Glassy, Gardner-like phenomenology in minimally polydisperse crystalline systems

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We report on a nonequilibrium phase of matter, the minimally disordered crystal phase, which we find exists between the maximally amorphous glasses and the ideal crystal. Even though these near crystals appear highly ordered, they display glassy and jamming features akin to those observed in amorphous solids. Structurally, they exhibit a power-law scaling in their probability distribution of weak forces and small interparticle gaps as well as a flat density of vibrational states. Dynamically, they display anomalous aging above a characteristic pressure. Quantitatively, this disordered crystal phase has much in common with the Gardner-like phase seen in maximally disordered solids. Near crystals should be amenable to experimental realizations in commercially available particulate systems and are to be indispensable in verifying the theory of amorphous materials.

I. INTRODUCTION

Supercooling a liquid to form a glass and crunching grains until they jam both lead to solids that are amorphous. Because the two protocols are far out of equilibrium, however, their end products need not have much in common. Twenty years ago, Liu and Nagel nonetheless postulated the existence of a deep connection between them [1], and a formal relationship has recently been uncovered for certain models [2]. At the crux of the latter lies the Gardner transition [3,4], which for a mean-field model of hard spheres is intermediate between glass formation and jamming [2,5–7]. At this transition, the phase space of a mechanically stable glass basin splits into an intricate and hierarchical arrangement of marginally stable subbasins; jamming occurs deep within this marginal phase. Remarkably, mean-field theory (MFT) further predicts materials features that are robustly universal down to dimension $d = 2$ [2]. For instance, amorphous packings of hard spheres exhibit distinctive power-law-distributed small interparticle gaps and weak contact forces with exponents that are numerically consistent with MFT [2,8–12]. A similarly stunning agreement is observed for the distribution of vibrational excitations at and around these jammed configurations [13–16].

While the description of crystalline solids has long been well established and that of amorphous solids is under increasingly strong theoretical control, a large conceptual gap persists in between these two materials poles. Various proposals to reconcile them have recently emerged. Goodrich *et al.* found that athermal crystals with discrete disorder, such as vacancies and interstitials, display structural and rheological properties similar to those of amorphous solids [17]. Such crystals also

undergo a relatively sharp amorphization transition as the particle-size dispersity (polydispersity) increases [18,19]. For jammed packings specifically, Tong *et al.* proposed that a disordered crystal phase underlies distinct scaling exponents for certain rheological quantities, such as the ratio of the shear to bulk modulus [19]. The microscopic origin of these anomalies in slightly disordered crystals, however, remains far from understood.

In this Rapid Communication, we investigate the out-of-equilibrium physics of crystals of weakly polydisperse hard particles [20]. Disorder is introduced continuously in otherwise perfect crystals of hard spheres by scaling particle radii by a factor drawn from a log-normal distribution of unit mean and standard deviations [21]. The chosen crystal symmetry, HS1 [22] [[23], Sec. II], contains no particle with coplanar neighbors—unlike face-centered cubic (FCC) and many other crystal symmetries—hence, the role of low-energy buckling excitations is minimal [12]. We study both the relaxation dynamics of finite-pressure crystals and the structure of infinite-pressure jammed packings. Remarkably, even though these solids appear crystalline (Fig. 1), we find that their structure and dynamics exhibit most of the glassy properties of amorphous solids, in line with the MFT predictions for high-density amorphous solids.

