Negative compressibility, negative Poisson's ratio, and stability

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1 Introduction Reversal of physical properties with respect to their usual condition can be counter-intuitive and interesting. For example, Poisson's ratio refers to the ratio of transverse contraction strain to longitudinal extension strain during stretching. Poisson's ratio is usually positive as one can see in the stretching of a rubber band. Negative values are permitted by the theory of elasticity as presented in detail below. Polymer foams [1] with negative Poisson's ratio have been made and characterized, and negative Poisson's ratio was predicted to occur in model systems [2, 3] and in various anisotropic single crystals [4, 5]. Negative Poisson's ratio has been observed in metal foams [6] and microporous polymers [7]. Poisson's ratio is a cross property, with no energy associated with it, so there is no restriction that it cannot be negative. The same is true for the thermal expansion. For example, negative thermal expansion of arbitrarily large magnitude in designed composites has been analyzed [8]. Various models with negative thermal expansion are known [9, 10]. In the Appendix A we solve a very simple model illustrating such a behavior.

Negative specific heat, though forbidden in classical thermodynamics, occurs in stars and star clusters [11, 12]. The apparent paradox is explained [13] by observing that an extensive system is implicitly assumed in thermodynamic analyses, in which a canonical ensemble of subsystems is in equilibrium. Stars contain an internal power source from nuclear fusion, however that is not the essential stabilizing element. The essential physics here is the notion of a partition of the total energy. In a model system [14], negative specific heat was attained by coupling a compressed ideal gas with a nonlinear spring containing stored energy. It is also possible for a negative specific heat to occur in systems which are not in equilibrium [15], for example rapidly cooled amorphous materials near the glass transition temperature.

Negative pressure is also forbidden at equilibrium by thermodynamics for any positive temperature and for stable potentials with finite interaction range and finite attractive forces. This is because when such a system is divided into two (or a finite number of) macroscopic parts its free energy is lower than that of a system at negative pressure. (For solids the time necessary for the breakage can be very long.) However, it can occur in unstable and metastable states [16]. For tethered potentials [17, 18] the negative pressure is allowed even at equilibrium. It has been shown for various interaction potentials [18–20] that Poisson's ratio should be negative in a range of densities in solids at negative pressures. Recent study of frequency dependent Poisson's ratio in fluids at negative pressures [21] showed that infinite frequency Poisson's ratio is positive both at the densities corresponding to metastable and unstable states.

Negative *structural* stiffness is well known in certain post-buckled configurations of structures [22]. Under some

conditions a structure with negative stiffness may be stable if constrained. In theory, negative material stiffness can occur in ferroelastic [23] phase transformation, but the associated instability is associated with the phase change. Negative moduli arise within the context of Landau theory [24] from the formation of two local minima in the strain energy function. As a control parameter such as temperature is lowered, an energy function with a single minimum gradually flattens, then develops two minima. The curvature of this energy profile represents a modulus, so the modulus softens during cooling, then becomes negative. This condition is unstable. Bands of material form, visible as the twin crystal structures associated with ferroelastic transformation. Solids with negative *material* stiffness i.e. negative elastic modulus, can be stabilized with sufficient constraint. Negative shear modulus entails instability in which the material forms domains even if it is constrained, but a particle sufficiently small can be single domain, owing to surface energy effects. Such particles were used as inclusions constrained in a composite, to achieve large mechanical damping and anomalies in modulus [25] in the composite. Negative *material* stiffness, specifically the bulk modulus, of a constrained solid elastic object of any size is stable within the theory of elasticity, as described below. Negative bulk modulus (inverse compressibility) is, however, considered to be forbidden in the context of thermodynamics. In this paper, the role of negative bulk modulus is considered. Experimental observations of negative bulk modulus in pre-strained foam are presented and interpreted.

2 Experiment: negative incremental bulk modulus in foam Stable negative structural stiffness is known, both theoretically and experimentally, in postbuckled structural elements. For example, single cells of foam exhibit a non-monotonic load deformation characteristic [26]. Recently, stable negative bulk modulus of a material has been observed experimentally in constrained foam [27] subjected to hydrostatic compression under displacement control. Since a pre-deformation was required to observe the effect, it is a negative incremental bulk modulus or inverse compressibility. Results are reviewed and additional results are presented.

