A reduced thermodynamic description of phase separation in a quasi-one-dimensional granular gas.

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We describe simulations of a quasi-one-dimensional, vibrated granular gas which exhibits an apparent phase separation into a liquid-like phase and a gas-like phase. In thermal equilibrium, such a phase separation in one-dimension is prohibited by entropic considerations. We propose that the granular gas minimises a function of the conserved mechanical variables alone: the particle number and volume. Simulations in small cells can be used to extract the equation of state and predict the coexisting pressure and densities, as confirmation of the minimisation principle. Fluctuations in the system manifest themselves as persistent density waves but they do not destroy the phase-separated state.

Systems driven far from equilibrium often exhibit complex collective behaviour such as phase-separation, pattern formation and self-organisation [1–3]. In thermodynamic equilibrium, systems evolve to minimise the appropriate free energy, a principle that lies at the heart of statistical mechanics [4]. No such principle can generally be applied to explain emergent behaviour in far-from-equilibrium systems.

One of the simplest possible realisations of a far-from-equilibrium system is that of a driven gas of identical spheres that undergo dissipative collisions, namely a granular gas [5, 6]. In both experiment and simulation, non-ideal behaviour analogous to a liquid-gas phase separation with an emergent surface tension has been observed in a confined, periodically vibrated, quasi-2D system [7, 8]. An equal-areas construction was employed to predict the coexisting densities to a reasonable degree of accuracy [9]. However, the validity of this approach has been called into question due to a breach of detailed balance [10]. Similarly, the breakdown of detailed balance in the interfacial region has been argued to explain an unequal-areas rule in active Brownian particles [11].

A quasi-1D granular gas driven by thermalised boundaries also exhibits a phase separation analogous to a van der Waals gas in equilibrium [12–15]. The general applicability of an equal-areas rule in this case has been questioned due to the proximity of the critical point [16]. In thermodynamic equilibrium a 1D gas of particles with short-ranged interactions would not be expected to phase separate at all, due to the dominance of thermal fluctuations. As such the existence of a 1D phase separation in granular matter illustrates a striking difference between equilibrium and non-equilibrium systems. Can a modified version of thermodynamics provide a framework to describe phase separation in a 1D granular gas?

In this article we describe simulations of a confined, periodically-vibrated, quasi-1D granular gas, carried out to investigate phase separation in a one-dimensional non-equilibrium system. Surprisingly, we find that this system can be described by a reduced form of thermodynamics in which kinetic, thermal, variables play no significant role.

Our main results are as follows. (i) A finite-size scaling analysis shows that the system exhibits a true 1D phase separation into a liquid-like phase and a gas-like phase. (ii) We propose that this two-phase coexistence can be described by a function of state $W(N, V)$, where $N$ is the number of particles in the cell and $V$ is the volume of the cell; in the steady state $W(N, V)$ is minimised. (iii) Simulations in small cells can be used to extract the pressure as a function of the volume per particle, $p(v)$, which acts as a non-isothermal equation of state. For a range of small system sizes, an equal-areas construction on $p(v)$ can be used to determine the coexisting pressure and densities, justifying the above assumption. (iv) Gradient terms may be added to $W(N, V)$ to construct an energy functional which accurately describes the steady-state, interfacial profile. (v) In this non-equilibrium steady state a single domain of the dense phase persists and exhibits periodic oscillations in its length with a dominant frequency.

We have carried out computer simulations of $N$ spheres of diameter $d$ in a cell of height $10d$, length $L$ in the range $10d$ to $25600d$ and thickness $d$ (to confine the motion of the spheres to a plane) [17]. The cell is shaken sinusoidally in the direction of the height with an amplitude, $A$, typically of around $1.2d$. The frequency of vibration is $50Hz$, the diameter $d = 1mm$ and the particle density was taken to be that of bronze. Periodic boundary conditions are imposed in the long direction. The effects of gravity and friction are ignored. Particle interactions are modelled by a linear spring-dashpot force, with the coefficient of restitution equal to $\varepsilon = 0.7$. Our findings are robust to changes in $\varepsilon$, the addition of gravity, the geometry of the cell and the mass of the particles.

