Singularities in Hessian element distributions of amorphous media

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Outline

Amorphous Materials

Figure: Amorphous materials display characteristics that are both liquid and solid-like.

Amorphous Materials

- Materials that **do not form periodic spatial patterns**.
- Many properties displaying **extreme deviations from equilibrium**.
- Display **non-Debye** behaviour in density of states.
- **Localised modes** that makes the vibrational density of states non-trivial.
- Can be broadly classified as **athermal**.

The Hessian

- The Hessian matrix is defined to be

$$\mathcal{H}^{ij}_{\alpha\beta}(\mathrm{r}^{ij}) = \frac{\partial^2 U\left[\{\mathrm{r}^i\}\right]}{\partial r^{ij}_{\alpha} \partial r^{ij}_{\beta}} \tag{1}$$

- Here $\vec{r}^{ij} := \vec{r}^{i} - \vec{r}^{j}$ is the **inter-particle distance vector** between particles i and j.
- When the total potential energy is the **sum of two-particle, central potentials**:

$$U\left[\{\mathrm{r}^{ij}\}\right] = \sum_{ij} \psi^{ij}(r^{ij}) \tag{2}$$

- The Hessian for radially symmetric potentials is

$$\mathcal{H}^{ij}_{\alpha\beta}(\mathrm{r}^{ij}) = -\left(\frac{\psi^{ij}_{rr}}{(r^{ij})^2} - \frac{\psi^{ij}_{r}}{(r^{ij})^3}\right) r^{ij}_{\alpha} r^{ij}_{\beta} - \delta_{\alpha\beta}\frac{\psi^{ij}_{r}}{r^{ij}} \tag{3}$$

Amorphous Materials

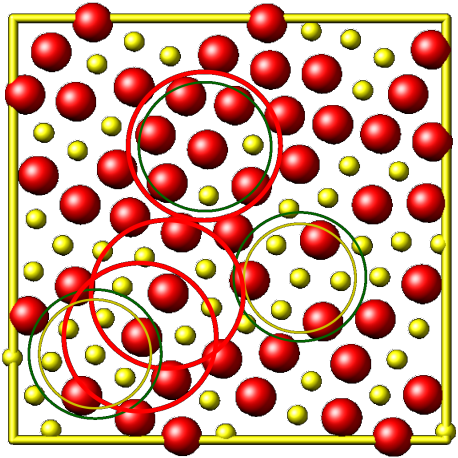


Figure: An energy minimised structure of a 100-particle system of a glass forming model. The rings indicate interaction radii.

Hessian Matrix of Amorphous Systems

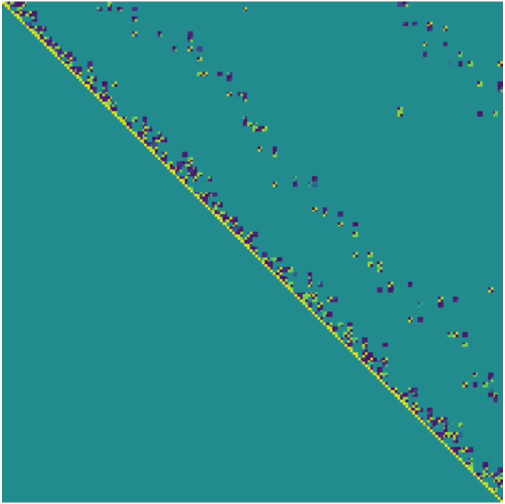


Figure: A typical Hessian matrix of a 100-particle system of a glass forming model.

