How do dynamic heterogeneities evolve in time?

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Abstract

We present simulations of a hard disc system and analyze the time evolution of the dynamic heterogeneities. We characterize the time evolution of slow regions and slow particles individually. The motion of slow clusters turns out to be very restricted, i.e. a cluster is generated and annihilated in a spatial region four times the size of its maximum extent. The residual motion of the cluster can be traced back to subdiffusive motion of the constituent particles and the process of absorption and loss of adjacent particles. The subdiffusive dynamics is independent of how long the particles remain slow. Clusters of fast particles show an even smaller reach, which seems to be due to their short life time.

Key words: dynamic heterogeneities, supercooled liquid, computer simulation
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Dedicated to Prof. Hans Sillescu on occasion of his 65\textsuperscript{th} birthday.

1 Introduction

In the last decade many important pieces of information have been gained about the microscopic details of the glass formation process by experiments as well as simulations [1–3]. One specific aspect deals with the nature of dynamic heterogeneities [4]. It has been realized that dynamic heterogeneities are one of the key ingredients for understanding the nature of non-exponential relaxation and the decoupling of translational and rotational dynamics [5]. Their presence has been uniquely shown by very different experiments like NMR [6], solvation...
dynamics [7], and optical [8] and dielectric dynamic hole burning [9]. Whereas these methods can be used for bulk probes, fascinating new experiments have been recently developed which can be also used for mesoscopic samples [10,11].

Most experiments have concentrated on two different aspects of dynamic heterogeneities. First, what is the exchange time scale on which slow molecules become fast? Second, on which length scale are slow (or fast) molecules clustered in the sample? For temperatures several Kelvin above $T_g$ all experiments clearly revealed that the exchange time scale is of the order of the $\alpha$ relaxation. This means that on average after one relaxation process the dynamics of a slow molecule is statistically uncorrelated with its initial dynamics. This result has been mainly obtained for the rotational dynamics of the molecules. Furthermore the length scale of dynamic heterogeneities could be directly measured via multidimensional NMR experiments for which the information about the length scale can be obtained from spin diffusion. Typical length scales are of the order of 3 nm [12,13].

In recent years several computer simulations on glass forming systems have been performed [14–18], in order to elucidate the properties of dynamic heterogeneities above the mode coupling temperature $T_c$ [19] (and thus still far above $T_g$). Many details about the relevance of dynamic heterogeneities, their time scale, and length scale are therefore known today. For example it could be shown that the length scale strongly increases with decreasing temperature (above $T_c$) and that the degree of cooperativity depends on the time scale with a maximum at a few times the $\alpha$ relaxation time [20–22]. Furthermore a strong relation between dynamic heterogeneities and the non-gaussian parameter has been found [23].

To the best of our knowledge no specific information is available about the time evolution of the dynamic heterogeneities in space. The goal of this paper is to analyze the time evolution of dynamic heterogeneities for the translational motion of a simple model glass former. In what follows we analyze how the slow particles as well as the slow regions, i.e. subsets of adjacent slow particles, move around. Both aspects are necessary for a full characterization of dynamic heterogeneities. Note that also most experiments mentioned above are sensitive to the properties of the slow molecules. Further, we provide a comparison with the dynamics of fast clusters. This is a first step to back up possible scenarios of the time evolution of dynamic heterogeneities, as indicated e.g. in [24].
2 Simulation

We performed simulations on two- and three-dimensional hard sphere systems. Here we present the results for the 2D system in order to optimize visualization. The simulation box contains 9201 particles and the total simulation time is 5000 \( \tau_\alpha \). We choose a Monte Carlo algorithm for the time evolution of the system. Our main results are for the packing fraction \( \rho = 0.77 \). In order to hamper crystallization we choose a polydispersity of 25%. Periodic boundary conditions are used.

One technical question deals with the determination of slow particles as well as slow regions. Choosing the mean square displacement as a criterion may give misleading results since by chance fast particles can be back at the origin after some time. In this respect it has proven useful to monitor the respective neighborhoods of the individual particles. We define the nearest neighbors via a modified Voronoi construction, taking into account the different particle sizes [25]. Then particles, which are slow on a time scale \( \tau \), can be identified via the criterion that the number of neighbor changes during this time interval is smaller than some fixed number \( k_{NN} \). Particles leaving or entering a neighborhood are counted as neighbor changes. Here we choose \( k_{NN} = 5 \), which means that particles with an exchange of two neighbors are considered as slow. This is a sensible choice since on average, a particle is surrounded by six others. On this basis we define a particle to be slow on a time scale \( \tau \) at time \( t \) if there exists a time interval \( t \in [t_0, t_1] \) such that \( t_1 - t_0 = \tau \) and the particle performs less than 5 neighbor changes during this time interval.

