Negative Poisson's Ratio Materials via Isotropic Interactions

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We show that under tension a classical many-body system with only isotropic pair interactions in a crystalline state can, counterintuitively, have a negative Poisson's ratio, or auxetic behavior. We derive the conditions under which the triangular lattice in two dimensions and lattices with cubic symmetry in three dimensions exhibit a negative Poisson's ratio. In the former case, the simple Lennard-Jones potential can give rise to auxetic behavior. In the latter case, a negative Poisson's ratio can be exhibited even when the material is constrained to be elastically isotropic.

Materials with a negative Poisson's ratio (NPR), the so-called "auxetics," are those that when stretched in a particular direction expand in an orthogonal direction. NPR behavior is a counterintuitive material property that has been observed only in a handful of materials that often have intricate structures and characteristic lengths much larger than an atomic bond length. NPR materials have a great deal of technological potential, for example, to increase the sensitivity of piezoelectric transducers [1], as components in microelectromechanical systems, and as shock absorbers and fasteners [2,3].

A negative Poisson's ratio had not been observed in any elastically isotropic material until the discovery of certain foam structures with reentrant structures [4]. NPR behavior has also been observed in multiple-length-scale laminate composites [5], polymeric and metallic foams [6], inverted honeycomb and other structures fabricated using soft lithography [2], and scaffold structures made out of springs, hinges, and rods [7]. It has been found in cubic atomic solids when they are stretched in the [110] direction [8].

In this Letter, we derive conditions for which NPR behavior is exhibited in classical many-body systems; this continues a research program in which interparticle interactions are sought for targeted material properties. Examples of such *inverse problems* include optimization of pair potentials to give rise to negative thermal expansion [9], and a method to derive potentials that yield targeted classical ground states [10].

We report here that under tension two- and three-dimensional systems with isotropic two-body interaction potentials can show NPR behavior in the crystal phase as long as certain linear equalities and inequalities involving the interaction potential are satisfied. This is an unexpected result, since an inherently anisotropic behavior arises from isotropic interactions; indeed, most previously discovered NPR materials exhibit complex, carefully designed anisotropic interactions. We show this to be the case at zero temperature for the elastically isotropic triangular lattice in

two dimensions, and for the fcc lattice in three dimensions. In the latter case, NPR behavior is exhibited even when the material is constrained to be elastically isotropic. We first describe the calculation of the Poisson's ratio for any dimension. Then, we present results for the two- and three-dimensional cases, including the elastic constants and NPR constraints. In order to demonstrate that NPR behavior is achievable at positive pressure, we present an example in which this is achieved by including three-body interactions in two or three dimensions.

Consider a set of $N + 1$ particles, with positions $\{\mathbf{r}_n\}$ ($n \geq 0$), that occupy a particular Bravais lattice in a state of zero strain. Under strain that is uniform throughout space, the new positions of the particles are

$$\mathbf{x}_n = (\mathbf{I} + \mathbf{E}) \cdot \mathbf{r}_n, \qquad (1)$$

where $\mathbf{I}$ is the unit tensor in d dimensions and $\mathbf{E}$ is the second-rank strain tensor with components ε_{ij}. The latter is constrained to be symmetric (i.e., $\varepsilon_{ij} = \varepsilon_{ji}$) in order to remove simple rotation. For simplicity, we take the origin to be at $\mathbf{r}_0$, and thus the energy per particle of the system can be written as

$$u = \frac{1}{2} \sum_{n=1}^{N} \phi(|\mathbf{x}_n|), \qquad (2)$$

where ϕ is the pair interaction potential and N is the total number of particles excluding that at the origin. At zero temperature, the enthalpy and Gibbs free energy per particle are equivalent and equal to $g = u + pv$, where $p = -du/dv$, and v is the d-dimensional specific volume. The equilibrium volume is found by minimizing g with respect to v at fixed p. In order to calculate the second-order elastic constants and Poisson's ratio, g is expanded to quadratic order in the strain tensor ε_{ij}. The expansion is taken around equilibrium; thus, it contains no linear terms, and can be written as $g \simeq g_0 + \frac{v}{2} \lambda_{ijkl} \varepsilon_{ij} \varepsilon_{kl}$, where g_0 is the zero-strain free energy, λ_{ijkl} are the second-order elastic

constants of the system [11], and the Einstein convention is used. The Poisson's ratio $\nu = -\varepsilon_T/\varepsilon_L$ is calculated by imposing a strain, $\varepsilon_L = \varepsilon_{ij}n_i n_j$, and minimizing the free energy to find the strain in a transverse direction, $\varepsilon_T = \varepsilon_{ij}n'_i n'_j$, where **n** and **n'** are unit vectors in the original and transverse directions, respectively.

