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1998 J. Phys.: Condens. Matter 10 4387

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## Pressure and entropy of hard-sphere crystals

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Received 21 April 1997, in final form 3 February 1998

**Abstract.** The pressure and entropy of the face-centred cubic and hexagonal close-packed hard-sphere crystals were measured. At the melting density, the hcp crystal has a higher pressure. A precise equation of state is reported for the crystals. The equation extrapolates to a spinodal instability in the metastable low-density crystal.

### 1. Introduction

Nearly half of the elements are known to form face-centred cubic (fcc) or hexagonal close-packed (hcp) crystals, and the two crystal types occur in nature with about equal frequency. For rigid spheres, these structures provide the most efficient packings, in which the spheres occupy  $\sqrt{2}\pi/6$  or 74% of the space.

This study of the crystals was motivated by Woodcock's report [1] of a Gibbs free-energy difference,  $\Delta G = 0.005(1)NkT$ , favouring the fcc crystal. Throughout this paper  $\Delta X$  means  $X_{\text{hcp}} - X_{\text{fcc}}$ ,  $N$  is the number of spheres,  $k$  is Boltzmann's constant,  $T$  is the temperature and a number in brackets gives the uncertainty in the last digit quoted. Woodcock's result is five times larger than expected from the entropy difference,  $\Delta S \approx -0.001(1)Nk$ , reported by Frenkel and Ladd [2], which has been verified by more precise measurements [3, 4] since Woodcock's report [1]. Much, but not all, of the discrepancy is explained by the finding that there is a significant pressure difference between the two crystals near the melting density.

### 2. Methods and results

The simulations used standard molecular dynamics methods [6, 7] with periodic boundaries. They were performed with a constant number of spheres, at constant volume  $V$  and energy  $U$ . The fcc crystals were simulated in a cubic box. The hcp crystals were simulated in rectangular boxes with side lengths in the ratios  $11\sqrt{3}:15:22\sqrt{(2/3)}$  ( $N = 7260$ ),  $9\sqrt{3}:13:18\sqrt{(2/3)}$  ( $N = 4212$ ),  $7\sqrt{3}:10:14\sqrt{(2/3)}$  ( $N = 1960$ ) and  $4\sqrt{3}:8:8\sqrt{(2/3)}$  ( $N = 512$ ). The density,  $z = (N/V)\sigma^3/\sqrt{2}$ , is expressed relative to close packing.

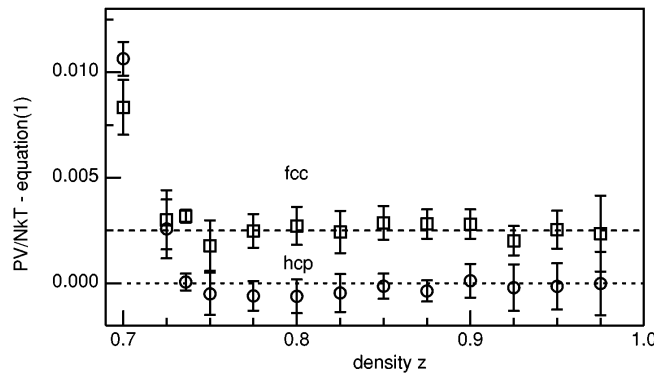
Figure 1 shows that pressures measured above the melting density,  $z_m = 0.736$  [8], are precisely represented by the simple empirical equation of state

$$PV/NkT = 3/(1 - z) - a(z - b)/(z - c) \quad (1)$$

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**Table 1.** The parameters in equations (1) and (2) and a comparison of the values of  $\Delta_{ig}S(z_m)/Nk$  calculated from equation (2) with independent values obtained for crystals of  $N = 12\,096$  spheres [12] at  $z_m = 0.736$ .  $S_0(\text{hcp})$  was adjusted to be consistent with the precise measurement of  $\Delta S$  [4] at  $z = 0.7778$ . To agree with [12], both values of  $S_0$  should be 0.0014 more negative.

Crystal	$a$	$b$	$c$	$S_0$	$\Delta_{ig}S/Nk$	$\Delta_{ig}S/Nk$ [12]
hcp	0.5935	0.7080	0.601	-2.5335	-5.9186(14)	-5.920 03(13)
fcc	0.5921	0.7072	0.601	-2.531	-5.9178(14)	-5.919 16(13)