Amorphous versus Crystal Hessians

- Amorphous Hessians contain a preponderance of small elements

V. V. Krishnan, S. Karmakar, K. Ramola, Phys. Rev. Research 2, 042025 (2020).

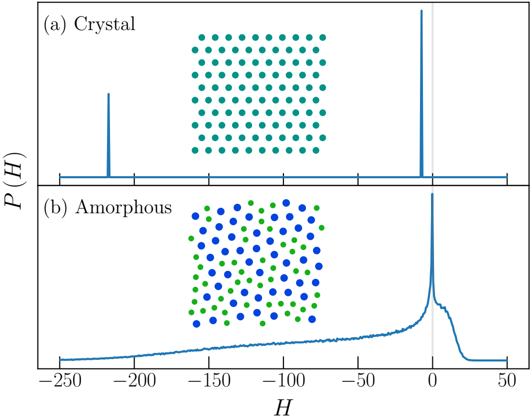


Figure: Comparison of energy minimised configurations in (a) a mono-disperse crystal and (b) an amorphous glass consisting of two types of particles.

Potentials and Smoothness

- In simulations, interaction potentials are **cut-off** at a finite distance for computational expediency, and are **smoothed** to relevant degrees.

- The potential is smooth to 'n' derivatives at cut-off (r_c):

$$\left.\frac{d^m\psi}{dr^m}\right|_{r_c} = 0 \quad \forall \quad m \in \{0,\ldots,n\} \tag{4}$$

- For n=2:

$$\psi(r) \sim r^{-10} + c + br^2 + ar^4 \quad \text{with} \quad (\psi(r_c) = \psi'(r_c) = \psi''(r_c) = 0)$$

- For n=3:

$$\psi(r) \sim r^{-10} + c + br^2 + ar^4 + dr^6 \quad \text{with}$$
$$(\psi(r_c) = \psi'(r_c) = \psi''(r_c) = \psi'''(r_c) = 0)$$

Potentials and Iso-Hessian Contours

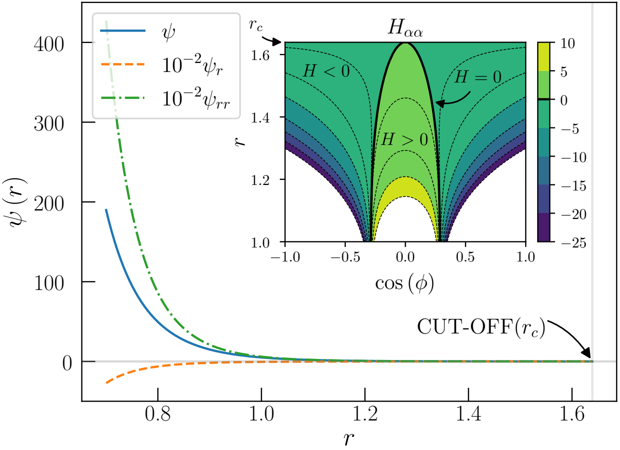


Figure: The R10 potential $\psi(r) \sim r^{-10} + c + br^2 + ar^4$ for A-B interactions, smoothed to two derivatives ($n = 2$) at the cut-off.

Symmetry Considerations

- **Diagonal elements** in 2D and 3D ($\alpha = \beta$): By symmetry *xx*, *yy* and *zz* Hessian elements are the same, and therefore we only consider one of them.
- **Off-Diagonal elements** in 2D and 3D ($\alpha \neq \beta$): By symmetry the *xy*, *yz* and *zx* Hessian elements are the same, and therefore we only consider one of them.
- **In two dimensions** the inter-particle distance vector is determined by its magnitude r and angle (ϕ) with respect to the x-axis.
- **In three dimensions** the inter-particle distance vector is determined by its magnitude, the polar angle (θ) subtended on the z-axis, and the azimuthal angle (ϕ) on the $x - y$ plane.