Regions of slow particles (slow clusters) are identified via a straightforward cluster analysis. Starting from a slow particle one has to check which other slow particles are connected with this slow particle via other slow particles, i.e. by a chain of slow nearest neighbors.

3 Results

First we show that the time scale on which nearest neighbor changes occur is strongly related to the time scale of structural relaxation. For this purpose we define the function \( C_5(t) \) which counts the fraction of particles with less than 5 neighbor changes between time 0 and time \( t \). In Fig.1 we show the time-dependence of \( C_5(t) \) for different densities. As known from other observables the dynamics is dramatically reduced when approaching high densities. In the inset we show the decay time of \( C_5(t) \) as defined by the criterion \( C_5(\tau_{nn}) = 1/e \), together with the alpha relaxation time \( \tau_\alpha \) which has been extracted from the incoherent scattering function (see [22] for more details). Evidently \( \tau_\alpha \) and
\( \tau_{nn} \) are basically proportional to each other. Thus \( \tau_{nn} \) is also an appropriate time scale to characterize structural relaxation. For the analysis of cluster dynamics, we define slow particles on the time scale \( \tau = 200 \tau_\alpha \). In this way we select ca. 7% of all particles for the density \( \rho = 0.77 \) which will be dealt with exclusively now. Before quantifying the time evolution of slow clusters we visualize the dynamics of a single slow cluster, defined at \( t = 0 \). In Fig. 2(a) configurations are shown for \( t = 0 \) and \( t = 25 \tau_\alpha \). The particles belonging to the slow cluster are highlighted by black circles. One can clearly see that the constituents of the slow cluster as well as some adjacent particles on the left side are moving highly collectively. The dynamics closely resembles the motion of a small crystallite in a fluid. Note, however, that the slow cluster is fully amorphous, showing no crystalline structural features. Of course, there also exist some other slow particles, which do not belong to the selected slow cluster. The dynamics of the same cluster during the time interval \([50 \tau_\alpha, 75 \tau_\alpha]\), has many features of the initial dynamics. Again we see the cooperative dynamics of this system. Comparison of Figs. 2(a) and (b) also shows that the full cluster has shifted rightwards. Thus there exists some type of cluster dynamics, which, however, seems to be very slow. In Fig. 2(c), showing the dynamics during the time interval \([500 \tau_\alpha, 525 \tau_\alpha]\) one can clearly see that several particles from the surface have left the cluster and thus became fast during \( 75 \tau_\alpha \) and \( 500 \tau_\alpha \). On a qualitative level this scenario may be denoted surface-melting. From the shaded Voronoi areas we see that the cluster also may grow by attaching new slow particles. Finally in Fig. 2(d) the cluster breaks in its individual parts - the life time of the slow cluster is over. Note that this cluster has lived for a time as long as \( 1300 \tau_\alpha \).

Fig. 1. Time dependence of \( C_5(t) \) for different densities. In the inset the density dependence of \( \tau_{nn} \) is compared with that of the alpha relaxation time \( \tau_\alpha \).
Fig. 2. Time evolution of a slow cluster. The constituents of the slow cluster are highlighted. Shown are the configurations in the intervals (a) $[0, 25\tau_{\alpha}]$, (b) $[50\tau_{\alpha}, 75\tau_{\alpha}]$, (c) $[500\tau_{\alpha}, 525\tau_{\alpha}]$, and (d) $[1300\tau_{\alpha}, 1325\tau_{\alpha}]$. The configurations at the beginning and the end of the time interval are connected by straight lines. The shaded Voronoi polygons reflect the set of slow particles at the beginning of the above intervals. The position in (a) of the dark particle is shown as a black dot in (b).

This cluster was one of the longest-living structures in our simulation. Nevertheless the time evolution is typical for many other slow clusters appearing and disappearing during the course of the simulation. In particular we always observe the highly cooperative nature of the dynamics. This observation directly implies that it is not possible for particles to enter into the core of a slow
cluster. We have not seen such an event during our simulations. The dynamics of the cluster has two facets. First, the highlighted particles were moving also during the time where they belonged to the slow cluster. We call this real dynamics. Additionally, the set of particles belonging to the slow cluster, may vary with time. From Fig.2(b) to (c), the slow cluster has lost 38 members but gained 17 new. This type of time evolution will be denoted as fictive dynamics.

