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Anharmonic and quasi-localized vibrations in jammed solids
—Modes for mechanical failure

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Abstract – We study harmonic and anharmonic properties of the vibrational modes in 3-dimensional jammed packings of frictionless spheres interacting via repulsive, finite-range potentials. A crossover frequency is apparent in the density of states, the diffusivity and the participation ratio of the normal modes of vibration. At this frequency, which shifts to zero at the jamming threshold, the vibrational modes have a very small participation ratio implying that the modes are quasi-localized. The lowest-frequency modes are the most anharmonic, with the strongest response to pressure and the lowest-energy barriers to mechanical failure.

Introduction. – A starting point for understanding any solid is a calculation of its harmonic vibrational excitations. However, many important properties require an understanding of anharmonic effects as well. For example, in a crystal, heat transport and thermal expansion are governed by anharmonic coupling of the modes [1]. Anharmonic effects become even more essential when one considers how a solid, be it crystalline or amorphous, disintegrates and loses rigidity [2]. Such behavior requires the system to depart from the harmonic regime as it continually moves over potential-energy barriers to explore different configurations. In this letter we describe the harmonic response and discuss the anharmonic properties and energy barriers associated with the normal modes of a model amorphous solid compressed above the jamming threshold.

At the jamming transition, the system is precariously perched between a solid and a liquid. The vibrations calculated for such a solid composed of soft frictionless spheres interacting via repulsive forces possess decidedly unusual properties [3–5], some of which have now been observed in experiments [6–8]. Rather than having Debye behavior in which the density of normal modes, \(D(\omega)\), at low frequency, \(\omega\), varies as \(D(\omega) \propto \omega^{d-1}\) in \(d\) dimensions, the density of states at the transition packing fraction, \(\phi_c\), has a plateau that extends all the way down to zero frequency. Thus, there are many more low-frequency modes than can be accounted for simply by plane-wave excitations. Upon compression to a packing fraction \(\phi > \phi_c\), the plateau persists but only above a characteristic frequency, \(\omega^*\).

Here we show that as the frequency is lowered, the modes become progressively more heterogeneous with a lower-than-average mode coordination number. Below \(\omega^*\), the modes have high-displacement amplitudes in small, confined regions. Upon compression or application of shear stress, such modes can destabilize the system if their frequency passes through zero. These modes also have the lowest-energy barriers to particle rearrangements; even at low temperature, they can be sufficiently excited to force the system into different configurations. On approaching the unjamming transition, the barriers between nearby configurations must shrink to zero. Thus the jamming transition is not only marked by critical behavior in the harmonic properties of the solid [9] but also by diverging anharmonic effects.

Methods. – We analyze the same system studied previously [3,5,9,10]. Our packings consist of \(500 \leq N \leq 10000\) frictionless spheres of mass \(m\) in a three-dimensional box with periodic boundary conditions. To avoid crystallization, we use a binary mixture of spheres with diameters...
\[\sigma_L / \sigma_S = 1.4\]. The particles interact via a repulsive harmonic potential, \(V(r_{ij}) = \epsilon (1 - r_{ij} / \sigma_{ij})^2 / 2\) when the distance between the centers of particles \(i\) and \(j\), \(r_{ij}\), is smaller than the sum of their radii, \(\sigma_{ij}\), and 0 otherwise. Here \(\epsilon\) is the energy scale. We use units where \(\epsilon = 1\), \(\sigma_S = 1\), and \(m = 1\). The jammed solids were generated through conjugate gradient energy minimization \[11\]. We tuned the volume fraction and successively minimized the energy until a jammed solid at \(\Delta \phi \equiv \phi - \phi_c\) was obtained.

For comparison, we also constructed an unstressed counterpart for each configuration studied. Such systems offer special insights. To obtain unstressed systems, we replace the interaction between each pair of particles by an unstretched spring with the same spring constant, \(V''\), as in the original system. Thus, the pressure is automatically zero for this random spring network that has the identical geometry and coordination as the original sphere packing. By comparing the stressed system to its unstressed counterpart, we can untangle the separate effects of coordination and pressure.

We diagonalize the Hessian matrix of the jammed solids \[12\] to obtain the frequency \(\omega_n\) and normalized polarization vector \(e_{n,i}\) of each particle \(i\) in mode \(n\). From these quantities, we calculate the density of states, \(D(\omega)\), and the energy diffusivity, \(d(\omega)\) \[5,10\], which can be understood physically as follows. Consider a wavepacket narrowly peaked at a frequency \(\omega\) and localized at the origin. Over time, the wavepacket spreads out so it can eventually be characterized by a time-independent diffusivity given by the square of the width of the wavepacket at time \(t\), divided by \(t\).

