Diffusivity of the Hard-Sphere Model in the Region of Fluid Metastability

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New data are analyzed for the hard-sphere fluid at densities $\rho\sigma^3 = 0.95$–1.08 in the metastable range. In this region the diffusion coeffiecient behaves as in laboratory fluids, following a Doolittle equation with normal parameters rather than a Batchinski-Hildebrand equation. The diffusing, internally equilibrated, metastable fluid can be arrested at different densities by sudden "quenching" to obtain the glassy state. A new high-density limit for random close packing, 3% greater than that of Bernal packing, is identified.

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Data obtained by Alder, Gass, and Wainwright, in part of their classical studies of the hard-sphere system in its stable fluid range,[1] have been used to show[2] that the diffusivity D is a linear function of the system volume, implying that

$$D = A(V/V_0^{\mathrm{BH}} - 1), \tag{1}$$

which is the same relation found for liquid metals and simple molecular fluids by Batchinski[3] and Hildebrand[4] (hence V_0^{BH}). On the other hand Doolittle[5] showed that for viscous molecular liquids, in which D is much smaller than for liquid metals, fluidity φ (=viscosity^{-1}), and hence diffusivity, go like

$$\varphi \propto D = A' \exp[-B/(V - V_0^{\mathrm{D}})]. \tag{2}$$

It can be argued[4] that departures from behavior described by Eq. (1) occur because of a "cog-wheel" effect which would not apply to atomic systems. On the other hand it can also be argued[6] that "backscattering" effects neglected in the Enskog theory would lead to behavior described by Eq. (2) for atomic fluids also. There exists therefore some interest in testing the behavior of a suitable model atomic system in the low-diffusivity regime to establish the appropriate phenomenology for atomic liquids at high packing densities.[7]

Because it seems that the hard-sphere system may be more crystallization resistant than other metastable atomic systems,[7] we have extended Alder, Gass, and Wainwright's study to densities 14% above the value $\rho\sigma^3 = 0.95$, $V = 1.50V_{\mathrm{fcc}}$ (V_{fcc} is the close-packed volume) of the phase transition between equilibrium fluid and solid where the earlier study stopped. The algorithm is essentially that of Alder and Wainwright, and contains a compression rate parameter which can be set equal to 0 for study of (metastable) equilibrium properties. Equilibration occurs rapidly near the solid-liquid-transition density, but increasingly slowly as the density is increased. Runs of up to 10^6 collisions (approximately 200 psec of real time for a collision time of 10^{-13} sec) were made, to ensure that the equilibrium value of the diffusivity was measured in each case. Equilibration was judged from constancy of the pressure, calculated both from the virial theorem and from the collision rate itself, and from the linearity of the plot of mean-square displacement $\overline{l}^2$ vs time t ($D = \overline{l}^2/6t$).

Values of the diffusivity were obtained at fifteen different densities, ranging from that of the liquid-solid transition ($\rho\sigma^3 = 0.943$) up to $\rho\sigma^3 = 1.08$. At the latter density crystallization occurred after 0.25×10^6 collisions, as a quite sudden event reflected by an increase in $\overline{l}^2$ vs t plot slope and a decrease in the pressure. Any attempt to reequilibrate, starting with uncrystallized configuration, but running at higher densities, resulted in immediate crystallization. Details are given in a separate publication.[8]

Results are presented in Fig. 1 with a reduced *volume* scale, since the earlier data, given as an inset in Fig. 1, showed that D is linear in volume rather than in density. The range of diffusivity covered in this work is indicated by the shaded area in the inset in Fig. 1. The linear extrapolation of the high-diffusivity data to low diffusivities is shown by the dashed line in Fig. 1. It is clear that the simple linear volume dependence of D breaks down for hard spheres in the low-diffusivity regime.

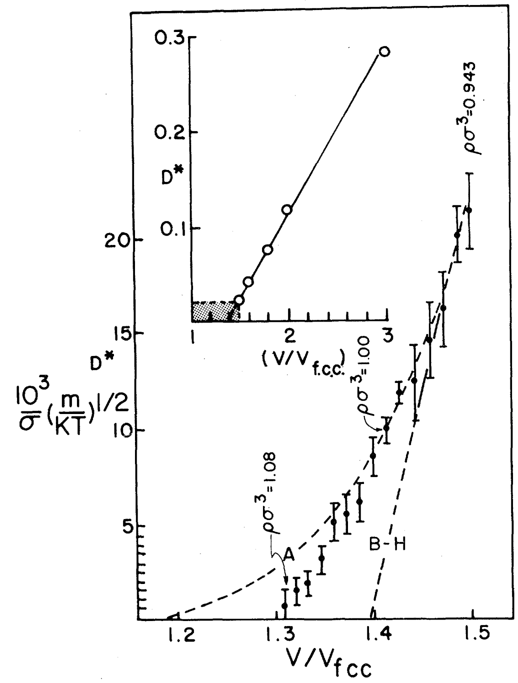

FIG. 1. Variation of hard-sphere diffusivity with volume reduced by the close-packed volume. Dashed lines show predictions of Eq. (1), and also of the Arrhenius equation with use of parameters which fit the high-diffusivity data shown in the inset. Error bars are standard deviations of best fit for plots of l^2 vs t in the long-time region. The last point is especially uncertain. Inset: Data in stable fluid region from Ref. 1. Shaded area shows D and V/V_{fcc} range covered in the present study.

