Two-step melting transition in confined hard spheres in three dimensions

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It is shown that certain geometrical constraints on a system of hard spheres lead to two distinct finite-size analogs of melting transitions upon decreasing the average number of spheres at constant volume. Melting takes place from an ordered crystal via an intermediate structure to a fluid. Sphere centers in the intermediate state have a high probability to be found in localized regions that are dramatically different in size and shape.

A collection of atoms may undergo phase transitions to and from a gas, liquid, and solid. Solids come in many structures, and upon variation of pressure and/or temperature, phase transitions between different solid structures may occur. For example, carbon may order into graphite and diamond, and tin into its gray and white form. These structures are transformed into one another by symmetry-breaking, first-order phase transitions (in these examples from a soft to a strong solid). From computer simulations it follows that solids may also undergo symmetry-conserved transitions [1]. Highly charged colloids may undergo a body-centered-cubic (bcc) to face-centered-cubic (fcc) transition (see [2] and references therein), which can be reproduced by computer simulation by assuming long-ranged repulsive interactions (Yukawa potential) between the spheres [3].

For hard disks in two dimensions, it is still being disputed whether such a system, upon decreasing the number density, melts in two continuous steps via an hexatic phase [Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) theory; see [4] and references therein] or if the melting transition is first order [5].

The simplest model of interacting atoms in three dimensions (3D), hard spheres under thermal agitation, has a single freezing transition from a fluid to a (fcc) solid [6,7]. When hard spheres are confined in one direction, i.e., between two parallel plates, they exhibit many phase transitions; see [8,9] and references therein. In particular, when the plate separation is kept constant in between approximately 1.2 and 2 sphere diameters, and upon increasing the number density of the spheres, a first-order phase transition from a fluid to a solid is found, followed by a solid-solid transition. The structure of the solid phases depend on the plate separation.

In this Brief Report, systems of hard spheres that are confined in all three directions are studied. Very small systems (down to eight spheres) already show the signature of the freezing transition [10,11]. Here the question is addressed as to what the role of geometrical constraints is on the character of the freezing transition. Geometrical constraints are imposed by the shapes of the boxes that keep the spheres together. Besides being interesting from a fundamental point of view, the answer to this question may be relevant to the behavior of simple fluids in highly porous media. In the case of magnetically interacting colloids, geometrical constraints dramatically change the phase behavior as was recently reported in [12].

The central quantity from which all thermodynamic functions are calculated is the configurationally averaged volume that is available for the center of an $(N+1)$th hard sphere in a system containing N hard spheres in a volume V, $V_0^{(N)}$. Speedy [13] derived an exact relation between available volume (named "spare volume" by the author) of a system of N hard spheres and the configuration integral, which implies that the (reduced) configurational part of the Helmholtz free energy of a system containing N spheres is exactly given by the recursive relation [11]

$$\beta F_N = \beta F_{N-1} - \ln\left(\frac{v_0^{(N-1)}}{N}\right), \qquad (1)$$

in which the reduced available volume $v_0^{(N)} = V_0^{(N)}/D^3$, where D is the diameter of a hard sphere. $\beta = 1/kT$, with k Boltzmann's constant and T the absolute temperature. A small-system analog of a first-order phase transition in the canonical ensemble is evident if the Helmholtz free energy as a function of the number of spheres has a region that is "concave from below." Strong evidence of a first-order phase transition in the grand ensemble follows from two peaks of the grand distribution function [14]
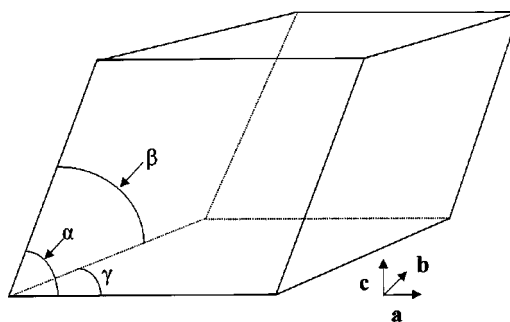
$$P_N = \frac{z^N q_N}{\Xi}, \qquad (2)$$

FIG. 1. Boxes of different geometry, that define the angles and length ratios given in Table I.

