

Negative Poisson ratio in a two-dimensional "isotropic" solid

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A two-dimensional system of hard cyclic hexamers is shown to display an anomalous (negative) Poisson ratio in a high-density crystalline phase. The anomaly can be reproduced qualitatively by a simple free-volume (FV) approximation. The FV approximation and a lattice model indicate the crucial role of broken mirror symmetry for this phenomenon.

I. INTRODUCTION

Everyday experience teaches us that elastic materials, like rubber, when compressed (stretched) in one direction increase (decrease) their transverse dimensions. The quantitative measure of shape changes of a material under a uniaxial compression is the Poisson ratio (PR) ν_P , defined as the negative of the ratio of the transverse strain to the longitudinal strain, when the stress parallel to the longitudinal direction is changed.¹ For rubber, as well as for all known isotropic materials the PR is positive.^{1,2} This is a rather paradoxical situation because thermodynamic stability conditions do permit negative values of this quantity: $-1 \leq \nu_P \leq 0.5$ in three dimensions (3D) and $-1 \leq \nu_P \leq 1$ in two dimensions (2D). Thus a fundamental question arises: Does an isotropic material with negative PR exist at all? In the present paper we show that it is possible to find a simple system with a negative (anomalous) PR. The particular system we consider below is a two-dimensional molecular system of hard cyclic hexamers (2D HCH's). A hard cyclic hexamer molecule consists of six equidiameter hard disks ("atoms") whose centers form a perfect hexagon of sides equal to the disk diameter σ . The high-density phase of 2D HCH's, referred to as "tilted" for a slight rotation of the molecular axes with respect to the crystalline ones,^{3,4} displays the sixfold symmetry axis but shows no mirror symmetry. It has been already suggested that in this particular phase ν_P may be negative.⁵ Since in two dimensions the sixfold axis is equivalent to the isotropic symmetry within the second-order elasticity,² the 2D HCH system in its tilted phase might be thought of as the first known example of an isotropic solid displaying the mentioned anomaly. Because of poor statistics, the preliminary results presented in Ref. 5 were not conclusive and necessity of further studies was pointed out. A step forward has been made in Ref. 6, where a static lattice model, within which the negative sign of PR could be proven in a rigorous manner, was considered. The essential conclusion was that the molecular tilt is crucial for the presence of the PR anomaly. Furthermore, it has been shown that the lattice model (neglecting completely molecular motions) needs strong nonconvexity of the molecules to display the PR anomaly.

The main aim of the present study is to check whether

the system of rather moderately nonconvex 2D HCH molecules does exhibit the anomaly suggested in the Ref. 5. A few Monte Carlo (MC) runs described in Sec. II prove that the PR is indeed negative at high densities. In Sec. III we consider ability of the simplest theoretical approximations to reproduce the anomaly. In the last part the results are summarized and some speculations about the 3D case are described.

II. MC METHOD AND RESULTS

Elastic constants (compliances), needed to determine the value of the PR, are the second-order derivatives of the free energy (free enthalpy) versus the strain (thermodynamic tension) tensor components.⁷ As such they require more computational effort comparing to the first-order derivatives like, e.g., pressure. The known in the literature methods determining the elastic properties of a body can be grouped into (i) the isostrain methods,⁸⁻¹² keeping the shape of the sample fixed, and (ii) the iso-stress (isotension) methods,^{13-16,5} in which the shape fluctuates under a constant stress (tension). Methods from the first group are, in general, better in respect of convergence than those of the second group. However, these from the second—can be attractive in the case of hard nonspherical interactions, as they do not require calculations of pressurelike quantities. In the present work the fluctuation version of the isotension method was used. The details of the simulation procedure and the elastic constants calculations were very similar to those in the case of hard disks¹⁶ and are not repeated here.¹⁷ The number of the molecules was chosen to be $N=56$, the acceptance ratio was kept close to 50%, and the runs consisted of 3×10^5 MC steps per molecule (after equilibration $\sim 10^5$ MC steps). The resulting elastic moduli $\lambda_{\xi\eta\xi\eta}$ (compressibility-related modulus) and $\lambda_{\xi\xi\eta\eta}$ (shear-related modulus) are presented in Table I.¹⁸ In Fig. 1 two typical plots of the elastic moduli dependence on the length of the MC runs are shown. They are similar to analogous plots drawn for spherically symmetric interactions in Ref. 15 and indicate rather slow convergence of the studied quantities with increasing number of MC steps also with presence of the orientational degrees of freedom.¹⁵

