Statistical Mechanics of segregation in binary granular mixtures

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We discuss mixing/segregation phenomena in a schematic hard spheres lattice model for binary mixtures of granular media, by analytical evaluation, within Bethe-Peierls approximation, of Edwards’ partition function. The presence of fluid-crystal phase transitions in the system drives segregation as a form of phase separation. Within a pure phase, gravity can also induce a kind of vertical segregation not associated to phase transitions.

Granular mixtures subject to shaking can mix or, under different conditions, spontaneously segregate their components according to criteria which, although of deep practical and conceptual importance, are still largely unclear \cite{1,2}. In this respect, microscopical grains properties are known to play a role since, for example, smaller grains appear to filter beneath larger ones (the so called “percolation” phenomena \cite{3,4}). “Inertia” \cite{5}, “convection” \cite{6} and “dynamical” effects in general are also known to be relevant \cite{7}. Interestingly, recent simulations and experiments have outlined that segregation processes can also involve “global” mechanisms: phenomena such as “condensation” \cite{8} or, more generally, “phase separation” \cite{9} have been found, recalling well known properties in the Statistical Mechanics of thermal fluids, such as colloidal mixtures (see Refs in \cite{9,10}). Actually, even though granular media are not characterized by Boltzmann distributions \cite{11}, fluidized mixtures have been schematically treated as standard fluids under gravity in presence of a finite bath temperature \cite{8,12}.

A different Statistical Mechanics approach was introduced by Edwards \cite{13,14,16} (see \cite{2} for a review). This was explicitly designed to deal with non-thermal systems, such as granular media in their “jammed states” (i.e., not in their fluidized regime): time averages of a granular system (subject to some drive, e.g., tapping) observed at rest, are supposed to coincide with suitable ensemble averages over its “mechanically stable” states, i.e., those where the system is found still. Even though the limit of validity of such an approach must be still assessed, it appears to be well grounded in several cases \cite{2,15,14,16}. In particular, it was shown to hold in a schematic model of granular mixtures: a lattice binary hard spheres system under gravity subject to sequences of taps \cite{14}. In this paper we analytically solve, at the level of Bethe approximation, the partition function à la Edwards of such a model and derive its phase diagram and mixing/segregation properties as a function of grains masses, sizes, number and, see below, “configurational temperatures”.

Our model exhibits phase transitions from fluid to crystalline phases. As much as in thermal media, this induces segregation effects associated to the presence of phase separation phenomena, with the formation of coexisting phases rich in small or large grains. Gravity drives vertical segregation, where large grains can be found on average above (the well known “Brazil nut” effect, BNE \cite{1}) or below small grains (reverse BNE, RBNE \cite{8,17}). When associated to phase separation, we have a form of strong segregation, as opposed to mixing, or similarly weak segregation, observed within a given phase. Coarsening phenomena, as those experimentally observed \cite{18}, are predicted to occur for suitable values of the system parameters.

The model under investigation \cite{14} is a binary hard sphere mixture made of two species, 1 (small) and 2 (large) with grain diameters $a_0 = 1$ and $\sqrt{2}a_0$, under gravity on a cubic lattice, of spacing $a_0$, confined in a rigid box. On each lattice site we define an occupancy $\gamma_{i,1}$, $\gamma_{i,2}$, $\gamma_{i,12}$ and $\gamma_{i,21}$. Their conjugated to the heights of the two species and $\mathcal{H}_{HC}$ is the hard core potential, preventing two nearest neighbor sites to be both occupied if at least one contains a large grain.