The number of independent elastic constants is determined by the dimensionality and rotational symmetry of the lattice in question. For example, in two dimensions, square lattices have three independent elastic constants, and triangular lattices are "elastically isotropic" (i.e., elastic properties are independent of direction) and thus have only two [11]. Lattices with cubic symmetry have three independent elastic constants, the least of any crystal structure in three dimensions.

Two dimensions: Triangular lattice example.—This analysis can be applied to any structure in two dimensions, but perhaps the simplest case is the triangular lattice. The free energy (neglecting g_0, an irrelevant offset) is

$$g_{\text{tri}} = \upsilon\{2\lambda_1(\varepsilon_{xx} + \varepsilon_{yy})^2 + \lambda_2[(\varepsilon_{xx} - \varepsilon_{yy})^2 + 4\varepsilon_{xy}^2]\}, \quad (3)$$

where λ_1 and λ_2 are the elastic constants and υ is the two-dimensional "volume," namely, the area. Since both terms are quadratic invariants of the strain tensor, g is rotationally invariant. This property holds true of the Poisson's ratio, which is

$$\nu_{\text{tri}} = \frac{2\lambda_1 - \lambda_2}{2\lambda_1 + \lambda_2}. \quad (4)$$

The free energy expansion must be a positive-definite quadratic form, or else the lattice is unstable. Thus, the eigenvalues of the Hessian matrix of g_{tri} must be positive. This is true if and only if $\lambda_1 > 0$ and $\lambda_2 > 0$. The Poisson's ratio must thus fall within the range $-1 < \nu_{\text{tri}} < 1$. By expanding Eq. (2) as well as the area to quadratic order in the strain tensor, we obtain the elastic constants in terms of the first and second derivatives of the pair potential, evaluated at the neighbor distances of the lattice:

$$\lambda_1 = \frac{1}{32\upsilon}\sum_{i=1}^{N}[|\mathbf{r}_i|^2\phi''(|\mathbf{r}_i|) - |\mathbf{r}_i|\phi'(|\mathbf{r}_i|)],$$

$$\lambda_2 = \frac{1}{4\upsilon}\sum_{i=1}^{N}\left[\left(\frac{x_i^2 y_i^2}{|\mathbf{r}_i|^2}\right)\phi''(|\mathbf{r}_i|) + \left(\frac{|\mathbf{r}_i|}{2} - \frac{x_i^2 y_i^2}{|\mathbf{r}_i|^3}\right)\phi'(|\mathbf{r}_i|)\right], \quad (5)$$

where the sum is over every particle except that at the origin, and x_i's and y_i's are the Cartesian coordinates of the particles in the unstrained lattice. The Poisson's ratio, given in Eq. (4), can be written as

$$\nu_{\text{tri}} = \frac{1 + 2p\kappa_T}{3 - 2p\kappa_T}, \quad (6)$$

where κ_T and p are defined by

$$\frac{1}{\kappa_T} = \left[-\upsilon\frac{dp}{d\upsilon}\right] = \frac{1}{8\upsilon}\sum_{i=1}^{N}[|\mathbf{r}_i|^2\phi''(|\mathbf{r}_i|) - |\mathbf{r}_i|\phi'(|\mathbf{r}_i|)],$$

$$\text{and} \quad p = -\frac{du}{d\upsilon} = -\frac{1}{4\upsilon}\sum_{i=1}^{N}|\mathbf{r}_i|\phi'(|\mathbf{r}_i|). \quad (7)$$

Thus, the Poisson's ratio, given in Eq. (6), cannot be negative as long as $p > 0$, since for mechanical stability $\kappa_T > 0$. Importantly, it is only for negative pressures, i.e., when the system is under tension, that ν_{tri} can be negative.

