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Short-range correlations control the G/K and Poisson ratios of amorphous solids and metallic glasses

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The bulk modulus of many amorphous materials, such as metallic glasses, behaves nearly in agreement with the assumption of affine deformation, namely that the atoms are displaced just by the amount prescribed by the applied strain. In contrast, the shear modulus behaves as for nonaffine deformations, with additional displacements due to the structural disorder which induce a marked material softening to shear. The consequence is an anomalously large ratio of the bulk modulus to the shear modulus for disordered materials characterized by dense atomic packing, but not for random networks with point atoms. We explain this phenomenon with a microscopic derivation of the elastic moduli of amorphous solids accounting for the interplay of nonaffinity and short-range particle correlations due to excluded volume. Short-range order is responsible for a reduction of the nonaffinity which is much stronger under compression, where the geometric coupling between nonaffinity and the deformation field is strong, whilst under shear this coupling is weak. Predictions of the Poisson ratio based on this model allow us to rationalize the trends as a function of coordination and atomic packing observed with many amorphous materials. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4862403>]

I. INTRODUCTION

In a disordered solid, every microscopic building block (atom, molecule, particle) is surrounded by its bonded (nearest) neighbors which are placed at random around it. As we apply a deformation to a solid, the atoms tend to affinely follow the macroscopic strain. In so doing, the bonded neighbors transmit forces to their neighbors. Due to the lack of local inversion symmetry in disordered systems, and in chiral lattices as well, the forces transmitted by the bonded neighbors do not cancel as they would do in an ordered lattice. The result is a net force f_i acting on every atom i during the deformation, in addition to the effects of an affine strain. To equilibrate this force such that mechanical equilibrium is reached, additional nonaffine displacements arise.¹⁻⁴ Nonaffine displacements induce a significant reduction in the shear elastic constant of amorphous solids, which are in general less rigid than crystalline solids.⁵⁻⁷ For metallic glasses, it is well documented that the shear elastic constant may be up to 50% lower than the one of the corresponding crystal of the same composition.⁸ In the limit of weak disorder (e.g., crystals with defects) other mechanisms may be active, such as local cancellation of first and second-order terms in the free energy expansion.⁹

For a broad class of amorphous materials (e.g., amorphous metals), however, the elastic response under compression appears to be little affected by nonaffinity and in fact the bulk or compression modulus K of these materials is comparable to that of the corresponding crystals with the same composition, thus behaving as if the deformation was nearly affine.^{6,10} Such discrepancy was noticed long ago in numerical calculations of amorphous packings of atoms interacting via the attractive Morse potential at $T=0$: an early model of metallic glasses.¹⁰ Already in that study, the discrepancy was correctly attributed to the bulk modulus

behaving quasi-affinely whereas the shear modulus behaves nonaffinely. Recently, it has been suggested¹¹ that there might be a correlation between the density of the packing and the Poisson ratio ν , which is uniquely determined by the ratio K/G . In particular, a ratio $K/G \simeq 2.4$ is typical of bulk metallic glasses, with high atomic packing density. This is a higher ratio compared to the one of the corresponding crystals with the same composition.^{8,11} For network glasses with lower packing density, instead, the nonaffine theory for the random network model (where the atomic radius is much smaller than the bond length) gives¹³ $K/G \simeq 5/3$, independent of the bonding type (whether purely central-force or covalent), which is in excellent agreement with numerical random-network simulations of amorphous diamond.¹² Finally, also in numerical simulations of Lennard-Jones glass,¹⁶ it has been shown that while the nonaffine correction to the shear modulus is substantial, leading to the softening of response with respect to the affine case, the nonaffine correction to the bulk modulus is negligible.

The mystery, which has to be solved, is then why in denser atomic packings (where the atomic excluded volume correlations are stronger) the response to compression tends to be nearly affine. This question cannot be resolved unless one sets up a microscopic analytical description where nonaffinity is taken into account along with a reasonable description of structural disorder and local atomic packing. This is precisely what we do here, which leads us to show that the quasi-affinity of the bulk modulus in amorphous materials is due to excluded atomic-volume correlations between atoms which lead to a local *short-range order*. This reduces the nonaffine displacements significantly under isotropic compression, at the same time producing a negligible effect on the nonaffinity in shear. In systems where the atomic size is small with respect to the range of bonding as in random networks (e.g., network glasses), this effect is small and in fact the response is strongly

nonaffine for both the bulk and the shear moduli.^{12–15} Also, our theory is able to provide a first analytical explanation of the trends discussed in Ref. 11 for the dependence of ν upon both the atomic packing and the coordination in bulk metallic glasses.

