Condensation of Hard Spheres Under Gravity

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(May 19, 2018)

Abstract

Starting from Enskog equation of hard spheres of mass m and diameter D under the gravity g, we first derive the exact equation of motion for the equilibrium density profile at a temperature T and examine its solutions via the gradient expansion. The solutions exist only when \( \beta \mu \leq \mu_0 \approx 21.756 \) in 2 dimensions and \( \mu_0 \approx 15.299 \) in 3 dimensions, where \( \mu \) is the dimensionless initial layer thickness and \( \beta = mgD/T \). When this inequality breaks down, a fraction of particles condense from the bottom up to the Fermi surface.

PACS numbers: 05.20-y, 81.35+k, 05.20.Dd, 05.70.Fh

Granular materials are basically a collection of hard spheres that interact with each other via hard sphere potential [1]. For this reason, many of the properties of excited granular materials may be understood from the atomistic view of molecular gases, in particular from the viewpoint of kinetic theory [2]. There are, however, several distinctions between molecular gases and granular materials: First, granular materials are macroscopic particles with finite diameter, and thus they cannot be compressed indefinitely. Second, the gravity plays an important role in the collective response of granular materials to external stimuli, largely because of the ordering of grains induced by the gravity. For example, one of the

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notable characteristics of the excited granular materials in a confined system under gravity is the appearance of a thin boundary layer near the surface that separates a fluidized region from a rigid solid region. This has been known for long time as is evidently seen in shearing experiments [3], avalanches [4], and grains subjected to weak excitations [5,6]. In this limit, those grains in a solid region are effectively frozen, and thus do not participate in dynamical processes. Now, the kinetic theory relies on two particle collision dynamics, and has been applied to systems where all the granular particles are in motion colliding with each other. But if a portion of grains are frozen and remain largely motionless, the kinetic theory or in general the continuum theory may pose some problems. Consider for example a system of strongly excited granular particles under gravity, where all the grains undergo collisions and thus the kinetic theory is valid. If we decrease the strength of excitation, then the particles at the bottom will freeze themselves, and the boundary layer will develop at the top. The question we address in this Letter is: How does the kinetic theory describe such process?

In a recent paper [6], it has been demonstrated that the granular statistics in the presence of gravity does not follow the usual Boltzmann statistics as in molecular gases, where all the particles are dynamically active, but a new Fermi statistics, where most of the particles are effectively frozen and only a portion of particles near the surface participate in the dynamical process. This is due to the excluded volume effect and the ordering of potential energy by gravity, and the mechanism associated with this Fermi statistics is similar to that of the Fermi gas in a metal. The existence of a thin boundary layer in granular materials should be viewed from such perspective.

Our specific objective of this Letter is to use the kinetic theory, in particular the Enskog equation of hard spheres of mass $m$ and diameter $D$, to explore whether or not the kinetic theory can describe the cross over from Boltzmann to Fermi statistics and if so, under what conditions it occurs. Our particularly interesting discovery is that the prediction of the Enskog equation is only valid when $\beta \mu \leq \mu_0$, where $\mu$ is the dimensionless initial layer thickness of the granules (or the Fermi energy), $\beta = mgD/T$ with $T$ the temperature, and
the critical value, $\mu_0$, is determined to be $\mu_0 = 21.756$ in 2d and $\mu_0 = 15.299$ in 3d. When this inequality is violated, Enskog equation does not conserve the particles, and the missing particles condense from the bottom up to the Fermi surface. This way, the hard sphere Enskog gas appears to contain the essence of Fermi statistics and Bose condensation.

