Non-chiral, molecular model of negative Poisson ratio in two dimensions

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Abstract

A two-dimensional model of tri-atomic molecules (in which 'atoms' are
distributed on vertices of equilateral triangles, and which are further referred
to as cyclic trimers) is solved exactly in the static (zero-temperature) limit
for the nearest-neighbour site–site interactions. It is shown that the cyclic
trimers form a mechanically stable and elastically isotropic *non-chiral* phase
of *negative* Poisson ratio. The properties of the system are illustrated by
three examples of atom–atom interaction potentials: (i) the purely repulsive
(*n*-inverse-power) potential, (ii) the purely attractive (*n*-power) potential and
(iii) the Lennard-Jones potential which shows both the repulsive and the
attractive part. The analytic form of the dependence of the Poisson ratio
on the interatomic potential is obtained. It is shown that the Poisson ratio
depends, in a universal way, only on the trimer anisotropy parameter both (1)
in the limit of $n \to \infty$ for cases (i) and (ii), as well as (2) at the zero external
pressure for any potential with a doubly differentiable minimum, case (iii) is
an example.

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1. Introduction

When pulled (pushed), rubber as well as other typical isotropic materials expand (shrink) their
transverse dimensions. The quantitative measure of such a deformation is the Poisson ratio,
ν_P, which is defined as the *negative* ratio of the transverse strain change to the longitudinal
strain change caused by infinitesimal change of the longitudinal stress. The minus sign makes
the Poisson ratio *positive* for common materials [1]. Although the theory of elasticity does not
exclude the existence of materials with $\nu_P < 0$, i.e. which expand (shrink) transversely when
pulled (pushed) longitudinally, materials of negative ν_P were not known in nature for a long

time [1]. Manufacturing of isotropic foams of negative Poisson ratio [2] caused increasing interest in systems exhibiting $\nu_P < 0$. Such systems were coined *auxetics* [3], which name will be used in the present work for its brevity. Recently, the notion of auxetic systems has been extended to anisotropic systems (axial auxetics) [4]. The interest in auxetics grows (for reviews see, e.g., [5–7]) because of various practical and potential applications of these unusual systems: air filters, strain sensors, press-fit fasteners, pads under carpeting, wrestling mats, doubly curved panels of synclastic shapes, vascular implants, fillings for highway joints, shock and sound absorbers, packing materials, etc [5–8]. One of the ways of better understanding auxetic systems and their properties is by studying various model systems.

Following the early mechanical models [2, 9, 10], most of the works on auxetics have concentrated on studies of some (mostly artificial) structures (on the macro-, meso- and micro-level) exhibiting negative Poisson ratio [2, 11–30]. (References to many other works in this direction can be found in [5–7].) Some works have also been devoted to studies of general conditions at which auxetic behaviour can be observed, in particular, (i) conditions of negative pressure [31–33], (ii) in the vicinity of some phase transitions where the bulk modulus decreases rapidly whereas the shear modulus shows relatively smaller change [34, 35] or (iii) in the neighbourhood of the percolation threshold for systems composed of particles which can form sufficiently many connections with other particles [36]. Recent works suggest that the negative Poisson ratio is not so exceptional in nature [4, 37–39] as one might expect on the basis of classic textbooks on elasticity [1].

As is well known, except for special situations (e.g. corresponding to phase transitions), at given thermodynamic conditions only a single phase can be thermodynamically stable for a given intermolecular interaction potential. The structure of the phase is uniquely defined by the thermodynamic conditions and the intermolecular interaction potential. In consequence, the elastic properties and, in particular, Poisson ratio of any structure which is in thermodynamic equilibrium at given thermodynamic conditions is *uniquely* determined by the intermolecular interaction potential.

Thus, a natural question arises: can one choose the intermolecular interaction potential in such a way as to obtain a thermodynamically stable, elastically isotropic, auxetic phase in a system of particles interacting through this potential?

In other words, can one find or build such a molecule (or molecules) which will form a thermodynamically stable auxetic phase? In two dimensions, the positive answer to this question was given in [40], where a 'molecular' model of cyclic hexamers (i.e. molecules composed of six 'atoms' placed on the vertices of a perfect hexagon, see figure 1) was constructed and solved exactly at zero temperature, and in [41–43] where the phase exhibiting the negative Poisson ratio was proved to be thermodynamically stable in a range of densities at positive temperatures. The negative Poisson ratio of the hexamer system results only from the intermolecular interaction potential. This is in contrast to most of other works in which the Poisson ratio is a *product* of both an artificial structure of the material used and its intermolecular interaction potential.

The hexamer structure is elastically isotropic by symmetry alone, i.e. its (second-order) elastic properties are direction independent for *any* interaction potential which makes the structure stable. The auxetic phase of the hexamers is however *chiral*. The chirality of the phase, related to the lack of the mirror symmetry of its structure, is caused by a tilt of the molecular axis with respect to the crystalline axis (figure 1). This molecular tilt varies when the system density is changed or when the structure is deformed.

