Rigidity in Solids

by

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Abstract

We address the question of whether solids may be distinguished from fluids by their response to shear stress.

* Research supported in part by NSF Grant DMS-0700120

I. Introduction

Our focus is the theoretical modeling, within statistical mechanics, of the solid/fluid phase transition of matter in thermal equilibrium, for instance the ice/water transition, at high pressure and temperature, and in particular the use of rigidity to distinguish the phases.

There are no analytic proofs of a solid/fluid transition in any statistical mechanics model which uses particles in space interacting through simple short range forces (see however [1]), though there are many simulations showing the transition, both Monte Carlo and molecular dynamics. Since we concentrate on the transition at high pressure and temperature, at which short range repulsion dominates the interparticle interaction, the classical hard sphere model is appropriate [2, page 84]; again there are no proofs of a phase transition in this model, but there are many simulations [2,3]. Traditionally such a transition is "understood" theoretically through an order parameter associated with some global (emergent) property of the bulk material, in particular the molecular-level crystalline symmetry which can be detected experimentally in X-ray scattering [4]. This paper follows an alternative proposal of Anderson [5], namely the use of rigidity, the response to stress, to distinguish the phases, for instance in a hard sphere model.

Stress, both pressure and shear, will be understood here as an external influence (force per unit area) on the boundary of a finite sample of the material, with pressure acting on the volume and shear on the shape; its extension to a uniform stress field inside the material is an important issue to be addressed, both in modeling and in real materials. Pressure is commonly incorporated in statistical mechanics as a parameter in a pressure ensemble, controlling the fluctuations of volume. A similar approach can be followed for shear, using a set of parameters controlling fluctuations of the shape of the container, though this is much less common; see however [6,7].

One might in principle be able to distinguish ice from water through statistical mechanics estimates of compressibility ($-[\partial V/\partial p]/V$), in which V is volume and p is pressure. Unfortunately the compressibility of ice and water are both high and the difference is relatively small, a common circumstance for a solid/fluid transition. However the difference in the corresponding elastic shear constants is, experimentally, much greater, since elastic shear constants are negligible for (isotropic) fluids. This suggests an advantage in using shear instead of pressure to distinguish a solid from its melt.

But, as emphasized for instance in the recent paper of Sausset et al [8], for a material in equilibrium any linear response to macroscopic shear must be transient in time, making it harder to model an elastic shear constant within equilibrium statistical mechanics. Indeed, there are proofs that the free energy of equilibrium statistical mechanics is independent of the shape of the material [9,10], which suggests that shear stress be properly considered as taking a material out of equilibrium. In [8] solids are treated as highly viscous fluids and solids are distinguished from fluids by a dynamical feature, the divergence of the viscosity as the shear stress vanishes. Since we are using an equilibrium model we focus instead on a spatial issue, namely the question whether the response to shear is localized at the boundary or is (uniformly) distributed throughout the material. We also concentrate on the response to shear stress in the limit of zero shear, computed before any bulk limit. (At zero shear stress the shape of the material is unconstrained; imagine a triaxial shear cell, with negligible friction and in zero gravity.) Mathematically, we are taking advantage of the fact that the limit of vanishing shear need not commute with the infinite volume limit.

Our approach is based on the following idea. A configuration of hard spheres at high pressure must be approximately crystalline, with most particles trapped in a cage of neighbors. A macroscopic change in container shape can be accommodated by adjustments only near the boundary, without affecting the structure in the bulk interior; see Fig. 1. On the contrary a very small change of shape cannot be accommodated in this way and might result in a small deformation of internal structure throughout the configuration rather than just near the boundary; see Fig. 2.