II. GLASSY DYNAMICS

We probe the dynamics of 300–400 copies of systems with $N = 2\,000$ particles initialized near the melting density of the HS1 lattice and annealed following a standard protocol [6]. First, we run isothermal-isobaric, constant NPT, Monte Carlo (MC) simulations using a relatively high pressure quench, until a target packing fraction, φ, is reached. Isothermal-isochoric, constant NVT, Monte Carlo simulations are then run using only local particle displacements [[23], Sec. III A]. The roughness of the caging landscape is ascertained by the long-time behavior of the mean-squared displacement of the
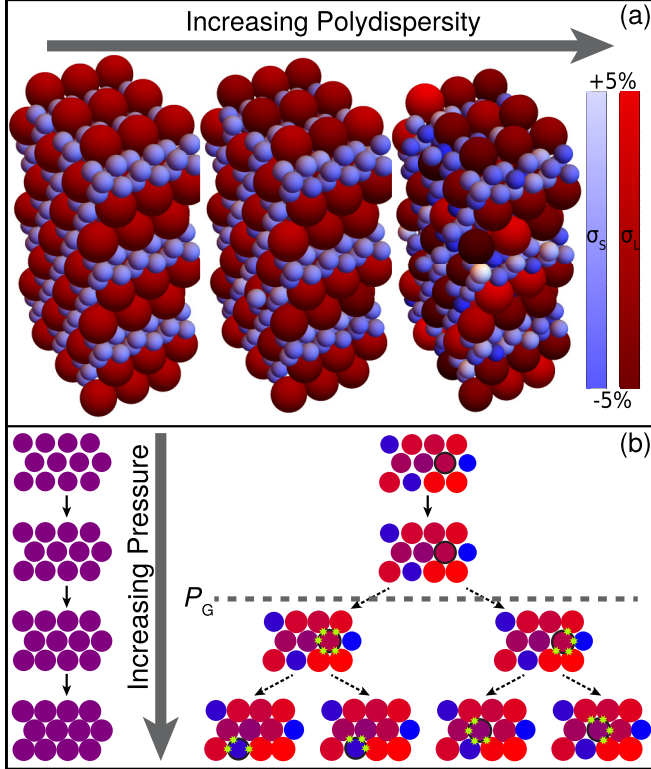
FIG. 1. (a) Jammed HS1 packings with $s = 0.0$, 0.01, and 0.03, from left to right. Color encodes the particle diameter, σ_i. Even the most disordered system appears crystalline. Note that the unit cell of a perfect HS1 crystal comprises 4 larger particles and 12 smaller particles, which for a diameter ratio of 1:0.5147 achieves close packing, $\varphi_{cp} = 0.7573$. (b) Schematic of a Gardner-like scenario for polydisperse crystals. While a monodisperse packing has but one well-separated densest packing, the number of nearby optima in a polydisperse system can be large. Beyond a threshold pressure, P_G, constraints on that optimum start to lock in. A particle (outlined in black) is free to collide with all its nearest neighbors at low pressures but is forced to have one or another set of contacts (green stars) as pressure increases beyond P_G.

particle positions, $\vec{r}$,

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

where t_w is the time (measured in sweeps of N MC steps) after reaching a target φ. For a simple, mechanically stable thermal solid, $\Delta(t, t_w)$ is expected to plateau quickly because all particles can efficiently sample their local cage. For a marginally stable solid, by contrast, $\Delta(t, t_w)$ is expected to exhibit significant aging, a reflection of the difficulty of sampling the complex caging landscape associated with this regime [6]. In the latter case, the long-time limit of $\Delta(t, t_w)$ is computationally out of reach, even for the relatively small systems studied here. We thus also compute the distance between two system copies, A and B,

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

with the same φ and quenched disorder, but evolved from different stochastic trajectories, such that $\Delta_{AB} = \Delta(t \to \infty, t_w)$.

