

Effect of monovacancies on the relative stability of fcc and hcp hard-sphere crystals

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The relative stability of perfect face-centered-cubic (fcc) and hexagonal-close-packed (hcp) hard-sphere crystals has been explored by different researchers over several decades.¹⁻¹⁰ Molecular simulations show that the free energy difference between the phases is small, and while the results vary in detail somewhat, the clear consensus prevails that fcc is the more stable phase at all densities. So far the comparison has been done only on defect-free close-packed hard-sphere crystals. Even though the existence of point defects results in a measurable shifting of the free energy of fcc hard-sphere crystals at melting,¹⁰ there exists no published results comparing the stability of hard-sphere crystals containing vacancies. Interest in this question is heightened by the recent results of Pronk and Frenkel,¹¹ who found a surprising difference in the elastic constants of fcc and hcp hard-sphere crystals. In light of these results, one might question whether there are significant differences in the susceptibility of the free energy to other types of changes, and, in particular, to changes involving the formation of vacancies. If so, the difference in the response of the free energy to vacancy formation might be enough to alter the relative stability of the phases.

In this paper we address this issue and examine the effect of monovacancies on the free energy difference of close-packed hard-sphere crystals. We consider only noninteracting monovacancy defects, as the concentration of other point defects such as interstitials and divacancies is much smaller.^{12,13} The monovacancy free energy and concentration are obtained via Monte Carlo simulations with a biased insertion method interpreted in a grand-canonical formalism proposed by Pronk and Frenkel.¹² We conducted such simulations using 216 particles positioned at $6 \times 6 \times 6$ lattice sites in a rhombohedral box. Previous studies have found that finite-size effects on the vacancy free energy are negligible for systems of this size, even in comparison to the small effects of interest here.¹⁴ Initial configurations of fcc and hcp crystals were obtained by stacking hexagonal layers in *ABC* and *AB* arrangements, respectively; the hcp stacking was compressed slightly, in accord with the finding of Pronk and Frenkel.¹¹ Simulations were performed for densities $\rho\sigma^3$ (where ρ is the number density and σ is the hard-sphere diameter) within the range from 1.0376 (melting) to 1.2.

First we investigate the effect of monovacancies on the free energy of each crystal structure, calculated by

$$\Delta f_{\alpha} = f_{1,\alpha} x_{v,\alpha}, \quad (1)$$

where Δf_{α} is for crystal structure α the difference in the free energy per lattice site between a perfect hard-sphere crystal and one containing monovacancies, $f_{1,\alpha}$ is the change in free energy when creating a monovacancy by deleting a particle from its lattice site, and $x_{v,\alpha}$ is the fraction of the crystal lattice sites that are vacant in an equilibrium system.¹² Table I presents the complete results. Polson *et al.*¹⁰ reported the value of Δf_{fcc} as $(3 \times 10^{-3})k_{\text{B}}T$ near melting, $\rho\sigma^3 = 1.0409$ (where k_{B} is Boltzmann's constant and T is the temperature). Our data agree with their result. Even though free-energy changes are small, both crystal structures clearly show a shift of the free energy by about $(2.3 \times 10^{-3})k_{\text{B}}T$ at the melting point due to the presence of vacancies.

Second, we compare the difference in the effect of the vacancies to the difference between the free energies of the defect-free crystalline phases. The latter quantity was obtained at $\rho\sigma^3 = 1.0409$ using the value reported by Bolhuis *et al.*,⁷ while differences at other densities were obtained by thermodynamic integration using Speedy's equation of state.⁹ Comparisons are made of the Helmholtz free energy for different crystals at the same density; negligible changes are introduced if instead considering the Gibbs free energy of crystals at the same pressure. Results are included in Table I. The close-packing hcp-fcc free-energy difference reported by Bolhuis *et al.*⁷ is included to show that the lower-density

TABLE I. Relative free energies (per lattice site) of hard-sphere crystals for several densities. Under "Free energy," Δf_{fcc} is the difference between the free energy of a perfect fcc crystal and one with an equilibrium number of monovacancy defects, while Δf_{hcp} is the same for hcp crystals. The third column is the difference between the two to the left of it, and describes the net effect of monovacancies on the relative stability of fcc and hcp phases. The last column is the free-energy difference between the defect-free crystals. Confidence limits (67%) are indicated.

$\rho\sigma^3$	Free energy $\times 10^6 (k_{\text{B}}T)$			
	Δf_{fcc}	Δf_{hcp}	$\Delta f_{\text{fcc}} - \Delta f_{\text{hcp}}$	$f_{\text{hcp}} - f_{\text{fcc}}$
1.0376	2248 \pm 18	2251 \pm 20	-3 \pm 27	860 \pm 200 ^a
1.05	1393 \pm 11	1391 \pm 11	2 \pm 16	897 \pm 200 ^a
1.1	170.1 \pm 10.0	168 \pm 11	2.1 \pm 15	1015 \pm 200 ^a
1.2	0.2624 \pm 0.0017	0.2621 \pm 0.0016	0.0003 \pm 0.0023	1152 \pm 200 ^a
1.414				940 \pm 300 ^b

^aReference 7 at $\rho\sigma^3 = 1.0409$ with thermodynamic integration using the equation of state of Ref. 9.

^bReference 7.

values given by integration of the equation of state are reasonable. Table I shows that the change in the free energy in each phase due to monovacancies is considerably larger than the free energy difference between the phases. However, the effect of the monovacancies on the free energy is almost exactly the same for both phases. The difference in the effect is listed as $\Delta f_{\text{fcc}} - \Delta f_{\text{hcp}}$ in the table and is very small—within the confidence limits of the calculations, the difference is zero. Moreover, the confidence limits of the vacancy effects are themselves still smaller than the difference in free energy of the defect-free phases (given in the rightmost column), so there is no question that the presence of monovacancies does not change the relative stability of the phases.

We conclude that the relative stability of stress-free fcc and hcp crystals is not affected by the presence of monovacancies, and fcc remains the more stable phase over all solid-phase densities.

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