

# Cavities in the hard-disk crystal: A Monte Carlo simulation study

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The equilibrium pressure in a crystal composed of hard spheres or disks may be determined from the statistical geometry of a single isolated monocavity (one large enough for addition of only one particle). Additional knowledge of the equilibrium concentration of monocavities permits evaluation of the chemical potential and absolute entropy. We have used Monte Carlo simulation to examine isolated monocavities in the rigid-disk crystal near close packing. The resulting pressures compare very favorably with those from previous simulations, and with asymptotic high-compression equations of state. The monocavities exhibit fluctuating polygonal shapes; the number of sides varies from three to six, with four the most probable occurrence.

## I. THEORY

Geometry has become a major emphasis in the ongoing study of hard-particle systems. Indeed, at thermodynamic equilibrium, the hard-sphere pressure equation of state as derived by Speedy<sup>1</sup> involves only geometric variables:

$$\frac{p}{\rho kT} = 1 + \frac{\sigma}{2D} \frac{S_0}{V_0}, \quad (1)$$

where  $\rho = N/V$  is the density of the system,  $k$  is the Boltzmann constant,  $T$  is the temperature,  $\sigma$  is the hard-sphere diameter, and  $D$  is the dimensionality of the system. We will use three-dimensional language, although the focus of our work is the two-dimensional hard-disk system. If imaginary spheres of radius  $\sigma$  are placed around each hard sphere and the centers of all other particles are then excluded from those imaginary spheres, the volume outside the excluded region is the available space  $V_0$ . The area of the interface between the available space and the excluded region is denoted by  $S_0$ . The chemical potential may also be written in terms of the available space:

$$\mu = kT \ln \left( \frac{\lambda^D N}{V_0} \right), \quad (2)$$

where  $\lambda$  is the thermal deBroglie wavelength and  $N$  is the number of particles.

The quantities  $V_0$  and  $S_0$  and, therefore, the pressure may also be written in terms of the configuration average of the individual volumes  $\langle v \rangle$  and surfaces  $\langle s \rangle$  of all cavities.<sup>2</sup> A cavity is a connected subset of the total volume into which the addition of the center of another sphere is possible without sphere overlap. A cavity should not be confused with a vacancy in the high-compression regime, for it is possible to have a vacancy in the crystalline structure, e.g., a lattice defect, to which a particle could not be added; a vacancy is not necessarily also a cavity. All of the cavities together compose the available space; therefore, if there are  $N_c$  cavities,

$$V_0 = N_c \langle v \rangle \quad (3a)$$

$$S_0 = N_c \langle s \rangle. \quad (3b)$$

Substitution of these into Eq. (1) yields<sup>2</sup>

$$\frac{p}{\rho kT} = 1 + \frac{\sigma}{2D} \frac{\langle s \rangle}{\langle v \rangle}. \quad (4)$$

Equation (4) predicts that the pressure of a hard-disk system may be determined by the evaluation of the statistical geometric quantities  $\langle s \rangle$  and  $\langle v \rangle$  alone. For this reason, we undertook a Monte Carlo simulative study of both of these quantities in order to see how well the pressure obtained by this means near the close-packed limit compared with that obtained by other means. Speedy and Reiss<sup>3</sup> (SR) have reported the evaluation of  $\langle s \rangle$  by molecular dynamics at a few disk densities near close packing. Those authors calculated the total available surface  $S_0$  and the total available volume  $V_0$  from an empirical equation of state and Eqs. (1) and (2). Using the simulated values of  $\langle s \rangle$  and the calculated values of the total available surface they calculated  $N_c$  using Eq. (3b). The values of  $N_c$  and calculated values of the total available volume  $V_0$  were then used to calculate  $\langle v \rangle$  from Eq. (3a). SR found good agreement between their calculated pressures [Eq. (4)] and those obtained by nongeometric methods. Our results, covering more densities in the region near close packing, are derived entirely from the geometry of a single monocavity. We have also been able to examine some new geometric characteristics of monocavities.

