

Amorphous state studies with the Gaussian core model

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Properties of the supercooled amorphous state have been studied for the Gaussian core model at reduced density $\rho^* = 1$. By monitoring the self-diffusion constant and mean energy during a slow cooling to absolute zero, a glass transition was observed separating supercooled fluid from a rigid amorphous packing. At this glass transition the Wendt-Abraham criterion for the pair correlation function ($g_{\min}^{(2)}/g_{\max}^{(2)} = 0.14$) is satisfied. However, former suggestions that second-peak splitting in $g^{(2)}$ universally signifies the glassy state for monatomic substances are not supported.

I. INTRODUCTION

Amorphous solids have been prepared for a wide variety of substances including metals,¹ semiconductors,² polymers,³ and even water.⁴ The properties of these solids differ in significant ways from those of the corresponding crystalline phases, thereby offering new opportunities for materials applications. In addition to conventional experimental studies, computer simulations for amorphous solids have also produced insights into structures and properties, particularly for monatomic substances that are difficult to prepare in noncrystalline form in the laboratory.

Thus far the most detailed computer simulations of amorphous solids have concentrated on the Lennard-Jones (L-J) system^{5,6}; that is, a collection of particles interacting through additive pair potentials of the form:

$$\phi_{LJ}(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]. \quad (1.1)$$

This model is thought to yield a reasonably good description of the noble gases when appropriate values are assigned to the energy and length parameters ϵ and σ . One of the most important results emerging from these L-J simulations has been quantitative determination of the pair correlation function for the amorphous state, and the resulting formulation by Wendt and Abraham⁸ of a criterion for the glass transition in terms of that pair correlation function.

In order to widen understanding of the amorphous solid state generally, and of the glass transition specifically, it is desirable to carry out computer simulations for several types of interactions that differ substantially from that of the L-J case. The present paper offers a contribution toward that end. It investigates the amorphous solid state and glass transition properties for the Gaussian core model (GCM), for which Eq. (1.1) is replaced by ($\epsilon, \sigma > 0$):

$$\phi_{GCM}(r) = \epsilon \exp[-(\sigma/r)^2]. \quad (1.2)$$

Several important differences between L-J and GCM ought to be noted. First, it is obvious that Eq. (1.2) exhibits no attractive forces so that any dense phase can exist only by virtue of boundary restraints. Second, it has been established by previous molecular dynamics work⁷ that the GCM displays anomalous "waterlike" behavior in its fluid phase, which alone would set it apart from the L-J case. Third, the thermodynamic freezing point in the GCM is strongly depressed by increasing

the density,⁸ and this enhances the ability to study the behavior of the system under slow cooling through the normal freezing point without occurrence of spontaneous crystallization. It is this last property which has allowed us to observe, we believe, a sharp glass transition between the supercooled fluid and a rigid amorphous state.

II. GENERAL PROCEDURE

Details of the molecular dynamics method as applied to the Gaussian core model have been described in a previous paper.⁷ For the present study we have utilized $N=432$ particles confined to a cubical cell and subjected to periodic boundary conditions. The reduced density was fixed at

$$\rho^* = N\sigma^3/V = 1; \quad (2.1)$$

at this density the stable crystal form at low temperature is known to be body-centered cubic.⁸ Since 432 is an integer of the form $2n^3$ the particles can indeed produce such a crystal in the given periodic cell without defects.

It is convenient to measure time, distance, and temperature, respectively, in terms of the following reduced variables:

$$\begin{aligned} t^* &= (\epsilon/m\sigma^2)^{1/2}t \\ \mathbf{r}^* &= \mathbf{r}/\sigma \\ T^* &= k_B T/\epsilon, \end{aligned} \quad (2.2)$$

where m is the particle mass and k_B is Boltzmann's constant. One aspect of particle kinetics is conveyed by the reduced self-diffusion constant:

$$D^* = \lim_{t^* \rightarrow \infty} \langle (\Delta \mathbf{r}_i^*)^2 \rangle / (6t^*), \quad (2.3)$$

which as shown is usually evaluated from mean-square particle displacement vs time.

The rate at which the system undergoes configurational changes from one packing geometry to another can be measured roughly by the time it takes a particle to diffuse a nearest-neighbor distance [in the sense of Eq. (2.3)]. At $\rho^* = 1$ the thermodynamic freezing point is thought to be⁷

$$T_f^* \cong 6.0 \times 10^{-4}, \quad (2.4)$$

at which

$$D^* \cong 6.0 \times 10^{-4}. \quad (2.5)$$

TABLE I. Properties of Gaussian core model packings at $\rho^* = 1$, $T^* = 0$.