We also calculate geometrical properties of each mode. The participation ratio \(p(\omega_n)\) quantifies how extensive a mode is and ranges from 0 (fully localized) to 1 (fully extended):

\[p(\omega_n) = \frac{\left(\sum_i |e_{n,i}|^2\right)^2}{N \sum_i |e_{n,i}|^4}.\]  

We also compute \(z(\omega_n)\), the effective coordination number weighted by the polarization vectors in each mode:

\[z(\omega_n) = \sum_i z_i |e_{n,i}|^2,\]  

with \(z_i\) the number of interacting neighbors of sphere \(i\).

To quantify the anharmonicity of each mode we compute the Gruneisen parameter, \(\gamma(\omega_n)\), which measures the frequency shift of a mode with compression

\[\gamma(\omega_n) = \frac{d(\ln \omega_n)}{d(\ln \phi)} \text{.}\]  

In jammed solids, both the pressure \(P\) and coordination number \(z\) vary with compression and affect the frequency of the modes \[9,13,14\]. Therefore, eq. (3) is rewritten as

\[\gamma(\omega_n) = \gamma_P(\omega_n) + \gamma_\phi(\omega_n)\]

\[= \frac{\phi}{\omega_n} \left(\frac{\partial \omega_n}{\partial P}\right)_z \frac{\partial P}{\partial \phi} + \frac{\phi}{\omega_n} \left(\frac{\partial \omega_n}{\partial z}\right)_P \frac{\partial z}{\partial \phi}.\]  

Near \(\phi_c\), there is always a small fraction \(\xi\) of particles that are rattlers\footnote{1}. The rattlers may become network particles upon compression and contribute to \(\gamma_\phi\): \(\gamma_\phi(\omega_n) = -\frac{\partial^2 \omega_n}{\partial (\phi \Delta \phi)} + \xi \frac{\partial^2 \omega_n}{\partial \phi^2}_P \frac{\partial \phi}{\partial \Delta \phi}\), where \(\left(\frac{\partial \omega_n}{\partial \phi}\right)_P\) and \(\left(\frac{\partial^2 \omega_n}{\partial \phi^2}\right)_P\) are the change of \(\omega_n\) with respect to \(\phi\) without and with the change of the number of rattlers, respectively.

We measured \(\gamma_\phi\) in the linear-response regime without changing the number of particle interactions. We measured \(\gamma_\phi\) at fixed pressure by adding unstretched springs with spring constant \(V''\) between neighboring particles that do not interact but would touch under compression. We do the same for a rattler and its neighbors. The derivative \(\partial z / \partial \phi\) was calculated from the increase of \(z\) with compression as computed, \(\gamma_\phi\), in ref. \[9\]. We have calculated \(\gamma_\phi\) and \(\gamma_\phi\) for Hertzian as well as harmonic repulsions, to verify that the results are unaffected by the discontinuity in the curvature of the potential at contact that arises in the harmonic case.

We also compute \(u_{\max}(\omega_n)\), which is how far the \(n\)-th normal mode can be displaced (leaving all other modes excited) before the system crosses an energy barrier and flows to a different configuration. To measure \(u_{\max}(\omega_n)\), we first displaced the jammed state at \(R_0 = (r_1, r_2, \ldots, r_N)\) along \(e_n\) to \(R(u, \omega_n) = R_0 + u e_n\), and then quenched the perturbed system to the local energy minimum. When \(u < u_{\max}(\omega_n)\), the system returns to \(R_0\), but when \(u > u_{\max}(\omega_n)\) the local energy minimum changes.

Thus, \(u_{\max}(\omega_n)\) sets the maximum displacement of the \(n\)-th mode below which \(R\) remains in the same energy basin.

The energy barrier of the basin of attraction along mode \(n\) is \(V_{\max}(\omega_n) = V(R(u_{\max}(\omega_n), \omega_n)) - V(R_0)\), where \(V(R)\) is the potential energy per particle at \(R\). Because the jammed solid configurations are amorphous, there is no symmetry and \(u_{\max}\) and \(V_{\max}\) will be different for the + and − directions of each mode. We define \(u_{\max}(\omega_n)\) and \(V_{\max}(\omega_n)\) as the minimum values over these two directions. In general, the basins have a complex boundary \[15\] so that linear combinations of different normal modes will give different magnitudes for the maximum displacements and energy barriers. The results presented here for \(V_{\max}\) provide an upper bound on the minimum-energy barrier at frequency \(\omega\).

