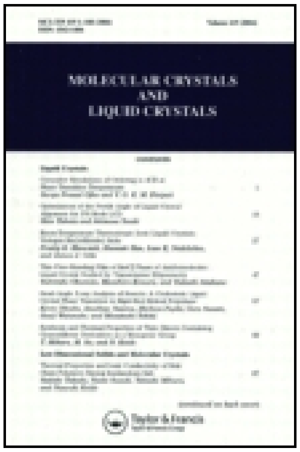

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Modified Lebwohl—Lasher Model for Investigation of Nematic — Isotropic Phase Transition in Liquid Crystals

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Modified Lebwohl–Lasher Model for Investigation of Nematic – Isotropic Phase Transition in Liquid Crystals

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We propose a lattice model of elongated molecules interacting *via* an angular part of the Berne–Pechukas potential. Monte Carlo simulations of this model are performed near the nematic to isotropic phase transition. We found that this transition is a stronger first order in the case of more elongated molecules. The comparison with the other simulations and the experimental data is performed.

Keywords: Liquid crystals; nematic; phase transitions; Monte Carlo; simulations

PACS Numbers: 02.70.Lq; 61.30.Cz; 64.70.Md

1. INTRODUCTION

Phase transitions in liquid crystals (LCs) attract much attention from both theoretical and experimental points of view [1, 2]. The rich phase diagrams in these systems can be explained by a competition between anisotropic interactions of a different kind [3, 4]. This fact complicates theoretical description of the phase transitions in LCs, for which purpose only quite simple models are used. The most intensively studied is nematic to isotropic (NI) transition. Maier–Saupe mean-field type theory [5] predicts the NI transition to be a first order, but it overestimates the scalar order parameter

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at the transition and its latent heat as compared to the experiment. An alternative mean-field theory with both energetic and steric effects [6, 7], as well as two particle [8] and four particle [9] cluster expansions were developed to improve the description of the NI transition. On the other side, Onsager theory describes the NI transition in a system of long thin hard rods [10], taking into account only pure steric effects of excluded volume. This theory concludes a very strong density driven first order NI transition. Third, widely used, Landau - de Gennes phenomenological theory of the NI transition [1, 11] is based on the expansion of the free energy in powers of the order parameter and contains a few phenomenological parameters which can be fitted with the experimental data. It predicts the order of transition due to the symmetry considerations, and estimates pretransitional behaviour of the pair correlations and some other properties [11].

The breakthrough in understanding of phase transitions in LCs on the microscopical level was achieved by computer simulations of correspondent model systems. It is evident that the success of such simulations depends on the optimal balance between following two requirements. First, the model has to describe the important features of given phenomena, and second, the model has to be reasonably simple for performing computer simulations. One can emphasize three main types of model systems for describing of LCs: hard particles systems [12–17], lattice models with simple anisotropic forces [18–25] and the Gay–Berne model for anisotropic fluid [26–32].

As far as the present report considers simulations of lattice models with simple anisotropic forces we will discuss this type of models in more detail. The first work in this direction by Lebwohl and Lasher (LL) started Monte Carlo (MC) simulations of the NI transition in a system of rotating molecules confined to the sites of a simple cubic lattice. The interaction potential in this model has a simple anisotropic form [18]:

