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A thermodynamic approach to slowly sheared granular matter

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Abstract

Recent theories postulate that the non-equilibrium behaviour of systems experiencing jamming or structural arrest could be described by equilibrium thermodynamic concepts. If a thermodynamic framework can describe the behaviour 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 support the thermodynamic picture.

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1. Introduction

The focus of this study is on the study of complex, out-of-equilibrium, jammed systems [1]. In particular, we consider the following systems: Granular materials and compressed emulsions under slow shear motion. Refs. [2–5], and colloidal suspensions undergoing structural arrest and jamming at high-volume fractions [6].

These disordered systems are but a few 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 their characteristic relaxation time. Consequently,

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the behaviour of these systems is very difficult to understand as the general tools of statistical mechanics are insufficient.

It is thought that there is a need for a new theoretical description for jammed matter, as well as new experimental evidence to unify the predicted state for all varieties of jammed systems. The prediction of how these different systems jam with respect to the applied stress, density and temperature has led to a speculative "phase diagram" proposed by Liu and Nagel [5]. It links the behaviour of several very different systems by the dynamics of their approach to jamming. When the external driving force is too small, these materials become amorphous solids and develop a yield stress. If it were true that temperature and applied stress play a similar role in unjamming the systems according to the proposed phase diagram, one could imagine describing driven, athermal systems of different types by concepts of statistical mechanics, and characterizing them by an effective temperature.

Background. Previous work: A new set of ideas was introduced more than a decade ago by S.F. Edwards and coworkers from Cambridge University to describe the aforementioned systems [7]. The key to the novel theoretical approach is the proposal of a statistical ensemble, and through it, thermodynamic notions such as entropy and temperature. Although the idea of a thermodynamic description of granular matter was recognized as attractive, it was not universally accepted. This controversy as to the validity of the proposed theory stems from there being no known first principle justification of Edwards' statistical ensemble, such as there is for ordinary statistical mechanics of liquids or gases (Liouville's theorem). Since the observable properties such as temperature, stress and density can be computed by consideration of only the blocked configurations in a given system, it is possible to test the thermodynamics numerically and by experimentation. Thus, this thermodynamic approach is intimately related to the ideas put forward in the jamming phase diagram.

Recently, theoretical and numerical work on schematic models for glassy systems and granular matter has yielded evidence supporting the existence of effective temperatures with a thermodynamic meaning for several out-of-equilibrium systems [8–15]. This has spurred a renewed interest in the out-of-equilibrium thermodynamics as a whole. In particular, in a recent work in collaboration with J. Kurchan from ESPCI, Paris we have shown evidence of the existence of an effective temperature and of the validity of a thermodynamic picture for granular materials at least in certain limits [16]. We performed a numerical study specially conceived to be reproducible in the laboratory, using a realistic model of sheared granular matter. The existence of a well-defined thermodynamic temperature leads the way to a development of a thermodynamics formulation for all jammed materials. Here we review this work.

2. Theoretical considerations: effective temperature and thermodynamics

The thermodynamic picture which we are trying 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. Systems like granular matter are both far from equilibrium and athermal, therefore, the

thermodynamic approach is rather more complex. The absence of a well-defined thermodynamic temperature in situations of slow dense flow is due to the fact that the typical energy needed to change the positions of the jammed particles and droplets is very large compared to their thermal energy at room temperature. Hence, the energy to induce slow flow is supplied by an external driving force and dissipated by inelastic interactions and a slippage between particles. This is a very different "heat exchange mechanism" from that of a Brownian thermal bath in a molecular systems. In the case of a thermal system such as a colloidal suspension of micrometer PMMA particles, Brownian motion is observed at low concentrations. However, when the volume fraction of the suspension is increased towards the glass transition (volume fraction ~ 0.58), they undergo a structural arrest which can be studied in terms of the same concepts we will develop for granular materials [6].

Edwards formulation for granular matter: The granular thermodynamics proposed by Edwards is based on two postulates:

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

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

This formulation immediately leads to an entropy $S_{\mathrm{Edw}}(E,V) = \ln \Omega_{\mathrm{jam}}(E,V)$ as the logarithm of the number of jammed configurations $\Omega_{\mathrm{jam}}(E,V)$, and the corresponding temperature

$$T_{\mathrm{Edw}}^{-1} = \frac{\partial S_{\mathrm{Edw}}}{\partial E} \tag{1}$$

and compactivity $X^{-1} = \partial S_{\mathrm{Edw}}/\partial V$.