Specifically, open cell foams were obtained from Foamade Industries, (Auburn Hills, MI, USA), and from Foamex International Inc (Eddystone, PA, USA). These foams had pore sizes of 2.5 mm (10 pores per inch (ppi)) and 0.4 mm (60 ppi). Cubes, cylinders and spheres were sectioned from the bulk foam for testing. Experimentally, foams were hydrostatically compressed under control of volumetric deformation. To do this, known volumes of water were injected by a calibrated screw piston into a volumetric test chamber fabricated from a 1 liter, polycarbonate bottle. To prevent the water from entering the interstices of the foam, specimens were sealed inside a cylindrical natural latex rubber membrane 0.076 mm thick. A thin pressure relief tube was provided to allow air within the foam to es-
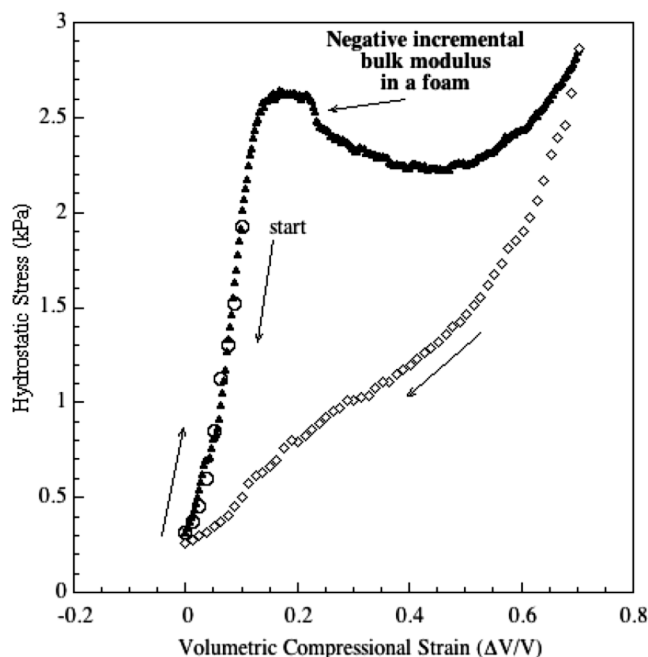

Figure 1 Hydrostatic stress with respect to volumetric compressional strain [27] for an open cell foam described in text. The region where the bulk modulus (and, hence, the compressibility) is negative is indicated.

cape as the foam was compressed. Water was then injected in small increments of about 0.14 mL. After each increment the pressure sensor was allowed to settle. A typical test to 40% strain typically took up to 5 hours.

Typical results for a spherical specimen are shown in Fig. 1. Non-monotonic behaviour was observed provided the foam specimen had small cells (0.4 mm) and was spherical in shape. Beyond about 20% volumetric strain in hydrostatic compression, the pressure-volume curve had a nonmonotonic region indicative of negative bulk modulus. Foams with large cells of 2.5 mm size were sufficiently anisotropic that the anisotropy of deformation was observed visually. The nonmonotonic effect, hence negative compressibility, is attributed to symmetric buckling of the foam cell ribs. Too much anisotropy in the structure spoils the symmetry, so that the compliant direction deforms via cell bending without buckling. Volumetric compression was also used in the preparation of the original negative Poisson's ratio foams [1]. The optimal volumetric compression was about a factor of 3 to 4 depending on the type of starting foam. Therefore a region of negative compressibility was traversed during the preparation process, though it was not measured at the time.

3 Stability in elasticity theory and in thermodynamics In this section the role of negative compressibility in elasticity theory and in thermodynamics is considered. Specifically, elasticity theory allows negative compressibility in a constrained object, but thermodynamic presentations of stability suggest negative compressibility

