

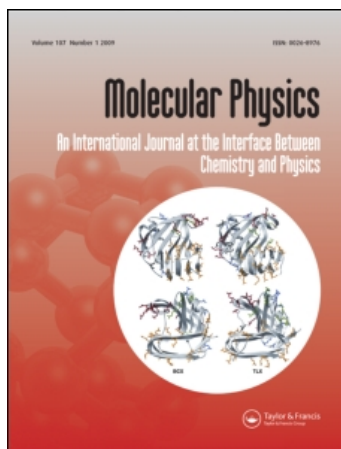
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Constant thermodynamic tension Monte Carlo studies of elastic properties of a two-dimensional system of hard cyclic hexamers†

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A constant thermodynamic tension Monte Carlo method is introduced and applied studies of the elastic properties of a two-dimensional system of hard cyclic hexamers. Elastic compliances and elastic constants are determined at a number of different values of the pressure. The existence of the phase transition between a tilted and a straight phase is confirmed. The results obtained strongly suggest that the Poisson modulus can be negative in the tilted phase.

1. Introduction

In the last few years significant progress in the field of computer simulations has been made, Andersen introduced a molecular dynamics (MD) method allowing the cubic volume of MD cell to vary at constant pressure and/or temperature [1]. This method, useful in studies of liquids, generates the isobaric-isoenthalpic ensemble in place of the microcanonical one, generated by conventional MD. Parrinello and Rahman generalized this method to an arbitrary cell varying both in its volume and shape. Their method allows one to study not only systems under a hydrostatic pressure [2] but also under an anisotropic stress [3-5]. Nosé and Klein extended constant pressure MD with variable shape to molecules [6, 7]. The next step forward was made by Nosé, who introduced a new constant temperature MD [8-10], generating canonical and isobaric-isothermal ensembles. Ray and Rahman have combined his method with a modified Parrinello-Rahman method [11, 12] in which the thermodynamic tension replaces the stress.

Apart from many advantages, MD methods with constant pressure or tension display a fundamental limitation: they cannot be used to study discontinuous potentials. Although it is generally recognized that real physical systems interact via continuous potentials, still a large class of interesting and important models, like the hard core models [13-16], are defined in terms of discontinuous potentials. In such cases constant pressure [17-19] or tension (stress [20]) Monte Carlo (MC) methods are attractive since they do not require any microscopic definition of pressure or tension (stress). In these MC methods the size and shape of the box is also allowed to vary under condition of constant thermodynamic pressure and/or tension. In the

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present paper the constant thermodynamic tension MC method with variable box shape is applied to the study of the elastic properties and phase transformations of the two-dimensional (2D) system of hard cyclic hexamers (HCH).

The HCH system is interesting for a number of reasons: it can be considered as a very crude model for benzene molecules adsorbed on a surface; the existence of structures with different orientational order in the solid density range found in previous studies [21, 22, 18], make it a very simple 2D model of a plastic crystal; its high density phase seems to show long-range orientational order which is uncommon in continuous 2D systems [23, 24]. The HCH molecule of figure 1 consists of six hard discs (atoms) of diameter $\sigma = 1$, located at vertices of a regular hexagon of

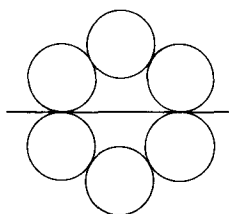


Figure 1. Geometry of a hard cyclic hexamer. The straight line indicates the molecular axis.

