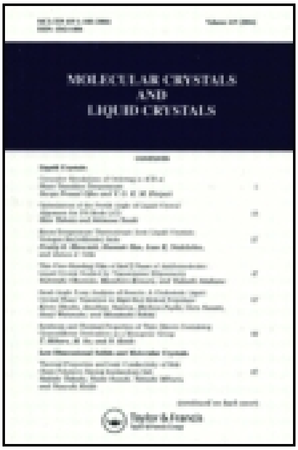

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A. Ts. Sarkissyan [a] & S. M. Yailoyan [a]
[a] Institute of Applied Problems of Physics, Armenian Academy of Sciences, 25 Nersisyan Str., Yerevan, 375014, Armenia
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Calculation of the Thermodynamic Function of Some Liquid Crystals by the Monte-Carlo Method

A. TS. SARKISSYAN and S. M. YAILOYAN

Institute of Applied Problems of Physics, Armenian Academy of Sciences, 25 Nersisyan Str., Yerevan, 375014 Armenia

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The Monte-Carlo method in the canonical NVT-ensemble is used to consider a system of 64 ellipsoidal, interacting particles (molecules). Their interactions are calculated, using the modified Lennard-Jones potential. The calculations were performed in a parallelepipedic box, using periodic boundary conditions. The particle eccentricity (length-to-width ratio), necessary for calculations, was selected in accordance with the data of conformational analysis of such nematic liquid crystal molecules as 4-cyanphenyl ether *n*-heptylbenzoic acid and 4-*n*-butyl-4′-*n*′-heptanoil-oxiazoxibenzene. Similar calculations have been also performed for the case when each of the ensemble particles is presented as a cluster of several molecules. The interaction among them has been also calculated by the Lennard-Jones potential. Here ellipsoidal particle dimensions have been determined due to the data on the position of molecules inside the cluster, obtained by the method of atom-atom potentials. We have considered clusters consisting of two and four molecules. It is shown that the short-range order effects taken into account affect and specify the results for the specific heat and the order parameter.

Keywords: nematic liquid crystals, Monte-Carlo calculations, molecular interactions

At present, the Monte-Carlo (MC) method applied to the study of properties of liquid crystals (LC) is used without taking account of the structure of molecules considered as hard particles of a cylindrical symmetry. It is a sufficiently rough approximation and, therefore, results obtained by the MC method are in bad agreement with experimental data. To improve results of calculation by this method, it is necessary to select as a precise model as possible which will allow us to take account of the molecular structure and short-range order, as well as the role they play in the determination of equilibrium thermodynamic feature of LC.

Analyzing different descriptions of energy interaction we arrive at the conclusion of the advantage of rather simple and universal Gaussian overlap model potentials,[1] which allows us to take account of the molecule anisotropy. To describe nematic LC, it is useful to apply a specially constructed Lennard-Jones potential[2] defining the interaction between two ellipsoidal particles:

$$V_{ij} = \frac{4\varepsilon}{(\sigma/\sigma_{\perp})^2}\left[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^{6}\right], \qquad (1)$$

where
$$\varepsilon(\mathbf{u}_i, \mathbf{u}_j) = \varepsilon_0[1 - \varkappa^2(\mathbf{u}_i \cdot \mathbf{u}_j)]^{-1/2}, \tag{2}$$

$$\sigma(\mathbf{u}_i, \mathbf{u}_j, \mathbf{r}_{ij}) = \sigma_\perp \left\{ 1 - \frac{1}{2}\varkappa \left[\frac{\left(\frac{\mathbf{r}_{ij}\cdot\mathbf{u}_i}{r_{ij}} + \frac{\mathbf{r}_{ij}\cdot\mathbf{u}_j}{r_{ij}} \right)^2}{1 + \varkappa(\mathbf{u}_i\cdot\mathbf{u}_j)} + \frac{\left(\frac{\mathbf{r}_{ij}\cdot\mathbf{u}_i}{r_{ij}} - \frac{\mathbf{r}_{ij}\cdot\mathbf{u}_j}{r_{ij}} \right)^2}{1 - \varkappa(\mathbf{u}_i\cdot\mathbf{u}_j)} \right] \right\}^{-1/2}, \tag{3}$$

$$\varkappa = \frac{(\sigma_\parallel/\sigma_\perp)^2 - 1}{(\sigma_\parallel/\sigma_\perp)^2 + 1}. \tag{4}$$

Here $\mathbf{u}_i$ and $\mathbf{u}_j$ are unit vectors directed along the long axes of the rotation ellipsoids, $\mathbf{r}_{ij}$ is the vectors connecting their centres of mass, $\sigma_\parallel$ and $\sigma_\perp$—are the ellipsoid axes, and ε_0 is the energy parameter of the potential.