State	bcc	A1 ^a	A2	A3	A4
Φ^*/N	2.284296878	2.284538845	2.284513292	2.284506531	2.284523683
p^*	2.783195310	2.7819862	2.78208410	2.78214843	2.78204213
$\langle z \rangle$	8.0000	8.0867	7.9568	8.0639	7.9067
Approx. cooling rate ^b	...	-2×10^{-6}	-7×10^{-7}	-3.8×10^{-8}	-5×10^{-3}

^aThis case was previously reported in Ref. 7.

^b $\partial T^*/\partial t^*$.

Consequently the configurational interchange time is estimated to be

$$\tau^* \cong 3 \times 10^2 \quad (2.6)$$

at the freezing point. This is about twice the corresponding time that can be estimated from our prior study⁷ of the GCM at $\rho^* = 0.4$ (for which $T_f^* \cong 6.2 \times 10^{-3}$), and explains in part the ease with which the GCM at high density can be supercooled without spontaneous freezing.

In order to create a low temperature amorphous state, the system is first equilibrated at a temperature well above T_f^* . The temperature is then reduced stepwise by scaling down all particle momenta at regular intervals whose length can be adjusted to suit one's interest. In the course of our various studies of the GCM several amorphous packings at $\rho^* = 1$ have been prepared. Four are listed in Table I along with a few of their properties at $T^* = 0$. The corresponding properties for the perfect bcc crystal at $T^* = 0$ are also included for comparison. The properties listed include:

(a) reduced potential energy per particle, Φ^*/N , where

$$\Phi^* = \sum \phi_{\text{GCM}}(ij); \quad (2.7)$$

(b) reduced pressure p^* ;

(c) average coordination number $\langle z \rangle$, defined by occurrence of neighbors within distance 1.1755 (the mean of first and second neighbor distances in the bcc crystal);

(d) approximate cooling rate to $T^* = 0$.

The first two of these properties, whether for the crystalline or the amorphous state, are dominated by contributions that are mandated by the relatively high density.

The properties of the four amorphous states A1...A4 are clearly not identical, but they seem to cluster around values that might be taken as characteristic of the amorphous state.

The potential energy per particle is naturally higher than that of the crystal, while the pressure is lower (the system expands on freezing at constant pressure in this density range). The average coordination number evidently can vary slightly in either direction from the crystal value.

If there are systematic variations with history of the amorphous state properties they probably are not sim-

ple enough to infer from Table I with confidence. Having established that a rough consistency exists between independently prepared amorphous packings, we will concentrate attention exclusively on one of these, A3, in the remainder of this paper. This is the case for which the cooling process was carried out most systematically and carefully, and it is the case for which the most data was collected.

III. SELF-DIFFUSION RATE

Beginning with already supercooled fluid at:

$$T^* = 3.3 \times 10^{-4} \quad (3.1)$$

a series of further cooling stages, each of magnitude

$$\Delta T^* = -3 \times 10^{-5} \quad (3.2)$$

was carried out finally to produce zero-temperature amorphous state A3. Before and after each cooling step, the system evolved at constant total energy for 800 time units. For the purpose of computing statistical averages this 800-unit period was broken up into four equal intervals of 200 units. The first of these four was regarded as a period of thermal relaxation, and disregarded; averages for the last three were intercompared for consistency and then lumped together to represent the given temperature state.

Since the mean-square particle displacement was monitored during each 200-unit interval, it was possible to estimate D^* during the cooling process. In particular the average slope of $\langle (\Delta \mathbf{r}_i^*)^2 \rangle$ vs t^* over the last half of each interval was employed. The results have been plotted in Fig. 1.

Within the statistical uncertainty of the data, Fig. 1 shows that D^* drops essentially to zero at a positive temperature,

$$T_f^* \cong 1.7 \times 10^{-4}. \quad (3.3)$$

As the notation indicates we identify this temperature as the boundary between mobile fluid and rigid glass, i. e., the glass transition temperature.

The D^* values shown in Fig. 1 for the supercooled fluid above T_f^* fit smoothly onto values previously determined at somewhat higher temperatures, both in the supercooled and normal fluid ranges. In fact the three highest-temperature points in the figure were taken from this earlier work.

