Phase Separation and Coarsening in Electrostatically Driven Granular Media

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A continuum model for the phase separation and coarsening, observed in electrostatically driven granular media, is formulated in terms of a Ginzburg-Landau equation subject to conservation of the total number of grains. In the regime of well-developed clusters, the continuum model is used to derive “sharp-interface” equations that govern the dynamics of the interphase boundary. The model captures the essential physics of this system.

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Despite extensive work in the last two decades, the physics of granular flow is still poorly understood, especially in the limit of strongly inelastic granular collisions when no first-principles hydrodynamic description is available\textsuperscript{1}. Additional complications include contact interactions which become dominant when the grain size goes below 0.1 mm. As particles may acquire an electric charge, a new type of dynamics appears which is governed by the interplay between long-range electromagnetic and short-range contact forces. In this regime, electrostatic excitation of granular media becomes possible. It offers an opportunity for an investigation of granular systems consisting of small particles.

Recently, off-equilibrium phase separation and coarsening in electrostatically driven granular submonolayers was reported\textsuperscript{1}. The inset of Fig. 1 shows a schematic of the setting. Conducting particles are placed between the plates of a plane capacitor which is energized by a constant (DC) or alternating (AC) electric field $E$. When particles are in contact with the capacitor plate, they acquire an electric charge. If the electric field exceeds a critical value, the resulting (upward) electric force overcomes the gravity force $mg$ ($g$ is gravity acceleration and $m$ is mass of particle) and pushes the particles upward. When a particle hits the upper plate, it gets the opposite charge and falls back. Changing the frequency $\omega$ of the AC field $E(t) = E_0 \cos(\omega t)$, one can control the particle elevation and avoid the collisions with the upper plate.

It was found in Ref.\textsuperscript{1} that the particles remain immobile on the bottom plate at $E < E_1$ (the precipitate state). If the electric field is larger than a second threshold value, $E_2 > E_1$, the system is in a gas-like state. This second field $E_2$ is $50\%-70\%$ larger than $E_1$. It was found that, upon decreasing the field below $E_2$ (in the interval $E_1 < E < E_2$) there is nucleation of precipitate, and small densely packed clusters form and start to grow. The clusters then exhibit Ostwald ripening\textsuperscript{3}: smaller clusters shrink, while larger clusters grow at their expense. Molecular dynamics simulations showed qualitative agreement with experimental results on phase separation and coarsening\textsuperscript{3}.

In this Letter we develop a continuum description of these phenomena. The model captures the essential phenomenology, correctly reproducing different possible morphologies of coarsening and providing a correct quantitative description of its dynamic scaling behavior.

Let the granulate consist of $N \gg 1$ identical spherical particles with mass $m$ and radius $r$ (which is small compared with the plate spacing $h$). The continuum version of the model employs two fields: the densities of the precipitate, $n(r, t)$ and gas phase $n_g(r, t)$, where $r = (x, y)$ and $x$ and $y$ are the horizontal coordinates. For concreteness, we will consider a low-frequency electric field (so that the gas density is almost independent of the vertical coordinate) and measure $n_g$ in cm$^{-2}$.

The phase separation is caused by electrostatic screening\textsuperscript{4}: a decrease in the vertical electric force $F$, exerted on a grain in contact with the bottom plate, caused by the presence of other grains. Thus, the $F(n)$ dependence is an important element of our model. This dependence can be easily found in the dilute limit $n a^2 \ll 1$. Consider two grains lying on the bottom plate the distance $L \gg a$ apart. The second grain and its mirror image in the plane form a dipole with the dipole moment of order of $\sigma^3 E$. This dipole produces an electric field at the location of the first grain: $\delta E \sim -\sigma/L^3 E$. Therefore, the net force acting on the first grain is reduced and becomes $F_0[1 - \kappa(\sigma/L)^3]$. If there are many grains lying far apart, we can simply sum up these vertical forces and obtain the net force

$$F(n) = F_0(1 - k_1 \sigma^3 n^{3/2}). \quad (1)$$

Here $F_0 = 1.36 \ldots \sigma^2 E^2$ is the vertical force exerted on a single grain in contact with the bottom plate\textsuperscript{5}, and $\kappa$, $k_1 = O(1)$ are numerical factors.