II. DERIVATION

A. Nonaffine elastic response

We work under the same assumptions that were used in the numerical simulations of Weaire *et al.*,¹⁰ namely: (i) $T=0$; (ii) pairwise central force interatomic potentials. In addition, since our theory is completely analytical, we use the harmonic approximation, which is valid at low T where metallic glasses are known to be relatively harmonic.¹⁷ While the importance of directional (e.g., bond-bending or covalent-like) components of the interatomic potentials is still an open issue, and the same caveats of Weaire *et al.*¹⁰ apply also here, one cannot exclude that realistic calculations may be done using our analytical framework in combination with the pseudopotential theory of metals for the pairwise interatomic interactions.¹⁸

Under these assumptions, the generic elastic constant $C_{i\zeta\kappa\chi}$ of an amorphous solid at low T can be written as^{16,21}

$$C_{i\zeta\kappa\chi} = C_{i\zeta\kappa\chi}^A - \sum_{i<j} \Xi_i^{i\zeta} (\underline{H}_{ij})^{-1} \Xi_j^{\kappa\chi}, \quad (1)$$

where $i\zeta\kappa\chi$ label the Cartesian components of the applied strain field. For a shear deformation γ in the xy plane we would have $i\zeta\kappa\chi = xyxy$. The affine part is the standard Born-Huang expression²² in terms of a lattice sum over nearest-neighbors (NN), which in the case of harmonic bond potential $\frac{1}{2}\kappa(R_{ij} - R_0)^2$ takes the form: $C_{i\zeta\kappa\chi}^A = \frac{R_0^{2\kappa}}{2V} \sum_{i<j} c_{ij} n_{ij}^i n_{ij}^{\zeta} n_{ij}^{\kappa} n_{ij}^{\chi}$, where, in $d=2$, $\underline{n}_{ij} = (\cos\phi_{ij}, \sin\phi_{ij})$ is the unit vector defining the orientation of a bond ij in terms of its angle ϕ_{ij} . Note that in $d=3$ there is an additional azimuthal angle θ_{ij} which defines the bond orientation. c_{ij} is the occupation matrix ($c_{ij} = 1$ for two bonded NN atoms and $c_{ij} = 0$ otherwise). $R_{ij} = |\underline{R}_j - \underline{R}_i|$, and κ is the bond stiffness.

$C_{i\zeta\kappa\chi}^{NA} = \sum_{i<j} \Xi_i^{i\zeta} (\underline{H}_{ij})^{-1} \Xi_j^{\kappa\chi}$ in Eq. (1) is the nonaffine correction term. It is positive, which reflects, based on Eq. (1), the reduction in stored elastic energy due to nonaffinity. The Hessian matrix \underline{H}_{ij} is the standard (real-space) dynamical matrix of the solid.²³ The vector $\Xi_i^{i\zeta}$ measures the increment of local force \underline{f}_i on an atom in response to the deformation of its environment (γ , in the case of shear). Note that this definition implies that this driving force for the local nonaffine relaxation is proportional to the applied affine strain, $\underline{f}_i = \Xi_i^{xy} \gamma$, for shear in the xy plane. This is in agreement with previous numerical characterizations of the nonaffine displacement field.² It has been shown that for harmonic lattices:¹⁶ $\Xi_i^{xy} = -R_0\kappa \sum_j \underline{n}_{ij} n_{ij}^x n_{ij}^y$. Since the sum runs over bonds to the nearest-neighbors j of the atom i , it is evident that in a monoatomic crystal for each bond involving i there is a mirror-image bond across a reflection plane of the crystal. In this case every bond in the sum cancels with its mirror-image and $\Xi_i^{i\zeta} = 0$, $\forall i$ in many crystal lattices.

In contrast, in the presence of lattice disorder (or in certain low-symmetry crystalline lattices), $\Xi_i^{i\zeta} \neq 0$. Let \underline{v}_k be the k eigenvector of the Hessian, associated with the k th vibrational eigenmode and with the k th eigenvalue λ_k . The set of eigenvectors \underline{v}_k with $k = 1 \dots dN$ is an orthonormal basis (ONB) in (dN) -dimensional space and therefore any (dN) -dimensional vector can be expanded in this basis. Using this fact and applying the eigenvalue equation for the Hessian $\underline{H}\underline{v}_k = \lambda_k \underline{v}_k$, after some manipulation one obtains¹⁶

$$C_{i\zeta\kappa\chi} = C_{i\zeta\kappa\chi}^A - \frac{1}{V} \sum_k \frac{(\Xi_i^{i\zeta} \cdot \underline{v}_k)(\Xi_j^{\kappa\chi} \cdot \underline{v}_k)}{\lambda_k}. \quad (2)$$

The presence of the eigenvalue at the denominator goes back to the fact that the inverse of the Hessian is used. The sum over modes does not include the zero-energy rigid-body translations for which $\lambda = 0$, which ensures that the Hessian is invertible and the sum does not diverge.¹⁶

Each (dN) -dimensional eigenvector of the dynamical matrix can be decomposed as $\underline{v}_k = \underline{a}_i \otimes \underline{e}_\alpha$, that is, into a direct product of a N -dimensional vector \underline{a}_i ($i = 1 \dots N$) with a d -dimensional vector \underline{e}_α ($\alpha = x, y, \dots$), the latter taken to be the unit vector basis of the Euclidean space. Rigorously, one should first evaluate the sum in Eq. (2) and then take the average over the disorder. Since this is not possible analytically, we first calculate the averages and then we sum, with a typical mean-field approach. Then the nonaffine contribution, as shown in Appendix A, becomes

$$C_{i\zeta\kappa\chi}^{NA} = \frac{\kappa^2 R_0^2}{V} \sum_{i<j,p<q} a_i a_p c_{ij} c_{pq} \sum_\alpha \frac{\langle n_{ij}^\alpha n_{ij}^\zeta n_{pq}^\alpha n_{pq}^\kappa n_{pq}^\chi \rangle}{\lambda_{i,\alpha}}. \quad (3)$$