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TABLE I. Quantities that define the box geometries as depicted in Fig. 1. Only in the geometries I and Ib can N_{max} spheres be ordered into the equivalent of an fcc or hcp lattice for a (very) small system. The other geometries allow only distorted configurations with respect to this ''true'' close packing.

Code	α	β	γ	$|\vec{a}|:|\vec{b}|:|\vec{c}|$	N_{max}	(Close-packed volume)/D^3
I	65.91	69.30	60	$1:1:\sqrt{2/3}$	8	$1/\sqrt{2}$
Ib	65.91	69.30	60	$1:1:\sqrt{2/3}$	27	$4\sqrt{2}$
II	90	69.30	60	$1:1:\sqrt{2/3}$	8	$3/4$
IIb	90	69.30	60	$1:1:\sqrt{2/3}$	27	6
III	90	90	60	$1:1:\sqrt{2/3}$	8	$\sqrt{3}/2$
IV	90	90	90	$1:1:1$	8	1

with the reduced canonical partition function $q_N = e^{-\beta F_N}$ and the reduced activity $z = (D^3/\Lambda^3)e^{\beta\mu}$, where Λ is the thermal de Broglie wavelength of a hard sphere and μ is the chemical potential. $\Xi = \sum_{N=0}^{N_{max}} z^N q_N$ is the grand partition function in which N_{max} is the maximum number of spheres that can be crammed into V.

The systems of hard spheres are contained in boxes with smooth hard walls and varying geometry. Their volume could be varied isomorphically.

The four different geometries of the boxes that were used are defined by Fig. 1, together with Table I. These boxes envelop the centers of the hard spheres (part of the spheres can thus be outside the boxes), and their volumes define $V_0^{(0)}$.

Table I summarizes the values of the angles, defined by Fig. 1, and the ratios of the axis lengths that characterize a box geometry. The sequence I, II, III, IV corresponds to an increasing number of cubic axes in the boxes and thus a decreasing packing efficiency. The close-packed volume is defined as the volume of the box at which N_{max} spheres are close packed in the particular geometry defined by the values of the angles. For example, the box of the geometry encoded by I fits a true close-packed configuration of eight hard spheres when its reduced volume equals $1/\sqrt{2}$. In the situation that the system I is close packed, all centers of the hard spheres are fixed at the corners of the box. The code Ib (IIb) refers to a box of the same geometry as I (II), but it is dilated to fit (at most) 27 spheres. This situation was chosen in order to study effects of the size of the system while keeping the geometry constant.

Throughout this paper, the volumes of the boxes are expressed relative to the close-packed geometry I; that is, it is defined by $\eta = v_0^{(0)}/(1/\sqrt{2})$ if $N_{max} = 8$ and $\eta = v_0^{(0)}/4\sqrt{2}$ if $N_{max} = 27$.

The available volumes were computed numerically, as in [11]. For the geometries I(b), III, and IV, its behavior qualitatively looks like what was found in [11] where geometry I(b) was studied; i.e., at constant $\eta > 2$ (approximately), the available volume continuously decreases with the number of spheres, but when η becomes small, the available volume for the small systems ($N_{max} = 8$) decreases up to $N = 4$ (system I) or $N = 6$ (systems III and IV), and subsequently increases. In
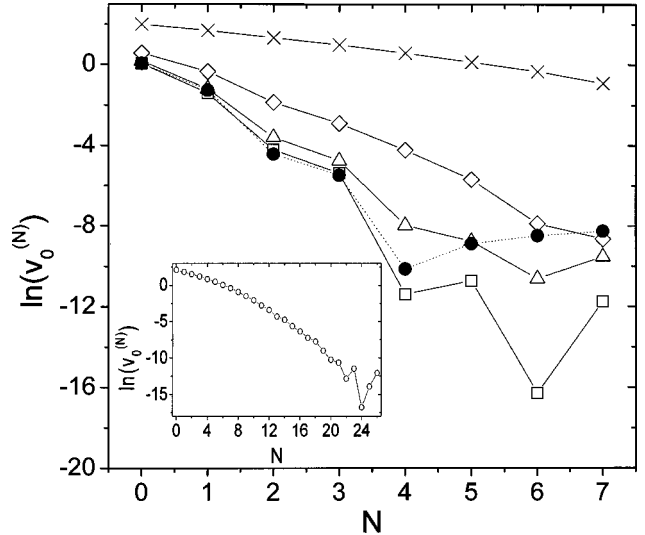

