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NEGATIVE POISSON RATIOS AT NEGATIVE PRESSURES

KRZYSZTOF W. WOJCIECHOWSKI

Instytut Fizyki Molekularnej PAN
Smoluchowskiego 17/19, 60-179 Poznań, Poland
and
International Centre for Theoretical Physics, Trieste, Italy

ABSTRACT: Typical isotropic materials exhibit positive Poisson ratios, i.e. shrink (expand) transversely when stretched (compressed) longitudinally. Presented theoretical analysis and computer simulations of model systems strongly suggest that at dimensionality $d \geq 2$, typical isotropic systems should behave in the opposite way, i.e. exhibit negative Poisson ratio, at some isotropic tensions (negative pressures).

1. INTRODUCTION

Poisson ratio, ν, being the negative of the ratio of the transverse to the longitudinal strain when the stress along the longitudinal direction is changed, is non-negative for materials known in nature [1]. Manufacturing materials with negative Poisson ratio [2, 3], coined *auxetics* [4], has attracted to them a broad interest of scientists and engineers (for a review see Refs. [4-7]). The interest comes not only from the counterintuitive features of auxetics, which require understanding and proper description, but also from many potential applications of such materials. Various theoretical models in which ν can be negative were proposed [8-17]. All of these studies suggested that the occurence of a negative Poisson ratio requires either special structure of the system or special form of interacting particles. Recently, however, it was found that some two dimensional (2D) systems exhibit negative Poisson ratios in a range of isotropic tension (negative pressure) [18], without special requirements concerning the structure of the system or the form of interactions. In the present communication we indicate that the result of Ref. [18] can be generalized to any dimensionality not less than two. This offers a very simple way to obtain the auxetic behaviour in real systems [19].

2. ELASTICITY OF D DIMENSIONAL ISOTROPIC MEDIA

Deformation of an elastic body can be described by the (Lagrange) strain tensor, ε_{ij}, defined as:

$$\varepsilon_{ij} = (\partial_i u_j + \partial_j u_i + \partial_i u_k \partial_j u_k)/2 ,$$

where $u_i = x_i - X_i$ is the displacement vector of a material point from the initial position, X_i, to the final position, x_i, and ∂_i means differentiation with respect to X_i. (Summation convention is used only for repeating *Latin* indices. Further on, we will assume that *Greek* indices require specification of the character and the range of summation.) Representing x_i by a locally affine transformation of the initial coordinates X_i one can write:

$$u_i = A_{ij}X_j - X_i = (A_{ij} - \delta_{ij})X_j,$$

what allows one to write the strain tensor in the following form:

$$\varepsilon_{ij} = (A_{ki}A_{kj} - \delta_{ij})/2. \tag{1}$$

First, let us consider the case of an isotropic elastic medium of dimensionality $D \geq 2$ which is in equilibrium at zero external pressure. The free energy change, ΔF, caused by a deformation of the system, from its equilibrium state with $\varepsilon_{ij} = 0$ to a state of non-zero strain, can be written as an expansion in powers of invariants constructed from the components of the strain tensor. For small deformations this expansion can be truncated at second order terms, and for a unit volume of the isotropic material it can be written as [1]:

$$\Delta F = \frac{\lambda}{2}\varepsilon_{ii}^2 + \mu\varepsilon_{ij}\varepsilon_{ij} = \frac{K}{2}\varepsilon_{ii}^2 + \mu(\varepsilon_{ij} - \frac{1}{D}\delta_{ij}\varepsilon_{kk})(\varepsilon_{ij} - \frac{1}{D}\delta_{ij}\varepsilon_{kk}), \tag{2}$$

where λ is the Lame constant, μ is the shear module and $K = \lambda + 2\mu/D$ is the bulk module.

Stability of the equilibrium state requires that the free energy change accompanying a deformation has to be positive for $\varepsilon_{ij} \neq 0$, what implies that K and μ in Eq.(2) must be greater than zero. It is easy to see, however, that the Lame constant λ can be negative.