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cannot occur. In isotropic elastic solids, the 'allowable' range of Poisson's ratio ν is

$$-1 < \nu < 0.5 . \tag{1}$$

It corresponds to the requirement that the shear, G, and bulk, K, moduli [28] be positive for *stability* of an unconstrained block of material. The lack of constraint is equivalent to a surface traction boundary condition in the language of elasticity theory. This stability condition is equivalent to a statement that the elastic modulus tensor is positive definite. If a solid elastic object is constrained (a boundary condition of prescribed displacement in the language of elasticity), the condition of unique solutions [29] and stability [30] becomes that of strong ellipticity. Strong ellipticity entails

$$C_{ijkl} n_i n_j m_k m_l > 0 , \tag{2}$$

for all nonzero vectors n_i and m_i and C_{ijkl} as the modulus tensor. The speed $v = \sqrt{C_{2323}/\rho}$ of shear waves must be real or the waves will grow exponentially, so $G = C_{2323} > 0$. Similarly since the speed of longitudinal waves is real, $C_{1111} > 0$. The corresponding range of isotropic elastic constants is [31]

$$G > 0 \quad \text{and} \quad \text{a)} \, \nu < 0.5 \quad \text{or} \quad \text{b)} \, \nu > 1 . \tag{3}$$

The second condition (3b) for strong ellipticity entails the constrained tensorial modulus be positive, $C_{1111} > 0$. Since $E = 2G(1+\nu)$, this allows negative Young's modulus E and bulk modulus K, specifically

$$\text{a)} -\infty < E < \infty \quad \text{or} \quad \text{b)} -4G/3 < K < \infty . \tag{4}$$

Displacement type boundary value problems have unique solutions if [32] the elastic constants are in the range for strong ellipticity. The condition of strong ellipticity is less stringent than that of positive definiteness.

In the context of thermodynamics, it is claimed that the compressibility (inverse bulk modulus) must be positive. Since that claim contradicts the above result of elasticity theory, it is of interest to study the assumptions made. The continuum has a non-denumerable infinite number of degrees of freedom, while a solid made of atoms has a finite, albeit large, number of degrees of freedom. If, however the atoms are in vibratory motion due to non-zero temperature, then the solid of atoms has a form of freedom not present in the continuum.

Thermodynamics suggests a size dependent metastability in fluids associated with negative compressibility, owing to the nonzero size of atoms and nonzero temperature [33]. The treatment of Van der Waals is applicable to fluids, which have zero shear modulus. The non-monotonic portion of the pressure – volume relation is therefore associated with instability, specifically the condensation of liquid droplets in a gas. If there is in fact a corresponding metastability in solids, the time scale may, however, exceed experimental time scales. Within continuum mechanics,

there is no size limitation for a constrained object of negative bulk modulus to be stable.

There exists exactly solvable two dimensional system of infinitely many interacting hard discs constrained in a strip shaped region in which negative compressibility is inferred from analysis of collisions of the discs [34, 35] and the system remains internally stable when the volume and the shape of the strip are fixed. This result concerning the two dimensional model can be extended to three dimensions (spheres in a cylinder). These results do not contradict van Hove's theorem [36] on non-existence of phase transitions in one-dimensional systems with short-range interactions since some assumptions of this theorem are not fulfilled by the models. The mentioned systems of hard discs and spheres are infinite only in one direction. In the Appendix B we show examples of two and three dimensional constrained systems which are infinite in all directions and, when their volume is fixed, are internally stable despite showing negative compressibility.

The thermodynamic proof of Münster [37] of positive compressibility assumes a system of particles without internal degrees of freedom and without external fields. It is also assumed that the potentials for particle interaction are stable. These assumptions appear to preclude consideration in the analysis of composite systems with pre-strain of constrained inclusions or phase transforming materials which are unstable in the absence of constraint. Indeed it is claimed that this class of thermodynamic state functions can never lead to an unstable state as obtained from the van der Waals equation of state. The proof of Kubo [38] of positive compressibility depends on assuming that a matrix of coefficients is positive definite. Moreover the restriction on compressibility is obtained from a single matrix element without any thermal coupling. This proof therefore is based on restrictive assumptions corresponding to an object with a free surface, hence it is equivalent to Eq. (1) and does not contradict the result of Eq. (3). The proof of Wallace [39] of positive compressibility also depends on the notion of a positive definite matrix. Constant volume is considered in the context of heat capacity, but not in the context of compressibility. Therefore the Wallace result corresponds to Eq. (1) for an unconstrained object and does not contradict the result of Eq. (3) for a constrained solid.

4 Thermoelastic coupling and restrictions on sign of the compliance Any difference between stability conditions in elasticity and in thermodynamics may be associated with coupled fields. Consider, therefore, thermoelastic damping in order to understand stability conditions associated with negative moduli. This energy dissipation results from the fact that adiabatic and isothermal moduli differ, and the time scale for observation may be neither fast enough to be adiabatic nor slow enough to be isothermal.

