

TWO-DIMENSIONAL ISOTROPIC SYSTEM WITH A NEGATIVE POISSON RATIO[☆]

K.W. WOJCIECHOWSKI

Institute of Molecular Physics, Polish Academy of Sciences, Smoluchowskiego 17/19, 60-179 Poznań, Poland

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A two-dimensional (2D) lattice model of hexagonal molecules on a triangular lattice interacting via a nearest-neighbour n -inverse-power site-site potential is shown to display an anomalous (negative) Poisson ratio at high densities when the anisotropy (non-convexity) of the molecules is substantial. It is suggested that such a behaviour may be observed in some real systems.

It is well known that a piece of simple rubber compressed (stretched) in one direction will increase (decrease) its transverse size. The negative of the ratio of the transverse strain to the longitudinal strain, when the stress parallel to the longitudinal direction is changed, is called the Poisson ratio [1]. Its value is positive for rubber as well as for most of materials in nature [1,2]. Exceptions to this "rule" were found in certain crystals showing the anomalous behaviour in one or more directions [2]. Such crystals are usually of low symmetry [2], and no elastically isotropic material of the negative Poisson ratio is known to exist [1].

A positive Poisson ratio of an elastically isotropic and stable material is equivalent to positive values of its Lamé coefficients. These coefficients were expected to be always positive for isotropic systems [1]. Recent Monte Carlo studies have indicated the possibility of a negative Poisson ratio, i.e. negative value of one of these coefficients, in a 2D elastically isotropic system of hard anisotropic (non-convex) molecules [3]. This very simple system is still too complicated for an analytical treatment. The static version of its lattice analog can be, however, solved exactly. The elastic properties of the last system are the subject of the present work. Elementary calculations prove the negative sign of the Poisson ratio of the system at sufficiently high densities.

The system consists of N ($N \rightarrow \infty$) molecules with

centres fixed in sites of a 2D triangular lattice with periodic boundary conditions. The lattice vectors are equal: $\mathbf{a}_1 = a\hat{x}$ and $\mathbf{a}_2 = a(\hat{x} + \sqrt{3}\hat{y})/2$, where a is the lattice spacing and \hat{x} , \hat{y} are the coordinate axis unit vectors. Each molecule, further referred to as a hexamer, contains six interaction sites placed on vertices of a perfect hexagon of side length equal to σ which is treated as the length unit ($\sigma = 1$). Only the sites of the neighbouring molecules interact, and the interaction is via an n -inverse-power potential ($n \geq 3$). To avoid penetration of the molecular interiors by interaction sites of the other molecules, the perfect hexagons forming the molecules are assumed to be hard (the same can be reached, without changing the described later qualitative results, e.g., by introducing an additional, sharply repulsive, interaction site in the molecular centre). When no hard hexagons overlap, the energy of the system is

$$U(a, \{\phi_i\}) = \sum_{i=1}^N \sum_{j=\text{nn}.i}^6 u(\mathbf{R}_{ij}, \phi_i, \phi_j), \quad (1)$$

where the intermolecular potential is

$$u(\mathbf{R}_{ij}, \phi_i, \phi_j) = \sum_{\alpha, \beta=1}^6 (b/R_{ij}^{\alpha\beta})^n. \quad (2)$$

ϕ_i defines the orientation of molecule i as the smallest angle between the x -axis and bisectrices of the hexagon's sides, $R_{ij}^{\alpha\beta}$ is the distance from the site α of molecule i to the site β of molecule j , and b is a positive real parameter ("atomic diameter"). The

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configurations with overlapping hard hexagons are forbidden as their energy is infinite.

The above system is a 2D generalization of the lattice model considered by Runge and Chester [4]. The presence of orientational degree of freedom makes it, however, analytically intractable at any non-zero temperature. For this reason further considerations are restricted to the static limit.

Analysis of the energy dependence of a pair of hexamers with molecular centres lying on the x -axis and being separated by a distance a proves that this energy is minimal when both the molecules have the same orientation $\phi(a)$. At finite n the angle $\phi(a)$ is equal to zero when a is large, and bifurcates into two symmetric non-zero values at a certain (transition) distance when a is decreased. This transition distance increases with n , tending to infinity in the limit $n \rightarrow \infty$ for which the orientation $\phi_\infty(a)$ is expressed by

$$\phi_\infty(a) = \arctan\{1/[2\sqrt{3} + (4a^2 + 11 - 4\sqrt{12a^2 - 3})^{1/2}]\}. \quad (3)$$