In view of the precipitous decline of D^* toward zero at

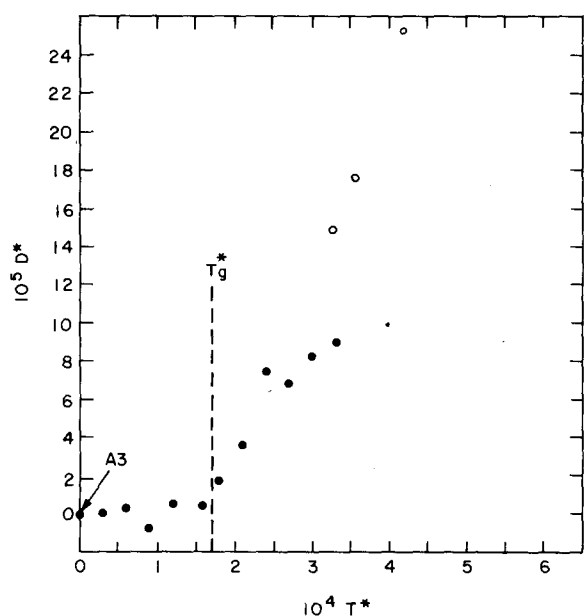


FIG. 1. Self-diffusion constants for the Gaussian core model during slow supercooling. The reduced density is $\rho^* = 1$. The final amorphous state produced by this cooling has been denoted in the text by A3. Open circles signify data from earlier work.

T_g^* it seems unlikely that a substantially depressed glass transition could easily be found by even slower cooling. The preparation procedure for A3 described above was itself quite demanding, since it consumed about 800 hours of CPU time on a moderately fast digital computer.

IV. MEAN INTERACTION ENERGY

Any mechanically stable packing P of the particles at $T^* = 0$, whether it is amorphous or crystalline, corresponds to a local minimum in Φ^* . (Note that the molecular dynamics simulation is carried out under the constraint of fixed center of mass.) The limiting low-temperature motions of this classical assembly will be superpositions of harmonic motions about this local minimum. Therefore the mean interaction energy in this very low temperature regime will have the form:

$$\langle \Phi^* \rangle = \Phi^*(P) + 3(N-1)T^*/2 + O(T^{*2}). \quad (4.1)$$

Here $\Phi^*(P)$ represents the interaction energy at the local minimum for packing P , four examples of which were given in Table I.

At higher temperatures anharmonic contributions appear. In order to examine these contributions it is useful to consider the quantity:

$$\Delta(T^*) = [\langle \Phi^* \rangle - \Phi^*(P) - 3(N-1)T^*/2] / N \quad (4.2)$$

in other words the mean anharmonic potential energy per particle. Figure 2 shows Δ for amorphous packing A3, along with the curve for the defect-free bcc crystal.

Not surprisingly, Δ manifests the same sudden transition at T_g^* [Eq. (3.3)] that we have identified from the self-diffusion constant D^* . The jump in Δ as T^* rises through T_g^* evidently reflects the fact that as particles develop sufficient amplitudes of motion to begin freeing

themselves of imprisoning neighbors, they wander into previously unexplored regions of high anharmonicity.

Notice in Fig. 2 that even in the rigid glass there is greater anharmonicity than in the perfect crystal. We interpret this to mean that the amorphous state offers a higher density of low frequency "soft" modes than does the perfect crystal. At a given energy of excitation such soft modes would entail relatively large anharmonic corrections to harmonic behavior.

The rather large jump in Δ at T_g^* by itself might seem to suggest a latent heat associated with the glass transition. However the data are too sparse at present to support such a conclusion yet, and it is conventionally presumed that glass transitions have no latent heat. Further simulation studies will be required to illuminate this point.

V. PAIR CORRELATION FUNCTION

The pair correlation function $g^{(2)}$ evaluated for the supercooled GCM continues to show the same qualitative behavior that obtains in the stable fluid above T_g^* . Successive shells of neighbors continuously reveal increasing distinctiveness, as T^* declines, through increasing amplitude of oscillation between successive maxima and minima.

