Liquid-solid transition of hard spheres under gravity

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We investigate the liquid-solid transition of two-dimensional hard spheres in the presence of gravity. We determine the transition temperature and the fraction of particles in the solid regime as a function of temperature via event-driven molecular-dynamics simulations and compare them with the theoretical predictions. We then examine the configurational statistics of a vibrating bed from the viewpoint of the liquid-solid transition by explicitly determining the transition temperature and the effective temperature T of the bed, and present a relation between T and the vibration strength.

The hard-sphere model has been quite successful in explaining the macroscopic properties of dense fluids, or gases, from the microscopic point of view [1]. At the molecular level, the potential energy of the hard spheres due to gravity is small in comparison to the thermal fluctuations and it has usually been ignored. However, when the mass of the constituent particle is macroscopic in quantity, as in the case of granular materials [2], gravity cannot be ignored. The purpose of this paper is to demonstrate the existence of a gravity-induced liquid-solid phase transition of hard spheres. This transition is an intrinsic transition associated with any system where the excluded volume interaction is dominant. Such a system cannot be compressed indefinitely, and must exhibit a coherent low-energy state. In the hard-sphere system, gravity introduces a potential energy, and each available site is associated with an energy state. Then, the formation of a solid at the bottom below the transition point is nothing but a massive occupation of the low-energy state at the low temperature, which is the Fermi gas in metals, the Bose condensate in the two-dimensional quantum Hall systems [3], the energy storage mechanism into a single state for biological systems [4], a mechanism to produce coherent light in the context of lasers [5], and the liquid-solid transition in a hard-sphere system under gravity, which is the subject of the current work. We will determine via the even-driven molecular-dynamics simulation the transition point and the thickness of the boundary layers as a function of external parameters, and make a careful comparison with the theoretical predictions [6]. Next, a nontrivial by-product of our investigation is to view the configurational statistics of the vibrating bed [7,8] from the viewpoint of the liquid-solid transition of hard spheres. This will certainly help one to compare the configurational statistics and other thermodynamic properties of vibrating beds with those equilibrium properties of hard-sphere systems.

Transition temperature and the thickness of boundary layers. Consider a collection of elastic hard spheres of mass m and diameter D, confined in a two-dimensional (x,z) container with an open boundary at the top. Gravity acts along the negative-z direction. The system is in contact with the thermal reservoir at a temperature T in such a way that the average kinetic energy of each hard sphere, $T = m \langle v_x^2 + v_z^2 \rangle / 2$ with $\langle \cdots \rangle$ being the configurational average. We now start from $T=0$, at which point all the particles are essentially in a solid regime, and the density profile is simply

a rectangle. If we gradually increase the temperature, fluidization starts from the surface, and the boundary layers appear. One may estimate the thickness of the boundary layer h by a simple energy balance between the kinetic and potential energy: $mgDh \approx \frac{1}{2} m \langle v^2 \rangle \approx T$. From this, one may obtain the size of the solidlike regime, or equivalently, its dimensionless height, say $\zeta_F(T)$,

$$\zeta_F(T) = \mu - h = \mu - \frac{T}{mgD}, \tag{1}$$

where μ is the number of layers of the original rectangle and h is the layer thickness in units of D. Equation (1) predicts the existence of a critical temperature T_c at which point a phase transition from a one-phase (liquid) to a two-phase regime (liquid-solid) occurs. By setting, $\zeta_F(T_c) = 0$, we find the mean-field result: $T_c^{M.F} = \mu mgD$. Since the boundary layer exists only when both phases coexist, T_c must be the temperature at which point the system becomes fully fluidized. One may equally define the critical temperature as a point at which the density at the bottom layer ϕ_o becomes the closed-packed density ϕ_c, i.e., $\phi_o(T_c) = \phi_c$. We now rewrite Eq. (1) in terms of the critical temperature, and recast the size of the solid region, in term of T/T_c, as

$$\zeta_F(T)/\mu = \left(1 - \frac{T}{T_c}\right). \tag{2}$$

A more precise estimate of the transition temperature was given in Ref. [6] within the framework of the Enskog theory [9]. In particular, the following expression for the density profile $\phi(\zeta)$ was obtained as a function of the dimensionless variable $\zeta = z/D$,

