Supplementary Material for: Glassy, Gardner-like Phenomenology in Minimally Polydisperse Crystalline Systems

Patrick Charbonneau,[1,2] Eric I. Corwin,[3] Lin Fu,[1] Georgios Tsekenis,[3,*] and Michael van der Naald[3]

[1] *Department of Chemistry, Duke University, Durham, North Carolina 27708, USA*
[2] *Department of Physics, Duke University, Durham, North Carolina 27708, USA*
[3] *Department of Physics, University of Oregon, Eugene, Oregon 97403, USA*

This Supplementary Material details the crystal structure and the choice of polydispersity as well as the thermal hard sphere simulation and athermal soft spheres energy minimization schemes.

POLYDISPERSE CRYSTAL

The binary crystal studied in this work is based on the Hudson Structure One (HS1) [1], whose unit cell contains four larger particles and 12 smaller particles. It has orthorhombic periodicity with dimensions $a : b : c = 1 : 1.4980 : 2.6014$ and for a ratio of smaller to larger particle diameter $\sigma_S/\sigma_L \doteq 0.5147$ the HS1 crystal attains close packing with $\varphi_{cp} \doteq 0.7573$.

In order to introduce polydispersity in this crystal, the particle diameter (σ_L or σ_S) of each particle is rescaled

$$\sigma_i = \sigma_{L/S} \times R,$$

where R is a log-normal distributed random variable with unit mean and standard deviation s. This choice of distribution is fairly generic and avoids the generation of negative diameters.

SIMULATION METHODS

Gardner Phenomenology

Simulations are initialized from a perfectly ordered HS1 binary crystal with a lattice spacing just large enough for the overlaps resulting from the instance of polydispersity to be eliminated. Isothermal-isobaric, constant NPT, Monte Carlo (MC) simulations are then run to reach a target φ. Pressure P is kept constant by standard logarithmically-sampled volume moves. Because the initial configurations are well-ordered, conventional MC moves with a ratio between particle moves and volume moves being $N : 10$ (N being the number of particles) suffice to efficiently compress the system. Once the target density is reached, constant NVT simulations are performed using a local Metropolis dynamics. Step sizes of the different MC moves are tuned to ensure that the acceptance ratio stays between 40% and 50%.

Mean-Squared Displacement

A standard order parameter for glassiness is the plateau height of the mean-squared displacement of particles,

$$\Delta(t, t_w) = \frac{1}{N} \sum_{i=1}^{N} \left\langle |\vec{r}_i(t + t_w) - \vec{r}_i(t_w)|^2 \right\rangle ,$$

where t_w is the waiting time after the target pressure or density is reached and $\vec{r}_i$ is the position of particle i. We measure the early plateau height of $\Delta(t, t_w = 0)$ for different φ. For $\varphi \lesssim \varphi_G$, the early plateau height can be easily estimated because the $\Delta(t, 0)$ quickly reaches a well-defined constant. For $\varphi \lesssim \varphi_G$, however, a logarithmic aging $\Delta(t, 0) \sim \ln(t)$ quickly develops. In order to estimate the early plateau height, we fit the MSD beyond the transient with $\ln[\Delta(t, 0)] = Q_1 \ln(t) + Q_2$. The early $\Delta(t, 0)$ is taken to be the intercept of this fit at $t = 1$, i.e., $\Delta(t = 1, 0) = Q_2$. Note that this procedure generalizes naturally to systems with a well-defined plateau.

The long-time limit of $\Delta(t, t_w)$ quickly becomes computationally unattainable once $\varphi \gtrsim \varphi_G$. To more clearly reveal the effect of aging, we obtain the equilibrium $\Delta(t \to \infty, t_w \to \infty)$ from the distance Δ_{AB} between two different copies, A and B, with the same φ and particle polydispersity, compressed from the same initial configuration, but using a different stochastic trajectory

$$\Delta_{AB}(t) = \frac{1}{N} \sum_{i=1}^{N} \left\langle |\vec{r}_i^{\,A}(t) - \vec{r}_i^{\,B}(t)|^2 \right\rangle .$$

Note that $\Delta_{AB}(t)$ is calculated after aligning the centers of mass of the two copies. A few hundred realizations of disorder are used in the averaging for both $\Delta(t, t_w)$ and Δ_{AB}.