As stated, Edwards’ approach appears to hold with good approximation in this model \cite{14} under a tap dynamics (analogous to that used in the compaction of real granular media), which turns out to be characterized by two suitable “thermodynamic parameters”, conjugated to the heights of the two species and called configurational temperatures, $T_1^{conf}$ and $T_2^{conf}$. Their values are increasing functions of the tap amplitude, $\Gamma$, and tend to coincide for $\Gamma \to 0 \\& \\Gamma \to \infty$. In brief, the weight of a given microstate $r$ turns out to be $\Pi_r$: $\text{exp} \{-\mathcal{H}_{HC}(r) - \beta_1 m_1 g H_1(r) - \beta_2 m_2 g H_2(r)\} \cdot \Pi_r$, where $T_1^{conf} = \beta_1^{-1}$ and $T_2^{conf} = \beta_2^{-1}$. The operator $\Pi_r$ selects mechanically stable states: $\Pi_r = 1$ if $r$ is “stable”, else $\Pi_r = 0$. The system partition function à la Edwards is thus the following \cite{14}:

$$Z = \sum_r \text{e}^{-[\mathcal{H}_{HC}(r) + \beta_1 m_1 g H_1 + \beta_2 m_2 g H_2]} \cdot \Pi_r$$

where the sum is over all microstates $r$. Since the exact calculation of $Z$ is hardly feasible, we want to evaluate $Z$ here at a mean field level. To this aim we consider
a generalization of Bethe-Peierls method for anisotropic systems (due to gravity), i.e., we solve by recurrence relations the partition function of the system on the Bethe lattice shown in the inset of Fig. 1 (see also [18, 19]). The reader not interested in technicalities about calculations can jump to the paragraph after Eq. (2) where the results are discussed. In particular, we consider a 3D lattice box with $H$ horizontal layers (i.e., $z \in \{ 1, ..., H \}$) occupied by hard spheres. Each layer is a random graph of given connectivity, $k \geq 1$ (we take $k = 5$). Each site in layer $z$ is also connected to its homologous site in $z-1$ and $z+1$ (the total connectivity is thus $k+1$). The Hamiltonian is the one above plus two chemical potential terms to control the two species densities ($\mu_1, \mu_2$). Hard Core repulsion prevents two particles on connected sites to overlap. In the present lattice model we adopt a simple definition of “mechanical stability”: a grain is “stable” if it has a grain underneath. For a given grains configuration $r = \{ n_i \}$, the operator $\Pi_r$ has a tractable expression: $\Pi_r = \lim_{K \to \infty} \exp \{ -K \mathcal{H}_{Edw} \} \mathcal{H}_{Edw} = \sum_{i,z} \left[ \delta n_i^{z} \delta n_i^{z-1} \delta n_i^{z+1} + \delta n_i^{z} \delta n_i^{z-1} \delta n_i^{z+1} \delta n_i^{z+2} (1 - \delta n_i^{z+2}) \right]$. The local tree-like properties of our lattice allows to write down recursive equations à la Bethe found by iteration of the lattice structure. Details on calculations and notations can be found in [2, 18, 19], here we just recall the main lines. A “branch” of our lattice can iteratively grow in the “up”, “down” or “side” directions. The partition functions of new branches starting from a site $i$ at height $z$ can be recursively written in terms of their old ones. To this aim define $Z_{0,s}^{(i,z)}$ and $Z_{n,s}^{(i,z)}$ the partition functions of the “side” branch restricted respectively to configurations in which the site $i$ is empty or filled by a particle of specie $n$ (with $n = 1, 2$); analogously, $Z_{n,u}^{(i,z)}$, $Z_{0,u}^{(i,z)}$ and $Z_{n,d}^{(i,z)}$, $Z_{0,d}^{(i,z)}$ are the partition functions of the “up” (resp. “down”) branch restricted to configurations in which the site $i$ is filled by a grain of specie $n$, empty with the upper (resp. lower) site empty and empty with the upper (resp. lower) site filled by a grain of specie $n$. In order to write Bethe recursive equations, it is convenient to introduce the local “cavity fields” defined by: $e_n^{(i,z)} = Z_{n,s}^{(i,z)}/Z_{0,s}^{(i,z)}$, $e_n^{(u)} = Z_{n,u}^{(i,z)}/Z_{0,u}^{(i,z)}$, $e_n^{(d)} = Z_{n,d}^{(i,z)}/Z_{0,d}^{(i,z)}$, $e_n^{(z)} = Z_{n,d}^{(i,z)}/Z_{0,d}^{(i,z)}$ (with $n = 1, 2$). In these new variables the recursion relations are more easily written:

$$e_n^{(i,z)} = e^\beta_n(\mu_n - m_n g_Z) \left[ \prod_{j=1}^{k-1} \frac{A_n^{(j,z)}}{S^{(j,z)}} \right] T_n^{(i,z+1)} R_n^{(i,z-1)}$$  

$$e_n^{(u)} = e^\beta_n(\mu_n - m_n g_Z) \left[ \prod_{j=1}^{k-1} \frac{A_n^{(j,z)}}{S^{(j,z)}} \right] T_n^{(i,z+1)}$$  

$$e_n^{(d)} = e_n^{(i,z+1)}$$  

Here $n = 1, 2$, the products run on the neighbors, $j$, of site $i$, $A_n^{(j,z)} = 1 + 2 \delta n_i^{(j,z)}$, $T_1^{(j,z)} = 1 + e_n^{(j,z)}$, $T_2^{(j,z)} = 1 + e_n^{(j,z)} + e_n^{(j,z)}$, $R_n^{(i,z-1)} = 1 + e_n^{(i,z-1)}$, $Q_n^{(j,z)} = 1 + e_n^{(j,z)} + e_n^{(j,z)}$, $S_n^{(j,z)} = A_n^{(j,z)} + e_n^{(j,z)}$, $Q_n^{(j,z)} = 1 + e_n^{(j,z)}$ [1 + $e_n^{(j,z)}$].

![FIG. 1: Main frame](image)

**FIG. 1:** Main frame Phase diagram, from Bethe approximation, of the hard sphere binary mixture model confined to a single 2D horizontal layer. Here the control parameters are the densities per unit surface of small and large grains $N_1$, $N_2$. A Fluid and a Crystal phase are found, divided by a discontinuous melting transition. When the mixture is prepared with values of $N_1$ and $N_2$ out of the Fluid or Crystal phases (i.e., in the white area), it exhibits phase separation, associated to coarsening, in a fluid phase rich in small grains and a crystalline phase rich in large ones. This causes horizontal segregation of the two grains species. We also plot the metastable “supercooled” fluid region, where a coexistence line between two supercooled fluids, with different relative species concentrations, is found (dashed line) having a critical point (open dot). For high $N_2$, a 1-step Replica Symmetry Breaking glassy phase (described in details elsewhere [11]), metastable with respect to the crystal, is present. Inset A schematic picture of the 3D lattice model: we consider a binary mixture of hard spheres located on a Bethe lattice where each horizontal layer is a random graph of given connectivity. Homologous sites on neighboring layers are also linked and the overall vertex connectivity is $c \equiv k+1 = 6$.

From local fields the free energy, $F$, can be derived along with the quantities of interest, such as the density profile of small and large grains, $\rho_1(z)$ and $\rho_2(z)$, their density per unit surface $N_1 = \sum_z \rho_1(z)$ and $N_2 = \sum_z \rho_2(z)$ and average heights $h_n = \langle z_n \rangle = \sum_z z \rho_n(z) / \sum_z \rho_n(z)$ (with $n = 1, 2$). The system parameters (for a given grains sizes ratio) are four: the two
number densities per unit surface, $N_1$ and $N_2$ (conjugated to the chemical potentials), and the two configurational temperatures, or more precisely $m_1\beta_1$ and $m_2\beta_2$ (conjugated to gravitational energies). In the space of these parameters, the fluid phase corresponds to a solution of Bethe-Peierls equations where local fields in each layer are site independent. Such a solution, characterized by horizontal translational invariance, is given by the fixed points of Eqs. 2. With the standard Bethe-Peierls methods, a crystalline phase, characterized by the breakdown of the translational invariance (local fields are now different on neighboring sites), is also found. The typical resulting phase diagrams are shown in Figs 1 and 2.