FIG. 2. Available volumes $v_0^{(N)}$ (averaged over at least 10^4 configurations) as a function of the number of spheres, at several box volumes relative to the volume of the box where the maximum number of spheres are close packed, as quantified by η (see text). Geometry II (see Table I): $\eta = 4.79$ (crosses), $\eta = 2.48$ (diamonds), $\eta = 1.68$ (triangles), and $\eta = 1.49$ (squares). Also shown is the situation for geometry I with $\eta = 1.49$ (solid circles) as a comparison. Inset: situation for geometry IIb with $\eta = 1.47$. Here $v_0^{(N)}$ still has two minima. Uncertainties are on the order of the symbol size for the smallest values of $v_0^{(N)}$ and smaller for the other values.

[11] it was shown that this increase corresponds to a small-system analog of a first-order phase transition in the grand ensemble.

For the geometry encoded as II, the situation is more complicated, as shown in Fig. 2. As long as $\eta > 2$ (approximately), the available volume continuously decreases with N. At smaller η (1.7), a minimum at $N = 6$ occurs. But when η is decreased even further ($\eta = 1.49$ in this case), the available volume has two minima, one at $N = 4$ and one at $N = 6$. This behavior is still apparent in geometry IIb with $N_{max} = 27$ and $\eta = 1.47$: here, $v_0^{(N)}$ has two minima, one at $N = 22$ and one at $N = 24$. In the following we shall concentrate on this geometry, II(b), as the behavior of the other ones (III and IV) is not qualitatively different from I(b). It should be noted that apparently a single cubic axis in the (small) box geometry depicted in Fig. 1 embodies a crossover between a single minimum of $v_0^{(N)}$ at $N = 4$ (geometry I, no cubic axes) to a single minimum at $N = 6$ (geometries III and IV, with two and three cubic axes, respectively). In the case of the geometries III and IV, $v_0^{(N)}$ goes to zero if $N > 4$ and $\eta < 1.5$.

At equal volumes, the Helmholtz free energies [Eq. (1)] of geometries II(b)–IV are always equal to (at small N) or larger (at large N; $N > 4$ for the systems with $N_{max} = 8$) than that of geometry I(b), indicating that if the geometries of the boxes were considered as a constraint imposed on the systems, the geometries that are different from I(b) are metastable with respect to I(b) at high densities. This situation is illustrated in Fig. 3, where the Helmholtz free energy as a function of the number of spheres is plotted for the geometries I and II. It is also shown that geometry I has a region
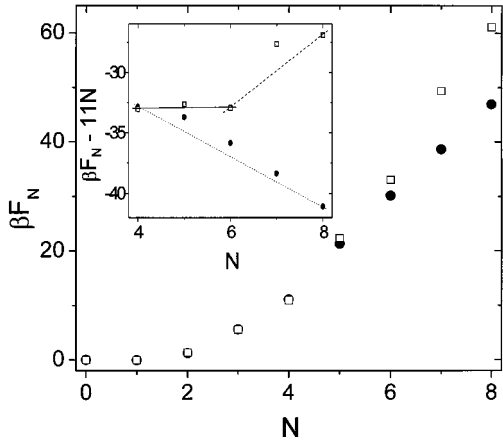
FIG. 3. Helmholtz free energies as a function of the number of spheres for systems I (solid circles) and II (open squares). Inset: expanded view with a linear term subtracted in order to clearly show the region where βF is concave from below. In both systems, $\eta = 1.49$.

