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Link to publication

Citation for published version (APA):

Gendelman, O., Lerner, E., Pollack, Y. G., Procaccia, I., Rainone, C., & Riechers, B. (2016).
Emergent interparticle interactions in thermal amorphous solids. *Physical Review E*, *94*(5),
[051001(R)]. https://doi.org/10.1103/PhysRevE.94.051001

Emergent interparticle interactions in thermal amorphous solids

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Amorphous media at finite temperatures, be them liquids, colloids, or glasses, are made of interacting particles that move chaotically due to thermal energy, continuously colliding and scattering off each other. When the average configuration in these systems relaxes only at long times, one can introduce effective interactions that keep the mean positions in mechanical equilibrium. We introduce a framework to determine the effective force laws that define an effective Hessian that can be employed to discuss stability properties and the density of states of the amorphous system. We exemplify the approach with a thermal glass of hard spheres; these experience zero forces when not in contact and infinite forces when they touch. Close to jamming we recapture the effective interactions that at temperature T depend on the gap h between spheres as T/h [C. Brito and M. Wyart, Europhys. Lett. **76**, 149 (2006)]. For hard spheres at lower densities or for systems whose binary bare interactions are longer ranged (at any density), the emergent force laws include ternary, quaternary, and generally higher-order many-body terms, leading to a temperature-dependent effective Hessian.

I. INTRODUCTION

The experimental determination of the interparticle forces in amorphous glassy systems is a nontrivial challenge that has motivated a great deal of effort both in athermal granular systems [1–3] and in thermal systems such as colloids [4–8]. The aim of this Rapid Communication is to introduce a method to determine the emergent force laws of the effective interactions between particles in thermal amorphous systems, especially in systems where direct measurements are either very difficult or even impossible. The suggested approach is only relevant for thermal amorphous systems that are arrested in the sense that the thermal dynamics of every particle is restricted to vibrations within a cage. We thus aim at glassy systems, at temperatures below the glass transition, or colloids at densities sufficiently high to suppress diffusion for sufficiently long times. Thus the basic prerequisite for the discussion below is the possibility to measure the average positions of the particles in the amorphous system, usually by averaging over the trajectory of each particle for times that are sufficiently long to produce a converged answer, but shorter than any relaxation time that destroys the cage structure to allow diffusion of the particles outside their cages. Denote then, in a system of N particles at temperature T, the average positions of the particles by $\{r_i\}_{i=1}^N$. These average positions define a configuration that is time independent. It is therefore legitimate and useful to ask what the effective forces are that are holding the configuration in force balance [9]. In the present Rapid Communication we exemplify the approach with thermal hard spheres near jamming and at lower densities. We will find that near jamming there exist almost only binary interactions and therefore binary effective forces f_{ij} are sufficient [10]. For hard sphere at lower densities and for systems with binary longer-range bare interactions, emergent

binary forces are not sufficient. Generically, the emergent effective forces will include also ternary, quaternary, and generally higher-order interactions.

Needless to say, the effective forces will generically turn out to be dependent on both the temperature and the density of the amorphous glass. However, once determined, they can be manipulated in much the same way as the given forces of athermal systems, including the availability of an effective Hessian from which one can determine stability properties and the density of states. The definition of such effective interactions opens a useful path for the discussion of thermal amorphous systems using a host of methods developed in the context of athermal systems.

II. THEORY: DETERMINING THE EFFECTIVE FORCES

When only binary effective forces are needed, the necessary algorithm for determining them had been already developed elsewhere [11] and it will only be summarized here briefly. Below we will extend the formalism for cases that call for higher-order effective interactions. To keep the notation as simple as possible, we describe the algorithm for systems in two dimensions [12], with an obvious generalization to three dimensions. The mechanical equilibrium constraints for the average positions read

$$\boldsymbol{M}|f_{ij}\rangle = 0, \tag{1}$$

where $|f_{ij}\rangle$ is a vector whose entries are the magnitudes of the c interparticle central forces $\boldsymbol{f}_{ij}$. The number c depends on the density and on the temperature. For simplicity we assume here periodic boundary conditions; otherwise walls introduce external forces that can be easily taken into account (cf. Ref. [11]). The matrix $\boldsymbol{M}$ contains the x and y components of the unit vectors $\hat{\boldsymbol{n}}_{ij} \equiv \boldsymbol{r}_{ij}/r_{ij}$, with $\boldsymbol{r}_{ij}$ being the vector distances between the particle positions $\boldsymbol{r}_{ij} \equiv \boldsymbol{r}_i - \boldsymbol{r}_j$. Explicit examples of such a matrix can be found in Ref. [13].

