

Supporting Information

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SI Text

Error and Uncertainty Analysis. The uncertainties in measured quantities, δ , are

$$\text{transmitted force } \delta_F = \begin{cases} 5 \times 10^{-3} \text{ N} & 1000 \text{ g-F transducer} \\ 5 \times 10^{-4} \text{ N} & 100 \text{ g-F transducer} \\ 5 \times 10^{-5} \text{ N} & 10 \text{ g-F transducer} \end{cases},$$

specimen diameter $\delta_D = 2 \mu\text{m}$,

specimen cross-sectional area $\delta_{A_o} = \sqrt{(\delta_D)^2 (\pi D)^2}$,

specimen length $\delta_{l_o} = 2 \mu\text{m}$,

specimen change in length $\delta_{\Delta l} = 10 \times 10^{-4} \times l_o$,

unfilled capillary mass $\delta_{m_{\text{unfilled}}} = 2 \mu\text{g}$,

filled capillary mass $\delta_{m_{\text{filled}}} = 2 \mu\text{g}$,

micropillar length in capillary $\delta_L = 10 \mu\text{m}$.

We assume an uncorrelated propagation of error. The uncertainties in the reported quantities $\langle \phi \rangle$, σ_{max} , and E_{load} are given by

$$\langle \phi \rangle = \frac{(m_{\text{filled}} - m_{\text{empty}}) / \rho_{\text{PS}}}{\pi(D/2)^2 L},$$

$$\delta_{\langle \phi \rangle} = \sqrt{(\delta_{m_{\text{filled}}})^2 \left(\frac{1}{\rho_{\text{PS}} A_o L} \right)^2 + (\delta_{m_{\text{empty}}})^2 \left(\frac{-1}{\rho_{\text{PS}} A_o L} \right)^2 + (\delta_{A_o})^2 \left(\frac{m_{\text{empty}} - m_{\text{filled}}}{\rho_{\text{PS}} A_o^2 L} \right)^2 + (\delta_L)^2 \left(\frac{m_{\text{empty}} - m_{\text{filled}}}{\rho_{\text{PS}} A_o L^2} \right)^2},$$

$$\sigma_{\text{max}} = \frac{F}{A_o},$$

$$\delta_{\sigma_{\text{max}}} = \sqrt{(\delta_{F_{\text{max}}})^2 \left(\frac{1}{A_o} \right)^2 + (\delta_{A_o})^2 \left(\frac{-F_{\text{max}}}{A_o^2} \right)^2},$$

$$E_{\text{load}} \propto \frac{F l_o}{A_o \Delta l},$$

$$\delta_{E_{\text{load}}} = \sqrt{(\delta_F)^2 \left(\frac{l_o}{A_o \Delta l} \right)^2 + (\delta_{l_o})^2 \left(\frac{F}{A_o \Delta l} \right)^2 + (\delta_{A_o})^2 \left(\frac{-F l_o}{A_o^2 \Delta l} \right)^2 + (\delta_{\Delta l})^2 \left(\frac{-F l_o}{A_o \Delta l^2} \right)^2}.$$

For the linear fit of $\sigma_{\text{max}} = \beta E_{\text{load}}$, we report the 95% CI for the regression analysis.

Effects of Dissipation in Stiffness Determination. Prior work (1) has shown that the micropillars are quite dissipative even at small strains. We define an efficiency, η , which is the ratio of work done by the pillar on loading to the work done on the pillar during loading

$$\eta = \frac{W_{\text{unload}}}{W_{\text{load}}} = \frac{E_{\text{unload}} \epsilon_{\text{elastic}}^2}{E_{\text{load}} \epsilon_{\text{total}}^2},$$

with $\epsilon_{\text{total}} = \epsilon_{\text{elastic}} + \epsilon_{\text{plastic}}$. By construction, $\eta = \frac{\epsilon_{\text{elastic}}}{\epsilon_{\text{total}}}$, so rearranging yields

$$E_{\text{load}} = \eta E_{\text{unload}}.$$

Assuming $\eta = 50\%$, we underestimate the elastic component of stiffness (E_{unload}) by a factor of 2, i.e., $2E_{\text{load}} = E_{\text{unload}}$. Because the transformation strain magnitude, ϵ^* , is inversely proportional to E ($\gamma_o^T \propto 1/E$; Eq. 4), we overestimate the transformation strain by a factor of 2 by using E_{load} in the energy analysis. Therefore, our reported value for γ_o^T should be considered an upper bound.

