Time and length scales in supercooled liquids

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We numerically obtain a quantitative demonstration that development of spatial correlations of mobility as temperature is lowered is responsible for the ''decoupling'' of transport properties of supercooled liquids. This result further demonstrates the necessity of a spatial description of the glass formation and therefore seriously challenges a number of popular alternative theoretical descriptions.

Transport coefficients in liquids approaching the calorimetric glass transition change by many orders of magnitude [1]. It was discovered about a decade ago that conventional hydrodynamic relations are not valid in supercooled liquids in the sense that various transport properties ''decouple'' from one another [2,3]. In a standard liquid the viscosity η, translational diffusion coefficient D, and temperature T are linked by the hydrodynamic Stokes-Einstein relation, $D\eta \propto T$, which breaks down for supercooled liquids. The product $D\eta$ can be orders of magnitude larger than its hydrodynamic expectation at the glass transition, a puzzling observation which has received considerable interest in the last decade [2–6].

We have numerically obtained a quantitative link between this decoupling phenomenon and the existence of spatial correlations in the dynamics of supercooled liquids, also called ''dynamic heterogeneity'' [6]. We define here dynamic heterogeneity as expressing the fact that local dynamics of the liquid becomes *spatially* more correlated as T decreases [7]. This naturally implies the existence of a wide distribution of relaxational time and length scales [7,8]. Decoupling results because different transport coefficients correspond to different averages over those broad distributions [5].

Increasing heterogeneity was previously reported in a number of numerical works [9], but its direct relevance to transport was not established. On the other hand, experiments have quantified decoupling [2,4,6], but spatial correlations were only indirectly measured [6,10] because they are presently inaccessible to scattering experiments since neutrons/light probe too small/large length scales, and no obvious temperature dependence was found [6,11]. The special feature of this work is therefore to reconcile in a direct manner two facets of the slow dynamics of supercooled liquids. Our results demonstrate the correctness of the widely shared belief that decoupling is most naturally interpreted in terms of heterogeneous dynamics, a result which has been actively sought in the last decade and has deep theoretical implications.

Our argument shall be presented in three steps. In large scale numerical simulations of a well-characterized liquid model [12], we first quantify dynamic heterogeneity, then decoupling, to finally establish in a third step the quantitative

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connection between these two aspects. We finally discuss the important theoretical consequences of our findings.

We investigate the binary Lennard-Jones mixture proposed in Ref. [12] with $N_A = 1097$ particles of type A and $N_B = 275$ particles of type B at density $\rho = 1.2$. The $N = N_A + N_B$ particles interact via a Lennard-Jones potential, $V(\mathbf{r}_{\alpha\beta}) = 4\epsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r_{\alpha\beta})^{12} - (\sigma_{\alpha\beta}/r_{\alpha\beta})^6]$, with $\alpha,\beta = A,B$. Time, energy, and length are measured in units of σ_{AA}, ϵ_{AA}, and $\sqrt{m_A \sigma_{AA}^2/\epsilon_{AA}}$, respectively. Other parameters are $\epsilon_{AB} = 1.5$, $\epsilon_{BB} = 0.5$, $\sigma_{BB} = 0.88$, $\sigma_{AB} = 0.8$. Newton equations are integrated via a leapfrog algorithm with time step 0.01. Velocity rescaling is used to thermalize the system. We study the system at equilibrium for a wide range of temperatures, $T \in [0.42, 2.0]$. Since we measure fluctuations of local dynamical quantities, extremely long simulations are necessary to ensure not only thermal equilibrium, but also that sufficient statistics is recorded. We use the parallelized algorithm developed by Plimpton [13], and at all T runs of length at least $100\tau_\alpha$ are performed. Our computer capabilities fix the lowest studied temperature. Characteristic temperatures for this system are the onset of slow dynamics, $T_o \approx 1.0$ and $T_c \approx 0.435$, the location of the mode-coupling singularity in the analysis of Ref. [12].

