Mechanical metamaterials with negative compressibility transitions

1. DESTABILISATION CONDITIONS

Role of Degenerate Equilibria. Consider the one-dimensional system governed by the potential energy $V = V(x, y, h, F)$ in Eq. (1) and represented in Fig. 2a (main text). The equilibria of the system correspond to critical points of $V$ for given $F$. These equilibria, denoted $x^*(F) = (x^*(F), y^*(F), h^*(F))$, are defined by

$$DV(x^*(F), F) = 0,$$  \hspace{1cm} (S1)

where $D = \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial h} \right)$ is the gradient operator. We assume that $V''_x(x) > 0$, $V''_y(y) > 0$, and $V''_h(h) > 0$ for all $x$, $y$, and $h$, which we refer to as a convexity assumption. This, combined with the assumption that $V_x(x)$ and $V_y(y)$ are attractive for some $x$ and $y$, implies that the corresponding forces become increasingly attractive for large $x$ and $y$, as in the case of spring-like potentials. We also assume that all the individual potentials are three times continuously differentiable, as required for some of the operations below. Under these assumptions, it follows that $h^* = x^* + y^*$ for all equilibria. This allows us to express the arguments of the potentials $V_x, V_y, V_z$, and $V_h$ (and of their derivatives) in equilibrium as $x^*, y^*, y^* - x^*$, and $x^* + y^*$, respectively.

The stability of an equilibrium is determined by the Hessian matrix of $V$, which we denote $D^2V$, provided that it is nonsingular. If all eigenvalues of $D^2V(x^*(F), F)$ are positive, $x^*(F)$ corresponds to a (nondegenerate) stable equilibrium. Given a stable equilibrium $x^*(F_0)$ at some applied $F_0$, the implicit function theorem guarantees a stable equilibrium $x^*(F)$ for $F$ in some open neighbourhood of $F_0$. By differentiating Eq. (S1) implicitly with respect to $F$ and solving for $\frac{dx^*}{dF}$, we find that $\frac{dx^*}{dF}$ is the ratio of a leading principal minor of $D^2V(x^*(F), F)$ and the determinant of $D^2V(x^*(F), F)$. But Sylvester’s criterion for positive definite matrices guarantees that if $x^*(F)$ is a stable equilibrium, all the leading principal minors and the determinant of $D^2V(x^*(F), F)$ are positive. Therefore, if a nondegenerate equilibrium is stable, $h^*$ will always increase with an infinitesimal increase in $F$. This demonstrates that we cannot achieve the desired negative compressibility in a continuous fashion, as we would expect from physical intuition.

It is possible, however, for stable equilibria to vanish as a result of a finite change in $F$. Stable equilibria can vanish only when $D^2V$ becomes a singular matrix, which, under our assumptions, is equivalent to

$$V''_x(y^* - x^*) + \frac{2V''_x(x^*)V''_y(y^*) + V''_h(x^* + y^*) (V''_x(x^*) + V''_y(y^*))}{V''_x(x^*) + V''_y(y^*) + 2V''_h(x^* + y^*)} = 0.$$  \hspace{1cm} (S2)

If this occurs for some equilibrium $x^*$ at some critical force $F_c$, we say that $x_c = x^*(F_c)$ is a degenerate equilibrium point. Note that subscript ‘c’ refers to critical points, and should not be confused with superscript ‘c’, which is used elsewhere to refer to coupling transitions.
Characterisation of Degenerate Equilibria. Understanding the “unfolding” of a degenerate equilibrium (i.e., the routes to it as the parameter $F$ is changed) is aided by diagonalising $D^2V(x_c, F_c)$. We introduce local coordinates $\eta = (\eta^0, \eta^1, \eta^2)$ around the degenerate equilibrium point using the linear transformation $\eta = U^{-1}x$, where $U$ is a unitary matrix whose columns are the normalised eigenvectors of $D^2V(x_c, F_c)$. With respect to the new coordinates, we have $\frac{\partial^2 V}{\partial \eta^i \partial \eta^j} = \lambda_i \delta_{ij}$, where $\lambda_i$ are the corresponding eigenvalues and $\delta_{ij}$ is the Kronecker delta. We assume that there is exactly one zero eigenvalue, $\lambda_0 = 0$, and two positive eigenvalues, $\lambda_{1,2} > 0$, as expected for a generic degenerate equilibrium point that might develop from a stable equilibrium. As shown below, an important expression involving the $\eta^i$’s is $\frac{\partial}{\partial \eta^i}$, which can be expressed as

$$\frac{\partial}{\partial \eta^0} = -\frac{(V_y'' + V_h') \frac{\partial}{\partial x} + (V_x'' + V_h'') \frac{\partial}{\partial y} + (V''_x - V''_y) \frac{\partial}{\partial \eta^0}}{\sqrt{(V_x'' - V_y'')^2 + (V_x + V_h'')^2 + (V_y + V_h'')^2}}, \quad (S3)$$

where we have dropped the arguments since it is implicitly clear that $V_x, V_y, V_z$, and $V_h$ are evaluated at the degenerate equilibrium point.

We seek an asymptotic expansion for any family of equilibria $\eta^*(F) = U^{-1}x^*(F)$ tending to $\eta_c = U^{-1}x_c$ as $\epsilon \equiv F - F_c \to 0$ (not to be confused with $\varepsilon$, which denotes strain). In this expansion, one might be tempted to use a series proceeding in integer powers of $\epsilon$. However, because of the degeneracy of the $\eta_c$ equilibrium, this series fails. The correct series, as it will become evident, proceeds in half-integer powers of $\epsilon$. That is, we take

$$\eta^{*i} - \eta^i_c = \alpha_i^1 \epsilon^{\frac{1}{2}} + \alpha_i^2 \epsilon^{\frac{3}{2}} + \cdots. \quad (S4)$$

Now, using Taylor’s theorem around $\eta = \eta_c$ and Eq. (S4), we expand the defining equation of equilibria,

$$DV(\eta^*(\epsilon), \epsilon) = 0, \quad (S5)$$

in powers of $\epsilon^{\frac{1}{2}}$ (for the sake of simplicity, we continue to use $V$ to denote the total potential, now as a function of the new coordinates and $\epsilon$). As usual, we find the coefficients of the series, $\alpha_j^i$, by equating the coefficients of each power of $\epsilon^{\frac{1}{2}}$ in this expansion to zero.

At order $\epsilon^{\frac{1}{2}}$, we have $\lambda_i \alpha_i^0 = 0$, which shows that $\alpha_1^1 = \alpha_2^1 = 0$. At order $\epsilon$, we have

$$\frac{1}{2} \frac{\partial^2 V}{\partial (\eta^0)^2} (\alpha_1^0)^2 + \lambda_i \alpha_i^2 = \frac{\partial h}{\partial \eta^0} = 0,$$ 

which for $i = 0$ leads to

$$\alpha_1^0 = \pm \sqrt{2 \left( \frac{\partial^3 V}{\partial (\eta^0)^3} \right)^{-1}} \times \frac{\partial h}{\partial \eta^0}. \quad (S6)$$

This reveals why we chose our series to proceed in half-integer powers of $\epsilon$: it allows us to find $\alpha_1^0$ at second order after the degeneracy made this impossible at first order. The expansion is well defined and will converge provided the degeneracy at $\eta_c$ is not of higher order. This condition will generally only fail for very special potentials, and even in those cases it will be recovered by a generic perturbation of the potentials.