The starting point of our investigation is the Enskog’s kinetic equation for elastic hard spheres \cite{7} of mass m and diameter D in the presence of gravity:

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla f - mg \frac{\partial f}{\partial v_z} = J_E$$  \hspace{1cm} (1)

where the Enskog’s collision operator is given by:

$$J_E = D^2 \int d^3 v_1 \int d^2 e e \cdot g[f(\mathbf{r}, \mathbf{v})f(\mathbf{r}+De, \mathbf{v}_1)'\chi(\mathbf{r}+\frac{1}{2}De) - f(\mathbf{r}, \mathbf{v})f(\mathbf{r}-De, \mathbf{v}_1)\chi(\mathbf{r}-\frac{1}{2}De)$$  \hspace{1cm} (2)

Here, \((\mathbf{v}, \mathbf{v}_1)\) and \((\mathbf{v}', \mathbf{v}_1')\) are the velocities of two colliding particles before and after the collision, and \(\mathbf{r}\) and \(\mathbf{r}'\) are the positions of the two particles when they are in contact, \(\mathbf{e}\) is the unit vector in the direction of \(\mathbf{r}-\mathbf{r}'\), \(\mathbf{V}\) is the relative particle flux given by \(\mathbf{V} = \mathbf{v} - \mathbf{v}_1\) and \(\mathbf{V}' = \mathbf{v}' - \mathbf{v}_1'\) \cite{2}. The + sign means that the integration should be carried out with the restriction that \(0 \leq \mathbf{e} \cdot \mathbf{V}\). From the geometry it is easy to show \(\mathbf{V}' = \mathbf{V} - 2\mathbf{e} \mathbf{e} \cdot \mathbf{V}\) and \(|\mathbf{V}'| = |\mathbf{V}|\). The correlation function, \(\chi\), is defined as \(F_2(\mathbf{r}, \mathbf{v}; \mathbf{r}_1, \mathbf{v}_1) = F_1(\mathbf{r}, \mathbf{v})F_1(\mathbf{r}, \mathbf{v}_1)\chi\), where \(F_2\) and \(F_1\) are the two and one particle distribution function respectively. Molecular chaos assumption in the usual Boltzmann collision operator sets \(\chi = 1\). In the case of dense gases, Enskog \cite{2,7} assumed that \(\chi\) might be given by the equilibrium two point correlation function estimated at the contact point. At equilibrium, we expect that the factorization of the space and velocity in the distribution function is valid. Thus, we set: \(f(\mathbf{r}, \mathbf{v}; t = \infty) = G(\mathbf{r})\phi(\mathbf{v})\). This is equivalent to the separation of the configurational statistics from the kinetics. In equilibrium statistics of elastic granular materials, \(\phi(\mathbf{v})\) is expected to be Gaussian, and the energy conservation requires that \(\phi(\mathbf{v}_1')\phi(\mathbf{v}') = \phi(\mathbf{v}_1)\phi(\mathbf{v})\). We note that \(\phi(\mathbf{v})\) is normalized to one: \(\int d^3 \mathbf{v} \phi(\mathbf{v}) = 1\). In the steady state, the left hand
said of eq.(1) then becomes:

\[ v_z \phi(v) \frac{\partial G}{\partial z} + \frac{mg}{T} G(z) \] (3)

In order to compute the right hand side, we first notice that the collision operator \( J_E \) (eq.(2)) is given by:

\[ J_E = D \phi(v) G(r) \left[ \int d^2 \phi(v_1) \right] \int d\theta e \left[ \chi(r - \frac{1}{2} De) G(r - De) - \chi(r + \frac{1}{2} De) G(r + De) \right] e \cdot V \] (4)

We now first compute the right hand side of eq.(1) under the factorization assumption. In this case, a care must be taken because the integral should be performed with the constraint \( e \cdot V \geq 0 \). However, if we change \( e \) to \(-e\) of the second term in the Enskog operator \( J_E \) (eq.(4)), we find it becomes:

\[ - \int_{e \cdot V \geq 0} d\theta \chi(r + \frac{1}{2} De) G(r + De) e \cdot V = \int_{e \cdot V \leq 0} d\theta e \cdot V \chi(r - \frac{1}{2} De) G(r - De) \] (5)

