclude that there is a crossover that manifests itself, *inter alia*, in a change from \(\tau_\alpha = \exp(k_1 \xi_{\alpha})\) to \(\tau_\alpha = \exp(k_2 \xi_{\alpha})\) (Fig. 1c), where \(k_i\) and \(k_2\) are fit parameters.

We should emphasize the difference between \(\xi^{sm}\) and \(\xi_\alpha\): \(\xi^{sm}\) pertains to a nonlinear response of a fluid’s dynamics to the pinning of one half of the particles, whereas \(\xi_\alpha\) characterizes the size of dynamic heterogeneities in an unperturbed bulk fluid. Although a length evaluated from a linear response function can be easily related to behaviour in an unperturbed fluid, such a relation is much less clear for the nonlinear response.

Kob et al.\(^1\)

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**Figure 1** Relationship between length scales in glass-forming liquids. a, A comparison of the temperature dependence of \(\xi_\alpha(t)\) (circles) and \(\xi^{sm}\) (squares; ref. 1). b, The four-point structure factor \(S_n(q,\tau)\) (symbols) and the Ornstein-Zernicke fits, \(\xi_\alpha(\tau)/(1 + \xi_\alpha(\tau)q^2)\) used to determine \(\xi_\alpha(\tau)\) (solid lines). c, The relationship between \(\tau_\alpha\) and \(\xi_\alpha(\tau)\) showing a crossover from \(\tau_\alpha = \exp(k_1 \xi_{\alpha})\) to \(\tau_\alpha = \exp(k_2 \xi_{\alpha})\).
and this Correspondence highlight the importance of: (1) establishing a connection between nonlinear response and dynamics in an unperturbed bulk fluid; (2) determining which length scale is the most relevant one for the understanding of glassy dynamics in the bulk; and (3) extending simulations beyond the mode-coupling crossover.

Kob et al. reply — In their Correspondence, Flenner and Szamel compare the temperature dependence of an alternative dynamic length scale, $\xi$, with that of $\xi^{dyn}$, which we studied. Using computer simulations of the same system, they conclude that these two length scales have a different temperature dependence. In particular, $\xi$ does not follow the striking non-monotonic temperature dependence we reported for $\xi^{dyn}$. Although both types of measurements aim at quantifying the spatial extent of dynamic correlations in supercooled liquids, the two procedures differ on essential points, which we now discuss.

Whereas we measured up to the distance at which the value of the relaxation time is affected by the presence of an amorphous wall, Flenner and Szamel quantify instead the spatial extent of spontaneous dynamic fluctuations at low wavevectors for a fixed timescale (the bulk relaxation time). These two measurements need not be directly related, although they seem to coincide at moderate temperatures (Fig. 1 of ref. 1). Although four-point functions as measured by Flenner and Szamel have played a pivotal role in previous analysis of dynamic heterogeneity, theoretical work has also revealed a number of shortcomings. Most notably, four-point functions display a strong dependence on the statistical ensemble chosen to perform measurements. As a result, they receive distinct contributions from density and energy fluctuations and show, even in idealized cases, complex scaling properties, which complicates the direct extraction of a correlation length. A second difficulty lies in the fact that these various contributions have different temperature dependences, with a crossover taking place very close to the mode-coupling temperature where the subtle effects we reported occur. We remark that $\xi$ corresponds to the temperature scale where $\xi$ and $\xi^{dyn}$ start to differ. These known weaknesses of four-point functions had in fact motivated our study of an alternative correlation length scale that is free of such ambiguities.

Given these important differences, it is not clear how a non-monotonic temperature evolution of dynamic correlations will manifest itself in the numerical data of Flenner and Szamel. Although the authors argue that the evolution of $\xi$ with the relaxation time shows a crossover (Fig. 1c in ref. 1), we point out that the presented data does not clearly show such a change in behaviour. Another possibility, not explored by Flenner and Szamel, could be that the functional form of the four-point correlation function $S(q,t)$ as investigated by these authors changes with temperature, in agreement with the idea that the geometry of the relaxing entities changes with temperature, as we argued. As the reported effect is small (Fig. 2b in ref. 2), one would presumably need a relative accuracy of $S(q,t)$ of better than 1% at low wavevectors. The data shown by Flenner and Szamel demonstrate that at present this remains technically difficult.

Finally, the crossover we report also coincides with the emergence of non-trivial static correlations in the system, a result that cannot be obtained using purely dynamic correlations. Overall, this suggests that the approach of pinning particles, for which no a priori knowledge of the nature of the relaxing entities is needed, is extremely helpful for studying small but important effects in the relaxation properties of glass-forming systems that cannot be drawn from the measurements of Flenner and Szamel. We point out that since our results were published, we have independently confirmed the qualitative change of transport properties in our system near the mode-coupling crossover by analysing the temperature evolution of dynamical finite size effects.

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Origin of the Au/Ge(001) metallic state

To the Editor — The physical realization of two-dimensional electron systems, such as semiconductor heterostructures, graphene and topological insulators, has revealed a cornucopia of new and exciting physics. It has been predicted that one-dimensional electron systems will also open up a new realm of physical phenomena, driven by the appearance of spin and charge collective modes and non-Fermi-liquid behaviour. The exploration of this new field has barely begun, its promises have not yet materialized, and the extent of its potential for new physics and devices remains largely untapped. However, a great leap forward has been made recently by Blumenstein and colleagues. In their