Although no analytic expression for $F(n)$ is presently available for intermediate and large $n$, it is clear that $F(n)$ should decrease with $n$\textsuperscript{5}. A decreasing $F(n)$ dependence leads, at intermediate values of $E$, to a segregation instability and bistability. Indeed, the density value $n = n_*$ such that $F(n_*) = mg$ is in an unstable equilibrium. For $n < n_*$, $F(n)$ exceeds $mg$ so the particles
“evaporate” until the “empty state” \( n = 0 \) is reached. If \( n > n_+ \), \( F(n) < mg \) and the particles remain immobile. However, as gas particles hit these regions and (because of strong inelasticity of collisions) get attached to them, \( n \) grows until the densely packed state \( n = n_c \sim \sigma^{-2} \) is reached. This simple argument ignores conservation of the total number of particles and cluster edge effects that we account for in the following.

The vertical force exerted on a particle decreases with an increase of the number of neighboring particles \( \bar{3} \): the force exerted on a particle located at the cluster edge, \( F_c \), is larger than the force on a particle in the bulk of the cluster \( F_b \), but smaller than the force on a single particle \( F_0 \). In addition, in a coarse-grained description (which should be valid for clusters with many particles) \( F_c \) should depend on the local curvature of the cluster edge. Although no general relation for \( F_c \) is presently available, a clear signature of these cluster edge effects appears already in the dilute limit where quantitative relations can be obtained. First, for an inhomogeneous density distribution, the density \( n(r) \) in Eq. (1) should be replaced by a locally averaged density \( \bar{n}(r) \), the averaging being performed over a region which size is of the order of the interparticle distance. For a weakly inhomogeneous coverage, one can expand \( n(r) \) around a point \( r_0 \) up to \( (r - r_0)^2 \). Then, averaging the result over a circle of radius \( n(r_0)^{-1/2} \), we obtain \( \bar{n}(r) = n(r) + O(\nabla^2 n/n) \). Substituting it in Eq. (1), we arrive at

\[
F(n, \nabla^2 n) = F_0(1 - k_1 \sigma^3 n^{3/2} - k_2 \sigma^3 n^{-1/2} \nabla^2 n),
\]

where \( k_2 = O(1) \) is another numerical factor. The cluster edge effects are described by the \( \nabla^2 \)-term.

Now we start formulating our model. The precipitate number density \( n(r, t) \) will serve as the order parameter, the two phases corresponding to \( n = 0 \) and \( n = n_c \). In its turn, the gas density \( n_g(t) \) plays the role of the “mean field”. (We assume that the density relaxation in the gas phase is fast compared to the cluster-gas exchange dynamics. Therefore, \( n_g \) is approximately constant in space and depends only on time.) First, consider a uniform precipitate in the dilute limit: \( n + n_g \ll n_c \). The precipitate will “evaporate” if \( F_0 > mg \). On the contrary, the gas will precipitate if \( F_0 < mg \). The typical time scales of each of these two processes are of order of \( \tau = \min [(g/h)^{1/2}, \omega^{-1}] \). A simple dynamic equation

\[
\frac{dn}{dt} = \frac{C}{\tau} n_g \theta(\Gamma) + n \theta(-\Gamma),
\]

subject to conservation law \( n + n_g = N/L^2 = \text{const} \), accounts for these facts. Here \( \Gamma = 1 - F_0/mg \) and \( \theta(\ldots) \) is the \( \theta \)-function. The numerical factor \( C = O(1) \) accounts for a possible difference between the time scales of “evaporation” and precipitation. The factor \( \Gamma \) in front of the brackets of Eq. (3) takes care, in the simplest possible way, of the continuity of transition between the regimes of \( F_0 > mg \) and \( F_0 < mg \).

For higher precipitate densities one needs to account for additional effects. First, because of the screening, the lifting force decreases with \( n/n_c \). For simplicity, we assume a linear dependence \( F_0(1 - bn/n_c) \), for all densities \( 0 \leq n/n_c \leq 1 \). Here \( b \) is a numerical constant (using the estimate of \( F(n = n_c) \) from Ref. \( \bar{3} \), we have \( b \approx 8/9 \)). Second, we account for the inhomogeneity of the precipitate by adopting the \( \nabla^2 n \) term from Eq. (1), with a diffusion coefficient \( D \sim \sigma^2/\tau \). Third, we introduce an additional factor \( (n_c - n)/n_c \) in the first term in the r.h.s. of Eq. (1). It accounts, in a simple way, for a slowdown of precipitation from the gas phase: at finite \( n/n_c \), a part of the bottom plate is already occupied by grains.