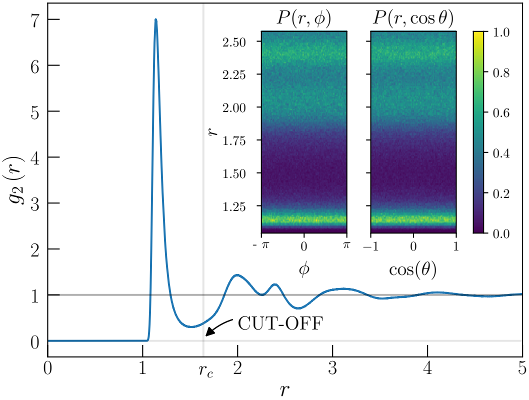


Figure: Numerically sampled radial distribution function of A-B particle pairs in the R10 system in three dimensions.

Probability transformations

- Integrating over Iso-Hessian Contours

$$P(H) = \int dr\, d\Omega\, P(r, \Omega)\, \delta\Big(H - \mathcal{H}^{ij}_{\alpha\beta}(\mathrm{r}^{ij})\Big) \tag{5}$$

- Assuming isotropy $(P(r, \Omega) = P(r)P(\Omega))$,

$$P(H) = \int_0^{r_c} dr\ P(r)\ \frac{P(\Omega)}{\left|\frac{\partial H}{\partial \Omega}\right|} = \int_0^{r_c} dr\ P(r)\ \mathcal{P}(H, r) \tag{6}$$

- The distribution of angles is

$$P_{2D}(\phi) = P_{3D}(\phi) = \frac{1}{2\pi} \text{ and } P_{3D}(\cos\theta) = \frac{1}{2} \tag{7}$$

- The distribution of inter-particle distances is

$$P(r) \sim g_2(r)\Theta(r_c - r) \tag{8}$$

Partial Integrand — 2D, Diagonal

- The diagonal Hessian element, in two dimensions is

$$H_{xx}^{2D} = -\left(\psi_{rr} - \frac{\psi_r}{r}\right)\cos^2\phi - \frac{\psi_r}{r} \tag{9}$$

- Using the partial integrand

$$\mathcal{P}(H, r) = \left[\left|\frac{\partial H}{\partial \Omega}\right|\right]^{-1} P\left(\Omega\right) \tag{10}$$

- with $\Omega \equiv \cos\phi$ with the distribution $P_{2D}\left(\Omega\right) = 1/\left(\pi\sqrt{1-\Omega^2}\right)$ yields

$$\mathcal{P}_{\alpha\alpha}^{2D}\left(H, r\right) = \left|4\pi^2\left(H + \frac{\psi_r}{r}\right)\left(H + \psi_{rr}\right)\right|^{-1/2} \tag{11}$$

Partial Integrand — 2D, Off-Diagonal

- The off-diagonal Hessian element, in two dimensions is

$$\mathcal{H}_{xy}^{2D} = -\left(\psi_{rr}^{ij} - \frac{\psi_r^{ij}}{r}\right)\cos\phi\sin\phi. \tag{12}$$

- Using the partial integrand

$$\mathcal{P}(H,r) = \left[\left|\frac{\partial H}{\partial \Omega}\right|\right]^{-1} P\left(\Omega\right)$$

- with $\Omega \equiv \cos\phi$ with the distribution $P_{2D}\left(\Omega\right) = 1/\left(\pi\sqrt{1-\Omega^2}\right)$ yields

$$\mathcal{P}_{\alpha\beta}^{2D}\left(H,r\right) = \left[\sqrt{\left|\left(\psi_{rr} - \frac{\psi_r}{r}\right)^2 - 4H^2\right|}\right]^{-1}, \tag{13}$$

Partial Integrand — 3D, Diagonal

- The diagonal Hessian element, in three dimensions is

$$\mathcal{H}_{zz}^{ij}\left(r^{ij},\theta\right) = -\left(\psi_{rr}^{ij} - \frac{\psi_r^{ij}}{r}\right)\cos^2\theta - \frac{\psi_r^{ij}}{r}. \tag{14}$$