Hence, we can now remove the restriction \( e \cdot V \geq 0 \) in eq.(4) and integrate over the whole space. After some algebra, we obtain:

\[ J_E = D \phi(v) G(r) \left[ \int d^2 \phi(v_1) \right] v \cdot I \] (6)

where

\[ I = \int_{all\, space} d\theta e \chi(r - \frac{1}{2} De) G(r - De) \]

\[ = \frac{1}{2} \int_{all\, space} d\theta e \left[ \chi(r - \frac{1}{2} De) G(r - De) - \chi(r + \frac{1}{2} De) G(r + De) \right] \] (7)

In obtaining (7), we utilized the fact that \( \int d^2 \phi(v_1) v_1 = 0 \) by symmetry. Our next step is to compute \( I \). To this end, we first rewrite \( I \):

\[ I = \int d\theta e \chi(r - \frac{1}{2} De) G(r - De) - \int d\theta e \chi(r + \frac{1}{2} De) G(r + De) \]

\[ = \frac{1}{2} \int d\theta e \left[ \chi(r - \frac{1}{2} De) G(r - De) - \chi(r + \frac{1}{2} De) G(r + De) \right] \] (8)
Notice that $I_x$ (and $I_y$) will vanish by symmetry and only the vertical component, $I_z$, survives. Using $e = (\sin \theta, \cos \theta)$ in 2d, we find:

$$I_z = \frac{1}{2} \int_0^{2\pi} d\theta \cos \theta [\chi(z - \frac{1}{2} D \cos \theta)G(z - D \cos \theta) - \chi(z + \frac{1}{2} D \cos \theta)G(z + D \cos \theta)] \quad (9)$$

At equilibrium, $\phi(v; T) = \phi(\frac{mv^2}{2T})$. We now put this functional form along with $G(z; T) = G(\frac{mgz}{T})$ to the right hand side of (1) and cancel $v_z \phi(v)$ term. Next, in a free volume theory, particles are confined in a cage. Hence, if we use a simple cubic lattice as a basic lattice, the closed packed volume fraction $\rho_c = N/V = N/D^2 N = 1/D^2$. If we define the dimensionless density $\phi(z) = G(z)/\rho_c = D^2 G(z)$ or $\phi(\zeta, \beta) = D^2 G(z)$ with $\zeta = z/D$, we then obtain the exact dimensionless equation of motion for $\phi(\zeta, \beta)$:

$$\frac{d\phi(\zeta)}{d\zeta} + \beta \phi(\zeta) = \phi(\zeta) I_\zeta(\zeta) \quad (10)$$

where

$$I_\zeta(\zeta) = \frac{1}{2} \int_0^{2\pi} d\theta \cos \theta [\chi(\zeta - \frac{1}{2} \cos \theta)\phi(\zeta - \cos \theta) - \chi(\zeta + \frac{1}{2} \cos \theta)\phi(\zeta + \cos \theta)] \quad (11)$$

For 3d, the corresponding equation for the density $\phi(\zeta) = D^3 G(z)$ is given by:

$$\frac{d\phi}{d\zeta} + \beta \phi = \phi I_\zeta(\zeta) \quad (12)$$

with

$$I_\zeta(\zeta) = \pi \int_0^{\pi} d\theta \sin \theta \cos \theta [\chi(\zeta - \cos \theta/2)\phi(\zeta - \cos \theta) - \chi(\zeta + \cos \theta/2)\phi(\zeta + \cos \theta)] \quad (13)$$

Several forms for the equilibrium correlation function $\chi$ have been proposed, but we use the following widely used forms: For 2d, we use the form proposed by Ree and Hoover [8]: $\chi(\phi) = (1 - \alpha_1 \phi + \alpha_2 \phi^2)/((1 - \alpha \phi)^2$, while for 3d, we use the form suggested by Carnahan and Starling [9]: $\chi(\phi) = (1 - \pi \phi/12)/(1 - \pi \phi/6)^3$

Since the total number of particles, $N$, remain fixed, the following normalization condition should be satisfied for both 2d and 3d.
\[ \int_{o}^{\infty} d\zeta \phi(\zeta; \beta) = \mu \]  