Next the interparticle force magnitudes are presented as Taylor-Laurent polynomials

$$f_{ij}^{AB} = \sum_{k=\ell_1}^{\ell_2} a_k^{AB} \left(r_{ij} - r_0^{AB} \right)^k, \tag{2}$$

where ℓ_1, ℓ_2 are the most negative and most positive powers in the expansion, respectively. Below we will define the number of terms in the expansion as $\ell \equiv \ell_2 - \ell_1 + 1$. Here AB denotes the interaction type. For example, in the case of a binary system these will be AA, BB, and AB, as determined by the nature of the particles i, j. In general we can have n types of particles. Further, r_0^{AB} are the positions of the possible singularities around which we expand the forces for each type of interaction. The coefficients a_k^{AB} can be grouped into a vector $|a\rangle$ of size $n(n+1)\ell/2$ and the force vector can now be written as

$$|f_{ij}\rangle = S|a\rangle, \tag{3}$$

where S is the appropriate $c \times n(n+1)\ell/2$ matrix containing the Taylor-Laurent monomials.

To have a unique solution for the coefficients of the Taylor-Laurent expansion we need to fix one scale parameter. While in experiment we would measure the pressure (see Ref. [11] for details), in simulation of hard spheres we have to calculate the impulse applied in collisions (divided by duration) $\sum \Delta \boldsymbol{p}_{ij}/\Delta t$, where the sum is over all the collisions of the same pair of particles and Δt is the time of measurement. Given the vector distances between the average position of the particles, say, $\boldsymbol{r}_{ij}$ we can calculate the virial υ as

$$\upsilon \equiv \left\langle \boldsymbol{r}_{ij} \left| \sum \Delta \boldsymbol{p}_{ij} \middle/ \Delta t \right. \right\rangle. \tag{4}$$

The problem of finding the effective forces then takes the form

$$\begin{pmatrix} M \\ \langle r_{ij}| \end{pmatrix} |f_{ij}\rangle = \begin{pmatrix} MS \\ \langle r_{ij}|S \end{pmatrix} |a\rangle \equiv Y|a\rangle = \begin{pmatrix} 0 \\ \vdots \\ \upsilon \end{pmatrix} \equiv |t\rangle, \tag{5}$$

where Y is a $(2N+1) \times \ell$ matrix. We now multiply by Y^T from the left

$$Y^T Y |a\rangle = Y^T |t\rangle. \tag{6}$$

The set of unknown coefficients $|a\rangle$ is then solved for using standard least-squares methods.

One should note at this point that indeed the calculation of the impulse $\sum \Delta \boldsymbol{p}_{ij}/\Delta t$ provides a direct measurement of the effective forces between particles (see, for example, Refs. [14,15]). The procedure proposed here provides, however, the emergent effective force laws and not just the forces. Moreover, while in numerical simulations the measurement of the impulse is possible, it would be a hopeless proposition in any experimental setting, where nevertheless the measurement of the pressure and mean positions are readily available. The method proposed here remains valid when the pressure instead of the virial is provided (cf. Ref. [11]).

III. EXAMPLE: THERMAL HARD SPHERES

To exemplify the above procedure we choose a two-dimensional hard-sphere event-driven simulation of over 10^7 collisions with a system size of $N = 400$ particles with periodic boundary conditions. The particles follow ballistic trajectories until they make contact and undergo an elastic collision. The particle radii R are slightly polydispersed around a binary distribution with mean values and standard deviation of $\langle R_A \rangle = 0.5, \sigma_{R_A} = 0.0081, \langle R_B \rangle = 0.7$, and $\sigma_{R_B} = 0.0123$. A jammed state is used as the initial configuration to be expanded as explained below. The system has constant volume V and a constant energy $T = 1$ (in units for which Boltzmann constant is unity), with the initial momenta $|p\rangle$ of the particles chosen randomly, with constant distributions on p_x and p_y separately in the interval $[-1,1)$, subject to the constraint that $T = m\langle p|p\rangle$. In hard spheres the temperature only sets the time scales, so we set $T = 1$ and run the system at different densities as determined by the volume. To analyze systems with different packing fractions, the jammed state is expanded during the initialization of the simulation. Expansions from an initial box of length L_{init} to length L are applied such that