In previous experiments, we quantified the dissipation in a specimen when compressed to small strains as a function of RH. Briefly, we found a strong dependence of η on RH with a significant decrease in η —equivalently, an increase in dissipation—for RH above $\sim 40\%$. An example of an experimental compression cycle at $RH = 50\%$ is shown in Fig. S3.

Gibbs Free Energy of an Inclusion in an Elastic Matrix. For completeness, we reproduce the derivation by Mura (2) of the change in the Gibbs free energy, G , of an inclusion in an elastic matrix with an applied traction. Define

$$\epsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \equiv \text{total strain},$$

$$\epsilon_{ij}^* \equiv \text{eigenstrain or transformation strain},$$

$$e_{ij} \equiv \text{elastic strain},$$

$$\sigma_{ij} = C_{ijkl} e_{kl} \equiv \text{stress}.$$

The elastic strain energy of a body subjected to an applied traction σ_{ij}^∞ and an internal stress due to an inclusion σ_{ij} is given by

$$W^* = \frac{1}{2} \int_V (\sigma_{ij}^\infty + \sigma_{ij}) (\epsilon_{ij}^\infty + \epsilon_{ij} - \epsilon_{ij}^*) dV \quad \text{with} \quad \sigma_{ij}^\infty = C_{ijkl} \epsilon_{ij}^\infty.$$

Equilibrium ensures that $\sigma_{ij,j} = 0$ and $\sigma_{ij} n_j = 0$ at the surface S . Integration by parts gives

$$\begin{aligned} \int_V \sigma_{ij} (\epsilon_{ij}^\infty + \epsilon_{ij}) dV &= \int_V \sigma_{ij} (u_{i,j}^\infty + u_{i,j}) dV, \\ &= \sigma_{ij} (u_{ij}^\infty + u_{ij}) \Big|_{V=S} - \int_V \sigma_{ij,j} (u_{ij}^\infty + u_{ij}) dV = 0. \end{aligned}$$

Similarly, $\sigma_{ij,j}^\infty = 0$. Because $\epsilon_{ij}^\infty = e_{ij}^\infty$ and $e_{ij} = \epsilon_{ij} - \epsilon_{ij}^*$ and using the symmetry $C_{ijkl} = C_{klij}$

$$\begin{aligned} \int_V \sigma_{ij}^{\infty} (\epsilon_{ij} - \epsilon_{ij}^*) dV &= \int_V C_{ijkl} u_{k,l}^{\infty} (u_{i,j} - \epsilon_{ij}^*) dV = \int_V u_{k,l}^{\infty} C_{kl ij} e_{ij} dV, \\ &= \int_V u_{k,l}^{\infty} \sigma_{kl} dV = u_{kl} \sigma_{kl} \Big|_{V=S} - \int_V u_{k,l}^{\infty} \sigma_{k,l} dV = 0. \end{aligned}$$

So

$$W^* = -\frac{1}{2} \int_V \sigma_{ij} \epsilon_{ij}^* dV + \frac{1}{2} \int_V \sigma_{ij}^{\infty} \epsilon_{ij}^{\infty} dV.$$

The total potential energy is given by

$$G = W^* - \int_S F_i^{\infty} (u_i + u_i^{\infty}) dS,$$

where the second term is the work done at the boundary by the applied traction, and $F_i^{\infty} = \sigma_{ij}^{\infty} n_j$. Without any inclusions ($\epsilon_{ij}^* = 0$), $G = G_o$

$$G_o = \frac{1}{2} \int_V \sigma_{ij}^{\infty} \epsilon_{ij}^{\infty} dV - \int_S F_i^{\infty} u_i^{\infty} dS.$$

Without any applied tractions ($\sigma_{ij}^{\infty} = 0$), $G = G_1$

$$G_1 = -\frac{1}{2} \int_V \sigma_{ij} \epsilon_{ij}^* dV.$$

The interaction between the strain field generated by the inclusions and the applied traction is

$$\begin{aligned} \Delta G &= G - G_o - G_1 = - \int_S \sigma_{ij}^{\infty} u_i n_j dS = - \int_V \sigma_{ij}^{\infty} u_{i,j} dV \\ &= - \int_V \sigma_{ij}^{\infty} (u_{i,j} - \epsilon_{ij}^*) dV - \int_V \sigma_{ij}^{\infty} \epsilon_{ij}^* dV = - \int_V \sigma_{ij}^{\infty} \epsilon_{ij}^* dV. \end{aligned}$$

by Gauss's theorem and the fact that $\int_V \sigma_{ij}^{\infty} (u_{i,j} - \epsilon_{ij}^*) dV = 0$ (see above). Therefore, with spatially homogeneous stress and strain fields

$$\Delta G = - \int_V \sigma_{ij}^{\infty} \epsilon_{ij}^* dV = - \sigma_{ij}^{\infty} \epsilon_{ij}^*.$$

For the case where the body is under an applied traction and inclusions are introduced, the change in free energy is given by

$$\Delta \bar{G} = G - G_o = \Delta G + G_1 = -\frac{1}{2} \sigma_{ij} \epsilon_{ij}^* - \sigma_{ij}^{\infty} \epsilon_{ij}^*,$$

which is Eq. 1.