side σ . At high densities the molecules form a so-called tilted phase, in which their centres of mass vibrate around sites of a hexagonal lattice and their axes librate around directions slightly rotated with respect to crystal axes. The molecular axis is defined here as the line joining the molecular centre of mass and the contact point of neighbouring discs (see figure 1). When the relative area parameter d , which is the ratio of the actual area to the area of the system at close packing, exceeds a particular value, the system transforms to the straight phase: the lattice of the centres of mass remains hexagonal but the mean directions of molecular axes are now aligned with the crystal axes. Apart from vibrational and librational motions molecules undergo jump-like reorientations of $\sim \pi/3$ [21]. MC simulations [18] showed that this transformation takes place in the range $1.16 < d < 1.19$ and appears to be first-order, in surprisingly good agreement with a free volume approximation [22]. Mechanical simulations (MS) located the transition range at lower relative areas [21, 22]. This discrepancy can be explained by: the effective weakening of the hard potential in a MS caused by the small vertical motions of molecules, and the influence of the hard hexagonal box, used in the MS, which favours the straight phase. As d is increased the frequency of orientational jumps and the molecular motions become increasingly similar to those of a free rotator. Single particle density profiles observed by the MS in the straight phase showed clearly six-fold orientational symmetry (in agreement with MC experiments) at $d \lesssim 1.28$, whereas at $d \gtrsim 1.35$ their symmetry was practically isotropic. This suggested a second possible transition: from the straight to a rotator phase. Detailed MC investigations of the orientational singlet distribution function (OSDF) showed [18], however, that even at $d \gtrsim 1.35$ it displays a maximum for the molecular axes parallel to the crystalline ones. In spite of this, the existence of a 'rotator' phase cannot be ruled out [18].

2. Generalities

Let the homogeneous transformation of a crystal from an initial configuration \mathbf{X} of volume V_0 to a final configuration \mathbf{x} of volume V define the strain tensor $\boldsymbol{\varepsilon}$

$$\varepsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial X_j} + \frac{\partial u_j}{\partial X_i} + \frac{\partial u_k}{\partial X_i} \frac{\partial u_k}{\partial X_j} \right), \quad (1)$$

where \mathbf{u} is the displacement vector equal to

$$u_i = x_i - X_i, \quad (2)$$

and the Einstein convention is used for the summation of indices throughout the paper. In view of the rotational and translational invariance, the free energy $F(\mathbf{x})$ at the configuration \mathbf{x} depends only on the initial configuration \mathbf{X} and the strain tensor $\boldsymbol{\varepsilon}$. For small strains $F(\mathbf{x})$ can be expanded in a series [25]

$$F(\mathbf{x}) = F(\mathbf{X}; \boldsymbol{\varepsilon}) = F(\mathbf{X}) + V_0 \sigma_{ij}(\mathbf{X}) \varepsilon_{ij} + \frac{V_0}{2} C_{ijkl}(\mathbf{X}) \varepsilon_{ij} \varepsilon_{kl}, \quad (3)$$

where $\sigma_{ij}(\mathbf{X})$ is the stress tensor at \mathbf{X} and $C_{ijkl}(\mathbf{X})$ is the isothermal tensor of the elastic constants at \mathbf{X} . Terms containing $\boldsymbol{\varepsilon}$ with powers higher than two are neglected. The stress and the elastic constants at the configuration \mathbf{X} can be easily obtained from (3) as

$$\sigma_{ij}(\mathbf{X}) = \frac{1}{V_0} \frac{\partial}{\partial \varepsilon_{ij}} F(\mathbf{X}; \boldsymbol{\varepsilon}) \Big|_{\mathbf{x}}, \quad (4a)$$

$$C_{ijkl}(\mathbf{X}) = \frac{1}{V_0} \frac{\partial^2}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} F(\mathbf{X}; \boldsymbol{\varepsilon}) \Big|_{\mathbf{x}}. \quad (4b)$$

