

## Freezing transition of two-dimensional Lennard-Jones fluids

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We have investigated, employing the techniques of molecular-dynamics computer simulation, the onset of the freezing region of a two-dimensional fluid interacting with a Lennard-Jones potential. We have studied the pair-distribution function  $g(r)$  and its Fourier transform  $S(q)$  for unique, qualitative, and quantitative structural characteristics associated with the onset of freezing and for the validity of a universal freezing criterion. We conclude that such a criterion exists, but its value is sensitive to even slight changes in density and temperature.

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### I. INTRODUCTION

Molecular-dynamics (MD) simulation has been a very useful tool in the study of atomic properties of fluids. In this paper, we wish to study the onset of the glass transition in two-dimensional (2D) Lennard-Jones (LJ) fluids through an investigation of the salient features of the pair-distribution function (PDF) and of the structure factor.

A freezing criterion based on the structural properties of three-dimensional dense fluids has been formulated [1] and investigated [2]. The criterion is that the crystallization should occur when  $S(q_0)$ , the first maximum of the structure factor, reaches the value 2.85. Wendt and Abraham [3] defined an empirical parameter  $R$ , which is the ratio of the first minimum  $g_{\min}$  to the first maximum  $g_{\max}$  of the PDF to characterize the onset of the amorphous state. By employing Monte Carlo methods to study the PDF of Lennard-Jones fluids, they stated the criteria that the onset of freezing occurs when  $R$  is approximately equal to 0.14.

In two dimensions, equivalent freezing criteria have not been adequately tested. Caillol *et al.* [4], comparing the structure factor of the hard disk and of the one-component plasma (OCP) with a  $\ln r$  potential at their respective freezing transitions, concluded that "any classical 2D fluid with central pair interaction freezes when  $S(q_0)$  is approximately 4.4, provided of course the transition is of first order." Gann *et al.* [5] studied 2D OCP with a  $1/r$  potential and, though they could not obtain a good estimate of  $S(q_0)$  at freezing, suggested that it is larger than the 3D value. A MD study of 2D fluids with an inverse-twelfth-power repulsive interaction [6], showed a very rapid growth of  $S(q_0)$  close to freezing and a value of around 5.0 at the onset of freezing.

However, these studies involve repulsive potentials or a OCP in which one parameter alone determines the transition. The onset of the glass-transition region as a function of *both* temperature and density has not received significant attention. In this paper we report the results

of a two-dimensional MD simulation of the Lennard-Jones (6-12 type) system near the freezing transition. Section II describes some details of the MD method and the thermodynamic states studied while Sec. III contains discussions of the pair-distribution function  $g(r)$  and its Fourier transform, the structure factor  $S(q)$ . Existence of unique or distinctive structural features associated with the liquid-to-glass transition region is then discussed. Concluding remarks are found in Sec. IV.

### II. COMPUTATIONAL METHODS

MD calculations were performed for a system with 128 particles of mass  $m$  interacting with the Lennard-Jones pair potential

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

The particles were confined to a square box of length  $L = \sqrt{(128/n^*)}\sigma$ , where  $n^* = n\sigma^2$  is the dimensionless density. The potential was cut off at half the box length, which, for the densities under consideration, was approximately  $6.5\sigma$  and periodic boundary conditions imposed in the usual fashion. Other dimensionless units that are being 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 Verlet's algorithm. After establishing an equilibrium configuration, a MD run was carried out for 6000 time steps with  $\Delta t^* = 0.032$  that corresponds to about  $10^{-14}$  sec using argon LJ parameters.  $r(t)$  for these time steps were stored to facilitate the calculation of  $g(r)$ . One run with  $N = 242$  was made to see the influence of the number of particles on the pair-distribution function and the conclusion was that the effect was negligible.

The thermodynamic states investigated were all close to the freezing line as indicated in Fig. 1. This phase diagram, which clearly indicates a first-order transition, was obtained by Abraham [7]. In the first set, an isotherm defined by  $T^* = 0.48$  with densities  $n^* = 0.75, 0.78, 0.79$ ,

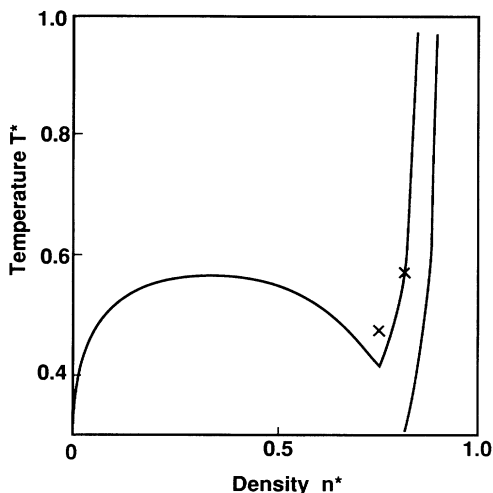


FIG. 1. Phase diagram for the two-dimensional Lennard-Jones system. The crosses indicate the  $(n^*, T^*)$  states (0.75, 0.48) and (0.81, 0.58).

and 0.80 was chosen, while in the second set an isochore of  $n^*=0.81$  with temperatures of  $T^*=0.58$  and 0.59 was chosen. Just for reference, the  $(n^*, T^*)$  states (0.75, 0.48) and (0.81, 0.58) are shown in the figure by crosses.