In this way one arrives at a scalar Ginzburg-Landau equation (GLE). We will be using this equation in the phase coexistence regime \( mg < F_0 < mg/(1 - b) \). (A more detailed condition will be derived below.) The equation can be written in a scaled form:

\[
\frac{dn}{dt} = \phi(n, n_g, n_+) + \nabla^2 n, \tag{4}
\]

where

\[
\phi = (n - n_+) \times \begin{cases} n, & \text{if } 0 \leq n \leq n_+ \\ C n_g (1 - n), & \text{if } n_+ \leq n \leq 1 \end{cases}
\]

Here \( n_+ = (1/b)(1 - mg/F_0) \). The coordinates (and the system size \( L \), see below) are scaled by \( \delta = (D\tau/\lambda)^{1/2}/n_c \), the time is scaled by \( \tau mg/bF_0 \). The precipitate and gas densities (and \( n_+ \)) are scaled by \( n_c \). Finally, \( \lambda = bF_0/mgn_c^2 \).

The dynamics are constrained by the conservation of the total number of particles. In the scaled units

\[
L^{-2} \int_0^L \int_0^L n(x, y, t) dx dy + n_g(t) = \varepsilon, \tag{6}
\]

where \( \varepsilon \) is the (constant) area fraction of the granulate.

At fixed \( n_g \) and \( 0 < n_+ < 1 \), the function \( \phi(n, n_g, n_+) \) describes bistability: it has two stable zeros: at finite \( n/n_c \), \( \phi = 0 \). Second, we account for the inhomogeneity of the precipitate by adopting the \( \nabla^2 n \) term from Eq. (1), with a diffusion coefficient \( D \sim \sigma^2/\tau \). Third, we introduce an additional factor \( (n_c - n)/n_c \) in the first term in the r.h.s. of Eq. (1). It accounts, in a simple way, for a slowdown of precipitation from the gas phase: at finite \( n/n_c \), a part of the bottom plate is already occupied by grains.

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\[
\int_0^1 \phi(n, n_g, n_+) dn = 0
\]

approximately holds. For the present model, a straightforward calculation yields
\[ n_g^e = \frac{n^3}{C (1-n^e)^3}. \]

When \( n_g = n_g^e \), a planar interface of the precipitate is in a dynamic equilibrium: it neither advances nor retreats if fluctuations are neglected. For curved interfaces there is an additional, slower coarsening stage of the dynamics, governed by the cluster edge curvature. Its characteristic time \( t_2 \propto L^2 \).

A detailed analysis of this system is possible in the asymptotic sharp-interface limit. The sharp-interface equations become valid towards the end of the \( t_1 \)-stage, when the precipitate in the clusters is already densely packed \((n = 1)\), and the gas density \( n_g \) is close to \( n_g^e \). In this limit, the conservation law (7) reads

\[ \frac{A(t)}{E^2} = \varepsilon - n_g^e, \]

where \( A(t) \) is the total area of the precipitate. Demanding \( A > 0 \) and using Eq. (7), we obtain a condition for the two-phase coexistence:

\[ \varepsilon > \frac{n^3}{C (1-n^e)^3}. \]

Using our model expression for \( n^e \), we can write

\[ 1 < \frac{F_0}{mg} < \left[ 1 - b \left( 1 + \frac{1}{\sqrt{C \varepsilon}} \right)^{-1} \right]^{-1}. \]

One should compare the more restrictive condition (10) with the “naive” condition \( 1 < F_0/mg < (1-b)^{-1} \). For example, for \( \varepsilon = 0.25, C = 1\), and \( b = 8/9\) the “naive” condition gives \( 1 < F_0/mg < 9\), whereas Eq. (10) gives \( 1 < F_0/mg < 1.5\). The latter condition agrees better with experiment [3]. Even better agreement is achieved if one chooses \( C \approx 10\).

The normal component of the interface speed is (11):

\[ v_n = \nu C \frac{(1-n^e)^3}{n^{3/2}} (n_g - n_g^e) - \mathcal{K}, \]

where \( \mathcal{K} \) is the local curvature of the interface and \( \nu = 5(9 + 2\sqrt{3})/138 \approx 0.45 \).

Given the initial location of all interfaces, Eqs. (8) and (9) provide a proper description of the late-time coarsening dynamics. Furthermore, these equations can be mapped into equations of interface-controlled transport which appeared in other contexts. This enables one to readily present a number of important results for several coarsening configurations: (1) A planar or circular interfaces are stable with respect to small modulations \([8,11]\); (2) The radius of a single cluster which can be in a stable dynamic equilibrium with the gas phase has a non-zero lower bound. This lower bound scales with the system size (like \( L^{2/3} \)), but is independent of \( N \); (3) Multiple clusters exhibit Ostwald ripening; \([6,11,12]\); (4) If there are many clusters, their size distribution exhibits dynamic scaling. The number of clusters decays with time like \( t^{-1} \), while the average distribution grows like \( t^{1/2} \); (5) Depending on the initial parameters, a “hole” (empty region) inside a cluster will either shrink to zero, or expand and come out of the cluster \([3]\). It should be stressed that these results are insensitive to the exact form of the bistable function \( \phi \).

