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Thermodynamics and effective temperatures in sheared granular matter and emulsions

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Abstract. Recent theories postulate that the non-equilibrium behavior of systems experiencing jamming or structural arrest could be described by equilibrium thermodynamic concepts. If a thermodynamic framework can describe the behavior of systems far from equilibrium, then an effective temperature with a true thermodynamic meaning exists as a key parameter in characterizing the material's properties. In order to examine the validity of the thermodynamics for jammed systems, we perform a numerical experiment with a realistic granular matter model specially conceived to be reproducible in the laboratory. The results strongly support the thermodynamic picture.

PACS. 81.05.Rm Porous materials; granular materials – 83.80.Lz Physiological materials (*e.g.* blood, collagen, etc.)

1 Introduction

In particulate materials, such as emulsions and granular media, a "jammed" system results if particles are packed together so that all particles are touching their neighbors, provided the density is sufficiently high. In granular systems and compressed emulsions there is no kinetic energy of consequence; the typical energy required to change the positions of the jammed particles is very large compared to the thermal energy at room temperature. As a result, the material remains arrested in a metastable state and is able to withstand an applied stress.

The focus of this paper is the study of a thermodynamic formulation for systems undergoing structural arrest or approaching the jammed state. In particular we study: densely packed granular materials [1–3] and compressed emulsion systems [4–6].

The similarities between a driven granular system and a system of molecules in a fluid have prompted the use of statistical ideas to describe granular matter [7], such as, for example, kinetic theories of gases to study rapid flows of low-density systems of inelastic particles [8]. In this context, it is customary to associate the mean kinetic energy of the particles with a "granular temperature".

On the other hand, systems like slowly moving and highly compacted granular materials and compressed emulsions are both far from equilibrium and jammed, therefore the thermodynamic approach is rather more complex. These disordered systems are examples of out-of-equilibrium systems belonging to a new class of "jammed materials", characterized by slow relaxation dynamics. These systems involve many-body interactions leading to a collective structural evolution, much slower than the microscopic motion of the constitutive particles. Jammed matter is very often out of equilibrium, since a laboratory experiment generally takes place on time scales shorter than the characteristic relaxation time of the matter. Consequently, the behavior of these systems is very difficult to understand as the general tools of statistical mechanics are insufficient. The thermodynamic picture which we are aiming to explore is the application of the powerful tools of equilibrium statistical mechanics to help explain a different set of natural phenomena —the physics of static and weakly driven jammed matter.

1.1 Background

A new train of ideas was initiated more than a decade ago by Edwards and co-workers from Cambridge University: the proposal of a statistical ensemble [9], and through it, thermodynamic notions such as entropy and temperature (the latter unrelated to the "granular temperature" above). Recent work has yielded evidence supporting the existence of effective temperatures for several systems such as foams, Lennard-Jones glasses, finite-dimensional models of the glass transition, and lattice gases [10–17]. Recent experimental work [18] has provided further evidence of the validity of the thermodynamic framework. In particular, in a recent numerical study we showed preliminary

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evidence for the existence of an effective temperature and the validity of the thermodynamics for granular materials within certain limits [17]. The existence of a well-defined temperature leads the way to a development of a thermodynamic formulation for all jammed materials and has initiated a renewed interest in describing such systems as a whole. In what follows we review our recent findings.

2 Numerical results

2.1 Einstein relation and effective temperature

Consider a "tracer" body of arbitrary shape immersed in a liquid in thermal equilibrium. As a consequence of the irregular bombardment by the particles of the surrounding liquid, the tracer performs a diffusive, fluctuating "Brownian" motion. The motion is unbiased, and for large times the average square of the displacement goes as $\langle |x(t) - x(0)|^2 \rangle = 2Dt$, where D is the diffusivity. On the other hand, if we pull gently on the tracer with a constant force f, the liquid responds with a viscous, dissipative force. The averaged displacement after a large time is $\langle [x(t) - x(0)] \rangle = f\chi t$, where χ is the mobility. Although both D and χ strongly depend on the shape and size of the tracer, simulation results show they are related by the Einstein relation $T = D/\chi$ (a form of the Fluctuation-Dissipation Theorem, FDT), where T is the temperature of the liquid.

2.2 Test for particulate systems

The Einstein relation is strictly speaking only valid for equilibrium thermal systems. The existence of its application in out-of-equilibrium particulate systems under slow shear begs exploration. In the absence of a first principle derivation, one needs to ascertain its validity for every particular case experimentally, or numerically at the least.