Let $V$ denote $(\frac{\partial^3 V}{\partial (\eta^0)^3})^{-1} \times \frac{\partial h}{\partial \eta^0}$ and assume that it is nonzero and finite. Then, for $2V \epsilon > 0$, we have two families of equilibrium points tending to $\eta_c$ as $\epsilon \to 0$, one of stable equilibria given by the plus sign and one of unstable equilibria given by the minus sign in Eq. (S6). For $2V \epsilon < 0$, on the other hand, there are no equilibria in a neighbourhood of $\eta_c$. Thus, in the formation of a degenerate equilibrium point, one stable and one unstable equilibrium
collide as $F$ tends to $F_c$, and annihilate each other at $x_c$. This occurs for $F > F_c$ if $\mathcal{V} > 0$ and for $F < F_c$ if $\mathcal{V} < 0$.

This result is rather general and applies to the constituent systems considered in our study for a large class of potentials. In the language of catastrophe theory [36], the bifurcation just described is called a fold. The sign of $\mathcal{V}$ thus determines the direction in which the fold opens. Using Eq. (S3) and our convexity assumption, this term can be expressed as

$$\mathcal{V} = \frac{2(\gamma_1 + \gamma_2)(1 + 3\gamma_1\gamma_2)}{2\gamma_1^2 V_x'' + 2\gamma_2^2 V_y'' + V_z'' + (\gamma_1 + \gamma_2)^3 V''_h}, \quad (S7)$$

where $\gamma_1 = -\frac{V_y'' + V_h''}{V_x'' + V_y'' + 2V_h''}$ and $\gamma_2 = \frac{V_x'' + V_h''}{V_x'' + V_y'' + 2V_h''}$, and $1 + 3\gamma_1\gamma_2$ is a strictly positive factor.

Equation (S7), together with the equilibrium condition, Eq. (S1), and the degeneracy condition, Eq. (S2), allows us to design our system so that it undergoes destabilisations in a predictable manner. We simply choose potentials that have a degenerate equilibrium at a desired applied force and ensure that the sign of $\mathcal{V}$ will make the fold open in the desired direction. In the decoupling transitions we consider, this sign is negative, so that the destabilisation leading to contraction occurs as the tensional force $F$ is increased.

2. CONDITION FOR NEGATIVE COMPRESSIBILITY TRANSITIONS

To generate potentials that exhibit the desired negative compressibility transitions, we assume that for small $F$ the only equilibrium, $x_0^*(F)$, is one in which $z^*$ is confined near a minimum of $V_z$ in the vicinity of $z = 0$ (i.e., the central particles are coupled together by a weak bond). We also assume that as $F$ is increased, this bond is stretched up to a point where the tension becomes too high for the bond to be maintained (i.e., the central particles decouple). Using Eq. (S2) and Eq. (S7), we can ensure that this occurs as $F$ tends to some prescribed $F_c$, which leads the equilibrium $x_0^*$ to tend to a degenerate equilibrium point $x_c$, and then disappear under further increase of $F$. The decoupling of the central particles that results from the increase of the force through $F_c$ causes the system to switch to a different equilibrium, $x_1^*(F)$. According to Eq. (S1), we must have

$$F_c = V'_x(x_c) + V'_y(y_c) + V'_h(x_c + y_c) = V'_x(x_1^*(F_c)) + V'_y(y_1^*(F_c)) + V'_h(x_1^*(F_c) + y_1^*(F_c)). \quad (S8)$$

Since $V'_x$, $V'_y$, and $V'_h$ are monotone functions (by our convexity assumption) and the labels $x$ and $y$ can be exchanged, we can conclude without loss of generality that $x_1^*(F_c) \leq x_c$ and $y_1^*(F_c) \geq y_c$.

Therefore, to achieve the desired behaviour we must ensure that the amount by which $x$ decreases is larger than the amount by which $y$ increases during the decoupling transition. This can be accomplished by making the $V_x$ potential “soft” in the neighbourhood of $x_c$ but “hardened” below it, and making the $V_y$ potential “soft” in the neighbourhood of $y_c$ but “hardened” above it. The potentials used in the main text were chosen to do just this.
3. POTENTIALS USED IN NUMERICAL SIMULATIONS

The potentials \( V_x \) and \( V_y \) used in our study are derived from

\[
V_{\alpha}(r) = k_{\alpha_0}(\alpha_1 - \alpha_0)r + \frac{1}{4}(r - \alpha_1)^2(k_{\alpha_0} + k_{\alpha_1}) - \frac{1}{4}(k_{\alpha_0} - k_{\alpha_1})(r - \alpha_1)g_{\alpha}(r)
- \frac{1}{4}(k_{\alpha_0} - k_{\alpha_1}) \frac{R_\alpha^2}{\sqrt{(1 + k_{\alpha_0}^2)(1 + k_{\alpha_1}^2)}} \log [(r - \alpha_1) + g_{\alpha}(r)], \tag{S9}
\]

where

\[
g_{\alpha}(r) = \sqrt{(r - \alpha_1)^2 + \frac{R_\alpha^2}{\sqrt{(1 + k_{\alpha_0}^2)(1 + k_{\alpha_1}^2)}}}.	ag{S10}
\]

This potential produces hyperbolic forces with asymptotic slopes \( k_{\alpha_0} \) and \( k_{\alpha_1} \), where \( \alpha_1 \) determines the centre of the hyperbola, \( R_\alpha \) indexes different hyperbolas for given asymptotes, and \( k_{\alpha_0}\alpha_0 \) produces a constant force. In the limit \( R_\alpha \to 0 \), the hyperbola converges to the corresponding branch of the asymptotes everywhere, and \( \alpha_0 \) becomes the equilibrium length. The other potentials are

\[
V_z(z) = \zeta \left[ \left( \frac{z_0}{z} \right)^{12} - 2 \left( \frac{z_0}{z} \right)^6 \right],
\]

\[
V_h(h) = k_h(h - h_0)^2.	ag{S12}
\]

That is, \( V_z \) is the Lennard-Jones potential while \( V_h(h) \) is a harmonic potential. Using Eq. (S9) with \( \alpha \) representing \( x \) and \( y \), we first considered \( R_x = R_y = 0.05 \), which leads to smooth but nonlinear forces. The other parameters used to define \( V_x \) and \( V_y \) were \( k_{x_0} = 11, k_{x_1} = 2, x_0 = 2, x_1 = 2.2, k_{y_0} = 0.5, k_{y_1} = 20, y_0 = 2.225 \), and \( y_1 = 3.3 \). The parameters for \( V_h \) were \( k_h = 0.3 \) and \( h_0 = 4.225 \). The parameters for \( V_z \) were then chosen as \( \zeta = 0.26 \) and \( z_0 = 0.225 \) in order the achieve the desired behaviour.