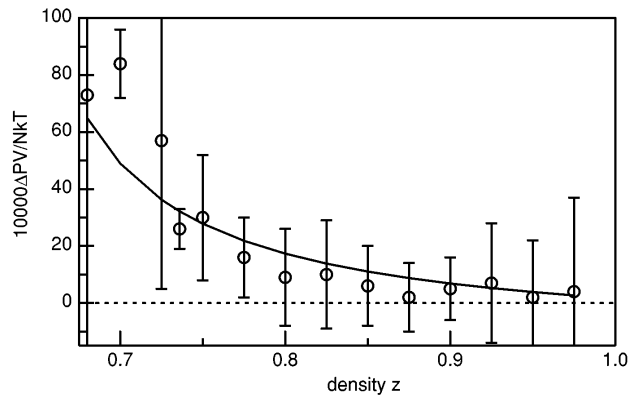


**Figure 1.** The pressure  $PV/NkT$  of the fcc and hcp hard-sphere crystals, relative to values calculated from equation (1) with the constants from table 1, versus the density relative to close packing,  $z$ . To separate the points, the fcc results are shifted up by 0.0025. Results are for  $N = 2048$  (fcc) or  $N = 1960$  (hcp). The pressure was measured in runs of 20 million collisions except at the densities  $z = 0.68, 0.7$  and  $0.736$  (the melting density [8]), where runs of 300 million collisions were used to improve the precision. In the density range where the crystal is stable, the maximum deviation of any point from equation (1) is 0.0007. At  $z = 0.68$  the measured  $PV/NkT$  is 0.08(3) higher than values extrapolated with equation (1). For crystals of 500 spheres, the pressures are 0.003 lower near the melting density and the difference is smaller at higher density.

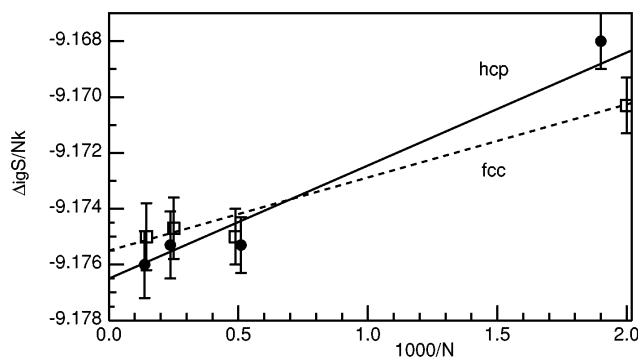
with the constants  $a$ ,  $b$  and  $c$  listed in table 1. The measured pressures are higher than values extrapolated with equation (1) when  $z < z_m$ . Equation (1) agrees with the empirical equation of Hoste and Van Dael [9] to within 0.02 in  $PV/NkT$  and it agrees with the most precise data reported by Alder *et al* [10], for  $N = 500$  spheres, to within less than half their estimated uncertainties.

Figure 2 shows that the pressure of the hcp crystal is systematically higher than that of the fcc crystal, at the same volume, implying that the fcc crystal is denser at the same pressure. The difference is smaller than the uncertainty away from the melting density but, when the uncertainty is reduced by running the simulations for long times, the difference  $\Delta PV/NkT = 0.0026(7)$ , is measurable at the melting density. Woodcock [5] has confirmed this difference, in the cell model [1, 8], and reports  $\Delta PV/NkT = 0.0029(5)$  ( $N = 12\,000$ ) at the melting density.

The entropy was measured with the tether method [11] at density  $z = 0.9$ , for crystals of up to 7260 spheres. The method is as described previously [11] except that the pressure on the tether cell wall was measured in runs of 10 to 30 million collisions at each tether length, the centre of mass of the spheres was allowed to drift freely and no corrections [11] were applied. More precise results [3, 4] have been reported since these measurements



**Figure 2.** The difference in pressure,  $\Delta PV/NkT$ , between the hcp and fcc crystals versus the density  $z$ . The line is from equation (1) with constants from table 1.



**Figure 3.** The entropy of the fcc and hcp crystals, relative to the entropy of an ideal gas at the same  $N$ ,  $V$  and  $T$ , plotted against  $1000/N$  where  $N$  is the number of spheres in the simulation. Note that the sign of the entropy difference changes with  $N$ .

were made, so they are reported briefly, for the purpose of comparing methods. Figure 3 shows the system size dependence of  $\Delta_{ig}^c S$ , the entropy of the crystal relative to an ideal gas at the same volume and temperature (using Stirling's approximation, to second order, for  $\ln\{N!\}$ ).  $\Delta_{ig}^c S$  is independent of  $N$  for  $N > 2000$ , to within the uncertainty. The entropy at any other density is obtained by integrating the thermodynamic relation  $(\partial S/\partial V)_U = P/T$ , using equation (1) for the pressure, which gives

$$\Delta_{ig}^c S(z)/Nk = -3 \ln\{z/(1-z)\} + (1 + ab/c) \ln\{z\} + a(1 - b/c) \ln\{z - c\} + S_0. \quad (2)$$

The constant of integration  $S_0$ , where values are listed in table 1, is determined by the entropy in the thermodynamic limit from figure 3. The entropy at the melting density, from equation (2), is compared with independent measurements [3, 12] in table 1. The methods agree to within the estimated uncertainty. All of the entropy measurements [1–5, 12] refer to crystals without vacancies. The equilibrium vacancy concentration in the crystals is about 1 vacancy per 10000 spheres near the melting density [13]. Adding a vacancy to a crystal of 10000 spheres involves the work  $10^{-4}PV \approx 0.001NkT$ , corresponding to an entropy change of  $0.001Nk$ , which is similar to the uncertainty in the entropies shown in table 1.