We performed molecular-dynamics (MD) simulations for a binary system of large and small soft spheres in a periodic 3D cell [17]. In the model, deformable spherical grains interact with one another *via* non-linear elastic Hertz normal forces, and non-linear elastic and path-dependent Mindlin transverse forces [19]. The normal force, F_n, has the typical 3/2 power law dependence on the overlap between two spheres in contact, while the transverse force, F_t, depends on both the shear and normal displacements between the spheres. For two spherical grains with radii R_1 and R_2: $F_\mathrm{n} = \frac{2}{3}\, k_\mathrm{n} R^{1/2} w^{3/2}$, $\Delta F_\mathrm{t} = k_\mathrm{t}(Rw)^{1/2}\Delta s$. Here $R = 2R_1R_2/(R_1 + R_2)$, the normal overlap is $w = (1/2)[(R_1+R_2) - |\mathbf{x}_1 - \mathbf{x}_2|] > 0$, and $\mathbf{x}_1$, $\mathbf{x}_2$ are the positions of the grain centers. The normal force acts only in compression, $F_\mathrm{n} = 0$, when $w < 0$. The variable s is defined such that the relative shear displacement between the two grain centers is $2s$. The prefactors $k_\mathrm{n} = 4G/(1-\nu)$ and $k_\mathrm{t} = 8G/(2-\nu)$ are defined in terms of the shear modulus G and Poisson's ratio ν of the material from which the grains are made (typically $G = 29$ GPa and $\nu = 0.2$, for spherical glass beads). We assume a distribution of grain radii in which $R_1 = 0.105$ mm for half the grains and $R_2 = 0.075$ mm for the other half. The observables are measured in reduced units: length in units of R, force in units of GR^2, time in units of $\sqrt{\rho R^2/G}$, where ρ is the density of the particles. Internal dissipation is included in two ways: 1) *via* a viscous damping term proportional to the relative normal and tangential velocities, and 2) *via* sliding friction: when F_t exceeds the Coulomb threshold, μF_n, the grains slide and $F_\mathrm{t} = \mu F_\mathrm{n}$, where μ is the friction coefficient between the spheres (typically $\mu = 0.3$).

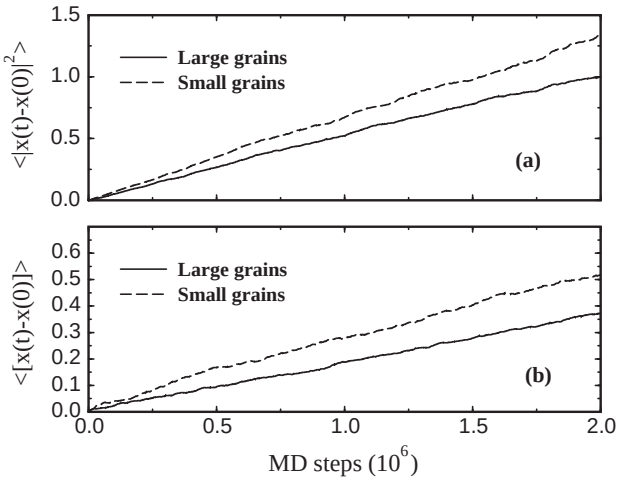

Fig. 1. (a) Diffusion and (b) response function for the large and small particles in a sheared granular material measured perpendicular to the shear plane as a function of time in MD steps. Both quantities depend linearly on time at the late stages of the evolution. The response function is measured by applying a constant force f in the x-direction to each type of particle. The obtained diffusivities and mobilities depend on the particles size as expected.

We apply a gentle shear in the y-direction at constant volume by moving the periodic images at the top and bottom of the cell with velocities $\dot{\gamma}L/2$, where $\dot{\gamma}$ is the shear rate (Lees-Edwards boundary conditions). In this simple shear flow the gradient of the velocity along z is uniform (no shear bands). We focus our study on the slow shear rate, quasi-static limit where the system is always close to jamming, but moves just barely enough to avoid stick-slip motion [20]. Here the external pressure is large enough ($\sim$ 10 MPa in a typical simulation) and the average coordination number is high enough (typically ~ 7) that deformation and elasticity of the particles play the dominant role, as opposed to the collision-dominated rapid-flow regime described by kinetic theories. We checked that shear induced segregation is absent at the times scales of our simulations. The contacts between particles are enduring and the internal stresses in the system are transmitted *via* a network of "force chains" [7] independent of the shear rate.