The subscript \mathbf{X} on the right means that the derivative is taken at \mathbf{X} (i.e. at $\boldsymbol{\varepsilon} = 0$). For large strains the quantity thermodynamically conjugated to the strain (referred to \mathbf{X}) is, however, not the stress but the thermodynamic tension [26]

$$\begin{aligned} t_{ij}(\mathbf{x}) &= \frac{1}{V_0} \frac{\partial}{\partial \varepsilon_{ij}} F(\mathbf{X}; \boldsymbol{\varepsilon}) \Big|_{\mathbf{x}} \\ &= \frac{1}{V_0} \frac{\partial \eta_{rs}}{\partial \varepsilon_{ij}} \frac{\partial}{\partial \eta_{rs}} F(\mathbf{x}; \boldsymbol{\eta}) \Big|_{\mathbf{x}} \\ &= \frac{V}{V_0} \frac{\partial X_r}{\partial x_i} \frac{\partial X_s}{\partial x_j} \sigma_{rs}(\mathbf{x}). \end{aligned} \quad (5a)$$

where \mathbf{x} under the bars indicate that derivatives are taken at \mathbf{x} , $\boldsymbol{\eta}$ is the strain referred to \mathbf{x} , and $\boldsymbol{\sigma}(\mathbf{x})$ is the stress at \mathbf{x} . At the initial (reference) state the thermodynamic tension coincides with the stress. It is easy to see that

$$\frac{\partial t_{ij}}{\partial \varepsilon_{kl}} \Big|_{\mathbf{x}} = C_{ijkl}(\mathbf{X}). \quad (5b)$$

Since our present interests are limited to a two-dimensional crystal of hexagonal symmetry under the isotropic pressure

$$\sigma_{ij} = -p \delta_{ij} \quad (6)$$

we give a number of formulae valid for this particular case. The free energy change, corresponding to the strain ϵ , reduces to [27]

$$\Delta F = F(\mathbf{x}) - F(\mathbf{X}) = V_0 \{ -p(\epsilon_{xx} + \epsilon_{yy}) + 2\lambda_1(\epsilon_{xx} + \epsilon_{yy})^2 + \lambda_2[(\epsilon_{xx} - \epsilon_{yy})^2 + 4\epsilon_{xy}^2] \}, \quad (7)$$

which leads to the following equalities:

$$\left. \begin{aligned} C_{11} &= C_{xxxx} = C_{yyyy} = 2(2\lambda_1 + \lambda_2), \\ C_{12} &= C_{xxyy} = C_{yyxx} = 2(2\lambda_1 - \lambda_2), \\ C_{66} &= C_{xyxy} = C_{xyyx} = C_{yxxy} = C_{yxyx} = 2\lambda_2. \end{aligned} \right\} \quad (8)$$

Combining (8) with (7) and using the definition of the thermodynamic tension one obtains

$$\left. \begin{aligned} t_{xx} &= -p + C_{11}\epsilon_{xx} + C_{12}\epsilon_{yy}, \\ t_{yy} &= -p + C_{12}\epsilon_{xx} + C_{11}\epsilon_{yy}, \\ t_{xy} &= 2C_{66}\epsilon_{xy}. \end{aligned} \right\} \quad (9)$$

The factor 2 (not 4, as would follow from the derivative of ΔF with respect to ϵ_{xy}) comes from the equality $\epsilon_{xy} = \epsilon_{yx}$ included explicitly in (7). Inverting (9) we obtain

$$\left. \begin{aligned} \epsilon_{xx} &= S_{11}\tau_{xx} + S_{12}\tau_{yy}, \\ \epsilon_{yy} &= S_{12}\tau_{xx} + S_{11}\tau_{yy}, \\ \epsilon_{xy} &= \frac{1}{2}S_{66}\tau_{xy}, \end{aligned} \right\} \quad (10)$$

where

$$\left. \begin{aligned} \tau_{ij} &= t_{ij} - (-p\delta_{ij}) = t_{ij} + p\delta_{ij}, \\ S_{11} &= C_{11}(C_{11}^2 - C_{12}^2)^{-1} = \frac{1}{16\lambda_1} + \frac{1}{8\lambda_2}, \\ S_{12} &= -C_{11}(C_{11}^2 - C_{12}^2)^{-1} = \frac{1}{16\lambda_1} - \frac{1}{8\lambda_2}, \\ S_{66} &= \frac{1}{C_{66}} = \frac{1}{2\lambda_2}. \end{aligned} \right\} \quad (11)$$

