

Fluid order and freezing

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Fluid order and freezing

Abstract. Computer calculations have been performed to investigate the short range order near the freezing point, for fluids of particles interacting with an inverse twelfth power potential and with the Lennard-Jones potential. For these potentials, it is found that the onset of freezing is marked by the number of neighbours within a certain radius exceeding that of a close packed system of rigid spheres of a diameter determined by the free energy minimization procedure of Mansoori and Canfield.

Recently, evidence of an upper bound on the density for the stability of a hard sphere fluid has been pointed out (Hutchinson and Conkie 1971). This bound appears to be related to the phase transition in that system.

The bound is obtained by considering a function $N(R)$ which gives the mean number of neighbouring particles contained within a sphere of radius R about any given particle

$$N(R) = 4\pi n \int_0^R r^2 g(r) dr \quad (1)$$

where $g(r)$ is the pair distribution function and n is the number density. It is intuitively obvious that for hard spheres $N(R)$ cannot exceed $N_c(R)$, its value for the hcp close packed solid, at any value of R . It has been observed, from computer results (Hutchinson and Conkie 1971) that in the region of the hard sphere (freezing point) transition the fluid $N(R)$ approaches $N_c(R)$ of the close packed solid at a value of R corresponding to the third neighbour distance.

The question arises as to whether this result is unique to hard spheres or if it has a more general bearing on the liquid–solid transition. To investigate this, we have studied $N(R)$ for systems of particles interacting with the potentials

$$\phi(R) = 4\epsilon \left(\frac{\sigma}{R}\right)^{12} \quad (2)$$

and

$$\phi(R) = 4\epsilon \left\{ \left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^6 \right\}. \quad (3)$$

The melting curves for both these potentials have been determined accurately by Monte Carlo methods (Hoover *et al.* 1970 and Hansen 1970). It should be noted that the potential of equation (2) is effectively the high temperature form of (3). $N(R)$ was calculated using the Harwell molecular dynamics program (Beeman and Schofield, unpublished) using 500 particles.

The results for the inverse twelfth power potential are shown in figure 1. $N(R)$ was calculated for: (i) the fcc solid (the stable configuration with this potential) near the melting point, (ii) the fluid near the freezing density, (iii) the fluid in the unstable

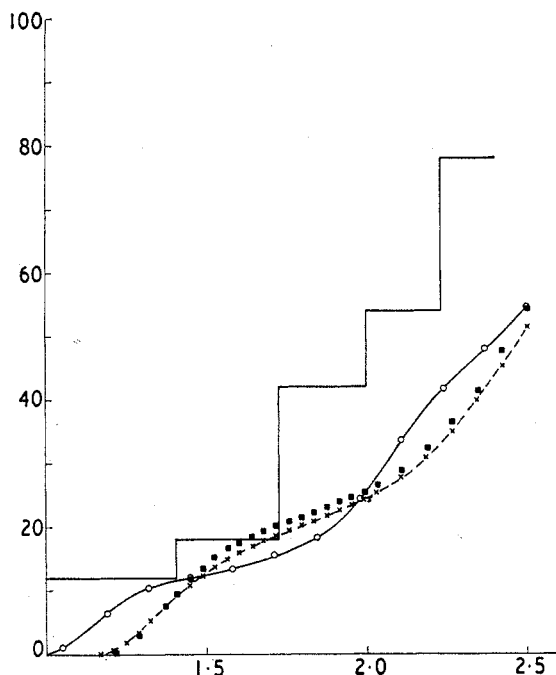


Figure 1. Packing fraction, $N(R) = 4\pi n \int_0^R r^2 dr g(r)$ for $\phi(r) = 4\epsilon(\sigma/r)^{12}$. Equivalent hard sphere diameter $d = (\epsilon/kT)^{1/12}\sigma$. — $N_c(R)$ fcc contact close packed lattice of hard spheres diameter d ; —○—○— solid at melting point, $nd^3 = 0.838$; —×—×— fluid at freezing point, $nd^3 = 0.815$; ■ unstable fluid, $nd^3 = 0.863$.

(supercooled) region at a density much higher than freezing. Since for an inverse power potential distance scales with temperature as $(\epsilon/kT)^{1/m}\sigma$ it is appropriate in this case to plot $N(R)$ against R/d where

$$d = \left(\frac{\epsilon}{kT}\right)^{1/12} \sigma. \quad (4)$$

Also shown in figure 1 is $N(R)$ for a contact fcc lattice for spheres of diameter d which we denote by $N_c(R)$. The three cases correspond to values of the density nd^3 of 0.838, 0.815 and 0.863 respectively at $\epsilon/kT = 1.0$. The close packed lattice density corresponds to $nd^3 = \sqrt{2}$.