Evidence to support the theory: Some insight into the validity of the thermodynamics first came from glass theory, by exploiting the analogy between the relaxation of powders [9] and aging in glassy systems. Recent analytic schemes for out-of-equilibrium glassy systems have shown that the Einstein relation gives rise to a well-defined "effective temperature" which is different from the bath temperature. It governs the heat flow, the slow components of fluctuations and responses of all observables [17,18]. The existence of an effective temperature with a thermodynamic meaning suggests a hidden form of 'ergodicity' for the slow modes of relaxation, which turns out to be closely related to Edwards' statistical ideas [7] for systems undergoing slow compaction. Explicit checks of this approach have been made so far within the mean-field/mode-coupling models of the glass transition [18], as well as for schematic finite-dimensional models of glassy systems [10,13–15].

Test for granular systems: In order to test the existence of an effective temperature with a thermodynamic meaning for dense slowly moving granular matter, we have recently performed a numerical study of a diffusion-mobility experiment in conditions that can be reproduced in the laboratory [16]. The results strongly support the thermodynamic picture.

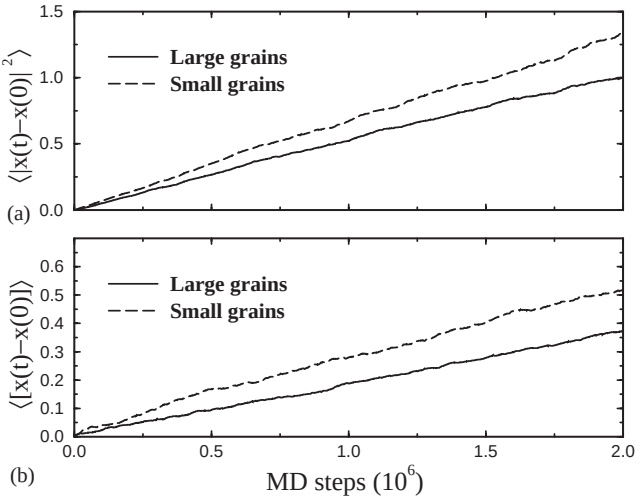

Fig. 1. (a) Diffusion and (b) response function for the large and small particles in a sheared granular material measured perpendicular to the shear plane as a function of time in MD steps. Both quantities depend linearly on time at the late stages of the evolution.

We performed molecular dynamics (MD) simulations for a binary system of large and small soft spheres in a periodic 3D cell. We applied a gentle simple shear flow at constant volume and measured the spontaneous fluctuations $\langle |x(t) - x(t_w)|^2 \rangle$ and force-induced displacements $\langle [x(t) - x(t_w)] \rangle / f$, where f is a small external force, for two types of tracers with different sizes. The results are shown in Fig. 1. We notice that the diffusivities and the mobilities are different for the two type of particles, as expected. However, when we draw the parametric plot of $\langle |x(t) - x(0)|^2 \rangle$ vs. $\langle [x(t) - x(0)] \rangle / f$ (Fig. 2) we find parallel straight lines for large time scales, implying an extended Einstein relation:

$$\langle |x(t) - x(0)|^2 \rangle = 2T_{\text{eff}} \frac{\langle [x(t) - x(0)] \rangle}{f} \tag{2}$$

valid for both particles *with the same* T_{eff} *for large time scales*. This suggests that T_{eff} can be considered to be the temperature of the slow modes.

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) and find that T_{eff} is well defined at long time scales for this case as well (see Fig. 1). Thus, our results suggest that the validity of an effective 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 proposed ideas by Edwards.

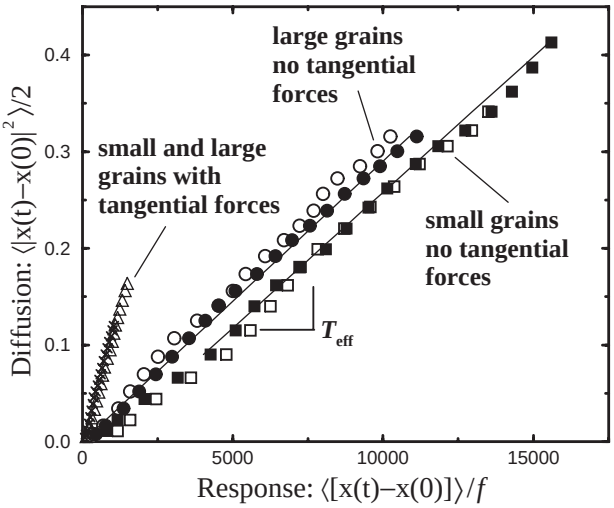

Fig. 2. Parametric plot of diffusion vs. response function for small and large grains and for spheres interacting with tangential forces and without tangential forces (Coulomb frictionless). The fitting at long time scales shows the existence of a well-defined temperature which is the same for small and large grains: $T_{\rm eff} = 2.8 \times 10^{-5}$ for grains without transverse forces and $T_{\rm eff} = 1.2 \times 10^{-4}$ for grains with Mindlin transverse forces and Coulomb friction. These effective temperatures are very large, i.e., $\sim 10^{14}$ times kT at room temperature, as expected.