$$H = -\varepsilon \sum_{\langle ij \rangle} P_2(\cos\theta_{ij}), \qquad (1)$$

where the sum includes all pairs $\langle i, j\rangle$ of the nearest neighbours, θ_{ij} is the angle between the long axes of neighbouring molecules, ε is the strength parameter and $P_2(x) = 1/2(3x^2 - 1)$ is the second Legendre polynomial. Lebwohl and Lasher estimated the transition temperature T_{NI}, the scalar order parameter at the transition S_{NI}, the latent heat and showed that the NI transition is a weak first order [18]. Later this model was subsequently studied in greater detail by Jansen *et al.* [19]. These authors improved the accuracy of simulations and calculated the magnetically induced birefringence and the scattering of light by orientational fluctuations in the isotropic phase. Extended LL model in which the restriction to a lattice sites was removed was simulated by Luckhurst and Romano [20]. A molecular dynamics study of the dynamical properties of the NI transition in the LL model was performed by Zannoni and Guerra [21]. Then, this model was revisited by Luckhurst and Simpson [22] to achieve more accurate results for the internal energy, the heat capacity and the latent heat at the transition, as well as the transition temperature T_{NI}. Results of MC simulations of the LL model were essentially reestimated by Fabbri and Zannoni [23]. The larger lattice of molecules (30^3) was simulated and the number of simulation runs was significantly higher than in the previous simulations. This allowed more precise estimates for the transition temperature T_{NI}, as well as for the scalar order parameters $S \equiv \langle P_2 \rangle$, $\langle P_4 \rangle$, the internal energy and the heat capacity in the transition region. Particular attention was paid to the pair correlations $G_2(r)$ and $G_4(r)$. The difference between T_{NI} and the isotropic phase limiting instability temperature T^* was obtained with reasonable accuracy, agreeing well with the experiments on real nematics.

Zhang, Mouritsen and Zuckermann used the modern numerical techniques of finite-size scaling analysis [33] and histogram reweighing technique [34] to simulate the NI transition in the LL model with greater accuracy [24]. Unambiguous numerical evidence is found in favour of a weak first order transition, and the precise estimates for T_{NI} and pseudospinodal points were done. The transition enthalpy obtained from these simulations is in satisfactory agreement with the experimental data on *octyl-cyanobiphenyl* (8CB) [35]. Pseudospinodal points are located by analyzing the free energy as the function of the scalar order parameter with two minima in the transition region. Correlation functions for the order parameter fluctuations just above the NI transition are investigated by Greeff and Lee [25]. At those temperatures for which the distribution of the order parameter fluctuations in Gaussian, the inverse susceptibility is found to follow Landau theory behaviour.

The interest to polymer dispersed liquid crystals (PDLCs) stimulates computer simulations of the model nematic droplets. The droplets of the LL model in the form of irregular spheres obtained from a cubic lattice were simulated by Chiccoli *et al.*, for different boundary conditions [36–38]. The effect of external field is also investigated [39]. The polarized light textures and Deuterium NMR lineshapes obtained from MC simulations show the qualitatively agreement with the experimental data [40]. The model droplets consisting up to 12,000 molecules were considered.

Thus, despite the simplicity and limited reliability of the LL model, it plays the role of a canonical model undergoing a pure orientational phase transition, and it is intensively used to simulate various related phenomena. The sizes of simulated systems (10,000–30,000 particles for the bulk behaviour and 12,000 for the model droplets) are large enough to study the thermodynamics of the phase transition of any type. For this reason, models of the same level of simplicity as the LL model still seemed to be useful for the investigation of correspondent phase transitions in anisotropic systems.

Concerning the extension of the LL model one can mention computer simulations of the pure P_4 model [41], pure P_6, P_8 models [42], as well as the model with the linear combination of a predominant P_2 and a minor P_4 term [43]. In the last case one can modulate a first order character of the NI transition by a suitable choice of the parameters of the potential. The attempt towards computer simulation of some more realistic lattice model was made by Humpries *et al.* [44], those authors used the potential of anisotropic dispersion forces. Their results show that the NI transition in such a model does not differ essentially from the transition in the LL model. The scalar order parameter at the transition is slightly higher and this produces a larger entropy of the transition, but both these values are insensitive to varying the relative anisotropy in the polarizability of the system.

The aim of this report is to extend the LL model and to investigate the correspondent NI transition by means of MC simulations. To this end we will use instead of a simple anisotropic potential (1) the angular part of the Berne–Pechukas (BP) potential [45–47]. The BP potential will be simplified to fit the requirements of a simple lattice model with the pure orientational interactions. The only additional degree of freedom appeared by means of our extension is the molecular anisotropy which is connected with the elongation of molecules. As the result, the possibility to investigate the NI transition in the lattice models with the different molecular anisotropy appears. This is done in the presented report.

The outline of this report is as follows. Description of the modified LL model with the angular part of the BP potential is given in Section 2. Results of MC simulations of this model near the NI transition, comparisons with the experiments, as well as conclusions are given in Section 3.