Figure 1 shows the curves of the energy dependence of two interacting particles on the distance between their mass centres for four relative orientations of the ellipsoid long axes—a parallel position "||", a perpendicular position in one plane "⊥", a straight-line position "— —" and a interacting position "||·". A qualitatively true description of the interaction between the real LC molecules is given by the potential (1) taking account of both the anisotrope "soft" repulsion and the dispersional attraction. Selecting parameters of the potential (1) accordingly, it is also possible to achieve agreement between the dispersion energy of the LC molecule interaction and the attraction energy of ellipsoid particles. From Figure 1 we can see that the potential pit depth and the maximum attraction distance change essentially for the potential (1) depending on the orientation of interacting particles in accordance with the terms of the McLachlan's strict theory on the interaction of macrobodies.[3]

In the present paper the MC method with the canonical NVT-ensemble is applied to the study of a system of 64 molecules, or rotation ellipsoids, interacting in accordance with the potential (1). Calculations were performed in a parallelepipedic box with its edges $L_x = L_y < L_z$ $(L_z/L_x \approx \sigma_\parallel/\sigma_\perp)$ the long edge being parallel to the primary directions of long axes of molecules. The faces were restricted by usual periodic boundary conditions, thus sharply reducing the error caused by the small quantity of particles in the main sample, and it became possible to study an infinite, translational-and-periodical system. Each particle had five degrees of freedom.

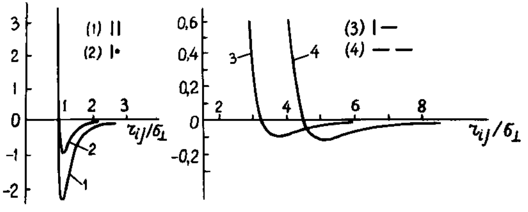

FIGURE 1 Curves of the potential energy of two interacting particles for different relative orientations. The ellipsoid axis values are selected according to the data on the geometry of the CPEHBA molecule: $\sigma_\perp = 20.15$ Å, $\sigma_\parallel = 4.48$ Å.

Position of the mass centres were determined by three Cartesian coordinates. Rotational motion of particles were described with the help of two polar angles ϑ and φ.

In their initial position the mass centres of ellipsoidal particles were ordered their axes being strictly parallel, i.e. the orientational-order parameter $S = 1$. Constant average values of calculated thermodynamic functions testify to the equilibrium achieved in the system. It should be noted that the final results were obtained after averaging approximately over 10^5 configurations.

Investigation objects were nematic LC of CPEHBA (*n*-cyanphenyl ether *n*'-heptylbenzoic acid), BHAOB (4-*n*-butyl-4'-heptanoil-oxiazoxibenzene) and their equimolar mixture, more general expressions[2] being used for ε and σ, in case of interaction between heterogeneous molecules:

$$\varepsilon(\mathbf{u}_1, \mathbf{u}_2) = \varepsilon_0^*[1 - \varkappa_1\varkappa_2(\mathbf{u}_1 \cdot \mathbf{u}_2)^2]^{-1/2}, \tag{5}$$

$$\sigma(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r}_{12}) = \sigma_\perp^*$$

$$\cdot \left\{ 1 - \frac{\varkappa_1 \left(\frac{\mathbf{r}_{12} \cdot \mathbf{u}_1}{r_{12}}\right) + \varkappa_2 \left(\frac{\mathbf{r}_{12} \cdot \mathbf{u}_2}{r_{12}}\right) - 2\varkappa_1\varkappa_2 \left(\frac{\mathbf{r}_{12} \cdot \mathbf{u}_1}{r_{12}}\right) \cdot \left(\frac{\mathbf{r}_{12} \cdot \mathbf{u}_2}{r_{12}}\right) (\mathbf{u}_1 \cdot \mathbf{u}_2)}{1 - \varkappa_1\varkappa_2(\mathbf{u}_1 \cdot \mathbf{u}_2)} \right\} \tag{6}$$