(in between $N = 4$ and 8) that is concave from below, indicating that in an ensemble of boxes with geometry I, if the number of spheres in the system is such that on average $N = 5 - 7$ (per box), the system reduces its Helmholtz free energy by splitting into $N = 4$ and 8 (the fractions of boxes with $N = 4$ and 8 being determined by the lever rule), as was indeed found to happen in the grand ensemble [11]. It is also clear from Fig. 3 that geometry II has two regions that are concave from below, indicating two small-system analogs of
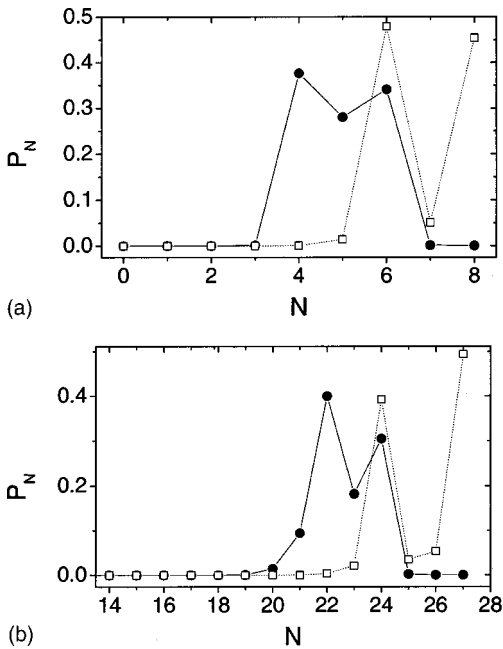

FIG. 4. P_N vs N for different values of $\ln(z)$. (a) Geometry II and $\eta = 1.49$; solid circles correspond to $\ln(z) = 12.7$ where the first maximum of $\sigma_N^2 = \langle N^2 \rangle - \langle N \rangle^2$ appears. Open squares: $\ln(z) = 16$ (second maximum of σ_N^2). (b) Geometry IIb with $\eta = 1.47$; solid circles represent $\ln(z) = 15.2$ (first maximum of σ_N^2), and open squares $\ln(z) = 17.6$ (second maximum of σ_N^2).
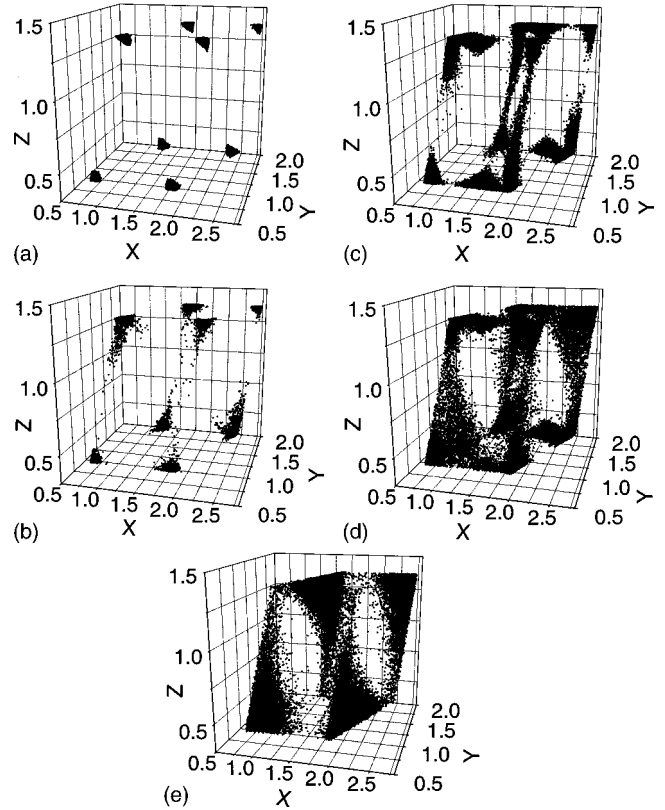