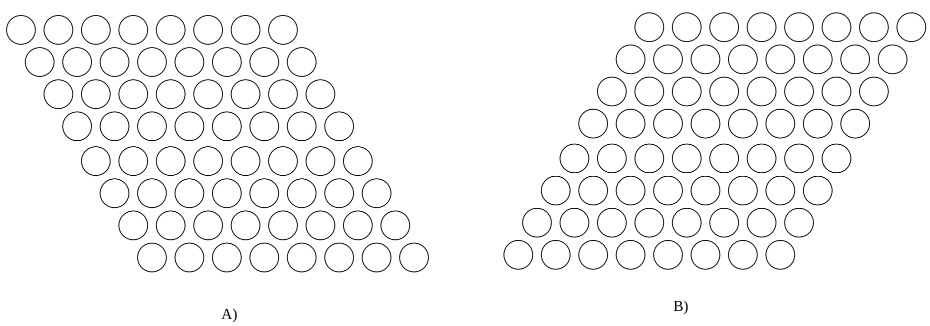

Figure 1. The result of a macroscopic change of strain: the interiors of A) and B) are the same.

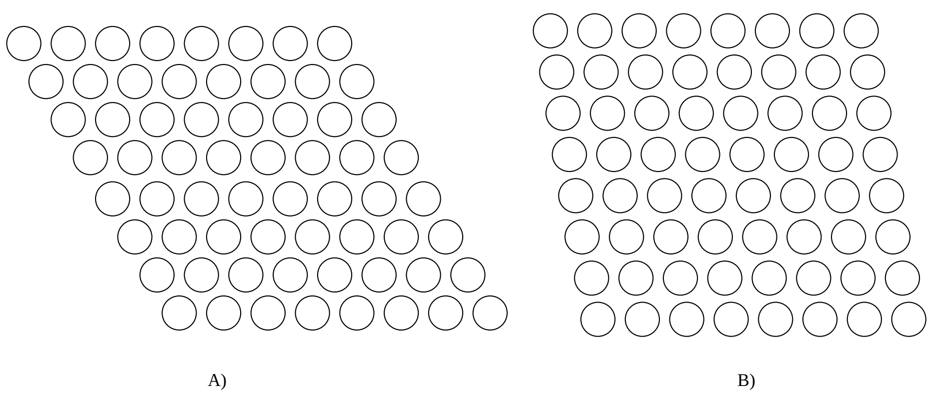

Figure 2. The result of a small change of strain: the interiors of A) and B) are different, the underlying lattice becoming distorted.

In other words, there may be a regime in which the response to shear is linear and extends throughout the material, but such a regime, measured by the angle of deformation, would have to vanish with the size of the system, constituting an equilibrium alternative to the dynamical effect discussed by Sausset et al. If indeed the response extends throughout the material, which is by no means evident, it would be appropriate to measure it, in a finite system at constant high pressure, by the rate of change in density ϕ with respect to f, computed at shear $f = 0$. We expect this to be large in magnitude at high pressure, in the solid phase. At low pressure the model should represent a fluid with negligible response, and we propose this difference as a means of detecting the solid/fluid phase transition.

In the remainder of this paper we give indirect support to the proposition that for infinitesimal shear the material responds linearly throughout the finite sample. We do this by simulation of the two dimensional hard disk model, in a stress (pressure and shear) ensemble. Our measurements in this model show an emerging resistance to shear at volume fraction about 0.7, very close to the known transition(s) for hard disks. Our simulation does not show the details of the transition, which are well displayed in the recent tour-de-force by Bernard and Krauth [11]. Instead, the point of this work is merely to illustrate the feasibility of using density response to infinitesimal shear to probe a solid/fluid phase transition, in the tradition of Anderson [5].

II. The Model and Simulations

We consider arrangements of a fixed number N of hard disks of radius σ inside various parallelograms, with the volume and shape of the parallelograms allowed to vary. More precisely, we consider arrangements of disks inside boundaries formed by placing disks along the edges of parallelograms at regular intervals as in Fig. 3. These boundary disks lie on a regular triangular lattice when the underlying parallelogram is rectangular, and all the parallelograms are related to each other via maps (on the boundary disk centers) of the form $(x, y) \to (\lambda x + \nu\lambda y, \lambda y)$ for real positive λ, ν.

