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## Localization and glass transition in two-dimensional liquids

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**Abstract.** Molecular dynamic computer simulations of a two-dimensional Lennard-Jones liquid, along several isotherms, have been carried out to search for a distinct transition from a compressed liquid to an amorphous solid. The dynamics of the transition is examined in terms of tagged-particle van Hove correlation functions, for times up to 600 ps. The onset of localization and the transition to non-ergodicity occur simultaneously and abruptly within a very narrow range of density. Further analysis of the data on the intermediate scattering function indicate a good fit to a stretched exponential with an exponent  $\beta$  equal to 0.62 and that this exponent is nearly independent of temperature. Thus, for the time scales investigated by this simulation, it is concluded that the transition observed is a glass transition.

### 1. Introduction

In three-dimensional liquids, a sharp transition from ergodic to non-ergodic behaviour is predicted by mode-coupling theories [1] and is labelled as an 'ideal' glass transition. Dynamically, this transition is signalled by a structural arrest, or, in other words, a decay to a non-zero value, at very long times, of density correlation functions. However, both in experiments and in computer simulation, activated processes blur this transition and restore ergodicity at sufficiently long times. Molecular dynamic (MD) simulations on Lennard-Jones fluids [2, 3] point to the existence of such a transition. A system is ergodic if, for a given time interval, the time-averaged and ensemble-averaged quantities yield the same results. As the glass transition is approached, this time interval increases rapidly and becomes longer than the MD observational time. Nevertheless, evidence from MD simulations [4, 5] indicates the onset of localization and the loss of ergodicity occurring in a narrow range of temperature (or equivalently density) and it is suggested that this may be a universal feature (independent of the precise inter-molecular potential) of glass-forming substances. Light-scattering experiments on colloidal systems [6] confirm the onset of localization occurring over a narrow range of density.

Even though there exists a substantial amount of MD simulation research [7, 8] and some experimental research [9] on two-dimensional systems, the nature of freezing and melting in such systems is still a subject of some debate and almost nothing has been done on the question of the existence of a glassy state. Even with the difficulty of producing experimentally a true two-dimensional liquid, this problem is of conceptual interest and can be clarified only through computer simulations. Two-dimensional systems pose unique problems: for example, the existence of a glassy state requiring the self-diffusion coefficient going to zero. However, it is known that the diffusion coefficient, as defined by the Green-Kubo time integral of the velocity autocorrelation function, does not exist in two-dimensions. Because of this, localization and long-range crystalline order, in the *strictest* sense, cannot exist in two dimensions. One could analyse the 'long time' behaviour of an

effective diffusion coefficient, defined as the slope of the mean-square displacement, to look for indications of a long-living metastable glass state and even possibly of a liquid-glass transition, but the very nature of an MD simulation limits one in terms of observational times. Thus we can only draw conjectures on the existence of glassy states in two dimensions.

Nevertheless, it is clearly of interest to study whether and how localization and non-ergodicity occur in two dimensions and whether dimensionality affects the universality of these phenomena. We can investigate, through MD simulations distinctive and possibly unique structural and dynamical features associated with the transition region of non-ergodicity, reached by compressing a simple liquid at equilibrium. In this way, we are systematically simulating equilibrium and non-equilibrium properties of various metastable states as the fluid progresses from a normal liquid state to a disordered amorphous state. By resorting to compression at a constant temperature, we more nearly approximate experimental situations. In a previous paper [10], our MD results on compressed two-dimensional Lennard-Jones liquids suggested a transition, signalled by changes in the pair distribution function and by a structural slowing down in density correlation functions at times of the order of tens of picoseconds. In this paper, we explore this transition in more detail, studying the density dependence of the pair distribution function  $g(r)$ , the van Hove self-correlation function in  $r$ -space  $G_s(r, t)$ , its Fourier transform in  $q$ -space  $F_s(q, t)$  and the non-Gaussian parameter  $A(t)$ , and develop diagnostic statements regarding the onset of localization and non-ergodicity. Our results indicate quite an abrupt and discontinuous change in the behaviour of these structural and dynamic quantities as a function of density. This can be interpreted as defining the supercooled/compressed liquid-amorphous solid boundary in the temperature-density phase diagram. The results for the intermediate self-scattering function  $F_s(q, t)$  have been analysed in terms of the Kohlrausch-Williams-Watts (KWW) [11] form of the correlation function. This is expressed as a stretched exponential,  $\exp[-(t/\tau)^\beta]$ . Mode-coupling theories indicate such a stretching of the spectrum near the glass transition, with  $0 < \beta < 1$ .