Remark 1. It is worth noting here that both the hexamer molecule and the auxetic phase of the hexamers possess the centre of symmetry. At first glance, this may seem to be in contradiction
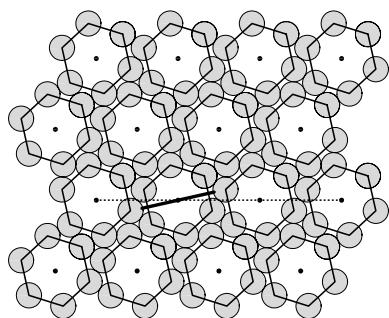
Figure 1. Geometry of the close packed structure of hard cyclic hexamers when the disc (grey colour) diameter is equal to 7/10 of the side length of the hexagon on whose vertices the disc centres are located. (The energy of the system is infinite when any two discs belonging to different hexamers or any two hexagons overlap and zero otherwise.) It can be seen that the structure shows a sixfold symmetry axis (which is sufficient to make its elastic properties direction independent for small deformations [1]) and the inversion centre. Because the hexamer axes (one of them is marked by a thick full line) are slightly tilted with respect to the crystalline axes (one of them is marked by a dotted line), this structure (referred to in [41] as the 'tilted' structure) does not show mirror symmetry, i.e. it is *chiral*. The particles shown here form a thermodynamically stable phase of negative Poisson ratio both at close packing in the static case [40] and in the whole range of thermodynamic stability of the tilted phase at positive temperatures [43].

with the general theory which states that isotropic phases with the centre of symmetry are *not* chiral [44, 45]. To solve the 'puzzle' it is sufficient to note two facts: (i) the system is two dimensional and (ii) the sixfold axis does not imply that the system is rigorously isotropic. Namely, the presence of the sixfold axis, sufficient to make the fourth rank tensor of the elastic constants in the plane perpendicular to the axis isotropic, does not mean that the system is invariant with respect to infinitesimal rotations. In consequence, neither the mirror symmetry implies the centre of symmetry nor the centre of symmetry implies the mirror symmetry for the structure considered. This is in contrast to a three-dimensional isotropic system in which each of these two elements implies the other one, i.e. *either* of these two elements of symmetry excludes chirality.

Recently, it has been suggested that molecular rotation is important for obtaining negative Poisson ratio [23, 46, 47]. Hence, in the context of the chiral nature of the auxetic phase obtained for the hexamers and molecular rotation implied by the chirality, one can pose the question: is it possible to construct a molecule forming a crystalline auxetic phase which is non-chiral and elastically isotropic? Such a phase might exhibit a negative Poisson ratio without *any* internal rotation. This question is of interest from the point of view of fundamental research as the known models of auxetics, which can be applied on a micro- or meso-scopic level, require rotation of certain components constituting the models [2, 11, 12–16, 18–22, 38, 40, 48].

Obviously, one could try to eliminate the chirality in the hexamer system by mixing grains of opposite molecular orientations. Such a solution, however, does not eliminate molecular rotation and the price for applying it is an increase in the Poisson ratio. (The latter because at the grain boundaries the molecules do not fit each other and tend to form a locally *straight phase* [41], which shows a positive Poisson ratio [41, 42].) For this reason, in the present paper, another two-dimensional molecular model system is constructed and solved exactly, which gives a positive answer to the question above.
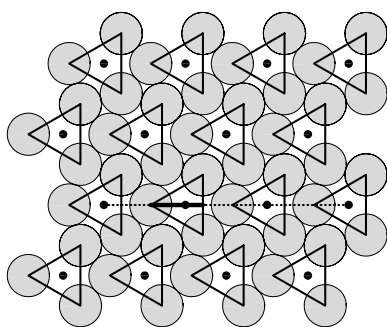
Figure 2. Geometry of the close packed structure of hard cyclic trimers when the disc-atom (grey colour) diameter, b, is equal to 7/10 of the side length of the triangle on which vertices the disc centres are located. (The energy of the system is infinite when any two discs/atoms belonging to different trimers or any two triangles overlap and zero otherwise.) It can be seen that the structure shows the threefold symmetry axis which makes it elastically isotropic for small deformations. The structure also shows mirror symmetry with respect to the crystalline axes (one of them is marked by the dashed line) which are oriented along molecular axes (one of them is marked by a thick full line), which means that the structure is *not* chiral, despite neither the molecule nor the structure showing an inversion centre. It is worth adding that the hard particles shown in this picture form a mechanically stable phase of negative Poisson ratio both at close packing in the static case (see the present paper) and in the whole range of mechanic stability of the solid phase at positive temperatures down to melting [49].

