Phase Separation and Coarsening in Electrostatically Driven Granular Media

I. S. Aranson,[1] B. Meerson,[1,2] P. V. Sasorov,[3] and V. M. Vinokur[1]

[1]*Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, Illinois 60439*
[2]*Racah Institute of Physics, Hebrew University of Jerusalem, Jerusalem 91904, Israel*
[3]*Institute of Theoretical and Experimental Physics, Moscow 117259, Russia*

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A continuum model for the phase separation and coarsening 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 [1,2]. 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.

Recently, off-equilibrium phase separation and coarsening in electrostatically driven granular submonolayers was observed [3,4]. The inset of Fig. 1 shows a schematic of experimental setting. Conducting particles are placed between the plates of a plane capacitor. When particles are in contact with the capacitor plate, they acquire an electric charge. If the electric field E exceeds a critical value, the resulting (upward) electric force overcomes the gravity force mg and pushes the particles upward. When a particle hits the upper plate, it gets the opposite charge and falls back. Changing the frequency of the alternating field, one can control the particle elevation and avoid the collisions with the upper plate.

It was found [3] that the particles remain immobile on the bottom plate at $E < E_1$ (the precipitate state). If the field E is larger than a second threshold value, $E_2 > E_1$, the system is in a gaslike state. This second field E_2 is 50%–70% larger than E_1. Upon decreasing E 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 coarsening of the Ostwald-ripening type: smaller clusters shrink, larger clusters grow. Remarkably, this coarsening process exhibits dynamic scaling typical for *interface-controlled* systems [5]. Molecular dynamics simulations showed qualitative agreement with experimental results [3].

In this Letter we develop a continuum description of this fascinating system. Our model captures the essential phenomenology, reproducing different morphologies of coarsening and the correct dynamic scaling. It establishes important connections with other nonequilibrium physical systems. It also gives new predictions, both qualitative and quantitative. We verified some of these predictions in specially performed experiments (see below properties 1, 2, and 4 and a discussion of the novel "hole" morphology).

Model.—Let the granulate consist of $N \gg 1$ identical spherical particles with mass m and radius σ (which is small compared with the plate spacing h). We will focus on the evolution of the number densities of the precipitate, $n(\mathbf{r}, t)$ and gas $n_g(\mathbf{r}, t)$, where $\mathbf{r} = (x, y)$ 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}. It was found in Ref. [3] that the phase segregation in this system is caused by electrostatic screening: 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. Correspondingly, the $F(n)$ dependence will become an important element of our model. This dependence can be easily found in the dilute limit

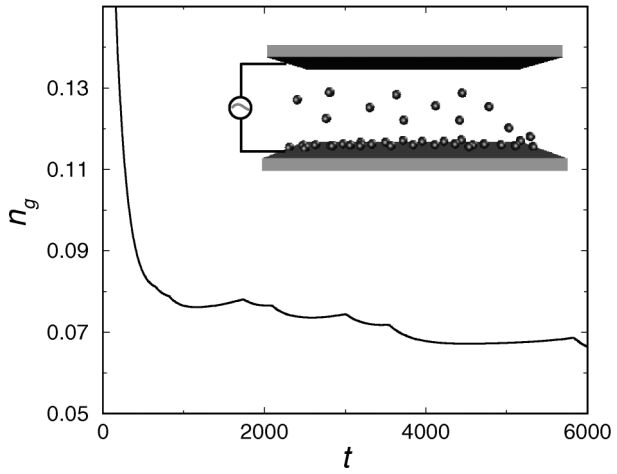

FIG. 1. The density of the gas phase n_g (normalized to n_c) vs time as predicted by the numerical simulations with Eqs. (4)–(6). Inset: schematic of the experimental setting [3].

$n\sigma^2 \ll 1$. Consider two grains lying on the bottom plate the distance $L \gg \sigma$ 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 [3], and κ, $k_1 = \mathcal{O}(1)$ are numerical factors.

Although no analytic expression for $F(n)$ is available for intermediate and large n, it is clear that $F(n)$ should decrease with n [3]. 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 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.

Two additional crucial elements of our model come from the fact that the vertical force exerted on a particle decreases with an increase of the number of neighboring particles [3]. The force exerted on a particle located at the cluster edge, F_e, 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 (valid for clusters with many particles) F_e should depend on the local curvature of the cluster edge. 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 $n(\mathbf{r})$ in Eq. (1) should be replaced by a *locally averaged* density $\overline{n}(\mathbf{r})$, 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 $n(\mathbf{r})$ around a point $\mathbf{r}_0$ up to $(\mathbf{r} - \mathbf{r}_0)^2$. Then, averaging the result over a circle of radius $\sim n(\mathbf{r}_0)^{-1/2}$, we obtain $\overline{n}(\mathbf{r}) = n(\mathbf{r}) + \mathcal{O}(\nabla^2 n/n)$. Substituting it in Eq. (1), we arrive at

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

where $k_2 = \mathcal{O}(1)$ is another numerical factor. The cluster edge effects are described by the ∇^2 term.