It may be questioned whether σ is the appropriate hard sphere diameter for the closed packed system with which comparison is made. For the pure repulsive potential (2) its estimation by the free energy minimization method of Mansoori and Canfield (1969), gives $d/\sigma = 1.02$ which is near enough to unity for qualitative purposes.

As in the case of hard spheres, we see that the freezing transition appears to be related to $N(R)$ rising to touch $N_c(R)$ at $R = R_3$ the third neighbour distance, so that the instability of the fluid phase is again determined by $N(R)$ exceeding $N_c(R)$ at some value of R .

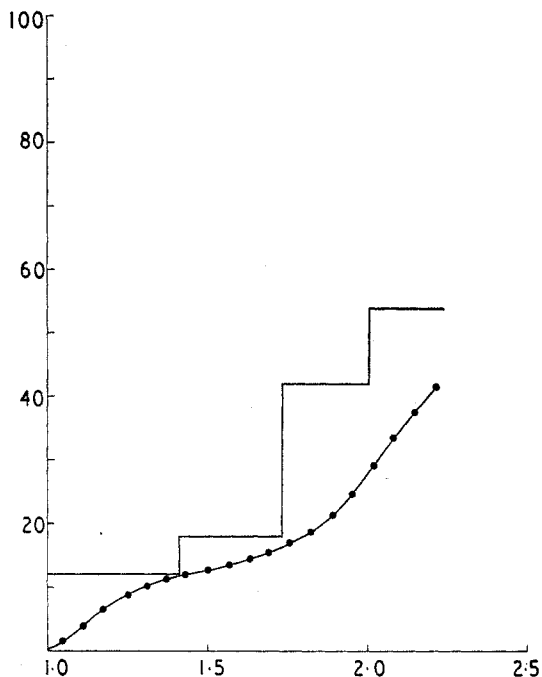


Figure 2. Packing fraction, $N(R) = 4\pi n \int_0^R r^2 dr g(r)$ for

$$\phi(r) = 4\epsilon\{(\sigma/R)^{12} - (\sigma/R)^6\}.$$

Equivalent hard sphere diameter $d = \sigma$. — $N_c(R)$ fcc constant close packed lattice of hard spheres, diameter d ; —●—●— liquid at freezing point, $n\sigma^3 = 0.87$, $kT/\epsilon = 0.75$.

In figure 2 are shown the results for the Lennard-Jones potential (equation (3)) at a density $n\sigma^3 = 0.875$ and temperature $kT/\epsilon \simeq 0.75$, a point very close to the freezing curve for this potential (Hansen 1970). Also shown is the fcc $N_c(R)$ for hard spheres of diameter σ . (For this phase point the equivalent hard sphere diameter d chosen by the procedure of Mansoori and Canfield, is again very close to σ .)

It can be seen that at the transition $N(R)$ again rises to touch $N_c(R)$, but this time at the second neighbour distance R_2 . Clearly this must reflect the effect of the $(\sigma/R)^6$ part of the potential in reducing the repulsion at short distances, allowing the closer approach of particles.

The calculations, shown in figure 1, for the repulsive potential indicate that the number of neighbours within a sphere of radius R_3 is considerably higher in the liquid at the freezing point than in the solid at the melting point, even though the solid density is about 2.5% higher. This excess becomes more pronounced in the metastable liquid and it can be argued that it is this local excess which produces the increase in free energy that leaves the solid the more stable state. Moreover the liquid

$N(R)$ is initially ($R \lesssim R_2$) less than that of the solid, and thus it is clear that the liquid structure is not that of a 'loosely packed solid' as is often suggested. We may note that an initial depletion of neighbours followed by an excess is to be expected in order to satisfy the thermodynamic constraint of equal pressure and temperature at the phase transition.

Finally, we should like to commend the use of the function $N(R)$ in the discussion of short range order in the liquid state. Although it reveals the 'structure' less dramatically than $g(R)$, the mean number of neighbours within a radius R , or the inverse function $R(N)$, the radius within which the mean number of neighbours is N , are more precise functions than the rather nebulously defined 'coordination number' often quoted. The significant volume to consider appears to be that occupied by twenty or thirty particles. It will be interesting to investigate whether the criterion for the stable fluid $N(R) < N_c(R)$ holds for other types of interaction.

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