We employ a "stress ensemble" which uses parameters p and f to control the volume V and shape α, respectively, of the parallelograms. (Here p is pressure and f is a component of shear stress.) More precisely, we consider probability measures (states) which minimize the free energy

$$F(p, f) = S - \beta pV + \beta f\alpha V. \tag{1}$$

Here β is the inverse temperature and α is the angle of inclination of a parallelogram, with $\alpha = 0$ representing a rectangle (see Fig. 3). Such an ensemble has partition function

$$Z_{p,f} = \int_0^\infty \int_0^\infty \left(\int_{V,\alpha} dC \right) \exp(-\beta pV + \beta f\alpha V) dV d\alpha, \tag{2}$$

where $\int dC$ represents integration over all arrangements of hard disks in a parallelogram of volume V and shape α. (Temperature plays a simple role in hard core models such as this, so we will assume that numerically $\beta = 1$ where convenient. Also we are using the usual "reduced" ensemble in which the velocity variables have been integrated out.) By the change of coordinates

$$\psi_{V,\alpha} : (x, y) \to (V^{-1/2}(x - \tan(\alpha)y), V^{-1/2}y), \tag{3}$$

considered as a function on the disk centers, the partition function may be rewritten as

$$Z_{p,f} = \int_0^\infty \int_0^\infty \int_\Omega \Phi(\psi_{V,\alpha}^{-1}(Q)) V^N \exp(-\beta pV + \beta f\alpha V) dQ dV d\alpha, \tag{4}$$

where $\Phi(C) = 1$ if no two disks of radius σ with centers from C overlap, $\Phi(C) = 0$ otherwise, and $\Omega \subset \mathbb{R}^2$ is a fixed rectangular area. The probability density of an arrangement of hard disks in a parallelogram of volume V and shape α is then proportional to

$$V^N \exp(-\beta pV + \beta f\alpha V). \tag{5}$$

Because we are interested only in infinitesimal shear, we impose the restriction $0 \leq \alpha \leq 0.01$, with α measured in radians. (For the densities and α we consider, the boundary disks do not come close to overlapping.)

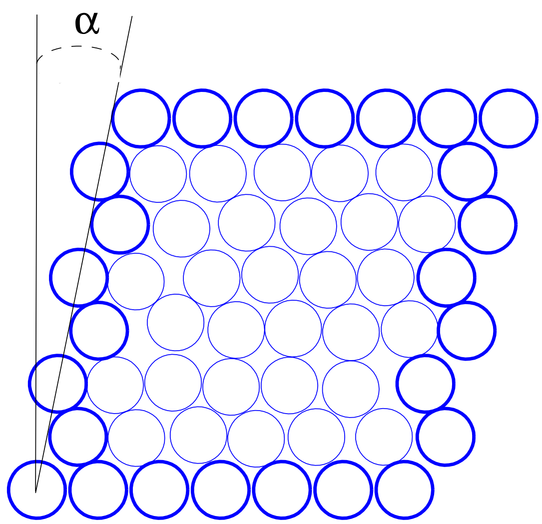

Figure 3. An arrangement of disks in a parallelogram. Boundary disks are in bold; α is the angle formed between the boundary disks and a vertical line.

Let $\phi_{p,f}$ be the average volume fraction of arrangements at fixed p and f. To measure the volume response of arrangements of disks to an infinitesimal change in shape, we estimate the derivative

$$\Gamma(p) := \left.\frac{\partial \phi_{p,f}}{\partial f}\right|_{f=0}. \tag{6}$$

By definition the average volume fraction $\phi_{p,f}$ is given by

$$\phi_{p,f} = \int_0^\infty \int_0^\infty \int_\Omega \Phi(\psi_{V,\alpha}^{-1}(Q))(N\pi\sigma^2/V) V^N \exp(-\beta pV + \beta f\alpha V) dQ dV d\alpha. \tag{7}$$