Differentiating the free energy, ΔF, with respect to ε_{ij} one obtains the stress tensor σ_{ij} as a function of the strain tensor ε_{ij}. The resulting formula can be inverted, giving

$$\varepsilon_{ij} = \frac{1}{D^2K}\delta_{ij}\sigma_{kk} + \frac{1}{2\mu}(\sigma_{ij} - \frac{1}{D}\delta_{ij}\sigma_{kk}). \tag{3}$$

Assuming that the only non-zero component of the stress tensor is σ_{xx}, one can express the Poisson ratio as a function of K and μ:

$$\nu \equiv -\frac{\varepsilon_{yy}}{\varepsilon_{xx}} = \frac{DK - 2\mu}{(D-1)DK + 2\mu} = \frac{\lambda}{(D-1)\lambda + 2\mu}. \tag{4}$$

It is easy to check that for a stable system the positive sign of λ is equivalent to the positive sign of ν. Taking however into account that for stable systems only K and μ must be positive, one obtains:

$$-1 \leq \nu \leq \frac{1}{D-1}. \tag{5}$$

The above inequalities mean that negative values of the Poisson ratio are not excluded by the stability requirements. Moreover, it is easy to notice that for infinitely dimensional systems ν cannot be positive. (This, however, does not answer the question whether "typical" infinitely dimensional systems are auxetic or behave like cork.)

Remark: It follows from Eq. (4) that to obtain negative value of ν, the ratio μ/K should be larger that $D/2$.

Let us consider, in turn, the case when the zero strain corresponds to an equilibrium state of an isotropic material at *non-zero* external pressure p. In such a case the free energy expansion, analogous to Eq. (2), reads:

$$\begin{aligned}\Delta F &= -p\varepsilon_{ii} + \frac{\lambda}{2}\varepsilon_{ii}^2 + \mu\varepsilon_{ij}\varepsilon_{ij} = \\ &= -p\varepsilon_{ii} + \frac{K}{2}\varepsilon_{ii}^2 + \mu(\varepsilon_{ij} - \frac{1}{D}\delta_{ij}\varepsilon_{kk})(\varepsilon_{ij} - \frac{1}{D}\delta_{ij}\varepsilon_{kk}),\end{aligned} \tag{6}$$

where the expansion coefficients K and μ are, in general, not equal to the bulk module and the shear module, respectively. The attractive feature of the above expansion is that in crystals with a centre of symmetry, at zero temperature, its coefficients fulfil the Cauchy relation [20], implying that $\lambda = \mu$. To find the stability conditions for the system under pressure p, however, it is more convenient to expand the free enthalpy (i.e. the Gibbs free energy) change, ΔG, accompanying a small strain ε_{ij}. Such expansion can be written as:

$$\begin{aligned}\Delta F + p\Delta V \equiv \Delta G &= \frac{\bar{\lambda}}{2}\varepsilon_{ii}^2 + \bar{\mu}\varepsilon_{ij}\varepsilon_{ij} = \\ &= \frac{\bar{K}}{2}\varepsilon_{ii}^2 + \bar{\mu}(\varepsilon_{ij} - \frac{1}{D}\delta_{ij}\varepsilon_{kk})(\varepsilon_{ij} - \frac{1}{D}\delta_{ij}\varepsilon_{kk}),\end{aligned} \tag{7}$$

where $\bar{K}$ and $\bar{\mu}$ are the bulk and shear module, respectively, and $\bar{K} = \bar{\lambda} + 2\bar{\mu}/D$. ΔV is the increase of the initial unit volume V_0 caused by the strain ε_{ij}.

Stability of the system is equivalent to the requirement that G is minimal at $\varepsilon_{ij} = 0$. Within the above (second order) expansion, the latter condition is equivalent to positivity of both $\bar{K}$ and $\bar{\mu}$. Differentiating ΔG with respect to ε_{ij} one obtains the change of the stress in the system as a function of the strain. Inverting these formulae leads to the analogue of Eq. (3) with K, μ replaced by $\bar{K}$, $\bar{\mu}$. Thus, the Poisson ratio can be expressed by the analogue of Eq. (4) with the same replacement:

$$\nu = \frac{D\bar{K} - 2\bar{\mu}}{(D-1)D\bar{K} + 2\bar{\mu}} \tag{8}$$

The relation between the coefficients K, μ in Eq. (6) and those in Eq. (7) can be established by expanding the volume change into ε_{ij}. Using the definition of volume in the D-dimensional space and Eq. (1) one can write:

$$\frac{V}{V_0} = \det[A_{ij}] = (\det[A_{ik}A_{kj}])^{1/2} = (\det[2\varepsilon_{ij} + \delta_{ij}])^{1/2}. \tag{9}$$