**Nature of the vibrational modes: harmonic properties.** In fig. 1, we show several properties of the modes as a function of frequency for both an unstressed (left column) and a stressed (right column) configuration at the relatively large compression of \(\Delta \phi = 0.1\). We first consider the harmonic properties: the density of states \(D(\omega)\) \[3\], the energy diffusivity \(d(\omega)\) \[5,10\], the participation ratio \(p(\omega)\) \[4\] and the mode-average coordination number \(z(\omega)\).
In the unstressed system, there are three regimes as observed previously for stressed systems [4]: i) At low \( \omega \) there is a regime of low scattering where the modes are weakly-scattered plane waves. These modes appear as peaks in the density of states, the diffusivity and the participation ratio, since they are quantized by the finite size of our system. In this regime, the diffusivity decreases sharply with increasing \( \omega \) in a manner consistent with Rayleigh scattering. ii) At intermediate frequencies, above a characteristic frequency (denoted by a vertical dashed line in the left column of fig. 1) that scales as \( \omega^* \propto \Delta c^{0.5} \), there is strong scattering of the plane waves [5,10]. In this regime, the density of states is high and the energy diffusivity is small and nearly constant. iii) At high frequencies, the modes are localized.

Signatures of the crossover at \( \omega^* \) appear in all quantities studied in the unstressed systems. Previously, it was shown that the rise in the density of states at \( \omega^* \) corresponds to a boson peak [3] and that the leveling off of the energy diffusivity at \( \omega^* \) corresponds to a crossover in the energy transport from a weak to a strong scattering regime [5,10]. Figure 1 also plots the participation ratio for every mode. For the unstressed systems, \( p(\omega_n) \) has a pronounced dip at \( \omega^* \) indicating that the modes in this regime are more localized than elsewhere in the spectrum (except for the Anderson-localized modes at high frequency). Above \( \omega^* \), the modes are extended with a roughly constant participation ratio \( p(\omega) \approx 0.5 \). The drop in the participation ratio near \( \omega^* \) is perhaps not surprising if one considers that \( \omega^* \) marks a dramatic drop in the density of vibrational modes, which can lead to localization. In this case, plane waves below \( \omega^* \) hybridize with these modes, so that the resulting vibrations are quasi-localized; they are not truly localized but rather are confined in small spatial regions with a small plane-wave background elsewhere. Previous studies have suggested that bilinear coupling between localized vibrations and plane waves should lead to quasilocalized modes near the boson peak frequency. Moreover, this frequency should nearly coincide with the transport crossover frequency at which the mean free path becomes of the same order as the phonon wavelength [16–19]. Above this frequency the vibrational modes are expected to be delocalized and diffusive. This scenario proposed in the context of the soft potential model is consistent with our findings.

Figure 1(d) shows that these quasi-localized modes are concentrated in regions where the number of interacting neighbors is lower than average: \( z(\omega) \) has a dip at \( \omega^* \), implying that large particle displacements in the quasi-localized modes predominantly exist in low-coordination regions.

The characteristic behaviors described above for \( \text{D}(\omega),\ d(\omega),\ p(\omega) \) and \( z(\omega) \) at \( \omega^* \) are observed at all compressions in which \( \omega^* \) falls within the observable range for our simulations. In our finite-sized systems, plane waves exist at the quantized frequencies \( \omega_{n_1} = 2\pi c_{T,L} \sqrt{n_1^2 + n_2^2 + n_3^2}/L \), which shift down with increasing system size \( L \propto N^{1/3} \), where \( c_{T,L} \) is the speed of transverse or longitudinal sound, \( n_x, n_y, n_z = 0, \pm 1, \pm 2, \ldots \), and \( L \) is the linear size of the system. The system size therefore limits the observable range of frequencies. At smaller compressions, where \( \omega^* \) lies below our accessible range, we see only regimes ii) and iii), corresponding to the plateau in the diffusivity and the localized modes at high \( \omega \).

The modes in a stressed system, as compared to its unstressed counterpart, are pushed to lower frequency since repulsive forces tend to lead to buckling instabilities of the force network [5,13,14]. The comparison of the right- and left-hand panels of fig. 1(c) shows that pressure pushes the low-participation ratio (quasi-localized) modes towards \( \omega = 0 \). As a result, regime i) is pushed down in frequency until it is below our frequency range.