Differentiating with respect to f, one obtains

$$\Gamma(p) = N\pi\sigma^2\langle\alpha\rangle_{p,0} - \phi_{p,0}\langle V\alpha\rangle_{p,0} \tag{8}$$

with $\langle\cdot\rangle_{p,f}$ representing an average value at fixed p and f. Applying equation (8), we obtain $\Gamma(p)$ from the average values of α and $V\alpha$, and from the average volume fraction $\phi_{p,0}$, in our simulations at pressure p with $f = 0$.

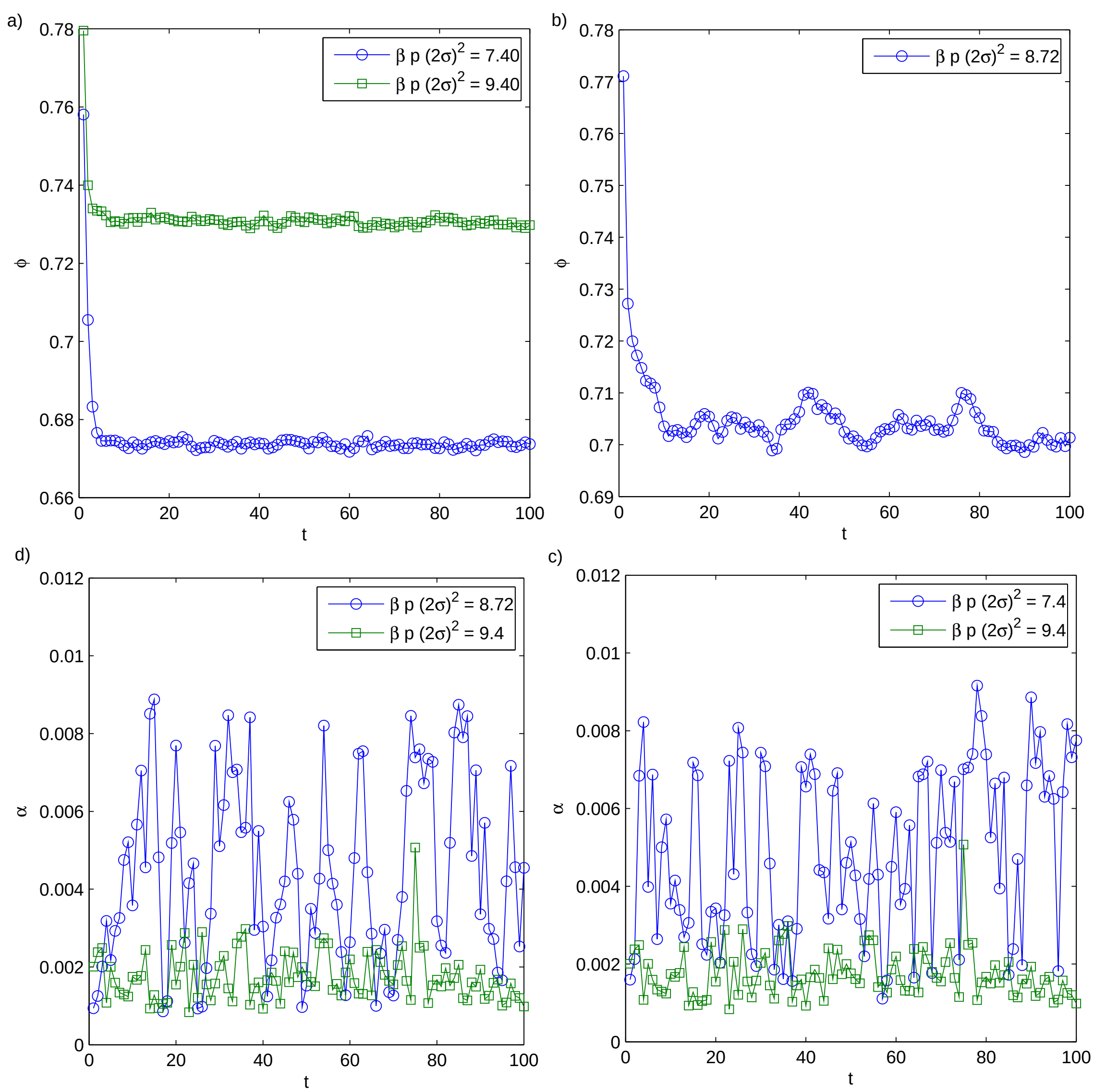

Figure 4. Time series for systems of $N = 10656$ disks, with t in units of 3.5×10^8 Monte Carlo steps, and at $f = 0$, clockwise from top left: a,b) Volume fraction ϕ vs. t; c,d) shape α vs. t.

Our simulations use Monte Carlo steps consisting of moves which change the size and shape of the arrangements of disks, as well as so-called "event-chain" movements of multiple disks [11]. In the former types of moves, the coordinates of disk centers (x, y) are mapped to $(\lambda x, \lambda y)$ or $(x + \rho y, y)$, respectively. Here $\lambda = (V + \eta\epsilon)^{1/2}/V^{1/2}$ and $\rho = \nu\delta$, where η, ν are (independent) random variables distributed uniformly in $(-1, 1)$, and ϵ and δ are positive real parameters.