Section 2 gives the details of the computer simulation and in section 3 we present the results for various static and dynamic correlation functions. Conclusions are presented in section 4.

## 2. Molecular dynamics experiment

The molecular dynamic computer simulations were carried out for a system of  $N$  ( $= 242$ ) particles of mass  $m$  interacting with the Lennard-Jones (LJ) potential

$$u(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]. \quad (1)$$

The particles were confined to a square box of length  $L = \sqrt{(N/n^*)} \sigma$  where  $n^* = n\sigma^2$  is the dimensionless density. The potential was cut off at half the box length, which does not pose any problems as this is at least  $6\sigma$ . Periodic boundary conditions were imposed in the usual fashion. Other dimensionless units used in this paper are distance  $r^* = r/\sigma$ , wave vector  $q^* = q\sigma$ , time  $t^* = t/\tau$  where  $\tau^2 = m\sigma^2/48\epsilon$  and temperature  $T^* = k_B T/\epsilon$ . Newton's equations of motion were integrated using the Verlet algorithm. The temperature was controlled by re-scaling the particle velocities every 50 time steps and equilibrium was considered to be achieved if the temperature drift was within 0.005 of the required temperature, when scaling was turned off. Initially, equilibration was achieved after a run extending for about  $10^4$  time steps, and after establishing an equilibrium configuration, the MD run was carried out for  $10^5$  time steps. The time step was chosen to be  $\Delta t^* = 0.032$ , corresponding to about  $10^{-14}$  s, using argon LJ parameters. The position vector  $r(t)$  and

velocity vector  $v(t)$  for these time steps were stored to facilitate evaluation of the correlation functions.

The temperature was kept constant at  $T^* = 0.50$ , close to the triple-point temperature of 0.43, and the system was compressed from a density of  $n^* = 0.79$  (the triple-point density is 0.77) to a density of 0.85 in steps of 0.01. At this temperature, it is expected that thermal motions would not contribute significantly and thus the onset of crystallization can be avoided. The compression to the next higher density was carried out by scaling all the particle positions by an appropriate factor that takes into account the decreased box length. Effects of system size were investigated in our previous paper [10], wherein it was found that errors with 242 particles were insignificant. To see the effects of temperature, the MD simulations were repeated for three other isotherms,  $T^* = 0.40$  (which is below the triple-point temperature), 0.60 and 0.70.

### 3. Results

Though we have calculated and analysed the static correlation functions  $g(r)$  and the dynamic quantities  $A(t)$ ,  $G_s(r, t)$  and  $F_s(q, t)$ , for a number of density states along all four isotherms, only the isotherm  $T^* = 0.50$  will be discussed here. The behaviours at other isotherms are strikingly similar. We have evaluated and analysed the pair distribution function (PDF)  $g(r)$  to see whether there are any static diagnostics of a transition. Previous MD studies [12] of  $g(r)$  have established the onset of freezing to be around  $n^* = 0.79$  at this temperature.  $g(r)$  varies quite smoothly over the range of densities investigated. The second peak just starts to exhibit a shoulder at  $n^* = 0.79$  and develops a split second peak at  $n^* = 0.82$ . Rather than looking at features of  $g(r)$  to define the transition, we look at a ratio involving the PDFs. In analyses of three-dimensional fluids, an empirical PDF parameter  $R = g_{\min}/g_{\max}$ , where  $g_{\max}$  and  $g_{\min}$  are the magnitudes of the first-shell maximum and the first minimum following this maximum, has been used to define the onset of freezing [13] and the liquid-glass transition [14]. This is plotted in figure 1 as a function of density. A discontinuous change in slope is seen to occur at  $n^* \simeq 0.83$ . This then could be taken as signalling a transition from a compressed liquid to an amorphous solid. Such a change in slope for the PDF parameter has been noted in computer simulations of three-dimensional liquids and used to define the glass transition [14]. As we shall see later, other dynamical quantities also show a discontinuous behaviour at this density, strongly suggesting the existence of a glass transition.

