

## Is There a Growing Correlation Length near the Glass Transition?

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**Abstract.** - We present the results of a molecular-dynamics study on a Lennard-Jones mixture. Measurements of density and bond-angle correlation functions show that the answer to the question posed in the title is NO. We also show that icosahedral order plays no special role in the glass transition, but that a normalized measure of the persistence of orientational correlations in the glass shows a systematic dependence on the spherical harmonic index  $l$ .

Over the years, several models and approximate treatments have been proposed to account for the glass transition [1]. The models are, broadly, of two types: *A*) kinetic models [2], in which the growth of relaxation times plays a primary role, and *B*) quasi-equilibrium models [3-5], which attribute this growth to an underlying continuous «phase transition» to an ideal glass. One feature of all class-*B*) models is that they tie the huge relaxation times to a growing correlation length of some sort, even if the theories do not explicitly state this. In this letter, we present the outcome of a search for such a length.

We base our results on a molecular-dynamics study of a Lennard-Jones mixture, in which we measured space- and time-dependent correlation functions as well as the behaviour of single-site autocorrelations for a range of system sizes from 32 to 256 particles. We studied both translational and orientational correlation functions. Over the range of temperatures explored, relaxation times grow by a factor of about 500, including a substantial range of non-Arrhenius growth. At the lowest temperatures, the system has frozen into a «glass» for the purposes of our simulation. Here are our main results:

1) neither a search for finite-size scaling nor a measurement of the space-time dependence of appropriately defined order-parameter correlation functions reveals *any* evidence for a growing length, even in the region of non-Arrhenius slowing-down,

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2) neither icosahedral [6] nor any other orientational ordering on intermediate scales [7] plays any special role in the glass transition in our system,

3) the analogue of an Edwards-Anderson [8] order parameter for orientational correlations in the frozen state shows a clear dependence on the order  $l$  of the spherical harmonic.

We believe that our results rule out some candidate theories of the glass transition, and raise some new questions about it. In particular, we speculate that many of the phenomena associated with the dynamics of dense liquids may be understood at the level of a few (say 8) particles.

We now describe our simulation. The systems we studied were 50-50 mixtures of Lennard-Jones particles of two types with different effective sizes but the same energy parameters. The potential between particles of type  $i$  and  $j$  is

$$V_{i,j} = 4\epsilon[(\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^6]$$

with  $\sigma_{11}/\sigma_{22} = 5/8$ , and  $\sigma_{12} = (\sigma_{11} + \sigma_{22})/2$ . The interactions were cut off at  $r = 2\sigma_{ij}$ . This mismatch was chosen, quite arbitrarily, to prevent crystallization. The simulation method was constant-volume molecular dynamics, using the Schofield [9] algorithm, with periodic boundary conditions. An effective density  $\rho^* = n\sigma_{11}^3 = 0.5$  was chosen,  $n$  being the total number density. Temperature was measured in units of  $T_0 = \epsilon/k_B$ , and time in units of  $t_0 = \sigma_{11} \sqrt{M/\epsilon/2\rho^*}^{1/3}$ . The temperature range covered was (in scaled units) from  $T^* = 5$  to  $T^* = 0.75$ . The longest time for which we have data is  $10^3 t_0$ . We present here data for system sizes of 32, 108 and 256 particles, on which, respectively, 8, 5 and 3 independent low-temperature runs were performed; we have also included sizes of 48, 96 and 160 particles in our simulations at higher temperatures. In each case the temperature, *i.e.* the average kinetic energy per particle, was allowed to stabilize for a few hundred time units before measurements were taken. Measurements of partial pair correlation functions as well as real-space images of particle positions were made to ensure that neither crystallization nor phase separation was taking place.

To study the nature of structural relaxation, several different measurements were made. We now discuss each of these in turn.