Figure 3 presents $g^{(2)}$ at $T^* = 1.57 \times 10^{-4}$, just below the glass transition. It is noteworthy that the second maximum around $r^* = 2$, though broad, shows no obvious sign of developing a split into two peaks. This "split second peak" has often been associated with formation of the glassy state for monatomic substances and in fact has been observed to occur in the L-J system.^{5,6}

The second maximum in $g^{(2)}$ remains intact without splitting until the lowest temperatures ($T^* < 10^{-6}$) are achieved. Figure 4 presents $g^{(2)}$ for structure A3 at $T^* = 0$. In principle this function consists of a sum of delta functions since particles are motionless, but data

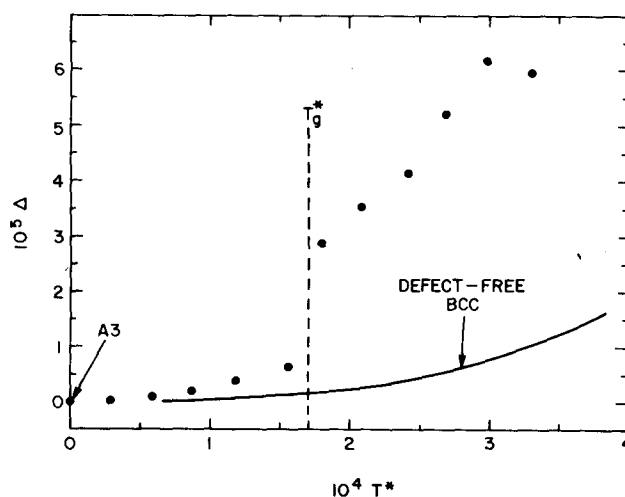


FIG. 2. Anharmonic contribution to the Gaussian core model potential energy. Δ is defined in Eq. (4.2). The curve shows the previously determined result for the perfect bcc crystal at the same density $\rho^* = 1$.

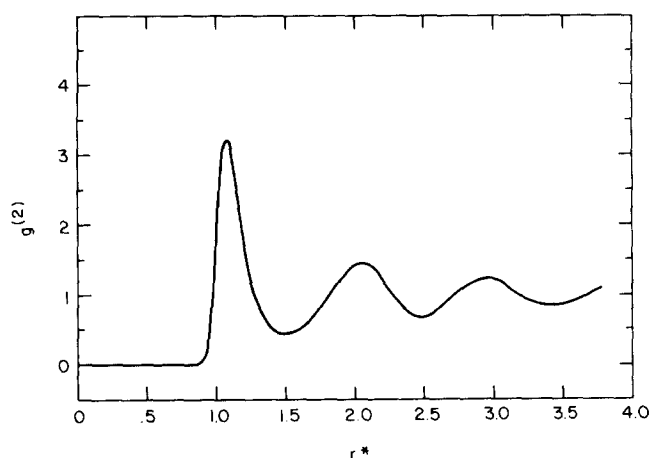


FIG. 3. Pair correlation function just below the apparent glass transition temperature. For this state $T^* = 1.57 \times 10^{-4}$, $\rho^* = 1$.

has been collected and reported in bins of width $\Delta r^* = 0.05$. As reported for a previous case (A1) in Ref. 7, the second peak finally seems to reveal a tendency toward splitting, but only weakly. Incidentally, this second peak region comprises third, fourth, and fifth neighbor shells in the bcc crystal.

It should be noted in passing that the magnitude of the first maximum in $g^{(2)}$ for the GCM in the glassy state is considerably less than the corresponding quantity for the L-J system. Figure 4 shows a value 3.58 for the GCM at $T^* = 0$, whereas a value close to 6.0 has been found for a glassy L-J state *above* absolute zero.⁵ Obviously, attractive forces reduce the dispersion of nearest-neighbor separations. It seems credible that such reduced dispersion might explain the greater tendency of the L-J system to yield a split second peak in $g^{(2)}$.

Although the present results tend to discredit second-peak splitting as a universal indicator of the glassy state they support another criterion that has been advanced. Wendt and Abraham⁶ noticed that the ratio of $g^{(2)}$ values at the first minimum and first maximum:

$$R = g_{\min}^{(2)} / g_{\max}^{(2)} \quad (5.1)$$

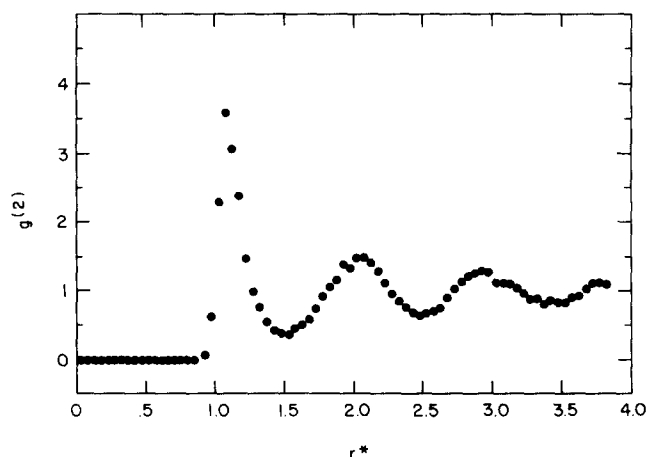


FIG. 4. Pair correlation function for the zero-temperature amorphous state A3.