It has been suggested [15] that the onset of a constant non-zero value, at long times, of the non-Gaussian parameter  $A(t)$ , defined as

$$A(t) = \langle [r(t) - r(0)]^4 \rangle / 2 \langle [r(t) - r(0)]^2 \rangle^2 - 1 \quad (2)$$

can be considered as an order parameter for the glass transition. Here the numerator is the mean quadric displacement and the denominator is the square of the mean square displacement. In figure 2,  $A(t)$  is plotted as a function of time for  $n^* = 0.81, 0.82, 0.83$  and 0.85. We note that while  $A(t)$  goes to zero reasonably quickly after achieving a maximum for the first two lower densities, there is an abrupt change in its behaviour at  $n^* = 0.83$ . The time scale for decay has increased quite dramatically as density is increased marginally from 0.82 to 0.83. The long-time decay does not seem to change appreciably on further compression. This analysis again shows a transition at  $n^* \simeq 0.83$ .

The phenomenon of localization can best be studied by looking at the space-time behaviour of the self-part  $G_s(r, t)$  of the density correlation function, defined as

$$G_s(r, t) = \frac{1}{N} \sum_1^n \langle [r_i(t) - r_i(0) - r] \rangle \quad (3)$$

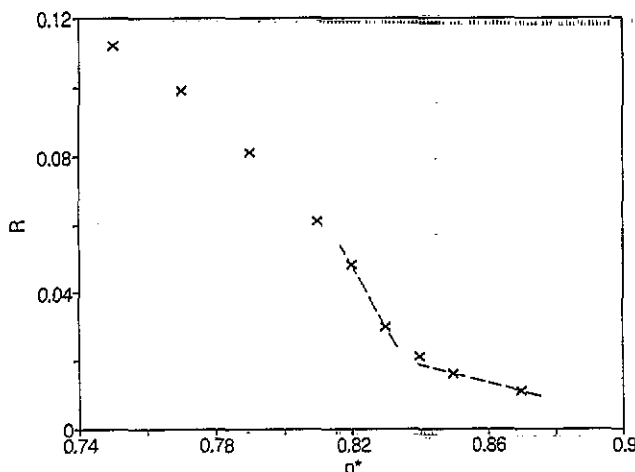


Figure 1. PDF parameter  $R$  ( $= g_{min}/g_{max}$ ) as a function of density  $n^*$ , along the isotherm  $T^* = 0.50$ .

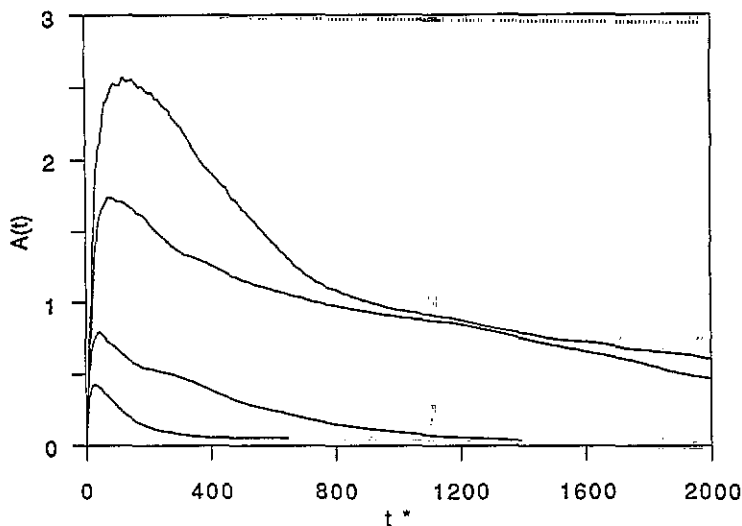


Figure 2. Non-Gaussian parameter  $A(t)$  as a function of  $t^*$  for  $n^* = 0.81, 0.82, 0.83$  and  $0.85$  along the isotherm  $T^* = 0.50$ . The lower curves correspond to lower densities.