- Using $\Omega \equiv \cos\theta$, with the distribution $P_{3D}\left(\cos\theta\right) = \frac{1}{2}$
- The partial integrand then becomes $\mathcal{P}_{zz}^{3D} = \left[2\left|\frac{\partial H}{\partial \cos\theta}\right|\right]^{-1}$.
- This can be simplified to yield

$$\mathcal{P}_{\alpha\alpha}^{3D}\left(H,r\right) = \left[2\sqrt{\left|\left(H + \frac{\psi_r}{r}\right)\left(\psi_{rr} - \frac{\psi_r}{r}\right)\right|}\right]^{-1}, \tag{15}$$

Partial Integrand — 3D, Off-Diagonal

- The off-diagonal Hessian element, in three dimensions is

$$\mathcal{H}^{ij}_{xz}(r,\theta,\phi) = -\left(\psi^{ij}_{rr} - \frac{\psi^{ij}_{r}}{r}\right)\cos\theta\sin\theta\cos\phi. \qquad (16)$$

- Choosing $\Omega \equiv \cos\phi$, and given that $P(\phi) = \frac{1}{2}$
- We arrive at the exact integral form $\mathcal{P}^{3D}_{xz} = \int \pi d(\cos\theta)\left[\left|\frac{\partial H}{\partial \cos\phi}\right|\sqrt{1-\cos^2\phi}\right]^{-1}$.
- This can be simplified to yield

$$\mathcal{P}^{3D}_{\alpha\beta} = \int_{-1}^{1} d(\cos\theta)\left[\sqrt{\left|\left(\psi_{rr} - \frac{\psi_r}{r}\right)^2 \sin^2\theta\cos^2\theta - H^2\right|}\right]^{-1}. \qquad (17)$$

Partial Integrands — All

$$\mathcal{P}^{2D}_{\alpha\alpha}(H,r) = \left| 4\pi^2 \left(H + \frac{\psi_r}{r} \right) (H + \psi_{rr}) \right|^{-1/2} \tag{18}$$

$$\mathcal{P}^{2D}_{\alpha\beta}(H,r) = \left| \pi^2 \left\{ \left(\psi_{rr} - \frac{\psi_r}{r} \right)^2 - 4H^2 \right\} \right|^{-1/2} \tag{19}$$

$$\mathcal{P}^{3D}_{\alpha\alpha}(H,r) = \left| 4 \left(H + \frac{\psi_r}{r} \right) \left(\psi_{rr} - \frac{\psi_r}{r} \right) \right|^{-1/2} \tag{20}$$

$$\mathcal{P}^{3D}_{\alpha\beta}(H,r) = \frac{\kappa}{H} \int_{-1}^{1} dx \left[x^2(1-x^2) - \kappa^2 \right]^{-1/2} \tag{21}$$

where

$$\kappa = H \left(\psi_{rr} - \frac{\psi_r}{r} \right)^{-1}$$

$P(H)$ using an exact radial distribution function

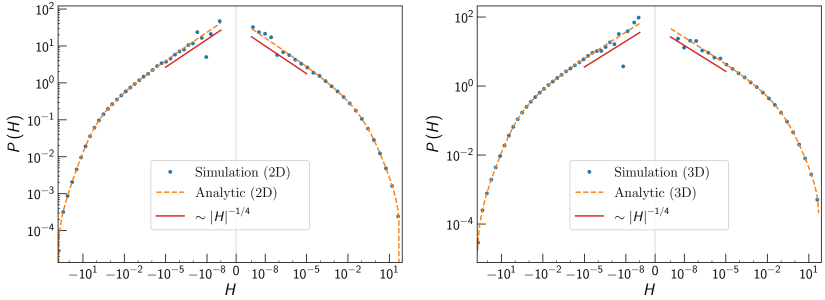


Figure: Distribution of diagonal Hessian elements ($\alpha = \beta$) corresponding to A-B interactions in the R10 model, using an exact form for the radial distribution function $g_2(r)$.

