

Molecular dynamics simulation study of the liquid crystal phase in small mesogene cluster (9CB)₂₀*

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Using the molecular dynamics (MD) technique, we have investigated a nano droplet composed of twenty mesogene molecules 4-*n*-alkyl-4-cyanobiphenyl (9CB). The geometry of the 9CB molecule was calculated with the DFT method. We treat 9CB molecules as rigid bodies, the intermolecular interaction is taken to be the full site-site pairwise additive Lennard-Jones (LJ) potential. We calculated the radial and orientational distribution functions in the temperature range of 100 to 350 K, as well as the linear and angular velocity autocorrelation functions and their Fourier transforms. We observed liquid crystal ordering in the studied nanoscale system, up to its vaporization temperature.

Keywords: *mesogene cluster, nanoscale liquid crystal, molecular dynamics simulation (MD), 9CB*

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1. Introduction

In the last decades, systems with liquid crystal molecules were extensively studied owing to their optoelectronic applications [1–6]. As experimental methods were not suitable for studying the motion of single molecules, molecular dynamics simulation studies of mesogenes became more popular [7–10]. When dealing with a simulation of the physical properties of liquid crystals, usually the initial choice to be made is between the use of phenomenological approaches (such as mean-field density functional theory) or molecular level methods (Gay-Berne [11], Lebwohl-Lasher [12]). Recently, a number of molecular dynamics studies of bulk liquid crystals samples have been carried out using fully atomistic models [13–15]. These simulations allow for a detailed description of the molecular structure and are essential for a quantitative investigation of liquid crystalline properties, which are sensitive to the molecular details. Fully atomistic computer experiment studies of nanoscopic mesogene droplets are so far scarce, but this issue will be increasingly important with the forthcoming advent

of nanotechnology. Particularly, one would like to know whether and how the peculiarities of dynamics of mesogene molecules near the surface of a nanoscale droplet influence the tendency of mesogenes to form liquid crystals. That is why we decided to investigate here an extremely small mesogene ensemble, composed of only twenty mesogenes. We have chosen the phenyl-based nematogen 9CB (4-*n*-alkyl-4-cyanobiphenyl) (Fig. 1), because of its known nematic and smectic phases in bulk sample near the room temperature [16, 17].

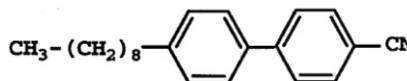


Fig. 1. The chemical formula of 9CB molecule.

2. Computational procedure

We have used the Van der Waals potential (Lennard-Jones + coulombic interaction) to describe the interaction between atoms (sites) of interacting mesogene molecules inside a (9CB)₂₀ cluster.

$$V(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}^6}{r_{ij}} \right) \right] + \frac{Z_i Z_j e^2}{4\pi\epsilon_0 r_{ij}} \quad (1)$$

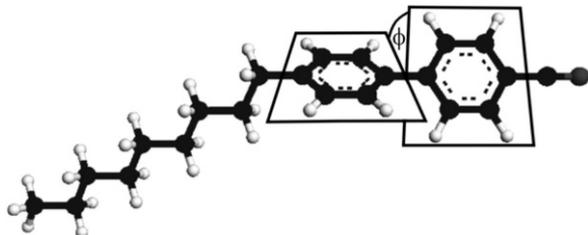
where r_{ij} is the distance between the i^{th} and j^{th} atoms of the pair of different molecules, Z_n is the

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Table 1. Lennard-Jones potential parameters.

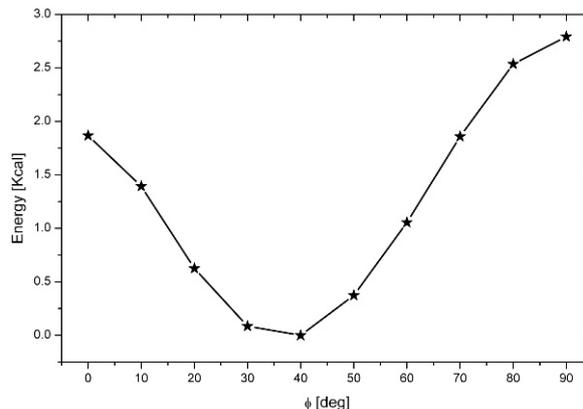
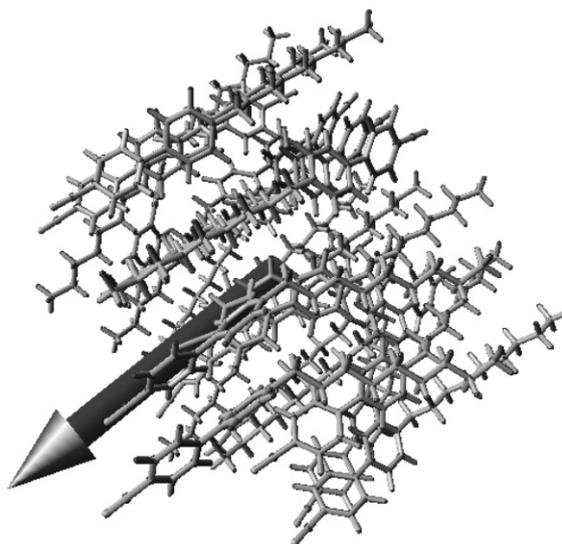
Atom	ϵ [10^{-21} J]	σ [10^{-10} m]	m [10^{-26} kg]
Carbon	0.386	3.4	0.199
Nitrogen	0.386	3.1	0.116
Hydrogen	0.171	2.81	0.017