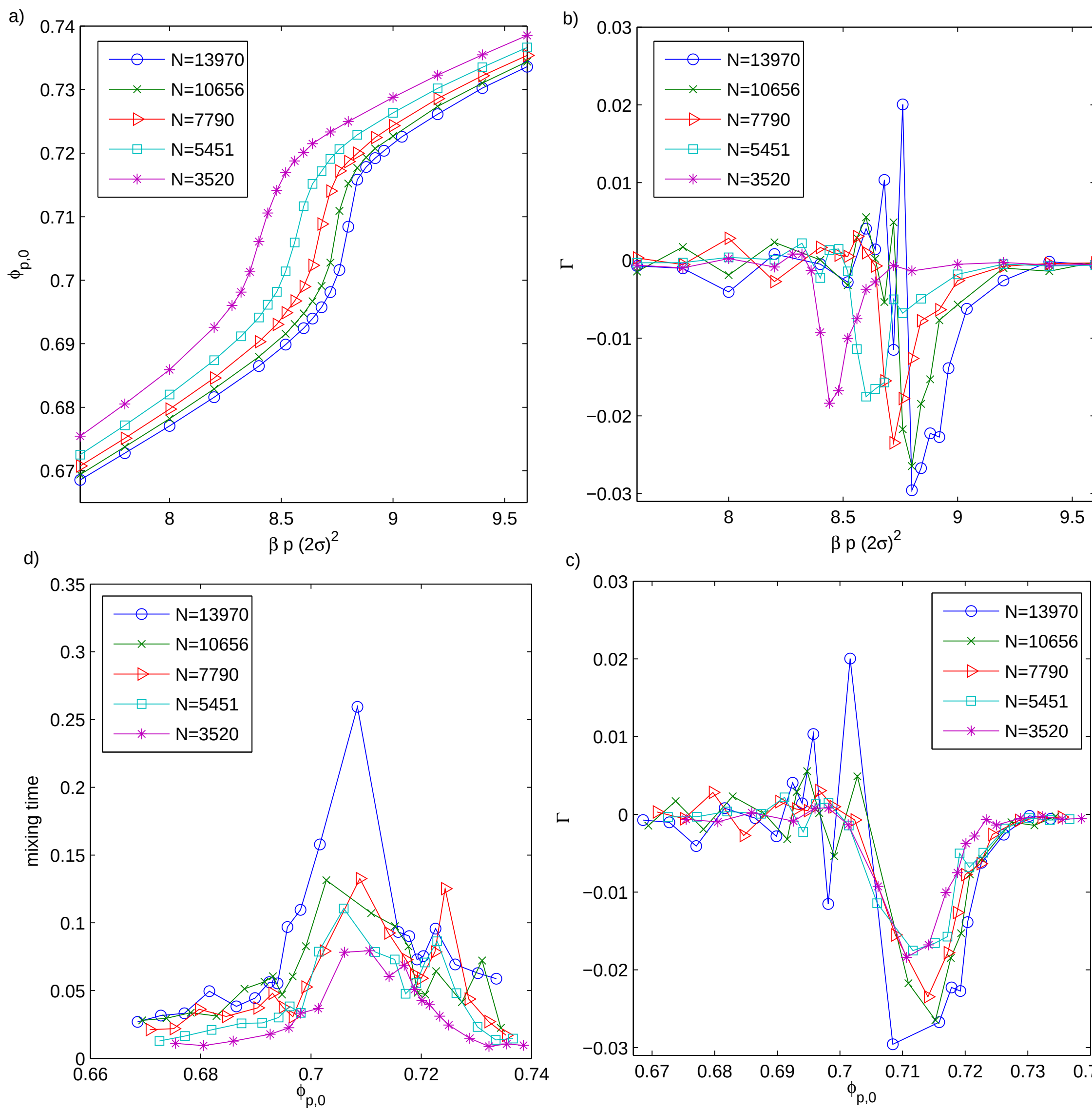

Figure 5. Volume fraction data, clockwise from top left: a) Average volume fraction $\phi_{p,0}$ vs. pressure $\beta p(2\sigma)^2$, with confidence intervals smaller than the data markers; b) Differential volume response Γ vs. pressure $\beta p(2\sigma)^2$; c) Differential volume response Γ vs. average volume fraction $\phi_{p,0}$; d) Mixing time, as a fraction of total number of Monte Carlo steps, vs. $\phi_{p,0}$.

If such a move results in overlap of disks, it is rejected. These types of moves are (each) attempted with frequency $N^{-1/2}/4$. In the latter type of move, employed recently in [11], a non-boundary disk and a random direction are selected, with the direction being up, down, left or right (that is, parallel to one of the coordinate axes). Additionally a displacement L is selected uniformly at random from the interval $(0, \sqrt{V - N\pi\sigma^2}/2)$. The particle is then moved along the chosen direction until it strikes another particle, at which point that particle moves in the same direction until it strikes another particle, and so on. The process continues until a total displacement of L is obtained, the total displacement being the sum of the displacements of all the particles.