- We use an exact form for the radial distribution function

$$g_2(r) = e^{-(r-1)}\Theta(r-1), \tag{22}$$

where $\Theta(r)$ is the Heaviside theta function.

Singular Distributions

Asymptotic limit

- In the limit of $r \to r_c$, the interaction potential can be approximated as

$$\begin{aligned} \psi(r) &= (r_c - r)^{n+1} f(r), \\ \psi_r / r &\approx C_1 (r_c - r)^n, \\ \psi_{rr} &\approx C_2 (r_c - r)^{n-1} \end{aligned} \tag{23}$$

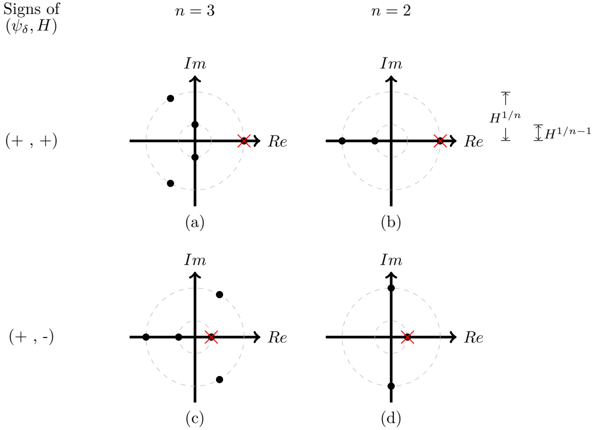
- Therefore the **partial integrand is singular** when

$$(r_c - r)^n = -\frac{H}{C_1}, \quad (r_c - r)^{n-1} = -\frac{H}{C_2} \tag{24}$$

- So, given a value of 'H', the singularity occurs at a **shifted value**:

$$r^* = r_c - s(H) \tag{25}$$

- The shift is determined by the **closest pole on the real axis**.



Signs of (ψ_δ, H)	Shift $s(H)$
$(+,+)$	$(H/C_1)^{1/n}$
$(+,-)$	$(H/C_2)^{1/n-1}$
$(-,+)$	$(H/C_2)^{1/n-1}$
$(-,-)$	$(H/C_1)^{1/n}$

Table: The various possible shifts $s(H)$ for the diagonal elements $(\alpha = \beta)$ in two dimensions.

- Define a **distance to the singular point**:

$$\epsilon = r^* - r = (r_c - s) - r \tag{26}$$

- The derivatives of the interaction potential simplify to

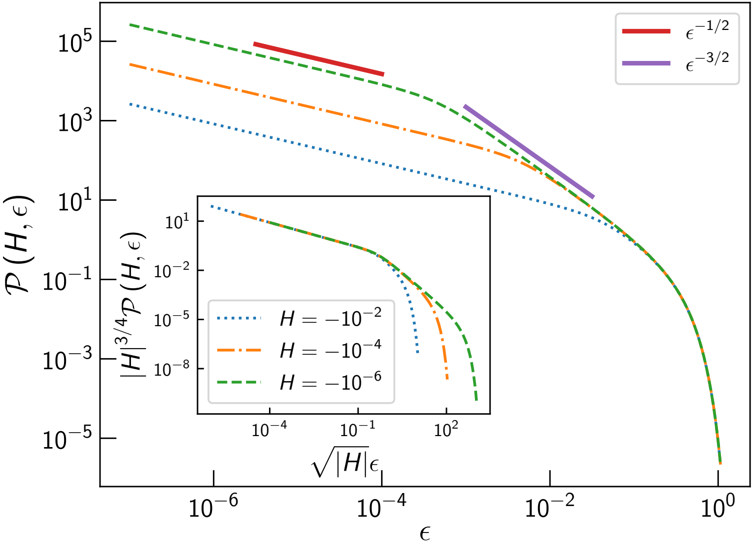
$$\psi_r/r \approx C_1(\epsilon + s)^n, \quad \psi_{rr} \approx C_2(\epsilon + s)^{n-1} \tag{27}$$