Using (10), (11) and (5a) for $\Delta\sigma_{ij} = -\Delta p\delta_{ij}$ we obtain

$$\epsilon_{xx} + \epsilon_{yy} = \frac{1}{8\lambda_1}(\tau_{xx} + \tau_{yy}) = -\frac{1}{8\lambda_1}\Delta p \frac{V}{V_0} \frac{\partial X_i}{\partial x_j} \frac{\partial X_i}{\partial x_j}. \quad (12)$$

Noting that

$$\frac{V}{V_0} = \det \left[\frac{\partial x_i}{\partial X_j} \right] \cong 1 + \epsilon_{ii} \quad (13)$$

(12) becomes

$$\frac{\Delta V}{V_0} = -\frac{\Delta p}{8\lambda_1} (1 + \epsilon_{ii}) \left(\frac{1}{1 + 2\epsilon_{xx}} + \frac{1}{1 + 2\epsilon_{yy}} \right) = -\frac{\Delta p}{4\lambda_1}. \quad (14)$$

which gives an expression for the isothermal compressibility, K_T ,

$$K_T = - \lim_{\Delta p \rightarrow 0} \frac{1}{V} \frac{\Delta V}{\Delta p} = \frac{1}{4\lambda_1}. \quad (15)$$

The results presented above can be summarized as follows. The elastic properties of a crystal of hexagonal symmetry under an isotropic pressure can be described (in linear elasticity) by two independent parameters (denoted here by λ_1, λ_2) and the pressure p .

3. Computational details

N HCH molecules are contained in a periodic box of sides **a** and **b**. These vectors can be regarded as columns of a 2×2 matrix **h**. The area of the cell is equal

$$V = \det \mathbf{h}. \quad (16)$$

The position \mathbf{r}_i of a particle $i = 1, \dots, N$ can be written in terms of the components $-\frac{1}{2} \leq \xi_i, \eta_i < \frac{1}{2}$ of a vector \mathbf{s}_i

$$\mathbf{r}_i = \mathbf{h} \cdot \mathbf{s}_i. \quad (17)$$

Components of images of particle i differ by integers in ξ_i, η_i . Molecular orientation is described by an angle $-\pi/6 \leq \varphi_i < \pi/6$ between a (fixed orientation) and a proper molecular axis. The other computational details are identical to those described in [18].

The total energy of the system under an external thermodynamic tension **t** is equal [28]

$$W_t = U - V_0 \text{Tr}(\mathbf{t} \cdot \boldsymbol{\varepsilon}), \quad (18)$$

where V_0 is the volume of a reference state defined by \mathbf{h}_0 , U represents the total potential energy of the system, and $\boldsymbol{\varepsilon}$ is the strain tensor

$$\boldsymbol{\varepsilon} = \frac{1}{2}(\mathbf{h}_0'^{-1} \mathbf{h}' \mathbf{h} \mathbf{h}_0^{-1} - \mathbf{I}); \quad (19)$$

the prime denotes the transpose of a matrix.

The choice of the reference state requires some attention. Usually it is chosen [26, 11, 12] as a state with zero stress. In such a case the free energy expansion (3) does not contain terms linear in the strain. However, in the case of purely repulsive potential there is no stable finite volume state at zero stress. Any choice of the reference state of a required symmetry seems to be as good as any other. It is to be noted that a natural reference state for hard core potentials, a close packed structure, cannot be used here since for this density the behaviour of the system is highly singular and (3) has no meaning.

It follows from (5b) that the elastic constants at the reference state are just the first derivatives of the tension components with respect to the strain components at zero strain. Thus, the most convenient way to obtain elastic constants at a given state is to choose it as the reference state. Since we are interested in elastic properties at certain values of pressure we will define the reference state for any pressure by the \mathbf{h}_0 -matrix equal to the mean value of **h** at this pressure

$$\mathbf{h}_0 = \langle \mathbf{h} \rangle_p. \quad (20)$$

To generate the reference states we used the formula for the energy of a system under an external pressure

$$W_p = U + pV. \quad (21)$$

Consequently, we introduced the thermodynamic tension not in the form (18) but as

$$W = U + pV - V_0 \text{Tr}(\boldsymbol{\tau} \cdot \boldsymbol{\varepsilon}), \quad (22)$$

with $\boldsymbol{\tau} = \mathbf{t} + p\mathbf{I}$ which reduces to (18) for small $\boldsymbol{\varepsilon}$ apart from the constant term V_0 .

