Time and length scales in supercooled liquids

Ludovic Berthier

Theoretical Physics, University of Oxford, 1 Keble Road, Oxford, OX1 3NP, UK
(Dated: October 29, 2018)

We numerically obtain the first 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.

PACS numbers: 64.70.Pf, 05.70.Jk

Transport coefficients in liquids approaching the calorimetric glass transition change by many orders of magnitude. 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. In a standard liquid the viscosity, \( \eta \), 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. Experiments have quantified decoupling \( \eta \), but spatial correlations were only indirectly measured \( D \). 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, and at all \( T \) runs of length at least \( 100 \tau_o \) 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. We use

\[
F_k(r, t) = \sum_{j=1}^{N} \delta(r_j(0) - r) \cos \left( ik \cdot [r_j(t) - r_j(0)] \right)
\]

(1)
as a natural local indicator of the dynamics, since \( F_k(k, t) = \langle F_k(r, t) \rangle \) is the real part of the standard self-intermediate scattering function; \( \langle \cdots \rangle \) stands for an ensemble average at temperature \( T \), while \( r_j(t) \) is the position of particle \( j \) at time \( t \). In our definition, dynamic heterogeneity implies that \( F_k(r, t) \) becomes long-ranged correlated as \( T \) is lowered, as can clearly be observed in the snapshots of Fig. 1.
FIG. 1: Snapshots of the simulation box where points with $\delta F = F_k(r, t) - F_s(k, t) > 0$ are represented with radii proportional to $\delta F$ at temperatures $T = 2.0, 0.6$ and $0.45$ (top to 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.

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 $F_k(r, t)$, for $k = 5.41$ and $t = \tau$, see Eq. (2). These data are discussed in detail in Ref. [16].

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, 15, 16]. We extract $\ell(T)$ from the wavevector dependence of the Fourier transform of the correlator $C_k(r)$:

$$C_k(r) = \frac{\langle F_k(0, \tau)F_k(r, \tau) \rangle - \langle F_k(r, \tau) \rangle^2}{\langle F_k(r, \tau)^2 \rangle - \langle F_k(r, \tau) \rangle^2}, \quad (2)$$

where $\tau = \tau(k = |k|, T)$ is the relaxation time defined in a standard way from the time decay of $F_s(k, t)$ [12]. The shape of $C_k(r)$, the temperature dependence of $\ell(T)$, and their theoretical interpretation in the context of a renormalization group analysis are the main object 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.

Secondly, to probe decoupling, we measure with a great precision the temperature and wavevector dependences of 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 wavevectors 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 wavevectors, $0 < k < k_0$, for which a crossover is observed in the temperature evolution of $\tau(k, T)$, uniquely governed by the value of the scaling
We find that \( X \) also corresponds to a very modest change of the coherence length even an increase of several decades in time scales corresponding to well below the mode-coupling temperature \( T_c \), directly demonstrating that the decoupling of different transport properties results from an increasingly spatially correlated dynamics.

\[
X(k, T) = \frac{\tau(k, T)D(T)}{\tau(k, T_o)D(T_o)}, \quad (3)
\]

since \( X(k, T) \) is wavevector 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 7 orders of magnitude can be collapsed on a unique, non-trivial curve, as shown in Fig. 4 so that

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

We find that \( \mathcal{A}(x) = 1 + x^2 \) 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 behaviour in (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 behaviour is qualitatively similar to our numerical investigations because even an increase of several decades in time scales corresponds to a 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 \( 1 > \alpha > 0 \). We find similarly that, at fixed \( k \), \( \tau D \sim \ell^\beta \).

The dynamic scaling discussed in Ref. [17], \( \ell \sim \tau^{1/z} \), yields indeed the observed power law, 

\[
D\eta \sim \eta^{\beta/z}, \quad (5)
\]

with an exponent \( \beta/z \approx 0.35 \). Various values for this exponent have been reported from experiments [7, 13] 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 \( \mathcal{A}(x) \) in Eq. (4) would automatically yield a smaller effective value of the exponent \( \beta/z \) on a restricted time window.

Finally, we discuss the theoretical interpretations and consequences of Fig. 4. These results constitute the first 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, 17, 20, 21, 22].

When a growing length scale for dynamic heterogeneity is included, our results are very naturally explained, just as the decoupling phenomenon is [3]. Tuning the wavevector in (1) amounts to probing the dynamics on different length scales, smoothly interpolating between \( D^{-1}(k \to 0) \) and \( \eta(k \approx k_o) \), 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 [5, 19]. This is at odds with the opposite belief

\[
FIG. 3: \text{Temperature dependence of } \tau(k, T) \text{ for various wavevectors, } k = 7.21, 6.61, 6.00, 5.41, 4.81, 4.21, 3.00, 2.40, 1.80, 1.20, \text{ and } 0.60 \text{ (bottom to top). The dashed line is } 10/D, \text{ indicative of the } \tau(k \to 0, T) \text{ limit. Decoupling is observed as the temperature dependence is stronger at large wavevectors.}
\]

\[
FIG. 4: \text{The quantity } X(k, T), \text{ Eq. (3), as a function of the scaling variable } k\ell(T) \text{ for various } T. \text{ The horizontal full line is the diffusive prediction, } \tau D k^2 \sim \text{const. Departure from diffusion arises at large } k\ell, \text{ directly demonstrating that the decoupling of different transport properties results from an increasingly spatially correlated dynamics.}
\]
that slow dynamics emerges because of the local blocking of the particles without any relevant length scale beyond the interparticle distance, the famous “cage effect” 22. Our results make it clear that the alpha-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 behaviour 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 11, 24. We note that the absence of non-trivial 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 new test to discriminate between the many theoretical approaches to the glass transition problem 11. 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 novelty 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 new way to access physically relevant length scales.