Figure 2(a) shows that aging, which is undetectable at low pressures, first appears and then becomes increasingly notable as pressure increases. The early plateau of $\Delta(t, t_w)$ correspondingly splits from Δ_{AB} [Fig. 2(b)] [[23], Sec. III A]. As in Ref. [6], the skewness, Γ_{AB} of the distribution of Δ_{AB} for different initial configurations also peaks in that regime, which provides a clear definition of φ_G [Fig. 2(c)]. Both effects are akin to the anomalous phenomenology observed in glassy hard spheres at high pressure [6]. Remarkably, as s decreases, the onset of aging and φ_G, are both pushed to increasingly larger pressures [Fig. 2(d)], while the equation of state is barely affected [[23], Sec. III A]. Microscopically, the Gardner-like regime appears when the typical interparticle spacing, which scales as $1/P$, becomes comparable to the polydispersity, i.e., $P_G \sim 1/s$ [Fig. 2(d)]. The anomalous regime thus only disappears for a perfect crystal, i.e., for $s \to 0$. This effect is reminiscent of the Gardner regime of amorphous hard spheres, which also steadily shrinks as the ideal glass limit is approached [2]. Although computer simulations, as considered here, do not cover the thermodynamic limit to determine whether a true phase transition takes place, our observations are consistent with the Gardner-like regime observed in numerical studies of hard-sphere glasses [6].

III. ISOSTATIC MECHANICAL EQUILIBRIUM

Having established that polydisperse hard sphere crystals display anomalous features at high but still finite pressure, we compare their microstructures at infinite pressure (jamming) with those of amorphous jammed configurations. Jammed packings of $N = 432$ polydisperse soft spheres in HS1 symmetry are obtained by minimizing the energy of 466–736 realizations for each s studied [11,26] [[23], Sec. III B]. (For $s \lesssim 0.01$, the unambiguous detection of small forces and gaps near the numerical accuracy of the simulation is prohibitively cumbersome.) The final configurations therefore coincide with the inherent structures of the polydisperse hard-sphere crystals. Just like amorphous jammed packings, these near-crystalline configurations contain but a small fraction of rattling particles and are otherwise perfectly isostatic. The interparticle forces, f, can thus be determined directly from the contact vectors [12].

Like their amorphous counterparts, our packings have power-law distributed small forces with different scaling exponent for contacts that give rise to localized excitations when opened and those associated with extended excitations [9,10,12] [[23], Sec. III B], i.e.,

$$\text{PDF}_e(f) \sim f^{\theta_e} \quad \text{and} \quad \text{PDF}_\ell(f) \sim f^{\theta_\ell}, \qquad (3)$$

respectively. Figures 3(a) and 3(b) reveal that the force scaling exponents are in good agreement with the MFT predictions, $\theta_e^{\text{MFT}} = 0.42311$ and $\theta_\ell^{\text{MFT}} = 0.17462$. The distribution of interparticle gaps, $h = \frac{r_{ij}}{(\sigma_i + \sigma_j)/2} - 1$, which is complementary to that of the forces [9–11], also displays a power-law tail,

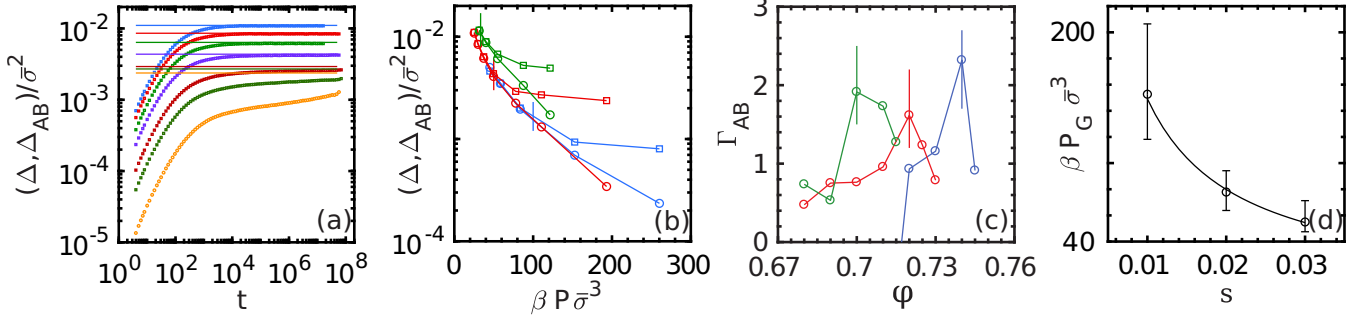$$\text{PDF}_h(h) \sim h^{-\gamma} \qquad (4)$$