Elastic constants can be obtained either by using a fluctuation theorem [4] or by numerical differentiation of the strain-tension isotherm. Here we used the later method which, although marginally more time consuming, gives more information about the system since it provides direct information on the stressed state.

4. Results and discussion

Calculations were performed on systems of $N = 56, 168$ and 504 HCH molecules. Most of the runs were carried out for $N = 168$ and averages were taken, after equilibration, over 9000 MC cycles. The runs for $N = 56$ and 504 lasted (after equilibrium) 18000 and 10800 MC steps per molecule, respectively. Calculations for $N = 504$ were initiated by replicating the equilibrium configuration of the $N = 56$ system.

Three forms of the thermodynamic tension tensor were applied. In uniaxial loading experiments one of the two forms:

$$\boldsymbol{\tau} = \begin{pmatrix} \tau_t & 0 \\ 0 & 0 \end{pmatrix}, \quad \boldsymbol{\tau} = \begin{pmatrix} 0 & 0 \\ 0 & \tau_t \end{pmatrix}, \quad (23)$$

was chosen corresponding, respectively, to a uniaxial loading in the x - and y -direction. In shear experiments, $\boldsymbol{\tau}$ was taken to be

$$\boldsymbol{\tau} = \begin{pmatrix} 0 & \tau_s \\ \tau_s & 0 \end{pmatrix}. \quad (24)$$

As mentioned before, the reference state was specified by a few 'values' of the h_0 -matrix corresponding to the system under a dimensionless hydrostatic pressure, $p\sigma^2/kT$. Values of $p\sigma^2/kT$ equal to 1.3, 1.6, 1.9, 2.3, 2.9, 3.4 and 4.1 were chosen in such a way that each of the three phases, described in the Introduction, is represented by two pressures, and the value 1.9 corresponds to the region of the transition between the straight and rotator phase (providing the transition exists). Since, as shown in previous studies [18] the system under the hydrostatic pressure displays hexagonal symmetry, the reference state in each of the cases under consideration can be defined by

$$\mathbf{h}_0 = \begin{pmatrix} a_0 & 0 \\ 0 & b_0 \end{pmatrix}. \quad (25)$$

The shape of the reference cell was a rectangle whose sides a_0 and b_0 were in the ratio [29]

$$\frac{a_0}{b_0} = \frac{4\sqrt{3}}{7} = 0.9897. \quad (26)$$

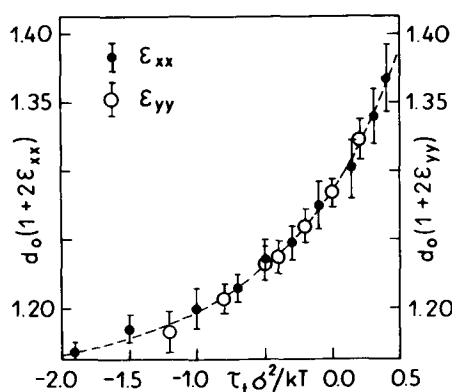


Figure 2. The dependence of the strain components ϵ_{xx} (full dots) and ϵ_{yy} (open circles) on the thermodynamic tension at uniaxial load. τ_t is equal to $p + t_{xx}$ and $p + t_{yy}$ respectively; $p\sigma^2/kT = 1.9$; $N = 168$. The broken line is drawn to guide the eye.

In order to fit a hexagonal crystal in such a MC cell the rows formed by neighbouring molecules were parallel to the x -axis for $N = 168$ and perpendicular to it for $N = 56$ and 504 .