$$L = L_{\text{init}}(1 + \epsilon), \tag{7}$$

with ϵ between 10^{-5} and 5.5×10^{-2}. The average positions are determined using averaging times that are well below the time for which particle diffusion destroys the meaning of the mean positions, but higher than the typical time between collisions. In practice, this means that we are limited in choosing the values of ϵ in Eq. (7). For value of $\epsilon \geqslant 5.5 \times 10^{-2}$ we cannot determine the mean positions of the particles with sufficient accuracy. To ensure that early dynamics due to the initial expansion do not affect the analysis, the first configuration of a simulation is discarded. To ensure that the noisy transition events from one stable configuration to another [14,15] do not affect the analysis, the first 10^4 collisions in the analyzed stable configuration are discarded.

For densities very close to jamming one expects the effective forces to remain binary [14,15]. In hard spheres the energy is simply T. If one assumes that the only important scale is the gap h between close-by particles, dimensional considerations predict that the effective forces would be simply T/h. As shown below, this simple assumption is likely to fail at lower densities [14,15]. We first examine the efficacy of our proposed method in supporting this binary effective force law.

IV. RESULTS

A. Binary effective forces

Having computed the average positions of the centers of mass $\boldsymbol{r}_i$ of all the N particles, we determine the vector distances $\boldsymbol{r}_{ij}$ and relative gaps between particles as h_{ij}, where

$$h_{ij} \equiv r_{ij} - R_i - R_j. \tag{8}$$

Identifying in Eq. (2) $r_0^{AB} = R_i^A + R_j^B$, we rewrite that equation in the form

$$f_{ij}^{AB} = \sum_{k=\ell_1}^{\ell_2} a_k^{AB} h_{ij}^k. \qquad (9)$$

This simplifies the S matrix in the present problem to the monomials in the gap values h_{ij}^k. For hard disks we expect that the effective interactions will depend only on the gap h_{ij} and we can simplify things further by dropping the distinction between particles of different size and the superscripts A,
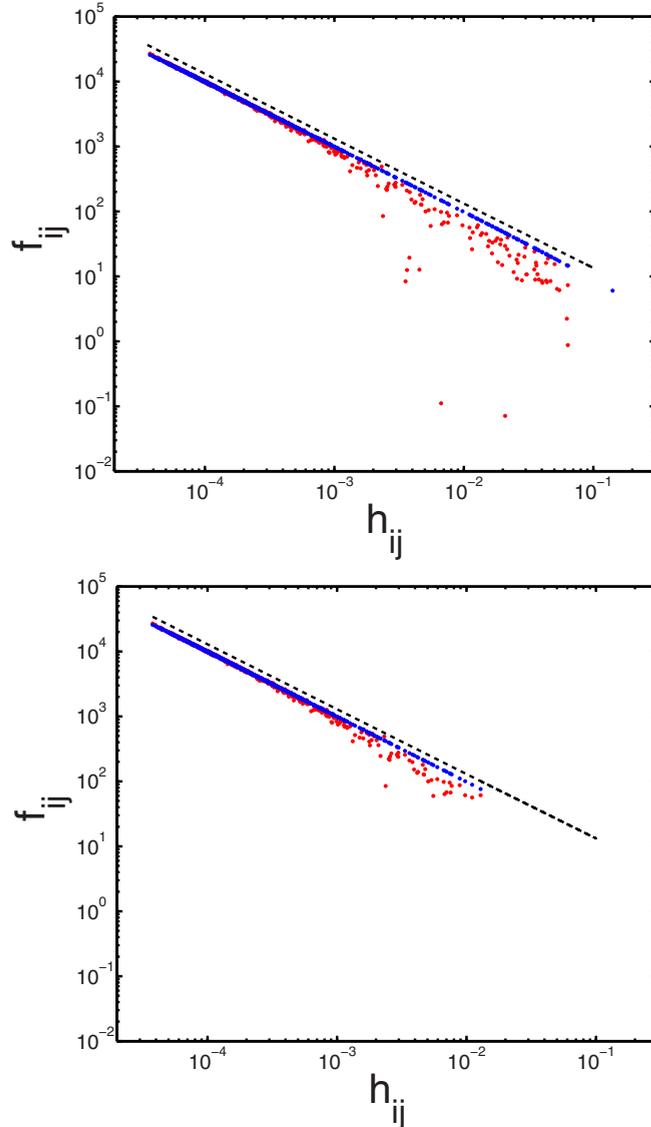