(14)

where \( \mu \equiv N/\Omega_x \) (or \( \mu \equiv N/\Omega_x\Omega_y \) in 3d) is the Fermi energy [6] and \( \Omega_x, \Omega_y \) are the degeneracies along the x and y axis. We now perform the gradient expansion of (11) and (13) and retain only the terms to first order in \( d\chi/d\zeta \). We find:

\[ \frac{d\phi}{d\zeta} + \beta \phi = -\frac{\pi}{2} \phi \left[ \frac{d\chi}{d\zeta} \phi + 2\chi \frac{d\phi}{d\zeta} \right] \]  

(2d)

\[ \frac{d\phi}{d\zeta} + \beta \phi = -\frac{2\pi}{3} \phi \left[ 2\frac{d\phi}{d\zeta} \chi + \phi \frac{d\chi}{d\zeta} \right] \]  

(3d)

(15a)  

(15b)

The solutions are readily obtained. For 2d, we find:

\[ -\beta(\zeta - \bar{\mu}) = \ln \phi + c_1 \phi + c_2 \log(1 - \alpha \phi) + c_3/(1 - \alpha \phi) + c_4/(1 - \alpha \phi)^2 \]  

(16a)

\[ \beta \bar{\mu} = \ln \phi_o + c_1 \phi_o + c_2 \ln(1 - \alpha \phi_o) + c_3/(1 - \alpha_o) + c_4/(1 - \alpha \phi_o)^2 \]  

(16b)

\begin{align*}
\beta \mu &= \phi_o + c_1 \phi_o^2/2 + c_2(\phi_o + \ln(1 - \alpha \phi_o)/\alpha) + c_3 \ln(1 - \alpha \phi_o)/\alpha \\
-(c_4/\alpha) [1/(1 - \alpha \phi_o) - 1] + c_3 \phi_o/(1 - \alpha \phi_o) + c_4 \phi_o/(1 - \alpha \phi_o)^2
\end{align*}

(16c)

where \( \phi_o \) is the density at \( \zeta = 0 \), and \( c_1 = 2\alpha_2/\alpha^2 \frac{\pi}{2} \approx 0.0855 \), \( c_2 = -\frac{\pi}{2} (\alpha_1 - 2\alpha_2/\alpha) / \alpha^2 \approx 0.710 \), \( c_3 = -c_2, c_4 = \frac{\pi}{2} (1 - \alpha_1/\alpha + \alpha_2/\alpha^2)/\alpha \approx 1.278 \). For 3d, we find:

\[ -\beta(\zeta - \bar{\mu}) = \ln \phi - 1/(1 - \alpha \phi)^2 + 2/(1 - \alpha \phi)^3 \]  

(17a)

\[ \beta \bar{\mu} = \ln(\phi_o) - 1/(1 - \alpha \phi_o)^2 + 2/(1 - \alpha \phi_o)^3 \]  

(17b)

\[ \beta \mu = \phi_o - \frac{2\phi_o}{1 - \alpha \phi_o} + \frac{2\phi_o}{(1 - \alpha \phi_o)^3} \]  

(17c)
where \( \alpha = \pi/6 \). For given values of \( \beta \) and \( \mu \), \( \phi_o \equiv \phi(\zeta = 0) \) will be determined by eq.(16c) and (17c). However, since the right hand sides are monotonically increasing functions for \( \phi_o \), \( \beta\mu \) must have the upper bound \( \mu_o \); namely, \( \mu_o = 21.756 \) in 2d and \( \mu_o = 15.299 \) in 3d, which are the values obtained by setting \( \phi_o = 1 \) in the right hand side of (16c) and (17c).