Even if the interaction potential extends only to the nearest neighbor in the triangular lattice and is zero beyond it, NPR behavior can be achieved at negative pressure, as long as

$$\phi'(a) > 0, \qquad \phi'(a) < a\phi''(a) < 5\phi'(a), \quad (8)$$

where $a = \sqrt{2\upsilon/\sqrt{3}}$ is the lattice constant. Figure 1 depicts these inequalities in a parameter space of $\phi'(a)$ and $\phi''(a)$. In the case that the potential extends beyond the first neighbor, corresponding inequalities to those in Eq. (8) can be found, involving the first and second derivatives of the potential at relevant neighbor distances.

To understand intuitively why NPR behavior only occurs at negative pressure, consider the function $\Phi(r^2) = \phi(r)$, which is the interaction potential rewritten in terms of the square of the interparticle distance. A condition for lattice stability is $\Phi''(a^2) > 0$, which physically means that the "effective repulsive spring constant" between nearest-neighbor particles must decrease with distance. Thus, if the bonds between neighboring particles are thought of as springs with zero rest length, an imposed outward strain has the effect of weakening the effective spring constants
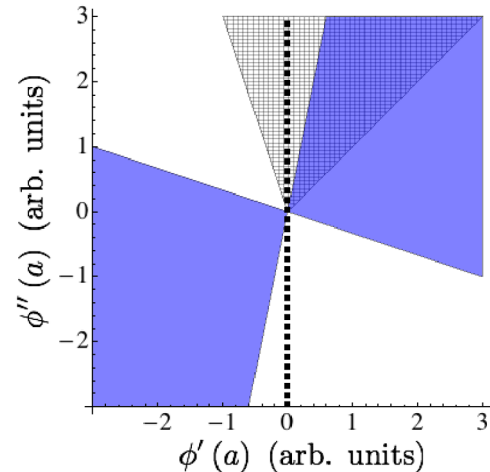

FIG. 1 (color online). Regime of negative Poisson's ratio in a triangular lattice, where the pair potential extends to the first neighbor only. The parameter space is composed of the first and second derivatives of the pair potential evaluated at the nearest-neighbor distance. In the continuously shaded region, ν_{tri}, given in Eq. (4), is negative. In the grid-shaded region, the lattice is stable. The overlap region is given in Eq. (8). The pressure is positive to the left of the dotted line and negative to the right.

of the bonds in the transverse direction. Under positive pressure, such a weakening causes a contraction, but under tension it causes an expansion.

When ϕ is taken to be the well-known 12-6 Lennard-Jones (LJ) potential, given by $\phi_{LJ}(r) = \epsilon[(b/r)^{12} - 2(b/r)^6]$, there is a range of lattice constants for which NPR behavior is exhibited, namely, $1.0596b < a < 1.0870b$, as demonstrated in Fig. 2. This corresponds to a pressure range of $-4.6363(\epsilon/b^2) > p > -4.8516(\epsilon/b^2)$. Therein, the Poisson's ratio takes on values of 0 through -1, the lower bound for stability. Note that a sufficient number of neighboring particles are included to accurately calculate the energy. That the Poisson's ratio is negative in this system is a surprising result, since the simple LJ potential has been studied extensively, and was not thought to exhibit this behavior.

Other two-dimensional crystals have been studied for a general ϕ, including the square lattice and non-Bravais crystals such as the honeycomb and kagome. In all cases, NPR behavior was only found under tension.

Three dimensions: Lattices with cubic symmetry.—Here we extend the previous analysis to lattices with cubic symmetry. The most common examples of these are the face-centered cubic (fcc), the body-centered cubic (bcc), and the simple cubic lattices. Such systems have three independent elastic constants and are generally not elastically isotropic. The most general expression for the Gibbs free energy of cubic systems is

$$g = v\{\tfrac{1}{2}\lambda_1(\varepsilon_{xx}^2 + \varepsilon_{yy}^2 + \varepsilon_{zz}^2) + \lambda_2(\varepsilon_{xx}\varepsilon_{yy} + \varepsilon_{xx}\varepsilon_{zz} + \varepsilon_{yy}\varepsilon_{zz})$$
$$+ 2\lambda_3(\varepsilon_{xy}^2 + \varepsilon_{xz}^2 + \varepsilon_{yz}^2)\}, \qquad (9)$$