Using, in part, a dynamic rather than a statistical thermodynamic argument, Hoover *et al.* have derived an equation of state for hard disks and spheres also dependent solely on geometric properties.<sup>4</sup> In this case, the variables are the free volume  $v_f$  and the surface area  $s_f$  of the free volume:

$$\frac{p}{\rho kT} = 1 + \frac{\sigma}{2D} \left\langle \frac{s_f}{v_f} \right\rangle, \quad (5)$$

where the average is over all allowable configurations of the spheres. The free volume is the volume through which the center of a particle in the system could move if all the other particles were fixed. It differs from the volume of a cavity in that it is the volume available to the center of a particle already in the system—one which has locally had an effect on the structure of the system. Speedy has proved the equivalence of the ratio of the average cavity surface to cavity

volume and the average of the ratio of the free surface to free volume<sup>2</sup> and has thereby validated Eq. (5) on a statistical thermodynamic basis. While the pressure may be determined from the geometry of the free volume alone, the chemical potential may not be calculated without knowledge of the equilibrium number of cavities. Cavities are essential to a complete geometric description of the thermodynamics of the hard-sphere crystal.

As the density of the system is increased from zero, the available space shrinks and passes through a critical percolation point where it disconnects into  $O(N)$  pieces. At crystalline densities, the available space is so small that only monocavities, i.e., cavities large enough to accept only one additional particle, are important. Because these monocavities are very dilute, we assume that they do not interact with each other, and, therefore, in the high-compression range, the configuration averages of the cavity volume and surface over all cavities may be replaced by the averages over a single monocavity. In a crystal, the pressure may be determined from Eq. (4) by the average volume and surface of a single cavity. In fact, SR (Ref. 5) have predicted by analogy with the exact one-dimensional case that the pressure at high compressions depends only on the average volume of a cavity. Equation (4) may be rewritten in terms of an average density-dependent shape factor  $a(z)$ ,

$$\frac{p}{\rho kT} = 1 + \frac{a(z)}{\langle v \rangle^{1/D}}, \quad (6)$$

where

$$a(z) = \frac{\sigma}{2D} \frac{\langle s \rangle}{\langle v \rangle^{(D-1)/D}}$$

and  $z$  is the density relative to the close-packed density. In one dimension,  $a(z) = \sigma$  for all densities, and it is expected that in the two-dimensional crystal,  $a(z)$  will be insensitive to density changes and will be approximately equal to  $\sigma$ .<sup>3</sup>

Schaaf and Reiss<sup>6</sup> have used a plausibility argument to derive an asymptotic form of the hard-sphere equation of state near the close-packed density using the geometric quantities  $V_0$  and  $S_0$ . SR (Ref. 5) proved the same result rigorously employing geometric considerations. The equivalent of this equation in two dimensions is

$$\frac{p}{\rho kT} = 1 + \frac{\rho^{1/2}}{\rho_c^{1/2} - \rho^{1/2}}, \quad (7)$$

where  $\rho_c$  is the close-packed density. It is important to note that the same asymptotic high-density expression for the pressure has also been derived from the configuration integral via a different route that neglects the existence of cavities completely.<sup>7-9</sup> The cavity is therefore a "thermometer" for the thermodynamic properties of the hard-sphere system.

## II. CALCULATION

We used the Monte Carlo method to calculate the average volume and surface of a monocavity in the high-density hard-disk system. As illustrated in Fig. 1, our initial configuration was a triangular lattice in a rectangular cell, with one disk removed to provide a vacancy. Periodic boundary con-

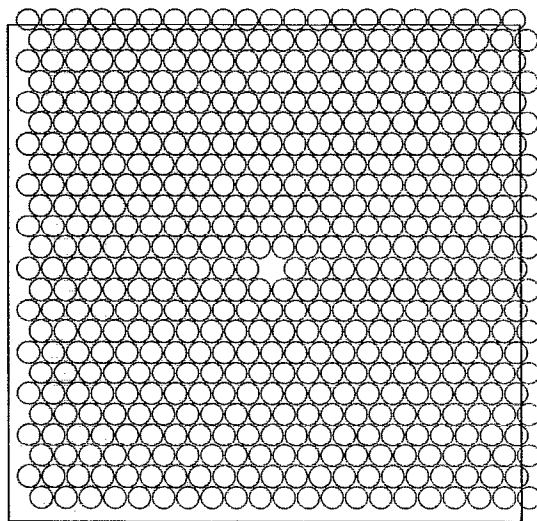


FIG. 1. The lattice configuration of hard disks with one vacancy is shown for  $z = 0.95$ . Simulations were performed on systems of 503 disks in a rectangular cell with periodic boundary conditions.