FIG. 1. Shown on top is a comparison of the computed effective forces for $\epsilon = 10^{-4}$. The blue line shows the results obtained from the present algorithm, i.e., T/h_{ij}. The red dots show the results of estimating the forces from the direct momentum transfer method. For small values of h_{ij} the agreement is excellent; it deteriorates at higher values. The black dashed line is the expected result C/h_{ij}, with $C > T$ to allow comparison. The bottom panel shows the same data plotted after excluding any particle pair that collided less than 100 times during the measurement period and the corresponding measured forces.

B, and AB. Taking then, for example, six monomials in Eq. (9) with $\ell_1 = -3$ and $\ell_2 = 3$ (without a constant term), we solve the problem set by Eq. (6) and find that $a_{-1} \approx T = 1$ and all the other coefficients vanish to high accuracy (better than 10^{-6}). This result should be compared with the direct measurement of the effective forces between the particles, which, as said above, can be evaluated from the momentum transfer, following verbatim the approach of Refs. [14,15]. The blue line in the top panel of Fig. 1 represents the solution described here for $\epsilon = 10^{-4}$ and the red dots are the estimates from the direct momentum transfer method. The black dashed line represents the law C/h_{ij} and coincides with the predicted emergent force law when $C = T$. The deviation of the red dots from the observed law indicates inaccuracies in the direct simulation that occur at larger values of h_{ij}. We have checked and determined that the infrequent collisions between spheres separated by high gaps cause the decline in accuracy of the direct measurements of the effective forces. The mean number of collisions between pairs in this simulation is 11 547. By demanding that there should be at least 100 collisions between an ij pair whose force f_{ij} is taken into account, we obtain the comparison shown in the bottom panel of Fig. 1. The improvement in agreement is obvious.

The first sign that these results are not necessarily generic appear while trying to repeat the same calculation for thermal glasses with Lennard-Jones bare forces. The effective binary forces contain a large number of Taylor-Laurent coefficients but fail to satisfy the mechanical constraints (1). The reason for this failure is deep. In the algorithm proposed above we allow only binary effective forces, with flexible Taylor-Laurent expansions, but only binary. This is appropriate in the dense hard sphere example since there are almost only binary interactions. In Lennard-Jones glasses even in very dense packings, any momentum exchange between two particles is strongly effected by other particles residing within the
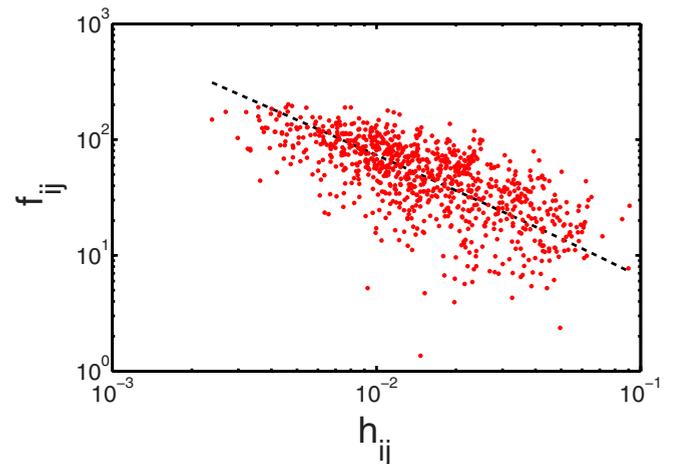