Consider [40, 41] a unit volume of *elastic* material with strain ε_{ij} and entropy S as dependent variables, and stress σ_{ij} and absolute temperature T as independent vari-

ables:

$$d\varepsilon_{ij} = \frac{\partial \varepsilon_{ij}}{\partial \sigma_{kl}}\bigg|_T d\sigma_{kl} + \frac{\partial \varepsilon_{ij}}{\partial T}\bigg|_\sigma dT \ , \tag{5}$$

$$dS = \frac{\partial S}{\partial \sigma_{kl}}\bigg|_T d\sigma_{kl} + \frac{\partial S}{\partial T}\bigg|_\sigma dT \ . \tag{6}$$

$(\partial \varepsilon_{ij}/\partial \sigma_{kl})$ represents elasticity, $(\partial \varepsilon_{ij}/\partial T)$ represents thermal expansion, $(\partial S/\partial \sigma_{kl})$ represents the piezocaloric effect in which heat is generated in response to stress, and $(\partial S/\partial T)$ represents heat capacity. In linear materials, the elasticity equations allowing for temperature changes become [41]

$$\varepsilon_{ij} = S_{ijkl}^T \sigma_{kl} + \alpha_{ij} \, \Delta T \ , \tag{7}$$

$$\Delta S = \alpha_{ij}\sigma_{ij} + \frac{C^\sigma}{T} \Delta T \ , \tag{8}$$

in which S_{ijkl}^T is the elastic compliance tensor at constant temperature, α_{ij} is the thermal expansion tensor, and C^σ is the heat capacity per unit volume at constant stress. In the isotropic case, $\alpha_{ij} = \alpha\delta_{ij}$.

The compliance S_{ijkl}^T is the isothermal compliance and is the compliance actually measured in an elastic material under deformation which is slow enough that any heat generated via the piezocaloric effect has time to flow, equalizing the temperature. The elastic compliance is different under deformation which is sufficiently fast that this heat has no time to diffuse (adiabatic condition, $dS = 0$). To calculate the adiabatic compliance, set $dS = 0$ in Eq. (6) and combine Eqs. (5),(6) to eliminate dT:

$$d\varepsilon_{ij} = \frac{\partial \varepsilon_{ij}}{\partial \sigma_{kl}}\bigg|_T d\sigma_{kl} - \frac{\dfrac{\partial \varepsilon_{ij}}{\partial T}\bigg|_\sigma \dfrac{\partial S}{\partial \sigma_{kl}}\bigg|_T}{\dfrac{\partial S}{\partial T_\sigma}\bigg|} d\sigma_{kl} \ . \tag{9}$$

Now $(\partial \varepsilon_{ij}/\partial T)_\sigma = (\partial S/\partial \sigma_{kl})_T$ since these derivatives can be expressed in terms of a thermodynamic potential function by virtue of the first and second laws of thermodynamics [41]. Dividing both sides of Eq. (9) by $d\sigma_{kl}$ to obtain the adiabatic compliance $(\partial \varepsilon_{ij}/\partial \sigma_{kl})S$,

$$\frac{\partial \varepsilon_{ij}}{\partial \sigma_{kl}}\bigg|_S - \frac{\partial \varepsilon_{ij}}{\partial \sigma_{kl}}\bigg|_T = -\frac{\partial \varepsilon_{ij}}{\partial T}\bigg|_\sigma \frac{\partial \varepsilon_{kl}}{\partial T}\bigg|_\sigma \frac{\partial T}{\partial S}\bigg|_\sigma \ . \tag{10}$$

If the material is linear, Eq. (10) becomes

$$S_{ijkl}^S - S_{ijkl}^T = -\alpha_{ij}\alpha_{kl}\frac{T}{C^\sigma} \ . \tag{11}$$

The adiabatic compliance S_{ijkl}^S differs from the isothermal compliance S_{ijkl}^T, and the difference depends on the thermal expansion and on the heat capacity.