Considering the fact that both the temperature \( T \) and the Fermi energy \( \mu \) are arbitrary control parameters, the existence of such bounds is a puzzle: if \( \beta\mu \) is less than \( \mu_o \), then the density profiles given by Eq.(16a) and (17a) are well determined, but if \( \beta\mu \) is greater than \( \mu_o \), then \( \phi_o \) must be one, and the particle conservation breaks down, namely

\[
\int_0^1 d\phi \zeta(\phi) = \int_0^{\infty} d\zeta \phi(\zeta) \equiv \mu_o/\beta < \mu
\]  

(18)

The central question is: where does the rest of the particles go? In order to gain some insight into this question, consider first the case of point particles under gravity, in which case the density profile is given by: \( \rho(\zeta) = \rho(0) \exp(-mg\zeta/T) \). If we put more particles into the system, we simply need to increase \( \rho(0) \) because the point particles can be compressed indefinitely, and the profile simply shifts to the right. We now replace these point particles with hard spheres, which cannot be compressed indefinitely. Suppose we start from a high temperature where all the particles are active. We then slowly decrease the temperature to suppress the thermal motion. At a certain temperature, the freezing of the particles will occur from the bottom [11], which will then spread out as the temperature is lowered down further, until at \( T=0 \) all the particles are frozen. Note that the frozen particles in the closed packed region behave like a solid. Such observation helps us to resolve the puzzle associated with the disappearance of particles, which must then condense from the bottom up to the lower part of the fluidized layer. We term this surface, which separates the frozen or a closed packed region with \( \phi = 1 \) from the fluidized region with \( \phi < 1 \), the Fermi surface. The location of the Fermi surface, \( \zeta_F \), is determined by the amount of the missing particles, namely, \( \zeta_F = \mu - \mu_o/\beta \). For nonzero \( \zeta_F \), we must put the missing particles below the Fermi surface and shift the bottom layer from \( \zeta = 0 \) to \( \zeta_F \). Such modified profile for \( \beta = 1 \) and
\( \mu = 100 \) in 2d is shown in Fig.1. In comparison, in Fig.1 is also shown the density profile for \( \beta = 10 \) and \( \mu = 100 \) for which \( \beta \mu \leq \mu_o \). We conclude that while the density profile obtained this way is not exactly the same as the Fermi profile, the essence of the Fermi statistics, namely the effect of excluded volume interactions, sets in when \( \beta \mu \geq \mu_o \). The condensation of particles from the bottom in one dimensional vibrating bed [12] and the clustering of particles near the bottom wall in two dimensional experiments [13] appear to be a strong confirmation of this scenario, which seems to be reminiscent of the Bose condensation of particles into the ground state.

We conclude with a few remarks. First, it remains to be seen whether the feature observed in this paper for hard spheres persists in the presence of dissipation, namely when particles collide inelastically. In this case, there are some evidences that the velocity distribution function is not Gaussian for strong dissipation, and the factorization assumption may not be valid. The future studies must focus on the accurate determination of this velocity profile, based on which an extension of the present analysis must be carried out. Second, we may define the freezing temperature \( T_c \) as the point where the particle conservation breaks down, namely

\[
T_c = mgD\mu/\mu_o
\]

which may be tested experimentally presumably by using the relation between \( T \) and the vibration strength \( \Gamma \) [6], or by Molecular Dynamics simulations. Finally, we point out that eqs. (15a) and (15b) can also be obtained from the force balance eq. for the pressure \( P; \rho g - dP/dz = P = T\rho/1 + A_d\rho D^d\chi(D)/2d \), where \( A_d = 4\pi \) for 3d and \( A_d = 2\pi \) for 2d.

The author is particularly grateful to A. J. McLennan for numerous discussions on kinetic theory and for several incisive suggestions over the course of this work. The author also wishes to thank H. Hayakawa for helpful discussions, S. Luding for ref. [12] and Joe Both and Paul Quinn for checking some of the algebras.
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[11] The freezing here does not mean the complete suppression of thermal motion. It means the suppression of the translational motion for those particles in a closed packed regime.

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Figure Caption

Fig.1. The crossover from Boltzmann to Fermi statistics as the temperature is lowered. For a given Fermi energy, $\mu = 100$, the density profiles are shown as a function of dimensionless height $\zeta$ for $\beta = 1/10$ and $\beta = 1$ (dotted line) for the two dimensional Enskog gas. For $\beta = 1$, grains freeze from the bottom up to the Fermi surface, and only those grains near the Fermi surface participate in the dynamical process.
