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INVESTIGATION OF NEMATIC-ISOTROPIC PHASE TRANSITION IN LIQUID CRYSTALS BY MONTE CARLO SIMULATIONS OF LATTICE MODELS

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Дослідження фазового переходу нематик-ізотропна рідина в рідких кристалах шляхом комп'ютерного експерименту на граткових моделях

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Анотація. Запропоновано граткову модель із видовжених молекул, які взаємодіють між собою за допомогою потенціалу Берне-Печукаса. За допомогою моделювання методом Монте Карло досліджено поведінку внутрішньої енергії, теплоємності та скалярного параметру впорядкування в околі переходу нематик-ізотропна (НІ) система. Показано, що при зростанні видовження молекул НІ перехід стає сильнішим переходом першого роду. Результати порівнюються із іншими даними комп'ютерного моделювання та з експериментом. Показано, що поведінка багатьох нематиків в околі НІ переходу може бути описана запропонованою моделлю із відносним видовженням молекул від 3 до 5.

Investigation of nematic-isotropic phase transition in liquid crystals by Monte Carlo simulations of lattice models

Ja.M.Ilnytskyi

Abstract. The lattice model of the elongated molecules interacting via the Berne-Pechukas potential is proposed. The Monte Carlo simulations of such a system is performed in the vicinity of the nematic-isotropic (NI) transition. The internal energy, heat capacity and scalar order parameter near transition are investigated. It is shown that for more elongated molecules NI transition becomes of more strong first order. The results are compared both with the results of other computer simulations and with the experiment. It is shown that the behaviour of many nematics in the vicinity of NI transition can be described by proposed model with the elongation ratio of molecules from 3 to 5.

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1. Introduction

Many molecular fluids consisting of anisometric molecules have one or several liquid crystalline phases [1]. The simplest among these phases is the nematic one (it appears in nematogenic liquid crystals) characterized by long range orientational and short range translational order. In the case of thermotropic nematogens it can be observed below the isotropic liquid phase. With the increase of temperature the nematic to isotropic (NI) transition takes place [1].

To favour orientational ordering the intermolecular interactions in nematogens have to be sufficiently anisotropic. In general they consist of both long-ranged anisotropic interactions and short-ranged repulsive ones, which complicates theoretical description of such systems. Maier-Saupe theory [2] gives the mean-field description of NI transition considering each molecule to be placed in the mean field of all others. Only long-ranged interactions are taken into account. This theory predicts that NI transition is of first order, but overestimates essentially the order parameter at transition and its latent heat as compared to the experiment. Mean-field theory with both energetic and steric effects [3,4], two particle [5] and four particle [6] cluster expansions were developed to describe NI transition too. These theoretical approaches do not include any details of the intermolecular interaction and thus are not able to describe wide variety of real nematogens. On the other side Onsager theory for NI transition describes the system of long thin hard rods [7] taking into account only pure steric effects of excluded volume. This theory gives very strong density driven first order NI transition. Landau-de Gennes phenomenological theory of NI transition [1,8] starts from the expansion of free energy in powers of order parameter and contains a few phenomenological parameters which can be fitted with the experiment. It predicts the order of transition due to symmetry considerations, estimates pretransitional behaviour of the pair correlations and other properties [8].

The great progress in identifying the microscopic nature of phases in liquid crystals was achieved by computer simulations which have been initiated for these systems more than 20 years ago. There are several approaches in providing computer simulations concerning NI transition. First one is the Monte Carlo (MC) study of the lattice version of Maier-Saupe model (called then as Lebwohl-Lasher model) performed by the different groups [9–14]. Molecular dynamics study of this model was also performed [15]. A MC study in which the restriction to lattice sites is removed and a scalar component added to the anisotropic potential has been done [16]. This approach consider NI transition as temperature

driven one and gives the behaviour of internal energy, heat capacity, and scalar order parameter (referred further as order parameter) in the vicinity of transition point, as well as pretransitional properties of pair correlations. The soft potential used in these simulations does not include the details of molecular shape which can be important at the typical densities in real nematics.

The second approach includes MC and molecular dynamics study of relatively dense systems of hard particles with strong short-ranged repulsive intermolecular interactions: for example the system of hard spherocylinders [17,18] spheroids [19,20], thin hard platelets [21] and of other shape (see [22]). Phase diagram includes in some cases both nematic and smectic phases, and NI transition is interpreted as density driven one. The molecules shape plays in this approach dominant role.

Other approaches are connected with the simulations of systems with more realistic intermolecular potentials like potential with dispersion forces [23], Berne-Pechukas [24–26] and Gay-Berne [27] potentials. The last one seemed to be the most realistic for description of liquids with elongated molecules and is used in many recent simulations. Adjustable parameters in this potential can be fitted to describe real intermolecular interaction in given mesogen. The phase diagram for Gay-Berne liquid of 256 particles was investigated by means of molecular dynamics simulations in wide range of temperatures [28]. Phases were identified by using computer graphics to vizualize configurations. System possesses an isotropic, nematic, smectic A, smectic B and a crystal phase. Phase diagram of the similar system was also investigated in [29] using molecular dynamics simulations in NVT ensemble. The isotropic liquid, nematic and smectic B phases were identified. The temperature stability of nematic phase is investigated. These simulations suggest that the anisotropic attractive interactions play a crucial role in the formation of smectic B phase. The adjustable parameters of Gay-Berne potential were fitted for the case of *p-terphenyl* and molecular dynamics study of 256 molecules was performed in [30]. Isotropic, nematic and smectic A phases observed. Model parameters for *p-azoxyanisole* (PAA) were adjusted in [31] and again molecular dynamic study of 256 molecules is done. The temperature dependencies of rotational and shear viscosities are in a good agreement with the experimental data. Other bibliography on related subjects can be find in corresponding literature [1,32–34].