- and the partial integrand is

$$\mathcal{P}^{2D}_{\alpha\alpha}(H, \epsilon) \sim \left[(H + C_1(\epsilon + s)^n)\left(H + C_2(\epsilon + s)^{n-1}\right)\right]^{-1/2} \tag{28}$$

Singular Distributions

Asymptotics ($n = 2$)



Singular Distributions

Asymptotic integral

- In the case of $n=2$, we have two regimes: $\epsilon \in [\sqrt{H}, \infty)$ and $\epsilon \in [0, \sqrt{H})$:

$$I_1(H) \sim \int_{\sqrt{H}}^{\infty} \left[(\epsilon^2)(\epsilon)\right]^{-\frac{1}{2}} = \int_{\sqrt{H}}^{\infty} \epsilon^{-\frac{3}{2}} = \epsilon^{-\frac{1}{2}}\Big|_{\sqrt{H}}^{\infty} \sim H^{-\frac{1}{4}} \quad (29)$$

$$I_2(H) \sim \int_0^{\sqrt{H}} [(H)(\epsilon)]^{-\frac{1}{2}} = H^{-\frac{1}{2}} \int_0^{\sqrt{H}} \epsilon^{-\frac{1}{2}} = H^{-\frac{1}{2}}\, \epsilon^{\frac{1}{2}}\Big|_0^{\sqrt{H}} = \boxed{H^{-\frac{1}{4}}} \quad (30)$$

- For a general n, when $H \times \psi_\delta > 0$, there are two intervals: $[0, H^{1/n})$, and $[H^{1/n}, \infty)$, and

$$I_1(H) \sim \int_{H^{\frac{1}{n}}}^{\infty} \left[(\epsilon^n)(\epsilon^{n-1})\right]^{-\frac{1}{2}} = \int_{H^{\frac{1}{n}}}^{\infty} \epsilon^{-n+\frac{1}{2}} = H^{-1+\frac{3}{2n}}. \quad (31)$$

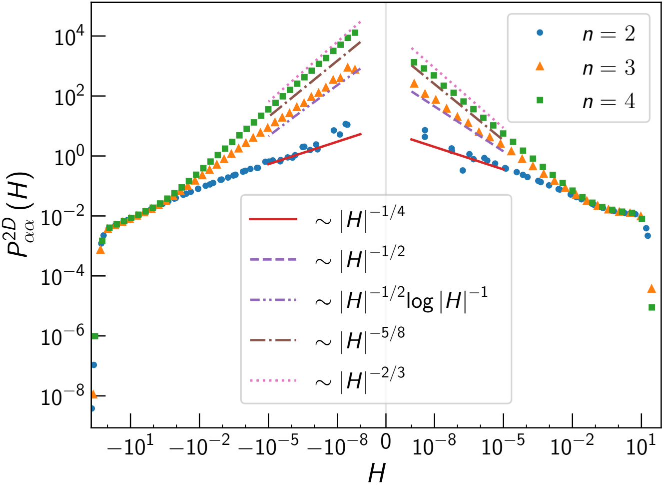
$$I_2(H) \sim \int_0^{H^{\frac{1}{n}}} \left[(\epsilon H^{\frac{n-1}{n}})(H^{\frac{n-1}{n}})\right]^{-\frac{1}{2}} = H^{-1+\frac{1}{2n}} \int_0^{H^{\frac{1}{n}}} \epsilon^{-1/2} \boxed{\sim H^{-1+\frac{3}{2n}}}. \quad (32)$$