ditions applied. The system as described provides no means for the escape of the defect. The initial vacancy in the lattice was also a cavity because the densities studied were below the close-packed limit. The size of a cavity relative to the radius of an exclusion circle is so small for the high compressions examined that the curvature of the cavity boundary was negligible, and the cavity was taken to be a polygon. Let the lattice point from which the single disk was removed be considered the cavity center. In the lattice, the sides of the polygon were the tangents to the exclusion circles of the cavity nearest neighbors at the point on the exclusion-circle perimeter which was closest to the cavity center. The lattice cavity was a regular hexagon (see Fig. 2). As the cavity neighbors were moved in the Monte Carlo process, the size and shape of the cavity changed. It was assumed that the

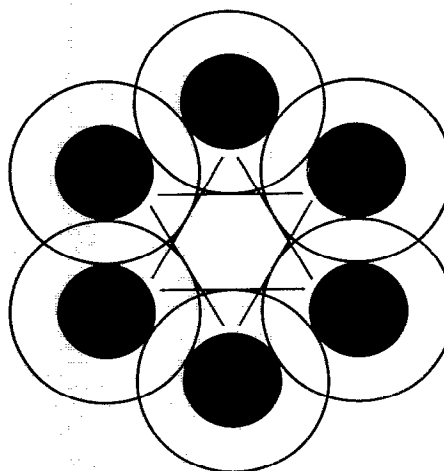


FIG. 2. The cavity in the lattice configuration is shown. The dark disks are the hard particles, with the surrounding circles the exclusion circles. Tangents to the exclusion circles form the polygon which approximates the cavity. If parallel sides cross, the cavity is eliminated.

TABLE I. Results of the Monte Carlo simulation for the percentage of vacancies examined that were also cavities, average cavity surface, volume, pressure, and shape factor [Eq. (5)] are given. The surface and volume values are reduced in terms of the lattice spacing of the particles  $l = 1/z^{1/2}$ .

$z$	% cavities	$\langle s \rangle / (l-1)$	$\langle v \rangle / (l-1)^2$	$p/pkT$	$a(z)/\sigma$
0.95	43.9	3.834	0.950	39.851	0.984
0.96	46.3	3.819	0.920	51.330	0.995
0.97	48.8	3.827	0.928	68.140	0.993
1/1.02	50.0	3.880	0.946	103.998	0.997
0.982	49.7	3.885	0.962	111.664	0.990
0.984	49.9	3.764	0.888	131.927	0.999
0.986	51.8	3.766	0.897	149.438	0.994
0.988	50.3	3.772	0.896	174.820	0.996

sides of the polygon moved parallel to themselves. The possible number of sides for the polygon ranged from three to six, and if two parallel sides crossed each other (corresponding to a particle's moving toward the vacancy such a distance that its exclusion sphere encompassed the available space), the polygon was eliminated. The polygon was also eliminated whenever there was no overlap of the quadrilaterals formed by two sets of parallel-side pairs. In each such case, although the polygonal cavity vanished, the vacancy remained.

The simulated systems contained 503 disks, with at least  $20 \times 10^6$  Monte Carlo single-particle steps allowed for equilibration. The step size was selected such that 50% of the trial moves were accepted. The calculations were divided into 20 blocks, each with 600 measurements of the cavity polygon separated by 3020 Monte Carlo steps, for a total of 12 000 measurements. For each configuration for which the cavity polygon was measured, a set of linear inequalities was used to determine whether the polygon had vanished. For cavities with nonzero content, the number of sides and the points of intersection of those sides were determined. The content and perimeter of the polygon were calculated from the points of intersection of the sides.