To answer the question of how closely the hard-sphere behavior is following that typical of molecular liquids studied in the laboratory it is necessary to provide some basis for comparison, i.e., some corresponding-states criterion. This is a problem because critical constants cannot be used, and melting constants are erratic functions of the crystal type. However, the characteristic linear volume dependence found for the diffusivities at high values (inset in Fig. 1) suggests a reasonable choice for comparisons of isothermal behavior, viz., the volume V_0^{BH} in Eq. (1).

Using this as a reference volume, the diffusivities of the hard-sphere fluid and laboratory fluids may be compared if the hard-sphere diffusivities D^* are converted from the dimensionless units natural to the machine calculations to the normal units square centimeters per second. The conversion formula is

$$D = D^*\sigma(kT/m)^{1/2} = 8.158\times10^{-5}T^{1/2}D^*, \qquad (3)$$

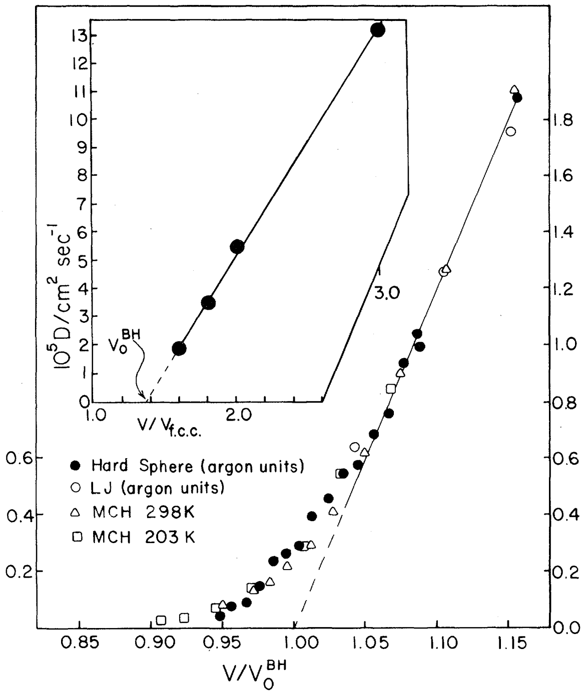

FIG. 2. Comparsion of the present hard-sphere diffusivities, in argon units, with LJ and laboratory data for methyl cyclohexane (MCH) (data of Ref. 10), using reduced volume units. Inset: Ref. 1 data in argon units and method of defining the reference volume V_0^{BH}.

and requires that mass m and size σ parameters be assigned to the hard-sphere data. Natural choices are the mass and diameter of the argon atom. Choosing a temperature of 90 K to correspond with the temperature at which the isothermal diffusivity of Lennard-Jones (LJ) argon has been studied,[9] we obtain the linear plot of D versus volume relative to the volume at close packing shown in the inset in Fig. 2. This extrapolates to $D=0$ at $V_0^{\mathrm{BH}}=1.38$, which then serves as our reference volume for the hard-sphere fluid. The low-temperature data of the present study are shown on an expanded scale as a function of the reduced volume scale V/V_0^{BH}, in Fig. 2.

For comparison with laboratory liquid data, we chose the cases of "LJ argon," also studied by simulation,[9] and methyl cyclohexane, a simple hydrocarbon which remains fluid to very low temperatures, and whose diffusion behavior as a function of volume has been accurately determined by Jonas, Hasha, and Huang using spin-echo measurements up to 1-kbar pressure.[10] Reference volumes for "LJ argon" and methyl cyclohexane (studied at two temperatures) have been obtained in the manner described above, and the diffusivities for these liquids then plotted on the same reduced scale in Fig. 2.

It is seen immediately that the form of departure from the Batchinski-Hildebrand linear law is very similar for all three fluids, the differences appearing to be within the computational noise limits except at the lowest V. Consequently, we can enquire whether the deviations from the BH linear law may be accounted for by the Doolittle form of the volume dependence [Eq. (2)]. Figure 3 shows the hard-sphere diffusion data plotted in the Doolittle form with two choices of V_0^D. The choice $V_0^D = V_{\mathrm{fcc}}$ [Fig. 3(a)] suggested by an Eq. (2) analysis of the data available previously[11] fails to linearize the data, but a second choice, which we have designated V_K, numerically $1.16V_{\mathrm{fcc}}$, does linearize the data within their uncertainty. The symbol V_K is chosen because this is the volume at which extrapolations of the best hard-sphere fluid equation of state[7,8] indicate that the fluid entropy would become the same as that of the ordered solid (the entropy problem to which attention was first drawn by Kauzmann[12]). That the diffusion coefficient is tending to zero at the same condition as the excess entropy tends to vanish implies that the hard-sphere model behaves in a manner characteristic of a wide range of experimental systems studied as a function of temperature.[6] Furthermore, the slope of the plot in Fig. 3(a) corresponds to a volume $0.68V_K$ which is comparable with the empirical relation between B and V_0^D of Eq. (2).[5]

