Size segregation in granular media induced by phase transition

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In order to study analytically the nature of the size segregation in granular mixtures, we introduce a mean field theory in the framework of a statistical mechanics approach, based on Edwards’ original ideas. For simplicity we apply the theory to a lattice model for hard sphere binary mixture under gravity, and we find a new purely thermodynamic mechanism which gives rise to the size segregation phenomenon. By varying the number of small grains and the mass ratio, we find a crossover from Brasil nut to reverse Brasil nut effect, which becomes a true phase transition when the number of small grains is larger then a critical value. We suggest that this transition is induced by the effective attraction between large grains due to the presence of small ones (depletion force). Finally the theoretical results are confirmed by numerical simulations of the 3d system under taps.

In the last decades a great attention has been devoted to the study of the problem of vertically shaken granular mixtures under gravity. It was observed that such systems depending on the control parameters can mix or segregate their components spontaneously according to a mechanism which is still largely unclear, although of deep practical and conceptual relevance \cite{3, 2}. Rosato et al. \cite{2} showed that large grains surrounded by a sea of smaller ones rise to the top when subjected to vertical shaking. This is the well known “Brazil Nut Effect” (BNE), while the opposite one (i.e. large grains on the bottom and small ones on the top) is known as “Reverse Brazil Nut Effect” (RBNE) \cite{4, 5}. The BNE was originally explained \cite{3} in terms of a geometric effect, based on “percolation” arguments. Along with geometry, dynamical effects, such as convection \cite{4} or inertia \cite{5}, were shown to play a crucial role. The hydrodynamic equations for binary mixtures \cite{6} were also applied, and in this framework the regimes of BNE and RBNE \cite{7} were found to depend on the presence of inelastic dissipation.

Recent results finally outlined that segregation processes may involve global mechanisms, such as condensation \cite{8} or phase separation \cite{9}. This suggested a change of perspective on the issue and the idea to formulate a statistical mechanics description of these phenomena \cite{10, 11, 12}. To this aim, in Ref.s \cite{10, 11} the interplay between size and mass was studied and a phase diagram for BNE/RBNE transition based on the competition between percolation and condensation was proposed.

In the present paper, applying a statistical mechanics approach for non-thermal systems \cite{13, 14}, a new purely thermodynamic mechanism is found responsible for size segregation. We follow a statistical mechanics approach for granular materials under taps, which was recently developed \cite{15} on the basis of Edwards’ original ideas \cite{16, 17}. This approach postulates that time averages coincide with suitable ensemble averages over the mechanically stable states (i.e. those where the system is found at rest). Such hypothesis was shown \cite{15} to hold with good approximation in a lattice model for granular mixtures under taps. In order to study size segregation, in this framework we apply a mean field theory to such model.

We find that, by fixing the number of grains of the two species, it is possible to obtain a smooth crossover from BNE to RBNE by changing the mass ratio of the grains. However if the number of small grains increases above a critical value, a sharp transition occurs resulting in a phase separation between the two species: Vertical size segregation is induced by the presence of gravity which forces the heavier phase to move downward. At the critical point, critical fluctuations are found typical of a second order phase transition. We suggest that this demixing phase separation is due to the presence of the depletion force. This is an effective attraction between large grains, obtained by tracing over all the degrees of freedom of small grains. The strength of the interaction is proportional to the number of small grains. The depletion force, typically present in thermal binary mixtures \cite{10}, in fact may be also present in 3d granular mixtures under gravity \cite{17}. The theoretical results are confirmed by numerical simulations of the 3d system.

The model – The model \cite{16, 17} is a hard sphere binary mixture under gravity made up of two species, 1 (small) and 2 (large), respectively with diameter $a_0 = 1$ and $\sqrt{2}a_0$, and masses $m_1$ and $m_2$. In order to simplify the calculations we divide the space in cubic cells of linear size $a_0$ whose vertices can be or not occupied by grains. Each site of the lattice is labeled by the two indices $i = 1, \ldots, L^2$ and $z = 1, \ldots, L_z$, where $L$ and $L_z$ are respectively the horizontal and vertical dimensions of the lattice. A microstate of the model is completely identified by the occupancy variables $\{n^z_i\}$, associated to each site of the lattice: $n^z_i = 0, 1, 2$ respectively if the site $(i, z)$ is empty, filled by a small grain or by a large one.