### III. RESULTS

The simulated averages of the cavity volume and surface are reported in Table I, along with the pressures, calculated

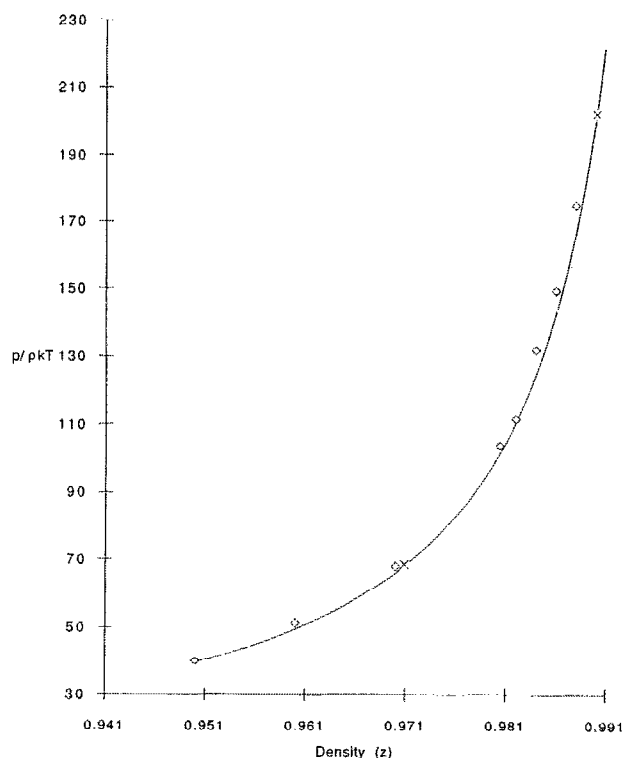


FIG. 3. The asymptotic high-density equation of state [Eq. (7)] (solid line) is compared with the pressure calculated by Monte Carlo using Eq. (4) (diamonds). The crosses show the pressure Alder *et al.* (Ref. 10) calculated by simulation of the virial of intermolecular force.

by Eq. (4). Approximately 50% of the vacancies examined for each density over the entire range studied were also cavities. SR have used molecular dynamics to calculate the cavity surface.<sup>3</sup> As outlined earlier, they determined the cavity volume from the simulated value of the cavity surface and values for  $S_0$  and  $V_0$  derived from Eqs. (1) and (2) and an empirical equation of state. The highest densities at which SR performed these calculations were  $z = 0.95$  and  $1/1.02$ . Their pressure at  $z = 0.95$  agrees with ours to within 0.04 (0.1% relative difference), the simulated average cavity surface to within  $10^{-3}$ , and the average cavity volume to within  $10^{-5}$ . Their pressure at  $z = 1/1.02$  agrees with ours to within 2.2 (2% relative difference), the simulated average cavity

TABLE II. The percentage of cavities with three, four, five, and six sides at each density is given (in the column marked "%"), along with the average cavity surface and volume for the cavities with those numbers of sides. The surface and volume values are reduced in terms of the lattice spacing of the particles  $l = 1/z^{1/2}$ .

$z$	%	3 sides				4 sides				5 sides				6 sides			
		$\langle s \rangle / (l-1)$	$\langle v \rangle / (l-1)^2$	%		$\langle s \rangle / (l-1)$	$\langle v \rangle / (l-1)^2$	%		$\langle s \rangle / (l-1)$	$\langle v \rangle / (l-1)^2$	%		$\langle s \rangle / (l-1)$	$\langle v \rangle / (l-1)^2$	%	
0.95	21.21	2.021	0.338	46.78		3.541	0.628	23.86		5.170	1.543	8.15		6.334	2.653		
0.96	21.70	2.022	0.338	45.94		3.578	0.615	24.53		5.026	1.455	7.83		6.431	2.644		
0.97	20.13	1.954	0.301	47.53		3.546	0.624	24.07		5.070	1.471	8.27		6.384	2.625		
1/1.02	19.23	2.068	0.346	47.58		3.572	0.623	24.88		5.043	1.458	8.31		6.354	2.654		
0.982	19.51	2.006	0.325	47.24		3.563	0.627	24.71		5.099	1.505	8.54		6.446	2.698		
0.984	19.35	1.839	0.262	48.71		3.539	0.617	24.71		4.995	1.433	7.23		6.230	2.517		
0.986	20.48	1.893	0.291	46.96		3.536	0.606	24.66		4.916	1.398	7.90		6.394	2.628		
0.988	19.08	1.919	0.302	48.10		3.482	0.589	24.68		4.918	1.392	8.14		6.361	2.600		