The considered system is shown in figure 2, and the idea of its construction is based on the observation that a three-fold axis is sufficient to make any two-dimensional periodic structure elastically isotropic for small deformations. (The proof follows precisely that presented in [1] for the hexagonal crystals.) It can be seen in figure 2 that although neither the cyclic trimers nor the presented structure is centrosymmetric, the structure (which shows mirror symmetry with respect to the crystalline axes) is *not* chiral. The reasoning presented in remark 1 helps to explain this, at first glance surprising, fact.

The aim of the present paper is to analyse the dependence of the Poisson ratio on the anisotropy of the 'molecular' system which is shown in figure 2. The studies will be exemplified by three kinds of atom–atom interactions in the system: (i) purely repulsive n-inverse-power potentials, (ii) purely attractive n-inverse-power potentials and (iii) the Lennard-Jones potential containing both the repulsive part and the attractive one. The investigations are performed at zero temperature (static case) which allows one to solve the system exactly by analytic methods. For the cases (i) and (ii) the limits $n \to \infty$ are also obtained, which correspond to the hard trimer and the tethered [31, 32, 50, 51] trimer, respectively.

The paper is organized as follows. In section 2 the model is presented, in section 3 the general solution of the model is described and some examples are discussed, and (the final) section 4 contains summary and conclusions.

2. The system

It will be assumed that the studied system consists of $N \to \infty$ cyclic trimers and the trimer mass centres form a triangular lattice. (The assumption that $N \to \infty$ allows one to avoid any unwanted effects which might be introduced by the system boundaries.) Each cyclic trimer consists of three 'atoms' whose centres form a perfect triangle (further referred to as
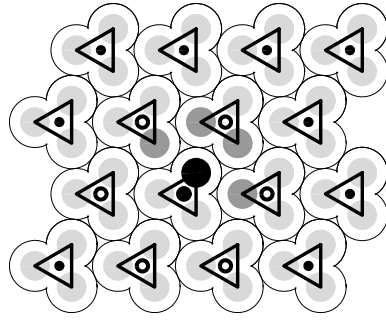
Figure 3. The triangular lattice of cyclic trimers when the atomic diameter (in σ units) is equal to $b = 0.7$ and the distance (in σ units) between the interacting atoms is equal to $r_0 = 1.2$. The atoms interacting with the black atom are marked by dark grey. The centres of the trimers which are nearest neighbours of the trimer whose centre is marked by a larger dot are indicated by open circles.

the molecular interior) of side length equal to σ, which will be taken as the length unit within this paper. (Within this paper the trimers are considered as rigid molecules, i.e. no internal forces responsible for stability of the molecules are discussed.) To simplify the calculations it is convenient to assume that the trimers interact using the atom–atom (site–site) interaction potential, $u(r)$, and only the atoms which are the nearest neighbours of a given atom and belong to other molecules can interact with this atom (see figure 3). Thus, the total potential energy of the system, E_{tot}, can be written as

$$E_{\text{tot}} = \sum_{1 \leqslant i < j \leqslant N} \sum_{k,l=\text{n.n.}} u\left(r_{k_i l_j}\right) \tag{1}$$

where the second summation concerns only the nearest-neighbouring atoms k_i, l_j of the molecules i, j which are taken into account in the first summation.

Three forms of the atom–atom (site–site) interaction potential will be discussed in this paper: (i) the purely repulsive inverse-power potential,

$$u(r) = \epsilon \left(\frac{b}{r}\right)^n \tag{2}$$

(ii) the purely attractive power potential

$$u(r) = \epsilon \left(\frac{r}{b}\right)^n \tag{3}$$

and (iii) the Lennard-Jones (LJ) potential (repulsive at small distances and attractive at large distances)

$$u(r) = \epsilon \left[\left(\frac{r}{b}\right)^{-12} - 2\left(\frac{r}{b}\right)^{-6}\right] \tag{4}$$

where ϵ, b are positive and finite. The parameter b will be further referred to as the atomic diameter. Within this work the atomic diameter b and the distance r_0 between the neighbouring atoms of different molecules in the triangular structure are divided by σ, i.e. are dimensionless quantities.

Remark 2. The strictly attractive potential (3) requires a comment. Unlike typically used interaction potentials, one must apply *negative* pressure to systems interacting through potentials of the form (3) as they collapse otherwise (i.e. at any positive or zero pressure). Even at negative pressures, thermodynamic stability requires in this case an assumption that

each atom can interact with only a *finite* number of other atoms. Otherwise, as the total energy (for pairwise interactions) would be proportional to the square of the number of the particles, the system would have to collapse even at negative pressures. The convention of the nearest-neighbour interaction, introduced in this paper, allows one to avoid system collapse.