### 1. Density autocorrelation functions.

For all density correlation functions, the system was divided into cubic cells of size  $\sigma_{11}^3$ , labelled by  $i$ . For convenience, a lattice-gas variable  $n(i, t) = \text{sgn}[m_i(t) - \bar{m}]$  was used, where  $m_i(t)$  is the number of particles in cell  $i$  at time  $t$ , and  $\bar{m}$  is the average number of particles per cell. We measured

$$C_2(t) = \langle n(i, t_0) n(i, t_0 + t) \rangle,$$

where  $\langle \rangle$  denotes an average over  $i$  and  $t_0$ . Note  $C_2(t=0) = 1$  by definition. In the fluid phase,  $C_2(t \rightarrow \infty) = m_0^2$ , where  $m_0 = \langle n(i, t) \rangle = 0$  for  $N = 32, 108, 256$ , because in each of these cases, the number of cubic cells  $= 2N$ . For  $T^* > 1.33$ ,  $C_2(t)$  decays to  $m_0^2$  within the total time of the simulation ( $10^3 t_0$ ), whereas at lower values of  $T^*$ , the asymptotic value of  $C_2$  is not reached. From this we identify a «glass transition» at  $T^* = T_g^* = 1$ , which is consistent with the onset of arrested single-particle diffusion. For each size a relaxation time was

extracted:

$$\tau \equiv \int_0^{\tau_{\max}} [C_2(t) - m_0^2] / (1 - m_0^2) dt.$$

For  $T < T_g$ , only a lower bound to  $\tau$  may be obtained. The results of this are summarized in fig. 1, whence it can be seen that

a) the relaxation time grows in a non-Arrhenius manner as the temperature is lowered;

b) the growth is independent of sample sizes from 32 to 256 particles; therefore, there is no evidence for a growing correlation length; if anything,  $\tau$  appears to be larger for smaller  $N$ .

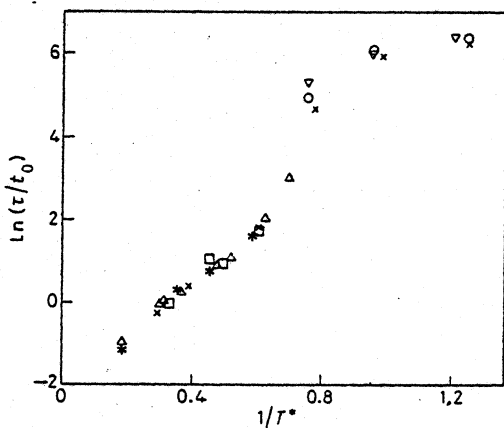


Fig. 1.

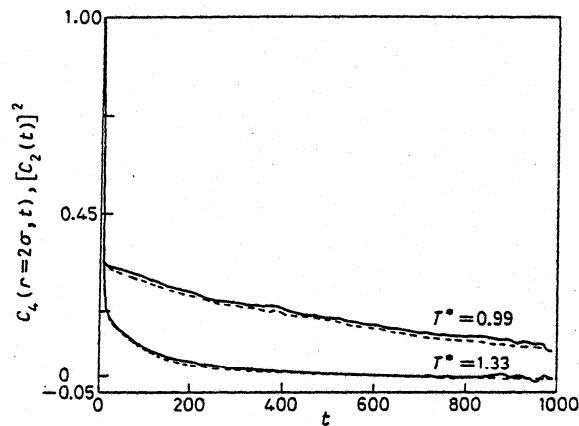


Fig. 2.

Fig. 1. - Logarithm of relaxation time ( $\ln(\tau/t_0)$ ) vs. inverse scaled temperature ( $1/T^*$ ). The lowest-temperature data represent only a lower bound to the actual relaxation times. Note the sample-size independence of  $\tau/t_0$ .  $\times N = 256$ ,  $* N = 160$ ,  $\circ N = 108$ ,  $\Delta N = 96$ ,  $\square N = 48$ ,  $\nabla N = 32$ .

Fig. 2. - Four-point density correlation function  $C_4(r=2\sigma_{11}, t)$  (—) and square of  $C_2(t)$  (---), the density autocorrelation function, vs. time for the  $N = 256$  sample at two different temperatures.