$$-\beta(\zeta - \bar{\mu}) = \ln \phi + c_1 \phi + c_2 \ln(1 - \alpha \phi) + c_3/(1 - \alpha \phi)$$
$$+ c_4/(1 - \alpha \phi)^2 \tag{3a}$$

with the constant $\beta \bar{\mu}$ given by

$$\beta \bar{\mu} = \ln \phi_o + c_1 \phi_o + c_2 \ln(1 - \alpha \phi_o)$$
$$+ c_3/(1 - \alpha_o \phi_o) + c_4/(1 - \alpha \phi_o)^2, \tag{3b}$$

where $\beta = mgD/T$, and $c_1 = 2\alpha_2/\alpha^2 (\pi/2) \approx 0.0855$, $c_2 = -(\pi/2)(\alpha_1 - 2\alpha_2/\alpha)/\alpha^2 \approx -0.710$ $c_3 = -c_2$, $c_4 = (\pi/2)$

$\times(1 - \alpha_1/\alpha + \alpha_2/\alpha^2)/\alpha \approx 1.278$, with $\alpha = 0.489\,351\,\pi/2 \approx 0.768\,67$. Note that the relation between the volume fraction ν and ϕ is given by $\nu = \pi(D/2)^2 N/V = \pi\phi/4$. If one integrates the density profile, and imposes the sum rule, $\int_0^\infty \phi(\zeta)d\zeta = \phi_o\mu$, then one finds that this sum rule breaks down at the temperature T_c,

$$T_c = mgD\mu\phi_o/\mu_o. \qquad (4)$$

The departure from the mean-field theory is the appearance of a factor ϕ_o/μ_o in Eq. (4), where $\phi_o = (4/\pi)(\pi/2\sqrt{3}) = 1.154\,700\,538\ldots$ and $\mu_o = 111.522\,74\ldots$. Equation (2) remains unchanged. We now present MD data to test Eqs. (2) and (4).

Molecular-dynamics simulations of gravity-induced liquid-solid transition. We have used the event-driven (ED) molecular-dynamics code, and refer the readers to Ref. [10] for details of the algorithm regarding the collision dynamics that take into account the rotation of hard spheres, and a way to handle the inelastic collapse. The thermal reservoir of our system was modeled using white-noise driving [11], which kicks each particle so that the average kinetic temperature of each particle is the same as that of the reservoir, and hence, the kinetic temperature of the system. Note that we are *not* driving the system by connecting the bottom wall to the temperature reservoir, which was often used as a model for a vibrating bed.

We present in Fig. 1 a typical configuration below the transition temperature ($T < T_c$), at which about 17 layers of particles condense and form a crystal near the bottom [Fig. 1(a)]. More precisely, the particles first form a loose hexagonal crystal and progressively evolve into a compact hexagonal lattice structure. The solid line in the density profile [Fig. 1(b)] is the Enskog profile given by Eq. (3a), which was *shifted* to fit the data beyond the crystal regime. We point out here that (i) this shift is *not* an arbitrary parameter, but should be uniquely chosen to fit the data, and (ii) this shift in fact determines the *measured* size of the solid by simulations. The density in the solid regime is then fit by a straight line as shown in the figure. The oscillations in the solid regime are real, but it is simply the finite-size effect, i.e., the hexagonal packing in a finite lattice has two more particles in alternative layers. This oscillation must disappear in the thermodynamic limit.