First, we measure the temperature dependent coherence length $\ell(T)$, associated with the ordering of the liquid's dynamics by measuring spatial correlations between individual particle relaxations [9]. We use

$$F_{\mathbf{k}}(\mathbf{r},t) = \sum_{j=1}^{N} \delta(\mathbf{r}_j(0) - \mathbf{r})\cos\{i\mathbf{k}\cdot[\mathbf{r}_j(t) - \mathbf{r}_j(0)]\} \quad (1)$$

as a natural local indicator of the dynamics, since $F_s(\mathbf{k},t) = \langle F_{\mathbf{k}}(\mathbf{r},t)\rangle$ is the real part of the standard self-intermediate scattering function; $\langle\cdots\rangle$ stands for an ensemble average at temperature T, while $\mathbf{r}_j(t)$ is the position of particle j at time t. In our definition, dynamic heterogeneity implies that $F_{\mathbf{k}}(\mathbf{r},t)$ becomes long-ranged correlated as T is lowered [14], as can clearly be observed in the snapshots of Fig. 1.

The measurement of the mean size of the dynamic clusters shown in Fig. 1 involves the study of a two-point, two-time correlation function as already discussed in several papers [7,9,14–16]. We extract $\ell(T)$ from the wave vector dependence of the Fourier transform of the correlator $C_{\mathbf{k}}(\mathbf{r})$:
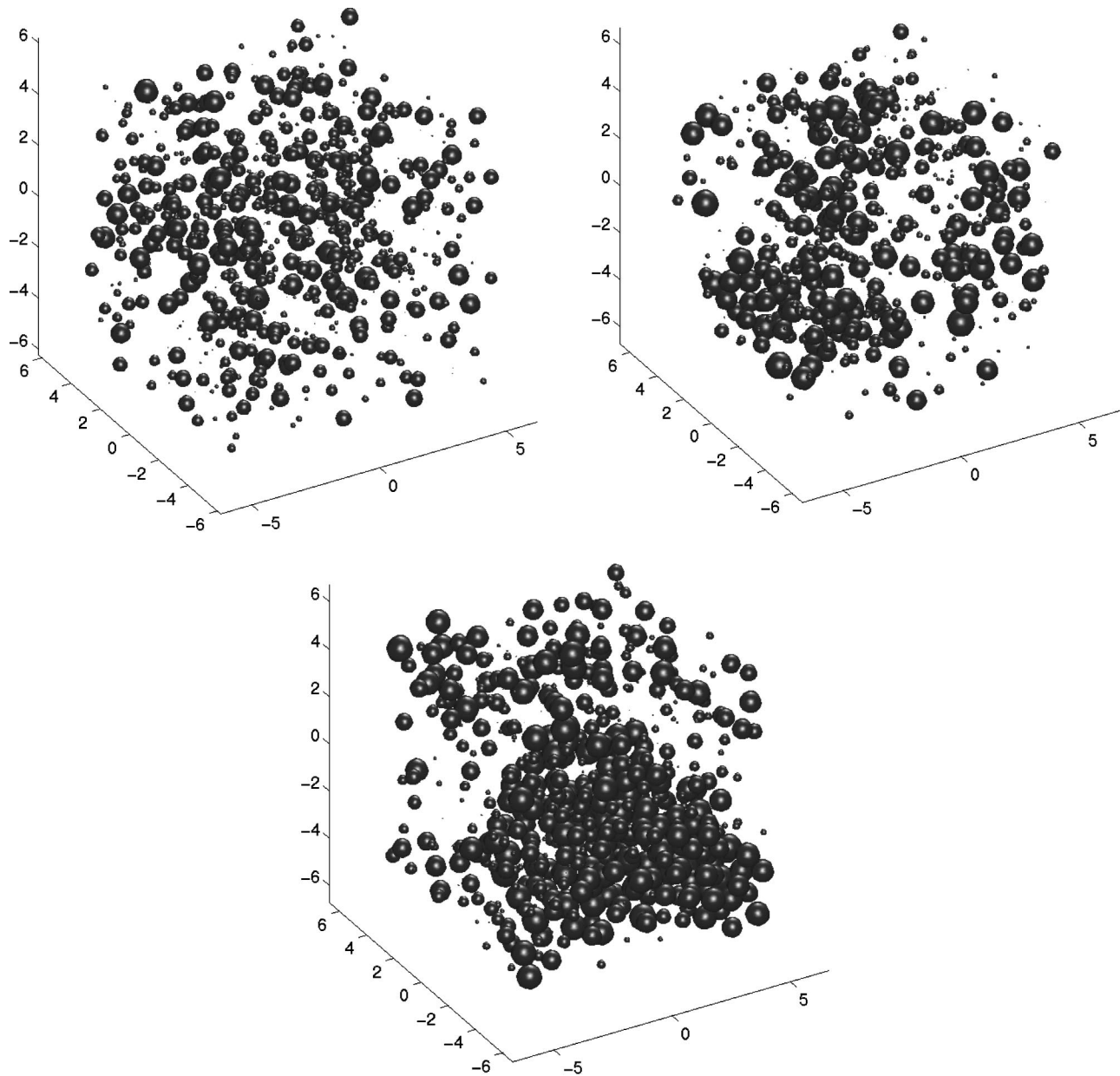
FIG. 1. Snapshots of the simulation box where points with $\delta F = F_{\mathbf{k}}(\mathbf{r},t) - F_s(\mathbf{k},t) > 0$ are represented with radii proportional to δF at temperatures $T = 2.0$ (top left), 0.6 (top right), and 0.45 (bottom), with $k = 5.41$, $t = \tau(k = 5.41, T)$. Increasing spatial correlations of the particles' individual dynamics when T is lowered is evident.