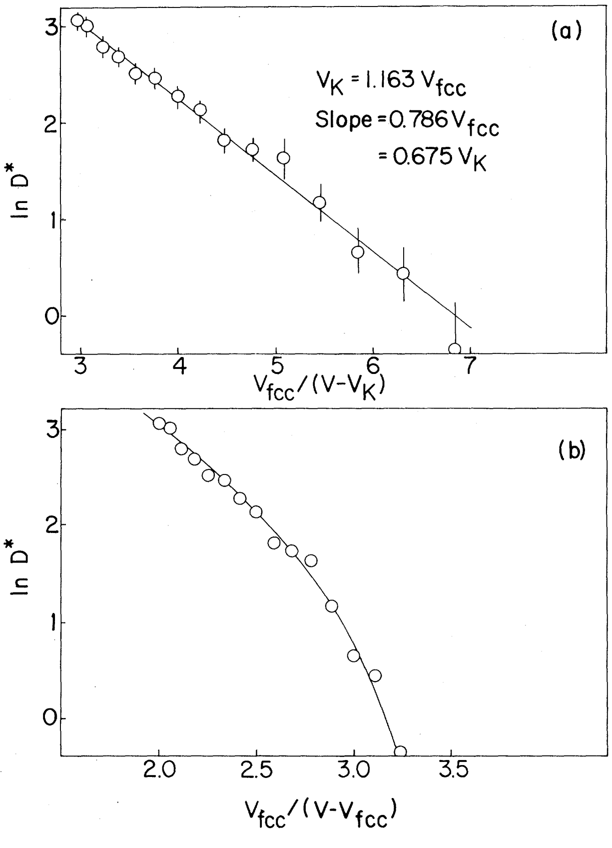

FIG. 3. Test of Eq. (2) for two choices of V_0^D. V_{fcc} is the ordered close-packed volume and V_K is the volume at which the extrapolated fluid entropy intersects the ordered solid value. This is the same volume as the so-called Bernal volume, which, however, is found in this study to be 3% greater than the limiting low value for "random" packing.

Some theoretical justification for the Doolittle form has been given by the treatments of Cohen and Turnbull[6] and, latterly, Cohen and Grest.[13] The success of the Doolittle equation for hard spheres evidenced herein should not, however, be construed immediately as a vindication of the underlying models; these are based on the idea that there exists "free volume" in the structure which redistributes in such a way as to permit a fraction of particle-size displacements which are designated "diffusive." With use of accurate hard-sphere equation-of-state data and the Widom expression[14] for the excess chemical potential $\Delta\mu$,

$$\Delta\mu = kT\ln(V_h/V) \tag{4}$$

(where V_h is the cavity volume $\sum n_i v_i$, the v_i being volumes in the structure large enough to accept a whole hard sphere), it would appear that the probability of finding a particle-size hole in a 512-particle sample around the freezing density,[15] during the period in which diffusion is substantial (several atomic diameters), is quite negligible. On this basis it would seem that the theories arrive at the right diffusion expression from a model which oversimplifies the actual transport mechanism.

At this point we make two additional observations of considerable interest and some irony. The first is that the value of V_K corresponds closely with the Bernal volume which is generally believed to be the limiting high density for amorphous packing of hard spheres. The second is that the Bernal volume is *not* the limiting high density for hard-sphere amorphous packing, shown as follows: If the equilibrated fluid configuration at $\rho\sigma^3 = 1.08$ is *suddenly* compressed, thereby avoiding crystallization, the density increases along a glassy-state path with the same slope as for the ordered solid,[8] and tends to a limiting high density which is nearly 3% greater than that of Bernal packing. Because any attempt to further condense the structure in the *fluid* regime leads to immediate crystallization, it seems that this new density, corresponding to $V=1.133V_{\text{fcc}}$, must be a final limit for amorphous-phase packing of hard spheres. Use of this volume as V_0 in the Doolittle equation gives as good a fit to the Doolittle equation as that using V_K ($1.163V_{\text{fcc}}$), and yields a slope of $1.02V_0$ which accords with Doolittle's original finding.[5]

A final question of interest concerns the relation of this latter random packing to ordered packing and possible connections with the probability of passing from one state to the other. The radial distribution functions of the prequenched fluid structures, *which at densities less than 1.08 were time-independent and stable against nucleation for very long periods*, showed increasingly the presence of near-neighbor distances characteristic of crystal packing as pressure increased.[8] In addition, an increasingly severe distortion of the "split second peak," commonly associated with amorphous packing, occurred in favor of the inner peak. The fluid thus seems to be preparing itself for eventual nucleation, the probability of which must be a very sharp function of volume, approaching unity for short times at $\sim\rho=1.09$. A critical nucleus (which once formed grows very rapidly) contains only some 15–50 atoms[16,17] however, so that it is of doubtful value to think of the fluid at less than the critical nucleation density as containing microcrystallites.

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