For this choice of parameters, the resulting equilibria configurations for these potentials are shown in Fig. S1, where we plot both \( h^* = x^* + y^* \) and \( z^* = y^* - x^* \) as a function of \( F \). In this high-dimensional representation, we see that the stable and unstable equilibrium points define a single curve, which exhibits two folds as one moves along the \( F \) axis. It is only when we project the equilibria into the \( h-F \) plane that the hysteresis loop appears to intersect itself. Our observation of the desired behaviour does not depend sensitively on the specific choice of the parameters or potentials.

For conceptual simplicity, in all simulations presented in the main text we considered \( R_x = R_y = 0 \), which reduces the potentials \( V_x \) and \( V_y \) to

\[
V_x(x) = \begin{cases} 
\frac{1}{2}k_{x_0}(x - x_0)^2 + \frac{1}{2}k_{x_0}(x_1^2 - x_0^2), & \text{for } x \leq x_1, \\
\frac{1}{2}k_{x_1}(x - x_1)^2 + k_{x_0}(x_1 - x_0)x, & \text{for } x > x_1,
\end{cases}
\]

\[
V_y(y) = \begin{cases} 
\frac{1}{2}k_{y_0}(y - y_0)^2 + \frac{1}{2}k_{y_0}(y_1^2 - y_0^2), & \text{for } y \leq y_1, \\
\frac{1}{2}k_{y_1}(y - y_1)^2 + k_{y_0}(y_1 - y_0)y, & \text{for } y > y_1.
\end{cases}
\]

These potentials describe piecewise linear forces, which facilitate interpretation of our results, particularly in connection with Eq. (S8). This choice was also used in Figs. S3 and S4. In all cases, the other parameters and potentials were chosen as defined above.
4. LINEAR SYSTEMS WITH NEGATIVE COMPRESSION TRANSITIONS

Our analysis allowed us to make precise predictions about the destabilisations in our system, but it involved using non-harmonic potentials to achieve the desired behaviour. Nonlinear forces are in fact necessary for our one-dimensional system to exhibit the desired behaviour. On the other hand, if we allow particles to move in two or three dimensions, we can actually achieve similar behaviour using only linear springs, albeit in a more complex system. In two and three dimensions, destabilisations can be achieved through buckling rather than decoupling (buckling transitions with positive compressibility are in fact easy to design for practical applications [37]). Specifically, consider a triangle formed by three particles, in which two particles are fixed and connected to the third particle by identical springs of natural length larger than half the distance between the first two. If we flatten the triangle by pulling the third particle down towards the other two, then when the triangle flattens out completely, this vertex will “buckle through” and the triangle will invert. In Fig. S2, we demonstrate that this kind of destabilisation can also lead to the desired behaviour.

5. METAMATERIALS

5. LATTICE, EFFECTIVE PARAMETERS, AND TEMPERATURE SCALE

In coupling together constituents on a two-dimensional square lattice or three-dimensional cubic lattice to form a metamaterial, the constituents specified by \( V = V(x, y, h, F) \) define links between adjacent lattice points in the horizontal and vertical directions. Unless otherwise noted, we focus on the two-dimensional case, in which case the unit cell then consists of five particles. Because in the metamaterial external forces are not applied on a microscopic scale, the role of the force \( F \) is now played by the applied stress \( \sigma \), which is a thermodynamic variable prescribed macroscopically. We also define the thermodynamic variable conjugate to \( \sigma \), the strain \( \varepsilon \), which can be used to prescribe the macroscopic size of the material. As we are ultimately interested in the bulk properties of the material, the boundary effects are assumed to be relatively unimportant. We thus approximate the lattice as being infinitely large and focus on a finite square “N-cell” of constituents within the lattice, where \( N \) is the length of the sides of this cell in units of the lattice spacing (i.e., one N-cell consists of \( N^2 \) unit cells). We assume \( N \) to be much larger than 1.

In the lattice, the \( V_h \) potential describes interactions between each exterior particle of the constituents (black particles in Fig. 2a,b, main text) and the closest particles of the same type along the horizontal, vertical, and diagonal directions (at distances given by the lattice spacing and \( \sqrt{2} \) times the lattice spacing). These interactions give rise to resistance to shear, which is important to maintain the structure of the lattice. To obtain the same zero temperature equilibria as for the isolated constituents while accounting for the fact that each such particle interacts via \( V_h \) with 8 others in the lattice, we renormalise the parameters associated with this potential. The spring constant \( k_h \) is reduced by a factor of 3 and the equilibrium length \( h_0 \) is increased by a factor of \( 3/(1 + \sqrt{2}) \). With this renormalisation, the effective resistance to changes of \( h \) in the lattice will be (within the mean field approximation) the same as for the isolated constituents, which facilitates comparisons between these two scales.

Using our potentials, we can define a reference temperature \( T_0 \) by setting \( k_BT_0 \) equal to the potential barrier separating the two minima of the potential energy at the stress for which
the values of the minima are equal. When \( T \) is comparable to or larger than \( T_0 \), thermal fluctuations will easily overcome the energy barrier, and thermodynamic equilibrium will prevail. However, when \( T \) is much smaller than \( T_0 \), the energy barrier will be difficult to overcome, and metastability can persist for long periods.

### 6. LATTICE VIBRATIONS AND TIME SCALES

The frequencies of the small-amplitude vibrations in the lattice define a set of natural time scales for the proposed material. Assuming that all the constituents in the lattice are oscillating around the same equilibrium state given by some \( x^* \) and \( y^* \), we can derive a dispersion relation for all such vibrations using a wave ansatz in the equations of motion of the particles, and expanding up to linear order in the wave amplitude. We first define

\[
f(k_x, k_y, k_z, k_h, k; \omega) = \left[ 4k_h + \frac{2(k_x + k_y)^2}{k_x + k_y - m\omega^2} - \frac{2(k_x - k_y)^2}{k_x + k_y + 2k_z - m\omega^2} \right] \sin^2 \left( \frac{k}{2} \right)
\]

\[
F(k, l) = f(k_x, k_y, k_z, k_h, k, \omega) + f \left( \frac{F_{x'}}{x^*}, \frac{F_{y'}}{y^* - x^*}, \frac{F_z}{x^* + y^*}, \frac{F_{h'\lambda}}{l, \omega} \right)
\]

\[
G(k, l) = 2 \left[ k_{h,d} + \frac{F_{h'}}{\sqrt{2}(x^* + y^*)} \right] \sin^2 \left( \frac{k + l}{2} \right) - \sin^2 \left( \frac{k - l}{2} \right),
\]

where \( F_{x'} = V_x'(x^*), F_y = V_y'(y^*), F_z = V_z'(y^* - x^*), F_{h'\lambda} = V_h'(x^* + y^*), \) and \( k_{h,d} = V_h''(\sqrt{2}(x^* + y^*)), k_{x'} = V_{x'}'(x^*), k_y = V_{y'}'(y^*), k_z = V_{z'}'(y^* - x^*), k_h = V_h''(x^* + y^*), \) and \( k_{h,d} = V_h''(\sqrt{2}(x^* + y^*)). \)