After a transient of the order of the inverse shear rate, we start measuring the spontaneous $\langle |x(t) - x(0)|^2 \rangle$ and force-induced displacements $\langle [x(t) - x(0)] \rangle / f$ along the x-direction for the two types of particles with different

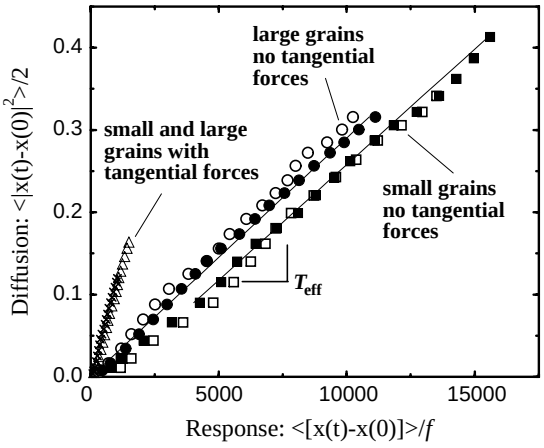

Fig. 2. Parametric plot of diffusion *vs.* response function for small and large grains and for spheres interacting with tangential forces and without tangential forces (Coulomb frictionless). The fitting at long time scales shows the existence of a well-defined temperature which is the same for small and large grains: $T_{\rm FDT} = 2.8 \times 10^{-5}$ for grains without transverse forces and $T_{\rm FDT} = 1.2 \times 10^{-4}$ for grains with Mindlin transverse forces and Coulomb friction. We calculate the response function for several small external fields and find the same temperature indicating that we are in the linear response regime. Averages are taken over 30 realizations. Plotted are results for a system without transverse forces using $f = 1.7 \times 10^{-5}$ (small grains □, large grains ○) and $f = 2.6 \times 10^{-5}$ (small grains ■, large grains ●). For a system with tangential forces and Coulomb friction we show the case $f = 6 \times 10^{-5}$ (small grains △, large grains ×).

sizes. We find that the diffusivities and the mobilities are different for the two types of particles, since they have different sizes (Fig. 1). However, when we draw the parametric plot of $\langle |x(t) - x(0)|^2 \rangle$ *versus* $\langle [x(t) - x(0)] \rangle / f$ (Fig. 2), we find parallel straight lines for large time scales, implying an extended Einstein relation:

$$\langle |x(t) - x(t_w)|^2 \rangle = 2\ T_{\rm FDT} \frac{\langle [x(t) - x(t_w)] \rangle}{f}, \qquad (1)$$

valid for both particles *with the same* FDT temperature $T_{\rm FDT}$ for widely separated time scales $t \gg t_w$. This suggests that $T_{\rm FDT}$ can be considered to be the temperature of the slow modes.

For small time scales (fast rearrangements, near the origin in Fig. 2) the fluctuation-dissipation plot shows that there is not a well-defined Einstein-relation temperature. We expect this result since the fast motion of the grains depends on the microscopic interactions dominated by inelastic collisions. We also calculate the "granular kinetic temperature" defined in terms of the velocity fluctuations in the x-direction. Unlike $T_{\rm FDT}$, we find that this temperature is different for the two types of particles, and their values are two orders of magnitude smaller than $T_{\rm FDT}$. We expect this result since the kinetic granular temperature is dominated by the fast (high-frequency) modes, which are not thermalised to $T_{\rm FDT}$.

We also repeat the numerical experiment for a system of Hertz spheres without transverse forces ($\mu = 0$: experimental realizations of elastic spheres with viscous forces but without sliding friction are foams and compressed emulsions [4,5]) and find that $T_{\rm FDT}$ is well defined at long time scales for this case as well (see Fig. 2). Thus, our results suggest that the validity of a structural temperature for long-scale displacements (larger than a fraction of the particle size) holds in the presence of viscous forces between grains or even of a sliding threshold (Coulomb's law).

The fact that slow relaxation modes can be characterized by a temperature immediately raises the question of the existence of a hidden form of ergodicity for the structural motion, allowing a construction of a statistical mechanics ensemble of the slow motion of grains. This argument leads us back to the ideas of the thermodynamics of jammed states.

2.3 Thermodynamics based on jammed states

The statistical ensemble for dense, static and slow-moving granular materials and glasses is based on the notion of the material exploring a number of jammed configurational states [9]. The statistical ensemble is based on two postulates:

1) While in the Gibbs construction for equilibrium statistical mechanics one assumes that the physical quantities are obtained as an average over all possible configurations at a given energy, the granular ensemble consists of only the static or jammed configurations at the appropriate energy and volume.