When the atoms interact through the hard potential (infinite when they overlap, $r_0 < b$, and zero otherwise, $r_0 \geqslant b$), it is easy to note that to eliminate the possibility of penetration of the molecular interior of a given molecule by centres of atoms belonging to other molecules, the range in which the parameter b can vary must be restricted to $1/2 \leqslant b < \infty$. For such hard trimers (composed of hard atoms) the molecular shape clearly depends on the atomic diameter b and the latter can be used as a measure of the molecular anisotropy. Instead of using b which covers an infinitely long interval, however, it is more convenient to introduce the trimer anisotropy parameter

$$\alpha_b \equiv \frac{1}{2b} \tag{5}$$

which varies from zero to unity. (The latter parameter is equal to 5/7 for the structure shown in figure 2.) The limit $\alpha_b = 0$ corresponds to isotropic molecules. The extreme anisotropy limit, $\alpha_b = 1$, corresponds to the situation when atomic centres of neighbouring trimers can reach the border of the molecular interior of a given trimer.

As is easy to note, the first two of the potentials studied in this paper, (2) and (3), are self-similar for finite n, i.e. the atomic diameter b is only a scaling factor for finite n, and the system properties are essentially determined by r_0, being the distance of the nearest-neighbouring atoms of the neighbouring trimers. For this reason, it is convenient to characterize the molecular anisotropy by replacing b by r_0 for the potentials (2) and (3),

$$\alpha \equiv \frac{1}{2r_0} \tag{6}$$

where $r^* = r_0/b$. It is worth stressing that the assumption that centres of atoms belonging to a given trimer cannot penetrate the interior of any other trimer and the interiors cannot overlap implies that $0 \leqslant \alpha < 1$, whereas $0 \leqslant \alpha_b \equiv (\alpha r^*) < r^*$, in general.

Using α instead of α_b one can compare systems with finite n directly with those corresponding to the limit $n \to \infty$. In the latter limit the potential (2) corresponds to the *hard potential* (infinity when $r_0 < b$ and zero otherwise) and the condition $r_0 = b$ gives, the so-called, *close packed structure* which corresponds to minimum distances between the interacting atoms. (At zero temperature the close packed structure is stable at an infinitesimal positive pressure.) In the case of the potential (3), which for $n \to \infty$ tethers the interacting atoms allowing them to move freely within the distance b from each other and making further increase of the distance impossible [50, 51] (the energy is zero for $r_0 \leqslant b$ and infinity otherwise), the condition $r_0 = b$ gives a structure corresponding to the maximum distances between the interacting atoms. This structure, which is stable at zero temperature and infinitesimal *negative* pressure, is further referred to as the *extremely expanded structure*.

In contrast to the self-similar potentials, the parameter b is a relevant parameter characterizing the molecular interaction for the LJ potential (4). (The latter potential reaches its minimum value $u(b) = -1$ when the interacting atoms are precisely at the distance $r_0 = b$. In such a case the system is at zero external pressure.) Hence, to describe the trimers interacting using the LJ potential one could use the parameter α_b defined in (5). As the possible values of α_b for the potential (4) are restricted from the above by r^* instead of unity, to compare the properties of the considered crystalline phase of the LJ trimers with the results obtained for the purely attractive and purely repulsive trimers, it is more convenient to represent the studied

quantities as functions of the distance of the interacting atoms, r_0, and, in consequence, to use α instead of α_b also in this case.

Remark 3. One should add here that, unlike the hexamers described in [40], the trimers defined above may show some structural degeneracy. This means that structures other than that shown in figures 2 and 3, but of the same energy per molecule, can be formed by the trimers defined above. These can be either crystalline structures (e.g. obtained by making neighbouring rows of the trimers oriented anti-parallelly) or aperiodic ones, like those described in the case of the two-dimensional dimers [52, 53] (when $b = 1$) or dumb-bells [52, 54] (when $b \approx 1$). Any degeneracy in the trimer system can be easily removed, however, e.g. by introducing an additional interaction between the molecular mass centres which favours the triangular lattice of the trimer mass centres. To remove the degeneracy in the zero-temperature limit, studied in this work, the additional interaction can be arbitrarily weak. As the elastic properties of the system will not be influenced by sufficiently weak additional interaction, one can neglect this interaction in the calculations of the elastic constants considering at the same time the triangular structure as the stable one; this solution is adopted in the present paper.

3. The solution and examples

The solution method of the system considered in this work follows that of [40]. This section starts from some general considerations valid for any potential of the interacting atoms of the nearest-neighbouring trimers. Next the elastic properties of each of the three cases mentioned above are discussed.

3.1. The general case

The system of energy defined in (1) will be studied in the whole density range where the triangular lattices of the trimer mass centres (like those in figures 2 and 3) are mechanically stable. Elastic constants of the system will be obtained by deformations of the perfect triangular lattice corresponding to equilibrium at a given density.