For the hexagonal symmetry of the molecules and the lattice, the minimum energy orientations of the molecules neighbouring in the directions of \mathbf{a}_2 and $\mathbf{a}_3 = \mathbf{a}_2 - \mathbf{a}_1$ are also equal to $\phi(a)$. Hence, in the energy minimum state all the molecules of the lattice have the same orientation, $\pm\phi(a)$, and the state is stable versus changes of the molecular orientations. The energy of this configuration is

$$U(a) = 3Nu[\mathbf{a}\hat{x}, \phi(a), \phi(a)]. \quad (4)$$

In order to obtain the elastic properties of the system, one considers small uniform deformation of such a stable reference state. The deformations can be described by a matrix \mathbf{A} transforming the unit cell vectors from the reference state to the deformed one:

$$\mathbf{r}_i = \mathbf{A} \cdot \mathbf{a}_i \quad (i = 1, 2). \quad (5)$$

The matrix \mathbf{A} defines the (Lagrange) strain tensor ϵ [1]:

$$\epsilon = (\mathbf{A}' \cdot \mathbf{A} - \mathbf{I})/2, \quad (6)$$

where \mathbf{A}' is the transpose of \mathbf{A} . Change of the unit cell vectors is followed by a change in the molecular orientations which can be site dependent, in general. However, to obtain the second order elastic moduli

determining the Poisson ratio, it is sufficient to take into account only such of the (deformed) configurations in which all the molecules have the same orientation ϕ . This comes from the expansion of the energy change in the strain ϵ and the orientation changes $\delta\phi_i$. For a 2D lattice with a six-fold symmetry axis this expansion reads ^{#1}:

$$\begin{aligned} [U(a, \mathbf{A}, \{\phi_i\}) - U(a)]/V_{\text{ref}} &\equiv \Delta U/V_{\text{ref}} \\ &= -p(\epsilon_{xx} + \epsilon_{yy}) + 2\lambda_1(\epsilon_{xx} + \epsilon_{yy})^2 \\ &\quad + \lambda_2[(\epsilon_{xx} - \epsilon_{yy})^2 + 4\epsilon_{xy}^2] \\ &\quad + (1/N)(\epsilon_{xx} + \epsilon_{yy})\lambda_3 \cdot \delta\phi + (1/2N)\delta\phi \cdot \lambda_4 \cdot \delta\phi, \end{aligned} \quad (7)$$

where $V_{\text{ref}} = Nv(a)$ is the area, p is the isotropic pressure, and λ_i ($i = 1, \dots, 4$) are the elastic moduli at the reference state triangular lattice of the lattice spacing a . λ_3 and $\delta\phi$ are single-column matrices of N elements λ_3 and $\delta\phi_i$, respectively, and λ_4 is an $N \times N$ matrix of the second derivatives of ΔU with respect to $\delta\phi_i$ and $\delta\phi_j$ divided by $v(a)$. The equilibrium condition requires the first derivative of ΔU versus $\delta\phi$ to be equal to zero. Hence,

$$\lambda_4 \cdot \delta\phi = -(\epsilon_{xx} + \epsilon_{yy})\lambda_3.$$

Since the matrix λ_4 is cyclic (this follows from the periodic boundary conditions imposed) and positively defined ^{#2} (the reference state is stable versus changes of the molecular orientations) all the elements of $\delta\phi$ in the above equation are the same. Thus, the differences (if any) between orientations of the molecules are small quantities of order higher than one in ϵ , and can be neglected in the second order expansion. All the $\delta\phi_i$ are then equal to $\delta\phi$ and the above expansion simplifies to

$$\begin{aligned} \Delta U/V_{\text{ref}} &= -p(\epsilon_{xx} + \epsilon_{yy}) + 2\lambda_1(\epsilon_{xx} + \epsilon_{yy})^2 \\ &\quad + \lambda_2[(\epsilon_{xx} - \epsilon_{yy})^2 + 4\epsilon_{xy}^2] \\ &\quad + \lambda_3(\epsilon_{xx} + \epsilon_{yy})\delta\phi + \lambda_4(\delta\phi)^2/2, \end{aligned} \quad (8)$$

where λ_4 is the sum of the elements of any single row

^{#1} The symmetry arguments are analogous to those in ref. [1].

^{#2} At the isolated value of the lattice spacing where the angle $\phi(a)$ bifurcates, the matrix λ_4 is not defined positively. The properties of the system at this lattice spacing can be obtained by considering the limits of a greater/smaller than the bifurcation value.

of λ_4 (for $N \gg 1$ this sum is independent of N because the interaction range is finite).