The precipitate number density $n(\mathbf{r}, t)$ serves as the order parameter of our continuous model, the two phases corresponding to $n = 0$ and $n = n_c$ [6]. 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.) To derive the governing equation for n, we 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

$$\frac{dn}{dt} = \frac{\Gamma}{\tau}[Cn_g\theta(\Gamma) + n\theta(-\Gamma)], \quad (3)$$

subject to conservation law $n + n_g = N/L^2 = \text{const}$, accounts for these facts. Here $\Gamma = 1 - F_0/mg$ and $\theta(\cdots)$ is a step function. The numerical factor $C = \mathcal{O}(1)$ accounts for a possible difference between the time scales of "evaporation" and precipitation. The factor Γ 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 $F_0 < mg$.

Going to higher precipitate densities, we account for three basic effects: (a) 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 $0 \le n/n_c \le 1$. Here b is a numerical constant [using the estimate of $F(n = n_c)$ from Ref. [3], we have $b \simeq 8/9$]. (b) We introduce an additional factor $(n_c - n)/n_c$ in the first term in the right-hand side of Eq. (3). 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. (c) We account for the inhomogeneity of the precipitate by adopting a simplified version of the $\nabla^2 n$ term from Eq. (2), with a diffusion coefficient $D \sim \sigma^2/\tau$. Thus we arrive at a scalar Ginzburg-Landau equation (GLE). We will use this equation in the phase coexistence regime $mg < F_0 < mg/(1 - b)$. (A more restrictive condition for the phase coexistence will be obtained below.) GLE can be written in a scaled form:

$$\frac{\partial n}{\partial t} = \phi(n, n_g, n_*) + \nabla^2 n, \quad (4)$$

where

$$\phi = (n - n_*) \times \begin{cases} n, & \text{if } 0 \le n \le n_*, \\ Cn_g(1 - n), & \text{if } n_* \le n \le 1. \end{cases} \quad (5)$$

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

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

where ε 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 $n = 0$ and $n = 1$, and an unstable zero at $n = n_*$. Equations (4)–(6) serve as the continuum version of our model. Remarkably, similar equations (with different forms of function ϕ and conservation laws) have appeared in other contexts [7–10]. The dynamics of a globally conserved bistable system involve *three* characteristic time scales. Phase separation occurs on the fastest time scale t_0, determined by the properties of the function ϕ; it is independent of the characteristic cluster size l. On a longer time scale $t_1 \propto l$, the time-dependent gas density $n_g(t)$ becomes close to special "equilibrium" value n_g^{eq} which satisfies the Maxwell rule $\int_0^1 \phi(n, n_g, n_*)\, dn = 0$. A direct calculation yields

$$n_g^{eq} = \frac{n_*^3}{C(1 - n_*)^3}. \tag{7}$$

When $n_g = n_g^{eq}$, a *planar* interface of the precipitate is in a dynamic equilibrium: it neither advances nor retreats if fluctuations are neglected. *Curved* interfaces define an additional, slower *coarsening* stage governed by the cluster edge curvature. Its characteristic time $t_2 \propto l^2$ [9].

Sharp-interface equations.—These 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^{eq}. The conservation law (6) reads

$$A(t) = L^2[\varepsilon - n_g(t)], \tag{8}$$

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:

$$\varepsilon > \frac{n_*^3}{C(1 - n_*)^3}. \tag{9}$$

Using our model expression for n_*, we can write

$$1 < \frac{F_0}{mg} < \left[1 - b\left(1 + \frac{1}{\sqrt[3]{C\varepsilon}}\right)^{-1}\right]^{-1}. \tag{10}$$

The quantity in the right side of Eq. (10) corresponds to the threshold value E_2 of the electric field found in experiment [3]. It is instructive to compare this value with the "naïve" estimate $F_0/mg = (1 - b)^{-1}$. For example, for $\varepsilon = 0.25$, $C = 1$, and $b = 8/9$ the naïve estimate gives $F_0/mg = 9$, whereas Eq. (10) gives $F_0/mg = 1.5$. The latter condition agrees better with experiment [3]. Even better agreement is achieved if one chooses $C \simeq 10$.