where  $r_i(t)$  denotes the position vector of particle  $i$  at time  $t$ . This correlation function provides a detailed description of the motion of individual particles. In a normal liquid or a slightly compressed liquid,  $G_s(r, t)$  should go over reasonably rapidly to the hydrodynamic limit

$$G_s(r, t) \simeq (1/4\pi Dt) \exp(-r^2/4Dt) \quad (4)$$

where  $D$  is to be interpreted, in two dimensions, as an effective diffusion coefficient, obtained from the slope of the mean-square displacement at sufficiently long times. Figure 3 shows plots of  $P(r, t) = r^* G_s(r, t)$ , at specific densities, as a function of  $r^*$  and at various times. The times chosen are  $t^* = 205, 410, 615$  and  $820$ , with the largest  $t^*$  corresponding to about 250 ps, using argon LJ parameters.  $2\pi r G_s(r, t)$  yields the distribution of particles that have moved a distance  $r$  in time  $t$ . At the compressed liquid density of 0.79, the peak of  $P(r, t)$  moves to the right quickly and the hydrodynamic limit, shown by crosses, is reproduced quite accurately for  $t^* \simeq 820$ . Further compression to 0.82 shows a qualitatively similar behaviour, though the single-particle motion has slowed down significantly and it

takes longer to reach the hydrodynamic limit. However a further small change in density to 0.83 brings about an abrupt and a dramatic change in the behaviour of  $P(r, t)$ . The position of the mean peak is now independent of time, even for the longest time investigated, implying localization. The amplitude and area of the main peak decrease slowly with time and a side peak at  $r \simeq \sigma$  develops. The behaviour at higher density is very similar.

The above analysis indicates a clear and abrupt transition from 'liquid-like' motion to 'solid-like' motion of particles and that the transition occurs in a very narrow range of density. The density at which this transition takes place coincides with that observed for other properties discussed earlier.

We note that for  $n^* \geq 0.83$ , the main peak of  $P(r, t)$  does not change with time, at least for the observational MD times. This implies a frozen but disordered structure, akin to a glassy state. The formation of a side peak, at distances comparable to interatomic separation, seems to indicate the emergence of a 'hopping' process in an otherwise translational single-particle dynamics. In this region then, the system is in a frozen, disordered structure where most atoms vibrate around fixed equilibrium positions, but there are occasional individual or correlated jumps to other potential energy minima. Such a hypothesis was put forward more than 20 years ago [16].

From the position of the frozen main peak, we can come to some conclusions regarding Lindemann ratio,  $L = \sqrt{\langle u^2 \rangle} / d$  where  $u$  is the root-mean-square displacement of a particle from its equilibrium position is a crystal and  $d$  is the nearest-neighbour distance, which we will take to be the position of the first peak of the pair distribution function  $g(r)$ . In three-dimensional crystals, the peak of  $P(r, t)$  is related to  $u$ , which is related to the Debye-Waller factor,  $\exp(-2W)$ . In two dimensions, it can be shown that this factor is exactly zero. This then implies that  $u$  is infinite and therefore long-range crystalline order can never really exist in two dimensions. However since the divergence is of a logarithmic type and hence very slow, one can still relate  $u$  to the peak of  $P(r, t)$  for times available in a typical MD simulation. Previous study [10] has shown that the 'long-time' behaviour of  $F_s(q, t)$  at localization can be well represented by a Gaussian in  $q$  and that the product of the half width and the root-mean-square displacement is approximately constant. This implies that we can assume a Debye-Waller form

$$F_s(q, t = \text{large}) = \exp(-q^2 \langle u^2 \rangle) \quad (5)$$

in two dimensions also. This yields, on Fourier transformation,

$$G_s(r, t) = (1/4\pi \langle u^2 \rangle) \exp(-r^2/4 \langle u^2 \rangle). \quad (6)$$