In order to quantify the time evolution of dynamic heterogeneities we will be guided by two questions: How does the slow cluster move in space during its life time and which particles contribute to this slow cluster? To answer these questions, we introduce four observables: (i) A is the absolute area one distinct slow cluster covers during its lifetime. For the definition of A the Voronoi areas of all members of the cluster at all times are superimposed. (ii) M is the maximum cluster size during its life time. We only consider clusters with \( M > 10 \) average particle sizes. (iii) \( A_p \) is defined in analogy to A but counts the total number of different particles which were members of the cluster during its life time. (iv) \( M_p \) denotes in analogy to M the maximum size of the slow cluster in terms of particles. In particular we are interested in the ratios \( A/M \geq 1 \) and \( A_p/M_p \geq 1 \). First we discuss the possible scenarios in terms of both values. If dynamic heterogeneities were dominated by extrinsic forces (e.g. dynamics of interacting ions in a basically fixed disordered network) there would exist fixed areas in space where the dynamics would be slower all the time. Whenever a particle entered this area it would become slow. Since many particles will enter and leave one expects \( A/M \ll A_p/M_p \). Intuitively this means that the (here totally immobile) slow regions move slower than the slow particles. In contrast, if the dynamic heterogeneities are not related to fixed structural variations in the probe it is hard to imagine that the dynamics of slow regions is slower than the dynamics of the constituting slow particles. This general physical reason implies \( A/M \geq A_p/M_p \geq 1 \). In the case \( A/M \approx 1 \) the time evolution of the slow cluster can be characterized as a local process of generation and annihilation. No dynamics is involved. For \( A/M > 1 \) the dynamics of the slow regions can be characterized by two independent contributions which correspond to the real and fictive dynamics, introduced above. First, in the case \( A_p/M_p = 1 \) the dynamics of the slow region is fully related to the dynamics of the constituting slow particles, thus it is real. Second, in the opposite case \( A/M = A_p/M_p \) the dynamics of the slow cluster is exclusively due to changes in the set of slow particles belonging to the slow cluster. Thus it is fictive.

For our analysis we only consider clusters with \( M > 10 \) average particle sizes. In Fig.3 the distribution of \( A/M \) and \( A_p/M_p \) is plotted for all relevant clusters during our analysis. The average value of \( A/M \) is 4.3. This result indicates that in agreement with the example of Fig.2 there is only a minor time evolution of the slow clusters. However, the generation and annihilation process of a typical slow cluster is not fully local. As discussed above, the value of \( A_p/M_p \) contains the relevant information about the number of particles involved in...
Fig. 3. The distribution of the ratio \( A/M \) and \( A_p/M_p \) (see text) for all relevant slow clusters. The mean values are 4.3 and 1.8, respectively. The inset illustrates the definition of \( A \) and \( M \).

the time evolution of the clusters. One can see that its distribution is shifted to smaller values as compared to \( A/M \). We obtain \( \langle A_p/M_p \rangle = 1.8 \). A cluster of maximum size ten rambles therefore (on average) between 18 particles. The ratio \( \langle (A_p/M_p) - 1 \rangle / (\langle A/M \rangle - 1) \) is a good measure for the contribution of fictive dynamics to the overall dynamics. Here we see that approximately 3/4 of the cluster dynamics is due to real and one quarter due to fictive dynamics. Using a shorter time scale for the identification of slow particles (here we used \( \tau = 200\tau_\alpha \), see above) one would increase the contribution of fictive dynamics since it would be more easy for the slow cluster to attach adjacent particles. If we eventually reached a selection level of more than ca. 15%, the life time of clusters would become infinite due to fictive dynamics. In other words, there would always remain fragments of every cluster which would further bequest their origin to freshly emerging slow regions. For this reason, we have restricted the calculation of \( A/M \) to the 7% slowest particles, corresponding to a selection time of \( \tau = 200\tau_\alpha \).