Summary of Exponents

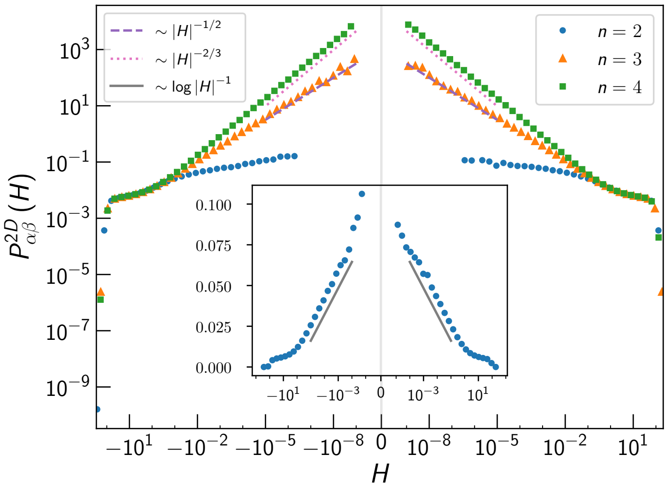
Element (H)	Smoothness (n)	$\lim_{H\to 0} P(H)$
Diagonal	$[2,\infty)^*$	$\|H\|^{-1+\frac{3}{2n}}$
($\alpha = \beta$)	$\{2\}^\dagger$	$\|H\|^{-1+\frac{3}{2n}}$
	$\{3\}^\dagger$	$\|H\|^{-\frac{1}{2}} \log\left(\|H\|^{-1}\right)$
	$(3,\infty)^\dagger$	$\|H\|^{-1+\frac{1}{n-1}}$
Off-Diagonal	$\{2\}$	$\log\left(\|H\|^{-1}\right)$
($\alpha \neq \beta$)	$(2,\infty)$	$\|H\|^{-1+\frac{1}{n-1}}$

Table: Asymptotic behaviour of Hessian element distributions in the limit $H \to 0$. Relative signs: $\psi_\delta \equiv \psi(r_c - \delta)$. The case $(*)$ corresponds to $H \times \psi_\delta > 0$, while $(\dagger)$ corresponds to $H \times \psi_\delta < 0$. The results are identical for both two and three dimensions.