2. THE MODEL

We consider a lattice model of molecules interacting *via* the angular part of the BP potential [45]. This potential is obtained by considering the overlap integral between two identical ellipsoidal Gaussians for arbitrary relative orientations of the Gaussians. The overlap potential is obtained by using orientationally dependent strength $\varepsilon(\hat{u}_i, \hat{u}_j)$ and range $\sigma(\hat{u}_i, \hat{u}_j, \hat{r})$ parameters in the Lennard-Jones potential [45]:

$$V_{BP}(\hat{u}_i, \hat{u}_j, \vec{r}) = 4\varepsilon(\hat{u}_i, \hat{u}_j)\left[\left(\frac{\sigma(\hat{u}_i, \hat{u}_j, \hat{r})}{r}\right)^{12} - \left(\frac{\sigma(\hat{u}_i, \hat{u}_j, \hat{r})}{r}\right)^{6}\right], \quad (2)$$

where

$$\varepsilon(\hat{u}_i, \hat{u}_j) = \varepsilon_0[1 - \chi^2(\hat{u}_i \cdot \hat{u}_j)^2]^{-1/2} \quad (3)$$

and

$$\sigma(\hat{u}_i, \hat{u}_j, \hat{r}) = \sigma_0\left\{1 - \frac{\chi}{2}\left[\frac{(\hat{r} \cdot \hat{u}_i + \hat{r} \cdot \hat{u}_j)^2}{1 + \chi(\hat{u}_i \cdot \hat{u}_j)} + \frac{(\hat{r} \cdot \hat{u}_i - \hat{r} \cdot \hat{u}_j)^2}{1 - \chi(\hat{u}_i \cdot \hat{u}_j)}\right]\right\}^{-1/2}.$$

Each unit vector $\hat{u}_i$ is directed along the long axis of the i-th ellipsoid, $\vec{r}$ is the center-of-mass distance vector between interacting ellipsoids and $\hat{r}$ is the unit vector along $\vec{r}$. The anisotropy of ellipsoids is characterized by an anisotropy parameter:

$$\chi = \frac{a^2 - 1}{a^2 + 1}, \quad a = \frac{\sigma_{\parallel}}{\sigma_{\perp}},$$

where $\sigma_{\parallel}$, $\sigma_{\perp}$ are their major and minor axes, and a is the elongation parameter. The distance $r = \sigma(\hat{u}_i, \hat{u}_j, \hat{r})$ is, to good accuracy, the separation at which two ellipsoids of relative orientation specified by unit vectors $(\hat{u}_i, \hat{u}_j, \hat{r})$ touch.

The angular part of the BP potential which is used in our lattice model is derived from (2) by eliminating the distance dependent part:

$$\left(\frac{\sigma(\hat{u}_i, \hat{u}_j, \hat{r})}{r}\right)^{12} - \left(\frac{\sigma(\hat{u}_i, \hat{u}_j, \hat{r})}{r}\right)^{6} = V_0 = \text{const.}$$

and therefore can be written in the form:

$$V_{\mathrm{BPA}}(\theta_{ij}) = 4V_0\varepsilon(\hat{u}_i, \hat{u}_j), \quad (4)$$

where θ_{ij} is the angle between $\hat{u}_i$ and $\hat{u}_j$. The value of V_0 has to be choosen from some normalization condition. It is easy to check that in the limit of small anisotropy one can expand (3) in powers of χ and to reproduce from $V_{\mathrm{BPA}}(\theta_{ij})$ the potential of the LL model (1):

$$\begin{aligned}\lim_{\chi\ll 1} V_{\mathrm{BPA}}(\theta_{ij}) &= -\frac{3}{2}\left(\frac{4}{3}\varepsilon_0\chi^2 V_0\right)\cos^2\theta_{ij} - 4\varepsilon_0 V_0 \\ &= -\varepsilon P_2(\cos\theta_{ij}) + \text{const.},\end{aligned} \tag{5}$$

where

$$\varepsilon = \frac{4}{3}\varepsilon_0\chi^2 V_0 \tag{6}$$

stands for the strength parameter of the LL model and will be used as the energy scale in our simulations. It has to be mentioned that ε is anisotropy dependent (*via* χ), which fact has to be taken into account when we wish to consider the dependence of the final physical characteristics (like the transition temperature, internal energy and oth.) on the molecular anisotropy. For the convenience we will normalize $V_{\mathrm{BPA}}(\theta_{ij})$ in such a manner that, at $\theta_{ij}=0$ and $\theta_{ij}=(\pi/2)$ it gives the same energy (in the units of ε) as (1) for arbitrary elongation of molecules a (see Fig. 1). This yields a following expression for a normalized angular part of the BP potential:

$$V_{\mathrm{BPA}}(\theta_{ij}) = -\frac{\varepsilon}{2}\left[\frac{6a}{(a-1)^2}\left([1-\chi^2\cos^2\theta_{ij}]^{-1/2}-1\right)-1\right]. \tag{7}$$