I thank S. Whitelam and J.P. Garrahan for a fruitful collaboration 16 and discussions, J.-L. Barrat, J.-P. Bouchaud and G. Tarjus for useful correspondence. This work is supported by CNRS (France), E.U. (Marie Curie Grant No. HPMF-CT-2002-01927), Worcester College Oxford (UK), and Oxford Supercomputing Centre at Oxford University (UK).

---

* Also at: Laboratoire des Verres, Université Montpellier II, 34095 Montpellier, France

[1] P.G. Debenedetti and F.H. Stillinger, Nature 410, 259 (2001).

[2] F. Fujara, B. Geil, H. Sillescu, and G. Fleischer, Z. Phys. B 88, 195 (1992).

[3] J.-L. Barrat, J.-N. Roux, and J.-P. Hansen, Chem. Phys. 149, 197 (1990).

[4] M.T. Cicerone and M.D. Ediger, J. Chem. Phys. 104, 7210 (1996); S.F. Swallen, P.A. Bonvallet, R.J. McMahon, and M.D. Ediger, Phys. Rev. Lett. 90, 015901 (2003).

[5] J.A. Hodgdon and F.H. Stillinger, Phys. Rev. E 48, 207 (1993); G. Tarjus and D. Kivelson, J. Chem. Phys. 103, 3071 (1995); D.N. Perera and P. Harrowell, J. Chem. Phys. 104, 2369 (1996); Y.J. Jung, J.P. Garrahan and D. Chandler, cond-mat/0311396.

[6] H. Sillescu, J. Non-Cryst. Solids 243, 81 (1999); M.D. Ediger, Annu. Rev. Phys. Chem. 51, 99 (2000).

[7] J.P. Garrahan and D. Chandler, Phys. Rev. Lett. 89, 035704 (2002).

[8] L. Berthier and J.P. Garrahan, J. Chem. Phys. 119, 4367 (2003).

[9] M.M. Hurley and P. Harrowell, Phys. Rev. E 52, 1694 (1995); Y. Hiwatari and T. Muranaka, J. Non-Cryst. Solids 235-237, 19 (1998); C. Bennemann, C. Donati, J. Baschnagel, and S.C. Glotzer, Nature 399, 246 (1999); S.C. Glotzer, V.N. Novikov, and T.B. Schroder, J. Chem. Phys. 112, 500 (2000); B. Doliwa and A. Heuer, Phys. Rev. E 61, 6989 (2000).

[10] U. Tracht, M. Wilhelm, A. Heuer, H. Feng, K. Schmidt-Rohr, and H.W. Spiess, Phys. Rev. Lett. 81, 2727 (1998); S.A. Reinsberg, X.H. Qiu, M. Wilhelm, H.W. Spiess, and M.D. Ediger, J. Chem. Phys. 114, 7299 (2001).}

[11] X.H. Qiu and M.D. Ediger, J. Phys. Chem. B 107, 459 (2003).

[12] W. Kob and H.C. Andersen, Phys. Rev. Lett. 73, 1376 (1994).

[13] S. Plimpton, J. Comput. Phys. 117, 1 (1995).

[14] L. Berthier, Phys. Rev. Lett. 91, 055701 (2003).

[15] S.C. Glotzer, J. Non-Cryst. Solids 274, 342 (2000).

[16] S. Whitelam, L. Berthier, and J.P. Garrahan, preprint cond-mat/0310207.

[17] R. Yamamoto and A. Onuki, Phys. Rev. E 58, 3515 (1998).

[18] L. Andreozzi, A. Di Schino, M. Giordano, and D. Leporini, Europhys. Lett. 38, 669 (1997).

[19] L. Berthier and J.P. Garrahan, Phys. Rev. E 68, 041201 (2003).

[20] J. Jäckle, J. Phys. C 14, 1423 (2002); J.P. Garrahan and D. Chandler, Proc. Natl. Acad. Sci. USA 100, 9710 (2003).

[21] D. Kivelson, S.A. Kivelson, X. Zhao, Z. Nussinov and G. Tarjus, Physica A 219, 27 (1995).

[22] X. Xia and P.G. Wolynes, Proc. Natl. Acad. Sci. USA 97, 2990 (2000).

[23] W. Götze and L. Sjögren, Rep. Prog. Phys. 55, 55 (1992).

[24] Y. Brumer and D.R. Reichman, preprint cond-mat/0306580.

[25] In S. Franz and G. Parisi, J. Phys. C 12, 6335 (2000), the volume integral of $\ell$ is shown to diverge at $T_o$ in the fully-connected spherical $p$-spin glass model. This suggests that non-trivial dynamic spatial correlations might underlie the mode-coupling instability at $T = T_o$.

[26] D. Turnbull and M.H. Cohen, J. Chem. Phys. 29, 1049 (1958); G.S. Grest and M.H. Cohen, Adv. Chem. Phys. 48, 454 (1981).

[27] M. Goldstein, J. Chem. Phys. 51, 3728 (1969). F.H. Stillinger, Science 267, 1935 (1995); D.J. Wales, Energy landscapes (CUP, Cambridge, 2003).