Expanding the determinant up to the second order in ε_{ij} and taking into account that the initial (equilibrium) volume, V_0, is chosen equal to unity, one obtains:

$$V = (\det[2\varepsilon_{ij} + \delta_{ij}])^{1/2} = 1 + \varepsilon_{kk} + \frac{1}{2}\varepsilon_{kk}^2 - \varepsilon_{ij}^2 + 0(\varepsilon^2),$$

where $o(\varepsilon^2)$ represents terms higher than of the second order in the components of the strain tensor. Hence, the increase of the initial volume caused by the strain ε_{ij} is equal:

$$V - 1 = \Delta V = \varepsilon_{kk} + \frac{1}{2}\varepsilon_{kk}^2 - \varepsilon_{ij}^2 + o(\varepsilon^2). \tag{10}$$

Substituting Eq. (10) to Eq. (7) one obtains:

$$\Delta F \equiv \Delta G - p\Delta V = -p\varepsilon_{ii} + \frac{\bar{\lambda} - p}{2}\varepsilon_{ii}^2 + (\bar{\mu} + p)\varepsilon_{ij}^2. \tag{11}$$

Comparing Eqs. (6) and (11) one concludes that:

$$\bar{\lambda} = \lambda + p, \quad \bar{\mu} = \mu - p, \quad \bar{K} = K + \frac{(D-2)p}{D}. \tag{12}$$

The above formulae suggest that at *negative* pressures the ratio $\bar{\mu}/\bar{K}$ can be large, leading to $\nu < 0$ (see Eq. (8)). Such a possibility will be examined in next sections.

3. HARMONIC CRYSTAL

Elastic properties of real crystals at low temperatures can be approximated by the harmonic crystal model [20]. In the case of *isotropic* harmonic crystal the Cauchy relations, which imply that $\lambda = \mu$, lead to:

$$\nu = \frac{D\bar{K} + 4p}{(D-1)D\bar{K} - 4p}. \tag{13}$$

The condition $\nu < 0$ requires either:

$$p < -\frac{D}{4}\bar{K} \tag{14}$$

or $p > D(D+1)\bar{K}/4$. The latter possibility has to be rejected as it holds true only for $\bar{\mu} < 0$, i.e. when the system is unstable.

For harmonic system at $T = 0$ the free energy of uniformly expanded or compressed system equals:

$$F = \frac{k}{2}(a - a_0)^2 \tag{15}$$

where k is a constant, and a describes the linear distance which is equal to a_0 at equilibrium without any external stress.

From the definition of the pressure and the bulk module, and the fact that the volume of the system is proportional to a^D, the condition for the negative value of ν, Eq. (14), can be rewritten as:

$$\frac{D+3}{D+2}a_0 < a < \frac{D-1}{D-2}a_0, \tag{16}$$

where the second inequality follows from the stability condition, $\bar{K} > 0$). The above equation means that the harmonic system exhibits $\nu < 0$ in a (D-dependent) range of negative pressures at any dimensionality.

4. TETHERED SOLID

At high temperatures when the thermal motions of the particles increase, the role of the anharmonic part of the interparticle interactions cannot be neglected. This introduces essential complications to the theory because anharmonic models cannot be solved analytically. To understand the tendencies accompanying the temperature increase, it is reasonable to study the very limit of anharmonicity – the hard body models. The simplest hard body model is the hard sphere system. Unfortunately, this model is stable only at positive pressures what does not allow for studying the influence of the negative pressure on the Poisson ratio. For this reason we consider certain generalization of this model, known as the *tethered* solid [21]. The interaction potential between the particles corresponds to a well whose walls are placed at $r = \sigma_{min}$ and $r = \sigma_{max}$; the interaction potential is zero within the well and infinity otherwise.

In the present paper we restrict our considerations to a particular case of the tethered solid with $\sigma_{min} = 0$; σ_{max} we take as unity. To calculate the free energy of the system we use the smoothed free volume theory [22]. The free volume treatment gives asymptotically exact equation of state in the close packing limit of hard spheres [23]. It offers also proper description of the density dependence of the elastic constants for hard spheres and discs [24, 25]. For the present model the free volume approximation gives:

$$\Delta F = -D\log(1 - a), \tag{17}$$

where a is the linear size parameter, $a \equiv (V/V_{max})^{1/D}$, and V_{max} is the maximum value of the volume of the system, V. The computer simulations performed for hard spheres in three and two dimensions [24, 25] revealed very week volume dependence of the ratio of $\lambda/\mu = \alpha$. Approximating this ratio by unity one can write ν in the same form as in Eq.(13). Explicit calculations of the pressure and the bulk module of the system lead to the following condition sufficient for $\nu < 0$:

$$1 - \frac{1}{D} < a < 1 - \frac{1}{D+4} \tag{18}$$

Remark: One can check that the qualitative conclusion that in the stability regime of the D dimensional tethered solid there is a pressure range in which ν is negative, remains correct even if one assumes that α is different from unity [19].