(Note that subscript ‘\( d \)’ refers to diagonal interactions and should not be confused with superscript ‘\( d' \), which is used elsewhere to refer to decoupling transitions.) Here, \( m \) is the particle mass (assumed to be the same for all particles in the lattice), \( k \) and \( l \) are the components of a wave vector (expressed in units of the inverse of the lattice spacing), and \( \omega \) is the angular frequency. Then, the dispersion relation is given by

\[
m\omega^2 \left[ m\omega^2 - F(k, l) - F(l, k) \right] + F(k, l)F(l, k) - G(k, l)G(l, k) = 0,
\]

where, like in Eqs. (S14) and (S15), the other arguments of \( F \) and \( G \) are omitted for notational convenience. For given \( k \) and \( l \), the frequencies of the vibration modes are solutions to a tenth order polynomial in \( \omega^2 \), so that there are ten branches of positive frequency, as expected given our five particle unit cell in two dimensions.

For the \( N \)-cell, the most important time scale is the inverse of the rate of the most prominent volume fluctuations. This corresponds to the acoustic longitudinal mode with wavenumbers \( l = 0 \) and \( k = \frac{\pi}{2N} \). For large \( N \), a perturbative expansion of Eq. (S16) gives the volume fluctuation period as

\[
\tau_V = \frac{4\sqrt{5mN}}{\sqrt{\frac{2k_x k_y + (k_x + k_y)k_z}{(k_x + k_y + 2k_z)} + k_{h,n} + k_{h,d} + \frac{F_{h'}}{\sqrt{2}(x^* + y^*)}}},
\]
which depends linearly on \( N \), as expected. But \( \tau_V \) also depends on \( k_x, k_y, k_z, k_{h_n}, k_{h_d}, x^*, y^* \), and \( F_{h_d} \), and hence on the applied stress or strain. When we use \( \tau_V \) as a reference time scale elsewhere, we are referring to the largest of its values in the relevant stress or strain ranges.

For the individual constituents, much faster times scales are relevant. For example, two of the solution branches of Eq. (S16) (one transverse and one longitudinal) correspond to optical modes in which the central particles in Fig. 2a (main text) move in opposite directions. These modes are of particular interest because they are precisely the vibrations that give rise to the couplings and decouplings of the constituents, and thus the frequencies of these modes indicate how often such transitions will occur. The exact calculation of the transition events would require full consideration of the entire vibrational spectrum, but such an approach is very difficult. The alternative we follow is to restrict our attention to the translationally invariant vibration modes, defined by \( k = l = 0 \), and assume this will give us indication of the microscopic time scales. From Eq. (S16), we find that the frequencies of the longitudinal and transverse optical modes (for both the coupled and the decoupled configuration) are

\[
\omega_L = \sqrt{\frac{k_x + k_y + 2k_z}{m}}, \quad \omega_T = \frac{1}{\sqrt{m}} \sqrt{\frac{F_x}{x^*} + \frac{F_y}{y^*} + 2 \frac{F_z}{y^* - x^*}},
\]

respectively. Below we use these frequencies to estimate the rates of transition events, which allows us to make accurate predictions about when the proposed material will exhibit the desired negative compressibility transition.

### 7. PERSISTENCE OF METASTABLE STATES

The local minima of the free energy are not significantly perturbed when the temperature is increased slightly above zero. However, at finite temperatures, transition events between local minima can occur spontaneously, and metastable states eventually decay. For a negative compressibility transition to be possible, it is necessary that the material remain in the metastable coupled state until the stress or strain becomes sufficiently large so that the decay into the decoupled state can produce a negative response. Whether this actually happens or not depends on both the temperature and the rate of change of applied stress or strain. To make this statement more precise, we have developed a simple model for the decay rate of metastable states. We assume that the time scale for which stress or strain is varied is much larger than the volume fluctuation rate. Under this condition, the quasi-static approximations are valid and the material can be assumed to be always near (metastable) equilibrium, except during the destabilisation transitions.

In order for a constituent to actually transition between the coupled and decoupled states, thermal fluctuations must be sufficiently large to overcome the free energy barrier separating the metastable state from the (thermodynamic) equilibrium state. We consider the expected frequency of events that overcome this free energy barrier, which we approximate as twice the potential energy differences between the unstable equilibrium and the coupled (\( 2V_b^c \)) or decoupled (\( 2V_b^d \)) stable equilibrium of the constituents (assuming they are initially coupled or decoupled, respectively). As indicated in Fig. S1, for each given stress or strain the
unstable equilibrium is indeed intermediate to the stable ones and hence defines the peak of the energy barrier. The factor two arises because the kinetic and potential energy contribute equally to the total energy.

The probability that thermal fluctuations exceed an energy of $2V_b$ is taken from the canonical ensemble as $e^{-\frac{2V_b}{k_BT}}$. The frequency at which the energy barrier is approached is taken as determined by the frequencies in Eqs. (S18) and (S19). During the decoupling transition, both transverse and longitudinal vibrations strain the bond, so we take the effective rate of energy barrier approach as $(\omega_L + \omega_T)$. On the other hand, for the coupling transition, we must have a coordinated approach in both the longitudinal and transverse directions, so we use a reduced frequency $(\omega_L^{-1} + \omega_T^{-1})^{-1}$. The rate of decoupling transitions for a single constituent is then taken as $\frac{\omega_L \omega_T}{2\pi(\omega_L + \omega_T)} e^{-\frac{2V_b}{k_BT}}$, and the rate of coupling transitions as $\frac{\omega_L \omega_T}{2\pi(\omega_L + \omega_T)} e^{-\frac{2V_b}{k_BT}}$.

Suppose we increased the applied tension on the $N$-cell at a constant rate such that in time $\tau$ the stress increased from $\sigma = 0$ to $\sigma = \Delta\sigma$. All of the $2N^2$ particle pairs interacting through the $V'_{\sigma}$ potential in the $N$-cell are initially coupled, but decouplings become possible when the stress increases past some $\sigma^c$, where the decoupled equilibrium appears. Then, applying our estimate for the transition frequency of each constituent, the expected number of decoupling transitions that will occur by the time the stress reaches some $\sigma$ is

$$n^d(\sigma; N, \tau, T) = 2N^2 \int_{\sigma^c}^{\sigma} \frac{\omega_L(\sigma') + \omega_T(\sigma')}{2\pi} e^{-\frac{2V_b(\sigma')}{k_BT}} d\sigma' \Delta\sigma,$$

(S20)

where $V'^c(\sigma')$, $\omega_L(\sigma')$, and $\omega_T(\sigma')$ are the average values of the corresponding quantities over all constituents in the $N$-cell when the stress is $\sigma'$. Here we assume that $\Delta\sigma > \sigma^d$ and that the integration is taken up to $\sigma^c < \sigma < \sigma^d$, since this calculation is tailored to accurately estimate only the beginning of the transition (the subsequent constituent transitions are discussed below).