The parameters of the expansion (8) can be calculated differentiating the energy of the unit cell,

$$u_c \equiv u_c(a, \mathbf{A}) = \sum_{i=1}^3 u[r_i, \phi, \phi] = U(a, \mathbf{A})/N, \quad (9)$$

divided by the area per molecule $v(a)$, with respect to the molecular orientation ϕ and the strain ϵ (the derivatives are taken at the reference state). In this calculation one can use the following transformation matrix:

$$\mathbf{A} = \begin{pmatrix} 1+\epsilon & 0 \\ 0 & 1+\eta \end{pmatrix} \quad (10)$$

(ϵ, η are small real numbers), which corresponds to the strain tensor

$$\epsilon = \begin{pmatrix} \epsilon + \epsilon^2/2 & 0 \\ 0 & \eta + \eta^2/2 \end{pmatrix}. \quad (11)$$

The pressure p can then be calculated as follows:

$$\begin{aligned} pv(a) &= - \left(\frac{\partial u_c}{\partial \epsilon_{xx}} \right)_{\epsilon_{yy}, \epsilon_{zz}=\epsilon_{yy}=0} \\ &= - \left(\frac{\partial u_c}{\partial \epsilon} \right)_{\eta} \bigg/ \frac{\partial \epsilon_{xx}}{\partial \epsilon} \bigg|_{\epsilon=\eta=0} = - \left(\frac{\partial u_c}{\partial \epsilon} \right)_{\eta} \bigg|_{\epsilon=\eta=0} \\ &= \frac{3}{2} nab^n \sum_{\alpha, \beta=1}^6 (R^{\alpha\beta})^{-(n+2)} R_x^{\alpha\beta}, \end{aligned} \quad (12a)$$

where $R_z^{\alpha\beta}$ ($z=x, y$) is the z -component of the vector $\mathbf{R}^{\alpha\beta}$ joining the interaction sites of two molecules of the reference orientation $\phi(a)$ and separated by a distance a . The other parameters, calculated in a similar way, are

$$\begin{aligned} \lambda_1 v(a) &= \frac{3}{16} nab^n \sum_{\alpha, \beta=1}^6 (R^{\alpha\beta})^{-(n+2)} \\ &\quad ([R_x^{\alpha\beta} - a] + (n+2)a(R_x^{\alpha\beta}/R^{\alpha\beta})^2], \end{aligned} \quad (12b)$$

$$\lambda_2 v(a) = \frac{3}{16} nab^n \sum_{\alpha, \beta=1}^6 (R^{\alpha\beta})^{-(n+2)} (2R_x^{\alpha\beta} + na), \quad (12c)$$

$$\begin{aligned} \lambda_3 v(a) &= -\frac{3}{2} n(n+2) a^2 b^n \\ &\quad \times \sum_{\alpha, \beta=1}^6 (R^{\alpha\beta})^{-(n+4)} R_x^{\alpha\beta} R_y^{\alpha\beta}, \end{aligned} \quad (12d)$$

$$\begin{aligned} \lambda_4 v(a) &= nab^n \sum_{\alpha, \beta=1}^6 (R^{\alpha\beta})^{-(n+2)} \\ &\quad \times [(R_x^{\alpha\beta} - a) + (n+2)a(R_y^{\alpha\beta}/R^{\alpha\beta})^2]. \end{aligned} \quad (12e)$$

In the expansion (8), the molecular orientation ϕ is treated as an independent thermodynamic variable. Being an internal variable, however, it has to minimize the energy of the system, i.e. the derivative of ΔU versus $\delta\phi$ must be zero:

$$0 = \lambda_3 (\epsilon_{xx} + \epsilon_{yy}) + \lambda_4 \delta\phi. \quad (13)$$

From eqs. (8) and (13) one obtains

$$\begin{aligned} \Delta U/V_{\text{ref}} &= -p(\epsilon_{xx} + \epsilon_{yy}) + 2\lambda_{\xi\eta\xi\eta}(\epsilon_{xx} + \epsilon_{yy})^2 \\ &\quad + \lambda_{\xi\xi\eta\eta}[(\epsilon_{xx} - \epsilon_{yy})^2 + 4\epsilon_{xy}^2], \end{aligned} \quad (14)$$

where

$$\begin{aligned} \lambda_{\xi\eta\xi\eta} &= \lambda_1 - \lambda_3^2/4\lambda_4, \\ \lambda_{\xi\xi\eta\eta} &= \lambda_2. \end{aligned} \quad (15)$$