As the system is isotropic, one needs only two elastic constants (and pressure) to describe its elastic properties. This can be seen by expanding the system energy per unit volume in powers of the (Lagrange) strain components [1]

$$E_{\text{tot}}/V_{\text{ref}} = -p(\varepsilon_{xx} + \varepsilon_{yy}) + 2\lambda_{\xi\eta\xi\eta}(\varepsilon_{xx} + \varepsilon_{yy})^2 + \lambda_{\xi\xi\eta\eta}\left[(\varepsilon_{xx} - \varepsilon_{yy})^2 + 4\varepsilon_{xy}^2\right] \tag{7}$$

where V_{ref} is the two-dimensional 'volume' (area) of the reference state; the linear terms in the strain components come from the fact that the pressure can be different from zero, in general. The bulk modulus, B, and the shear modulus, μ, are related to the above defined elastic constants as follows [40]

$$B = 4\lambda_{\xi\eta\xi\eta} \qquad \mu = 2\lambda_{\xi\xi\eta\eta} - p. \tag{8}$$

Periodicity of the system allows one to restrict further considerations to a single unit cell whose energy and volume will be denoted by E and v_{ref}, respectively. For the triangular lattice of the trimer mass centres (see figures 2 and 3), the volume of the unit cell can be expressed by the formula

$$v_{\text{ref}} = \frac{\sqrt{3}}{2}\left(\frac{\sqrt{3}}{2} + \sqrt{r_0^2 - \frac{1}{4}}\right)^2 \sigma^2 \tag{9}$$

where r_0 corresponds to the distance (in σ units) of the nearest-neighbouring atoms of the neighbouring trimers at the density considered.

Differentiating the system energy per unit volume with respect to ε_{xx} (or ε_{yy}) at the reference state, one obtains the pressure. It is convenient to express it by the distance r_0 between the nearest-neighbouring atoms of the neighbouring trimers

$$p = -\frac{1}{v_{\text{ref}}}\frac{\partial E}{\partial \varepsilon_{xx}}\bigg|_{\varepsilon=0} = \frac{-2\sqrt{12r_0^2-3}}{r_0(\sqrt{3}+\sqrt{4r_0^2-1})}\frac{u'(r_0)}{\sigma^2} \tag{10}$$

where $\varepsilon = 0$ indicates that after the differentiation all the strain tensor components should be replaced by zero.

By double differentiation of the energy per unit volume one obtains

$$\frac{1}{v_{\text{ref}}}\frac{\partial^2 E}{\partial \varepsilon_{xx}^2}\bigg|_{\varepsilon=0} = 4\lambda_{\xi\eta\xi\eta} + 2\lambda_{\xi\xi\eta\eta} \tag{11}$$

$$\frac{1}{v_{\text{ref}}}\frac{\partial^2 E}{\partial \varepsilon_{xx}\partial \varepsilon_{yy}}\bigg|_{\varepsilon=0} = 4\lambda_{\xi\eta\xi\eta} - 2\lambda_{\xi\xi\eta\eta}. \tag{12}$$

Combining (8) and (10)–(12) one gets

$$B = \frac{\left(3 - \sqrt{3}(4r_0^2-1)^{\frac{3}{2}}\right)}{4r_0^3(\sqrt{3}+\sqrt{4r_0^2-1})}\frac{u'(r_0)}{\sigma^2} + \frac{\sqrt{3}(-1+4r_0^2)}{4r_0^2}\frac{u''(r_0)}{\sigma^2} \tag{13}$$

$$\mu = \frac{3(1+\sqrt{12r_0^2-3})}{2r_0(\sqrt{3}+\sqrt{4r_0^2-1})}\frac{u'(r_0)}{\sigma^2} + \frac{\sqrt{3}}{2}\frac{u''(r_0)}{\sigma^2}. \tag{14}$$

The Poisson ratio can be obtained by substituting (13) and (14) into the formula [40]

$$\nu_P = \frac{B-\mu}{B+\mu} \tag{15}$$

which leads to

$$\nu_P = \frac{r_0(2r_0^2-1)u''(r_0)}{(1+2r_0^2)u'(r_0) + r_0(6r_0^2-1)u''(r_0)}$$
$$+ \frac{\left(3+\sqrt{12r_0^2-3} - 2r_0^2(3+5\sqrt{12r_0^2-3})\right)u'(r_0)}{\left(3+\sqrt{12r_0^2-3}\right)\left((1+2r_0^2)u'(r_0) + r_0(6r_0^2-1)u''(r_0)\right)}. \tag{16}$$