We will concentrate our attention on results obtained by computer simulations of Lebwohl-Lasher (LL) model which is the system of anisosymmetric molecules confined to the sites of simple cubic lattice and interacting via the simple anisotropic potential of Maier-Saupe type.

Hamiltonian of the model is written in the form [9]:

$$H = -\epsilon \sum_{<ij>} P_2(\cos\theta_{ij}), \qquad (1)$$

where the sum includes all pairs $< i, j >$ of nearest neighbours, θ_{ij} is the angle between long axes of i-th and j-th molecule, ϵ is the maximum interaction energy, and $P_2(x)$ is the second Legendre polinomial. This model was firstly proposed by Lebwohl and Lasher [9] to obtain more exact MC simulations as compared to mean-field approximation of [2]. It was shown by the authors that transition is definitely of first order, as well as estimations for transition temperature T_{NI}, order parameter in nematic phase at transition temperature S_{NI} and latent heat were obtained. Then this model was subsequently studied in greater detail by Jansen, Vertogen and Ypma [10]. These autors stated two aims: firstly, to improve the accuracy of the calculations, and secondly, to calculate the magnetically induced birefringence and the scattering of light by orientational fluctuations in the isotropic phase. Then LL model was revisited by Luckhurst and Simpson [11] to get more accurate data for internal energy, heat capacity and latent heat at the transition, as well as transition tempetature T_{NI}. MC data obtained by authors was extensively compared with results obtained within the cluster theories and with experimental data on real nematics. Molecular dynamics study of LL model was performed by Zannoni and Guerra [15]. MC data obtained from simulation of LL model were essentially reestimated by Fabbri and Zannoni [12]. The larger lattice of (30^3) molecules was simulated and the number of simulation runs was significantly higher than in previous simulations. This allowed to get more precise estimates for transition temperature T_{NI} as well as for order parameters $< P_2 > \equiv S$, $< P_4 >$, internal energy and heat capacity in transition region. Particular attention has been devoted to pair correlations $G_2(r)$, $G_4(r)$. The difference between T_{NI} and isotropic phase limiting instability temperature T^* was obtained with the good accuracy and agree well with the experiments on real nematics.

Lebwohl-Lasher model was revisited again by Zhang, Mouritsen and Zuckermann [13] using modern numerical techniques of analyzing phase transitions. The finite-size scaling analysis proposed by Lee and Kosterlitz [35] and Ferrenberg-Swendsen reweighting technique [36] were used. Unambiguos numerical evidence is found in favour of a weak first order transition and the presence of pseudospinodal points T^*, T^{**} which are extremely close to T_{NI}. Estimate for T_{NI} coincides with one from [12], and value for transition entalpy is in satisfactory agreement with experimental data on *octylcyanobiphenyl* (8CB) [37]. Pseusospinodal points T^*, T^{**} are located from the form of free energy as the function of order parameter with two minima in the transition region. Correlation functions for the order parameter fluctuations for the temperatures just above the transition are investigated by Greeff and Lee [14]. At those temperatures for which the distribution of order parameter fluctuations is Gaussian, inverse susceptibility is found to follow Landau theory behaviour, being proportional to $(T - T^*)$. The value for T^* is close to one from [12].

Despite the limited realibility of LL model (in fact it interpretates NI transition as a rotational order-disorder transition in an effective crystalline solid) it plays role of canonical model of a system which displays an orientational phase transition like an Ising model for order-disorder phenomena in alloys and magnetic systems. To bring more physics into LL model one has to replace the simple anisotropic potential of Maier-Saupe type in (1) by much more relistic one. Such attempt was made, for example, in [23] where the MC simulation of lattice model with anisotropic dispersion forces (being more realistic soft potential) is performed. But in this case it turned to be that NI transition in such model does not differ essentially from the transition in LL model. The order parameter at transition is slightly higher and this produce the larger entropy of the transition but both these values are insensative to varying the relative anisotropy in the polarizability in the system. Althought authors believe these differences to be significant they would emphasize that the transition is blurred by the relatively small ensemble used in the simulations (10^3 particles).

It is evident that increasing of the systems size together with the use of realistic potentials become very time consuming. The most computer simulations on Gay-Berne fluids are simulated on 256 particles [28–31] which system seemed to be too small for investigating phase transitions. For this reason models of the same level of simplicity as LL model seemed to be still useful for investigation of different phase transitions in anisotropic systems. The aim of this report is to modify the simple anisotropic potential of Maier-Saupe type used in LL model by including parameter of molecules elongation. The influence of this factor on phase transitions in hard particles systems is already investigated [22]. We will investigate the influence of this factor in the system of particles interacting via soft potential. This will be done by using the angular part of Berne-Pechukas potential [24] instead of simple anisotropic potential. This potential [24] is the single-site approximation of intermolecular site-site atomic potential between linear molecules and describes the pairwise interaction between two ellipsoids of revolution with given elongation.

The potential of Maier-Saupe type can be reproduced from this potential in the limit of almost spherical molecules. Comparing results of our simulations with experimental data for some nematics in the vicinity of NI transition gives us optimism that LL model modified in such a way gives one the possibility to simulate different real systems closer to their nature.