The elastic moduli $\lambda_{\xi\eta\xi\eta}$ and $\lambda_{\xi\xi\eta\eta}$ (the notation of ref. [1] is used) are these which are actually describing the considered system. The Poisson ratio ν_p of the system is then^{#3}

$$\nu_p = \frac{4\lambda_{\xi\eta\xi\eta} - 2\lambda_{\xi\xi\eta\eta} + p}{4\lambda_{\xi\eta\xi\eta} + 2\lambda_{\xi\xi\eta\eta} - p} = \frac{K - \mu}{K + \mu}, \quad (16)$$

where $K = 4\lambda_{\xi\eta\xi\eta}$ and $\mu = 2\lambda_{\xi\xi\eta\eta} - p$ are the bulk modulus and shear modulus, respectively. Following Landau and Lifshitz [1] it is easy to show that the thermodynamic stability condition requires positivity of K and μ only, and not ν_p . When μ exceeds K , the Poisson ratio becomes negative.

It follows from eqs. (12), (15) and (16) that the Poisson ratio does not depend on b when n is finite. The density dependence of ν_p is shown in fig. 1a for a few values of n . It is clearly visible that the Poisson ratio is negative at sufficiently high densities.

The limit $n \rightarrow \infty$ requires some comment. In this limit the molecules tend to hard hexamers consisting of six hard discs of diameter b with centres forming perfect hexagons of side length equal to unity. At $b=1$ such molecules are identical to those studied in ref. [3] and further referred to as perfect hard hexamers;

^{#3} The calculation is similar to that in the 3D isotropic case (see e.g. ref. [1]). The pressure enters the stress-strain relation as the system is under non-zero stress (see e.g. ref. [5]).

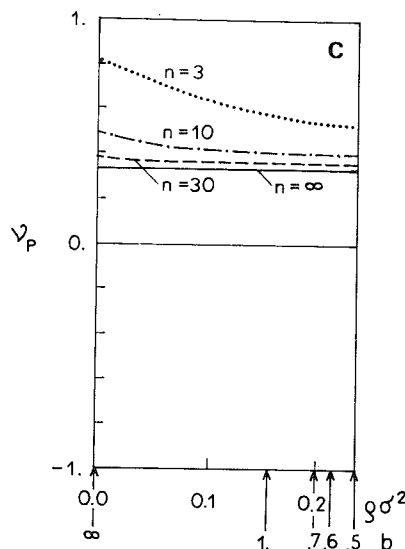
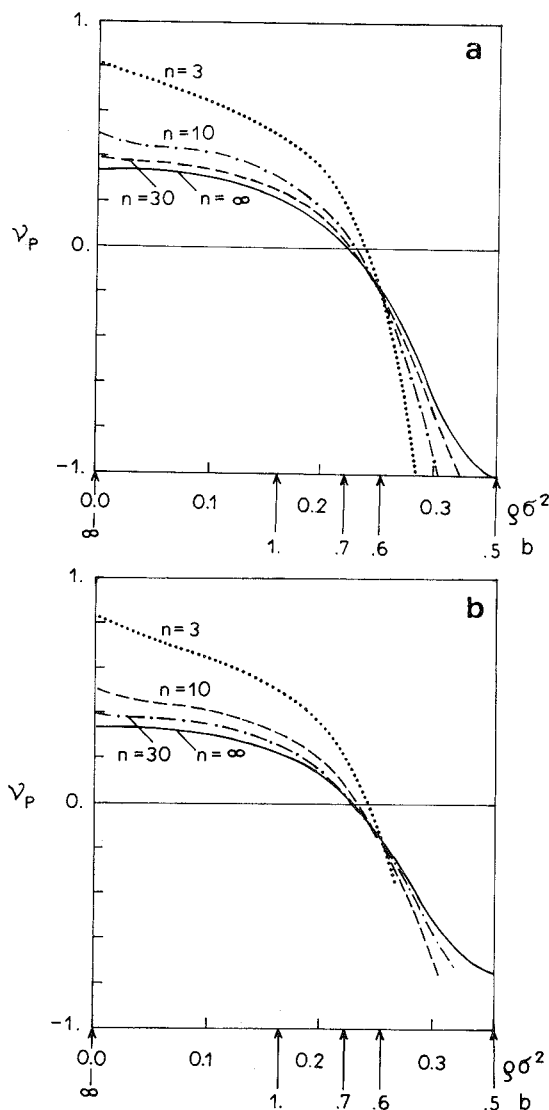