where

$$\varkappa_1 = \frac{(\sigma_{1_\parallel}/\sigma_{1_\perp})^2 - 1}{(\sigma_{1_\parallel}/\sigma_{1_\perp})^2 + 1}; \qquad \varkappa_2 = \frac{(\sigma_{2_\parallel}/\sigma_{2_\perp})^2 - 1}{(\sigma_{2_\parallel}/\sigma_{2_\perp})^2 + 1}, \tag{7}$$

$$\varepsilon_0^* = (\varepsilon_{0_1} \cdot \varepsilon_{0_2})^{1/2}; \qquad \sigma_\perp^* = (\sigma_{1_\perp} + \sigma_{1_\perp})^{1/2}, \tag{8}$$

Eccentricity of molecules, i.e. rotation ellipsoides (or the length-to-width ratio) was obtained from the data of conformation analysis which we performed in the atom-atom approximation.[4,5] These parameters, as well as some other values of the model under study, necessary for calculations, are given in Table I.

A nematic phase was detected at the pressure ($\eta = 0.397$ for CPEHBA and $\eta = 0.436$ for BHAOB), the same for different temperature values. Results of calculations for configuration energy U, specific heat C_v and orientational-order parameter S are presented in Figures 2 to 4 (see the curve (1) in Figures 3 and 4).

TABLE I

Parameters of the Lennard-Jones potential and some NVT-ensemble constants: η is the stacking coefficient, N/V is the density parameter, V_0 is the volume of one rotation ellipsoid, and k_B is the Boltzmann constant.

Substance	$\sigma_\perp$, Å	$\sigma_\parallel$, Å	ε_0/k_B, K	$\eta = V_0N/V$	N
CPEHBA	20.15	4.48	596.03	0.397	64
BHAOB	23.7	4.7	666.99	0.436	64

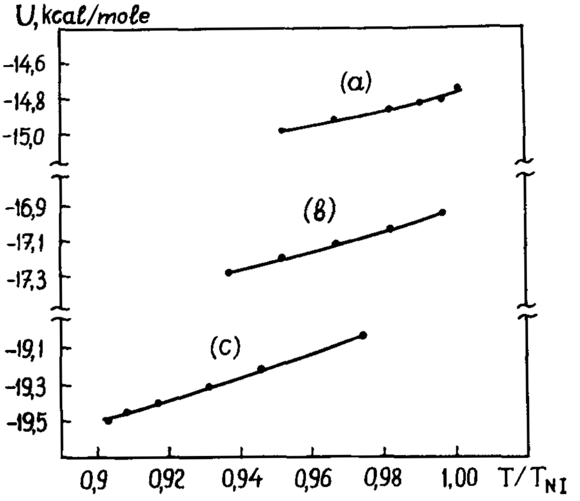

FIGURE 2 Configurational energy vs reduced temperature: (a) CPEHBA; (b) equimolar mixture CPEHBA + BHAOB; (c) BHAOB.

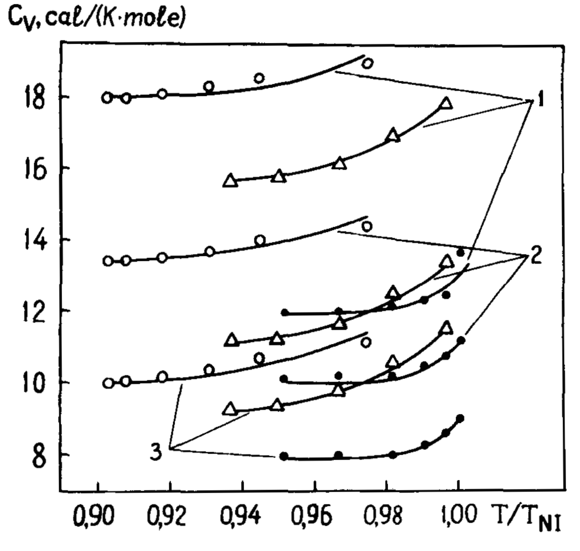

FIGURE 3 Specific heat C_v vs reduced temperature for (•) CPEHBA; (○) BHAOB and (△) equimolar mixture CPEHBA + BHAOB: 1 → $\gamma = 1$, 2 → $\gamma = 2$, 3 → $\gamma = 4$, γ is the number of molecules in NVT-ensemble's "elementary" object.