The outline of this report is as follows. Section 2 contains description of simulation method on pure LL model. We decided to perform our own simulations (despite the great amount of data avaliable in literature) firstly, to test out our procedure on well known model, and, secondly, to remove any method-relative effects in future comparing with simulation of modified LL model with Berne-Pechukas potential. Section 3 contains definition of modified LL model and its simulation for different elongation of molecules according to method described in section 2. The influence of molecules elongation on latent heat and order parameter is discussed. Section 4 contains comparing of our data with the experiments on real nematics. We compare both latent heat, value of order parameter at NI transition and extrapolate temperature dependence of order parameter to get effective index β. This section include the general conclusions too.

2. Monte Carlo simulation of Lebwohl-Lasher model

Here we present the details of Monte Carlo simulations of LL model in the vicinity of NI transition. We consider the system of 20^3 molecules confined in the sites of simple cubic lattice with the periodic boundary conditions. Each i-th molecule is characterized by unit vector $\vec{u}_i$ directed along its long axis. Each direction $\vec{u}_i$ was stored as the set of it's Cartesian coordinates (x_i, y_i, z_i). Pairwise interactions between nearest neighbours are considered to be of the simple anisotropic form (1).

Simulations at each temperature started from perfectly ordered state along OZ axis. Then we allow each molecule to rotate to new direction $\vec{u'}_i$. To satisfy the ergodicity condition we have to move in the phase space of configurations by reasonable steps, so the new direction $\vec{u'}_i$ can be choosen in the following way:

$$\vec{u'}_i = (x'_i, y'_i, z'_i) = \left(\frac{x_i + \delta \cdot p_1}{l_{u'}}, \frac{y_i + \delta \cdot p_2}{l_{u'}}, \frac{z_i + \delta \cdot p_3}{l_{u'}}\right), \qquad (2)$$

where $\delta < 1$ is the restriction parameter, $l_{u'}^2 = (x_i + \delta \cdot p_1)^2 + (y_i + \delta \cdot p_2)^2 + (z_i + \delta \cdot p_3)^2$ stay for normalization of $\vec{u'}_i$, $p_{1,2,3}$ are the pseudorandom numbers from -1 to $+1$, generated by generators [38]:

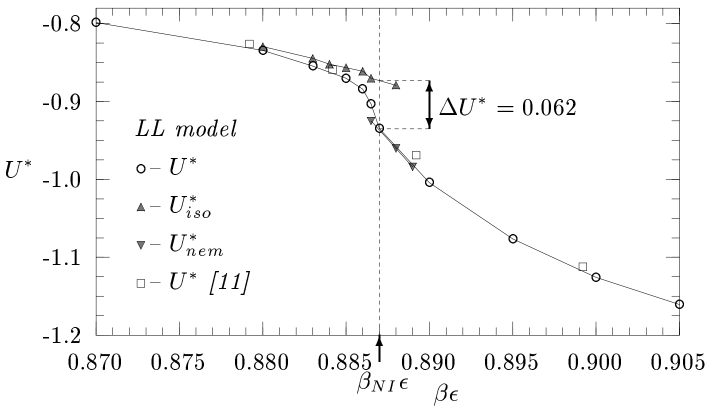

Figure 1: Dimensionless single-molecule internal energy U^* in the vicinity of NI transition for the Lebwohl-Lasher model (open circles – averaged energy, triangles – separated energies of coexisting phases, open squares – data from [11], ΔU^* – dimensionless latent heat).

$$p_{n+1}^{(\mathrm{fl})} = 2.0 \cdot \frac{x_{n+1}^{(\mathrm{fl})}}{m^{(\mathrm{fl})}} - 1.0, \qquad (3)$$

$$x_{n+1}^{(\mathrm{int})} = (a^{(\mathrm{int})} \cdot x_n^{(\mathrm{int})}) \;\&\; m^{(\mathrm{int})}. \qquad (4)$$

Here $a = 16807$, $m = 2^{31} - 1$, index $^{(\mathrm{int})}$ denote 32-bit integer type of variable, index $^{(\mathrm{fl})}$ floating-point type, & is bitwise AND operation between the integers. We use three independent generators of (4) type for each of $p_{1,2,3}$ started from different initial x_0.

The acceptance or rejection of new configuration is considered due to the standard Metropolis algorythm [38]. Restriction parameter δ restricts possible rotation of the molecule during one step and makes it possible to control the acceptance-rejection ratio. The same restriction for the spherical polar angle when working in spherical frame is usually used too [11]. One MC cycle is completed after allowing all molecules to change their orientation. We performed 10^5 cycles for the temperatures close to transition. The data obtained for dimensionless single-molecule internal energy:

$$U^* = \frac{< H >}{N \cdot \epsilon} \qquad (5)$$

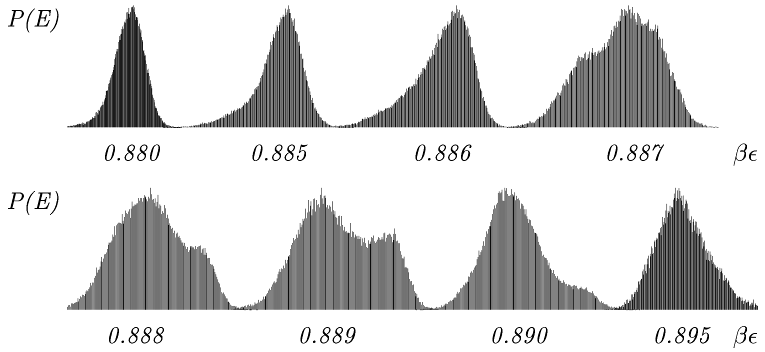

Figure 2: Histograms of internal energy distribution in the vicinity of NI transition for the Lebwohl-Lasher model.