Properties 1, 3 and 4 were already observed in experiment \([3]\). We checked predictions 1, 2 and 5 by performing additional experiments with cells similar to those described in Ref. [3]. The experimental results fully agree with these predictions.

![FIG. 1. The gas phase density \( n_g \) (normalized to \( n_c \)) vs. time. Inset: schematic of the experimental setting.](image)

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Though suitable for theoretical analysis, sharp-interface equations are less convenient for numerical simulations. We solved Eqs. (8)-(11) numerically in periodic boundary conditions. Figure 2 shows a typical simulated evolution of the precipitated phase. The initial conditions describe a situation when most of the particles are in the low-density precipitate (that is, in the unstable region). This corresponds to an up-quench of the electric field from \( E < E_1 \) to the coexistence region \( E_1 < E < E_2 \). At small times, “holes” in the precipitate develop and grow. At later times multiple clusters form and exhibit Ostwald ripening, in agreement with experiment. Figure 1 shows the time history of the gas density \( n_g \) (normalized to \( n_c \)). At late times, \( n_g \) approaches the value corresponding to the coexistence of a single cluster and gas phase \([3,11]\). For the set of parameters chosen for this simulation, the area rule value \( n_g^e = 0.05 \). The fine structure of the \( n_g(t) \) dependence (small peaks) corresponds to the disappearance of clusters \([1,11]\). In experiment, the current through the cell is carried by the grains belonging to the gas phase, so it should be proportional to \( n_g \). Therefore, the “mean field” \( n_g(t) \) is a directly observable quantity.

The “up-quench” type of morphology at small times
shown in Fig. 2 was not reported in Ref. [3], so we performed special experiments with electrostatic cells similar to those used in Ref. [3]. Starting from the gas phase \((E > E_2)\) and making a down-quench to \(E < E_1\), we first prepared a nearly uniform layer of precipitate. Then, after an up-quench into the coexistence region \(E_1 < E < E_2\), we observed the same type of morphology as shown in Fig. 2.

![Images of simulated dynamics for different time scales](Image)

**FIG. 2.** Simulated dynamics of the precipitate for \(t = 100\) (a), 160 (b), 300 (c) 600 (d) 4000 (e) and 6000 (f) scaled time units. White color corresponds to densely packed clusters \((n \simeq n_c)\), black to empty regions. The system dimensions (in the units of \(\delta\)) are 500 \(\times\) 500. The electric field \(E\) corresponds to \(n_\ast = 0.2\).

It should be noted that when \(F\) is only slightly larger than \(mg\), the interface width (which, at \(n_\ast \ll 1\), is proportional to \(n_\ast^{-3/2}\)) becomes comparable to the cluster size and/or intercluster distance. In this regime the sharp-interface theory is invalid. Still, the continuum theory should work.

The present model assumes a low-frequency electric field. In this case the gas particles typically perform an appreciable bounce motion, and a separate, mean-field treatment of the gas phase is legitimate. For very high frequencies, the particle motion becomes effectively restricted to the bottom plate. The corresponding coarsening dynamics can be quite different. One can expect that, at the high frequencies, the 1/2 growth exponent (observed in experiment [3] and predicted by our model) will cross over to the 1/3 growth exponent, typical for locally-conserved systems [14].

It is interesting to compare the phase separation properties of electrostatically driven granulates with those vibrated in the vertical direction mechanically [8]. Though these two types of systems strongly differ in details of particle interactions and motion, they have very similar phase diagrams and are strikingly similar in their phase transition morphologies. This gives an indication that a bistable Ginzburg-Landau equation subject to conservation of the number of particles can be relevant for the mechanically vibrated systems as well.

In summary, we have formulated a phenomenological theory of the dynamics of off-equilibrium phase separation in electrostatically driven conducting monodisperse particles. The theory includes both continuum, and sharp-interface formulations. It captures the essential physics of this system. Several new predictions of our model have been verified in experiment. A better quantitative understanding of this system requires additional quantitative experiments in different regimes of phase ordering. A comparison of the model with the new experiments will enable one to determine the unknown numerical coefficients of the model. These coefficients control the precise phase diagram, the interface velocity, the amplitudes of the dynamic scaling laws in the Ostwald ripening regime, etc. However, already at this stage we see a strong evidence in favor of quantitative relevance of the globally constrained GLE to this system.

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