The normal component of the interface speed is [10]

$$v_n = \nu C(1 - n_*)^3 n_*^{-3/2}(n_g - n_g^{eq}) - \mathcal{K}, \tag{11}$$

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 (11) provide a proper description of the late-time coarsening dynamics. Furthermore, these equations can be mapped into equations of *interface-controlled* transport that appeared in other contexts. This enables one to readily present a number of important results for several coarsening configurations: (1) A planar (a) or circular (b) interface is stable with respect to small modulations [9,11]. (2) The radius of a single cluster which is in a stable dynamic equilibrium with the gas phase has a nonzero lower bound [9,11]. (3) Multiple clusters exhibit Ostwald ripening [7–9,11], and their size distribution exhibits dynamic scaling. The number of clusters decays with time like t^{-1}, while the average cluster radius grows like $t^{1/2}$ [5,9,11]. (4) Depending on the initial parameters, an "inclusion" (empty region) inside a cluster will either shrink to zero or expand and come out of the cluster [12].

Properties 1 to 4 are insensitive to the exact form of the bistable function ϕ. Properties 1(b) and 3 were already observed in the original experiment [3]. Properties 1(a), 2, and 4 represent new predictions. We verified all of them by performing special experiments. In contrast to our previous studies [3], bigger cell (11×11 cm) and larger particles (165 μm Cu balls) were used. The typical number of particles in the cell was 200 000. The area fraction of granulate was also larger than in experiments [3].

Note that when F only slightly exceeds mg, the interface width (which, at $n_* \ll 1$, is proportional to $n_*^{-3/2}$) 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.

Simulations.—We solved Eqs. (4)–(6) numerically with periodic boundary conditions. Selected results are shown in Figs. 1 and 2. The upper row of Fig. 2 shows a typical evolution of the precipitated phase, as observed in the simulations. At $t = 0$ 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 one observes growing "holes" in the precipitate. At this early stage conservation of the number of particles is unimportant yet. At later times multiple clusters form and exhibit Ostwald ripening as expected. The lower row of Fig. 2 shows snapshots from experiment. Excellent agreement in morphology is observed, including the appearance of holes predicted by our model. Figure 1 shows the simulated time history of the gas density n_g. One can see that, at late times, n_g approaches the value corresponding to the coexistence of a single cluster and gas phase [9,11]. For the set of parameters chosen for this simulation, the Maxwell-rule value $n_g^{eq} = 0.05$. The fine structure of the $n_g(t)$ dependence (small peaks) corresponds to the disappearance of clusters [11,12]. 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 $n_g(t)$ should be a directly observable quantity, so our model gives a definite prediction of its dynamics.

Our 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

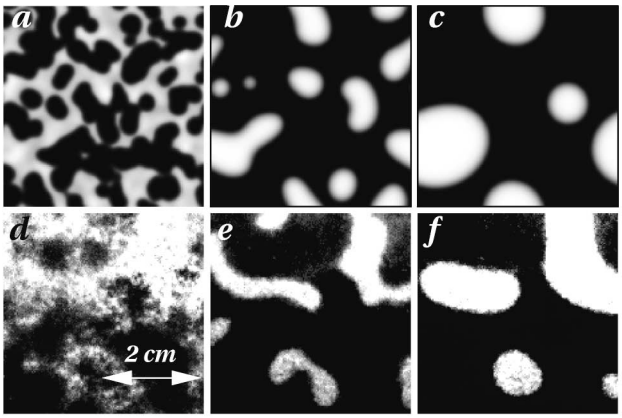

FIG. 2. Phase segregation and coarsening dynamics. The simulation images (a)–(c) are taken at $t = 100$ (a), 300 (b), and 4000 (c) scaled time units. White corresponds to densely packed clusters ($n \simeq n_c$), black to empty regions. The system dimensions (in the units of δ) are 500×500. The electric field E corresponds to $n_* = 0.2$. The experimental pictures (d)–(f) were obtained for dc electric field $E \approx 7$ kV/cm. Starting from the gas ($E > E_2$) and making a down-quench to $E < E_1$, we first prepared a nearly uniform layer of precipitate. Then the system was up-quenched into the coexistence region $E_1 < E < E_2$. Images correspond to times $t = 1$ sec (d), $t = 30$ sec (e), and $t = 200$ sec (f) after the up-quench.

gas phase is legitimate. For high frequencies, the particle motion becomes restricted to the bottom plate. Therefore, one can expect that, at the high frequencies, the $1/2$ growth exponent (observed in experiment [3] and explained by our model) will cross over to the $1/3$ exponent, typical for *locally* conserved systems [13].

It is interesting to compare the phase separation properties of electrostatically driven granulates with those vibrated in the vertical direction mechanically [14]. 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 indicates that a bistable Ginzburg-Landau equation subject to conservation of the number of particles can be relevant for the mechanically vibrated systems as well.

We have formulated a scalar Ginzburg-Landau theory of the off-equilibrium phase separation in electrostatically driven conducting monodisperse particles. The theory captures the essential physics of this system. Several new predictions of our model have been verified in specially performed experiments. 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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