The Poisson ratio,

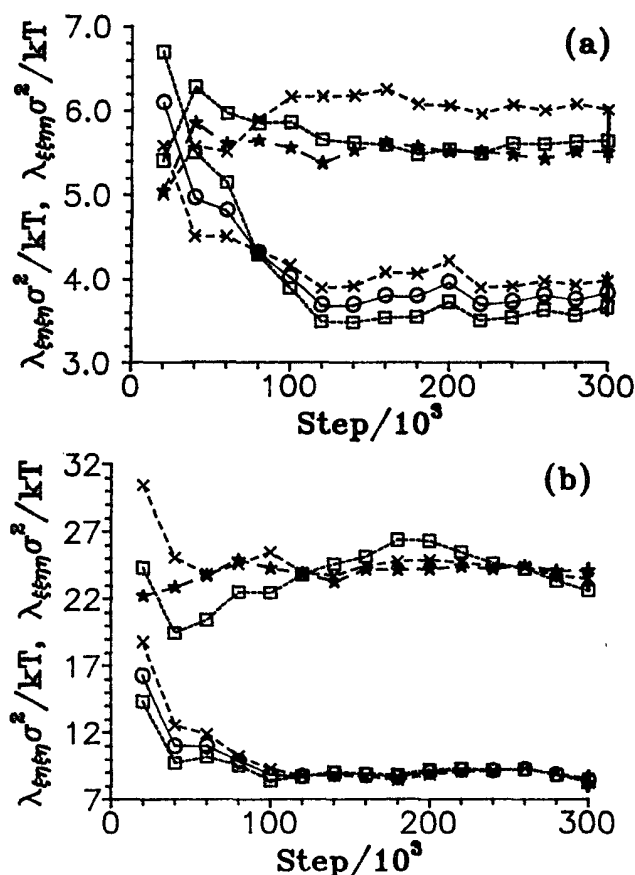


FIG. 1. Accumulation plots for the elastic moduli at two pressures below and above the phase transition between (a) the straight phase $p\sigma^2/kT=2.2$, and (b) the tilted phase, $p\sigma^2/kT=4.1$. Meaning of the symbols: (i) squares (crosses) were calculated from S_{xxxx} (S_{yyyy}) and S_{xxyy} using Eqs. 5(a) and 5(b) from Ref. 16, (ii) stars were calculated from S_{xxyy} using Eq. 5(c) in Ref. 16, and (iii) circles were obtained from area fluctuations [Eq. 5(d) in Ref. 16]. Thick vertical lines at the end of the plots are centered in the mean values of the elastic moduli and indicate the estimated errors (see Table I).

$$\nu_P \equiv \frac{4\lambda_{\xi\eta\xi\eta} - 2\lambda_{\xi\xi\eta\eta} + p}{4\lambda_{\xi\eta\xi\eta} + 2\lambda_{\xi\xi\eta\eta} - p}, \quad (1)$$

the ratio of the elastic moduli $r \equiv \lambda_{\xi\xi\eta\eta}/\lambda_{\xi\eta\xi\eta}$, and the

TABLE I. The relative volume and the elastic moduli of the 2D HCH system at a few different pressures. The errors of the relative area are given in the parentheses and concern the last digit.

$p\sigma^2/kT$	v/v_0	$\lambda_{\xi\eta\xi\eta}\sigma^2/kT$	$\lambda_{\xi\xi\eta\eta}\sigma^2/kT$
9.0	1.0579(3)	38.2 ± 3	126 ± 7
7.0	1.0748(4)	28.6 ± 2.0	76 ± 4
5.0	1.1059(6)	14.1 ± 1.1	38.6 ± 1.4
4.1	1.133(1)	8.2 ± 0.7	23.7 ± 1.0
3.5	1.188(1)	6.7 ± 0.6	12.7 ± 0.8
2.2	1.264(1)	3.82 ± 0.25	5.7 ± 0.3

mean tilt of the molecules ϕ are shown in Table II. It is visible that for high pressures, where the tilt is substantial, the PR is negative. Such a result was expected also for the pressure $p\sigma^2/kT=3.5$. At this pressure the system is close to the transition region^{4,5} (from the tilted to the straight phase) and all the data are clearly affected by relatively large fluctuations. More reliable results would require simulations of larger system. At the lowest pressure the system is in the straight phase, the tilt is zero, and PR is positive. It is worthwhile to note that the ratio of the elastic moduli r at this pressure corresponds to the typical hard-disk value of 1.5.