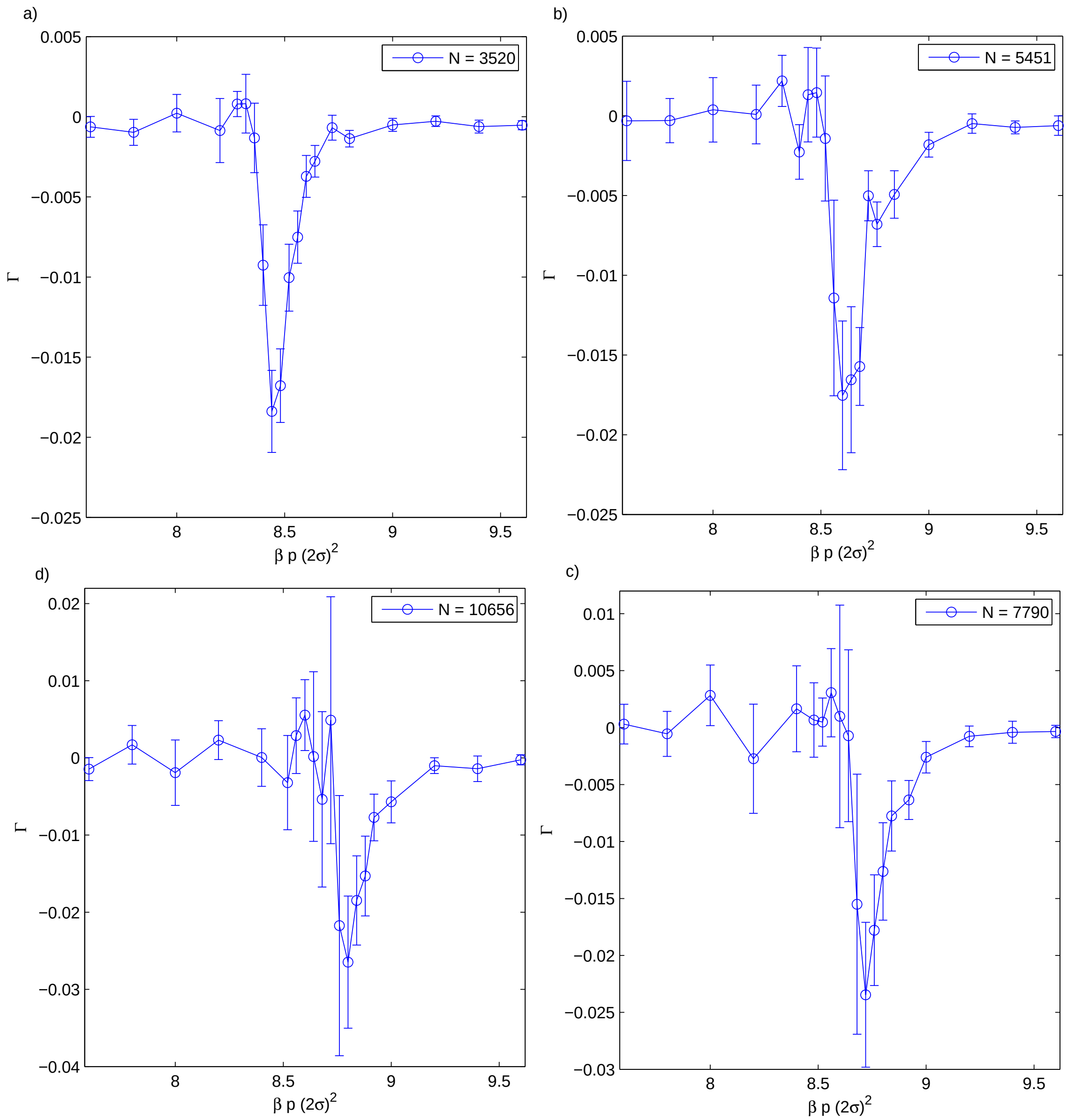

Figure 6. Confidence intervals for differential volume response Γ vs. pressure $\beta p(2\sigma)^2$, for systems with (clockwise from top left) $N = 3520$, $N = 5451$, $N = 7790$, and $N = 10656$.

If the process results in the displacement of a boundary particle, then the move is rejected. (It is in principle possible that such moves result in disks moving outside the boundary, but this does not occur for the pressures we simulate.) Such moves are attempted with frequency $1 - N^{-1/2}/2$.

We investigate systems with $N = 3520$, $N = 5451$, $N = 7790$, $N = 10656$, and $N = 13970$ disks, beginning with perfectly crystalline arrangements of the disks. At each pressure p we run these systems to 2×10^{10}, 2.5×10^{10}, 3×10^{10}, 3.5×10^{10}, and 4×10^{10} Monte Carlo steps, respectively. This results in about 2×10^7 displacements per particle, and about 10^7 fluctuations in volume and shape, for each p and system size N. We checked that our runs were long enough for volume fraction ϕ and shape α to equilibrate, after a burn-in time of at most about 10% of the run (with the exception of the shape α at large p, as discussed below); see Fig. 4. Therefore in our main data, shown in Fig. 5 (with confidence intervals in Fig. 6), we have thrown away the first 10% of each Monte Carlo run. Along with our main data we also measured mixing times, defined as the number of Monte Carlo steps before the standard (unbiased) autocorrelation of the time series for $\phi_{p,0}$ first crosses zero; see Fig. 5. Excluding the largest system ($N = 13970$), mixing times were no more than 15% of our Monte Carlo runs. For 90% confidence intervals, we run 10 independent copies of every simulation and use Student's t-distribution with 9 degrees of freedom on the average values obtained from each of the 10 copies; see Fig. 6. We do not compute confidence intervals for the largest system, $N = 13970$.