Introducing polydispersity changes particle sizes nonuniformly, and thus a finite-size system cannot reach its densest packing while maintaining the original aspect ratio of the simulation box. Even though the s considered here and the resulting cell anisotropy are very small, we employ anisotropic volume moves to compute $\Delta(t, t_w)$. For $\Delta_{AB}(t)$, however, only isotropic volume moves are used to ensure that independent system copies have the same dimensions.

Equation of State

The system pressure is calculated from the virial equation of state (EoS). In general, for a polydisperse system, this would require calculating of $N(N-1)/2$ distinct pair distribution functions. For hard interactions, however, a rescaling reduces the relationship to a single distribution function. Defining the rescaled quantities:

$$\bar{r}_{ij} = \frac{r_{ij}}{\sigma_{ij}}$$
$$\bar{u}_{ij} = \begin{cases} \infty, & \bar{r}_{ij} < 1 \\ 0, & \bar{r}_{ij} \geq 1 \end{cases}$$
$$\bar{\boldsymbol{f}}_{ij} = -\nabla \bar{u}_{ij}$$

where $r_{ij} = |\vec{r}_i - \vec{r}_j|$ is the distance between particles i and j, $\sigma_{ij} = (\sigma_i + \sigma_j)/2$, σ_i is the diameter of particle i, we can indeed rewrite the virial as

$$\begin{aligned}
\beta P &= \rho + \frac{\beta}{3V} \left\langle \sum_{i<j} \boldsymbol{f}_{ij} \cdot \vec{r}_{ij} \right\rangle \\
&= \rho + \frac{\beta}{3V} \sum_{i<j} \langle \boldsymbol{f}_{ij} \cdot \vec{r}_{ij} \rangle \\
&= \rho + \frac{\beta\rho^2}{3} \frac{1}{N(N-1)} \sum_{i<j} \int \boldsymbol{f}_{ij} \cdot \vec{r}_{ij} g(\vec{r}_{ij}) d\vec{r}_{ij} \\
&= \rho + \frac{4\beta\pi\rho^2}{3} \frac{1}{N(N-1)} \sum_{i<j} \sigma_{ij}^3 \int \bar{f}_{ij} \bar{r}_{ij}^3 \bar{g}(\bar{r}_{ij}) d\bar{r}_{ij} \\
&= \rho + \frac{4\pi\rho^2}{3} \bar{g}(1^+) \sum_{i<j} \frac{\sigma_{ij}^3}{N(N-1)},
\end{aligned}$$

where $\bar{g}(\bar{r})$ is a uniform rescaled pair distribution function [**?**] and the contact value $\bar{g}(1^+)$ is extrapolated from the first few non-zero values of $\bar{g}(\bar{r})$ using a quadratic fit. Note that the above expression reduces to the monodisperse case when $\sigma_i = \sigma_j = \sigma, \quad \forall i, j$.

Once a target φ is reached, 2×10^5 MC cycles are first run to equilibrate the system. The distribution function $\bar{g}(\bar{r})$ is then sampled every 100 MC cycles, and $\bar{g}(1+)$ is updated after each sampling. Except for the few largest φ, P quickly converges to its equilibrium value. For the few largest φ, the last recorded (out-of-equilibrium) value of P is reported.

Pressure diverges at a finite packing fraction as can be seen in Figure S1. Towards infinite pressure the system indeed appears to be asymptoting to its jamming behavior at φ_J. A collapse is thus obtained after rescaling the packing fraction with the distance to jamming (Figure S1, right panel).

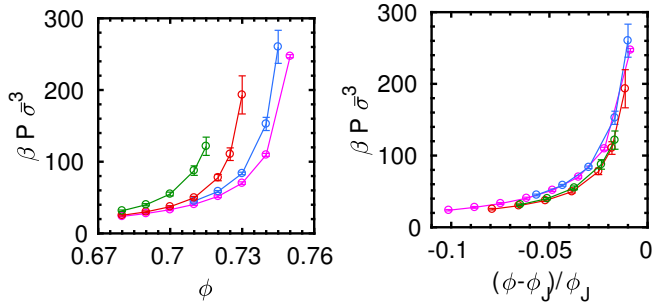

FIG. S1. The equation of state (left panel) for different polydispersities (from left to right), $s = 0.03$ (green), $s = 0.02$ (red), $s = 0.01$ (blue), $s = 0$ (purple). (right panel) Collapse of the EoS after rescaling with the jamming packing fraction φ_J.