It is worth noting that when the interatomic potential shows a smooth minimum at the distance r_0, i.e. when $u'(r_0) = 0$, or when the ratio of the first to the second derivative of the interaction potential at r_0 tends to zero, $u'(r_0)/u''(r_0) = 0$, the above formula simplifies to
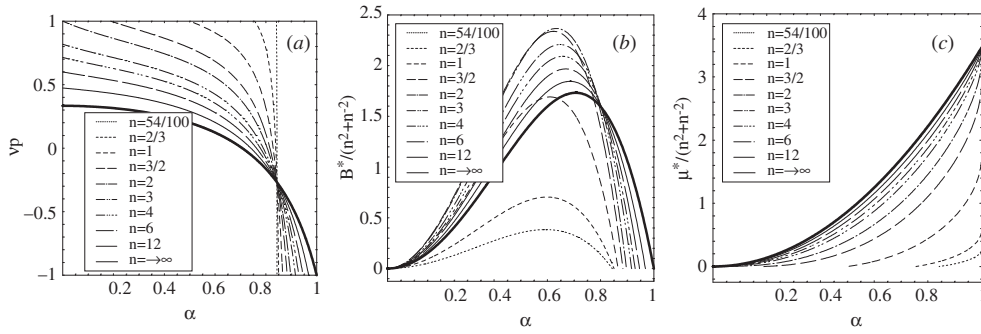
$$\nu_P = \frac{1-2r_0^2}{1-6r_0^2} \tag{17}$$

Figure 4. (*a*) The Poisson ratio, (*b*) the bulk modulus and (*c*) the shear modulus dependences on α for a few values of the exponent n in the case of the purely repulsive n-inverse-power atom–atom interaction (2). The thick line indicates the hard trimer system at close packing. The values of B, μ were divided by $n^2 + n^{-2}$ to reduce their amplitudes in a consistent way and to eliminate their singularities in the limit $n \to \infty$.

which leads to

$$\nu_P = \frac{1 - 2\alpha^2}{3 - 2\alpha^2} \tag{18}$$

where equation (6) defining α has been used. The same dependence of the Poisson ratio on the anisotropy parameter is obtained for the hard trimers and the tethered trimers for which $r_0 \equiv b$.

It can be seen that for $\alpha = 0$ (isotropic particles) one gets from (18) $\nu_P = 1/3$, which is the value of the Poisson ratio obtained for two-dimensional isotropic systems fulfilling the Cauchy relations [55]. For $\alpha = 1$ (extreme trimer anisotropy) the formula (18) gives $\nu_P = -1$, which is the minimum value of the Poisson ratio for any isotropic system.

Substituting the potentials (2)–(4) into equations (10), (13), (14) and (16) one can obtain the formulae for the pressure, the bulk modulus, the shear modulus and the Poisson ratio for the three examples considered in this paper. They are discussed in the following subsections.

3.2. The n-inverse-power repulsion

Using (16) and (6) the Poisson ratio for the repulsive self-similar potential (2) can be written as

$$\nu_P = \frac{3(2 + n)\alpha(-1 + 2\alpha^2) + \sqrt{3 - 3\alpha^2}(-6 - n + 2(2 + n)\alpha^2)}{(-2 - 3n + 2(2 + n)\alpha^2)(3\alpha + \sqrt{3 - 3\alpha^2})}. \tag{19}$$

In figure 4(*a*), plots of the anisotropy dependence of the Poisson ratio are shown for a few values of n. For each plot, the presented curve is drawn only in the ranges of α corresponding to the *mechanical stability* of the system, i.e. when B, $\mu > 0$. To demonstrate the mechanical stability explicitly, the bulk modulus and the shear modulus are drawn (only for such values of α for which they are positive) for the same n as in figures 4(*b*) and (*c*).

It is easy to see in figure 4 that when the molecular anisotropy is large enough (i.e. when the distances between the molecular centres are sufficiently small), the Poisson ratio is negative. It can also be seen that (in agreement with the stability requirements) the system is unstable when the absolute value of the Poisson ratio exceeds 1.

It is worth noting that in the case of the trimers one can choose the atomic inverse-power-interaction potential (with $0.537... < n \leqslant 2$) in such a way that when the density is changed,
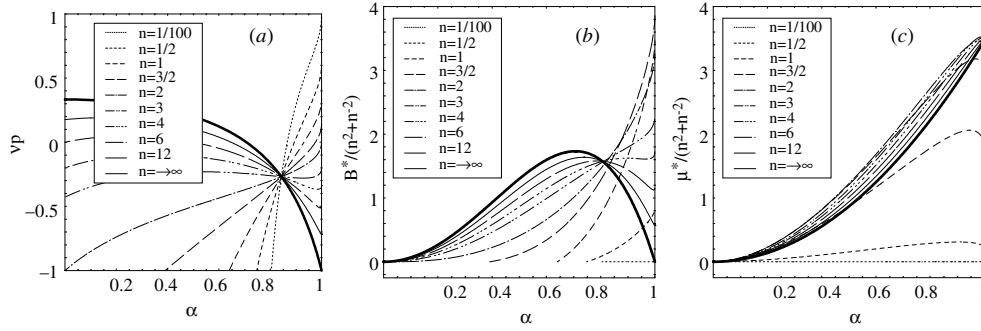
Figure 5. (a) The Poisson ratio, (b) the bulk modulus and (c) the shear modulus dependences on α for a few values of the exponent n in the case of the purely attractive n-power atom–atom interaction (3). The thick line indicates the tethered trimer system in the extreme expansion limit. The values of B, μ were divided by $n^2 + n^{-2}$ to reduce their amplitudes in a consistent way and to eliminate their singularities in the limit $n \rightarrow \infty$.