Findings are consistent with known results on binary hard spheres with no gravity [21]. A Fluid phase is found for small $N_2$ and, by increasing $N_2$, there is a discontinuous (except for $N_1 = 0$) melting transition to a Crystal phase. Whenever the system is prepared with values of $N_1$ and $N_2$ out of the regions where these phases are stable (i.e., in the white area of Fig 1), phase separation occurs between a fluid rich in small grains and a crystal rich in large grains [21]. This might correspond to a horizontal segregation in the grains mixture, as recently found in the form of coarsening phenomena in experiments on a monolayer by Reis and Mullin [9]. Fig. 1 also shows the “supercooled fluid” and “glassy” metastable phases (plotted with smaller fonts). Since nucleation times can be in practice very long (and enhanced by a degree of polidispersity), crystallization can be avoided and the metastable fluid observed. In such a region we find a coexistence line between a fluid rich in small grains and another one rich in big grains (dashed line in Fig. 1) with a second order critical point (big empty circle).

Fig. 2 shows the typical phase diagram of a 3D system in a case where $m_1\beta_1 > m_2\beta_2$. The pure Fluid and Crystal phases found in 2D are still present, even though their extension depends now on $\beta_1$ and $\beta_2$ (they shrink as $\beta_1$ and $\beta_2$ increase). There is also a region where the two phases coexist (marked Crystal&Fluid). Gravity breaks the system “up-down” symmetry, so the coexisting stable or metastable phases of the 2D case are vertically segregated. This separation mechanism underlies a form of strong vertical segregation (see Fig 2): here the crystal phase, rich in large grains, moves to the top and a clear cut BNE is found (as RBNE is observed in the opposite case, when $m_1\beta_1 < m_2\beta_2$). This kind of segregation is visualized by a plot of the density profiles which, in this region, show a clear separation of the two coexisting phases (see right inset of Fig 2). Opposed to such phase separation driven segregation, within the pure Fluid and Crystal phases one observes mixing or a form of weak vertical segregation since more mechanically stable states can be found with small grains at the bottom (as described by “percolation” mechanisms). This is shown, in a typical point of the Crystal phase, by the species density profiles plotted in the left inset of Fig 2: small grains are essentially mixed with large ones and, on average, slightly below. In the phase diagram of Fig 2 different forms of BNE can thus be found in different regions (similarly for RBNE in the case $m_1\beta_1 < m_2\beta_2$). In general, for a given grains sizes ratio, an interplay of mass densities and configurational temperatures difference drives the phases vertical positioning.

Due to the symmetry breaking field, in 3D no coarsening phenomena are usually associated to segregation, in contrast with the 2D case. Coarsening is expected to appear in the segregation process when both the phases densities and the configurational temperatures get close,
a phenomenon which could be confirmed by experiments or simulations.

These are the basic mechanisms which underly segregation/mixing phenomena and which give rise to a variety of behaviors as grains and system parameters are changed. This is illustrated by a few more examples in Fig. 3 selected to describe cases where the system moves from weak BNE to weak RBNE regions. The picture shows the usual vertical segregation parameter $\Delta h/h \equiv 2(\bar{h}_1 - h_2)/(\bar{h}_1 + h_2)$. In the main panel of Fig. 3 $\Delta h/h$ is plotted as a function of $N_2$ in a region where the system crosses from the fluid to the crystal phase (see Fig. 2), the full dot showing the phase transition point: well within the crystal, $\Delta h/h$ changes its sign passing from BNE, $\Delta h/h < 0$, to RBNE, $\Delta h/h > 0$. The insets of Fig. 3 show $\Delta h/h$ in the fluid phase as a function of $N_1$ and $T_1^{\text{conf}} = T_2^{\text{conf}} = T^{\text{conf}}$ respectively.

Summarizing, the present mean field Statistical Mechanics model of granular mixture, here analytically treated à la Edwards, allows to explain the basic mechanisms underlying a variety of mixing and segregation phenomena experimentally observed, ranging from BNE [1] and RBNE [8, 17], to coarsening effects [9]. Interestingly for non-thermal media, they turn out to be related to thermodynamic-like mechanisms taking place in the system phase diagram.

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