FIG. 2. Comparison of the measured forces (red dots) and the best fit to binary forces (dashed black line), for $\epsilon = 10^{-2}$. The measured forces are no longer a graph of h_{ij} since they reflect the existence of multiple-body interactions. The dashed line is a graph by construction, but obviously it does not represent the data well (see also Fig. 3).
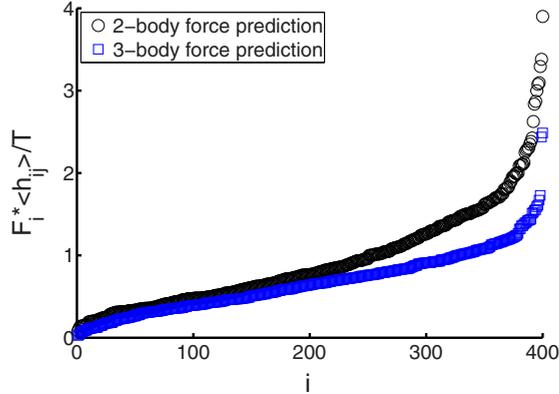
FIG. 3. Net forces on each particle, rescaled by $T/\langle h_{ij}\rangle$. We have reordered the indices of the particles according to the increasing magnitude of the net force. Black circles show the net forces computed from the best binary approximation. Blue squares represent the net forces computed with binary and some ternary contributions. The addition of even a limited number of ternary interactions improves the approximation.

interaction distance. Accordingly, we expect that the emergent effective interactions will contain ternary, quaternary, and higher-order terms, depending on the density, the range of interactions, and probably the temperature. In fact, the same issues appear also for hard spheres when we reduce the density, as we demonstrate next.

B. Binary and ternary effective forces

Reducing the density of the thermal hard spheres by using an expansion $\epsilon = 10^{-2}$ in Eq. 7 changes the situation altogether. First, the direct measurements of the forces do not yield a function of h_{ij}. This is demonstrated in Fig. 2, where the red dots represent the forces measured directly from momentum transfer, plotted against h_{ij}. The data scatter since not only are the forces functions of h_{ij}, but they are functions of more variables and do not fall on a graph as a function of h_{ij}. Trying to fit the "best" binary forces f_{ij} results in the black dashed line in Fig. 2. Obviously, this resulting function does not do justice to the scattered red dots; a good way to demonstrate the failure of the best binary approximation is to compute the net force on each particle $f_i = \sum_j f_{ij}$. This should vanish for every i if the approximation is good. In Fig. 3 we show the net forces f_i in order of increasing magnitude as black circles. Obviously, the situation calls for the introduction of additional terms to the emergent effective forces.

For the sake of brevity we will demonstrate here how the addition of a limited type of three-body terms leads to an improvement in satisfying the conditions of mechanical equilibrium of the mean positions. We will add only two types of terms, respecting the dimensionality of the binary forces,

i.e.,

$$f^{(2)}(h_{ij},h_{ik}) \equiv \frac{a^{(2)}T}{(h_{ij}h_{ik})^{1/2}},$$
$$f^{(3)}(h_{ij},h_{ik},h_{jk}) \equiv \frac{a^{(3)}T}{(h_{ij}h_{ik}h_{jk})^{1/3}}, \tag{10}$$

where $a^{(2)}$ and $a^{(3)}$ are dimensionless coefficients to be determined. We recognize that, in general, other three-body and higher-order terms may be necessary, but for the purposes of this Rapid Communication it will be enough to determine our effective forces in the present approximation as

$$\boldsymbol{f}_{ij} = -\hat{n}_{ij}\left(f_{ij}(h_{ij}) + \sum_k [f^{(2)}(h_{ij},h_{ik}) + f^{(3)}(h_{ij},h_{ik},h_{jk})]\right), \tag{11}$$

where the sum over k goes over $k \neq ij$. One should recognize that the resulting forces $\boldsymbol{f}_{ij}$ are not a function of h_{ij} as is required. The method described above can be easily extended to determine the best fit in this form and the results for the net forces when these terms are included are shown as the blue squares in Fig. 3. The improvement with respect to the binary approximation is obvious, although convergence certainly requires additional terms.

V. CONCLUSION

We have demonstrated an approach based on measuring the average positions of particles in thermal amorphous systems in which the structural relaxation is slow. This allows us to define and compute emergent effective force laws that hold the system stable. In general, the emergent forces include ternary, quaternary, and in general higher-order terms. Since the average positions are time independent, we can now study how the Hessian of the effective interactions can be used to predict the stability, the mechanical responses, and the density of states of thermal systems in much the same way as is done in athermal systems. The actual emergent theory, including a full consideration of the many-body interactions, is beyond the scope of this Rapid Communication. In particular, the convergence properties of this theory, both as a function of distance from jamming and as a function of the order of the many-body terms, call for an exciting and novel theory of thermal glasses.

ACKNOWLEDGMENTS

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