### III. POSITIONAL CORRELATIONS

The calculation of  $g(r)$  involves the relation

$$\langle n(r) \rangle = 2\pi r \Delta r n g(r), \quad (2)$$

where  $\langle n(r) \rangle$  is the average number of particles in an annulus of radius  $r$  and thickness  $\Delta r$ , centered at a given particle. The step in  $r$  used to calculate  $g(r)$  was taken to be  $0.005\sigma$  and averages carried out over 6000 time steps with every fourth time step as a new origin.

We have plotted the pair-distribution function for the isotherm  $T^*=0.48$  in Fig. 2. Concentrating on the first two peaks of the PDF, we note that two smooth peaks exist at  $n^*=0.75$  and as the density increases, the first peak becomes more pronounced in magnitude and narrower in width and the first minimum decreases in magnitude. The second peak starts to show signs of a gradual flattening out at  $n^*=0.79$  and if the density were further increased, an eventual bimodal splitting of the second peak would have been seen. The splitting of the second peak is the principal feature of the PDF of amorphous materials. However, we are interested in looking for the “signature” that the glass-transition region has been reached. The start of the flattening of the second peak in  $g(r)$  then likely indicates the freezing transition, which in our case is definitely below  $n^*=0.80$  and probably closer to 0.79. Applying then the Wendt and Abraham quantitative criteria for identifying the onset of freezing, we find that

$$R = (g_{\min}/g_{\max}) \approx 0.07. \quad (3)$$

In Fig. 3, we have plotted the PDF at a constant density of 0.81 at two different temperatures of 0.59 and 0.58. Again it is seen that the second peak is smooth at the

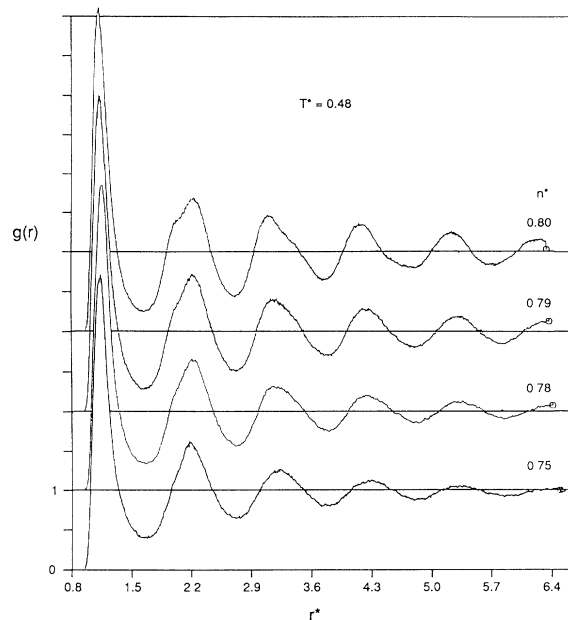


FIG. 2. Pair-distribution function along the isotherm  $T^*=0.48$  at various densities. The curves are displaced for clarity.

higher temperature and the flattening is just starting to show at the lower temperature. The value of  $R$  is again approximately 0.07.

It is also instructive to look at the structure factor to understand the phenomena. The structure factor is the Fourier transform of the PDF, which in two dimensions can be written as

$$S(q) = 1 + 2\pi n \int_0^\infty r J_0(qr) [g(r) - 1] dr, \quad (4)$$

where  $J_0$  is the Bessel function of order 0.  $g(r)$  obtained through MD calculations is valid only up to half the box length and so it was extrapolated further by an empirical formula,  $Ae^{-\alpha r} \sin(\beta r)$ . We also calculated  $S(q)$  through zero-time value of the intermediate scattering function

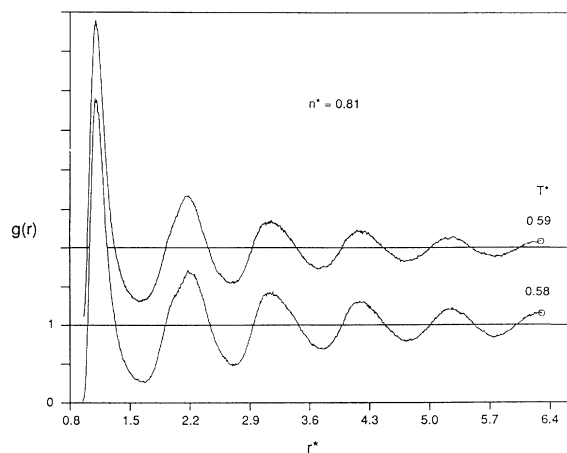


FIG. 3. Pair-distribution function along the isochore  $n^*=0.81$  at two temperatures.