The participation ratio data are consistent with earlier studies of the frequency-averaged participation ratio [4].
We show here for every mode \( n \) the value of \( p(\omega_n) \) to display fine structure that is not easily observed when \( p(\omega_n) \) is averaged within frequency bins. Figure 2 shows the participation ratio for the stressed systems at three compressions. In all cases, \( p(\omega_n) \) decreases dramatically and appears to reach the same very low value independent of the packing fraction. The only difference is that for higher values of \( \Delta \phi \), the anomalous modes do not persist to as low a frequency as they do for systems closer to the jamming threshold. Figure 2 shows that as the packing fraction of the system is decreased towards the unjamming transition, quasi-localized modes persist but shift to lower frequency. These results suggest that the characteristic size of high-displacement regions in quasi-localized modes does not scale as the cutting length introduced in ref. [13], which diverges with decreasing compression. Rather, the size can be arbitrarily small, as in ordinary localization, due to the expected drop in the density of states at the crossover between the Debye regime and the plateau in the density of states.

Because we are dealing with finite-size samples, it is difficult to ascertain whether the participation ratio can become arbitrarily small and approach zero in the thermodynamic limit. It is also difficult to determine the properties of the low-frequency modes in large systems where plane-wave modes are plentiful at low frequency. Since there is no symmetry to forbid it, the plane waves will hybridize with the excess modes to produce some low-amplitude plane-wave character at large distances. Figure 3 shows the participation ratio at different system sizes \( N \). At \( \omega \approx \omega_{\text{pu}} \), plane-wave peaks appear superimposed on a smooth background. The peaks shift downwards and increase with increasing \( N \), but the background remains unaffected. This \( N \)-independent background clearly shows the trend of decreasing participation ratio with decreasing frequency, suggesting that in the large-\( N \) limit, the participation ratio at \( \omega^* \) should approach arbitrarily small values at low frequencies.

**Nature of the vibrational modes: anharmonic properties.** – Figure 1 also shows one measure of the anharmonic behavior of the modes, the Grüneisen parameter, vs. frequency. We separately plot the pressure and coordination number contributions to the Grüneisen parameter \( \gamma_P(\omega) \) and \( \gamma_z(\omega) \) along with the total \( \gamma(\omega) = \gamma_P(\omega) + \gamma_z(\omega) \) for both unstressed and stressed systems.

The crossover frequency \( \omega^* \) from regime i) to regime ii) is determined by the extra coordination number above isostaticity \( \Delta z \) and pressure \( P \): \( \omega^* \sim \sqrt{A(\Delta z)^2 - BP} \), where \( A \) and \( B \) are positive constants [13,14]. Applying this to the entire spectrum above \( \omega^* \), we derive the frequency dependence of the Grüneisen parameters: \( \gamma_P(\omega) \sim -\omega^{-2} \), and \( \gamma_z(\omega) \sim -\omega^{-1} \). These scalings are verified in fig. 4. The different frequency dependences of \( \gamma_P \) and \( \gamma_z \) lead to a crossover frequency \( \omega_\gamma \) at which \( \gamma = \gamma_P + \gamma_z = 0 \). For \( \omega > \omega_\gamma \), the modes move upwards in frequency upon compression, while for \( \omega < \omega_\gamma \) the modes shift downwards.

The inset to fig. 4 shows \( \omega_\gamma \), estimated at various volume fractions for stressed systems: \( \omega_\gamma \sim (\Delta \phi)^{1/2} \). This is the...
Data were averaged over frequency bins. System sizes are then varied in the overall magnitude of several configurations. There is significant variation of its original energy basin. The results are shown for different realizations of jammed systems. Data were averaged over frequency bins.

same scaling as was found for \( \omega^* \), the onset of excess modes (the boson peak) in the density of states [3], and for \( \omega_d \), the onset of the low-diffusivity plateau [5,10]. Figure 1 shows that below \( \omega^* \), the Grüneisen parameter becomes enormous and negative in stressed systems. Thus the low-frequency modes are localized, highly anharmonic and unstable. This is completely different from the situation for crystals, where the Grüneisen parameter is small and independent of frequency: \( \gamma(\omega) = -1/6 \) in \( d \) dimensions, where \( c(\phi) \) is the speed of sound. For a 3-dimensional crystal of spheres interacting with finite-ranged harmonic repulsions, \( \gamma(\omega) = -1/6 \). The way that localization can affect the anharmonic properties of a mode has previously been explored [20]. The localized modes at high frequencies do not show large \( \gamma(\omega) \) in agreement with observations on Lennard-Jones glasses [20] and amorphous silicon [21].