FIG. 2. (a) $\Delta(t, 0)$ (squares) and $\Delta_{AB}(t) \equiv \Delta(\infty, 0)$ (lines) for HS1 crystals with $s = 0.02$. As φ increases (from top to bottom), $\Delta(t, 0)$ crosses over from having a well-defined long-time plateau to displaying logarithmic aging at $\varphi_G \approx 0.72$. (b) Evolution of Δ_{AB} and (early) plateau height of $\Delta(t, t_w)$ with pressure for $s = 0.01$ (blue), 0.02 (red), and 0.03 (green). (c) The skewness, Γ_{AB}, of the distributions of Δ_{AB} for each polydispersity peaks at φ_G denoted with vertical lines in (c) which in turn defines P_G denoted with vertical lines in (b). (d) The pressure, P_G, corresponding to φ_G increases with decreasing polydispersity. The solid line is a fit to an inverse relationship, which suggests that the anomalous regime only vanishes for $s \to 0$, where $P_G \to \infty$. For the sake of comparison, in previous works (with uniformly distributed polydispersity), equilibrium polydisperse FCC crystals become unstable to fractionation around $s \sim 0.08$ [24,25], and the athermal amorphization transition occurs around $s \sim 0.11$ [19].

[Fig. 3(c)]. The observed exponent, however, is visibly smaller than the MFT prediction, $\gamma^{\mathrm{MFT}} = 0.41269$, for all s considered. For the range of very small polydispersities considered, we nonetheless clearly observe that near-crystals have a complex particle microstructure concordant with that of amorphous solids.

The theory of marginally stable packings provides inequalities for these exponents [9,10,27], $\gamma \geqslant 1/(2 + \theta_e)$ and $\gamma \geqslant (1 - \theta_\ell)/2$, which were found to be saturated in amorphous solids [2,12]. Here, because the force scaling exponents are consistent with the MFT predictions while γ is markedly smaller, both inequalities are violated. Even though the treatment in Refs. [9,10,27] is seemingly independent of the degree of disorder, it implicitly assumes that the marginal solids have no structural correlations. While this may be a reasonably valid assumption for amorphous packings, it is clearly not the case here. How to include such correlations in the theory of marginality and what precise values should the critical exponents take in that context, however, remain open problems.

IV. HARMONIC EXCITATIONS

As a further test of the similarity between polydisperse crystals and amorphous solids, we consider the low-energy excitations around the jammed minima [14,16]. The eigenvalues λ_k and eigenvectors $\{\vec{u}_i\}_k$ of the Hessian computed from the contact vectors provide the harmonic frequencies, $\omega_k = \sqrt{\lambda_k}$, and normal modes, respectively. As in amorphous solids, we find the spectra of vibrational states to be flat at low frequencies [Fig. 3(d)], and the spatial extent of the normal modes to be nontrivial [Fig. 3(d), inset]. The eigenmodes, $\{\vec{u}_i(\omega_k)\}_k$, at a given ω_k indeed have an inverse participation ratio (IPR),

$$Y(\omega) = \frac{\sum_i^N |\vec{u}_i(\omega)|^4}{\left[\sum_i^N |\vec{u}_i(\omega)|^2\right]^2}, \qquad (5)$$