2) The strong ergodic hypothesis is that all jammed configurations of a given volume and energy can be taken to have equal statistical probabilities.

This formulation immediately leads to a configurational entropy (or "packing entropy") as the logarithm of the number of jammed configurations $\Omega_{\rm jammed}(E, V)$, and the corresponding configurational temperature

$$S_{\rm conf}(E, V) = \ln \Omega_{\rm jammed}(E, V)\,, \qquad T_{\rm conf}^{-1} = \frac{\partial S_{\rm conf}}{\partial E}. \quad (2)$$

An interpretation of the configurational temperature and entropy is given in Figure 3.

Next, we treat the question whether it is possible to relate the FDT temperature obtained above to the thermodynamic construction of slowly driven out-of-equilibrium systems proposed by Edwards.

2.4 Calculation of the configurational temperature

In order to calculate $T_{\rm conf}$ and compare with the obtained $T_{\rm FDT}$, we need to calculate the entropy of the packing. (For this calculation we concentrate on the case without tangential forces and sliding friction, in order to avoid path dependency which would lead to an ambiguity in the definition of jammed configurations —see below.) This

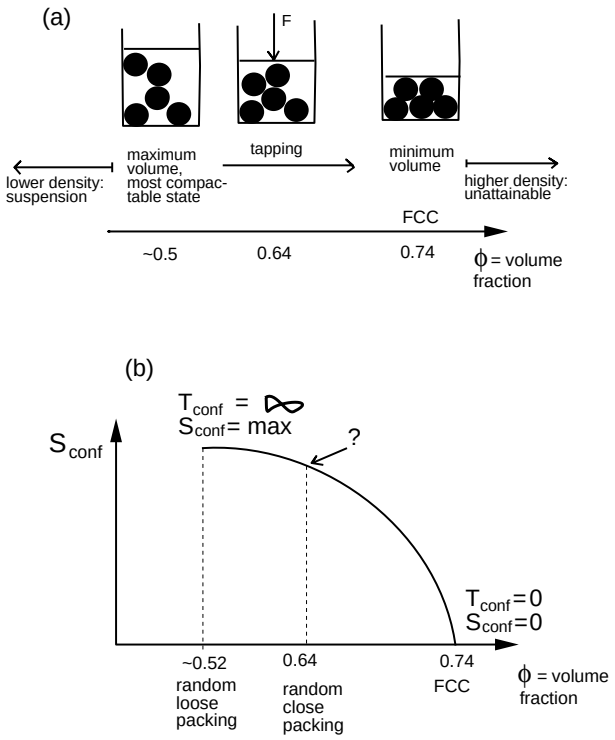

Fig. 3. (a) Interpretation of the configurational temperature and entropy in terms of different packings of granular materials. (b) A sketch of a possible result for the configurational entropy *versus* volume fraction.

is impossible to do directly, except for small systems. To do this in practice, we use a modification of the standard thermodynamics integration methods to compute the configurational entropy [21]. We resort here to an indirect "auxiliary model" method [12,17], modified to the case of deformable grains. In practice, it consists of computing, using any standard method (Monte Carlo, MD, etc.) the equilibrium properties of the granular system in the cell in the absence of viscous dissipation and external shear with the modified partition function

$$Z \simeq \sum \exp[-E/T^* - E_{\rm jammed}/T_{\rm aux}]\,, \qquad (3)$$

where E is the true deformation energy leading to the Hertz contact force, and

$$E_{\rm jammed} \propto \sum_a |\mathbf{F}_a|^2 \qquad (4)$$

is an energy term that vanishes in (and only in) the jammed configurations. (Here $\mathbf{F}_a$ is the total contact force exerted on particle a by its neighbours.)

Annealing $T_{\rm aux}$ to zero selects the jammed configurations ($\sum_a |\mathbf{F}_a|^2 \to 0$), while T^* fixes the Hertz energy E. Thus, the dynamical system studied previously *via* the Einstein relation is now augmented by a temperature T^* setting the mean elastic potential energy per grain, plus an additional auxiliary temperature, $T_{\rm aux}$, which relates to an energy $E_{\rm jammed}$ that vanishes if and only if the total force on each grain is zero (*i.e.* in the jammed configurations).