From equation (2),  $\Delta S$  varies by  $0.0003(2)Nk$  over the density range  $z_m \leq z \leq$

1 and  $\Delta S = -0.0008(23)Nk$  at the melting density. Bolhuis *et al* [3] report  $\Delta S = -0.00087(20)Nk$  ( $N = 12\,096$  at  $z_m$ ) and Bruce *et al* [4] report  $\Delta S = -0.00086(3)Nk$  ( $N = 5832$  at  $z = 0.7778$ ). These very precise measurements make obsolete the less precise value of  $\Delta S$  calculated here, though the agreement between the three very different methods is reassuring.

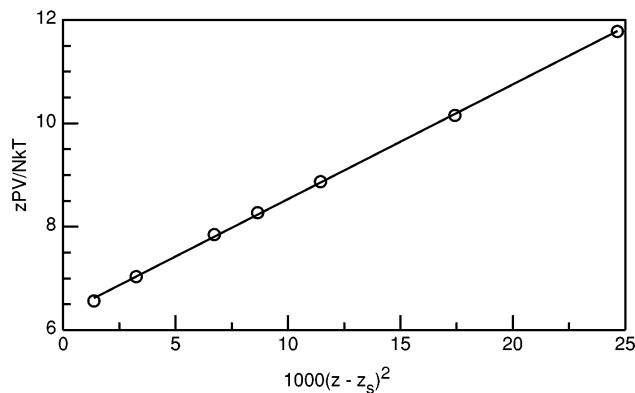
Woodcock [1] calculated

$$\Delta G(P) = \int_0^P \Delta V(P') dP' = 0.005(1)NkT \quad (3)$$

but he assumed that evaluating the integral up to the same density for each crystal was the same as evaluating it up to the same pressure  $P$ . In other words, he evaluated  $\Delta G(V)$  and assumed that  $G(P) = \Delta G(V)$ . To within a negligible correction term,  $\Delta G(P) = -T \Delta S(V) = \Delta G(V) - \Delta P V$  and the measured value of  $\Delta P V = 0.0026(7)NkT$  accounts for about 60% of the difference between Woodcock's result [1] and the others [2–4]. With a recalculation that avoids the above assumption, Woodcock [5] found  $\Delta S = -0.0026(10)Nk$  ( $N = 12\,000$  at  $z_m$ ), so a smaller discrepancy remains.

### 3. Discussion

The small differences between the pressure and entropy of the fcc and hcp crystals are summarized by equations (1) and (2) with the constants in table 1. The relative stability of the two crystals is now decided [2–5] in favour of the fcc crystal and the results of this work are obsolete in that respect.



**Figure 4.** The pressure  $PV/NkT$  of the fcc crystal plotted against  $1000(z - z_s)^2$ . Points are shown for the density range  $0.68 \leq z \leq 0.8$ . The straight line shows  $zPV/NkT = 6.31 + 222(z - 0.643)^2$ .

Equation (1) extrapolates to a spinodal instability [14–18], where  $(\partial P/\partial V)_T \rightarrow 0$  and the expansivity, compressibility and heat capacity of the metastable crystal diverge. The spinodal is located, by extrapolation of equation (1) or from figure 4, at  $z_s \approx 0.643$  where  $PV/NkT \approx 9.3$ . The crystals melt spontaneously when  $z \approx 0.67$ , so the spinodal is never reached. However, when the crystals are prevented from melting, by applying cell model constraints [1, 5, 8], or by tethering [11] the spheres to their lattice sites, the instability is evident. Woodcock's calculations [1] show it near  $z = 0.64$  where  $PV/NkT = 9.4$ , for the fcc cell model. His method [1, 5, 8] of calculating the entropy relies on integrating the

pressure of the cell model crystals through the instability. For the unconstrained crystals studied here, the increase in fluctuations near the spinodal shows up in the poor precision of the measured pressures at  $z = 0.68$  (figure 2).

Sciortino *et al* [17] have recently shown that when models for ice and silicates are stretched in simulation experiments, they also behave as though tending towards a spinodal, located just beyond the point where the crystals rupture. In particular, the pressure varies as

$$P = P_s + B(z - z_s)^2 \quad (4)$$

where  $P_s$  and  $z_s$  are the pressure and density at the spinodal and  $B$  is a constant. Equation (4) is the limiting form expected [14–16] near a mean-field spinodal. Figure 4 shows that the hard-sphere crystal follows the same form as ice [17], the silicates [17], liquid water [14–16] and other models [18] near their respective limits of stability, so this behaviour seems rather general.

### Acknowledgments

I thank P Bolhuis, D Frenkel, N B Wilding and L V Woodcock for sharing unpublished results and the Marsden Fund for support through contract GRN 501.

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