The critical temperature T_c is determined as the temperature at which point a *compact* hexagonal crystal is formed from the bottom layer, beyond which point the density at the bottom layer remains constant at $\phi_o = 1.15$, and this hexagonal structure is permanently retained. We point out that a loosely hexagonal crystal forms at a temperature T_c', which is somewhat larger than T_c. Between T_c and T_c', particles squeeze themselves, expelling holes, and progressively forming a compact hexagonal crystal. Note that a few vacancies created during this crystallization do not anneal but stay in the system [Fig. 1(a)]. Now, in order to carry out the quantitative analysis of the formation of a crystal beyond the transition temperature, we have *measured* the size of the solid as mentioned above, namely by shifting the Enskog profile [i.e., Fig. 1(b)], and plotted it at different temperature $T < T_c$ as a function of the scaled variable T/T_c for 1000 particles of $m = 2.090 \times 10^{-6}$, $D = 0.001$ m, and $\mu = 20$. The solid line
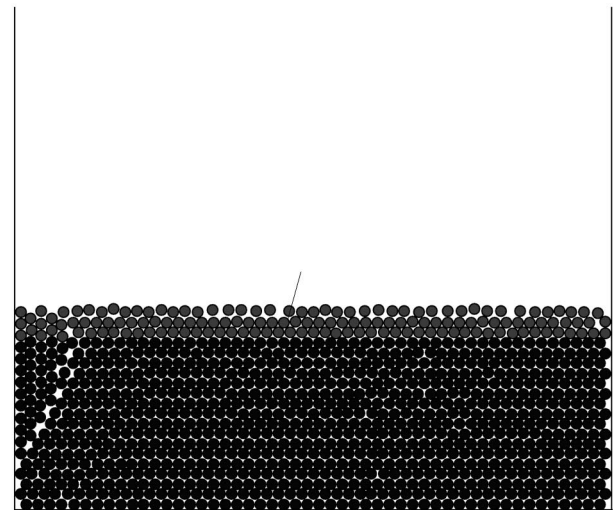
(a)
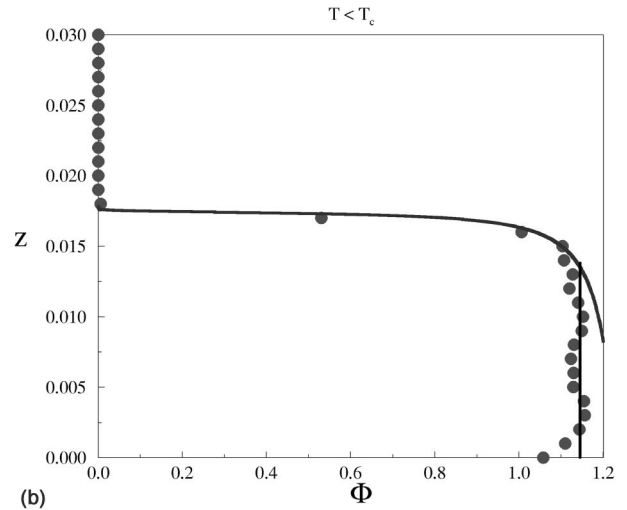
(b)

FIG. 1. (a) Snap shot at $T < T_c$, where about 17 layers (black grains) form a crystal and two layers at the top are fluidized. (b) The fitting of the density profile is the combination of the Enskog profile [Eq. (3)] and the rectangle (straight line). The vertical axis is the position z from the bottom, and the horizontal axis is the Φ.

in Fig. 2(a) is the prediction Eq. (2). The excellent agreement between the theory and simulations is a confirmation of (i) the existence of the gravity-induced liquid-solid transition of hard spheres, and (ii) the validity of the suggested mechanism of this transition via the disappearance of particles from the liquid and their settlement into the solid regime as predicted by Enskog theory [6]. We point out that the transition here is sharp, but because of the discrete nature of the hard spheres, it is somewhat difficult to measure the layer thickness of the solidified regime near T_c, when the layer thickness is less than *one* layer. This is the reason why the measurement was a little far away the transition temperature.