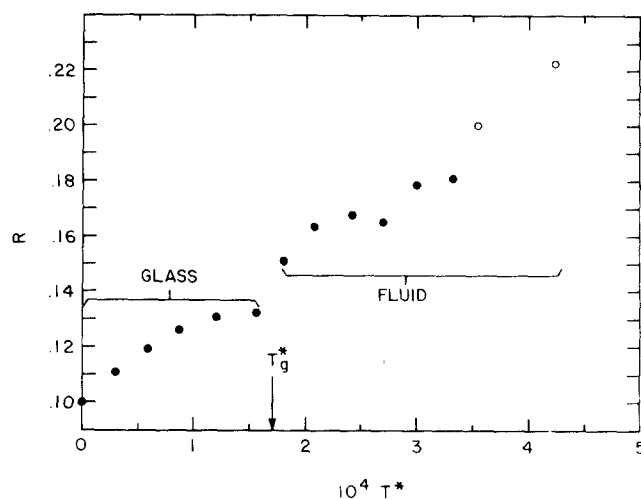


FIG. 5. Pair correlation function ratio [Eq. (5.1)] for the slowly supercooling amorphous system.

passed through a characteristic magnitude 0.14 when their L-J system passed into the glassy rigid state. We find that the same is true from our GCM calculations. Figure 5 shows R values that emerged from our slow cooling process that produced packing A3. Within statistical error R appears to decline smoothly with declining T^* , and indeed to pass through

$$R = 0.14 \quad (5.2)$$

at T_g^* .

For the purpose of interpreting information in the pair correlation function it is useful to have the distribution of coordination numbers z for the particles. The mean values of z can be inferred from $g^{(2)}$ itself, and these were shown in Table I for the cutoff distance 1.1755. However the full z distribution conveys structural information that cannot be extracted from $g^{(2)}$. Figure 6 presents the distribution for the zero-temperature packing A3, showing that although the bcc coordination number 8 is the most frequently occurring integer there exists a substantial dispersion. We have also found similar results for the other amorphous packings.

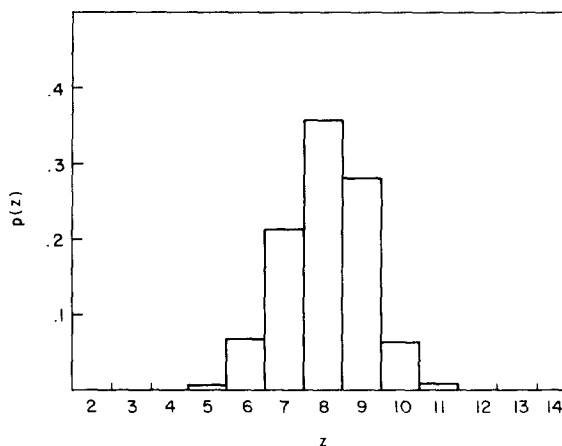


FIG. 6. Coordination number distribution for amorphous packing A3.

VI. DISCUSSION

Two major questions are raised by the present study, namely whether the Wendt-Abraham criterion (5.2) is universally valid for all monatomic glasses, and whether the glass transition is properly to be regarded as an inherent singular point that is independent of kinetic history. The former can be clarified by further simulations with widely differing potentials; the latter requires deep thought.

At low temperatures, motions that contribute to self diffusion are likely to involve simultaneous sliding of several particles along a curvilinear path toward a vacancy, or perhaps around a closed ring. It seems not unlikely that these collective motions would be "autocatalytic" or "cooperative." Very few would be in progress at any instant at very low temperature, but one which is in progress could locally enhance the prospect for another to begin by unlocking the packing. This is a situation that can produce a transition singularity as the density of collective local motions finally reaches a critical value dependent on their coupling. If this de-

scription is qualitatively correct, then a sudden increase in the self diffusion rate should occur at that transition, which by our procedure would be identified as a glass transition. We hope that sufficient insight will soon be forthcoming to evaluate this possibility.

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