In Eq. (3), the effect of microscopic structure is contained in the average over orientational disorder: $\langle n_{ij}^\alpha n_{ij}^\zeta n_{pq}^\alpha n_{pq}^\kappa n_{pq}^\chi \rangle$ where $\langle \dots \rangle = \int_0^{2\pi} \int_0^{2\pi} \dots f(\phi_{ij}, \phi_{pq}) d\phi_{ij} d\phi_{pq}$ for $d=2$ denotes the average over bond orientations according to an appropriate orientation distribution function $f(\phi_{ij}, \phi_{pq})$ for the angles ϕ_{ij} and ϕ_{pq} of the two bonds ij and pq , respectively. This distribution function contains the information on all possible correlations between ij and pq , i.e., the local short-range order. In the absence of any orientational correlations as in the random network model, the angles ϕ_{ij} and ϕ_{pq} are independent. Then, the double integral factorizes into the product of two integrals, both of the type: $\frac{1}{2\pi} \int_0^{2\pi} n_{ij}^\alpha n_{ij}^\zeta d\phi_{ij} = 0$, vanishing by symmetry. Hence, in the random network model, the only terms which survive are those for which either $ij = pq$ or $ij = qp$.

B. Short-range order and local packing

In the presence of excluded-volume repulsion between atoms, such as in metallic glasses^{6,10,11} or colloids,²⁴ it is still realistic that two *distinct* bonds ij and pq have uncorrelated orientations (leading to vanishing contributions to the sum) provided that the two bonds have no atom in common. If, however, $i = p$ and $j \neq q$ in the sum of Eq. (3), the two particles j and q cannot be placed independently at random around

the particle $i = p$, due to their mutual excluded volume. This situation is depicted in Fig. 1.

The extent of the excluded volume correlations is controlled by the ratio σ/R_0 , where σ is the hard-core cross section, i.e., the minimum distance at which the atoms can be without feeling a very large repulsion. In the limit $\sigma/R_0 \rightarrow 1$, this is equivalent closely-packed particles of diameter R_0 . In the limit $\sigma/R_0 \rightarrow 0$ we recover the random network model and there are no excluded volume correlations. We proceed by first deriving the theory for the limit of dense packings $\sigma/R_0 = 1$ which will be extended later to get a formula valid for arbitrary σ/R_0 .

To account for the excluded-volume correlations in the limit $\sigma/R_0 = 1$, we consider that whenever two bonds share one particle as in Fig. 1, the angular range where the second bond/particle can be placed with random likelihood is no longer 2π (in $d=2$) but it is given by 2π minus twice the angle occupied by the first bond/particle. If we denote by ϕ_{iq} the angle defining the orientation of the second bond, and $\phi_{ij} = \phi_{ij} + 2\psi$, it follows that the angle ψ can take any value with the same likelihood only in the range $\sin^{-1}(\sigma/2R_0) < \psi < \pi - \sin^{-1}(\sigma/2R_0)$. Upon setting $\psi^* \equiv \sin^{-1}(\sigma/2R_0)$, the angular average of these terms is given by

$$\begin{aligned} & \langle n_{ij}^\alpha n_{ij}^\xi n_{iq}^\alpha n_{iq}^\zeta \rangle \\ &= \int_{\psi^*}^{2\pi-\psi^*} d\psi \rho(\psi) \int_0^{2\pi} d\phi_{ij} \rho(\phi_{ij}) n_{ij}^\alpha n_{iq}^\alpha n_{iq}^\zeta n_{ij}^\xi n_{ij}^\xi, \quad (4) \end{aligned}$$

with the orientation distribution functions defined as

$$\rho(\psi) = \frac{1}{2\pi - 2\psi^*}, \quad \rho(\phi_{ij}) = \frac{1}{2\pi}. \quad (5)$$

With these correlation terms, the overall orientation average of the nonaffine term becomes

$$\begin{aligned} \langle n_{ij}^\alpha n_{ij}^\xi n_{pq}^\alpha n_{pq}^\zeta \rangle &= \delta_{ip}(1 - \delta_{jq})A_{\alpha,i\xi\kappa\zeta} - \delta_{iq}(1 - \delta_{jp})A_{\alpha,i\xi\kappa\zeta} \\ &+ (\delta_{ip}\delta_{jq} - \delta_{iq}\delta_{jp})B_{\alpha,i\xi\kappa\zeta} \\ &= (\delta_{ip} - \delta_{iq})A_{\alpha,i\xi\kappa\zeta} \\ &+ (\delta_{ip}\delta_{jq} - \delta_{iq}\delta_{jp})(B_{\alpha,i\xi\kappa\zeta} + A_{\alpha,i\xi\kappa\zeta}), \quad (6) \end{aligned}$$

where we defined $A_{\alpha,i\xi\kappa\zeta} \equiv \langle n_{ij}^\alpha n_{ij}^\xi n_{iq}^\alpha n_{iq}^\zeta \rangle$ and $B_{\alpha,i\xi\kappa\zeta} \equiv \langle n_{ij}^\alpha n_{ij}^\xi n_{ij}^\alpha n_{ij}^\zeta \rangle$. The first term in the r.h.s. of Eq. (6)