Next, we present our analysis of the vibrating bed from the viewpoint of the liquid-solid transition discussed above. See Fig. 3. It has been fairly well established that the configurational statistics of the vibrating beds seem identical to the equilibrium statistics of a molecular gas at an equal packing fraction [8], yet the relation between the vibrational strength, Γ, and the corresponding equilibrium kinetic tem-
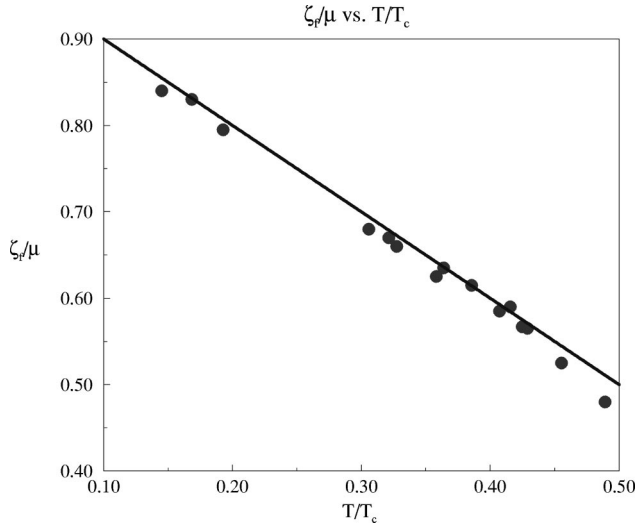
FIG. 2. The fraction of the hard spheres in the condensed regime as a function of T/T_c with $N=1000$, $\mu=20$, $g=981$ cm/sec^2, and $m=1.047\times10^{-6}$ (square). The data points are obtained by uniquely determining the shifting position of the Enskog profile, and the solid line is the prediction Eq. (2).

perature has remained largely undetermined. There has been a previous attempt to relate Γ to the Fermi temperature [12], which is not the same as the kinetic temperature, but essentially the compactivity [13]. In the present work, we will establish a specific relation between the vibration strength and the kinetic temperature, and test its validity via simulations.

At a low vibration strength, experimental data [7] seems to clearly indicate two distinctive regimes: the solid regime near the bottom where there are very little particle movements, and the liquid regime near the surface where particles are dynamically active exchanging their positions via collisions. Hence, the system presented in Ref. [7] is *below* the liquid-solid transition temperature. We will determine both the transition temperature T_c and the effective temperature of
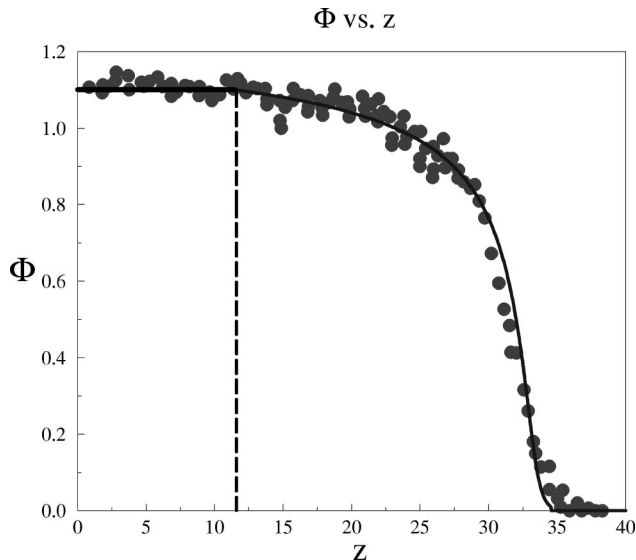

FIG. 3. Experimental density profile of the granular materials in a vibrating bed (Ref. [7]). The fit was by the Enskog profile near the surface and the rectangle below ζ_F.

the system, and then measure the size of the solid region and compare it with the prediction made by Eq. (2). The control parameters are given in Ref. [7], namely the particle diameter $D=2.99$ mm, and the dimensionless initial layer thickness $\mu=10.2$, from which we determine the normalized critical temperature of the vibrating bed $T_c/mg = \mu D \phi_o/\mu_o = 0.607$ mm. The effective temperature of the system is then determined by fitting the tail region and shifting the Enskog profile by ζ_o. We find $T/mg=0.36$ mm, and $\zeta_o=4.41$ layers from which we measure the size of the solid as $z_o=\phi_o\zeta_o/D=12$ mm≈4.0 layers, while the predicted dimensionless height of the solid region, ζ_F, is $\zeta_F = \mu(1-T/T_c)\approx4.15$ layers. The previous fitting of the density profile by the Fermi profile was also satisfactory, but was found to be most difficult near the rounded region, which the Enskog profile fits quite well (Fig. 3). One advantage of the present method of analyzing the configurational statistics of the vibrating bed might be that the global *kinetic* temperature can now be associated with the vibrating bed, and hence comparison can be made between the experimentally determined configurational statistics of the vibrating bed and those of the hard spheres in thermal contact with the heat reservoir. The specific relation between the two can be obtained by comparing the thermal expansion of the hard spheres and the kinetic expansion of the vibrating bed. The thermal expansion is simply the increase in the center of mass $\Delta z(T)$, which can be computed by the Enskog profile near the tail, and the solid rectangle. We find