Now, suppose that for $\sigma = \Delta\sigma$ the entire $N$-cell is in the decoupled equilibrium, and that $\sigma$ is decreased at constant rate so that after another time $\tau$ the stress returns to $\sigma = 0$. In this process, when the stress drops below some $\sigma^d$, where the coupled equilibrium reappears, couplings become possible. Then, as above, the expected number of coupling transitions that will occur by the time the stress drops to some $\sigma$ is

$$n^c(\sigma; N, \tau, T) = 2N^2 \int_{\sigma}^{\sigma^d} \frac{\omega_L(\sigma') + \omega_T(\sigma')}{2\pi(\omega_L(\sigma') + \omega_T(\sigma'))} e^{-\frac{2V_b(\sigma')}{k_BT}} d\sigma' \Delta\sigma,$$

(S21)

where $\Delta\sigma$ and the integration limit $\sigma$ fulfil the same assumptions as for Eq. (S20).

From these considerations, we can construct our simple model for the decay of metastable states. For this, we first note that the transition events are largely irreversible; they tend to go from metastable to stable states, and not the other way around. Moreover, and central to our argument, the transition events are not independent in the material. A single coupling or decoupling event produces a cascade of further transitions, and metastability can be completely and suddenly lost. Therefore, Eqs. (S20) and (S21) indicate when we should expect the decay of a metastable state to begin. So long as, say, $n^d(\sigma; \cdot) \ll 1$, we can assume that no decoupling events will occur in our $N$-cell between stress $\sigma^c$ and $\sigma$, and analogous conclusion can be derived from $n^c(\sigma; \cdot)$ for coupling transitions. We expect the decay of metastable states to begin when either $n^d \sim 1$ or $n^c \sim 1$. 

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This can be formalised by defining the effective energy barrier, $E_{b}^{c,d} = E_{b}^{c,d}(\sigma, N, \tau)$, as the solution of $n_{c,d}(\sigma; N, \tau, E_{b}^{c,d}/k_{B}) = 1$. In the derivation of Eqs. (S20) and (S21), we changed the integration variable from time to stress; changing it to strain leads to the corresponding equations for strain cycles, which define an effective energy barrier $E_{b}^{c,d}(\varepsilon, N, \tau)$ through $n_{c,d}(\varepsilon; N, \tau, E_{b}^{c,d}/k_{B}) = 1$ (where, for simplicity, we use the same notation for the $E_{b}^{c,d}$ and $n_{c,d}$ functions in both cycles). The results presented in Fig. 3 (main text) were obtained by integrating these equations numerically to estimate the stress and strain at which $n_{c} = 1$ and $n_{v} = 1$ for a range of values of $E_{b}^{c}$ and $E_{b}^{v}$, respectively, and then inverting the relationship.

The dependence of $E_{b}^{c,d}$ on the lattice size $N$ and cycling time $\tau$ can be made explicit after some approximations. First, note that the integrand in Eq. (S21) is dominated by the exponential factor, which increases as the stress increases. A similar statement holds for Eq. (S20). This justifies the following bounds:

$$n^{d}(\sigma; N, \tau, T) < N^{2\tau} \frac{\omega_{L}(\sigma) + \omega_{T}(\sigma)}{\pi} e^{-\frac{2V_{c}^{d}(\sigma)}{k_{B}T} \sigma - \sigma^{c}} \Delta \sigma,$$  \hspace{1cm} (S22)

$$n^{e}(\sigma; N, \tau, T) < N^{2\tau} \frac{\omega_{L}(\sigma)\omega_{T}(\sigma)}{\pi(\omega_{L}(\sigma) + \omega_{T}(\sigma))} e^{-\frac{2V_{c}^{d}(\sigma)}{k_{B}T} \sigma^{d} - \sigma \Delta \sigma}.$$  \hspace{1cm} (S23)

Then, the effective energy barrier for decoupling transitions at some $\sigma$ satisfies

$$E_{b}^{c}(\sigma, N, \tau) > \frac{2V_{c}^{d}(\sigma)}{\log \left[ \frac{N^{2} \sigma - \sigma^{c}}{\pi} \Delta \sigma \left( \omega_{L}(\sigma) + \omega_{T}(\sigma) \right) \right]},$$  \hspace{1cm} (S24)

and the effective energy barrier for coupling transitions at some $\sigma$ satisfies

$$E_{b}^{d}(\sigma, N, \tau) > \frac{2V_{b}^{d}(\sigma)}{\log \left[ \frac{N^{2} \sigma^{d} - \sigma}{\pi} \Delta \sigma \left( \omega_{L}(\sigma) + \omega_{T}(\sigma) \right) \right]}.$$  \hspace{1cm} (S25)

The same approach can be used to define effective energy barriers for constant-rate strain cycling as well.

These effective energy barriers, which must be overcome before the $N$-cell can make the decoupling and coupling transitions, decrease with increasing $N$ and $\tau$. It is important to note, however, that $N$ and $\tau$ enter only logarithmically, so that orders of magnitude changes in them produce only moderate changes in the effective energy barriers. This strengthens our results, given that in making the proposed material we want there to be a very large number of constituents and we want the effect to be apparent regardless of the rate of the external forces. In fact, it is not even necessary that $N$ be taken as large as the total size of the sample. Rather, $N$ should be taken as the typical size of the cell that is affected by a single transition event. This could be quite large if the material were a perfect crystal, but in a realistic material, domain boundaries and other impurities may prevent cascades from propagating endlessly. Even if this was not the case, additional design elements could be incorporated into the material to prevent cascades from propagating very far.

As evidenced in Fig. 3 (main text), the transitions become increasingly less sharp for larger temperatures. However, even at finite temperature, the decoupling transition exhibits clear signatures of the behaviour associated with negative compressibility observed in the zero temperature limit (Fig. 2, main text). The physical reason underlying this robust behaviour is as follows. During a decoupling transition of the material, the decoupling of an individual
constituent decreases local volume, and hence increases the force exerted on its neighbours. This triggers the decoupling of the neighbours, leading to a chain reaction that gives rise to the sharp transition observed in the material for both stress and strain cycles. Consistent with our simulations, this mechanisms dominate for small temperatures.

Finally, in relating our system’s phase transition to those frequently studied in statistical mechanics, we note that the degenerate equilibria that lead to the decoupling/coupling transitions in the $T \to 0$ limit can be identified as spinodal points [38]. In this context, the appearance of negative compressibility transitions can be interpreted as a manifestation of a spinodal curve extending outside of the coexistence curve at sufficiently low temperatures. The requirement that metastability survives sufficiently long for the decay to result in negative compressibility may then be related to the problem of spinodal decomposition [39].