Validity of the free volume approximation in the case of the tethered solid can be tested by comparing its results with the exact, in principle, data obtained via computer simulations. Various methods of determining the elastic properties of solids are known (for references see, e.g., Ref. [25]). The fluctuation method in which the compliances are computed from the correlations of the strain tensor fluctuations is, for its simplicity, the most attractive method for hard body interactions [25]. We will avoid here describing details of the simulations; they can be found in Ref. [19]. In Fig.1 we present the (predicted theoretically and computed by the Monte Carlo simulations) isotherm of the three dimensional tethered solid. Fig. 2 shows the comparison of the volume dependence of the negative Poisson ratio, obtained from the free volume approximation and computer simulations, of the three-dimensional tethered solid. One can see that the very simple free volume approximation offers quite accurate description of the system. The agreement is also fair in two dimensions [19]. This allows one to expect that the free volume approximation is correct, at least qualitatively, for higher dimensions.

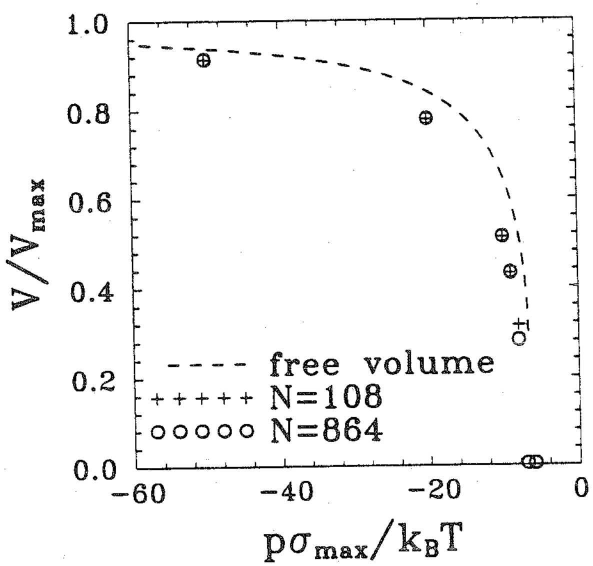

Fig. 1. The volume – pressure isotherm of the three dimensional tethered solid.

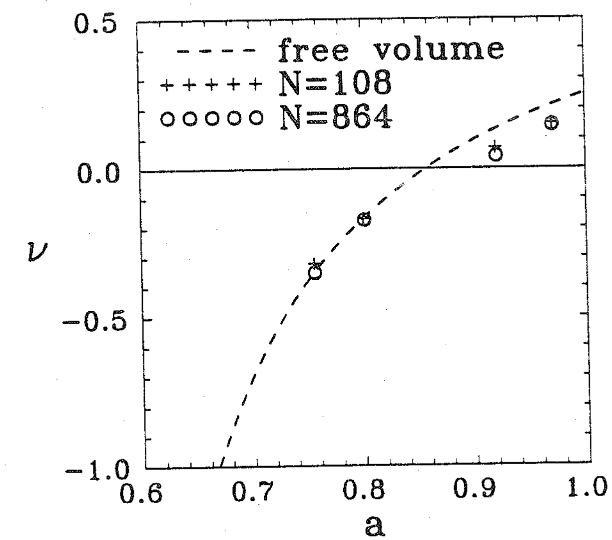

Fig. 2. The Poisson ratio as a function of the size parameter a in the three dimensional tethered solid. The MC runs, from which the presented quantities were computed, were (1-5) × 10^6 trial steps per particle long.

We should stress that the upper stability limit for the pressure of the tethered solid, [19],

$$p_{\min}\sigma_{\max}/kT \equiv p^*_{\min} = \frac{D^D}{(D-1)^{D-1}}$$

is in a good agreement with the simulation data both for two and three dimensional systems. This indicates that the collapse of the system, observed in simulations at certain p^*_{min}, is caused by reaching by the system the stability limit $\bar{K} = 0$.