where λ_1, λ_2, and λ_3 are the elastic constants, and v is the specific volume. The Poisson's ratio is a function of both the direction of the imposed strain and the chosen transverse direction. As an example, if the strain is imposed along the [100] direction, the Poisson's ratio is

$$\nu_{\text{cubic}}^{100} = \frac{\lambda_2}{\lambda_1 + \lambda_2}. \qquad (10)$$
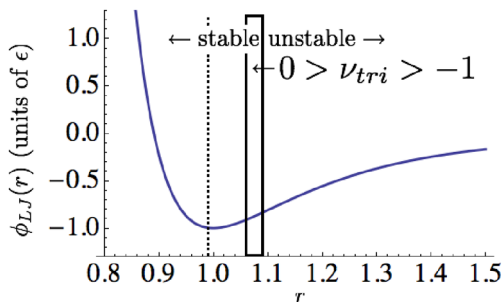

FIG. 2 (color online). Region of lattice constants (indicated by the rectangular box) for which the Poisson's ratio is negative in a triangular lattice, using the LJ interaction potential ϕ_{LJ}. Pressure is positive to the left of the dotted line and negative to the right; thus, NPR behavior only occurs at negative pressure. To the right of the rectangular box, the lattice becomes unstable.

In order for the Hessian of the quadratic form given in Eq. (9) to be positive definite, a necessary condition for lattice stability, we must have that $\lambda_1 > 0$, $\lambda_3 > 0$, and $-\lambda_1/2 < \lambda_2 < \lambda_1$. If we expand Eq. (2) to quadratic order in the strain tensor components, we obtain

$$\lambda_1 = -p + \frac{1}{2v}\sum_{i=1}^{N}\left(\frac{x_i}{|\mathbf{r}_i|}\right)^4[|\mathbf{r}_i|^2\phi''(|\mathbf{r}_i|)$$
$$- |\mathbf{r}_i|\phi'(|\mathbf{r}_i|)],$$

$$\lambda_2 = \frac{p}{2} + \frac{3}{2\kappa_T} - \frac{1}{4v}\sum_{i=1}^{N}\left(\frac{x_i}{|\mathbf{r}_i|}\right)^4[|\mathbf{r}_i|^2\phi''(|\mathbf{r}_i|)$$
$$- |\mathbf{r}_i|\phi'(|\mathbf{r}_i|)],$$

$$\lambda_3 = -p + \frac{1}{2v}\sum_{i=1}^{N}\left(\frac{x_i y_i}{|\mathbf{r}_i|^2}\right)^2[|\mathbf{r}_i|^2\phi''(|\mathbf{r}_i|)$$
$$- |\mathbf{r}_i|\phi'(|\mathbf{r}_i|)],$$

with $\quad \dfrac{1}{\kappa_T} = \dfrac{1}{18v}\sum_{i=1}^{N}\left(\dfrac{x_i}{|\mathbf{r}_i|^2}\right)^2[|\mathbf{r}_i|^2\phi''(|\mathbf{r}_i|) - |\mathbf{r}_i|\phi'(|\mathbf{r}_i|)],$

and $\quad p = -\dfrac{1}{6v}\sum_{i=1}^{N}|\mathbf{r}_i|\phi'(|\mathbf{r}_i|), \qquad (11)$

where p is the pressure and κ_T is the compressibility. Note that these expressions apply equally well to any Bravais lattice with cubic symmetry. If we impose an additional linear constraint on the elastic constants, we find that we can impose elastic isotropy on the system, namely, if we enforce the following:

$$\lambda_1 = \lambda_2 + 2\lambda_3, \qquad (12)$$

then the system becomes elastically isotropic because the free energy given in Eq. (9) can be written as a function only of quadratic invariants of the strain tensor. Even with this additional applied constraint, we find that the system can exhibit NPR behavior under tension, with the Poisson's ratio in any direction given by Eq. (10). The Poisson's ratio must fall between -1 and $+1/2$ in this case. If we consider a particular lattice we can, by employing Eqs. (10)–(12), find inequalities, which involve the pair potential evaluated at the neighbor distances, that describe the regime in which the Poisson's ratio is negative and the system is elastically isotropic. For each set of coordination shells included in the calculation, such inequalities can be found; none were found to allow for NPR behavior at positive pressure.