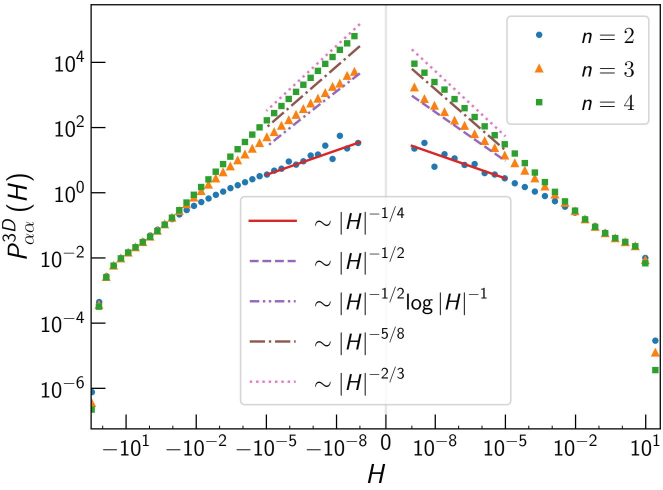
Diagonal Element Distributions: 2D



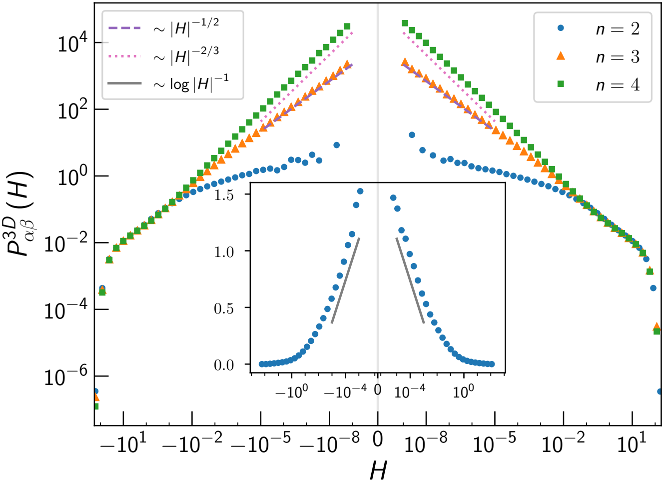
Off-Diagonal Element Distributions: 2D



Diagonal Element Distributions: 3D



Off-Diagonal Element Distributions: 3D



Minimum eigenvalue distributions

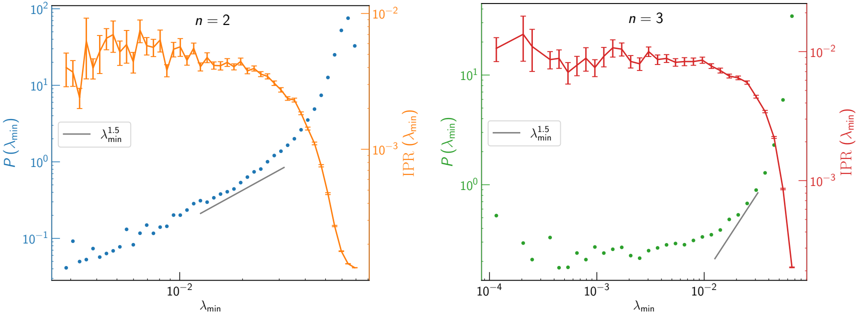


Figure: The distributions of the minimum eigenvalue of systems of size $N = 10,000$ in 2D, along with the Inverse Participation Ratios for systems with interaction potentials smooth to **(Left)** 2 and **(Right)** 3 derivatives at cut-off. The grey line corresponds to the universal ω^4 regime observed in the vibrational density of states of amorphous systems.

Minimum eigenvectors

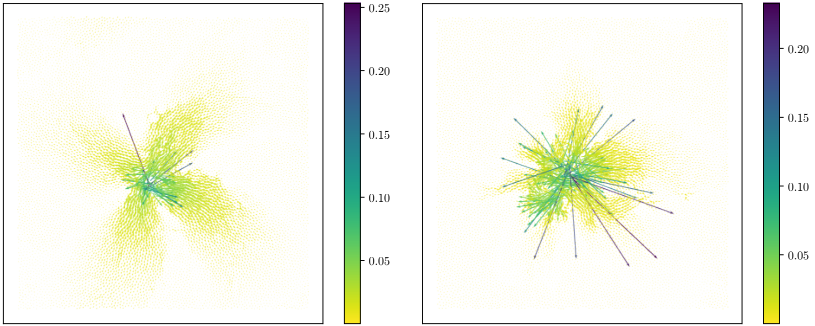


Figure: Minimum eigenvectors of 2D systems of 10,000 particles, corresponding to potentials with smoothness **(Left)** $n = 2$, and **(Right)** $n = 3$. These eigenmodes were picked from the low-end of the distribution of minimum eigenvalues, and belong to different regimes of $P(\lambda_{\text{min}})$.

Conclusions

- We have presented analytic results for the distribution of Hessian elements in disordered amorphous media in 2D and 3D.
- Our treatment is quite general, relying only on the **isotropy** of the underlying amorphous medium.
- We have shown that the Hessian matrices of amorphous materials display a **singularity that depends on the smoothness** of the interaction potential at the cut-off distance.
- Remarkably, the results for the cusp singularities are **exactly the same in both 2D and 3D**.
- We have shown numerically that such singularities **affect the low-lying eigenvalues** of the Hessian matrix that govern the stability or fragility of amorphous solids.

Outlook

- Such singularities are an important ingredient to be taken into account in **Random Matrix treatments** of Hessian matrices of amorphous materials.
- It would be interesting to extend our analytic results to **construct bounds on the vibrational density of states** of amorphous systems.
- It would be interesting to extend our results to jamming transitions, that are characterized by **diverging pair correlation functions** at the cut-off distance.

Thank You.