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In terms of these variables the model Hamiltonian is
\[
H = H_{HC} + m_1 g H_1 + m_2 g H_2,
\]
where \(H_1 = \sum_{i,z} \delta n_{i,z}^1\), \(H_2 = \sum_{i,z} \delta n_{i,z}^2\) respectively the heights of the two species, and \(H_{HC}\) is the hard core potential, preventing two nearest neighbor sites to be both occupied if at least one contains a large grain.

In Refs. [12, 19], under tapers is described with good approximation by a statistical mechanics approach based on Edwards’ originally ideas. In particular it was found that the weight of a microscopic state, \(\{n_{i,z}\}\), is given by
\[
P(\{n_{i,z}\}) = \Pi(\{n_{i,z}\}) \cdot e^{-\mathcal{H}_{HC}(\{n_{i,z}\}) - \beta_1 m_1 g H_1 - \beta_2 m_2 g H_2},
\]
where \(\Pi(\{n_{i,z}\})\) is a projector over the “mechanically stable” states, namely \(\Pi(\{n_{i,z}\}) = 1\) if \(\{n_{i,z}\}\) is mechanically stable, and \(\Pi(\{n_{i,z}\}) = 0\) otherwise, \(\beta_1\) and \(\beta_2\) are the variables conjugated respectively to the gravitational energies of the two species, and the two “configurational temperatures” \(T_1 = \beta_1^{-1}\) and \(T_2 = \beta_2^{-1}\) are increasing functions of the tap amplitude. The system partition function is given by \(Z = \sum_{\{n_{i,z}\}} P(\{n_{i,z}\})\) where the sum is over all the microstates but, due to the projector, only the mechanically stable ones are taken into account. In the following calculations we adopt a simple definition of “mechanical stability”: a grain is considered stable if it has a grain underneath [12].

**Mean field approximation** – In the present paper the partition function, \(Z\), is evaluated in mean field approximation: we consider a generalization of Bethe-Peierls method for anisotropic systems (due to gravity) already used in previous papers [12, 13, 20]. In particular, we consider a Bethe lattice made up by \(L_z\) horizontal layers (i.e., \(z \in \{1, ..., L_z\}\)) whose edges can be occupied by grains. Each layer is a random graph of given connectivity, \(k-1 = 4\). Each site in layer \(z\) is also connected to its homologous site in \(z-1\) and \(z+1\) (the total connectivity is thus \(k+1 = 6\)). We use the grancanonical ensemble by introducing two chemical potentials, \(\mu_1\) and \(\mu_2\), relative to species 1 and 2.

In the following we give the main ideas of the calculations and refer to a longer paper [21] for the details (see also [13]). The Bethe-Peierls recursion equations, which allow to calculate the partition function, are written in terms of the local “cavity fields” defined by:
\[
e^{n_{i,z}} = Z_{n,0,0}^{i,z} / Z_{0,0}^{i,z}, \quad e^{n_{i,z}} = Z_{n,0}^{i,z} / Z_{0,0}^{i,z}, \quad e^{n_{i,z}} = Z_{n,0}^{i,z} / Z_{0,0}^{i,z},
\]
with \(n = 1, 2\). Here \(Z_{n,0,0}^{i,z}\) and \(Z_{0,0}^{i,z}\) are the partition functions of the “side” branch restricted respectively to configurations where the site \((i, z)\) is empty or filled by a particle of specie \(n\); analogously, \(Z_{n,0}^{i,z}\), \(Z_{0,0}^{i,z}\), and \(Z_{n,0}^{i,z}\) (resp. \(Z_{n,0}^{i,z}\), \(Z_{0,0}^{i,z}\), and \(Z_{n,0}^{i,z}\)) are the partition functions of the “up” (resp. “down”) branch restricted to configurations where the site \((i, z)\) is filled by a grain of species \(n\), empty with the upper (resp. lower) site empty and empty with the upper (resp. lower) site filled by a grain of species \(n\).