This potential will be used in the simulations and we will refer to a lattice model with the nearest-neighbours interactions of this type as the modified Lebwohl-Lasher (MLL) model. As commented by Allen [48], this modification of the potential results in only using the BP formula as the basis for an idealized, simpler, angle-dependent potential (7) which extends the LL one (1). We are able, in principle, to expand (7) in series on Legendre polynomials P_{2l}, but we prefer to use the general formula. This way to extend the LL model is pretended to be a more natural than the use of the linear combination of P_{2l} with adjustable coefficients. We assume that the MLL model will retain the simplicity of the original LL model (the initial potential of which (1) is reproduced in the limit of small anisotropy (5)), but also will give the possibility to describe the NI transition in the real nematics more precisely.

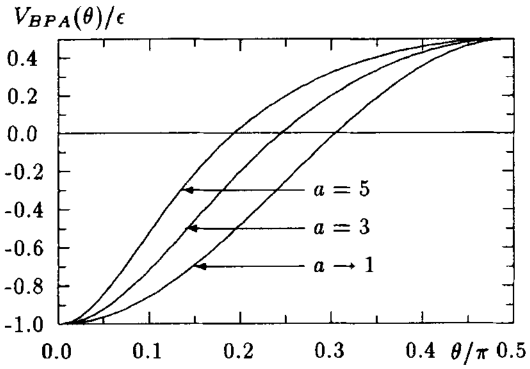

FIGURE 1 Angular part of the Berne-Pechukas potential $V_{\mathrm{BPA}}(\theta)$ *vs* the angle between the long axes of two interacting molecules θ for different cases of molecular elongation a ($a \to 1$ reproduces the LL model potential).

3. RESULTS

We used a standard NVT MC method [49] for simulation of the NI transition in the MLL model. The system of 20^3 molecules confined to the sites of a simple cubic lattice with the periodic boundary conditions is considered. Each i-th molecule is characterized by the unit vector $\hat{u}_i$ directed along its long axis, stored as a set of its Cartesian coordinates $\hat{u}_i = (x_i, y_i, z_i)$. The nearest neighbours interactions has a form of the normalized angular BP potential (7). The simulation at each temperature was started from the perfectly ordered configuration $\hat{u}_i = (0, 0, 1)$ for all i. After this we allow each molecule to rotate to a new direction $\hat{u}_i'$:

$$\hat{u}_i' = (x_i', y_i', z_i') = \frac{1}{l}(x_i + \delta \cdot p_1, y_i + \delta \cdot p_2, z_i + \delta \cdot p_3), \tag{8}$$

where p_1, p_2, p_3 are pseudorandom numbers from -1 to $+1$, l stays for the normalization of $\hat{u}_i'$ and δ restricts the maximal possible rotation. The acceptance or rejection of a new configuration is considered in accordance with the standard Metropolis algorithm [49]. The acceptance-rejection ratio is controlled to be around 0.4 by the choice of δ. One MC cycle is completed after allowing all molecules to change their orientation. We performed 10^5 cylces for the temperatures close to transition.