Derivation of the Stress Field for a Prescribed Transformation Strain. The tensorial infinitesimal strain, ϵ_{ij} , is given by

$$\epsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) = \begin{pmatrix} \epsilon_{11} & \epsilon_{12} & \epsilon_{13} \\ \epsilon_{12} & \epsilon_{22} & \epsilon_{23} \\ \epsilon_{13} & \epsilon_{23} & \epsilon_{33} \end{pmatrix} = \begin{pmatrix} \epsilon_{11} & \frac{\gamma_{12}}{2} & \frac{\gamma_{13}}{2} \\ \frac{\gamma_{12}}{2} & \epsilon_{22} & \frac{\gamma_{23}}{2} \\ \frac{\gamma_{13}}{2} & \frac{\gamma_{23}}{2} & \epsilon_{33} \end{pmatrix}.$$

Define the stiffness tensor, C_{ijkl} , for an isotropic homogeneous solid as

$$C_{ijkl} = \frac{E\nu}{(1+\nu)(1-2\nu)} \delta_{ij} \delta_{kl} + \frac{E}{2(1+\nu)} (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}),$$

and the constitutive relation

$$\sigma_{ij} = C_{ijkl} \epsilon_{kl},$$

where ϵ_{kl} is now the elastic component of the strain. Argon and Shi (3) use Eshelby's tensor for a spherical inclusion, given by

$$S_{ijkl} = \frac{5\nu - 1}{15(1-\nu)} \delta_{ij} \delta_{kl} + \frac{4-5\nu}{15(1-\nu)} (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}).$$

To relate the confined strain, ϵ_{ij}^C , to the transformation strain, ϵ_{ij}^T , of the inclusion

$$\epsilon_{ij}^C = S_{ijkl} \epsilon_{kl}^T.$$

The authors assume two components of ϵ_{kl}^T

$$\epsilon_{kl}^T = \frac{\epsilon_o^T}{3} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \frac{\gamma_o^T}{2} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

where the first term accounts for dilatation and the second for a pure shear. The stress inside the inclusion, σ_{ij}^I , is given by

$$\sigma_{ij}^I = C_{ijkl} (S_{klmn} \epsilon_{mn}^T - \epsilon_{kl}^T).$$

The elastic energy in both the inclusion and matrix is given as

$$E_{elastic} = -\frac{1}{2} \int_{\Omega_i} \sigma_{ij}^I \epsilon_{ij}^T dV.$$

For the case of a spherical inclusion, in which σ_{ij}^I and ϵ_{ij}^T are constants, this expression becomes

$$E_{elastic} = -\frac{1}{2} \sigma_{ij}^I \epsilon_{ij}^T \Omega_i.$$

Considering only the dilatational component of ϵ_{kl}^T and using the relationship $E = 2\mu(1+\nu)$

$$\begin{aligned} \sigma_{ij}^I &= \frac{2E\epsilon_o^T}{9(\nu-1)} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \text{and} \quad E_{elastic} = \frac{E}{9(1-\nu)} (\epsilon_o^T)^2 \\ &= \frac{2\mu(1+\nu)}{9(1-\nu)} (\epsilon_o^T)^2, \end{aligned}$$

which is the same as the second term of equation 7 in ref. 3. Now, considering only the shear component of ϵ_{kl}^T yields

$$\begin{aligned} \sigma_{ij}^I &= \frac{E\gamma_o^T(7-5\nu)}{30(\nu^2-1)} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \text{and} \\ E_{elastic} &= \frac{E(7-5\nu)}{60(1-\nu^2)} (\gamma_o^T)^2 = \frac{\mu(7-5\nu)}{30(1-\nu)} (\epsilon_o^T)^2, \end{aligned}$$

which is the same as the first term of equation 7 in ref. 3. In the presence of an applied far-field stress, the change in Gibb's free energy becomes (see previous section)

$$\Delta G = -\frac{1}{2} \sigma_{ij}^I \epsilon_{ij}^T \Omega_f - \sigma_{ij}^\infty \epsilon_{ij} \Omega_f.$$