The calculations are limited to the “fluid” phase corresponding to a solution of Bethe-Peierls equations where local fields in each layer are site independent [22]. Such a solution, characterized by horizontal translational invariance, is given by the fixed points of the following equations:
\[
e^{n_{i,z}} = \phi^{n_{i,z}} \left[ e^{n_{i,z}} \right]^{-k-2} P^{(n+1)} P^{(n+1)} / Q^{(z)},
\]
where \(n = 1, 2\), and \(\phi^{n_{i,z}} = e^{\beta_n (\mu_n - m_n g z)}\). The functions appearing in Eq. [3] have a simple expression in terms of the local fields [23]. From the local fields we calculate the free energy [24], \(F\), and all the quantities of interest, such as density profiles of small and large grains, \(\sigma_1(z)\) and \(\sigma_2(z)\), the grain number per unit surface, \(N_n = \sum_z \sigma_n(z)\), and their average height, \(h_n = \langle z_n \rangle = \sum_z z \sigma_n(z) / \sum_z \sigma_n(z)\) (with \(n = 1, 2\)).

![FIG. 1: (color online). Main frame ♦ as a function of δ in the mean field approximation for fixed value of \(N_2 = 0.685\), and \(N_1 = 0.5\) (blue curve), \(N_1 = 0.9\) (green curve), \(N_1 = N_1e = 1.37\) (red curve) and \(N_1 = 2.4\) (black curve) (\(N_1\) increases along the arrow). Inset: The susceptibility, \(\chi\), as a function of \(\delta\) for fixed value of \(N_2 = 0.685\), and \(N_1 = 0.5\) (blue curve), \(N_1 = 0.9\) (red curve) and \(N_1 = N_1e = 1.37\) (black curve) (\(N_1\) increases from bottom to top).]

In the following instead of using the chemical potential variables, \(\mu_1\) and \(\mu_2\), we use the conjugate variables, \(N_1\) and \(N_2\), respectively the number of the small and large grains per unit surface. For simplicity we fix the configurational temperatures, \(T_1 = T_2 = 1\), and the number
of large grains, $N_2$, and vary $N_1$. In order to study the BNE/RBNE transition we also vary the masses of the two species, $m_1$ and $m_2$ (keeping constant $m_1 + m_2$), and measure the height difference, $\Delta h = \frac{h_1-h_2}{h_1+h_2}$. This quantity, that is thus a function of $N_1$ and $\delta \equiv \frac{2m_1-m_2}{2m_1+m_2}$, is positive when small grains are in average above large grains (RBNE) and negative otherwise (BNE).

In the Main Frame of Fig. 1, $\frac{\Delta h}{h}$ is plotted for fixed $N_1$ as a function of $\delta$: The different curves correspond to increasing values of $N_1$ (along the arrow). We find that for low enough values of $N_1$, $\frac{\Delta h}{h}$ is a continuous monotonous decreasing function of $\delta$, due to entropic and buoyancy effect. By increasing $N_1$ above some critical value ($N_{1c} \approx 1.37$) $\frac{\Delta h}{h}$ instead exhibits first order transition with a finite jump from a positive value to a negative one at $\delta = \delta_{c_1}(N_1)$, where a BNE phase and a RBNE one coexist with the same free energy. As shown in Fig. 2 the jump becomes smaller and smaller approaching $N_{1c}$ from above, and goes to zero continuously at $N_{1c}$ (the critical point is $\delta_c$, $N_{1c}$), where $\delta_c \equiv \lim_{N_1 \to N_{1c}} \delta_{c_{1c}}(N_1)$.

Along the coexistence curve near the critical point in both phases the order parameter $\Delta h \simeq (N_{1c}^{-1} - N_{1c}^{-1})^{\beta}$, where, solving the mean field equations numerically, $\beta$ is found consistent with the mean field value $\beta = 0.5$.

As in any second order phase transition, the fluctuations of the order parameter diverge at the critical point. In the Inset of Fig. 1 the susceptibility, $\chi(\delta, N_1) \equiv N_{tot}(\langle \Delta h^2 \rangle - \langle \Delta h \rangle^2)$ (where $N_{tot}$ is the total number of grains) is plotted as a function of $\delta$ (the curves, from bottom to top, correspond to increasing values of $N_1$). As $N_1$ approaches $N_{1c}$, the susceptibility diverges at $\delta = \delta_c$. For $N_1 < N_{1c}$, $\chi(\delta, N_1)$ displays a maximum (for the value of $\delta$ where $\Delta h$ is zero), which diverges as a power at $N_{1c}$, $(N_{1c}^{-1} - N_{1c}^{-1})^{-\gamma}$ with an exponent $\gamma$ found, solving numerically the mean field equations, consistent with the mean field value $\gamma = 1.0$ (see Fig. 2).