We have seen that also the sluggish dynamics of the constituting particles is a relevant effect for the dynamics of slow clusters. In any event, most experiments are only sensitive to the single particle behavior. Therefore it may be of interest to study the single particle dynamics somewhat closer. Here we consider the mean square displacement \( \langle r^2(t, t_0) \rangle \) of particles which have less than 5 neighbor changes during the time interval \([0, t_0]\), and have the 5th neighbor change during the subsequent interval \([t_0, t_0 + \Delta t]\), where \( \Delta t = t_0/10 \). We first discuss the case \( t_0 = 200\tau_\alpha \) which corresponds to the rightmost curve in Fig.4. One can clearly see the change of slope around \( t = t_0 \). This effect is directly related to the fact that by definition all particles become mobile around \( t_0 \). Of
interest is the time regime $t < t_0$ during which the particles were slow. The dominant feature here is the subdiffusive dynamics with an exponent 0.65 during two decades of time. This quantifies the previous observation in Fig.2 that slow particles (and thus slow regions) are not totally immobile. Intuitively, the subdiffusive behavior implies that slow clusters are rattling back- and forth in effective cages formed by the surrounding fluid like particles. Interestingly, the curves for the other values of $t_0$ look very similar for their respective $t < t_0$. Thus the life time of a slow cluster and the dynamics during this life time are uncorrelated. From the numbers extracted from $C_5(t)$ (see Fig.1, one can estimate that more than 80% of all particles become fast before moving more than a nearest neighbour distance, i.e. $\langle r^2 \rangle \approx 4$. Thus on the length scale of the nearest neighbor distance a slow particle can be viewed as immobile until it becomes fast and subsequently contributes to the structural relaxation.

So far, we have concentrated on the regions of slow particles. One might expect that the time evolution of fast regions is quite different. To check this, we defined fast particles by not being slow on a time scale $\tau = 10\tau_\alpha$, which again yielded a selection of about 7%. Here we obtain $\langle A/M \rangle = 3.4$ and $\langle A_p/M_p \rangle = 2.8$. Thus, fast clusters are more localized than slow clusters. Furthermore, the ratio $(\langle A_p/M_p \rangle - 1)/\langle A/M \rangle = 0.75$ indicates that the real dynamics has only a little contribution to the overall time evolution. This
may come as a surprise since we are concerned with very mobile particles. Obvious explanations for this are the comparatively small life time of fast clusters and the lacking cooperativity of fast particles.

4 Discussion

Using appropriately defined observables, computer simulations can be used to obtain very detailed information about microscopic processes. Here we have specified the time evolution of slow particles and slow clusters. As main results we obtained that (i) the dynamics of particles in slow clusters is highly cooperative, thus excluding the dynamics of single particles through slow clusters, (ii) the dynamics of slow clusters is highly restricted in space, (iii) the residual dynamics is both due to temporal variation in shape as a result of adjacent fast particles becoming slow or slow particles from the surface becoming fast (fictive dynamics) and due to the motion of the constituting particles (real dynamics), (iv) the so-defined real dynamics is subdiffusive until the particle becomes fast and is independent from the time the particle remains slow, (v) clusters of fast particles move less than their slow counterparts. On a qualitative level the results (i)-(iii) can be already identified in Fig.2. They might give rise to some refinement of previous models of dynamic heterogeneities, see e.g. in [26,27].

Finally we would like to discuss two questions. What is the relation to experimental results and what is the underlying origin of these features which are at the core of the glass-forming process?

A discussion of the relation to experiments has to contain the statement that the time scales of experiments and simulations are vastly different. Therefore it is important to analyze whether or not properties of the glass formation process around \( T_g \) and \( T_c \) are different. Furthermore most experimental results have been gained for rotational dynamics whereas most simulations have concentrated on translational dynamics. It has been shown, however, from simulations of a molecular glass former that already above the mode coupling temperature the dynamic heterogeneities of rotational and translational dynamics are coupled in a nearly maximum way. Molecules with fast translational dynamics also rotate fast and vice versa [28,29]. In the temperature range several Kelvin above \( T_g \) experiments have revealed that on the time scale of \( \tau_\alpha \) a slow molecule becomes fast [8,30,31]. Note that during \( \tau_\alpha \) the mean square displacement of a molecule is of the order of the squared nearest neighbour distance. Therefore the experimental result, generalized to translational dynamics, implies that typical slow molecules become fast after moving a nearest neighbour distance. This is indeed the case, see Fig.4. According to measurements by the Ediger group [32] the behavior changes at \( T_g \) where
the life time of the slow molecules becomes much larger than the structural relaxation time.

The question of the origin of dynamic heterogeneities is very complex. One answer has been found in terms of energy landscapes for a Lennard-Jones system. For very small systems $N = 60$ particles it has been shown that the slow regions correspond to configurations very deep in the potential energy landscape [33]. High activation barriers have to be passed so that the system can become mobile again. Some correlations with the local potential energy have been also observed in simulations of larger Lennard-Jones systems [21]. For the hard disc system the potential energy landscape is not a convenient way of representation of different configurations. Rather one would like to use concepts like locally stable structures. We have seen that obvious quantities like particle sizes or local density fail to identify locally slow regions. It seems that the underlying reason for regions of the system to be slow is to be found in complex multi-particle correlations. These correlations prevent a local region to relax since, in analogy to a crystal, internal degrees of freedom are not present. The observation that the dynamics of a cluster is independent of its life time and thus of its stability shows that this is mainly related to the interaction with the adjacent fast particles and not with the internal structure. Currently we are trying to identify the relevant structural quantities which are the basis of dynamic heterogeneities.