$$\Delta z(T) = \frac{D\mu}{2}\left(\frac{2|\Lambda_1|\phi_o}{\mu_o^2}-1\right)\left(\frac{T}{T_c}\right)^2, \quad (5)$$

where the constant

$$|\Lambda_1| = \phi_o\int_o^1[f(\rho\phi_o)-f(\phi_o)][\rho\phi_o f'(\rho\phi_o)d\rho]$$

$$= 5503.531\,806$$

with $f(x)$ given in Eq. (3a). Note that the correction is second order in T. Let $H_o(\Gamma)$ be the single ball jump height on the surface [16]. Then, by equating $\Delta z(T)$ and $H_o(\Gamma)g/\omega^2$, we find the desired relation

$$\frac{T}{T_c} = \sqrt{\frac{2H_o(\Gamma)g}{D\omega^2\mu^2}\left(\frac{\mu_o^2}{2|\Lambda_1|\phi_o-\mu_o^2}\right)}, \quad (6)$$

where ω is the vibration frequency. Putting all the values, Eq. (6) predicts $T/T_c=0.663$, which is close to the measured value of 0.593 above.

In conclusion, two points are in order. First, we have demonstrated in this paper that the point at which the Enskog description of hard spheres fails indeed signals the liquid-solid transition, and such a failure arises via the breakdown in the particle conservation. The missing particles form a condensate at the bottom, which essentially determine the fraction of particles in the solid regime, and in turn the thickness of boundary layers. Since only a fraction of grains are mobilized under shear [14], and avalanches and many interesting dynamics occur in these thin boundary layers [2], such a determination should be of technological importance. Second, since Enskog theory is a truncation of Bogoliubov-Born-Green-Kirkwood, and Yvon (BBGKY) [15] hierarchy

at the third order, the existence of gravity-induced liquid-solid transitions of hard spheres must have some interesting consequences to higher-order kinetic theory, in particular with regard to the dynamic behaviors. Unlike particles in the liquid regime, those particles in the solid regime are largely confined in cages and fluctuate around fixed positions. Their motions resemble the lattice vibrations rather than binary collisions, and it may be a little peculiar, albeit not unphysical, to attempt to describe the lattice vibrations by the kinetic theory. If so, such a description must include much more than binary collisions. Hence, it is not unphysical to see that these particles disappear from the kinetic equation *at the level* of the Enskog approximation. However, as discussed in the beginning and demonstrated in this paper, this gravity-induced liquid-solid transition is not a peculiar phenomenon associated with the Enskog equation, but rather an intrinsic transition inherent in a system where an excluded volume interaction is dominant. The formation of a solid at the bottom is the appearance of a massive occupied low-energy state due to the Pauli exclusion principle. Therefore, the breakdown in the sum rule, the necessary shift of the density profile due to the formation, and its upward spread of the closed-packed regime *should* persist because the Pauli exclusion principle is in action in real space, even if one may use different approximations [16–18] or may try a different form for the pressure, such as the form suggested by Percus-Yevick [19], and/or in higher-order truncation. It only disappears in the limit when the closed volume packing density ν becomes one, which is possible only in the case of an ideal Appolonian packing [20]. Finally, we point out that the presence of dissipation does not alter the condensation picture at all [21], *if* the velocity distribution remains Gaussian. Recent experiments [22] have demonstrated the non-Gaussian nature of the velocity distribution, but if the dissipation is small, which is the case for the simulations carried out in this work, the deviation from Gaussian should be small. We also point out that for hard-sphere systems without gravity, there exists no typical energy scale, and thus any transition must be entropy driven, i.e., there exists no critical temperature, and the phase transition occurs at a critical volume fraction [23]. However, for the system considered in this paper, there exists a typical energy associated with the potential energy due to gravity, and thus this transition is not entropy driven, but energy driven, and there exists a critical temperature T_c.

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