It is convenient to introduce a dimensionless area parameter, d_0 , equal to the ratio of the actual area of the reference state, V_0 , to the area at close packing, V_{cp}

$$d_0 = V_0/V_{cp}. \quad (27)$$

We begin by describing the results obtained at $N = 168$. In figure 2 we present the strain as a function of tension in the case of the uniaxial loading at $p\sigma^2/kT = 1.9$. In agreement with symmetry arguments, the x - and y -direction experiments give the same results, within the experimental error. The isotherms for other pressures look similar, i.e. all of them are convex in the neighbourhood of $\tau_t = 0$ until the limit of stability is reached. At these tensions the shape of the box starts to flow and it is impossible to reach an equilibrium state. For obvious reasons, however, we do not expect that the constant tension MC method in the present form could be used to study conditions of mechanical stability of crystals.

From the $\epsilon_{xx} - \tau_t$ (or $\epsilon_{yy} - \tau_t$) dependence one can determine the strain-thermodynamic tension compliances S_{11} and S_{12} . Since at present there is no theory which quantitatively describes the experimentally obtained isotherms, we used a very simple method to determine the slope of the tangent to a given isotherm at zero tension. Namely, the required quantity was approximated by the mean value of the slopes of the linear regression obtained with a small number of points on the left or on the right the zero tension. Half of the absolute value of the difference between the two slopes was taken a measure of the error. In figure 3 the values of S_{11} determined in this way are plotted against pressure except for the value of $p\sigma^2/kT = 3.4$. At this pressure an anomaly was observed in the vicinity of $\tau_t = 0$ (see figure 4). This precludes the determination of S_{11} (and S_{12}). Analysis of the orientational order of the samples for each of the data points revealed that full dots were in the tilted phase while the open circles were in the straight one, indicating the occurrence of a tension induced phase transition.

Looking carefully at S_{11} as a function of $p\sigma^2/kT$ in figure 3, we can see a slight anomaly in the vicinity of $p\sigma^2/kT = 1.9$. In view of the limited number of experimental points and relatively large errors we cannot make firm conclusions on the

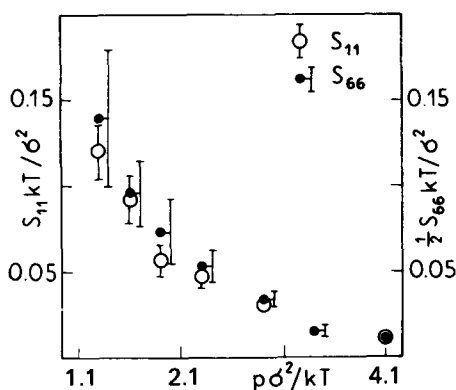


Figure 3. The strain-thermodynamic tension compliances S_{11} (open circles) and S_{66} (full dots) at a few values of $p\sigma^2/kT$. $N = 168$.

existence of a rotator phase. Furthermore, the compliance S_{66} , presented in the same figure, does not show any disturbances in the neighbourhood of this particular pressure. In contrast, S_{66} displays an anomaly in the range of $2.9 < p\sigma^2/k_B T < 3.4$, where the transition between the tilted and the straight phase occurs [18].

The absolute values of the compliance S_{12} are much smaller than S_{11} and S_{66} . In agreement with [11] they fulfil, with the estimated error, the relation

$$S_{12} = S_{11} - \frac{1}{2}S_{66}. \quad (28)$$

In almost all cases the values of S_{12} are negative, which means transverse dimensions will decrease (increase) upon application of a tensile (compressive) load which is the normal behaviour. However, at $p\sigma^2/kT = 4.1$, which corresponds to the tilted phase, the determined compliance, $S_{12} = 0.0019 \pm 0.0011$, is positive. Thus, at this value of pressure the system should behave in a different way: subjected to a tensile (compressive) uniaxial load it should increase (decrease) its transverse dimensions. If it were true, it would be the first known example [27] of a system with a negative value of the Poisson modulus. In the tilted phase, the tilt of molecules increases when the mean distance between them is reduced. Thus, if by an application of a