(where H is defined in (1)) are presented in fig.1. Our MC data for U^* coincides well with other ones for the same system size avaliable in literature [11]. Simple statistical averaging used for calculating of U^* in (5) (open circles in fig.1) produces a curve with the change of slope at transition temperature $\beta_{NI}\epsilon$. To find the latent heat of the transition one can use histograms of the energy distribution [12]. In the vicinity of transition these histograms demonstrate a two-hill shapes which indicate the coexistance of isotropic and nematic phases (fig.2). Corresponding cumulants of these distributions were discussed in details previously [12]. We can separate energy values of two phases by estimating maximums of these histograms, which are shown in fig.1 by triangles. Our estimation for latent heat for LL model is $\Delta U = \Delta U^* \varepsilon = 0.062\varepsilon$ in a good agreement with values $\Delta U = 0.1\varepsilon$ [10], $\Delta U = 0.07\varepsilon$ [11] and $\Delta U = 0.05\varepsilon$ [12].

The change of slope for U^* at the transition region leads to the peak in the single-molecule heat capacity c_V (fig.3):

$$c_V^* = \frac{1}{N}\left(\frac{\partial < H >}{\partial T}\right)_V = -(\beta\epsilon)^2\left(\frac{\partial U^*}{\partial(\beta\epsilon)}\right)_V .$$

To find this derivative we used both differentiation of cubic splain interpolation between U^* points with respect to $\beta\epsilon$ [11], and alternatively differentiation of linear interpolation between U^* points. Both methods coincide well and give peak for c_V^* at $\beta_{NI}\epsilon = 0.887$ close enough to results $\beta_{NI}\epsilon = 0.894$ [10], $\beta_{NI}\epsilon = 0.887$ [11], and $\beta_{NI}\epsilon = 0.890$ [12]. It has to be pointed that this procedure is very sensative to accuracy of energy data points, so calculation of c_V^* is useful in general for estimating of transition temperature and is not accurate enough to compare it with the experimental data.

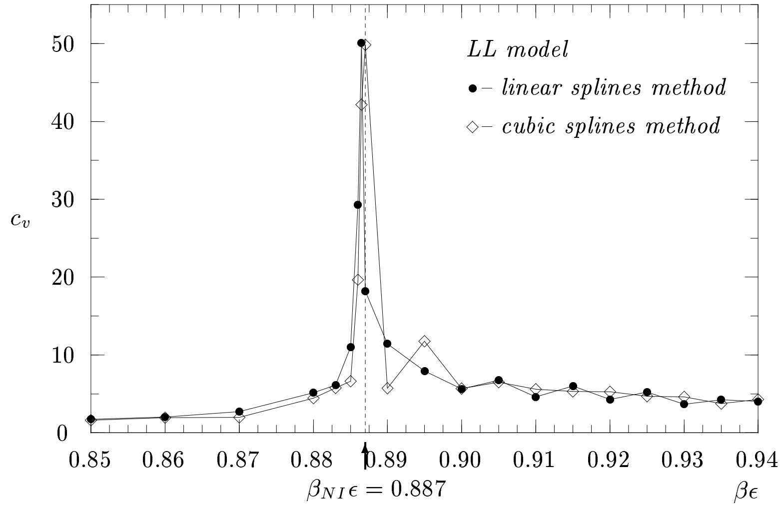

Figure 3: Position of the NI transition temperature from the peak of heat capacity for Lebwohl-Lasher model.

One of the most important aims of MC simulation in LL model is to evaluate scalar order parameter [1]:

$$S \equiv < P_2 > = < P_2(\cos\theta_i) >, \tag{6}$$

where θ_i is the angle between long axis of i-th molecule and director (preferred direction of nematic ordering). As it was pointed in [12] director can fluctuate from one simulation cycle to other, so order parameter is calculated with respect to the instantaneous prefered direction after given cycle. This is normally done [10–12] by the method proposed by Viellard-Baron [17]. According to this method the tensor order parameter [1]

$$S_{ij} = \frac{3}{2}\begin{pmatrix} < x_i^2 > -1/3 & < x_i y_i > & < x_i z_i > \\ < y_i x_i > & < y_i^2 > -1/3 & < y_i z_i > \\ < z_i x_i > & < z_i y_i > & < z_i^2 > -1/3 \end{pmatrix} \tag{7}$$

is calculated after each MC cycle and its eigenvalues λ_i are found. Diagonalization of S_{ij} corresponds to switching from laboratory frame to the director frame. The largest eigenvalue of S_{ij} gives the scalar order parameter

$$S = \max(\lambda_i).$$

Evaluation of S during simulations shows dramatic increasing of its fluctuations in the transition region. Typical behaviour of S as the function of Monte Carlo cycles at $\beta\epsilon = 0.886$ is shown in fig.4. It is evident that this figure shows the jumps between two coexisting phases: isotropic and nematic taking place simultaneously at this temperature. To separate values for order parameter in two coexisting phases we can use histograms of order parameter distribution. This turns to be possible only for some temperature points due to the fact that two maxima at histograms are too close and wide enough and thus intersect one another strongly. The behaviour of order parameter as the function of temperature is shown in fig.5. We found that the order parameter in nematic phase is $S_{NI} = 0.240$ which value is close to previous ones $S_{NI} = 0.333$ [10], $S_{NI} = 0.270$ [11], and $S_{NI} = 0.270$ [12]. Typical experimental values for S_{NI} are between 0.3 and 0.45 [39]. It should be noted that behaviour of S in the vicinity of β_{NI} is very sharp so value of S_{NI} is very sensative to correct determination of β_{NI} point.