Previous simulations showed that the NI transition in the LL model is a weak first order [18, 19, 22, 23]. We are interested in how the change of molecular elongation affects the order of transition in the MLL model. Two cases of molecular elongation $a=3$ and $a=5$ are considered (these values has also been used in computer simulations of hard ellipsoids model [14, 15]). The order of transition can be examined from the jump of a dimensionless single-molecule internal energy

$$U^* = \frac{\langle \sum_{\langle ij \rangle} V_{\mathrm{BPA}}(\theta_{ij}) \rangle}{N \cdot \varepsilon} \tag{9}$$

at the transition temperature. To extract this jump we separate the correspondent energies of the isotropic and the nematic phases in the closest vicinity of the transition. This is done by using the histograms of energy distribution and locating two maxima corresponding to each phase. The result is shown in Figure 2, where we presented the behaviour of the internal energy and its jump at the transition for the MLL model with molecular elongation $a=3$ and $a=5$. To compare with the case of the LL model, and to reduce the influence of simulational details, we performed our own simulations for the LL model instead of using results of other authors [18, 19, 22, 23]. We estimated the dimensionless latent heat of the transition ΔU^* in this case to be 0.062 in agreement with the other simulations 0.1 [19], 0.07 [22], 0.05 [23]. These values in the case of the MLL model appeared to be essentially higher (0.111 in $a=3$ case and 0.474 in $a=5$ case). The inverse

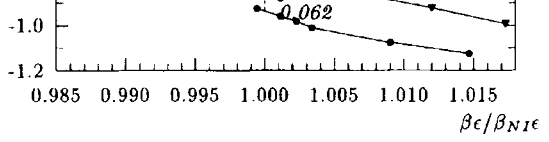

FIGURE 2 The dimensionless single-molecule internal energy U^* for the MLL model with molecular elongation $a=3$ (triangles, shifted by -0.2 along U^* axis for better visualization), $a=5$ (boxes) and for the LL model (circles) near their NI transitions. The energies of the system in the isotropic and the nematic phase were separated by the histogram technique. The numbers near the jumps of U^* show the dimensionless latent heat at the transition.

transition temperature $\beta_{\mathrm{NI}}\varepsilon$ in all cases is estimated from the peak of the heat capacity, which was derived by differentiating of cubic splain interpolation between U^* points with respect to $\beta\varepsilon$ [22]. For this purpose we used the values of average energy in the system at each temperature and no histogram data. The values for $\beta_{\mathrm{NI}}\varepsilon$ and dimensionless latent heat ΔU^* for different elongations of molecules are presented in the Table I. It has to be mentioned that both these quantities are dimensionless, so to examine the dependence of physical transition termperature T_{NI} and physical latent heat ΔU on the molecular anisotropy one has to take into account the correspondent dependence of ε on χ (see (6)). To do this we can write:

$$T_{\mathrm{NI}} = \frac{\varepsilon}{k_B \beta_{\mathrm{NI}}\varepsilon} = \mathrm{const.} \cdot \frac{\chi^2}{\beta_{\mathrm{NI}}\varepsilon}, \tag{10}$$

$$\Delta U = \Delta U^* \varepsilon = \mathrm{const.} \cdot \Delta U^* \chi^2, \tag{11}$$

where const. are certain anisotropy independent constants. Using these expressions together with the data listed in the Table I for $\beta_{\mathrm{NI}}\varepsilon$ and ΔU^* we obtain:

$$a = 3: \quad T_{\mathrm{NI}} = \mathrm{const.} \cdot 0.678, \quad \Delta U = \mathrm{const.} \cdot 0.071, \tag{12}$$

$$a = 5: \quad T_{\mathrm{NI}} = \mathrm{const.} \cdot 0.802, \quad \Delta U = \mathrm{const.} \cdot 0.404. \tag{13}$$

Thus, with the increasing of the molecular anisotropy the transition temperature increases, and the latent heat became essentially higher. However, we cannot list the correspondent values for the LL model in which case one has to perform the formal limit $\chi \to 0$. This is the reason we prefer to work within the ε scale and the values (12, 13) are listed exclusively as the indication that our results are physically correct.