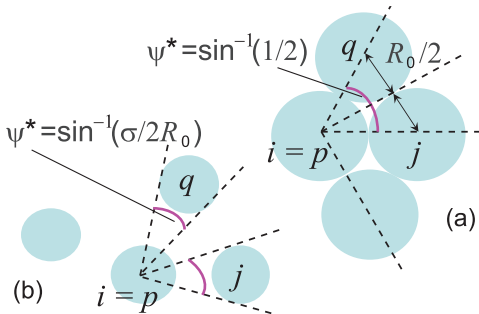


FIG. 1. (a) Illustration of the excluded-volume angle ψ^* between two bonds ij and iq shared by one atom $i = p$ when $\sigma/R_0 = 1$. (b) The same bonds with a smaller but non-zero excluded volume, $\sigma/R_0 < 1$. At $\sigma \rightarrow 0$ the exclusion $\psi^* = 0$.

accounts for the terms with $i = p$ and $j \neq q$. The minus sign in the second term on the r.h.s. (which accounts for the terms with $i = q$ and $j \neq p$) is due to frame-inversion in the second triplet: $\langle n_{ij}^\alpha n_{ij}^\xi n_{iq}^\alpha n_{iq}^\zeta \rangle = -\langle n_{ij}^\alpha n_{ij}^\xi n_{pi}^\alpha n_{pi}^\zeta \rangle = -A_{\alpha,i\xi\kappa\zeta}$. Overall, the B coefficients are the same encountered in the random network model¹³ and include only those terms for which $ij = pq$ or $ij = qp$. The coefficients A are zero in the random network model and include all terms where there is one particle in common between two bonds.

III. RESULTS AND DISCUSSION

A. Elastic constants

Upon substituting Eq. (6) into Eq. (3) and evaluating the sum over the modes in mean-field approximation, after some algebra which is listed in Appendix B, we arrive at the expression for the nonaffine contribution in the presence of excluded atomic-volume correlations

$$C_{i\xi\kappa\zeta}^{NA} \simeq \kappa R_0^2 d \frac{N}{V} \sum_{\alpha} (A_{\alpha,i\xi\kappa\zeta} + B_{\alpha,i\xi\kappa\zeta}). \quad (7)$$

The coefficients due to correlations are evaluated using the integral in Eq. (4) which in $d=2$ give

$$\begin{aligned} A_{x,xyxy} &= A_{y,xyxy} = -0.0129 \\ A_{x,xxxx} &= -0.116, \quad A_{y,xxxx} = -0.0129 \\ A_{x,xyyy} &= A_{y,xyyy} = -0.0387. \end{aligned} \quad (8)$$

The fact that $A_{\alpha,i\xi\kappa\zeta} < 0$, $\forall \alpha$ implies that the excluded-volume correlations act as to decrease the nonaffinity. This consideration is very important as it indicates that particle short-range correlations reduce the nonaffinity by increasing the likelihood, stochastically, of having bonds that are diametrically opposed across a common bonded neighbor at the center. As a result, there is a higher likelihood that some of the NN forces which contribute to f_{-i} (the driving force for the nonaffine motion) cancel mutually due to this effect, resulting in a decreased f_{-i} , and thus in a decreased nonaffinity. This effect critically depends upon the degree of geometric coupling between the imposed deformation and the structure, as discussed below. We also note that the A coefficients have their maximum absolute value in the limit $\sigma/R_0 = 1$ and their value decreases to zero in the limit $\sigma/R_0 \rightarrow 0$, where only the B coefficients survive, which are not affected by the σ/R_0 ratio.

The orientation-averaged affine contribution is $C_{i\xi\kappa\zeta}^A = \kappa R_0^2 \frac{N}{2V} \langle n_{ij}^\alpha n_{ij}^\xi n_{ij}^\alpha n_{ij}^\zeta \rangle$, where $\langle \dots \rangle = \int_0^{2\pi} \frac{1}{2\pi} \dots d\phi_{ij}$, in $d=2$, since the bond ij can have any orientation in the solid angle with the same likelihood $1/2\pi$. We should also recall that $B_{x,xxxx} = 5/16$, $B_{y,xxxx} = 1/16$, $B_{x,xyxy} = B_{y,xyxy} = 1/16$, $B_{x,xyyy} = B_{y,xyyy} = 1/16$. Then, we obtain the following estimates for the shear modulus and the bulk modulus of densely-packed amorphous solids ($\sigma/R_0 \rightarrow 1$) in $d=2$

$$\begin{aligned} G &= \frac{1}{16} \kappa R_0^2 \frac{N}{V} [(z-4) + 0.05] = \frac{1}{16} \kappa R_0^2 \frac{N}{V} (z-3.95) \\ K &= \frac{5}{48} \kappa R_0^2 \frac{N}{V} [(z-4) + 2.6] = \frac{5}{48} \kappa R_0^2 \frac{N}{V} (z-1.41). \end{aligned} \quad (9)$$

This is the most important result of this work; it should be discussed in comparison with the analogous result for random networks ($\sigma/R_0 = 0$), where both the shear modulus and the bulk modulus are $\propto (z - 4)$, i.e., vanish exactly when $z = 2d$. With excluded volume we have shown that the effect of correlations is to decrease the nonaffine correction to the moduli for both the shear modulus and the bulk modulus. However, whilst this correction is so small for the shear such that practically it cannot be assessed in simulations, the situation is very different for the bulk modulus. Here the nonaffinity is strongly suppressed by the excluded-volume correlations and $K \gg G$, because $K^{NA} \ll G^{NA}$.