FIG. 5. Positions of sphere centers of 10^4 configurations of geometry II and $\eta = 1.49$. (a) $N = 8$, (b) $N = 7$, (c) $N = 6$, (d) $N = 5$, and (e) $N = 4$. The x, y, z axes correspond to the directions of the vectors **a**, **b**, **c** in Fig. 1. Note that the z axis is somewhat expanded relative to the x and y axes.

phase transitions or a melting transition that occurs in two steps when decreasing the average number of spheres in the boxes. As shown in Fig. 4, where the grand probability distribution [Eq. (2)] is plotted, this behavior is corroborated in the grand ensemble: there are two values of $\ln(z)$ (the chemical potential) where the grand probability P_N has two peaks. Note that the transition at the larger values of $\ln(z)$ is the strongest of the two transitions; i.e., the probability of finding systems containing numbers of spheres in between the two peaks is very small relative to the first transition.
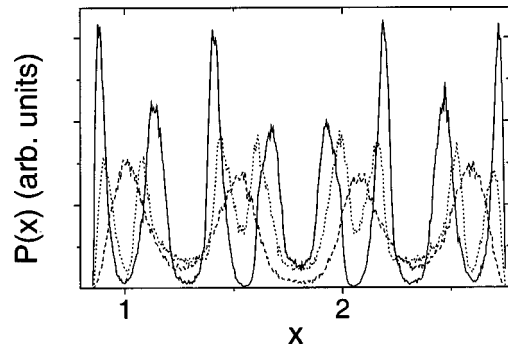

FIG. 6. Histogram of the positions of sphere centers along the x direction (in Fig. 5). Dashed line: $N = 4$. Dotted line: $N = 6$. Solid line: $N = 8$.

What is the structure of the system at high, intermediate, and low numbers of spheres in geometry II? The positions of the centers of N spheres, of 10^4 configurations, are plotted in Fig. 5. When $N=8$, the system clearly is a crystal, with eight well-defined lattice positions [Fig. 5(a)]. The system is a ''defective solid'' when $N=7$ [there are eight lattice positions for seven spheres, Fig. 5(b)]. When $N \leq 4$, the centers tend to occupy positions at the corners and along the walls, but there are no distinct lattice positions [Fig. 5(e)]. At intermediate values, in particular when $N=6$ [Fig. 5(c)], the sphere centers occupy localized lattice positions as well as regions that clearly are localized, but still occupy a relatively large volume of the box—they look more like ''streaks'' than they look like lattice positions. Similar structures have not been found in the boxes with geometries that are different from II(b). So for this structure to exist, hcp- (or fcc-) like configurations should be suppressed, while at the same time the system should be able to reach relatively high number densities. Looking at several configurations (not shown), it follows that the streaks in the z direction may contain a single sphere center that can be located anywhere in the streaks or two sphere centers with large probabilities of being located at the extreme extensions of the streaks. As shown in Fig. 6, where the histograms of the positions of the sphere centers along the x coordinate are plotted, the system with $N=6$ clearly has a symmetry that is different from the ''fluid'' $N=4$ and the crystal $N=8$. The situation is less obvious in the larger system of geometry IIb (not shown), which probably is related to the observation (Fig. 2) that the minima of $v_0^{(N)}$ tend to become closer to one another along the $N/N_{\max}$ axis when the system size is increased (the two minima should ultimately merge into a single one in the thermodynamic limit). This melting scenario is different from the situation where hard spheres are confined between parallel plates, where either fluid-solid or solid-solid transitions have been observed [8,9], and no structure has been found that is a mixture of localized and not-so-localized lattice positions, i.e., intermediate between fluid and solid.

By applying geometrical constraints to small systems, I have shown that melting of a small hard-sphere crystal can occur in two steps, where the structure of the intermediate state consists of localized regions of high probability to find a sphere center. Within the (single) crystal, these regions differ dramatically in size and shape.

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