$$C_{\mathbf{k}}(\mathbf{r}) = \frac{\langle F_{\mathbf{k}}(\mathbf{0},\tau) F_{\mathbf{k}}(\mathbf{r},\tau)\rangle - \langle F_{\mathbf{k}}(\mathbf{r},\tau)\rangle^2}{\langle F_{\mathbf{k}}(\mathbf{r},\tau)^2\rangle - \langle F_{\mathbf{k}}(\mathbf{r},\tau)\rangle^2}, \qquad (2)$$

where $\tau = \tau(k = |\mathbf{k}|, T)$ is the relaxation time defined in a standard way from the time decay of $F_s(\mathbf{k},t)$ [12]. The shape of $C_{\mathbf{k}}(\mathbf{r})$, the temperature dependence of $\ell(T)$, and their theoretical interpretation in the context of a renormalization group analysis are the main objects of Ref. [16], so that we only report the data for $\ell(T)$ in Fig. 2 without discussing them further in the present report. Note that this first step is also the most demanding in terms of numerical resources.

Second, to probe decoupling, we measure with a great precision the temperature and wave vector dependences of
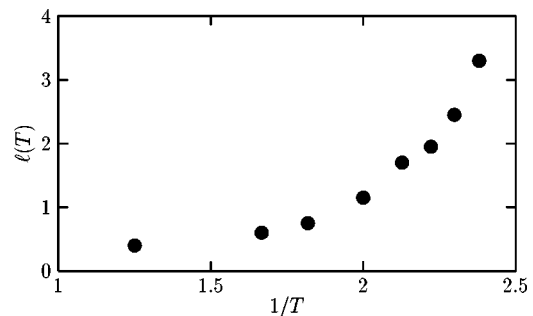