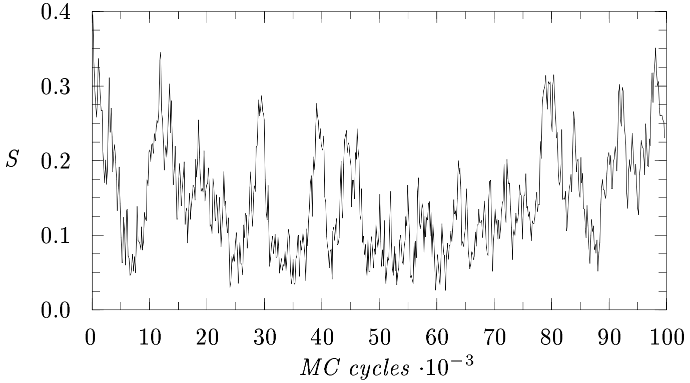

Figure 4: Typical behaviour of the order parameter S vs Monte Carlo cycles for temperatures close to NI transition (the case of Lebwohl-Lasher model, $\beta\epsilon = 0.886$).

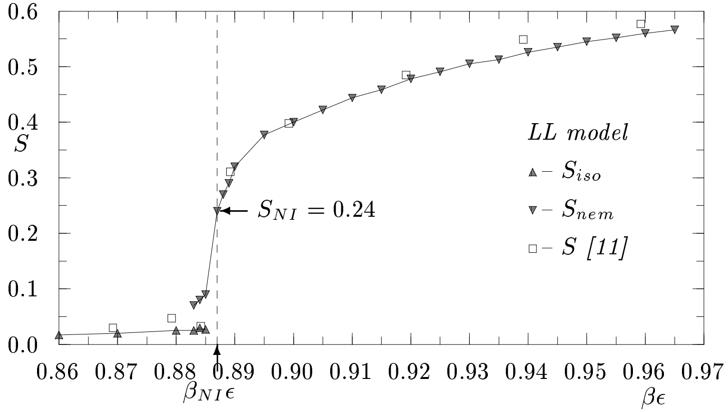

Figure 5: Order parameter S near NI transition for the Lebwohl-Lasher model (triangles – present data, squares – data from [11])

Thus, we to recalled standard computational method for simulation of LL model in the vicinity of NI transition [9–12]. Due to this we will omit corresponding explanations in the next section containing original results. On the other hand, in such way we will reduce the influence of the computational details when comparing simulations of LL and modified LL models being performed using unique simulational scheme.

3. Modified Lebwohl-Lasher model

As one can see LL model is capable to give the satisfactory quantitative description of NI transition in the liquid crystal materials. But the values for latent heat ΔU as well as nematic order parameter at transition point S_{NI} given by LL model are fixed and cannot cover entire interval of typical experimantal values for real nematics [39]. To bring more physics into this model one have to include additional parameters connected with the details of the intermolecular interaction. We suppose that this can be done by using more realistic Berne-Pechukas (BP) potential [24] (the predecessor of Gay-Berne potential [27]). In the case we still retain the lattice the translational part of this potential will be lost, and only angular part will be essential. This will retain intermolecular interaction in the system to be soft but brings the additional parameter of molecules elongation.

BP potential is the overlap potential which consider pairwise interaction between moleculs of ellipsoids of revolution shape instead of linear arrays of atoms. It has the Lennard-Jones form with the orientational dependent strength and range parameter [24]:

$$V_{BP}(\vec{u_i},\vec{u_j},\vec{r}) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right], \tag{8}$$

where

$$\epsilon_{ij} = \epsilon_0\left[1-\chi^2(\vec{u_i}\cdot\vec{u_j})^2\right]^{-1/2}, \tag{9}$$

and

$$\sigma_{ij} = \sigma_0\left\{1-\frac{\chi}{2}\left[\frac{(\hat{r}\vec{u_i}+\hat{r}\vec{u_j})^2}{1+\chi(\vec{u_i}\vec{u_j})}+\frac{(\hat{r}\vec{u_i}-\hat{r}\vec{u_j})^2}{1-\chi(\vec{u_i}\vec{u_j})}\right]\right\}^{-1/2}. \tag{10}$$

The anisotropy of molecules are characterized by the anisotropy parameter:

$$\chi = \frac{a^2-1}{a^2+1}, \qquad a = \frac{\sigma_{\|}}{\sigma_{\perp}}, \tag{11}$$

where $\sigma_{\|}, \sigma_{\perp}$ are major and minor axes of ellipsoids of revolution, and a is the elongation parameter. The distance $r = \sigma_{ij}$ is, to good accuracy, the separation at which two molecules of relative orientation specified by unit vectors $\vec{u_i}, \vec{u_j}, \hat{r}$ touch.