TABLE I The dimensionless inverse transition temperature $\beta_{\mathrm{NI}}\varepsilon$, the dimensionless latent heat ΔU^* and the scalar order parameter at the transition S_{NI} for the NI transition in the Lebwohl-Lasher (LL) and the modified Lebwohl-Lasher (MLL) models (see (12) and (13) and comment in the text about the correspondence of $\beta_{\mathrm{NI}}\varepsilon$ and ΔU^* to the physical transition temperature and latent heat)

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

Orientational order in the system is characterized by a set of the scalar order parameters [1, 23]. The most important among them is:

$$S \equiv \langle P_2 \rangle = \langle P_2(\cos\theta_i) \rangle, \tag{14}$$

where θ_i is the angle between the long axis of the i-th molecule and a director (unit vector which defines a preferred direction of nematic ordering). As far as the director can fluctuate from one MC cycle to another [23], the scalar order parameter is calculated with respect to the instantaneous director after each cycle. This is normally done [19, 22, 23] by a method proposed by Viellard–Baron [12]. The tensor order parameter [1]:

$$S_{ij} = \frac{3}{2}\begin{pmatrix} \langle x_i^2 \rangle - 1/3 & \langle x_i y_i \rangle & \langle x_i z_i \rangle \\ \langle y_i x_i \rangle & \langle y_i^2 \rangle - 1/3 & \langle y_i z_i \rangle \\ \langle z_i x_i \rangle & \langle z_i y_i \rangle & \langle z_i^2 \rangle - 1/3 \end{pmatrix} \tag{15}$$

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

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

The evaluation of S during simulations shows a dramatic increase of its fluctuations in the transition region. A typical behaviour of S as the function of MC cycle at the inverse temperature $\beta\epsilon = 0.886$ (for the case of the LL model) is shown in Figure 3. It is evident that this figure shows the jumps between the isotropic and the nematic phases, which coexist at this temperature. To separate the values of the scalar order parameter for each phase we use, as before, histograms of the scalar order parameter distribution. This is possible only for some temperature points with recognizable peaks. For other temperatures, the histogram maxima are not so well defined. For the case of the LL model we found that the scalar order parameter at the transition S_{NI} is 0.240 which value is close to the previously obtained ones 0.333 [19], 0.270 [22] and 0.270 [23]. It should be noted that the curve for S in the vicinity of β_{NI} is very steep so the value of S_{NI} is very sensitive to the accuracy of β_{NI}. The behaviour of the scalar order parameter as the function of the temperature for the MLL and the LL models is shown in Figure 4. We report higher values of S_{NI} with increasing of the molecular anisotropy (see Tab. I), so the case $a = 5$ demonstrate much more strong first order transition as compared to the other cases.

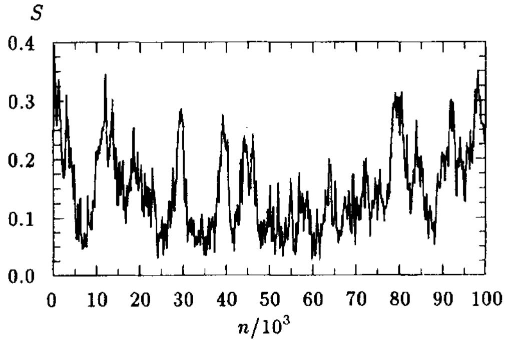

FIGURE 3 Typical behaviour of the scalar order parameter S as the function of performed Monte Carlo cycles n demonstrating the coexistence of two phases near the NI transition (the LL model, $\beta\varepsilon = 0.886$).

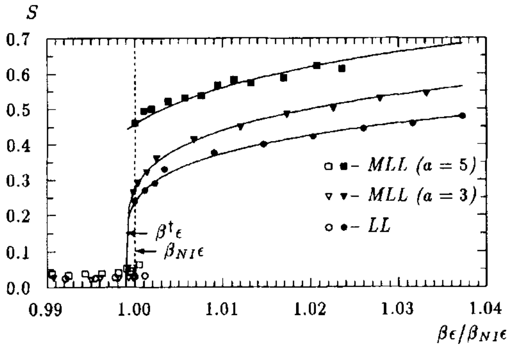

FIGURE 4 The scalar order parameter S for the MLL model with molecular elongation $a = 3$ (triangles), $a = 5$ (boxes) and for the LL model (circles) near their NI transitions (open symbols correspond to isotropic phase, see comment in the text). Solid curves represent extrapolations to fit the power-law dependence $S = S_0(\beta\varepsilon/\beta^\dagger\varepsilon - 1)^{\beta^*}$ in the vicinity of $\beta^\dagger$ point.