Next, we treat the question whether it is possible to relate the effective temperature obtained above to the thermodynamic construction of out-of-equilibrium systems proposed by Edwards. In order to calculate $T_{\rm Edw}$ and compare with the obtained $T_{\rm eff}$ we need to count the number of jammed configuration at a given energy and volume (for this calculation we concentrate in 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). Counting directly all jammed configurations is impossible, except for small systems. To do it in practice, we resort here to an indirect 'auxiliary model' method [10] suitably modified to the case of deformable grains. It consists of computing, using any standard method (Monte Carlo, MD, etc.) the equilibrium properties of the granular system in the periodic cell with the modified partition function $\sum \exp[-E/T^* - E_{\rm jammed}/T_{\rm aux}]$, where E is the elastic compressional potential energy leading to the Hertz contact force, and $E_{\rm jammed} \sim \sum_a |\vec{F}_a|^2$, with $\vec{F}_a$ the total contact force exerted on particle a by its neighbours. Thus, the dynamical system studied previously via the Einstein relation is now augmented by a temperature T^* setting the mean elastic energy per grain, plus an auxiliary temperature, $T_{\rm aux}$, which relates to the (artificial) term $E_{\rm jammed}$ which selects, in the limit $T_{\rm aux} \to 0$, the configurations where the grains are jammed ($E_{\rm jammed} \to 0$).

One can show, although this may not be immediately obvious, that the following protocol yields the correct Edwards temperature at energy E. One starts by equilibrating the system at high temperatures ($T_{\rm aux}$ and $T^* \sim \infty$), and anneals slowly the value $T_{\rm aux}$

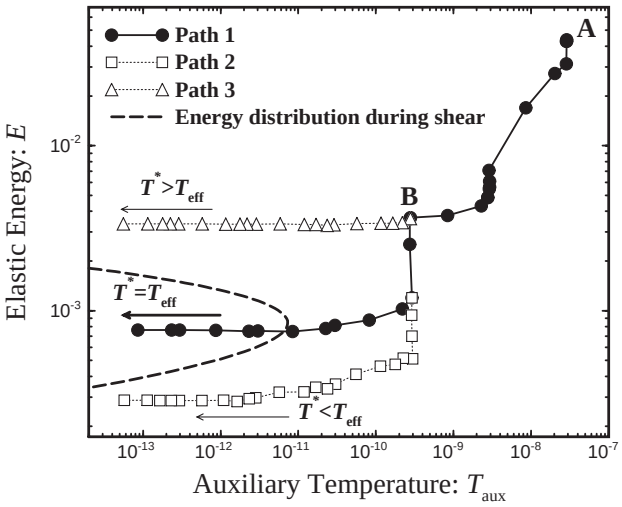

Fig. 3. Annealing procedure to calculate T_{Edw} at different elastic compressional energies. We plot the elastic energy vs. T_{aux} during the annealing together with the distribution of elastic energies obtained during shear (dashed curve, mean value $\langle E\rangle = 8.4\times 10^{-4}$). When we set $T^* = T_{eff}$ (Path 1), the final elastic compressional energy value when $T_{aux} \to 0$ falls inside the distribution of energies obtained, and it is very close to the mean value of the elastic energy during shear $\langle E\rangle$. This proves that $T_{eff} = T_{Edw}$ under the numerical accuracy of the simulations.

to zero while tuning T^* so as to achieve a given final elastic potential energy E. At the end of the procedure ($T_{aux} \to 0$) one reads directly Edwards' temperature as $T_{Edw}(E) = T^*(E)$. This simulation is performed with the same system parameters as in the previous dynamical simulations within the shearing cell, but without viscous internal dissipation and external shear. We note that the procedure is a calculational trick, and it does not correspond to any real experimental protocol.

In Fig. 3 we plot the elastic compressional energy as a function of T_{aux} for three annealing protocols using different values of T^* and the distribution of compressional elastic energies obtained during the shearing experiments superimposed. The y-intercept of each annealing curve gives, as mentioned above, the value of E at $T_{Edw} = T^*$. Only when we set T^* equal to T_{eff} (as obtained through the Einstein relation in the shearing cell), do we find that the final E coincides, within the accuracy of the simulations, with the mean elastic compressional potential energy of the system under shear (see Fig. 3). *This shows the agreement between Edwards' T_{Edw} and the effective temperature T_{eff}.*

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*, as long as we are in the slow flow regime of interest in this study.