Interestingly, the short-range order due to excluded volume, which breaks the statistically isotropic symmetry of the random network, induces a jump in G at $z = 2d$ and changes the order of the rigidity transition from the second-order of random networks¹² to a first-order transition where both moduli are finite at $z = 2d$ (recall^{19,20} that in packings there is a discontinuous jump in z which falls to zero below $z = 2d$). The qualitative predictions of the theory are illustrated in Fig. 2 for the two limiting cases of $\sigma/R_0 = 0$ (random networks, left) and $\sigma/R_0 = 1$ (dense packing, right).

The reason why the effect of excluded volume correlations is much stronger for compression than for shear lies in the fact that under compression the deformation field is always aligned with the bond vectors, if we consider one particle surrounded by its neighbors. Hence, when any two particles around a common neighbor happen to be one the mirror image of the other, as a result of the excluded volume

correlations, it is clear that the forces they communicate to their common neighbor must vanish, because, just like the bond vectors, they have the same orientation but opposite direction. Hence they give a zero contribution to the overall force $f_{\underline{i}}$ driving the nonaffinity of their common neighbor i .

In the case of shear, the orientations of the two particles that are the mirror image of each other cannot coincide with the orientations of the forces they transmit because the latter are dictated by the shear geometry which is strongly anisotropic. Indeed, the forces $f_{\underline{i}}$ from the neighbors j causing nonaffinity of any atom i are proportional to $\underline{n}_{ij}n_{ij}^i n_{ij}^k$, and it is evident that they depend on the coupling between the deformation field (encoded in the Cartesian labels) and the bond vectors \underline{n}_{ij} . Hence, in the case of shear, NN forces driving the nonaffinity of an atom i cannot have the same orientation even when the two bond vectors do, because of the coupling to the anisotropic shear field. As a result, the cancelation of forces contributing to $f_{\underline{i}}$ is much smaller in shear.

B. Poisson ratio

As a final illustration of this physical picture, we provide predictions for the Poisson ratio. In $d = 2$, based on the tensorial nature of stress and strain, and on dimensionality, the Poisson's ratio can be inferred²⁵ as $\nu = [(K/G) - 1] / [(K/G) + 1]$. As a first-order interpolation in the small parameter σ/R_0 , our theory gives

$$K/G \approx \frac{5}{3} + \left[\frac{5(z - 1.41)}{3(z - 3.95)} - \frac{5}{3} \right] \frac{\sigma}{R_0}. \quad (10)$$