In thermodynamic equilibrium, it is often difficult to determine the nature of a phase transition due to finite size and time effects [18]. In the following paragraphs we describe a number of tests that we have carried out in order to demonstrate that our system exhibits a true phase separation.

Initially, the particles are positioned randomly within the cell and given a small random velocity. The cell is shaken. For a range of amplitudes and mean number densities the particles spontaneously phase separate in the direction perpendicular to the vibration, $x$ [19]. This
The main panel of Fig. 1 shows the number of independent clusters, \( N_c \), as a function of time, \( t \), for different length systems with mean particle number density 0.1875 mm\(^{-3}\). The lines all have a constant slope, showing that \( N_c \) varies as \( t^{-1/2} \). The corresponding mean cluster size thus grows as \( t^{1/2} \), in contrast to the observed behaviour in 2D, where for the Cahn-Hilliard model with short-ranged interactions does not exhibit a phase transition in one dimension. In contrast, our tests have demonstrated that the dissipative granular gas can exhibit a true phase separation. However, the granular temperature i.e. the mean kinetic energy per particle is different in the two phases. Consequently, there is no need to introduce the concept of a granular gas temperature as the total kinetic energy is not conserved. Hence we propose that our system may be described in terms of a reduced form of thermodynamics based on conserved variables alone.

Consider a box shaken at a constant amplitude, \( A \), containing particles in a state in which it has phase separated into a dilute and a dense phase [22]. The dilute phase has a number density \( n_1 = N_1/V_1 \) and the dense phase has density \( n_2 = N_2/V_2 \). Particles can move from one phase to the other, resulting in fluctuations in the particle numbers and volumes of each phase.

For our granular system the total number of particles, \( N \), and the total volume, \( V \), are fixed. We postulate that there exists an extensive function of state of these conserved variables \( W(N, V) \) which, in the steady state, is minimised for a given amplitude of vibration. Note that the total kinetic energy of the particles, \( E \), is not fixed so that \( W(N, V) \) is not explicitly a function of \( E \). For the whole system the total \( W \) is

\[
W_T = W(N_1, V_1) + W(N_2, V_2),
\]

with \( N = N_1 + N_2 \) and \( V = V_1 + V_2 \).

Minimising \( W_T \) by varying \( N_1 \) and \( V_1 \) subject to the constraints of fixed particle number and fixed volume leads to

\[
\frac{\partial W}{\partial N} \bigg|_1 = \frac{\partial W}{\partial N} \bigg|_2 = \mu^*,
\]

\[
\frac{\partial W}{\partial V} \bigg|_1 = \frac{\partial W}{\partial V} \bigg|_2 = -p^*,
\]

where we define \( \mu^* \) and \( p^* \) to be, respectively, the granular chemical potential and granular pressure at two-phase coexistence. Away from coexistence we assert that

\[
p = -\frac{\partial W}{\partial V} \quad \text{and} \quad \mu = \frac{\partial W}{\partial N},
\]

so that \( dW = -pdV + \mu dN \). Extensivity of \( W \) requires \( W = -pV + \mu N \). Hence, by introducing the intensive
These findings show that the predictions based solely on agreement is very good throughout the phase diagram. The open circles, and those obtained directly from the densities in a phase-separated system (green filled circles). The equal-areas construction (green), and those obtained from density box simulations and the equal-areas construction (green). The percentage deviation in the pressure measured in a phase separated system and that obtained assuming an equal-areas construction on \( p(v) \) is valid, as a function of the small box length.

FIG. 2. The main panel shows pressure characteristics \( p(v) \) in Pascales obtained from simulations in small boxes, for lengths ranging from 100d down to 10d. For larger boxes (green) the curves deviate in the spinodal region due to partial phase separation. For smaller boxes (blue) the curves deviate in the bulk phases due to finite-size effects. The inset shows the percentage deviation in the pressure measured in a phase separated system and that obtained assuming an equal-areas construction on \( p(v) \) is valid, as a function of the small box length.