ν_P covers the interval $(-1, 1)$, i.e. the whole range of values allowed by the stability conditions, $B, \mu > 0$. This is in contrast to an atomic system with the same interaction potential on the triangular lattice, for which the Poisson ratio, equal to $(6 + n)/(2 + 3n)$, is the same in the whole density range. (Obviously, a mechanically stable triangular lattice can be formed only for $n > 2$, for which the Poisson ratio fulfils the condition $1/3 \leqslant \nu_P(n) < 1$, and $B, \mu > 0$.)

It is easy to note that for the inverse-power potential the following equality holds

$$u'(r_0)/u''(r_0) = -\frac{r_0}{n+1}. \qquad (20)$$

The equality (20) implies that in the limit $n \rightarrow \infty$ one gets $u'(r_0)/u''(r_0) \rightarrow 0$. This means that in the hard interaction limit ($n \rightarrow \infty$) one can neglect $u'(r_0)$ in the formula (16) which results in equation (18) for the Poisson ratio, see the continuous thick line in figure 4(a).

3.3. The n-power attraction

The Poisson ratio for the trimers interacting using the attractive self-similar potential (3) can be obtained from (19) by the replacement $n \rightarrow -n$. In figure 5(a) the Poisson ratio is shown for the purely attractive trimers for a few values of the exponent n, as well as in the limit of $n \rightarrow \infty$. Again, the curves are drawn only for those values of α for which the system is mechanically stable. As in the case of the purely repulsive trimers, the positivity of the corresponding moduli B, μ is shown in figures 5(b) and 5(c).

It can be seen in figure 5 that also for the purely attractive trimers it is possible to choose a single atomic potential (with $n \rightarrow 0$) for which the Poisson ratio covers the range from -1 to 1, i.e. the whole range allowed by the mechanical stability conditions. Again, this is in contrast to an atomic system with the same interaction potential on the triangular lattice, for which the Poisson ratio, equal to $(n - 6)/(3n - 2)$, is constant in the whole density range. The latter system can form a mechanically stable triangular lattice only for $n > 2$, for which the Poisson ratio fulfils the condition $-1 < \nu_P(n) \leqslant 1/3$, and for which $B > 0$ and $\mu > 0$.

The Poisson ratio of the tethered trimers (i.e. in the limit $n \rightarrow \infty$) of the anisotropy α at the extreme expansion can be obtained in an analogous way as in the case of the repulsive trimers. It is also expressed by the formula (18), i.e. it is negative when the trimer anisotropy parameter is large enough, as indicated by the continuous thick line in figure 5(a).
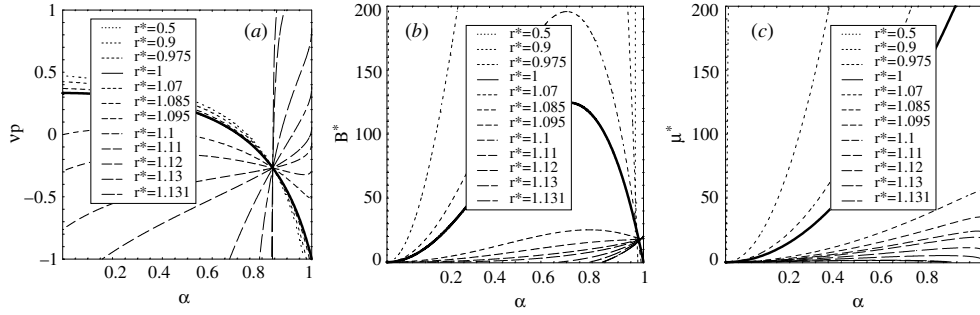
Figure 6. (a) The Poisson ratio, (b) the bulk modulus and (c) the shear modulus as functions of α for a few values of the interatomic distance parameter $r^* \equiv r_0/b$ in the case of the LJ atom–atom interaction (4). The thick line indicates the system at zero external pressure. The ranges $r^* < 1$ and $r^* > 1$ correspond, respectively, to repulsive and attractive interactions.