(ii) On the contrary, tangential forces and sliding friction may or may not block certain configurations, depending on how they are accessed: the ensemble of jammed

configurations is then ill-defined. We have not tried to construct a suitable ensemble in this case, but content ourselves with the observation that T_{eff} is also in this case independent of the particle size (Fig. 2)—our results suggest that thermodynamic concepts still apply, but the relevant ensemble for frictional systems necessarily 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 inhomogeneities and shear bands (by imposing a uniform shear rate), segregation of the species or long-range order. Thus, the experimental test of our computational results may be complicated by, for instance, the formation of shear bands which tend to be present in physical systems. Even though it remains to be seen whether the thermodynamic picture may account for these highly nonlinear and dissipative 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 first performed numerically a diffusion-mobility experiment with a dense slowly sheared granular systems specially conceived to be a 'dress rehearsal' for the real laboratory one. The independence of T_{eff} on the tracer' size provides a strong test for an underlying thermodynamics. We have then independently computed the configurational temperature T_{Edw} based on the entropy of jammed configurations and verified that, remarkably, it coincides with T_{eff}—thus supporting Edwards' statistical mechanical ideas. This last step cannot be performed in the laboratory, so the numerical simulation provides the missing link between thermodynamic ideas and diffusion-mobility checks.

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References

[1] R.P. Behringer, J.T. Jenkins (Eds.), Powders and Grains 97, Balkema, Rotterdam, 1997.
[2] H.M. Jaeger, S.R. Nagel, R.P. Behringer, The physics of granular materials, Rev. Mod. Phys. 68 (1996) 1259.
[3] M.-D. Lacasse, G.S. Grest, D. Levine, T.G. Mason, D.A. Weitz, Model for the elasticity of compressed emulsions, Phys. Rev. Lett. 76 (1996) 3448–3451.
[4] D.J. Durian, Foam mechanics at the bubble scale, Phys. Rev. Lett. 75 (1995) 4780–4783.
[5] A.J. Liu, S.R. Nagel, Jamming is not just cool any more, Nature 396 (1998) 21.
[6] E.R. Weeks, J.C. Crocker, A.C. Levitt, A. Schofield, D.A. Weitz, Three-dimensional direct image of structural relaxation near the colloidal glass transition, Science 287 (2000) 627.
[7] S.F. Edwards, The role of entropy in the specification of a powder, in: A. Mehta (Ed.), Granular Matter: An Interdisciplinary Approach, Springer, New York, 1994, pp. 121–140, and references therein.
[8] S.A. Langer, A.J. Liu, Sheared foam as a supercooled liquid? Europhysics Lett. 49 (2000) 68–73.
[9] J. Kurchan, Emergence of macroscopic temperatures in systems that are not thermodynamical microscopically: towards a thermodynamical description of slow granular rheology, J. Phys.: Condens. Matter 29 (2000) 6611.

[10] A. Barrat, J. Kurchan, V. Loreto, M. Sellitto, Edwards measures for powders and glasses, Phys. Rev. Lett. 85 (2000) 5034–5037;
A. Barrat, J. Kurchan, V. Loreto, M. Sellitto, Edwards' measures: a thermodynamic construction for dense granular media and glasses, Phys. Rev. E 63 (2001) 51301, and references therein.
[11] I.K. Ono, C.S. O'Hern, S.A. Langer, A.J. Liu, S.R. Nagel, Effective Temperatures of a Driven System Near Jamming, cond-mat/0110276.
[12] L. Berthier, J.-L. Barrat, Non-equilibrium dynamics and fluctuation–dissipation relation in a sheared fluid, cond-mat/0111312.
[13] M. Nicodemi, Dynamical response functions in models of vibrated granular media, Phys. Rev. Lett. 82 (1999) 3734–3737.
[14] J. Javier Brey, A. Prados, B. Sanchez-Rey, Thermodynamic description in a simple model for granular compaction, Physica A 275 (2000) 310–324.
[15] F. Sciortino, P. Tartaglia, Extension of the fluctuation–dissipation theorem to the physical aging of a model glass-forming liquid, Phys. Rev. Lett. 86 (2001) 107–110.
[16] H.A. Makse, J. Kurchan, Testing the thermodynamics approach to granular matter with a numerical model of a decisive experiment, Nature 415 (2002) 614–617.
[17] L.F. Cugliandolo, J. Kurchan, L. Peliti, Energy flow, partial equilibration, and effective temperatures in systems with slow dynamics, Phys. Rev. E 55 (1997) 3898–3914.
[18] J. Kurchan, Rheology and how to stop aging, in: A. Liu, S.R. Nagel (Eds.), Jamming and Rheology: Constrained Dynamics on Microscopic and Macroscopic Scales, Taylor & Francis, London, 2001, cond-mat/9812347.