8. MOLECULAR DYNAMICS SIMULATIONS

Following common practice, our molecular dynamics simulations employ periodic boundary conditions on the edges of the $N$-cell and assume that the results will not be significantly different from an infinitely large lattice. The general approach in molecular dynamics is to calculate the steady state distribution of a system by calculating time averages of a small number of components in a finite time. In our study of negative compressibility, we assume that we are dealing with relatively slow changes compared with the microscopic time scales. Therefore, while negative compressibility is not possible in a strict equilibrium sense, we can assume that the distribution around metastable states, and hence the decay of metastable states, is well predicted by molecular dynamics in the same sense that the equilibrium distribution is.

We consider both stress and strain cycling at constant rates and fixed temperatures. In both cases, we find it advantageous to express the positions of particles as scaled variables varying between zero and one. That is, if $(x_{i,j,k}, y_{i,j,k})$ is the position of the $k^{th}$ particle in the unit cell in the $i^{th}$ row and $j^{th}$ column of the $N$-cell, the scaled position $(\rho_{x,i,j,k}, \rho_{y,i,j,k})$ is defined by

$$ (x_{i,j,k}, y_{i,j,k}) = \left( L_x \rho_{x,i,j,k}, L_y \rho_{y,i,j,k} \right), $$

where $L_x$ is the length of the $i^{th}$ row of the $N$-cell and $L_y$ is the length of the $j^{th}$ column of the cell.

To maintain a constant temperature in the system, we employ a Nosé-Hoover chain [35], which is a generalisation of the Nosé-Hoover thermostat [40, 41] that couples additional dynamical variables to the momentum of the particles. We use a chain length of 50 thermostats to ensure that the heat released during the metastability decays is quickly removed from the system. For the relaxation times in the Nosé-Hoover chain, we use the volume fluctuation period of the $N$-cell. This ensures that the coupling to the heat bath does not dominate the microscopic interactions, which occur on time scales much faster than the volume fluctuation rate. This also ensures that the temperature remains essentially constant as the stress or strain varies, which occurs on a time scale much longer than the volume fluctuation rate.

For the strain cycles, we simply take $L_x$ and $L_y$ as functions of time. For the stress cycles, we must modify the equations of motion to incorporate applied stresses. To do so, we make all the $L_x$ and $L_y$ dynamical variables as well, and couple their evolution to the particles in a manner that maintains the applied external pressure. The Lagrangian for this extended
system is
\[ \mathcal{L} = \frac{1}{2} \sum_{i,j,k} \left[ (L_j^x \dot{\rho}_{i,j,k}^x)^2 + (L_j^y \dot{\rho}_{i,j,k}^y)^2 \right] + \sum_k \left[ \frac{1}{2} M (\dot{L}_k^x)^2 + (\dot{L}_k^y)^2 + \sigma (L_k^x + L_k^y) \right] - V_{\text{tot}}, \quad (S27) \]

where \( V_{\text{tot}} \) is the total potential energy (expressed in terms of the scaled variables) and \( M \) is the mass quantity associated with the variables \( L_i^x \) and \( L_i^y \). We include an additional constraint force in \( V_{\text{tot}} \), which prevents the centre of mass from moving by acting equally on all particles. By expanding the equations of motion generated by Eq. (S27) for a small amplitude volume fluctuation and setting the fluctuation rate to that from Eq. (S17), we can conclude that \( M = \frac{2\rho m N}{\pi^2} \). This technique was first described by Andersen [34] for the case of fluid systems, where it only allowed the size of the cell to vary while maintaining a fixed (usually cubic) shape. It was later expanded by Parrinello and Rahman [42] to allow for variation in the size and shape of the cell, where it proved successful in simulating solid-to-solid phase transitions. For our system, we take a slightly different generalisation than the Parrinello-Rahman barostat by allowing each row and column to vary in size (though not in orientation). We do so because in our system, entire rows and columns tend to decouple together without necessarily causing the adjacent constituents to undergo the same transition, but the Parrinello-Rahman does not allow individual rows or columns to change size in a manner that is independent from the other rows and columns. A Nosé-Hoover chain of 50 thermostats is again added to the equations of motion derived from Eq. (S27) to control the temperature of the particles. In addition, to prevent long-lived fluctuations in the \( L_i^x \) and \( L_i^y \), a separate Nosé-Hoover chain of 10 thermostats is added to the equations of motion to control the fluctuations of these extended variables. For these thermostats, a relaxation time of 10 volume fluctuation periods was used so as to minimally affect the evolution of the particles themselves while still eliminating the fluctuations that arise from the decay of the metastable states.

Figure S3 shows the hysteresis loops exhibited by an \( N \)-cell for \( N = 20 \) undergoing stress cycling for a range of temperatures and cycle times. Figure S4 shows the same system undergoing strain cycling for the same range of temperatures and cycle times. Higher temperatures and longer cycle times cause the metastable states to decay earlier in the cycle, as expected. However, the negative compressibility transitions are observed to persist for a wide range of small temperatures and for large cycle times (\( \tau \) as large as \( 10^3 \tau_V \) for \( T \) below \( 10^{-2} T_0 \)). To be able to generate non-uniform stresses, as shown in Fig. 2b (main text), we have relaxed the periodic boundary conditions and applied the stress directly to the boundary particles instead of using the barostat. This alternative approach was used in the simulations shown in the Supplementary Movie, which animates the response of the material to different stress profiles. The robustness of the negative compressibility observed in all these simulations demonstrate that our results do not depend on our implementation of the barostat. Furthermore, we have also benchmarked our barostat with both the Andersen barostat and the Parrinello-Rahman barostat.

9. PREVIOUS REFERENCES TO NEGATIVE COMPRESSIBILITY

As emphasised in the main text, there are fundamental stability limitations on the existence of negative compressibility systems. Our material is the first design in which one can create a rod that will contract when we pull on its ends; in this process, the forces we exert can be
applied directly to the material and the contraction of the rod is along the direction of the applied force. Ours is also the first closed system to exhibit contraction along all directions of an increasing tensional stress. Nevertheless, there exists a large body of literature describing different kinds of negative compressibilities in both theoretical and actual materials. It is then instructive to consider in further detail how the effect demonstrated in our study differs from what has been previously described.

There are four main contexts in which concepts associated with negative compressibility, negative stiffness, and negative elastic/bulk moduli have been considered in the literature:

1. *Response transverse to the applied stress.* The volume of most materials increases when they are tensioned along a specific direction. However, if the Poisson’s ratio sum is larger than 1, which is possible for anisotropic materials, the volume will in fact decrease due to the contraction of transverse directions, and this is referred to as *stretch densification* in the literature [7]. In this process, the direction along which the tension is applied will expand, as in ordinary materials. If hydrostatic pressure is applied to the boundaries of a three-dimensional sample, the same material will expand in one dimension (a behaviour often termed *negative linear compressibility*) or two dimensions (*negative area compressibility*) [7, 22, 23, 43], while it will necessarily contract in the third dimension such that the volume compressibility is positive. In this case, negative linear compressibility and negative area compressibility are manifestations of transverse response and as such cannot be observed if the stress is applied only to those dimensions. In this context, the compressibilities (and also the stretch densification) concern the response of the system to infinitesimal changes of applied stress. Negative (differential) volume compressibility defined as an increase in volume in response to an incremental increase in hydrostatic pressure is thermodynamically forbidden for any closed system in equilibrium.