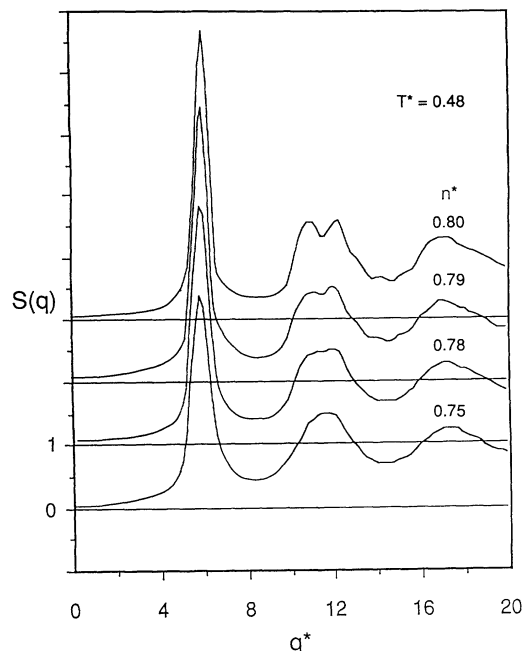


FIG. 4. Structure factor along the isotherm  $T^*=0.48$  at various densities. The curves are displaced for clarity.

$F(q,t)$ . The two values were in reasonably close agreement, but since the  $q$  values allowed in MD calculations are fixed and discrete, we have used Eq. (4) to determine  $S(q_0)$ . In Figs. 4 and 5 we have plotted the structure factor  $S(q)$  corresponding to the states in Figs. 2 and 3. It is to be noted that the height of the first peak of  $S(q)$  grows rapidly with the development of a prominent split second peak as the freezing transition is neared. It is interesting that  $S(q)$  reveals greater structure than is apparent in  $g(r)$ . For example, we can see a clear splitting of the second peak of  $S(q)$  at  $n^*=0.79$  while the corresponding  $g(r)$  barely shows the start of a flattening of its second peak. The height of the first peak,  $S(q_0)$  in the structure factor at the onset of freezing from both the figures is approximately 4.6.

We have also determined the diffusion coefficient from the slope of the mean-squared displacement  $\langle r^2(t) \rangle$  at long times. It is known that the velocity-correlation function in two-dimensions exhibits a  $1/t$  behavior for long times [8] and hence the diffusion coefficient, as defined by the Green-Kubo integral, does not exist. However,  $\langle r^2(t) \rangle$  shows a well-established linear behavior at long times. The diffusion coefficient  $D^* = D\tau/\sigma^2$  did not fall abruptly to zero as the transition was crossed. Its value was found to be still quite appreciable around the transition density and dropped from 0.0040 to 0.0020 as the density increased from  $n^*=0.78$  to 0.80. Similar behavior was noted with inverse-twelfth-power repulsive potential [6].

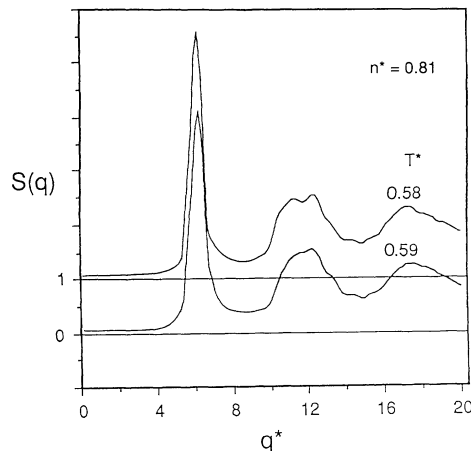


FIG. 5. Structure factor along the isochore  $n^*=0.81$  at two temperatures.

#### IV. CONCLUSIONS

We have investigated behavior of the pair-distribution function and the structure factor of a two-dimensional Lennard-Jones system to look for distinctive structural features associated with the onset of freezing. Based on our analysis, the “signatures” that the glass transition has been reached are the following: (a) the amplitude of the main peak,  $S(q_0)$  of the structure factor is approximately 4.6, (b) the parameter  $R = g_{\min}/g_{\max}$  equals approximately 0.07, (c) the first appearance of a shoulder in the second peak of the pair-distribution function, and (d) the first appearance of the splitting of the second peak of the structure factor. Of course, as we have seen, any one of the above implies all the others. It is a little difficult to state categorically whether a “universal” freezing criterion based on the amplitude of the main peak of the structure factor exists for two-dimensional systems as it seems to exist for three-dimensional systems. The rapid increase of the value of the main peak and its sensitivity to variations in density and temperature near the transition region do not readily yield precise numbers for the freezing criteria. In our case,  $S(q_0)$  increases from 3.8 to 4.8 as the density goes from 0.78 to 0.80, an increase of 27%. Similar rapid increases have been noted in other two-dimensional systems [6]. However, when we consider our work and those of others involving other two-dimensional potentials and systems, a value of 4.7 for  $S(q_0)$  as the universal freezing criterion for a two-dimensional classical fluid is most likely.

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