The non-zero positive noise of the order parameter in the isotropic phase which is observed during computer simulations (see Figs. 3 and 4) was discussed previously by other authors [16, 23]. This effect appears from the procedure of deriving the scalar order parameter as the largest eigenvalue (say, λ_3) of the tensor order parameter (15). When this procedure is performed in the case of a finite size system of N particles it leads to a noise of order $N^{-(1/2)}$ in the isotropic phase. Eppenga and Frenkel proposed to define the scalar order parameter *via* the middle eigenvalue: $S = -2\lambda_2$ [16], which will lead to the noise of order N^{-1} in the isotropic phase. But this is a matter of a discussion. In this paper the standard definition of the scalar order parameter is used.

Due to the results obtained for the latent heat of the transition and the scalar order parameter it can be pointed unambiguously that the NI transition becomes more strong first order with the increasing of molecular elongation. The same conclusion was made during simulations of pure P_4 [41], P_6, P_8 [42] models and for aP_2+bP_4 model for some values of a and b. Computer simulation of a lattice model with anisotropic dispersion forces gave also more strong first order transition as compared to the LL model [44]. It is also known from the simulations of the hard particles [17] that as the shape becomes more elongated, we expect to see progressive strengthening of transition, towards the Onsager limit [10].

As far as the simulated system was finite and contains 20^3 molecules with the periodic boundary conditions some considerations about the finite-size effects have to be discussed. The increasing of the lattice size would induce a slight lowering of the transition temperature and increasing of the peak heights for the heat capacity and susceptibility. These effects in the LL model was studied by Zhang *et al.* [24]. The transition temperature found by the extrapolation of the finite-size behaviour was estimated as $T_{NI}=1.1232 \pm 0.0001\varepsilon/k_B$. Fabbri and Zannnoni [23] obtained exactly the same result $T_{NI}=1.1232 \pm 0.0006\varepsilon/k_B$ previously. It was derived from the position of the heat capacity peak (the lattice of 30^3 size was used, no finite-size effects were taken into account). The use of a smaller system of 20^3 size lead to the value $T_{NI}=1.1274\varepsilon/k_B$ for the LL model, which is only 0.4% higher as compared to the finite-scaling analysis result. It is known that the finite-scaling effects will give the essential corrections to the singular behaviour of the heat capacity and susceptibility (particularly in estimating corresponding critical indices). Concerning the discontinuities of the internal energy and the order parameter (which are investigated in this paper), only the slight shifts along the temperature axis are expected to be observed. The other reason for the finite-scaling effects to be examined is to give conclusive numerical evidence for the presence of a very weak first-order transition (like in the cases of $3D$, 3-state Potts or the LL models). A finite-scaling analysis suggested by Lee and Kosterlitz [33] is used usually for this purpose. In our case the first order transition in enhanced strongly with the increasing of molecular elongation, so we conclude that there is no need of using such methods in the scope of problems discussed in a presented paper.

As compared to other lattice models the MLL model proposed here has the parameter of molecular elongation a which can be varied to refer to some real nematics. The latent heat and the scalar order parameter for both the simulations and the experiment can be compared. First of all we are able to compare our results for the scalar order parameter at the transition S_{NI} with the correspondent experimental data for 13 nematics collected by Haller [50]. The result is shown in Figure 5 where we can see that the typical experimental values of S_{NI} are scattered inside the interval bounded by our values which correspond to $a=3$ and $a=5$. This coinside well with the fact that most rod-like mesogens have length-to-breadth ratios between 3 and 4 [51]. But, as far as it is not straightforward to tell from experiment how the NI transition depend on the shape of the repulsive core of the molecules [51] the comparison with the real nematics by assuming for them a certain molecular elongation is a subject of discussion. However, there are some indications and it is commonly assumed that molecules of *p-methoxybenzylidene-n-butylaniline* (MBBA) have the elongation $a=3$ and molecules of *p-azoxyanisole* (PAA) $a=4$ [1, 30, 46, 52, 53]. Using these assumptions the additional check can be performed. Particularly, the experimental values for MBBA $S_{\mathrm{NI}}=0.283$, 0.332 [50] (empty circles in Fig. 5) are indeed very close to our result $S_{\mathrm{NI}}=0.285$ for $a=3$ case, and the experimental values for PAA $S_{\mathrm{NI}}=0.38$, 0.39 [50] (empty rombs in Fig. 5) are just at the middle between the results $a=3$ and $a=5$, thus corresponding to $a \approx 4$.