The above data should represent (within the experimental error and, perhaps, except the pressure $p\sigma^2/kT=3.5$) the ideal 2D HCH crystal in the thermodynamic limit.⁵ Thus, the anomalous behavior of the system at high densities can be thought of as proved. It is now reasonable to ask to what extent this anomaly can be reproduced by simplest theoretical approximations.

III. SIMPLE APPROXIMATIONS

The simplest model worth considering is a lattice model of hexagonal molecules with centers fixed in the triangular lattice sites and "atoms" interacting via an n -inverse-power potential:

$$u(r) = (\sigma/r)^n. \quad (2)$$

For a hard-sphere fcc crystal at the melting density such a model approximates the experimental PR surprisingly well.¹² Presence of the angular degree of freedom in the case of the hexagonal molecules is not a serious obstacle for analytic calculations in the zero-temperature limit, and in this limit the elastic properties of the system can be determined exactly.⁶ The calculated PR depends both on the density and the power n . For $n \rightarrow \infty$ when the interatomic interactions become hard, one obtains a density dependence of the PR for the "static" 2D HCH's. The PR values, as well as r and ϕ obtained in this approximation at densities corresponding to those studied in the MC simulations, are shown in Table II.¹⁹ As easy to note the PR is always positive and rather far from the experimental data. The disagreement between the experiment and theory is also visible in the values of r differing by a factor of order 2.

The above result indicates a rather accidental character of the mentioned agreement between the theory and experiment in the case of hard spheres at melting.¹² Actually, at any density of the fcc crystal, the model predicts the following proportionality: $p:C_{11}:C_{12}:C_{44} = 0.2:1:1$. Hence, the PR's²⁰ calculated within the model are density independent. The experimental results^{11,12} show both (i) a strong deviation from the Cauchy relation (C_{44} more than twice exceeds C_{12}) and (ii) a substantial density dependence of the standard PR (it increases about 50% by changing the relative density from 0.9 down to melting). In spite of the pointed out shortcomings, the model is the simplest one which can reflect some anomalies in the elastic properties of hard spheres (a negative PR at a certain orientation¹² can be obtained at

TABLE II. Comparison of ν_P , r , and ϕ values (i) found from the MC experiment, (ii) calculated for the lattice model (LM), and (iii) obtained from the FV approximation. (The calculated quantities correspond to the experimental relative densities ν/ν_0). The errors of ν_P^{MC} and r^{MC} do not exceed, respectively, 20% and 10% of their values. The errors of ϕ^{MC} concerning the last digit, are given in parentheses. The values of the PR, $\nu_P^{\text{FV},0}$, presented in the last column were calculated assuming that molecular orientations are frozen at the zero tilt (what is equivalent to impose the strain-orientation coupling λ_3 , see Ref. 6, equal zero) to eliminate an orientational instability of the FV model at this orientation.

ν_P^{MC}	r^{MC}	ϕ^{MC}	ν_P^{LM}	r^{LM}	ϕ^{LM}	ν_P^{FV}	r^{FV}	ϕ^{FV}	$\nu_P^{\text{FV},0}$
-0.23	3.3	0.1805(4)	0.235	0.238	0.1848	-0.789	17.07	0.1844	
-0.12	2.7	0.1771(4)	0.240	1.226	0.1833	-0.746	13.88	0.1827	
-0.12	2.7	0.1712(5)	0.247	1.207	0.1807	-0.680	10.70	0.1795	
-0.14	2.9	0.163(1)	0.254	1.192	0.1785	-0.634	9.14	0.1767	
0.10	1.9	0.04(4)	0.263	1.167	0.1742	-0.560	7.39	0.1709	0.023
0.25	1.5	0.000(6)	0.274	1.140	0.1688	-0.485	6.17	0.1627	0.041

finite n) and 2D HCH's (strongly nonconvex static hexamers exhibit a negative PR⁶).