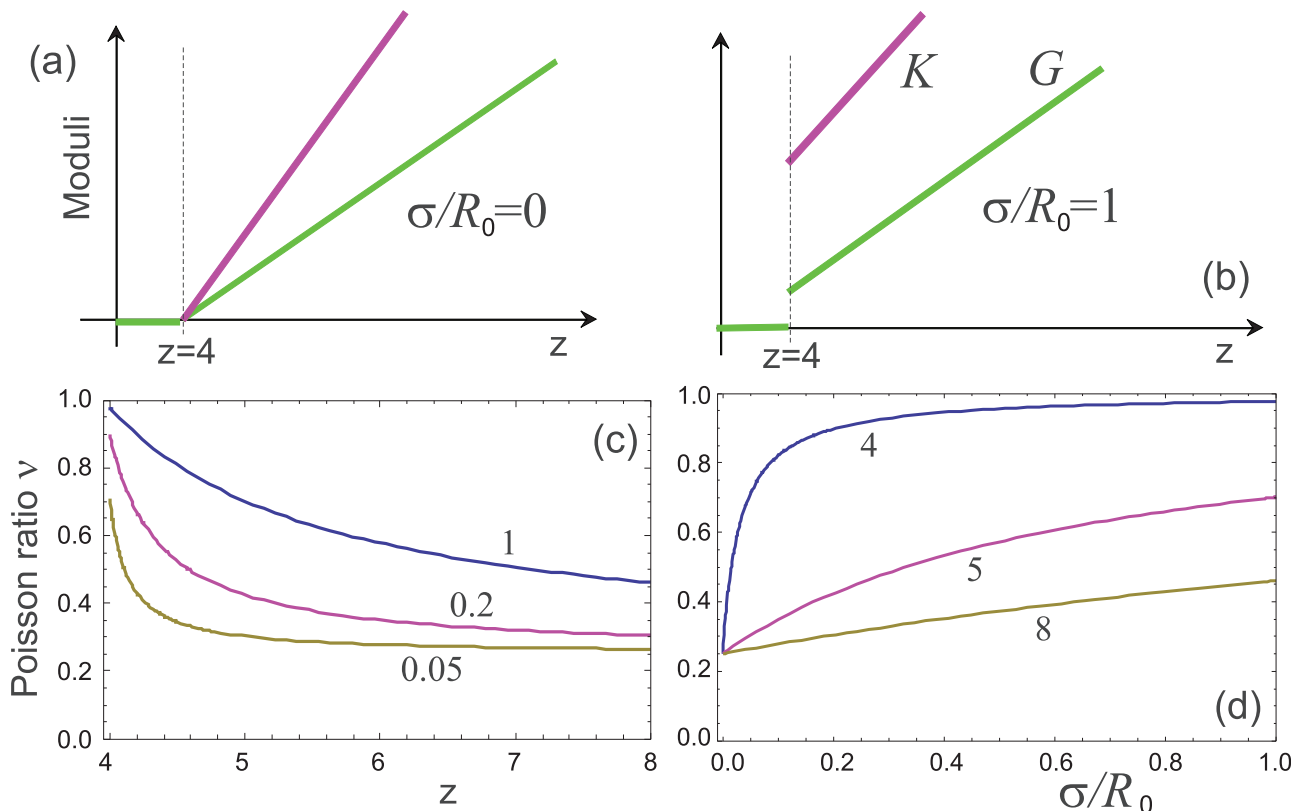


FIG. 2. (a) Qualitative predictions of the bulk and shear moduli dependence on z near the stability threshold for the limiting case of random networks, $\sigma/R_0 \rightarrow 0$, see Ref. 13. (b) Predictions of the theory in the limiting case of packings, $\sigma/R_0 \rightarrow 1$, Eq. (9). (c) Dependence of the Poisson ratio on the coordination z for $\sigma/R_0 = 1, 0.2$ and 0.05 , labeled on the plot. (d) Dependence of the Poisson ratio on the atomic packing parameter σ/R_0 for $z = 4, 5$, and 8 .

Substituting this formula in the definition of ν given above, predictions are obtained as a function of z and of the packing density parameter σ/R_0 and plotted in Figs. 2(c) and 2(d). ν is predicted to monotonically decrease as a function of the coordination number z , and to monotonically increase as a function of the atomic packing ratio σ/R_0 . Remarkably, both these $2d$ -model predictions seem to capture trends observed experimentally with many different amorphous materials, cf. Figs. 3 and 4(a) in the review.¹¹ The dimensionality appears not to have a dramatic effect on this mechanism.

IV. CONCLUSION

In summary, we have shown that nonaffine displacements may get strongly reduced in the compression of amorphous solids as soon as one includes short-range order due to the atomic mutual excluded volume, as is the case in metallic glasses.^{6,26–32} The extent of the nonaffinity reduction is highly dependent on the geometry of deformation, in particular on the coupling between the deformation field and the nearest-neighbor orientations. This coupling is maximum for hydrostatic compression, where the nonaffinity is strongly reduced, whereas it is small, but finite, for shear. We also showed that short-range order changes the order of the rigidity transition from the second-order of random networks¹² to first-order. Further, this theory provides a theoretical explanation for the trends observed in the Poisson ratio of many different materials upon varying the coordination and the atomic packing.¹¹ Our theory is currently limited to harmonic interactions and it can be expanded in future studies to include more realistic details of the interatomic potentials of materials. Furthermore, the relative softness of shear transverse modes with respect to longitudinal modes predicted by our theory may found a connection with the dominance of shear modes in the anomalous Boson peak seen in the vibrational density of states of glasses.³³ In a related context, it appears³⁴ that the Poisson ratio and the ratio K/G might play a role in determining the fragility of supercooled liquids, i.e., the temperature dependence of the viscosity close to the glass transition. Our work might lead to a more microscopic understanding of the relation between fragility, elasticity, and short-range correlations in supercooled liquids.

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APPENDIX A: DERIVATION OF EQ. (3)

The non-affine contribution to the elastic constants,

$$C_{i\xi\kappa\chi}^{NA} = \frac{1}{V} \sum_k \frac{(\underline{\Xi}_i^{i\xi} \cdot \underline{\mathbf{v}}_k)(\underline{\Xi}_i^{\kappa\chi} \cdot \underline{\mathbf{v}}_k)}{\lambda_k}, \quad (\text{A1})$$

is a sum over the $k = 1 \dots dN$ eigenmodes of the dynamical matrix of the lattice. The $dN \times dN$ dynamical matrix for harmonic lattices is given, in components, by

$$H_{ij}^{\alpha\beta} = \delta_{ij} \sum_s \kappa c_{is} n_{is}^\alpha n_{is}^\beta - (1 - \delta_{ij}) \kappa c_{ij} n_{ij}^\alpha n_{ij}^\beta. \quad (\text{A2})$$