Figure 5(a) shows another measure of anharmonicity: the maximum displacement \( u_{\text{max}} \) and energy barrier \( V_{\text{max}} \) along each mode, \( n \), before falling into another basin of attraction for stressed systems at \( N = 1000 \) and \( \Delta \varphi = 0.1 \). Seven configurations are shown to demonstrate that the trend in frequency is similar in all cases but that there is significant variation in the magnitudes of \( u_{\text{max}} \) and \( V_{\text{max}} \) between different realizations of jammed systems.

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Fig. 5: (Colour on-line) Spectra of (a) the maximum displacement \( u_{\text{max}} \) and (b) energy barrier \( V_{\text{max}} \) along each mode, \( n \), before falling into another basin of attraction for stressed systems at \( N = 1000 \) and \( \Delta \varphi = 0.1 \). Seven configurations are shown to demonstrate that the trend in frequency is similar in all cases but that there is significant variation in the magnitudes of \( u_{\text{max}} \) and \( V_{\text{max}} \) between different realizations of jammed systems. Data were averaged over frequency bins.

The energy barrier, \( V_{\text{max}} \), is shown in fig. 5(b). Note that the barrier height shows a very strong frequency dependence, with the lowest-frequency modes having the lowest-energy barriers. The increase is consistent with the expectation \( V_{\text{max}} \sim u_{\text{max}}^2 \). Thus at low temperatures, the low-frequency quasi-localized modes are the ones that will most easily be driven unstable by thermal energy, producing localized melting at low temperatures.

Conclusions. — We studied the harmonic and anharmonic properties of the vibrational modes in jammed packings of frictionless spheres. We find that the participation ratio of the modes drops with decreasing frequency so that modes become highly resonant, or quasi-localized, at a characteristic frequency that approaches zero at the jamming threshold. Their participation ratio remains low when the system size is increased. In some ways, these modes resemble the localized modes at the high-frequency end of the spectrum, in that both types of modes have small participation ratio and are localized in regions with fewer constraints than average. However, the quasi-localized modes are significantly different from the localized ones in that they are the most anharmonic modes in the system, with the largest negative Grüneisen parameters and the lowest-energy barriers for crossing into different basins in the potential-energy landscape.

Similar quasi-localized modes at low frequencies have been observed in simulations of amorphous silicon [21–23], Lennard-Jones glasses [24,25] and soft repulsive disks [26], as well as in experiments on amorphous polymers [27]. In silica, the modes also occur near the boson peak frequency [23], the high-displacement regions in these modes are preferentially situated on under-coordinated atoms [22], and the modes themselves have strong anharmonic corrections [21,23], consistent with our findings. Our results suggest that the existence of highly anharmonic, low-frequency, quasi-localized modes near the boson peak frequency is not just a feature of specific systems. Rather, it is a common feature of disordered packings, which can be understood within the jamming scenario as originating from zero-frequency modes at the isostatic jamming transition. The presence and importance of these modes can be tuned by varying the compression \( \phi - \phi_c \). With this control parameter, we have studied how different properties are related to one another and identified their common cause — the underlying isostatic jamming transition.

The strong anharmonicity and low-energy barriers associated with the low-frequency quasi-localized modes imply that when the system is compressed further or sheared, it is these modes that eventually go unstable and give rise to spatially heterogeneous elastic moduli [28] and initially localized rearrangements in the sample. This
neglected is controlled by the proximity to this transition. Anharmonic effects, such as those studied here, can be more anharmonic and smaller excitation energies should be achieved as the unjamming transition is approached; modes must become progressively localized at low frequency and associated with low-coordinated regions in disordered packings. These modes with low-energy barriers present a new avenue for material failure. They should play an especially important role in low-temperature glasses, where they are the only modes populated. This suggests that further work should be done to examine the relation of these modes to the physics of two-level systems, which are believed to be the dominant excitations in low-temperature glasses.

Finally, as noted above, the energy barriers of soft-sphere systems decrease to zero as the unjamming transition is approached; modes must become progressively more anharmonic and smaller excitation energies should suffice to force the system into new ground states. Not only does the jamming/unjamming transition create critical behavior in the harmonic properties of the solid [9] but also in its anharmonic response. The stress and temperature domain over which harmonic theory applies and anharmonic effects, such as those studied here, can be neglected is controlled by the proximity to this transition.

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