Equation (11) gives a relaxation strength

$$\Delta_{ijkl} = \frac{S_{ijkl}^T - S_{ijkl}^S}{S_{ijkl}^S} = \frac{\alpha_{ij}\alpha_{kl}}{S_{ijkl}^S}\frac{T}{C^\sigma} \ . \tag{12}$$

The relaxation strength is a measure of the magnitude of time (or frequency) dependence of a material; in the present context, conditions are intermediate between adiabatic and isothermal. The peak mechanical damping $\tan\delta_{peak}$ is half the relaxation strength, $\tan\delta_{peak} = \Delta/2$. Since the thermal expansion α_{ij} is diagonal, there is no relaxation associated with thermoelastic coupling in shear; a volume change is required.

As for stability, the mechanical damping is positive in passive materials. Negative damping entails acoustic amplification in the material, hence a divergence of wave amplitude. The corresponding condition $\Delta > 0$ implies a restriction on compliance S, provided the heat capacity is positive.

Consider a relaxation strength associated with volume change, e.g. bending. The relevant elastic constant for bending vibration in reeds [42] is Young's modulus $E = 1/S_{1111}$. Then the condition of passivity of a material in reed bending vibration will imply positive Young's modulus E provided the material has no other source of damping than thermo-elastic coupling. If the modulus is slightly negative, the instability will manifest as a slow build-up of vibration in the material until the stored energy is exhausted. If, however, the material has other sources of dissipation so that the total $\tan\delta > 0$, then negative Young's modulus will not entail instability *by this mechanism*. The bending of a reed, however, involves all surfaces free except one end. Therefore the restriction $E > 0$ in this case does not contradict the elasticity result *that a fully constrained object can be stable with $K < 0$*.

There is also a thermoelastic relaxation [43, 44] which gives rise to attenuation of longitudinal waves. The corresponding elastic constant is C_{1111}, which must be positive in a passive material with positive attenuation. But that constant is already known to be positive via the condition of strong ellipticity in elasticity. Therefore the condition of a passive material with positive damping in this case does not contradict the elasticity result that a fully constrained object with $K < 0$ or $E < 0$ can be stable.

5 Discussion Proofs, thermodynamic and otherwise, are based on assumptions. Some of these may seem so obvious that they are not stated. Although negative heat capacity appears to be excluded by thermodynamics, it occurs in stars and star clusters which admit long range gravitational forces and in systems which are not in equilibrium. These systems do not follow all the assumptions of thermodynamics. Thermodynamic demonstrations that compressibility must be positive all appear to deal with unconstrained systems, in agreement with elasticity. Study of thermo-elastic coupling discloses no new instability as a result of that coupling. Experiments on foam under hydrostatic compression shows that a negative incremental compressibility occurs. It is possible that some form of coupling between the stress field and atomic motion could give rise to a slow instability or metastable behavior in constrained systems with negative compressibility, but such an effect has not been found.

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In the Appendix B we describe a microscopic model composed of 'nodes' and connecting them identical 'bonds' (or 'pistons') whose length depends on force applied to their ends. The bonds are non-bendable and a constraint is imposed on the angles between the bonds – the angles cannot change. Hence, the system can change its size but has to preserve its shape. Thus, it is a perfect auxetic of Poisson's ratio -1. If the force-length dependence contains a van der Waals like loop then the loop survives also in the pressure-volume dependence of the system, i.e. the isotherm of the system has to contain a range where the bulk modulus (and, in consequence, also compressibility) must be negative. Obviously, when the volume is fixed, the system remains internally stable.

6 Conclusions To conclude, no convincing case has yet been found in thermodynamics that negative compressibility of a *constrained* solid object is inadmissible or unstable. Negative moduli have been inferred from behavior of composites with ferroelastic inclusions. Negative compressibility has been measured in constrained slow hydrostatic deformation of polymer foams. A simple 'microscopic' model has been presented which is internally stable at a fixed volume despite of the fact that, for a range of densities, it shows negative bulk modulus.

Appendix A
Simple model of negative thermal expansion In Fig. 2a one can see a one-dimensional model with the interaction potential

$$u(r) = \begin{cases} \dfrac{k}{2}(r - r_{\max})^2, & r \in (r_{\min}, r_{\max}), \\ \infty, & r \notin (r_{\min}, r_{\max}). \end{cases} \tag{13}$$

Taking $k = 1$, $r_{\min} = 0$ and $r_{\max} = 1$, one can express the free enthalpy per particle, g, as a function of external pressure, p, acting on the system

$$g(p) = -k_{\mathrm{B}}T \log \int \exp\left[-\frac{u(r) + pr}{k_{\mathrm{B}}T}\right] dr, \tag{14}$$

where k_{B} is the Boltzmann constant.
Remark: As the studied model is one-dimensional, the external pressure applied is just a force acting on the ends of the line along which the particles move. When the model is generalized to three dimensions the pressure has its standard interpretation.