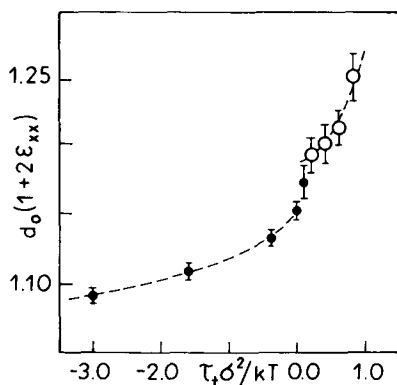


Figure 4. The $\varepsilon_{xx} - \tau_i$ isotherm at $p\sigma^2/kT = 3.4$ indicating the phase transition between the tilted phase (full dots) and the straight phase (open circles). The broken line is drawn to guide the eye.

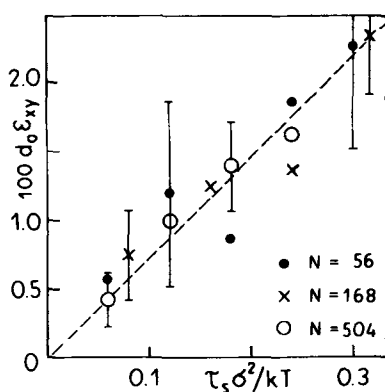


Figure 5. The dependence of the strain component ε_{xy} on the thermodynamic tension component $t_{xy} = \tau_s$ at shear for three different sizes of the system: $N = 56$ (full dots), $N = 168$ (crosses) and $N = 504$ (open circles). $p\sigma^2/kT = 2.3$. The broken line represents a linear fit obtained (in a wider range of τ_s) for $N = 168$.

uniaxial compressive load along one of the molecular axes the mean distance between molecules is reduced along this axis, the tilt increases and, consequently, the mean distances along other molecular axes decrease, which results in a decrease of transverse dimensions of a sample. Similar argument can be applied to a tensile load.

The experimentally determined compliances S_{11} and S_{66} enable one to calculate the quantities λ_1 and λ_2 . The latter can be obtained directly from S_{66} and then, substituted to S_{11} , to give λ_1 (see formulae [11]). One can compare the values of λ_1 obtained in this manner with those calculated from the isothermal compressibility (15) determined from the pressure-volume isotherms. Since, however, S_{66} is affected by a large error which is magnified in λ_1 , we applied a different method of comparison: the quantities $\lambda_2^{(6)}$ calculated from S_{66} were compared with $\lambda_2^{(6)}$ obtained from S_{11} and the isothermal compressibility K_T . The table shows that the differences do not exceed the combined experimental errors.

To check whether the obtained results depend on the size of the system a few runs were performed with $N = 56$ and $N = 504$ at $p\sigma^2/kT = 2.3$. In figures 5 and 6

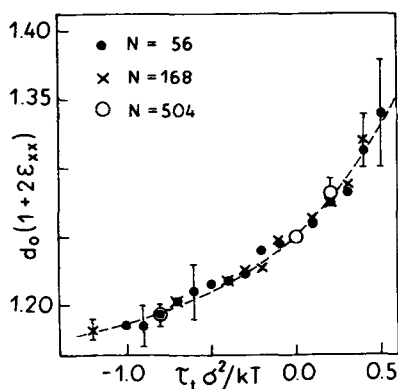


Figure 6. The dependence of the strain component ε_{xx} on the thermodynamic tension at uniaxial load. $\tau_t = p + t_{xx}$; other parameters the same as in figure 5. The broken line is drawn to guide the eye.

Elastic compliances and elastic constant λ_2 (determined by the two methods described in text) for the 2D-HCH-system at a number of pressures. $N = 168$.