## 2. Four-point density correlation functions.

Strictly speaking, a correlation length is defined by the decay of the spatial correlations of an order parameter. By analogy with spin glasses [10], a plausible order parameter [8] for a glass is

$$\lim_{t \rightarrow \infty} \langle n(r, 0) n(r, t) \rangle.$$

Therefore, the natural correlation functions to measure are

$$C_4(r, t) = [\langle n(r_0, t_0) n(r_0 + r, t_0) n(r_0, t_0 + t) n(r_0 + r, t_0 + t) \rangle],$$

and

$$C_4(r) = [\langle n(r_0, t_0) n(r_0 + r, t_0) \rangle^2] = \lim_{t \rightarrow \infty} C_4(r, t),$$

where  $\langle \rangle$  and  $[\ ]$  denote averages over the reference time  $t_0$  and reference space-point  $r_0$ , respectively.

The correlation function analogous <sup>(1)</sup> to  $C_4(r)$  for spin glasses has been found [10] to display a diverging correlation length at the spin glass transition. Note that if the range of correlations is smaller than  $r$ , then the four-point correlation function  $C_4(r, t)$  should be equal to  $[C_2(t)]^2$ . We find that the difference between  $C_4(r, t)$  and  $[C_2(t)]^2$  for  $r > 2\sigma_{11}$  goes to zero for all temperatures above the apparent freezing temperature (see fig. 2). Below this temperature, the difference between  $C_4(r, t)$  and  $[C_2(t)]^2$  appears to remain constant at a very small value ( $\sim 10^{-2}$ ) for all  $r > 2\sigma_{11}$ . Thus, we do not observe the development of any long-range spatial correlation in  $C_4(r, t)$ .

### 3. Orientational correlations.

Orientational order in three dimensions [8, 9] is characterized by spherical harmonic indices as follows. Associate a «bond» with each pair of particles (of type  $i, j$ ) whose centres lie less than a distance  $1 \cdot 2\sigma_{ij}$  apart. Let the orientation of the bond  $\alpha$  with respect to a reference coordinate system be given by the spherical polar angles  $(\theta_\alpha, \phi_\alpha)$ . Suppose the bond centre  $r_\alpha$  lies in a cubic cell with vertices  $[R_i, i = 1, 8]$ , with  $r_\alpha - R_i = d_{i\alpha}$ . Let  $Q_{lm}(r_\alpha, t) = Y_{lm}(\theta_\alpha(t), \phi_\alpha(t))$ , where the  $Y_{lm}$ 's are spherical harmonics of order  $(l, m)$ . For each vertex  $i$  define

$$W_{lm}(i, t) = \sum_\alpha w_\alpha^i Q_{lm}(r_\alpha, t),$$

where the sum is over all bond centres lying in cells with site  $i$  as one of the vertices, and

$$w_\alpha^i = \exp[-(d_{i\alpha}/\sigma_{11})] / \sum_j \exp[-d_{j\alpha}/\sigma_{11}].$$

This gives a space- and time-dependent bond-angle field, whose correlations can be measured. Define the  $l$ -dependent orientational susceptibility

$$X_l(t) = (4\pi/2l + 1) \left( \sum_m \langle |Z_{lm}(t)|^2 \rangle \right),$$

where  $Z_{lm}(t) = [Q_{lm}(r_\alpha, t)]$ ; here  $\langle \rangle$  indicates an average over time and  $[\ ]$  is an average over bonds.

The autocorrelation function is given by

$$G_l(t) = 4\pi/(2l + 1) \sum_m [\langle W_{lm}(l, t_0) W_{lm}^*(i, t_0 + t) \rangle];$$

here  $\langle \rangle$  indicates an average over time  $t_0$  and  $[\ ]$  is an average over sites  $i$ . We also define the normalized autocorrelation function

$$\tilde{G}_l(t) = G_l(t)/G_l(t=0).$$

<sup>(1)</sup> Since there is no quenched disorder in a liquid, the infinite-time-averaged  $C_4(r)$  must be equal to the square of the pair correlation function of the liquid. However, a computer simulation runs over a finite time over which some degrees of freedom are «frozen». It might therefore be hoped that they would act as quenched disorder for the rest, and that  $C_4$  could therefore contain a diverging correlation length. This appears *not* to be the case.