It is evident from this equation that  $\langle u^2 \rangle$  is the second moment of  $G_s(r, t)$  and further that it is related to the position of the frozen peak of  $rG_s(r, t)$ . We thus obtain  $u \equiv \sqrt{\langle u^2 \rangle} = r_m / \sqrt{2}$ , where  $r_m$  is the position of the frozen main peak of  $P(r, t)$ . The value of the Lindemann ratio  $L$ , for  $n^* = 0.83$  and 0.85, is approximately 0.16, comparable to its three-dimensional value. So if this is to be judged as a criterion for a glass transition, we see that this criterion is in agreement with the Lindemann melting criterion and that dimensionality has little effect on these criteria. It is also of interest to study the intermediate self-scattering function  $F_s(q, t)$ , which is the Fourier transform of  $G_s(r, t)$ :

$$F_s(q, t) = \frac{1}{N} \sum_1^N \langle \exp i\mathbf{q} \cdot [\mathbf{r}_j(t) - \mathbf{r}_j(0)] \rangle. \quad (7)$$

This correlation function, in mode-coupling theories in three dimensions, shows an abrupt change from ergodic to non-ergodic behaviour at the 'ideal' glass transition. This is signalled by a  $q$ -dependent non-zero limit of  $F_s(q, t)$  as  $t \rightarrow \infty$ , or, in other words, a structural