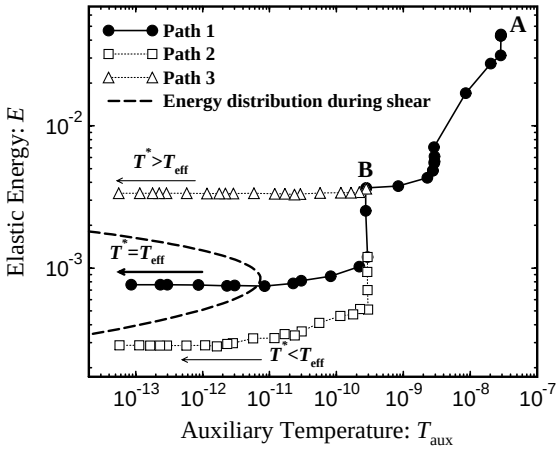

Fig. 4. Annealing procedure to calculate $T_{\rm conf}$ at different true energies. We plot the true deformation energy *versus* $T_{\rm aux}$ together with the distribution of deformation energies obtained during shear (dashed curve, mean value $\langle E\rangle = 8.4\times10^{-4}$).

We start by equilibrating the system at high temperatures ($T_{\rm aux}$ and $T^* \sim \infty$) and anneal slowly the value $T_{\rm aux}$ to zero and tune T^* to achieve a given final Hertz energy E. At the end of the procedure one reads directly Edwards' temperature as $T_{\rm conf}(E) = T^*(E)$, since in the limit $T_{\rm aux} \to 0$ we are sampling the configurations with vanishing fraction of moving particles at a given E.

Figure 4 shows various annealing protocols. We plot the value of the true deformation energy as a function of $T_{\rm aux}$ during annealing using different values of T^* as indicated in the figure. At the end of the annealing process the system stabilizes at a given deformation energy. We equilibrate the system for 40 million iterations at A: $(T^* = 3.4\times10^{-2}, T_{\rm aux} = 3\times10^{-8})$. We then anneal slowly both temperatures until B: $(T^* = 3.4\times10^{-4}, T_{\rm aux} = 3\times10^{-10})$, where we split the trajectory in three paths in the $(T^*, T_{\rm aux})$-plane. Path 1: we anneal $T_{\rm aux} \to 0$ and $T^* \to 2.8\times10^{-5}$ which corresponds to $T_{\rm FDT}$ obtained during shear (Fig. 2). Path 2: we anneal $T_{\rm aux} \to 0$ and $T^* \to 3.4\times10^{-6}$. Path 3: we anneal $T_{\rm aux} \to 0$ but keep $T^* = 3.4\times10^{-4}$ constant. When we set $T^* = T_{\rm FDT}$ (Path 1), the final true energy value when $T_{\rm aux} \to 0$ falls inside the distribution of energies obtained during shear and it is very close to the mean energy of the system under shear $\langle E\rangle$. This proves that $T_{\rm FDT} = T_{\rm conf}$ under the numerical accuracy of the simulations. For other values of $T^* \neq T_{\rm FDT}$ the final E falls out of the distribution obtained during shear (Paths 2 and 3). We also follow different trajectories (not shown in the figure) to $T^* \to 2.8\times10^{-5}, T_{\rm aux} \to 0$ and find the same results indicating that our procedure is independent of the annealing path.

3 Concluding remarks

We conclude with some remarks: i) Since the jammed configurations are the same whatever the inter-grain dissipation coefficient, Edwards' ensemble (and hence its temperature) are *insensitive to viscous dissipation.*

ii) On the contrary, tangential forces and sliding friction block certain configurations, depending on how they are accessed. The ensemble of jammed configurations is then ill-defined. We have not tried to construct any ensemble, but content ourselves with the observation that $T_{\rm FDT}$ is also in this case independent of the particle size (Fig. 2) —we suspect that thermodynamic concepts apply, but that the relevant ensemble goes beyond Edwards' construction as it stands.

iii) We have tested the validity of the thermodynamics in an ideal homogeneous system with periodic boundary conditions by explicitly avoiding structural features of dense granular flows such as shear bands and segregation of the species. Even though it remains to be seen whether the thermodynamic picture can account for these inhomogeneous effects, our ideal system may prove to be useful in deriving constitutive relations to be used in macroscopic theories of slow granular flows.

To summarize: we have performed numerically an experiment with dense granular systems specially conceived to be a "dress rehearsal" for the real laboratory one. The independence of the Einstein-relation temperature from the tracer provides a strong test for the thermodynamic ideas. We have also showed that this temperature, obtained from measurable quantities, indeed matches Edwards' one. Experimental verifications of the existance of effective temperature in sheared granular matter are ongoing. If this result is confirmed in the laboratory, this will give an experimental foundation for the use of the powerful tools of statistical mechanics as the framework to study this kind of far-from-equilibrium dissipative dynamical system.

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