2. *Response of mechanically open systems to hydrostatic pressure.* The volume of most materials decrease when they are hydrostatically pressured. Yet, volume increase under increased hydrostatic pressure is possible when the pressure is exerted through a medium that penetrates the material. The most common mechanism for this effect is infiltration of medium particles such that they occupy an increasingly larger volume inside the material as the pressure is increased, which has been demonstrated for porous materials [8, 9] and for the pressure denaturation of proteins [44] (a related effect is the expansion of voids with penetrating gas as pressure is increased [45]). In this case, the volume increase of the material can be accompanied by expansion in all directions. A different mechanism has been shown to be possible for certain grid- and truss-like systems whose edges are composed of two or more materials with different elastic moduli, where their different response to pressure leads to deformation of the lattice cells and possibly an increase in the system’s volume as the hydrostatic pressure is increased [10, 11]. Here, the medium is supposed to permeate the system and is necessary to communicate the applied pressure to all of its interior parts. These effects too, which depend on the system being open and the stress being exerted through a medium, have been called *negative compressibility* and/or *negative bulk modulus* by some authors.

3. *Response of (dynamically open) composites to acoustic waves.* Metamaterials can be designed to have resonances that exhibit *negative effective modulus* [6, 12–14], sometimes in conjunction with *negative effective density* [46–48], which leads to the acoustic
equivalent of a negative index of refraction. Such resonant composites can exhibit a number of unusual properties analogous to those found in electromagnetic metamaterials, such as negative group velocity. This is another context in which the terms negative bulk modulus and negative compressibility have been used, although clearly referring to the dynamic counterparts (i.e., the frequency-dependent relation between stress and strain). By construction, the unusual properties of acoustic metamaterials are only exhibited in response to acoustic waves, while ordinary behaviour is observed in response to quasi-static applications of stress.

4. Response of constrained materials to applied strain. Stable systems offer resistance to deformation, which corresponds to a positive slope for the relation between strain and stress and hence to a positive differential compressibility. Many systems also exhibit branches of negative slope in their stress-strain curves, which would correspond to negative differential compressibility, but these branches represent unstable configurations that cannot be realised when the applied stress is the control parameter. These branches can be stabilised by constraining the strain; such constrained systems are said to exhibit negative incremental stiffness, which physically means that an increase in deformation leads to a decrease in the restoration force in one of the components of the material. Indeed, in composite materials it is possible for a component of positive stiffness to provide such a constraint to a component of negative stiffness, as in the stabilisation of negative stiffness inclusions by a matrix [15, 16, 49] and in the stabilisation of a “negative compressibility” electron gas by the underlying positively-charged background in 2D interacting electron systems [50, 51]. As these examples illustrate, stability requires the strain to be completely or partially constrained in every portion of the material and not only at the boundaries (more about this below). Much research has been done on materials formed by systems that are constrained in this way (see Refs. [15, 16, 21, 49–54] and references therein), with the terminology negative bulk modulus and negative compressibility often employed here too. However, because the constraints do not allow contraction in response to tension or expansion in response to pressure, the interpretation of these terms is different in this context when compared with our study. In particular, in all materials with negative stiffness components, the composite itself must obey the thermodynamic restriction of positive differential volume compressibility.

The negative transverse effects mentioned in 1. are fundamentally different from the negative response transitions along the direction of applied stress considered in our study. In that case, the response is limited to be transverse due to thermodynamic restrictions. The negative responses mentioned in 2. avoid such restrictions because the systems are not closed. In that case, the pressure has to be applied through a medium—taking both the material and the surrounding medium as a closed system, the combined system will exhibit positive compressibility, i.e., it will contract upon increased pressure, and the same is true for the material in the absence of any medium. The negative responses mentioned in 3. also avoid the thermodynamic restrictions because the systems are not closed. In that case, the unusual properties are observed for acoustic waves, which requires the system to be dynamically excited, and hence are not thermodynamic equilibrium properties. In fact, if the system is open so that energy is supplied from an external source, it is easy to see that stable configurations can contract upon increase in tension and expand upon increase in pressure. This scenario includes interesting responses in fluid flow systems [55], but it is of limited interest in materials research since it concerns an externally driven response rather
than a spontaneous response of a material. The negative responses considered in 4. avoid the thermodynamic restrictions by means of constraints that effectively store energy in all portions of the system, but the resulting composites have positive compressibility. Thus, although these materials are interesting in their own right, they do not exhibit the negative compressibility transitions demonstrated in our study. In particular, a rod made of such materials will not contract when we pull on its ends.

A few more comments are in order concerning differences between these well-known negative responses and the negative compressibility transitions demonstrated in our study. First, our negative compressibility transitions are induced by changes in the applied stress whereas negative incremental stiffness requires the strain to be at least partially constrained. The mathematical and physical [56] differences between stress- and strain-driven transitions are in fact well appreciated. In particular, previous experimental observations of negative compressibility for strain-driven processes, such as in escape transitions of polymers [57], have reported positive compressibility for the stress-driven counterparts. Second, we emphasise that the stabilising constraints mentioned above with regards to negative incremental stiffness must be applied to every portion of the material rather than only to the boundaries, which is often not possible or not the physical situation of interest. If the strain is only applied to the boundaries, then the configurations corresponding to negative differential compressibility are no longer stable, and a phase mixture of two or more positive-compressibility phases will develop rather than a pure phase of negative compressibility. We do consider strain-driven cycles in our study, but we focus on applications of strain to the boundaries of the material, for which a phase mixture develops, as shown in Fig. 2d (main text) for the coupling transition. Therefore, as already noted for the unusual responses we observe in stress cycles (negative compressibility transitions), the unusual responses we observe in strain cycles (force amplification transitions) are fundamentally distinct from the negative responses considered in previous studies.

We emphasise that unstable, negative-slope branches in stress-strain curves, which underlie negative incremental stiffness, are also manifest in the macroscopic description of phase transitions. This is apparent in two main contexts:

5. Unstable branches of negative compressibility and stress-/strain-induced phase transitions. Models of materials undergoing first-order stress-induced phase transformations [31, 58–62], most noticeably those based on the Landau theory, generally possess free energies with concave regions. These regions correspond to unstable branches of negative differential compressibility in the stress-strain curve. According to such models, different phases of a material correspond to different branches of positive compressibility, and these branches are connected to each other by the unstable branches. As the external strain (applied to the boundaries) or the external stress (also applied to the boundaries) is varied, these materials jump between phases corresponding to branches of positive compressibility, while avoiding the unstable branches, and this is what gives rise to the phase transition. Thus, although there are branches that would correspond to negative differential compressibility, they are never actually observed (and hence only implicitly inferred from the destabilisations) unless additional stabilising constraints are imposed [63, 64].