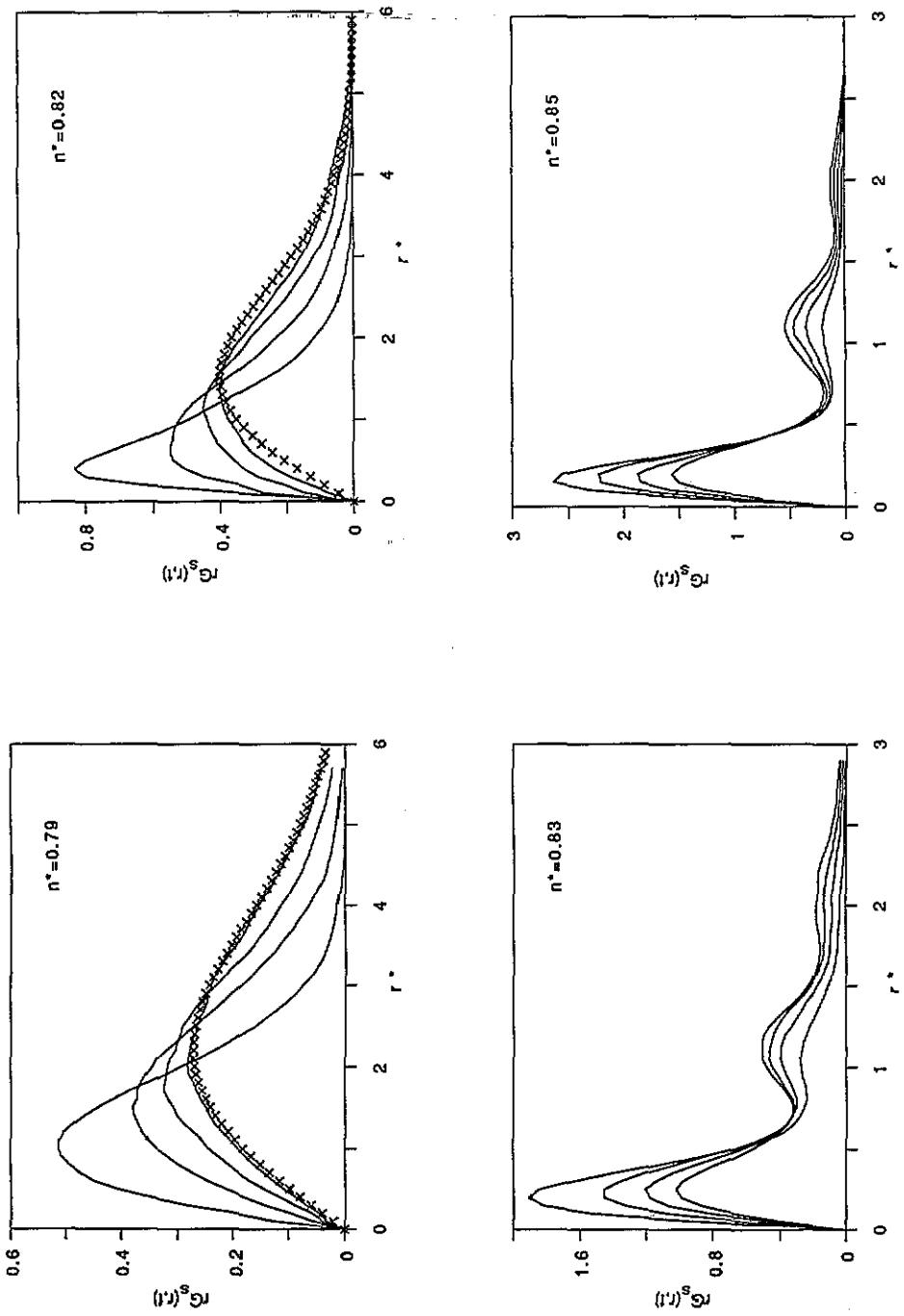


Figure 3. Plots of  $rG_s(r, t)$  as a function of  $r^*$  at  $t^* = 205, 410, 615$  and  $820$ . The density is indicated in each of the plots.  $T^* = 0.50$  in all cases. The crosses are the results for the hydrodynamic limit (equation (4)).

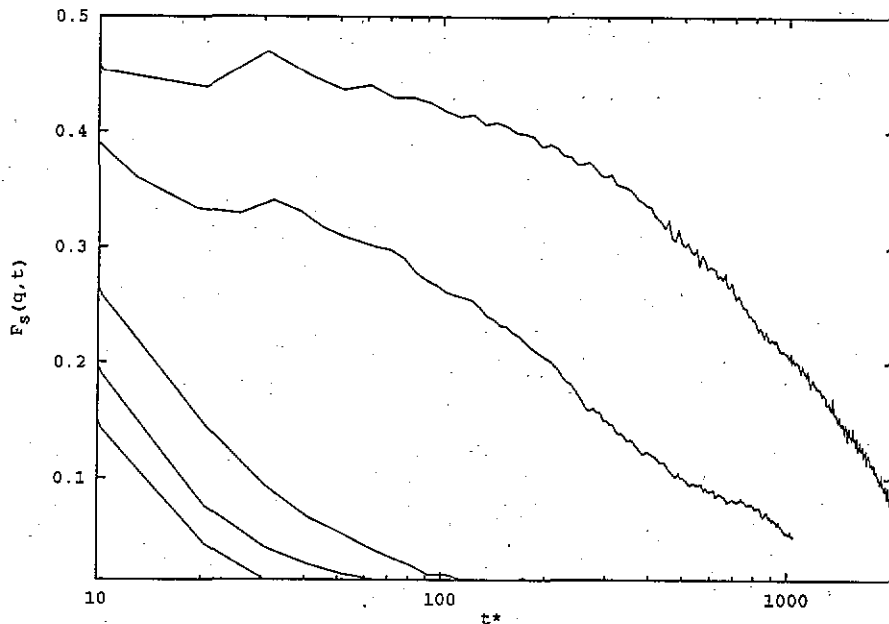


Figure 4. Time decay of the intermediate self-scattering function  $F_s(q, t)$  for  $q \simeq q_0$  at  $n^* = 0.79, 0.81, 0.82, 0.83$  and  $0.85$  along the isotherm  $T^* = 0.50$ . The lower curves correspond to lower densities.

arrest. Activated processes, which are ignored in an ideal glass transition, will tend to restore ergodicity at very long times.

In figure 4, MD results for  $F_s(q, t)$  for a value of  $q$  close to  $q_0$ , the position of the main peak of the static structure factor  $S(q)$ , are plotted for  $n^* = 0.79, 0.81, 0.82, 0.83$  and  $0.85$ . The lower curves correspond to lower densities.  $t^* = 2000$  corresponds to about 600 ps in argon and we must bear in mind that in a normal liquid, the time scales of decay are about two orders of magnitude less. It is seen from this figure that there is a distinct change in the decay pattern of  $F_s(q, t)$  when the density is changed marginally from 0.82 to 0.83. There is a change of about two orders of magnitude in the decay constant. However, complete structural arrest does not seem to have set in. Even though there is a localization at this density, as indicated by the frozen main peak of  $rG_s(r, t)$ , jump diffusion, as indicated by the amplitude of its second peak, provides a slow mechanism for structural relaxation.