Let us find BP potential in the limit of small anisotropy $\chi \ll 1$. To this end one can perform expansion of the square root in (9) in powers of χ and keep leading terms:

$$\begin{aligned}\lim_{\chi\ll 1} V_{BP}(\vec{u_i},\vec{u_j},\vec{r}) = &-\frac{3}{2}\left\{\frac{4}{3}\epsilon_0\chi^2\left[\left(\frac{\sigma_{ij}}{r}\right)^{6} - \left(\frac{\sigma_{ij}}{r}\right)^{12}\right]\right\}\cos^2\theta_{ij}\\ &-\left\{4\epsilon_0\left[\left(\frac{\sigma_{ij}}{r}\right)^{6} - \left(\frac{\sigma_{ij}}{r}\right)^{12}\right]\right\}\end{aligned} \tag{12}$$

Let us denote the distance dependent term by ϵ:

$$\epsilon = \frac{4}{3}\epsilon_0\chi^2\left[\left(\frac{\sigma_{ij}}{r}\right)^{6} - \left(\frac{\sigma_{ij}}{r}\right)^{12}\right]. \tag{13}$$

Then it is evident that in the case of:

$$\begin{aligned}&1.\quad \chi \ll 1,\\ &2.\quad \frac{\sigma_{ij}}{r} = \text{const.}\end{aligned} \tag{14}$$

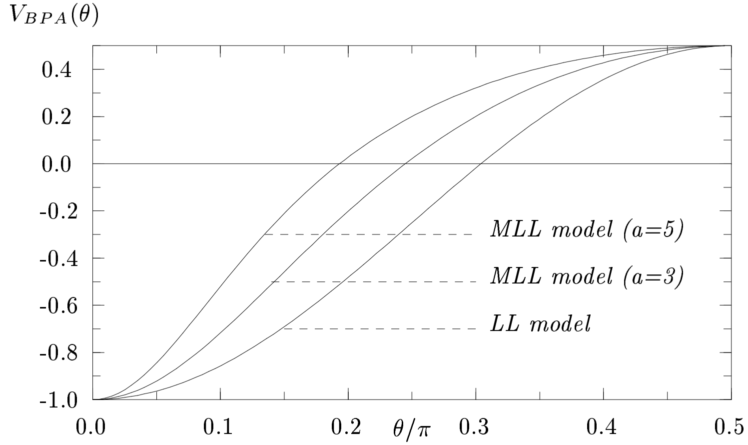

Figure 6: Angular part of Berne-Pechukas potential $V_{BPA}(\theta)$ vs angle between molecular axes θ for different elongation of molecules (LL model corresponds to $a \to 1$ case).

this limit reproduce the simple anisotropic potential of Maier-Saupe type:

$$\lim_{\chi\ll 1} V_{BP}(\vec{u_i},\vec{u_j},\vec{r}) = -\epsilon P_2(\cos\theta_{ij}) + \text{const.} \tag{15}$$

We will call the lattice model with BP potential as modified Lebwohl-Lasher (MLL) model. Due to retaining of the lattice we need indeed only angular part of this potential $V_{BPA}(\theta_{ij})$ which we normalize in such manner that at limiting values of angle $\theta = 0; \frac{\pi}{2}$ this potential have to coinside with the Maier-Saupe type one. This leads to:

$$V_{BPA}(\theta_{ij}) = -\frac{\epsilon}{2}\left[3\xi\left(\frac{1}{\sqrt{1-\chi^2\cos^2\theta_{ij}}}-1\right)-1\right], \tag{16}$$

where

$$\xi = \frac{\sqrt{1-\chi^2}}{1-\sqrt{1-\chi^2}} = 2\frac{a}{(a-1)^2}. \tag{17}$$

So within the MLL model one can consider more or less elongated molecules by varying the elongation parameter a which will change the form of interaction potential (16). As one can see in the fig.6 potential

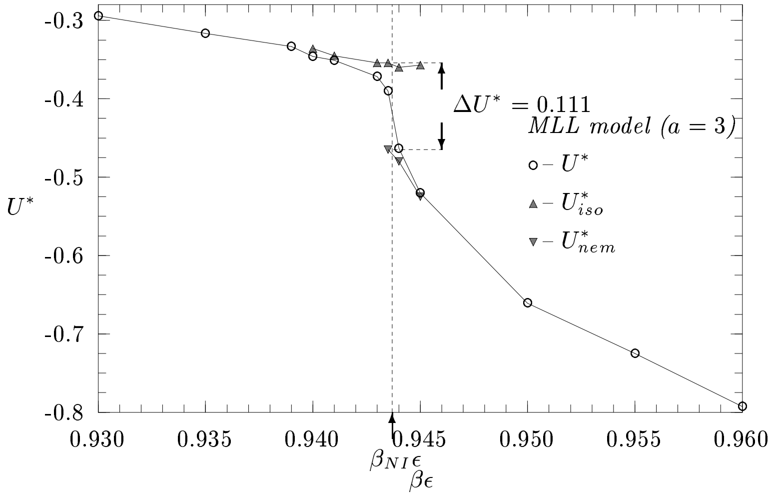

Figure 7: Dimensionless single-molecule internal energy U^* in the vicinity of NI transition for the modified Lebwohl-Lasher model with molecules elongation $a = 3$ (open circles – averaged energy, triangles – separated energies of coexisting phases, ΔU^* – dimensionless latent heat).

$V_{BPA}(\theta_{ij})$ with $a = 3, 5$ is more hard as compared to Maier-Saupe one when θ approaches $\pi/2$. On the other hand the LL model can be reproduced from MLL model in the case of almost spherical molecules $a \to 1$ ($\chi \ll 1$). To verify this fact numerically we performed simulation of MLL model for $a = 1.1$. It turned to be that we got exactly the same results as for the LL model in the previous section.