5. SUMMARY AND CONCLUSIONS

Exact calculations prove that at any dimensionality there exists a range of isotropic tensions (negative pressures) at which a harmonic system is stable and exhibits negative Poisson ratio. The same result can be obtained for the *D*-dimensional tethered solid within the free volume approximation. Computer simulations performed for two and three dimensional systems confirm the predictions of the free volume approximation [19]. The considered systems represent very different interaction potentials and opposite mechanisms of the elasticity. The properties of the harmonic system are determined by the energy only, whereas the properties of the (extremely anharmonic) tethered solid are determined by the entropy alone. This suggests that in other systems in which both the mechanisms are "mixed", the negative values of ν should also occur in certain ranges of negative pressures, as long as the temperature is sufficiently low to not break their stability.

As the occurrence of the negative Poisson ratio at negative pressures does not require preparing any special microscopic structure of the system, this mechanism may be interesting from the point of view of potential applications.

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References

[1] L. D. Landau and E. M. Lifshitz, *Theory of Elasticity*, Pergamon (1959).
[2] R. Lakes, Science **235**, 1038 (1987).
[3] B. D. Caddock and K. E. Evans, J. Phys. D **22**, 1877 (1989).
[4] K. E. Evans, Endeavour, New Series, **15**, 170 (1991).
[5] R. Lakes, J. Material Science **26**, 2287 (1991); R. Lakes, Nature **358**, 713 (1992); R. Lakes, Nature **361**, 511 (1993); R. Lakes, Adv. Materials **5**, 293 (1993).

[6] G. S. Ranganath, Current Sci. **63**, 160 (1992).
[7] K. W. Wojciechowski and A. C. Brańka, Mol. Phys. Reports **6**, 71 (1994). We should add here that Figures 8 and 9 were interchanged in that paper, and the factor (D-1) is lacking in the first term of the denominator in the last part of the formula (8) there; compare with Eq.(4).
[8] T. Hailing, G. A. Saunders, Y. K. Yogurtcu, H. Bach, S. Methfessel, J. Phys. C **17**, 4559 (1984).
[9] R. F. Almgren, Journal of Elasticity **15**, 427 (1985).
[10] A. G. Kolpakov, Prikl. Matem. Mekhan., **49**, 969 (1985).
[11] K. W. Wojciechowski, Mol. Phys. **61**, 1247 (1987); K. W. Wojciechowski and A. C. Brańka, Phys Rev. A**40**, 7222 (1989).
[12] R. J. Bathurst and L. Rothenburg, J. Appl. Mechanics. **55**, 17 (1988); R. J. Bathurst and L. Rothenburg, Int. J. Eng. Sci. **26**, 373 (1988).
[13] K. W. Wojciechowski, Phys. Lett. **137**, 61 (1989).
[14] K. E. Evans, J. Phys. **22**, 1870, 1989; K. E. Evans and B. D. Caddock, J. Phys. D **22**, 1883 (1989).
[16] L. Rothenburg, A. A. Berlin, R. J. Bathurst, Nature **354**, 470 (1991).
[17] G. Wei and S. F. Edwards, Computational Polymer Science, **2**, 44 (1992); G. Wei, J. Chem. Phys. **96**, 3226 (1992).
[18] D. H. Boal, U. Seifert, J. C. Schillcock, Phys. Rev. E **48**, 4274 (1993).
[19] K. W. Wojciechowski, to be published.
[20] J. H. Weiner, *Statistical Mechanics of Elasticity*, Wiley, New York (1983).
[21] Y. Kantor, M. Kardar, D. R. Nelson, Phys. Rev. Lett. **57**, 791 (1986); Y. Kantor, M. Kardar, D. R. Nelson, Phys. Rev. A**35**, 3056 (1987).
[22] J. A. Barker, in *Lattice Theories of the Liquid State*, Pergamon Press, New York (1963).
[23] Z. W. Salsburg and W. W. Wood, J. Chem. Phys. **37**, 1571 (1962).
[24] D. Frenkel and J. A. C. Ladd, Phys. Rev. Lett. **59**, 1169 (1987).
[25] K. W. Wojciechowski and A. C. Brańka, Phys. Lett. A **134**, 314 (1989).