This equation follows from replacing the harmonic potential $U(r_{ij}) = \frac{1}{2} \kappa (r_{ij} - R_0)^2$ in the definition of the dynamical matrix: $H_{ij}^{\alpha\beta} \equiv \partial^2 U / \partial r_i^\alpha \partial r_j^\beta$. R_0 is the rest length of the bonds and κ the bond spring constant. $\underline{\mathbf{v}}_k$ and λ_k in Eq. (A1) are eigenvectors and eigenvalues of the dynamical matrix, respectively. The inner product $(\underline{\Xi}_i^{i\xi} \cdot \underline{\mathbf{v}}_k)$ is the projection of the affine force field $\underline{\Xi}_i^{i\xi}$ (i.e., the force field exerted on every atom by the affine motions of its neighbors) on the eigenvector $\underline{\mathbf{v}}_k$. The analytical form of the affine fields is given by¹⁶ $\underline{\Xi}_{i,\kappa\chi}^\alpha = -R_0 \sum_j \kappa c_{ij} n_{ij}^\alpha n_{ij}^\kappa n_{ij}^\chi$. Thus, the evaluation of the non-affine term in the elastic moduli reduces to the task of evaluating the eigenmodes of the dynamical matrix, $\underline{\mathbf{v}}_k = \underline{\mathbf{a}}_i \otimes \underline{\mathbf{w}}_\alpha$ where $i = 1 \dots N$ and $\alpha = x_1, \dots, x_d$ denotes Cartesian components. In general, there are no analytical routes to evaluate the eigenvectors. Nevertheless, as we will show below, an analytical calculation is still possible if one has $\underline{\mathbf{w}}_\alpha = \underline{\mathbf{e}}_\alpha$ where $\underline{\mathbf{e}}_\alpha$ is the standard Cartesian basis of \mathbb{R}^d . Let us now justify the admissibility of this choice.

As is well known in algebra, if $\underline{\mathbf{v}}_k$ are the eigenvectors of a matrix $\underline{\mathbf{A}}$, the same eigenvectors are also eigenvectors of any matrix which commutes with $\underline{\mathbf{A}}$. Let us consider the matrix $\tilde{H}_{ij}^{\alpha\beta} = \frac{\kappa}{d} (\delta_{ij} \sum_j c_{ij} - (1 - \delta_{ij}) c_{ij}) \delta_{\alpha\beta}$, where $\delta_{\alpha\beta}$ is the Kronecker's delta. This matrix is obtained from the dynamical matrix by taking the isotropic angular average of its orientation-dependent terms. As one can easily verify by inspection, this matrix commutes with the dynamical matrix which implies that its eigenvectors are also eigenvectors of the dynamical matrix. Furthermore, the eigenvectors of this orientation-averaged matrix $\tilde{H}_{ij}^{\alpha\beta}$ are of the form: $\underline{\mathbf{v}}_k = \underline{\mathbf{a}}_i \otimes \underline{\mathbf{e}}_\alpha$. From the commutation of the two matrices, it follows that these are eigenvectors of $H_{ij}^{\alpha\beta}$ as well. Hence the eigenvalue equation for the dynamical matrix can be written as: $(\underline{\tilde{H}} \otimes \underline{\mathbf{I}})(\underline{\mathbf{a}} \otimes \underline{\mathbf{e}}) = \lambda_k (\underline{\mathbf{a}} \otimes \underline{\mathbf{e}})$, where $\underline{\tilde{H}} \equiv \frac{\kappa}{d} (\delta_{ij} \sum_j c_{ij} - (1 - \delta_{ij}) c_{ij})$ and $\underline{\mathbf{I}}$ denotes the $d \times d$ identity matrix. Then the inner products of the affine fields with the eigenvectors become¹³

$$\begin{aligned} & (\underline{\Xi}_i^{i\xi} \cdot \underline{\mathbf{v}}_i)(\underline{\Xi}_p^{\kappa\chi} \cdot \underline{\mathbf{v}}_p) \\ &= \kappa^2 R_0^2 \left(\sum_{i < j} a_i c_{ij} n_{ij}^\alpha n_{ij}^\kappa n_{ij}^\chi \right) \left(\sum_{p < q} a_p c_{pq} n_{pq}^\alpha n_{pq}^\kappa n_{pq}^\chi \right) \\ &= \kappa^2 R_0^2 \sum_{i < j, p < q} a_i a_p c_{ij} c_{pq} n_{ij}^\alpha n_{ij}^\kappa n_{ij}^\chi n_{pq}^\alpha n_{pq}^\kappa n_{pq}^\chi, \end{aligned} \quad (\text{A3})$$

where the sum runs over two pairs of NN atoms at the time, ij and pq . Upon taking the orientational average of the residual orientation-dependent factors in the previous equation we immediately recover Eq. (3).