In the present paper we have chosen as free parameters $N_1$ and $\delta$: $\delta$ plays the role of an external field, and $N_1$ plays the role of an inverse temperature, since it controls the amplitude of the depletion force $\left[16\right]$. To confirm this idea, we have studied the case of mixture of grains with the same radii ($R_2/R_1 = 1$), where the depletion force is completely absent. We find that the critical point disappears, and a smooth crossover from positive to negative values of $\Delta h$, varying the control parameters $N_1$ and $\delta$.

**Monte Carlo simulations** – The theoretical results obtained in mean field approximation are confirmed by Monte Carlo simulations of the model, Eq. [11], under taps [12, 22] on a cubic lattice. In Fig. 3 the height difference, $\frac{\Delta h}{h}$, and the susceptibility, $\chi$, are plotted as function of $\delta$ for fixed $N_2$ and increasing values of $N_1$.

As found in the mean field approximation, at fixed value of $N_1$, $\frac{\Delta h}{h}$ as a function of $\delta$ displays a steeper and steeper slope (and the susceptibility, $\chi$, a larger and larger maximum) as $N_1$ is increased. A power law divergence of the maximum of the susceptibility is found at $N_{1c} \simeq 2.2$, with an exponent $\gamma \approx 1.6$. As usually in mean field approximation, the critical point ($N_{1c}^{-1}$) is over-estimated.

As $N_1$ is further increased, $\frac{\Delta h}{h}$ obtained by varying $\delta$ at a given rate, becomes irreversible, and a strong hysteresis appears, signaling the presence of a first order transition.

**Conclusions** – We focus on the problem of the vertical size segregation in binary granular mixtures. In the
framework of a statistical mechanics approach to granular media, based on Edwards’ original ideas, we apply a mean field theory to a simple hard sphere lattice model under gravity, and explain BNE and RBNE with purely thermodynamic argument.

We find that by varying the control parameters a transition from BNE to RBNE can occur as a smooth crossover or as a sharp transition, depending whether one is above or below the critical point. The presence of such a critical point is manifested by the divergence of the height fluctuations of the two species. Therefore we suggest that it might be important to measure in experiments these fluctuations in the vicinity of the transition from BNE to RBNE. The larger the fluctuations the closer to the critical point are the control parameters.

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[22] Along with the fluid solution, also a crystalline solution characterized by the breakdown of the horizontal translational invariance, can be found. Here we consider the case where the crystallization is avoided.
[23] \( K_{\text{Edw}}(2) = A_n(2)/S(2) \) where \( A_n(2) = 1 + \delta_n e^{1_2} \) and \( S(2) = A_1(2) + e^{2_2} \). Moreover we have that \( P_{\text{Edw}}(2) = 1 + \delta_n e^{1_2} + \delta_n e^{2_2} + e^{1_2} + e^{2_2} \), \( F_{\text{Edw}}(2) = 0 \), \( Q(2) = 1 + e^{1_2} + e^{2_2} + e^{1_2} + e^{2_2} \). \( Q_{\text{Edw}}(2) = \sum_{h=0}^{H} \Delta F_{\text{Edw}}(h) \). The free energy, \( F \), is given by \( F = \sum_{h=0}^{H} \Delta F_{\text{Edw}}(h) - \frac{(k-1)}{2} \sum_{h=0}^{H} \Delta F_{\text{Edw}}(h) \sum_{h=0}^{H-1} \Delta F_{\text{Edw}}(h) \), where, \( e^{-\Delta F_{\text{Edw}}(h)} = (S(2)^{h-1} Q(2)^{h-1} + \sum_{n=1,2} \phi_n(2) \left( A_n(2)^{h-1} p_n(2)^{h-1} \right) \), \( e^{-\Delta F_{\text{Edw}}(h)} = 1 + \sum_{n=1,2} \phi_n(2) + e^{2_2} + e^{1_2} + e^{1_2} + e^{2_2} \). Each tap consists in raising the bath temperature to a finite value and, after a lapse of time quenching the bath temperature back to zero. The measurements are performed when the shake is off and the system is at rest.