The considered lattice model neglects, by definition, motions of the molecular mass centers. The most natural way to include these motions into consideration, avoiding any sophistication of the theory, is by applying the FV approximation.²¹ Here we restricted calculations to the simplest FV model in which (i) the central molecule moving within the FV cage has the same orientation as the molecules forming the FV cage, (ii) this orientation maximizes the smoothed area available for the center of the moving molecule, and (iii) this smoothing is done by replacing the circle arcs forming its boundaries by segments of straight lines.²² The resulting ν_P , r , and ϕ , at the appropriate densities, are given in the Table II. As could be expected, the quantitative agreement is very poor. However, the negative PR sign is what stays in agreement with the high-density experimental data. At lower densities the approximation gives qualitatively wrong (negative) PR values. This can be easily understood looking at the corresponding (calculated) tilt angles: they are large, which means that the FV system remains in the tilted phase even at low densities (no mechanism leading to the tilted-straight phase transition is incorporated into the approximation). Fixing the molecular orientations at the zero tilt, characteristic for the straight phase, one obtains qualitatively correct (positive) ν_P 's at these densities (see the last column in Table II). It is worthwhile to note that the FV approximation underestimates ν_P (and overestimates r) in contrast to the static lattice model which overestimates ν_P (underestimates r). It is easy to check that the same is true for hard disks¹⁶ and may be expected to hold for other potentials forming triangular lattice crystals.

The FV results can be improved by considering orientational vibrations of the central particle, e.g., along the lines sketched in Ref. 3(b). However, it seems that the various FV approximations are rather incapable of reproducing elastic properties *quantitatively*, which are well

seen in the case of hard disks²³ and hard spheres (see Ref. 12). Moreover, we are also skeptical concerning possibility of quantitative description of the system by introducing two-particle correlations. A theory in this spirit (second-order cluster variation method) has been proposed by Honda.²⁴ Main imperfections of this theory can be summarized as follows: (i) the crystal (meta-)stability region obtained in the theory^{24(b),24(c)} is narrower than the stability region determined in computer experiments,²⁵ and (ii) in the 2D single-occupancy case the theory predicts a strongly first-order phase transition (melting)^{24(b)} which is not observed in the computer simulations.²⁵ As the elastic properties are more sensitive on the theoretical approximations than the equation of state, the mentioned failures seem to discredit low-order cluster variation methods. Finally, it is an interesting question whether any present theory can describe quantitatively the anomalous elastic properties of the 2D HCH's.

IV. SUMMARY

The MC simulation proves a negative PR in the high-density 2D crystal formed by slightly nonspherical hard cyclic hexamers. The phenomenon can be qualitatively reproduced by a simple free-volume approximation. The system we considered is the first known nonzero temperature example, isotropic within the second-order elasticity, showing the PR sign anomaly. The FV approximation, the simple static model,⁶ and the present MC study indicate the crucial role of the nonconvex molecular shape which leads to mirror symmetry breaking in the tilted phase. These considerations can be a starting point to search for real systems of such a property.

It is an interesting, but still open problem, whether any 3D nonconvex molecular shape (forming a 3D solid) may lead to an isotropic 3D system with a negative Poisson ratio. It seems highly improbable that any periodic structure might exhibit such a property because no crys-

talline lattice in 3D is elastically isotropic.² However, as suggested recently,²⁶ nonspherical molecules may form thermodynamically stable nonperiodic solid structures. If elastically isotropic, such structures might be the solution of the problem.

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- ¹⁷The only difference was the presence of the orientational degree of freedom; its maximal changes (in rad) were equal to maximal translational changes of a single component of the molecular mass center (see Ref. 4).
- ¹⁸The Landau-Lifshitz notation (see the Ref. 2) is used. The symbols λ_1 and λ_2 used in Ref. 16 are reserved for the elastic moduli at fixed molecular orientation (compare to Ref. 6).
- ¹⁹The elastic constants of the model tend to zero with $n \rightarrow \infty$ and only their ratio is a nonzero quantity which can be compared with experiment.
- ²⁰As the fcc crystal is not isotropic in the second-order elasticity, its PR depends on the direction of the applied stress and the transverse direction chosen. In a standard definition of the PR in this structure both the directions are parallel to the fourfold symmetry axes.
- ²¹See, e.g., J. A. Barker, *Lattice Theories of the Liquid State* (MacMillan, New York, 1963).
- ²²The lines are tangent to the circles (generated by the atom-atom interaction) in points closest to the lattice position of the central molecule.
- ²³Various versions of the FV approximation applied to the hard-disk system describe reasonably well the compressibility modulus but fail in predicting the shear modulus. This can be explained using the expansion by F. H. Stillinger and Z. W. Salsburg, *J. Chem. Phys.* **46**, 3962 (1967): the compressibility is determined by the first (single-particle) cluster whereas higher (many-particle) clusters contribute to the shear modulus.
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