An explicit expression for \( w(n) \) can be obtained by direct integration of eqn (5). The resulting excess mechanical work \( \Delta w(n) \) at zero as obtained from the double tangent or equal-areas construction [24]. Physically, minimising \( \Delta w \) corresponds to minimising any mechanical work that could be released in exchanging particles from one phase to another at the coexistence pressure \( p^* \). As the system is dissipative, it is natural to expect that in the absence of fluctuations the system would relax to this minimum energy state. Note that the same equal-areas construction applies in thermodynamic equilibrium, but only if \( p(v) \) is an isotherm. In this case the mechanical work function defined here is equivalent to the Helmholtz free energy.

Figure 3 shows \( \Delta w(n) \) as a function of number density obtained from \( p(v) \) for a small cell, \( L = 16d \) and \( A/d = 1.2 \). The inset to Fig. 3 shows the time-averaged density profile in the corresponding system in a long cell that allows phase separation (green points). The shape of the interface was measured relative to the point where the local density is mid-way between the bulk liquid and gas densities, thereby negating the effects of interface motion. Many instantaneous configurations were then averaged to give the mean profile.

In equilibrium thermodynamics the interfacial profile can be constructed directly from the excess free energy.
density, and the assumption of a gradient squared term in the free energy functional [24]. If our granular system can be treated in the same fashion, we postulate the existence of the free energy functional \[24\]. If our granular system can separated system (green points) and a fit to the profile (black line). The solid line in the main panel shows that minimisation of the mechanical work functional can be used to construct the interfacial profile, as described in the text.

In our granular system a local energy functional is sufficient to provide a macroscopic description. However, an energy functional constructed solely from the pressure has no obvious connection to any large-deviation functional [25] and, as such, does not directly provide information about the fluctuations in the system. In order to investigate the fluctuations in the steady state we consider a system initialised in the phase-separated state and vibrated with \( A = 1.2d \). Such a configuration remains as a single dense domain, but the length of the domain exhibits breathing-like modes of oscillation [19].

To characterise these persistent fluctuations we have taken time-series of the domain length of the dense phase, \( l \), and Fourier transformed to get the frequency spectrum of the oscillations, shown in the inset to Fig. 4. We find that the frequency spectrum has a dominant frequency component, unlike the corresponding capillary-wave spectrum observed in systems in thermodynamic equilibrium where the equipartition theorem is applicable [24]. The main plot shows this dominant frequency, \( f_m \) (blue), as a function of the length \( L \), for systems with the same mean density. The data shows that \( f_m \) varies as \( L^{-1} \), suggesting that wave-like sound propagation occurs [26]. The speed of sound is of order 0.2 m s\(^{-1}\), which is comparable with the typical velocity scale set by the vibrating cell, \( A\omega = 0.36 \) m s\(^{-1}\).

The green data in Fig. 4 shows that the relative amplitude of these oscillations \( \delta l/L \) dies away as \( \delta l/L \sim L^{-1/2} \); the fact that both \( \delta l/l \) and \( f_m \) tend to zero as \( L \to \infty \) is our final piece of evidence indicating that the phase separated state is stable in the thermodynamic limit, in contrast to the corresponding equilibrium system which would break up into domains.

Our analysis shows that the granular gas can be described in terms of a reduced form of thermodynamics based on mechanical variables alone. The system evolves so as to minimise any residual mechanical work that can be released through inelastic collisions. Note that in thermodynamic equilibrium the principle of minimising mechanical work still holds. However, as energy is conserved the Maxwell construction must be evaluated along an isotherm. In this case minimising mechanical work is entirely equivalent to maximising entropy.

In the granular gas there is a decoupling of the kinetic and mechanical variables such that the appropriate
equation of state, $p(v)$, is not an ‘isotherm’. The minimisation of residual mechanical work allows a 1D dissipative gas to exhibit complex collective behaviour and emergent phenomena of the kind that are typical of far-from-equilibrium systems in general. As such it would be interesting to investigate whether our findings apply to other driven particle systems.

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