FIG. 2. Dependence of the coherence length $\ell(T)$ measuring the mean size of the clusters of Fig. 1 on the inverse temperature from the spatial fluctuations of $F_{\mathbf{k}}(\mathbf{r},t)$, for $k = 5.41$ and $t = \tau$, see Eq. (2). These data are discussed in detail in Ref. [16].
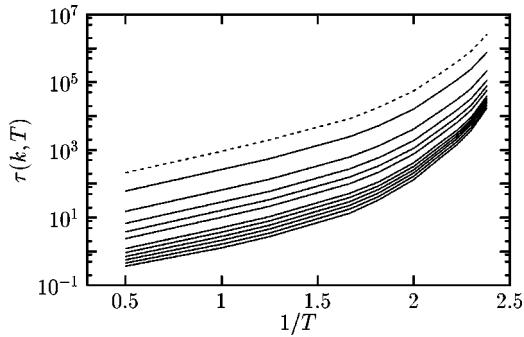
FIG. 3. Temperature dependence of $\tau(k,T)$ for various wave vectors, $k = 7.21, 6.61, 6.00, 5.41, 4.81, 4.21, 3.00, 2.40, 1.80, 1.20,$ and 0.60 (bottom to top). The dashed line is $10/D$, indicative of the $\tau(k \to 0, T)$ limit. Decoupling is observed as the temperature dependence is stronger at larger wave vectors.

FIG. 4. The quantity $X(k,T)$, Eq. (3), as a function of the scaling variable $k\ell(T)$ for various T. The horizontal full line is the diffusive prediction, $\tau D k^2 \sim \text{const}$. Departure from diffusion arises at large $k\ell$, directly demonstrating that the decoupling of different transport properties results from an increasingly spatially correlated dynamics.

the relaxation time $\tau(k,T)$ defined above. Our results are presented in Fig. 3. We find that the temperature dependence of $\tau(k \to 0, T)$ is the same as the inverse diffusion constant D^{-1}, as expected in a diffusive regime, while for wave vectors close to the first peak of the static structure factor, $k_0 \approx 7.2$, the temperature dependence is stronger, and follows that of the viscosity, establishing decoupling in our model system. This finding has already been reported in several numerical works [3,9,12,17], and is not unexpected in a system characterized by broad distributions of time scales.

We can now establish our main result which is the link between decoupling and dynamic heterogeneity. It stems from intermediate wave vectors, $0 < k < k_0$, for which a crossover is observed in the temperature evolution of $\tau(k,T)$, uniquely governed by the value of the scaling variable $k\ell(T)$. We find that $\tau(k,T)$ follows D^{-1} when $k\ell < 1$, or η for $k\ell > 1$. It is therefore useful to define the following ratio:

$$X(k,T) = \frac{\tau(k,T)D(T)}{\tau(k,T_o)D(T_o)}, \qquad (3)$$

since $X(k,T)$ is wave vector independent through the denominator, and is temperature independent if $\tau(k,T) \propto D^{-1}(T)$, so that by definition $X(k,T) = 1$ if no decoupling occurs.

Instead we find that time scales $\tau(k,T)$ spanning seven orders of magnitude can be collapsed on a unique, nontrivial curve, as shown in Fig. 4, so that

$$X(k,T) \simeq \mathcal{X}[k\ell(T)]. \qquad (4)$$

We find that $\mathcal{X}(x) = 1 + x^\beta$ with $\beta \approx 1.6$ represents the numerical data quite well, so that the diffusive regime is limited to small values of the scaling variable $k\ell$. Note that this scaling extends from the onset temperature T_o to well below the mode-coupling temperature T_c. From the scaling behavior (4), our main conclusion is therefore that dynamic heterogeneity emerging at T_o and increasing when T is lowered is directly responsible for decoupling.