Fig. 1. (a) Density dependence of the Poisson ratio, ν_P , at four different interaction strengths: $n=3$ (dotted), $n=10$ (dash-dotted), $n=30$ (dashed), and $n=\infty$ (full line). For finite n the curves are drawn only in the stability regions ($|\nu_P| \leq 1$) of the corresponding crystals which are unstable versus volume fluctuations at very high densities. For $n \rightarrow \infty$ the upper density limit of the system, determined by b , is indicated by arrows for a few values of b . At low densities ν_P tends to $(n+6)/(3n+2)$, the low density limit for a triangular lattice of points interacting with the n -inverse-power potential. (b) The same as in (a) with the fixed reference orientation. (c) The same as in (a) with $\phi=0$. The close packing densities of hard hexamers are in this case, obviously, lower than those in (a) and (b).

in the limit $b \rightarrow \infty$ one obtains hard discs. When $b > 0.5$, the minimal distance of the molecular centres is

$$d_0 = d_0(b) = [b^2 + 3 + 2\sqrt{3}\sqrt{b^2 - \frac{1}{4}}]^{1/2}.$$

The density of the molecules can then not be higher than that of hard discs of diameter d_0 , for which $\rho_0 \equiv \rho_0(b) = 1/v_0$, where $v_0 \equiv v_0(b) = \frac{1}{2}\sqrt{3}d_0^2$ is the close packing volume per particle [6]. Since the molecules can be packed without overlaps into a triangular lattice of lattice spacing d_0 and density ρ_0 (the molecular orientations are the same and equal to $\phi_\infty = \pm \arctan[1/2(\sqrt{3} + \sqrt{b^2 - \frac{1}{4}})]$), this is the

close packing density of the system. At any chosen b the Poisson ratio is then defined only in the range $0 \leq \rho \leq \rho_0$. Thus, the densities corresponding to the negative values of the Poisson ratio can be reached only at sufficiently small values of b , i.e. for sufficiently non-convex molecules. The maximal value of the "atomic diameter" for which the Poisson ratio can be zero is $b_m \approx 0.691$ which corresponds to a density $\rho_m \approx 0.225$.

For a static crystal of perfect hard hexamers the Poisson ratio is positive in the whole density range where the hexagonal crystal is stable (see fig. 1a). Computer simulations [7] prove, however, negative

values of the ratio at relative volumes $v/v_0 \lesssim 1.13$ (i.e. when the molecules are tilted with respect to the crystalline axes [8]). This "discrepancy" comes from the lack of fluctuations of the molecular orientations and mass centre positions in the static model. In the hard disc system the fluctuations increase the ratio $r \equiv \lambda_{\xi\eta\xi\eta} / \lambda_{\xi\eta\xi\eta}$ (i.e. decrease the Poisson ratio, according to eq. (16)) up to $r_{\text{simul}} \approx 1.5$ [9] comparing with $r_{\text{static}} = 1$ in the static model. A similar and even stronger effect appears also in the case of hard hexamers [7].

For comparison, the analogous figures are drawn for systems of the same molecules which: (i) keep the equilibrium reference orientation intact when the deformation is applied to the lattice, and (ii) have fixed orientation $\phi=0$. In the first case, fig. 1b, the Poisson ratio is also negative at high densities (small b), being obviously slightly higher than before (see eq. (15)). This means that when the molecules are tilted, the strong non-convexity leads to negative ν_P even without the strain-orientation coupling ($\lambda_3=0$). In the second case ν_P is positive even for highly non-convex molecular shape, fig. 1c. This proves that the molecular tilt equivalent to the lack of a "mirror" symmetry in the system is necessary for the effect.

The idea presented of constructing the isotropic model with negative Poisson ratio is based on using a lattice whose second order elastic properties are the same as those of the isotropic system. It is an intriguing, but still open question, whether this idea can be generalized to the 3D case.

Some real systems may display the anomaly described. The above discussion suggests searching either amongst crystals of non-convex hexagon-like molecules (e.g. similar to diazabicyclo-[2,2,2]-octane (DABCO), forming hexagonal layers with molecular axes tilted with respect to the crystalline

ones [10]) or in thin films of such molecules on surfaces of liquids.

Non-convex interparticle interactions, inducing in the case of hexamers the molecular tilt which is crucial for the phenomenon described, lead also to other striking behaviours demonstrated by very simple model systems [11,12]. The models prove that some of our intuitions, having their roots in experience with simple convex particles, are clearly incorrect in the case of dense non-convex molecule systems.

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