For uniaxial compression and our assumed orientation of the inclusion, the applied stress is

$$\sigma_{ij} = \frac{\sigma}{2} \begin{pmatrix} -1 & 1 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

Therefore, the change in free energy is

$$\Delta G = \frac{E}{\nu^2 - 1} \left[\frac{\nu + 1}{9} (\epsilon_o^T)^2 + \frac{7 - 5\nu}{60} (\gamma_o^T)^2 \right] - \frac{\sigma(2\epsilon_o^T - 3\gamma_o^T)}{6}.$$

Argon and Shi define the transformation dilatancy as

$$\beta = \frac{\epsilon_o^c}{\gamma_o^c} = \frac{45(1 - \nu)^2 \epsilon_o^T}{2(1 + \nu)(4 - 5\nu) \gamma_o^T}.$$

From measurements on an amorphous bubble raft, the authors estimate $\beta \approx 1$ (3). Therefore

$$\epsilon_o^T = \gamma_o^T \frac{2(1 + \nu)(4 - 5\nu)}{45(1 - \nu)^2},$$

with this relationship

$$\Delta G = \frac{\Omega E}{\nu^2 - 1} \left\{ \frac{\nu + 1}{9} \left[\frac{2(1 + \nu)(4 - 5\nu)}{45(1 - \nu)^2} \gamma_o^T \right]^2 + \frac{7 - 5\nu}{60} (\gamma_o^T)^2 \right\} + \frac{\Omega \sigma \gamma_o^T}{2} - \frac{\Omega \sigma \gamma_o^T}{3} \frac{2(1 + \nu)(4 - 5\nu)}{45(1 - \nu)^2}.$$

Setting $\Delta G = 0$ and rearranging yields

$$\frac{\sigma}{E} = \frac{\gamma_o^T [5,675\nu^5 - 33,365\nu^4 + 70,934\nu^3 - 74,578\nu^2 + 39,967\nu - 8,761]}{270(\nu - 1)^3 (155\nu^3 - 111\nu^2 - 147\nu + 119)} \equiv \gamma_o^T \theta(\nu).$$

1. Strickland DJ, et al. (2014) Synthesis and mechanical response of disordered colloidal micropillars. *Phys Chem Chem Phys* 16(22):10274–10285.
2. Mura T (1987) *Micromechanics of Defects in Solids* (Springer, Berlin), Vol 3.

3. Argon AS, Shi L (1983) Development of visco-plastic deformation in metallic glasses. *Acta Metall* 31(4):499–507.

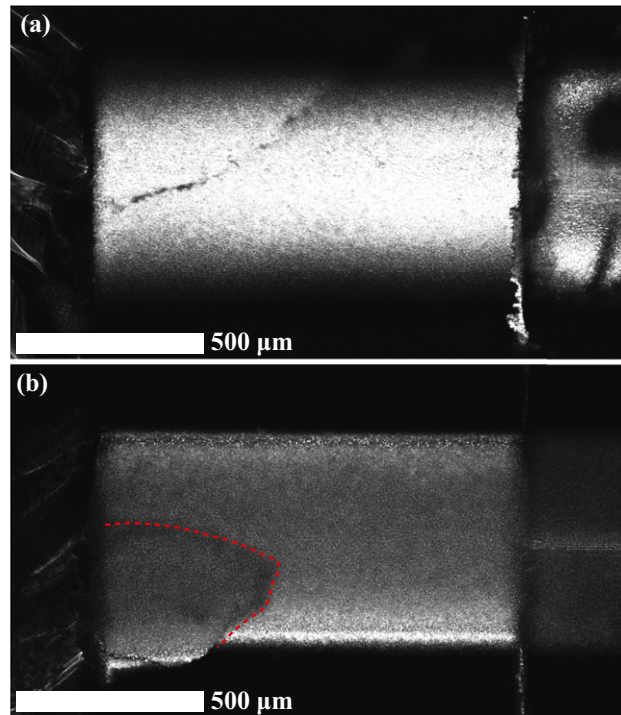


Fig. S1. Laser-scanning confocal micrographs of deformed micropillar specimens. (A) A specimen with $\phi = 0.559$ compressed at $RH = 60\%$. Failure results from the development of a shear band that propagates from the specimen/punch interface to the specimen surface. (B) A specimen with $\phi = 0.687$ compressed at $RH = 50\%$. The darker region outlined by the dashed red line has been sheared out of plane.