One of the major features related to glass transition is the stretching of the relaxation phenomena [17]. At or very near a glass transition, extremely slow structural relaxations are observed in the density correlation function and they are of a characteristic non-exponential type. They have been found to fit the KWW stretched exponential,  $\exp[-(t/\tau)^\beta]$ , with  $0 < \beta < 1$ . In figure 5(a), we have plotted  $F_s(q, t)$ , for  $q \simeq q_0$ , at  $T^* = 0.50$  and  $n^* = 0.83$ , with a solid curve and a best-fit stretched exponential curve with a dashed curve. The value of  $\beta$  is about 0.62, which is quite close to the three-dimensional LJ value of 0.68 [17]. In figure 5(b) and (c), we have plotted the same curves for  $T^* = 0.40$  ( $n^* = 0.81$ ) and  $0.60$  ( $n^* = 0.85$ ), with the same value of  $\beta$  to see whether the exponent is independent of temperature. It is seen that the fit is extremely good. This evidence points to this transition being a glass transition.

Based on the above analysis, the state specified by  $T^* = 0.50$  and  $n^* = 0.83$  defines the compressed liquid-amorphous solid phase boundary, which, for the observational times of



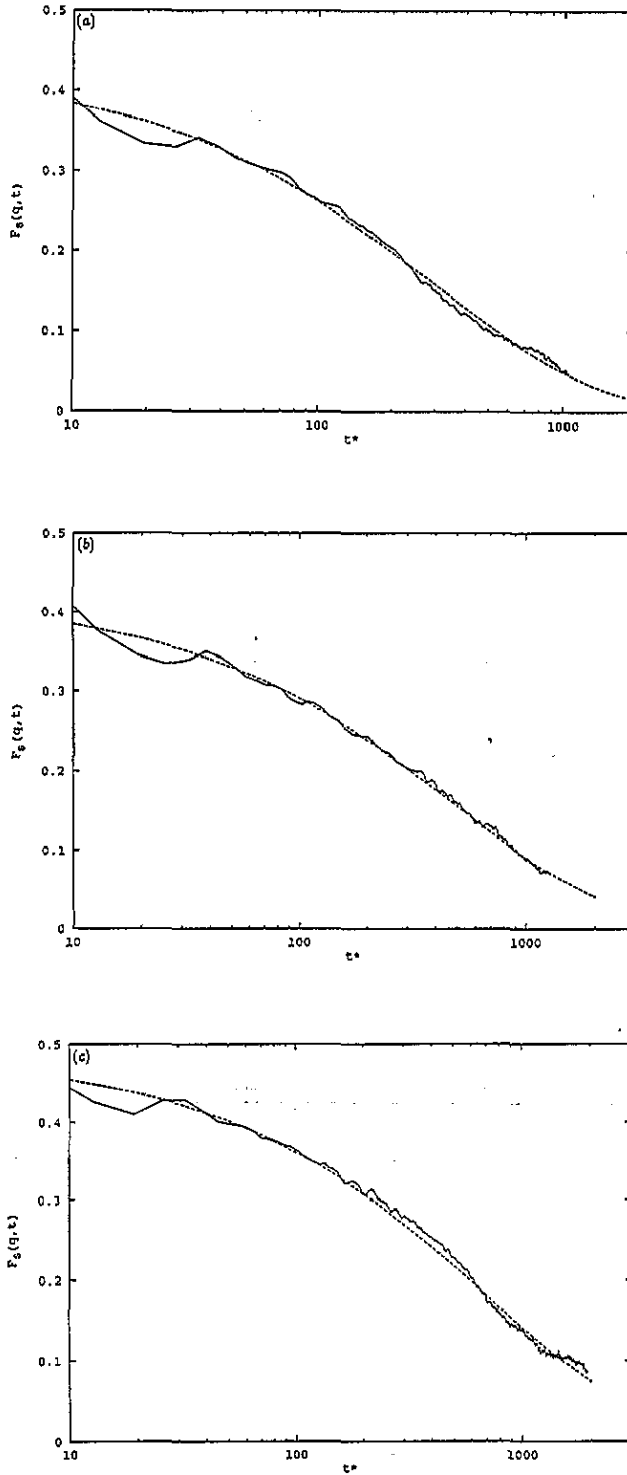


Figure 5. Time decay of the intermediate self-scattering function  $F_s(q, t)$  for  $q \simeq q_0$  (solid curve) and a stretched exponential fit,  $\exp[-(t/\tau)^\beta]$ , with  $\beta = 0.62$  (dashed curve) for (a)  $n^* = 0.83$ ,  $T^* = 0.50$ ; (b)  $n^* = 0.81$ ,  $T^* = 0.40$ ; (c)  $n^* = 0.85$ ,  $T^* = 0.60$ .