$p\sigma^2/kT$	V/V_{cp}^\dagger	$K_1 kT/\sigma^2 \ddagger$	$S_{11} kT/\sigma^2$	$S_{12} kT/\sigma^2$	$\frac{1}{2} S_{66} kT/\sigma^2$	$kT/\sigma^2 \lambda_2^{(s)}$	$kT/\sigma^2 \lambda_2^{(u)}$
1.3	1.372	0.158	0.120 ± 0.017	-0.030 ± 0.014	0.140 ± 0.040	0.56 ± 0.16	0.64 ± 0.08
1.6	1.321	0.108	0.091 ± 0.130	-0.020 ± 0.010	0.096 ± 0.019	0.38 ± 0.08	0.51 ± 0.06
1.9	1.285	0.078	0.057 ± 0.009	-0.016 ± 0.006	0.073 ± 0.018	0.29 ± 0.07	0.30 ± 0.04
2.3	1.246	0.057	0.047 ± 0.006	-0.014 ± 0.009	0.054 ± 0.009	0.21 ± 0.04	0.26 ± 0.03
2.9	1.210	0.041	0.031 ± 0.004	-0.005 ± 0.004	0.033 ± 0.004	0.132 ± 0.016	0.16 ± 0.02
3.4	1.159	0.039	—	—	0.016 ± 0.003	0.064 ± 0.012	—
4.1	1.129	0.027	0.0124 ± 0.0019	0.0019 ± 0.0011	0.011 ± 0.002	0.044 ± 0.008	0.045 ± 0.017

† Values of the relative area are taken from the previous studies [18]; errors do not exceed 1 per cent.

‡ Values of the isothermal compressibility are taken from [18]; errors do not exceed 5 per cent.

the uniaxial loading and shear isotherms are presented for each of the three systems studied. Within the estimated error the isotherms do not depend on N . We expect that our results should be valid for the non-defective crystal in the thermodynamic limit.

5. Summary and conclusions

The constant thermodynamic tension MC method with variable-shape cell was applied to study elastic properties of the 2D-HCH-system. The strain-thermodynamic tension compliances were determined from the isotherms corresponding to uniaxial loading and shear experiments. It was found that, as required by the symmetry, the compliances obey the relation $S_{11} + S_{12} = \frac{1}{2}S_{66}$. This proves that the method is self-consistent. To test its consistency with other methods elastic constants were determined at a number of pressures. Results obtained by the present method and by the constant pressure MC method with variable cell were the same within experimental error. No dependence of the results on N was observed at $N \geq 56$ and $p\sigma^2/kT = 2.3$, which suggests that the results obtained at $N = 168$ may be considered valid in the thermodynamic limit for a non-defective HCH crystal.

The anomaly visible in the pressure dependence of the compliance S_{66} confirms the existence of the transition from the tilted to the straight phase. This transition is visible also in the isotherm obtained by uniaxial loading at $p\sigma^2/kT = 3.4$. The existence of the second, straight to rotator, phase transition remains an open question.

At high density corresponding to $p\sigma^2/kT = 4.1$ the value of S_{12} was found to be positive, which corresponds to a negative Poisson modulus. If it is not an artifact, caused by approximations used in computation procedure, the HCH system is the first known example of a system displaying this unusual property [27]. Some real molecular crystals could display this property.

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- [28] For non-Bravais lattices the usual thermodynamic formalism for elasticity has been generalized to describe the internal degrees of freedom of the unit cell (see, e.g., BARRON, T. H. K., GIBBONS, T. G., and MUNN, R. W., 1971, *J. Phys. C*, **4**, 2805). When, as in the present case, only the zero internal thermodynamic tension is applied, the equilibrium values of the unit cell internal degrees of freedom are completely determined by the external thermodynamic tension and the standard description can be applied.
- [29] A square shape of the periodic box minimizes the influence of the boundary condition. This influence can be overwhelming for non-square boxes (see, e.g., WOJCIECHOWSKI, K. W., PIERAŃSKI, P., and MALECKI, J., 1983, *J. Phys. A*, **16**, 2197).