We find

i) that the autocorrelation functions decay to zero for  $T > T_g$ , but not for  $T < T_g$ , where  $T_g$  is the same as that obtained for the density autocorrelation function;

ii) that there is no tendency towards icosahedral order: all the  $X_l$ 's are small and approximately  $l$ -independent;

iii) that the relaxation time as measured from these correlation functions agrees approximately with that measured from the density correlation functions (if anything, the density correlation functions decay more slowly), questioning certain theories [11] of the glass transition which attribute the growing relaxation time mainly to orientational degrees of freedom; and

iv) that no effects of finite size can be seen here either.

The time-persistence of orientational correlations, as measured by  $\tilde{G}_l(t \rightarrow \infty)$ , shows a clear dependence on  $l$  which we do not understand. Our results on orientational correlations are shown in fig. 3.

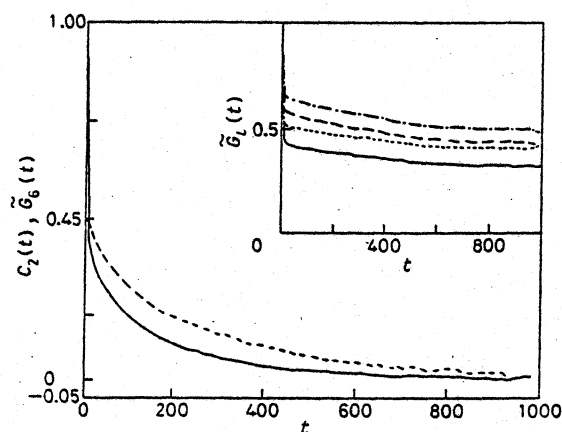


Fig. 3. - Normalized bond-angle ( $l=6$ ) (—) and density autocorrelation functions (---) vs. time, for the  $N=256$  sample at temperature  $T^*=1.33$ . Inset: normalized bond-angle autocorrelation function for different  $l$  values for the  $N=256$  sample, at  $T^*=0.77$ , which is below the transition: —  $l=2$ , ---  $l=4$ , - · - ·  $l=6$ , · · · ·  $l=8$ .

#### 4. Discussion.

Our most important conclusion is that the glass transition, at least over the range of temperatures studied, is not driven by a growing correlation length. Our study of space- and time-dependent correlations sets an upper bound of about one-particle size for the range of correlations in a liquid. Moreover, if we assume, based on many experiments and simulations [1] (including our own) that there is one timescale which dominates all relaxation measurements, then the search for finite-size scaling tells us *independently* that no matter *what* hidden order parameter is responsible for the glass transition, its correlation length remains smaller than  $2\sigma_{11}$ , which is the linear size appropriate to a 32-particle system with periodic boundary conditions. The spin-glass analogue and bond-angle correlation functions confirm this. In all, we believe we can rule out even the models of ref. [3] and [4] which can be shown to predict, close to the glass transition, an exponential dependence of relaxation

time on system size. Of course, it can always be argued that the true glass transition region, where  $\tau$  has grown by a factor  $\sim 10^{12}$ , is at much lower temperatures. This of course begs the question of the initial factor of  $10^3$  or so of growth in  $\tau$ , but apart from that we can only suggest that ingenious laboratory experiments (for example, measuring the structural relaxation time in dispersed liquid droplets of a range of sizes starting at 20 Å) be devised to search for finite-size effects near  $T_g$ .

Lastly, although icosahedral order plays no special role in the slowing-down of structural relaxation in these nearly simple liquids, there remains the puzzling systematic dependence of the persistence of correlations on the spherical harmonic index  $l$ .

After this work was completed, and while the manuscript was in preparation, we received a preprint from Ernst *et al.* [12] which also presents evidence for the absence of a growing correlation length near the glass transition in a similar system. The most important difference between their work (as well as similar studies by Pastore *et al.* [13]) and ours is that they look only at two-point, space- and time-dependent correlations of density and bond-angle fields whose analogue in a spin glass [10] would *not* reveal a diverging correlation length.

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