We may see that they are in good agreement with the experimentally observed trends in the changes of the nematic phases properties, though there is some qualitative discrepancy too. Thus, results of the MC calculations for the orientational-order parameter S give a correct picture of the parameter temperature changes, but quantitatively, they proved to be higher than the experimental values. This discrepancy takes place, as it is shown further, because the short-range order effects

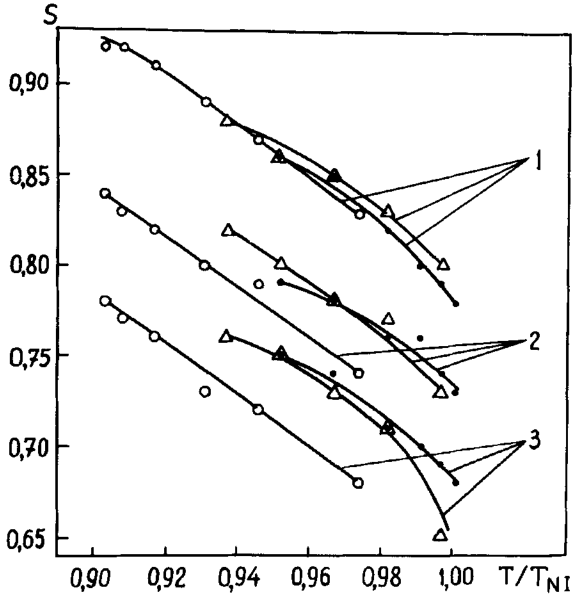

FIGURE 4 Dependence of orientational-order parameter S on reduced temperature for (•) CPEHBA, (○) BHAOB and (△) equimolar mixture CPEHBA + BHAOB: 1 → $\gamma = 1$, 2 → $\gamma = 2$, 3 → $\gamma = 4$. γ is the number of molecules in NVT-ensemble's "elementary" object.

TABLE II

Total values of energy U^* and specific heat C_v^* for CPEHBA and BHAOB due to translational, rotational and oscillation motions. U_0 is the system's energy at absolute zero temperature.

CPEHBA		BHAOB		
$(U^* - U_0)$, kcal/mole	C_v^*, cal/(K·mole)	$(U^* - U_0)$, kcal/mole	C_v^*, cal/(K·mole)	T, K
12.9860	82.5380	15.4381	102.4793	315
13.6456	85.6346	15.9637	104.2630	320
14.0436	86.8622	16.4789	106.1065	325
14.2985	87.6864	—	—	328
14.4864	88.2310	17.0073	106.8601	330
14.7318	89.6713	—	—	332
14.9308	89.7375	17.6024	110.0568	335
—	—	18.1112	111.5670	340
—	—	18.6728	113.2558	345

are neglected. Regarding the energy U and heat capacity C_v, we see the results of the MC calculations are lower than the experimental values[6], because neither intramolecular oscillations, nor contributions from translational and rotational motion molecules are taken into account in the applied model. A reasonable agreement with the known experimental data is achieved when these contributions to the values of configuration energy and heat capacity (Table II) are taken into account (by the oscillator method[7]).

MC calculations are also performed for the case when microclusters are considered as the "elementary" objects of NVT-ensemble, instead of single molecule. Interaction between the clusters were also computed with the help of the potential (1), dimensions of the rotation ellipsoids found from the data on the intracluster ordering of molecules, obtained by us by the method of atom-atom potentials. This approach accounts for the short-range order effects affecting thermodynamic properties of the NVT-ensemble.

The clusters under study consisted of 2 and 4 molecules. The calculation results are given on Figures 3 and 4. From these figures it is evident that the short-range order effects, taken into account, improve results for heat capacity and the order parameter ($S \approx 0.73$).

Good agreement between the experimental and calculated values, obtained in the present paper, raises hopes that the suggested model may be successfully used for describing thermodynamics of nematic crystals.

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