Differentiating g versus p one obtains the length per particle

$$l = \frac{\partial g}{\partial p}\bigg|_T, \tag{15}$$

from which the thermal expansion coefficient can be obtained as

$$\alpha = \frac{1}{l}\frac{\partial l}{\partial T}\bigg|_p. \tag{16}$$

It is easy to notice that at low pressures, for which the average length of the system is larger than $(r_{\min} + r_{\max})/2$, any increase of temperature causes better sampling of smaller distances in this model, i.e. the thermal expansion is negative at such pressures. This is shown in Fig. 2b.

Appendix B
An internally stable model with negative bulk modulus In Fig. 3a a simple two-dimensional model is shown for which the dependence of the force, F, on the distance, L, between the centers of interacting nodes (connected by non-bendable 'rods' or 'pistons') is given by (see Fig. 3b)

$$F(L) = \begin{cases} \dfrac{1}{L}, & L \in (0,1), \\ 1 - \sin(L-1), & L \in (1, 1+2\pi), \\ \dfrac{1}{L-2\pi}, & L \in (1+2\pi, \infty). \end{cases} \tag{17}$$
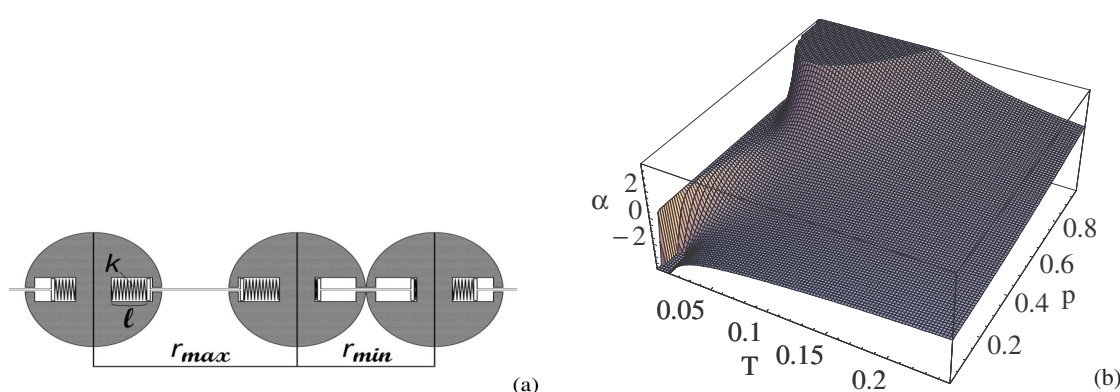