To investigate influence of molecules elongation on the NI transition we performed simulations for reasonable cases $a = 3$ and $a = 5$. These cases were also used in hard particles simulations [19,20]. Other possible reason is that, for example, molecules of typical nematogen PAA are roughly the rods with elongation parameter $a = 4$ [1]. All simulations are done using the method described in previous section. We observed more strong first order NI transition in both cases $a = 3$ and $a = 5$ as compared to LL model. The energy in the case of $a = 3$ is presented in fig.7. To separate energies of isotropic and nematic phases we used histograms of energy distribution. The NI transition in $a = 5$ case demonstrate very strong first order nature with relatively large latent heat $\Delta U = 0.474\varepsilon$ and with absence of coexisting phases (see fig.8). The last fact can be explained by the large potential barrier between two phases which cannot be easily overcomed during simulations.

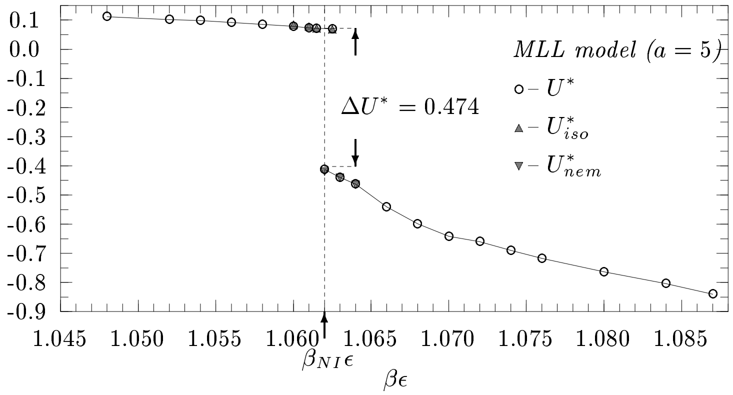

Figure 8: Dimensionless single-molecule internal energy U^* in the vicinity of NI transition for the modified Lebwohl-Lasher model with molecules elongation $a = 5$ (open circles – averaged energy, triangles – separated energies of coexisting phases, ΔU^* – dimensionless latent heat).

model	$\beta_{NI}\epsilon$	ΔU	S_{NI}
LL	0.887	0.062ϵ	0.240
MLL (a=3)	0.9437	0.111ϵ	0.285
MLL (a=5)	1.062	0.474ϵ	0.460

Table 1: Inverse transition temperature $\beta_{NI}\epsilon$, latent heat ΔU, and order parameter at transition S_{NI} for NI transitions at Lebwohl-Lasher (LL) and modified Lebwohl-Lasher (MLL) models.

Data for the order parameter S in the cases of $a = 3$ and $a = 5$ together with data for LL model are shown in fig.9. We got larger values for S_{NI} with increasing of a. Difference between cases $a = 5$ and $a = 3$ is much more essential than between $a = 3$ and LL model. The behaviour of S in the case of $a = 5$ demonstrate again much more strong first order transition as compared to other cases. We collected values for inverse

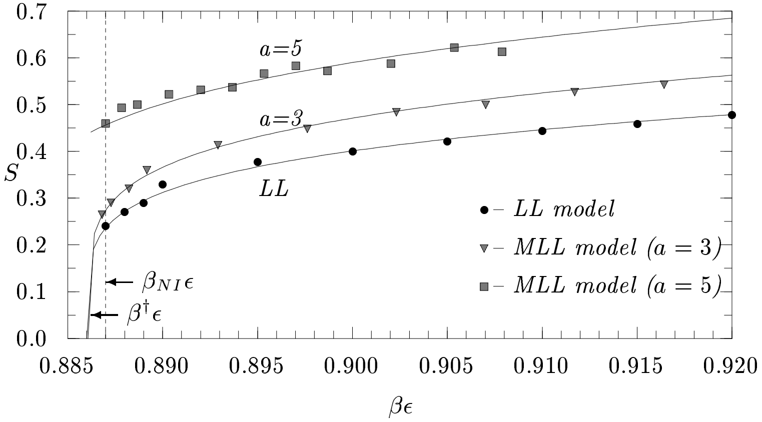

Figure 9: Behaviour of order parameter S near NI transition for models with different elongation of molecules ($\beta_{NI}\epsilon$ – inverse temperature of NI transition, $\beta^{\dagger}$ – inverse temperature of data extrapolation to fit power-law dependence).

transition temperature $\beta_{NI}\epsilon$, latent heat ΔU, and order parameter at transition S_{NI} in table 1.

Due to these results it can be pointed unambiguosly that NI transition in MLL model become more strong first order one with increasing of elongation parameter a. It is interesting to note, that computer simulations of lattice model with anisotropic dispersion forces gave also more strong first order transition as compared to LL model [23]. It is known [22] that as the shape becomes more elongated, we expect to see progressive strengthening of transition, towards the Onsager limit [7]. These results bring new light on comparing of MC data with entire set of experimental data on NI transition.