our computer simulation, can also be defined as the glass transition line. MD calculations of all of the above quantities, at temperatures of  $T^* = 0.40, 0.60$  and  $0.70$ , indicate very similar behaviour as a function of density and figure 6 shows the transition boundary, indicated by a dashed line, in the  $(T^*, n^*)$  phase diagram of a two-dimensional LJ fluid. The freezing line and the melting line shown in the figure are taken from [18].

#### 4. Conclusions

In this paper we have presented MD computer simulation results for a two-dimensional system interacting with an LJ potential in the vicinity of the glass transition density, if one were to exist in two-dimensions. We have computed several quantities pertaining to single-particle motion, namely, the PDF the non-Gaussian parameter and the self-part of the van Hove density correlation function in both  $r$ -space and  $q$ -space. All of the above quantities display a marked transition in their behaviour at the same density of  $n^* \simeq 0.83$  (at  $T^* = 0.50$ ), indicating an abrupt change in the nature of the particle dynamics at this density. The non-Gaussian parameter  $A(t)$ , has a very short decay time below this density and a decay time about two orders of magnitude greater beyond this density. The peak of  $rG_s(r, t)$  decays differently below and above this critical density. For densities less than 0.83, there is a single peak that moves to larger  $r$  and becomes broader with increasing time, while for densities equal to or greater than 0.83, it exhibits a double-peak structure, with a large main peak whose position is nearly frozen. This implies a strong localization of particles, at least for time scales probed by our MD simulation. The scattering function  $F_s(q, t)$  displays a severe structural slowing down at this crossover density.

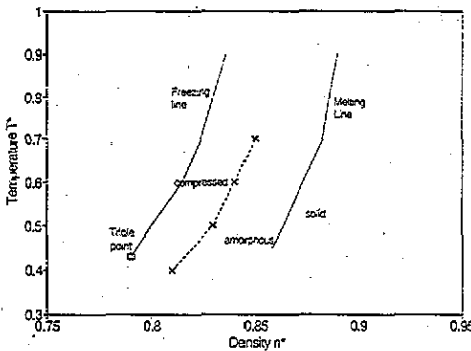


Figure 6. Phase diagram of a 2D LJ system indicating glass transition, shown by the dashed line.

The important question through is, what does this transition represent? From the phase diagram of a two-dimensional LJ fluid [18], it is known that, at  $T^* = 0.50$ , a density of  $n^* = 0.78$  represents a normal liquid and an  $n^* = 0.80$  represents a compressed liquid, and that the transition from a normal liquid to a compressed liquid is smooth and featureless when the above properties are analysed [11]. However, what we see here is an abrupt change in their behaviours, at  $n^* = 0.83$ . It appears as though we are in the vicinity of a glass transition.

One of the principal signatures of the existence of a glass transition is the non-exponential long-time decay of the density correlation function. The extremely slow decay

has been found to fit the KWW stretched exponential decay. Analysis of our data on the density self-correlation function indicates that the spectrum can indeed be fitted with a stretched exponential with an exponent  $\beta$  of 0.62, which does not seem to be sensitive to temperature changes. In addition, analysis of previous data [10] has shown that the Lamb-Mössbauer factor,  $[F_s(q, t = \text{large})]$ , for the density self-correlation function can be fitted very well by a Gaussian distribution, and the Debye-Waller factor,  $[F(q, t = \text{large})]$ , for the density correlation function seems to oscillate in phase with  $S(q)$ , the static structure factor. Thus a wide variety of analyses of our data clearly point to the existence of a glass transition in two dimensions, at least for time scales investigated in our computer simulations.

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