Inherent Structures

Athermal Energy Minimization Method

We prepare HS1 packings of harmonic soft spheres at jamming, starting from a packing fraction well above the crystal density, and then successively minimize the energy and shrink the particles until overlaps between spheres have all vanished. The preparation scheme follows that of Refs. 2 and 3 with initial packing fraction $\varphi_i = 0.8$ and convergence criterion that the packing (with rattlers removed) reaches isostatic equilibrium with $N_c = (N-1)d + 1$ contacts, as is expected for a system under periodic boundary conditions [2].

Force Network Calculation

Interparticle forces in isostatic packings can be uniquely determined from the contact vectors (see e.g., Ref. 2). Before calculating the forces, we remove all rattlers, which are particles that with fewer than $d+1$ contacts or with contacts that are co-hemispheric.

Extended and Localized Floppy Modes

In order to determine whether a contact is associated with an extended or a localized floppy mode, we follow the scheme described in Ref. 2 to extract the particle displacements in response to opening a contact.

More specifically, we solve for

$$H\delta\vec{r}^{(\tau)} = S^T\vec{\tau}$$

where S is the contact matrix, $H = S^T S$ is the Hessian of the packing and $\vec{\tau} = \delta_{\tau,<kl>}$ is a vector containing a unit entry at contact τ with all other contacts $< kl >$ zeroed. The solution of this equation gives the particle displacements, $\delta\vec{r}^{(\tau)}$, associated with opening contact τ.

A singular value decomposition of a non-square matrix can generally be expressed as $S = U\Sigma V^T$, where Σ is the rectangular diagonal matrix with the singular values (non-negative real numbers) in its diagonal, and U and V are the square matrices of the left-singular and right-singular eigenvectors. We can invert H by using only the non-zero singular values and the corresponding left and right eigenvectors of the contact matrix S^T. We then obtain

$$\delta\vec{r}^{(\tau)} = V\Sigma^{-1}U^T\vec{\tau},$$

which can be solved iteratively for each τ. The floppy modes fall naturally into two categories according to the relative value of their median, $V_{\text{median}} = \text{median}\{\delta r_i\}$, to their mean, $V_{\text{mean}} = \text{mean}\{\delta r_i\}$, displacements. Extended and localized modes are characterized by high and low ratios of $V_{\text{median}}/V_{\text{mean}}$ respectively with a split naturally occurring between them at $V_{\text{median}}/V_{\text{mean}} = 0.1$.

Gap Distribution

The gap between pairs of particles, $h = r_{ij}/\sigma_{ij} - 1$, is computed neglecting rattlers and pairs of particles already in contact.

Vibrational States

The vibrational states of the packing are obtained from the Hessian, which is computed as in Ref. [3]. We diagonalize H to compute its eigenvalues λ_k, and thus the vibrational frequencies, $\omega_k = \sqrt{\lambda_k}$, of the normal modes of the configuration. The inverse participation ratio (IPR) of the associated eigenvectors, $\{\vec{u}_i(\omega_k)\}_k$, provides a measure of the spatial extent of the normal modes. Note that because we are only interested in the spectrum of the mechanically rigid portion of the packing modes associated with rattlers are removed from the analysis.

* geotsek@gmail.com

[1] P. I. O'Toole and T. S. Hudson, The Journal of Physical Chemistry C **115**, 19037 (2011).

[2] P. Charbonneau, E. I. Corwin, G. Parisi, and F. Zamponi, Physical Review Letters **114**, 125504 (2015).

[3] P. Charbonneau, E. I. Corwin, G. Parisi, A. Poncet, and F. Zamponi, Physical Review Letters **117**, 045503 (2016).

[4] E. Bitzek, P. Koskinen, F. Gähler, M. Moseler, and P. Gumbsch, Physical Review Letters **97**, 170201 (2006).

[5] J. Kurchan, G. Parisi, P. Urbani, and F. Zamponi, The Journal of Physical Chemistry B **117**, 12979 (2013).