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References

[1] C. A. Angell. *Science*, 267(5206):1924–1935, 1995.
[2] K. L. Ngai. *J. Non-Cryst. Solids*, 275(1-2):7–51, 2000.
[3] W. Kob. *J. Phys.-Condes. Matter*, 11(10):R85–R115, 1999.
[4] H. Silleccu. *J. Non-Cryst. Solids*, 243(2-3):81–108, 1999.
[5] F. Fujara, B. Geil, H. Sillescu, and G. Fleischer. *Z. Phys. B-Condens. Mat.*, 88(2):195–204, 1992.
[6] K. Schmidt-Rohr and H. W. Spiess. *Phys. Rev. Lett.*, 66(23):3020–3023, 1991.
[7] M. Yang and R. Richert. *J. Chem. Phys.*, 115(6):2676–2680, 2001.
[8] M. Ediger. *J. Chem. Phys.*, 103(10):752, 1995.
[9] B. Schiener, R. Böhmer, A. Loidl, and R. V. Chamberlin. *Science*, 274:752, 1996.
[10] E. V. Russell and N. E. Israeloff. Nature, 408(6813):695–698, 2000.

[11] L. A. Deschenes and D. A. Vandenbout. Science, 292(5515):255–258, 2001.

[12] U. Tracht, M. Wilhelm, A. Heuer, H. Feng, K. Schmidt-Rohr, and H. W. Spiess. Phys. Rev. Lett., 81:2727, 1998.

[13] U. Tracht, A. Heuer, S. A. Reinsberg, and H. W. Spiess. Appl. Magn. Reson., 17(2-3):227–241, 1999.

[14] D. N. Perera and P. Harrowell. J. Chem. Phys., 104(6):2369–2375, 1996.

[15] W. Kob, C. Donati, S. J. Plimpton, P. H. Poole, and S. C. Glotzer. Phys. Rev. Lett., 79(15):2827–2830, 1997.

[16] A. Heuer and K. Okun. J. Chem. Phys, 106(14):6176–6186, 1997.

[17] S. C. Glotzer and C. Donati. J. Phys.-Condes. Matter, 11(10A):A285–A295, 1999.

[18] R. Yamamoto and A. Onuki. Phys. Rev. E, 58(3):3515–3529, 1998.

[19] W. Götze. in Liquids, Freezing and the Glass Transition, edited by J.P. Hansen, D. Levesque, and J. Zinn-Justin. (North-Holland, Amsterdam, 1989).

[20] C. Bennemann, C. Donati, J. Baschnagel, and S. C. Glotzer. Nature, 399(6733):246–249, 1999.

[21] C. Donati, S. C. Glotzer, P. H. Poole, W. Kob, and S. J. Plimpton. Phys. Rev. E, 60(3):3107–3119, 1999.

[22] B. Doliwa and A. Heuer. Phys. Rev. E, 61(6):6898–6908, 2000.

[23] B. Doliwa and A. Heuer. J. Phys.-Condes. Matter, 11(10A):A277–A283, 1999.

[24] M. Ediger. Science, 292(5515):233–234, 2001.

[25] M. Gavrilova and J. Rokne. Int. J. Comput. Math., 61(1-2):49–61, 1996.

[26] M. T. Cicerone, P. A. Wagner, and M. D. Ediger. J. Phys. Chem. B, 101(43):8727–8734, 1997.

[27] G. Diezemann. J. Chem. Phys., 107(23):10112–10120, 1997.

[28] S. H. Chen, P. Gallo, F. Sciortino, and P. Tartaglia. Phys. Rev. E, 56(4):4231–4243, 1997.

[29] J. Qian, R. Hentschke, and A. Heuer. J. Chem. Phys., 110(9):4514–4522, 1999.

[30] A. Heuer, M. Wilhelm, H. Zimmermann, and H. W. Spiess. Phys. Rev. Lett., 75:2851, 1995.

[31] R. Böhmer, G. Hinze, G. Diezemann, B. Geil, and H. Sillescu. Europhys. Lett., 36(14):55, 1996.

[32] C. Y. Wang and M. D. Ediger. J. Phys. Chem. B, 103(20):4177–4184, 1999.

[33] S. Büchner and A. Heuer. Phys. Rev. Lett., 84(10):2168–2171, 2000.