We find the volume response parameter $\Gamma(p)$ defined in (8) exhibits the following behavior (see Fig. 5). At low pressure p or volume fraction $\phi = \phi_{p,0}$, $\Gamma(p)$ is approximately zero, indicating there is no volume response to an infinitesimal shear. We interpret this as meaning the hard disk fluid does not resist a small shear stress. As ϕ rises above 0.70, the volume response Γ begins to deviate from zero. Our data is not fine enough to distinguish the details of the transitions shown in [11], and in particular does not justify estimating specific transition values for p.

We note that the volume response Γ measured in our simulations tapers off to zero. We do not expect this tapering to be accurate; instead we interpret this as a sign that the simulations begin to get "stuck" as densities increase. This is confirmed by checking that the simulations no longer explore the full range of shapes α; see Fig. 4c) -d). We expect the true behavior of Γ, as a function of ϕ, to be non-increasing, indicating a volume response into the nonfluid phases. We conclude, then, that the hard disk solid resists a small positive shear stress, while the fluid does not.

III. Summary

The rigidity of solids can be modeled in various ways. We have chosen to use equilibrium statistical mechanics, in large extent because it is the most convincing formalism in which to distinguish solids from fluids – our motivation for studying rigidity, following Anderson [5]. Even within equilibrium statistical mechanics one could model response to shear more simply with a harmonic crystal model [12: Chapter 22], with long range quadratic forces between particles assigned neighboring equilibrium sites. In fact this is commonly used to model sound (pressure) propagation, but does not exhibit a fluid phase and therefore does not allow comparison between solid and fluid phases, which is the purpose of our work.

The most awkward consequence of using equilibrium statistical mechanics is that to obtain the sharp solid/fluid distinction one must take the infinite volume limit while for infinite systems one cannot include shear stress, as noted in the introduction. Our solution to this was to incorporate the shear in finite volume, where there are no well defined solid or fluid phases but the system can accommodate shear stress, and measure the volume response in the limit of vanishing shear, before taking the infinite volume limit.

The other weakness of our approach is technical; in order to measure the volume response to stress we employed variation in both strain and volume, which is costly in simulation time compared to the usual Monte Carlo technique for the hard disk system, which uses fixed volume, strain and particle number. We favor this ensemble for its theoretical advantages: calculating response to stress in our ensemble is far simpler than in an ensemble which fixes, say, density and strain – in the latter, to estimate the response to stress one would have to calculate a numerical derivative as shear strain vanishes, whereas in our ensemble we can calculate the response directly from fluctuations. As a result of the large computation time associated with fluctuations in volume and strain, however, our data is not sufficient to demonstrate the details of the transitions as is done in [11]. We feel this is acceptable in exchange for demonstrating the feasibility of shear response as a theoretical tool to analyze the solid/fluid transition.

In conclusion we note that our approach is similar to the analysis of the dilatancy transition recently found experimentally [13] in (nonequilibrium) static, granular matter, and its modeling [14] with a stress ensemble. In effect we are proposing to model the solid/fluid transition of equilibrium matter as a dilatancy transition, a sharp change between the solid and fluid equilibrium phases in their response to (infinitesimal) shear, instead of by a change in symmetry of the molecular pattern, as is the common practice.

Acknowledgements. It is a pleasure to acknowledge useful discussions with Giulio Biroli, Daan Frenkel and Dan Stein.

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