Consider as an example the fcc lattice, which has 12 nearest neighbors (at distance $a/\sqrt{2}$) and 6 next-nearest neighbors at distance a, where a is the side length of the cubic cell. If the potential extends only to the nearest neighbor, NPR behavior is not possible. Both NPR behavior and elastic isotropy can be exhibited at negative pressure if the pair potential extends to the nearest and next-nearest neighbors, if the following constraints are satisfied:

$$4\phi'(a) - 4a\phi''(a) + a\phi''\left(\frac{a}{\sqrt{2}}\right) = \sqrt{2}\phi'\left(\frac{a}{\sqrt{2}}\right),$$

$$\sqrt{2}\phi'\left(\frac{a}{\sqrt{2}}\right) < a\phi''\left(\frac{a}{\sqrt{2}}\right)$$

$$< 4\phi'(a) + 5\sqrt{2}\phi'\left(\frac{a}{\sqrt{2}}\right),$$

$$\text{and} \quad 4\phi'(a) + 9\sqrt{2}\phi'\left(\frac{a}{\sqrt{2}}\right) < 5a\phi''\left(\frac{a}{\sqrt{2}}\right). \tag{13}$$

At zero pressure, the Poisson's ratio goes to $1/4$, as predicted by the Cauchy relations [12].

Our analysis suggests that NPR behavior does not occur at positive pressures in crystals when the system contains only pair interactions, and the material is elastically isotropic. However, we present here a three-body potential that yields NPR behavior in close-packed two- and three-dimensional lattices by construction at zero temperature and positive pressure. In order to produce this behavior, the potential has a built-in energy cost associated with deforming the equilateral triangles in the two-dimensional triangular lattice and the three-dimensional close-packed lattices. The three-body potential is given by

$$\phi_3(r, s, t) = \alpha f(r)f(s)f(t)F(r, s, t), \tag{14}$$

where α is a positive constant, r, s, and t are the side lengths of a triangle defined by a triplet of particles, f is some function that goes to zero sufficiently quickly that only nearest neighbors are within range of the potential, and

$$F(r, s, t) = \frac{(r + s + t)^2}{3^{3/2}[2(r^2 s^2 + r^2 t^2 + s^2 t^2) - r^4 - s^4 - t^4]^{1/2}} - 1, \tag{15}$$

a function that is zero if the triplet of particles defines an equilateral triangle, but is greater than zero otherwise. Thus, if an outward strain is imposed on the system, then regardless of the ambient pressure, the system will expand in the transverse direction, if α is sufficiently large.

In conclusion, we have shown that in two and three dimensions classical systems with only pair potentials can have a negative Poisson's ratio at zero temperature, a surprising result. To the authors' knowledge, this has not previously been made explicit [13]. However, this auxetic behavior is only present when the system is at negative pressure, and thus not in thermal equilibrium. NPR materials may potentially be experimentally produced using synthetic techniques that rely on kinetic effects; examples include tempered glass [15], and even colloidal crystals [16]. In two dimensions, it was proved that NPR behavior could be found at negative pressure; the proof was shown here for the triangular lattice, but a similar result also holds true for the square lattice. In three dimensions, a set of constraints on the pair interaction was found such that, if satisfied, the fcc lattice is both elastically isotropic and has NPR behavior at negative pressure. Although the fcc was chosen as an example, the calculation may be generalized

given the expressions for the elastic constants of cubic systems reported here. We also presented a three-body interaction potential that by construction gives rise to a solid with elastic isotropy and NPR behavior at zero temperature and arbitrary pressure (negative and positive values). This suggests that the requirement of negative pressure is limited to systems with only pair interactions. A general proof of such a statement does not exist and will be considered in future work. In other future work, we hope to describe under what conditions NPR behavior can be observed in colloidal crystals under tension, given the experimentally realizable interaction potentials between colloidal particles. Finding NPR behavior over a wide range in temperature and pressure is a challenging *optimization* problem that we also intend to address.

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[13] NPR behavior was found in network systems (vertices connected by flexible bonds) under tension [14]. The present work is fundamentally different in that we are considering a many-particle system in which an arbitrary number of neighboring particles may be incorporated and the pair potential is completely general. Moreover, unlike Ref. [14], we do not use a mean-field approximation.
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