4. Comparing with the experimental data

Our data for NI transition temperature, latent heat, and the order parameter obtained within the MLL model can be compared with the experimental data on real nematics. For example the set of experiments on 13 nematics in the vicinity of NI transition was collected by Haller [39]. Let us discuss firstly the behaviour of order parameter S in the vicinity

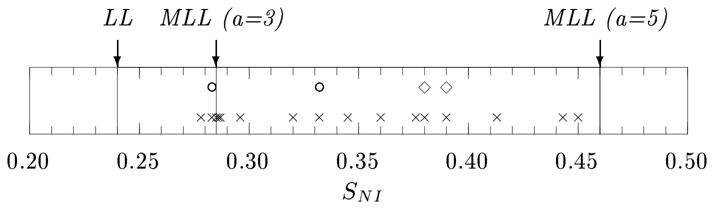

Figure 10: Comparing values for order parameter at transition S_{NI} obtained within the LL and MLL models with the experimental data. Crosses are experimental data for different nematogens, circles – particular data for MBBA, rombs – for PAA (all experimental data are taken from [39]).

of the NI transition (fig.9). As long as the NI transition is the first order the order parameter have some non-zero value at NI transition temperature S_{NI} and drops to zero sharply when temperature is increased. As was pointed in [39] one can extrapolate the gradual decrease of S until it becomes zero at hypothetical second-order phase transition temperature $T^{\dagger}$. Such extrapolation yields after scaling of experimental data following relation [39]:

$$S = (1 - T/T^{\dagger})^{\beta}, \tag{18}$$

where β is the critical index for order parameter in the hypothetical second-order transition at $T = T^{\dagger}$. In our case we can write the similar power law in terms of inverse temperature:

$$S = S_0(\beta\epsilon - \beta^{\dagger}\epsilon)^{\beta} \tag{19}$$

We performed several comparisons of our results with the experimental data. First of all we compared values for S_{NI} obtained for LL and MLL models with the experimental set of correspondent values for S_{NI}. This is illustrated in fig.10 where one can see that the typical experimental values for S_{NI} turned to be inside the interval between values obtained for MLL model at $a = 3$ and $a = 5$. Let us consider some typical nematogens. For example, from the rough steric point of view molecules of *p-methoxybenzylidene-n-butylaniline* (MBBA) correspond to elongation $a = 3$ and molecules of *p-azoxyanisole* (PAA) to $a = 4$. The experimental values for MBBA $S_{NI} = 0.283, 0.332$ [39] are indeed close enough to our result $S_{NI} = 0.285$ for $a = 3$ case, and the experimental values for PAA $S_{NI} = 0.38, 0.39$ [39] (filled rombs in fig.10) are just at the middle between results for $a = 3$ and $a = 5$. Other method to compare our results for order parameter with the experiment is to extrapolate our data in nematic phase to the point $\beta^{\dagger}\epsilon$ and to find the power law (19). For this purpose we plotted the dependence of S vs $\beta\epsilon$ in nematic phase in logarithmic scale (fig.11). The best fits were found with the value of exponent $\beta \sim 0.2$ (solid lines in fig.11). This value agree well with the experimental data being in the interval $\beta \in [0.17, 0.225]$ [39].

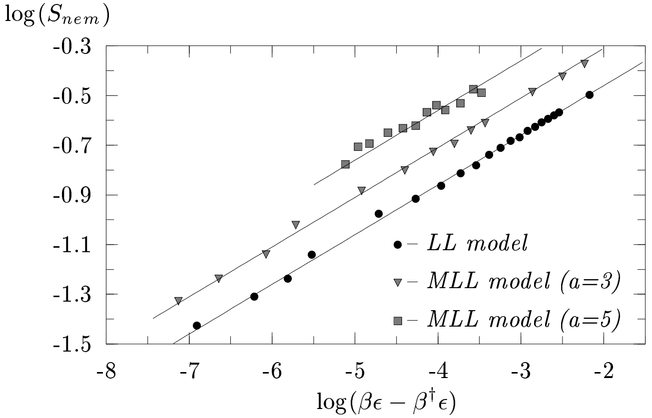

Figure 11: Fitting data for order parameter in nematic phase S_{nem} obtained for models with different elongation of molecules to power law $S_{nem} = S_0(\beta\epsilon - \beta^{\dagger}\epsilon)^{\beta}$ in logarythmic scale (effective index $\beta = 0.2$).

Other quantity can be compared with the experiment is the latent heat ΔU which coincides in our case with the enthalpy of the transition ΔH. We can use the experimental data obtained from studying of thermal behaviour of 8CB by adiabatic scanning calorimeter [37]. The result for the NI transition enthalpy is $\Delta H = 612 J/mol$ at transition temperature $T_{NI} = 40.8°C$. Fitting the transition temperature obtained for LL and MLL models to this value one can get energetic parameter ϵ and then value for transition enthalpy. We get $\Delta H = 143.23 J/mol$ for LL model, $\Delta H = 272.83 J/mol$ for MLL model (a=3) and $\Delta H = 1311.1 J/mol$ for MLL model (a=5). Despite the poor accuracy for these data we can state that the experimental value for ΔH is between our results found for MLL model at $a = 3$ and $a = 5$, so our results give the reasonable interval as compared to the experiment.

Thus, the modified Lebwohl-Lasher model being the lattice model of elongated molecules interacting via the angular part of Berne-Pechukas potential was proposed. The standard Metropolis Monte Carlo algorythm was used to simulate this sytem in the vicinity of nematic-isotropic transition. To separate the coexisting phases the histogram technique was used. Behaviour of the internal energy, heat capacity and order parameter in the vicinity of transition was investigated. As compared to pure LL model the additional parameter of molecules elongation a is present and the influence of this parameter on the phase transition is investigated. Simulations for the cases of molecules elongation $a = 3$ and $a = 5$ showed unambiguosly that nematic-isotropic transition become more strong first order one with the increasing of a. Comparing our results with the experimental data show that many real nematics in the vicinity of nematic-isotropic transition can be described well by proposed model with elongation of molecules from $a = 3$ to $a = 5$.

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