To consider the temperature behaviour of the scalar order parameter S, one can extrapolate its gradual decrease until it becomes zero at the hypothetical second-order phase transition temperature $T^{\dagger}$ (the correspondent inverse temperature is $\beta^{\dagger}$). After scaling of the experimental data we can write [50]:

$$S = S_0\left(\frac{\beta\varepsilon}{\beta^{\dagger}\varepsilon} - 1\right)^{\beta^*} \tag{16}$$

where β^* is the effective critical index. This index can be also estimated from extrapolation of our data for S in the nematic phase. For this purpose we

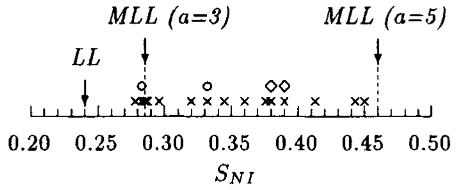

FIGURE 5 The scalar order parameter at the transition S_{NI} obtained within the LL and the MLL models (presented as the dash lines and arrows) as compared to the experimental data. Crosses represent data for the entire set of 13 nematogens, circles stay for MBBA, rombs stay for PAA (see comment in the text), all experimental data are taken from [50].

plotted the dependence of S *vs* $\beta\varepsilon/\beta^\dagger\varepsilon$ in the nematic phase in logarithmic scale (Fig. 6). Our data fits the best to the power law (16) when the value of exponent is $\beta^* = 0.2$ (solid lines in Fig. 4). This value agree well with the experimental data being in the interval $\beta^* \in [0.17, 0.225]$ [50].

Other quantity comparable with the experiment is the latent heat ΔU which coincides in the case of our model 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 [35]. The NI transition in this LC occurs at $T_{\mathrm{NI}} = 40.8°\mathrm{C}$, and the transition enthalpy is $\Delta H = 612$ J/mol. Using the value of $T_{\mathrm{NI}} = 40.8°\mathrm{C}$ we can get the strength parameter ε for the certain model and then the value of ΔH. We get $\Delta H = 143.23$ J/mol for the LL model, $\Delta H = 272.83$ J/mol for the MLL model ($a = 3$) and $\Delta H = 1311.1$ J/mol for the MLL model ($a = 5$). So we can notice, that our results for the latent heat of transition in the MLL model ($a = 3$ and $a = 5$) give the reasonable interval as compared with the experimental data.

Thus, we proposed the modified Lebwohl–Lasher model being a lattice model of elongated molecules interacting *via* the angular part of the Berne–Pechukas potential. This modification extends the initial model by introducing the parameter of molecular elongation a. Standard Metropolis Monte Carlo method for NVT ensemble was used to simulate this system in the vicinity of the nematic–isotropic transition. To separate the energy and the order parameter of the coexisting phases the histogram technique is used. The behaviour of the internal energy, the heat capacity and the scalar order parameter in the transition region indicates unambiguously that the nematic–isotropic transition becomes more strong first order with the increasing of a. The comparison of our results with the experimental data

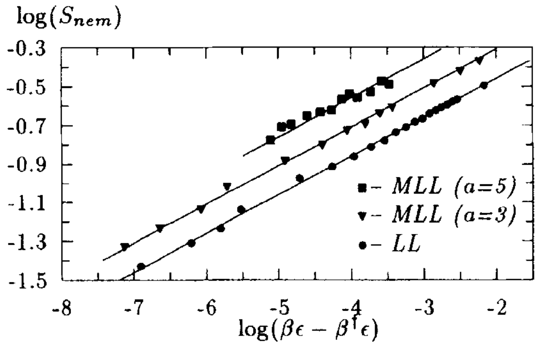

FIGURE 6 Fitting data for the scalar order parameter in nematic phase S_{nem} to the power law $S_{\mathrm{nem}} = S_0(\beta\varepsilon/\beta^\dagger\varepsilon - 1)^{\beta^*}$ in a logarythmic scale (effective index $\beta^* = 0.2$).

shows that many real nematics in the vicinity of the nematic–isotropic transition can be described by the proposed model with the molecular elongation from $a=3$ to $a=5$.

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