Decoupling phenomena have been experimentally characterized close to the calorimetric glass transition where they
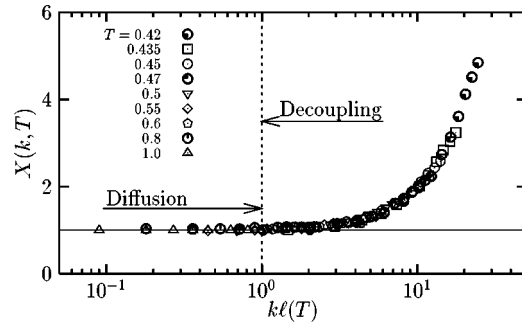
are more pronounced, as can be understood from Fig. 4. We believe, however, that the behavior is qualitatively similar to our numerical investigations because even an increase of several decades in time scales corresponds to a very modest change of the coherence length $\ell(T)$, which is the key quantity of the problem. Experiments report moreover that $D\eta \sim \eta^\alpha$ with $1 > \alpha > 0$ [2,4,6]. We find similarly that, at fixed k, $\tau D \sim \ell^\beta$. The dynamic scaling discussed in Ref. [16], $\ell \sim \tau^{1/z}$, yields indeed the observed power law,

$$D\eta \sim \eta^{\beta/z}, \qquad (5)$$

with an exponent $\beta/z \approx 0.35$. Various values for this exponent have been reported from experiments [6,18] and a precise characterization of all these exponents for various liquids on a wide range of length scales would be most useful. Note that the use of the crossover scaling function $\mathcal{X}(x)$ in Eq. (5) would automatically yield a smaller effective value of the exponent β/z on a restricted time window.

Finally, we discuss the theoretical interpretations and consequences of Fig. 4. These results constitute the direct demonstration that, much as in ordinary critical phenomena, large spatial correlations not only accompany but also influence the properties of supercooled liquids, and therefore the glass formation itself. Thus, they are a striking confirmation that spatial approaches are necessary to understand the formation of glasses, and several such quantitative approaches can be found in the literature [16,19–22].

When a growing length scale for dynamic heterogeneity is included, our results are very naturally explained, just as the decoupling phenomenon is [5]. Tuning the wave vector in Eq. (1) amounts to probing the dynamics on different length scales, smoothly interpolating between D^{-1} ($k \to 0$) and η ($k \approx k_0$), as is observed in Fig. 4 which clearly demonstrates that the crossover, $k\ell(T) \sim 1$, is ruled by the increasing correlation length of dynamic heterogeneity.

Our findings also confirm that dynamic heterogeneity is a central aspect of the dynamics of supercooled liquids in that time and length scales are intimately connected [7,19]. This is at odds with the opposite belief that slow dynamics emerges because of the local blocking of the particles with-

out any relevant length scale beyond the interparticle distance, the famous "cage effect" [23]. Our results make it clear that the α relaxation is instead a cooperative phenomenon where single particle dynamics are coherent on the length scale $\ell(T)$ much larger than k_0^{-1}, which is in turn directly responsible for the temperature behavior of the time scales. Moreover, $\ell(T)$ starts to grow significantly and connects to time scales even in the regime $T_c < T < T_o$ where a mode-coupling analysis supposedly applies [12,23]. This confirms that heterogeneous dynamics, decoupling, and activated dynamics set in at the onset temperature T_o which is therefore the key temperature scale of the problem, as opposed to T_c where no significant change of mechanism takes place [19,24]. We note that the absence of nontrivial spatial correlations [25], the incorrect identification of T_c as a key temperature scale, and the absence of decoupling in the present formulation of the mode-coupling theory represent major failures of this approach.

Our results constitute therefore a sharp test to discriminate between the many theoretical approaches to the glass transition problem [1]. Indeed, any theory in which time scales do not directly follow from the existence of spatial correlations growing when T is decreased below the onset temperature T_o

is seriously challenged by the present work. Quite importantly, this includes a number of approaches which have been nonetheless much applied to describe experimental results [23,26,27].

Our conclusions are drawn from a scaling relation discovered for a specific, yet paradigmatic, model system. Although we believe they are generic to supercooled liquids, the absence of any data on different systems emphasizes both the special feature of this work and the need for further detailed investigations of the slow dynamics of various supercooled liquids. It is clear, for instance, that the precise experimental characterization of $\ell(T)$ should become a central goal for future investigations, and the present work therefore suggests a way to access physically relevant length scales.

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