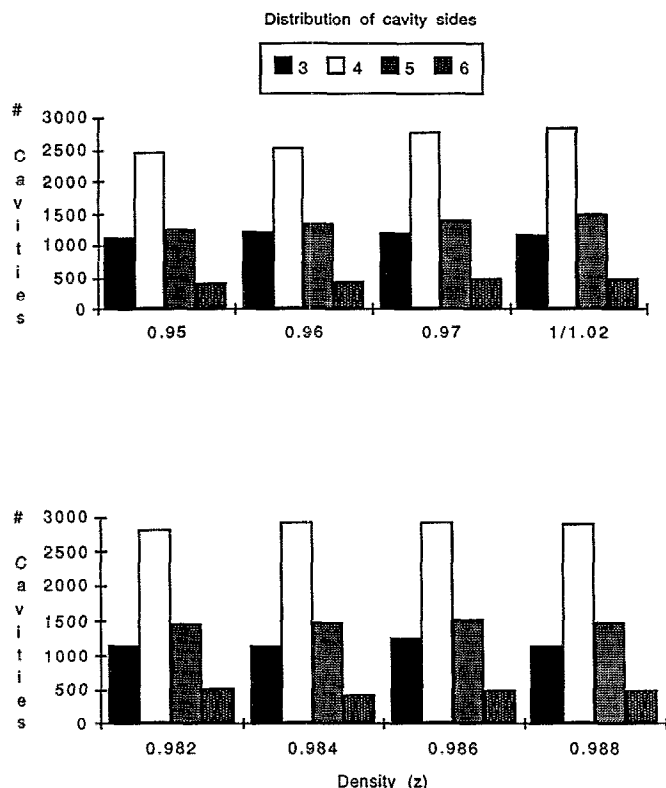


FIG. 4. The distribution of cavities with three, four, and five sides is shown for each density.

surface to within  $2 \times 10^{-4}$ , and the average cavity volume to within  $2 \times 10^{-6}$ . Hoover *et al.* used the Monte Carlo method to determine the pressure from the free volume and surface, using Eq. (5).<sup>4</sup> The highest density they studied was  $z = 0.95$ , where their pressure agrees with ours to within a relative difference of 0.3%. Table I also gives the simulated values of the shape factor  $a(z)$  relative to the particle diameter  $\sigma$ . As SR predicted and demonstrated in their molecular dynamics simulation,<sup>3</sup>  $a(z)$  does not depend strongly on the density in the crystalline regime and is approximately equal to the particle diameter. Our results confirm their findings for more densities near the close-packed limit.

Figure 3 shows the pressure calculated from Eqs. (4) and (7) as a function of density. The pressures we calculated

using the simulated geometric quantities (diamonds) agree quite well with the values predicted by the high-compression asymptotic form of the equation of state [Eq. (7); solid line in Fig. 3]. The crosses show the two pressures at these nearly close-packed densities which Alder *et al.*<sup>10</sup> calculated by simulation of the virial of the intermolecular force.

Table II gives the percentage of cavities at each density which had three, four, five, and six sides, along with the average area and surface of the cavities with those numbers of sides. Figure 4 shows the distribution of the number of cavity sides for each density studied with four the most probable outcome in all cases. The average number of sides per cavity also is approximately four over the density range studied, indicating that as the lattice was relaxed the particle neighbors tended to collapse into the available space of the cavity.

Speedy and Reiss have advanced a seemingly reasonable argument concluding that near the close-packed limit, cavities will virtually always exhibit simplectic shape: in two dimensions a triangle. Our results show that the collective behavior of the rigid-disk crystal is too complicated and subtle to respect "reasonable" arguments. It will be illuminating eventually to apply the approach used in this paper to the rigid-sphere crystal in three dimensions, where again cavities may exhibit shapes that are only occasionally simplectic (tetrahedral).

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