6. Unstable branches of negative compressibility and temperature-induced phase transitions. Models of ferroelastic materials [65] (the elastic analogues of ferromagnets) predict unstable branches in the stress-strain curve for sufficiently low temperatures,
which vanish at the critical temperature of a second-order phase transition [59, 60]. A related experimental observation is the softening of the bulk modulus, in which the bulk modulus approaches zero during temperature-induced transition [66–68]. Importantly, the bulk modulus is always observed to be positive in this process, as expected from stability. Theoretical considerations suggest that unstable branches of negative compressibility can be stabilised, but, as in the case of stress- and strain-induced transitions, stabilisation requires additional constraints [69, 70]. However, it is often only possible to control the strain applied to the boundaries of the material, which, as noted above, leads to a fundamentally different behaviour.

Equilibrium phase transitions cannot exhibit negative (volume) compressibility due to thermodynamic constraints [71]. However, materials undergoing phase transitions as those considered in 5. and 6. generally involve metastable configurations; hence, they could in principle exhibit negative compressibility transitions like those demonstrated here without violating thermodynamic stability constraints. Nevertheless, no negative compressibility transitions in such materials have been demonstrated in previous studies.


Fig. S1. High-dimensional representation of the stable and unstable equilibria of the constituents. The full hysteresis loop of the constituents does not lie in the $F$-$h$ plane, since there is an additional degree of freedom at each equilibrium configuration. Including an additional dimension, $z = y - x$, reveals that the hysteresis loop does not intersect itself and is instead twisted in three dimensions. This figure was generated using $R_x = R_y = 0.05$, which corresponds to smooth potentials; the projection in the $F$-$h$ plane is comparable to the $\sigma$-$\varepsilon$ projection shown in Fig. 2c,d (main text) for $R_x = R_y = 0$. Note that the intersection point shown in Fig. 2c,d thus corresponds to one coupled and one decoupled configuration. Because $z$ represents an internal degree of freedom, its value is not directly observed in compressibility and deformation measurements of the resulting material.
Fig. S2. Linear system exhibiting negative compressibility transition. a-b, System of 11 particles interacting via linear springs in an unbuckled (a) and in a buckled (b) configuration. The inter-particle forces are represented by dotted lines and their values are indicated by a continuous colour scale, which varies from red (repulsive forces) to grey (no force) to blue (attractive forces). When the system is tensioned by increasing the force $F$ applied to the black particles, a buckling destabilisation is induced during which the length $h$ of the system decreases (the increase in $F$ depicted in panel (b) is exaggerated for clarity). c, Hysteresis loop showing the behaviour of the length $h$ as the force $F$ is varied, which is in many aspects similar to the corresponding curve for the one-dimensional system considered in the other parts of our study (cf. Fig. 2c,d, main text). d, Force constants $k_{i,j}$ and natural lengths $r_{i,j}$ of the springs, which describe the interactions between particles $i$ and $j$ as being governed by the harmonic potential $V_{i,j}(r_i, r_j) = \frac{1}{2}k_{i,j}(|r_i - r_j| - r_{i,j})^2$. Functionally, the black particles are analogous to the exterior particles and the purple particles are analogous to the interior particles in Fig. 2a (main text). The green particles with their collective interactions are analogous to the $V_x$ bonds; by buckling at a certain applied force, they emulate the breaking of the weak bond in the original system. The springs connecting the black and purple particles are analogous to the $V_x$ bonds, which contract during the destabilisation. Finally, the orange particles and their collective interactions are analogous to the $V_y$ bonds, which expands minimally during the destabilisation.
Fig. S3. Hysteresis curves for stress cycles at various temperatures and cycle times. a-l. Each column corresponds to a different temperature and each row to a different cycle time. The arrows show the orientation of the evolution, with red indicating coupled and blue decoupled configurations. The $T = 0$ equilibria are indicated by the dotted lines, and are included as a reference. The predicted decrease in strain upon increase in tension is prominent for a wide range of small temperatures and up to the largest cycle times that we could simulate (left and centre columns). There is a noticeable but very small reduction of the effect as the cycle time increases. The effect is substantially reduced or lost only when the temperature is sufficiently large (right column). Each panel represents an average over 10 independent realisations of our molecular dynamics simulation for a square lattice of $20 \times 20$ unit cells.
Fig. S4. Hysteresis curves for strain cycles at various temperatures and cycle times. In close correspondence with the stress cycles shown in Fig. S3, the predicted sudden increase in tension upon increase in strain is observed for a wide range of small temperatures and for all cycle times simulated (left and centre columns). The extent of the effect exhibits only very weak dependence on the cycle time. The effect is lost at larger temperatures (right column). The parameters, temperatures, and cycle times are the same used in the corresponding panels of Fig. S3.
Supplementary Movie Legend

**Simulation of the material under stress.** a-d, Response of the material to uniform (a), diagonal (b), pinched (c), and splayed (d) stress profiles. The applied forces are indicated by the arrows, while red and blue indicate coupled and decoupled constituents, respectively. The time under each panel above indicates the time of the corresponding frame in the animation. The animation represents the results of our molecular dynamics simulations for a full stress cycle implemented on a square lattice of 20 × 20 unit cells, for temperature $T = 10^{-4}T_0$, cycle time $\tau = 10^{1.5}\tau_V$, and the same smooth potentials used in Fig. S1. To show that our results do not depend on the barostat in our molecular dynamics simulations, here we relaxed the periodic boundary conditions and applied the stress directly to the boundary particles.
**Table S1. Definitions and conventions.**

<table>
<thead>
<tr>
<th>Compressibility</th>
<th>The qualitative response in the strain of a sample of material when the externally applied stress is varied.</th>
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<tbody>
<tr>
<td>Differential compressibility</td>
<td>A quantitative measure of the compressibility, $\beta = \frac{1}{A(\sigma)} \frac{\partial A(\sigma)}{\partial \sigma}$, where $A(\sigma)$ is the area occupied by a two-dimensional sample of material subject to a uniform and isotropic applied stress $\sigma$. (The corresponding definitions in one and three dimensions are immediate.) This measure is most useful when infinitesimal changes in stress result in infinitesimal changes in strain.</td>
</tr>
<tr>
<td>Finite-difference compressibility</td>
<td>A quantitative measure of the compressibility, $\beta_\delta = \frac{1}{A(\sigma)} \frac{A(\sigma+\delta\sigma)-A(\sigma)}{\delta\sigma}$. This measure corresponds to the differential compressibility in the limit $\delta\sigma \to 0$ but is more useful when infinitesimal changes in applied stress result in finite changes in strain.</td>
</tr>
<tr>
<td>Negative compressibility transition</td>
<td>Transition in which an unconstrained material responds to a increase (decrease) in the applied stress with a decrease (increase) in the resulting strain. It manifests itself as an infinite negative value of the differential compressibility but as a finite negative value of the finite-difference compressibility.</td>
</tr>
<tr>
<td>Force amplification transition</td>
<td>Transition in which a material responds to a change in the applied strain with a discontinuous increase in the resulting restoration force. It manifests itself as an abrupt change to a different stable state (rather than the more common phase mixture), and as such is persistent upon small subsequent reduction of strain (although reversible upon complete relaxation of strain).</td>
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