consistent with them being mostly delocalized at intermediate frequencies with some degree of quasi-localization at low frequencies [18,28–30] [[23], Sec. III B]. Remarkably, the
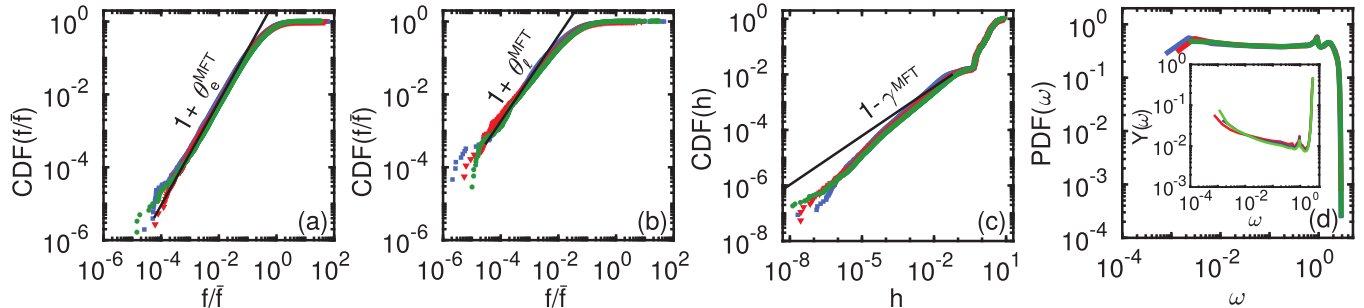

FIG. 3. Cumulative distribution function, $\mathrm{CDF}(x) = \int_0^x \mathrm{PDF}(x')dx'$, of contact forces between pairs of particles associated with (a) extended floppy modes and (b) localized floppy modes for $s = 0.01$ (blue squares), 0.02 (red triangles), and 0.03 (green circles). (c) CDF for small interparticle gaps in the same systems. MFT predictions for the power-law exponents, $1 + \theta_e^{\mathrm{MFT}} = 1.42311$, $1 + \theta_\ell^{\mathrm{MFT}} = 1.17462$, and $1 - \gamma^{\mathrm{MFT}} = 1 - 0.41269$, are given as black solid lines. While close agreement in observed in (a) and (b), a significant discrepancy is seen in (c). (d) The probability distribution of the frequency of harmonic vibrations has a spectrum identical to that of a disordered jammed packing for all polydispersities, while a standard Debye scaling would have $\sim \omega^{d-1}$. (Inset) Evolution of the average IPR with frequency. Low-frequency modes tend to be quasi-localized, as are those of fully amorphous solids. By contrast, at high frequency both the spectra and the IPR display crystal peaks.

high-frequency localized peaks of the crystal structure are also preserved. Because a similar normal mode distribution was observed in slightly disordered FCC packings [31], the density of vibrational states is likely universal in marginally stable packings.

V. CONCLUSION

Our work evinces that minuscule amounts of disorder are sufficient to blend the physics of crystals with that of amorphous solids. Perfect crystalline ground states are therefore a singular limit. Because relating microscopic features with macroscopic rheology is still unsolved, it is unclear whether our findings relate with those of the universality class proposed in Ref. [19], but this hypothesis deserves further consideration. The specific exponent values and their violation of the stability bounds for marginal solids observed in these systems should also motivate additional study.

The many structural and dynamical similitudes between crystals of polydisperse spheres and amorphous solids suggest that the former could be used to better understand the latter. The simplicity and stability of polydisperse crystals make them ideal for exploring the MFT Gardner transition scenario. Resolving whether a thermodynamic transition exists in finite-dimension [32–36] and for what interaction types [37], in particular, are of acute interest. Recent advances on the theory of glass formers with continuous interactions [38] suggest that a Gardner-like regime should also be observable in crystals formed of particles with continuous interactions, but only in very specific regimes. In practice this can and should be experimentally probed: both commercially manufactured colloids (with tunable interactions) and ball bearings (with very stiff Hertzian interactions) have nominal polydispersities on the order of or larger than that studied here. In colloidal systems the osmotic pressures needed to reach and exceed P_G are readily accessible, as are techniques for extremely high resolution single particle tracking [39]. Such easily accessible experimental systems could thus also be investigated to expand our understanding of rigidity in the entire spectrum from perfect order to maximal disorder [40].

Data associated with this work are available from the Duke Digital Repository [44].

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