Figure 2 (online colour at: www.pss-b.com) (a) One-dimensional model defined by Eq. (13). (b) Thermal expansion coefficient, $\alpha = (\partial l/\partial T)_p/l$, of the model as a function of pressure, p, and temperature, T.
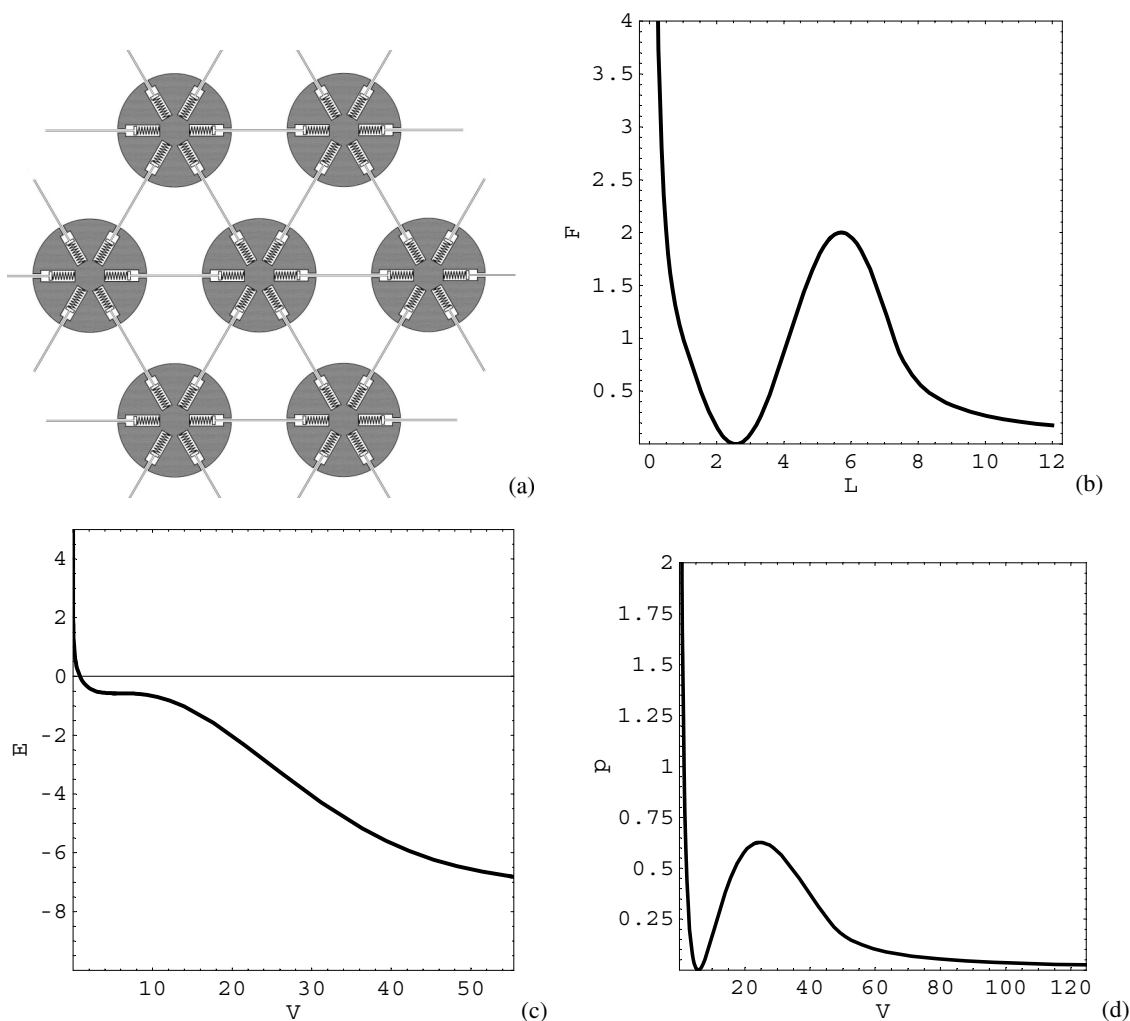
Figure 3 For the two-dimensional model shown in (a), if Poisson's ratio equals $\nu = -1$ and the length–force dependence of rods is given in (b), the energy on volume dependence is presented in (c), and at $T \rightarrow 0$ the pressure–volume dependence is given in (d). It can be seen that a volume range exists, in which the bulk modulus is negative.

Assuming that the angle between the rods is fixed and the rods are identical, one can easily obtain the energy of the system at a given volume, $V = \left(\sqrt{3}/2\right)L^2$, per particle

$$E(V) = \frac{-3 \int F(L)\,dL}{V}, \tag{18}$$

which is plotted in Fig. 3c. Differentiating the energy with respect to volume one gets the pressure, p, in the system

$$p(V) = -\frac{\partial E(V)}{\partial V}, \tag{19}$$

which is shown in Fig. 3d.

The above calculations concern the system at zero temperature. (One can expect, however, that at low temperatures the isotherms of the system will be very similar to that shown in Fig. 3d.) If one fixes the volume of the system then, because its Poisson's ratio is equal to -1, no internal transformation of its structure is possible and it will be stable even in the range of volumes where the bulk modulus is negative.

The number of nodes does not influence the mechanical properties of the above model, so it can be infinitely large in any direction.

Analogous models can be built in three dimensions, e.g. by replacing bonds of a fcc lattice by rods interacting through a potential similar to that described by Eq. (17).

One can expect that at low temperatures the isotherms of the system will be very similar to that shown in Fig. 3d, i.e. it will be possible to observe negative bulk modulus at some densities, whereas the system will be internally stable.

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