3.4. The Lennard–Jones interaction

For the atom–atom potential given by (4) the Poisson ratio reads

$$\nu_P = \frac{3\alpha(-1 + 2\alpha^2)(-7 + 4r^{*6}) + \sqrt{3 - 3\alpha^2}(9 - 14\alpha^2 + 2(-3 + 4\alpha^2)r^{*6})}{(3\alpha + \sqrt{3 - 3\alpha^2})(19 - 14\alpha^2 + 2(-5 + 4\alpha^2)r^{*6})}. \tag{21}$$

In figure 6(a) the Poisson ratio is shown as a function of the anisotropy parameter α. The curves are parametrized by the relative distance of the atoms $r^* \equiv r_0/b$. As in the former cases, the curves are drawn only in the ranges of those values of α for which the system is mechanically stable; the positivity of the corresponding moduli B, μ is shown in figures 6(b) and (c) where (as in the previous cases) these quantities are drawn only if they are positive.

It can be seen that also for the LJ potential, the molecular anisotropy increases the range which is covered by the Poisson ratio in comparison to the triangular lattice of atoms interacting using the same potential. For the atomic system, the Poisson ratio, given by the formula $\nu_P = [6(r^*)^6 - 9]/[10(r^*)^6 - 19]$, decreases from 9/19 at $r^* = 0$ to 1/3 at $r^* = 1$ (the mechanically stable range of positive pressures) and further to -1 at $r^* = (7/4)^{1/6}$ (the mechanically stable range of negative pressure). One should add here that from the point of view of the equilibrium thermodynamics the LJ system cannot be stable at *any* negative pressure when the temperature is positive. This is in contrast to the potential (3) which can grow to infinity with the increasing interatomic lattice spacing quickly enough to make the system stable at the negative pressure even when the temperature is positive.

Remark 4. The instability mentioned above is caused by the fact that the free energy of any stretched system interacting through a potential with a finite infimum (e.g. with a finite minimum) can be reduced if the system breaks down into parts. (The negative pressure corresponds to a particular case of the stretch, for which the stress in the system is isotropic.) This may seem paradoxical at first look, because by everyday experience there are many known objects which do not break down despite being stretched. The 'paradox' can be explained taking into account that generating a spontaneous fluctuation, which is necessary to destroy the metastable state of the stretched system, may require a very long time at low temperatures. The time effects are, however, neglected completely by the equilibrium thermodynamics. This

problem is discussed in detail in paragraph 12 of the Landau and Lifshits textbook on statistical mechanics [56].

As expected, it is seen in figure 6(*a*) that at $r^* = 1$ the Poisson ratio shows the same dependence on α as in the cases of hard trimers and tethered trimers.

4. Conclusions

An elastically isotropic, two-dimensional model system which is non-chiral, was constructed and solved exactly at the zero-temperature limit. Analytic formulae for the pressure and the elastic properties of the system, including the Poisson ratio, as functions of the molecular interaction potential were obtained. The ranges of stability were established for the parameters describing the studied model for some example potentials; auxetic behaviour was found in a broad range of parameters. In particular, the limiting cases of the repulsive interaction potential (hard trimers) and the attractive interaction potential (tethered trimers) were studied. It has been shown that the Poisson ratio shows the same dependence on the molecular shape parameter for the hard trimers at extreme compression (close packing) and for tethered trimers at extreme expansion. This dependence, which predicts negative Poisson ratio at high molecular anisotropy, is fulfilled also at zero external pressure for trimers interacting through any nearest-neighbour site–site potential of a circular symmetry which is doubly differentiable at its minimum.

Recently, it has been suggested that molecular rotation and anisotropy are important to obtain extreme values of the Poisson ratio [46]. Although this is certainly true in most of the known cases [2, 11, 12–16, 18–22, 38, 40, 48], the present model shows that (at least in two dimensions and for small deformations) the extreme values of the Poisson ratio can be obtained even for elastically isotropic structures and without *any* rotation of the molecules.

It is worth adding that extensive computer simulations of the hard cyclic trimers and tethered cyclic trimers discussed above have been performed at positive temperatures [49]. The simulations, which will be published elsewhere, have confirmed the existence of thermodynamically stable *auxetic phases* in a broad range of densities.

The models discussed in this paper are two dimensional and, as such, might be considered as unrealistic. The two-dimensional systems, however, can be thought of as models of three-dimensional *layers*. In such a context, the present paper and [40] can be thought of as indicating ways of preparing auxetic layers which are isotropic. Parallel layers can form three-dimensional materials whose elastic properties exhibit cylindrical symmetry and which are auxetic in the plane perpendicular to the cylindrical axis. The latter axis can be chiral or non-chiral, depending on the 'stacking' rules used.

The described models concern anisotropic molecules. To study the elastic properties of such systems one can use a more general version of the continuum elasticity theory, in which the elements of the continuum are described not only by their positional coordinates but also by their orientations [57, 47]. It seems interesting to analyse the static and dynamic properties of systems formed of layers of threefold and sixfold symmetry axes in the framework of such a generalized elasticity theory and compare them with the results of the standard elasticity theory [1]. This is planned as a subject of a future work.

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