APPENDIX B: DERIVATION OF EQ. (7)

Let us now evaluate the various terms separately within the sum in Eq. (6) of the main article. We shall first consider the term $(\delta_{ip} - \delta_{iq}) A_{\alpha, i\xi\kappa\chi}$. Upon replacing it in Eq. (3), we get $A_{\alpha, i\xi\kappa\chi} \sum_p a_p^2 - A_{\alpha, i\xi\kappa\chi} \sum_p a_p a_q c_{pq} = A_{\alpha, i\xi\kappa\chi} - A_{\alpha, i\xi\kappa\chi} \sum_{p < q} a_p a_q c_{pq}$, where clearly the second term is smaller than

the first because the mutual projection of the modes of two distinct particles is smaller than 1 (it is equal to 1 only when the two particles coincide, by orthonormality). To leading order, the term $A_{\alpha, i\tilde{\xi}\kappa\chi}$ thus gives a contribution to the nonaf-fine term which is equal to

$$\frac{\kappa^2 R_0^2}{V} \sum_{i,\alpha} \frac{dN}{\lambda_{i,\alpha}} \frac{A_{\alpha, i\tilde{\xi}\kappa\chi}}{\lambda_{i,\alpha}} \simeq \frac{\kappa^2 R_0^2}{V} (dN/\bar{\lambda}) \sum_{\alpha}^d A_{\alpha, i\tilde{\xi}\kappa\chi}, \quad (\text{B1})$$

where $\lambda_{i,\alpha}$ are the eigenvectors of the dynamical matrix and $\bar{\lambda}$ is the average eigenvalue, with the average taken over the disorder. The dynamical matrix averaged over the orientational disorder is given by $\tilde{H}_{ij}^{\alpha\beta} = \frac{\kappa}{d} (\delta_{ij} \sum_j c_{ij} - (1 - \delta_{ij}) c_{ij}) \delta_{\alpha\beta}$, and the d -fold degenerate eigenvalues of this matrix are also eigenvalues of the dynamical matrix. To find the mean eigenvalue we only need analyze the spectrum of eigenvalues $\tilde{\lambda}_i$ of the $N \times N$ matrix $\tilde{H}_{ij} = \frac{\kappa}{d} (\delta_{ij} \sum_j c_{ij} - (1 - \delta_{ij}) c_{ij})$, since $\tilde{\lambda}_{i,x} = \tilde{\lambda}_{i,y} = \dots = \tilde{\lambda}_i$. The average value of the eigenvalue spectrum is defined as: $\bar{\lambda} = \frac{1}{N} \sum_i^N \tilde{\lambda}_i$. From the trace definition we have that $\text{Tr}(\tilde{H}_{ij}) = \sum_i^N \tilde{\lambda}_i$. Hence, we get $\bar{\lambda} = 2(\kappa/dN) \sum_{i<j} c_{ij}$. The factor $\sum_{i<j} c_{ij}$ is a sum of independent binary (Bernoulli) random variables, hence it is itself a binary random variable characterized by the number of trials (which is equal the number of terms in the sum): $Q = N(N-1)/2$, and by the probability $P = z/(N-1)$ which is the probability of a successful trial ($c_{ij} = 1$ with success probability $P = z/(N-1)$). P represents the probability of picking two particles that are nearest neighbors when picking two particles at random in the solid. The expectation value is then $\sum_{i<j} c_{ij} = PQ$. Clearly this is an averaging taken over the realizations of positional disorder encoded in the binary occupancy variable c_{ij} . Using this, we obtain:

$$\bar{\lambda} = \frac{2\kappa}{dN} PQ = \frac{2\kappa}{dN} \frac{z}{N-1} \frac{N(N-1)}{2} = \frac{\kappa z}{d}. \quad (\text{B2})$$

The variance around the mean can also be calculated as for a binomial distribution, and is given by $\text{Var}(\bar{\lambda}) = (\frac{2\kappa}{dN})^2 PQ(1-P) = \frac{2\kappa^2}{d^2 N} (z - \frac{z^2}{N-1})$. In the thermodynamic limit $N \rightarrow \infty$, the variance is therefore zero (which is a reflection of the self-averaging principle) and in that limit we can write

$$\frac{\kappa^2 R_0^2}{V} \sum_{i,\alpha} \frac{dN}{\lambda_{i,\alpha}} \frac{A_{\alpha, i\tilde{\xi}\kappa\chi}}{\lambda_{i,\alpha}} \simeq \kappa R_0^2 \frac{N}{V} \frac{d}{z} \sum_{\alpha}^d A_{\alpha, i\tilde{\xi}\kappa\chi}. \quad (\text{B3})$$

By putting $(\delta_{ip} - \delta_{iq}) A_{\alpha, i\tilde{\xi}\kappa\chi} \simeq \delta_{ip} A_{\alpha, i\tilde{\xi}\kappa\chi}$, we overestimate this contribution and write, in good approximation

$$C_{i\tilde{\xi}\kappa\chi}^{NA} \simeq \kappa R_0^2 d \frac{N}{V} \sum_{\alpha}^d (A_{\alpha, i\tilde{\xi}\kappa\chi} + B_{\alpha, i\tilde{\xi}\kappa\chi}) + \kappa R_0^2 \frac{N}{V} \frac{d}{z} \sum_{\alpha}^d A_{\alpha, i\tilde{\xi}\kappa\chi}. \quad (\text{B4})$$

The second term in the r.h.s. of Eq. (B5) is smaller than the other term by at least a factor $1/z$, if not even smaller. Hence, in a further approximation, to leading order we can write

$$C_{i\tilde{\xi}\kappa\chi}^{NA} \simeq \kappa R_0^2 d \frac{N}{V} \sum_{\alpha}^d (A_{\alpha, i\tilde{\xi}\kappa\chi} + B_{\alpha, i\tilde{\xi}\kappa\chi}), \quad (\text{B5})$$

which is Eq. (7) in the main article.

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