Fig. 2. The definition of the angle ϕ between phenyl rings in 9CB molecule.

electric charge of n^{th} site. The Lennard-Jones interaction parameters between two different sites were calculated using Lorentz-Berthelot mixing rule [18]. All potential parameters and atomic masses used in the simulation are shown in Table 1. The mesogens were treated as rigid bodies with no internal degrees of freedom. The classical equations of motion were integrated up to 5 ns by the Adams-Moulton predictor-corrector algorithm [18]; the integration time step used was 0.5 fs which ensured good total energy conservation. The starting configuration was prepared via Monte Carlo potential energy minimization. The average energy was adjusted as desired by a process of velocities scaling using Berendsen algorithm. The cluster was equilibrated for 10^6 MD steps. The autocorrelation functions of linear \vec{v} and angular $\vec{\omega}$ velocities of 9CB molecule were calculated by averaging $\langle \vec{v}(0) \cdot \vec{v}(t) \rangle$ and $\langle \vec{\omega}(0) \cdot \vec{\omega}(t) \rangle$ over 10^4 time origins. The origins were separated by a time interval equal to 50 integration time steps. Our calculations were carried out for a constant energy ensemble for zero total linear and angular momentum.

3. Results

We started our computer experiment by first principle calculation of the geometry and atomic charge distribution of the 9CB molecule. In our *ab ini-*

Fig. 3. The plot of the ground state energy of (9CB)₂₀ cluster as a function of ϕ angle – DFT calculations.Fig. 4. The instantaneous configuration of (9CB)₂₀ cluster at $T = 120$ K. The arrow represents the director vector.

tio calculations we used the DFT approach with the B3LYP exchange-correlation functional and a 6-31G* basis set. All quantum calculations were performed using the GAMESS code [19]. The angle ϕ between two phenyl rings (see Fig. 2) was chosen so as to correspond to the conformation of the minimum ground state energy *i.e.* $\phi_{\text{min}} = 40$ degrees (Fig. 3). This conformation was used for the subsequent classical MD simulation. A representative snapshot of the instantaneous configuration of (9CB)₂₀ at the temperature $T = 120$ K (see Fig. 4) re-

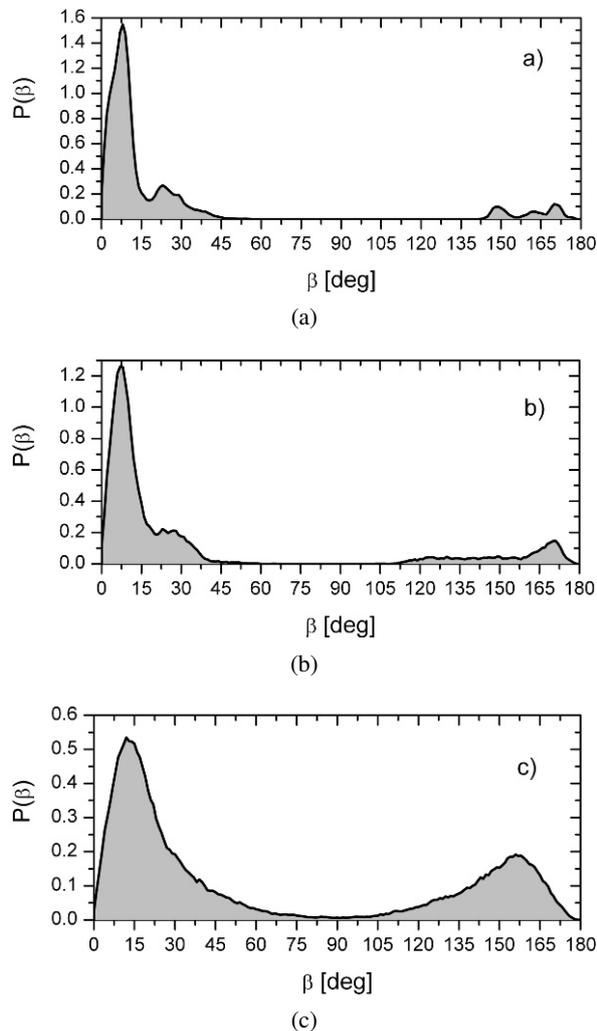


Fig. 5. The orientational distribution function $P(\beta)$ for $(9CB)_{20}$ cluster at a) $T = 120$ K, b) $T = 200$ K and c) $T = 304$ K.

veals the evident spatial ordering of 9CB molecules within the cluster volume. Their long axes of symmetry are oriented along roughly similar, apparently correlated directions. We verified that the kind of spatial ordering shown in the snapshot persisted also for higher temperature studied: $T = 200$ K and $T = 300$ K, although the mobility of boundary surface molecules increases at higher temperatures.

To investigate the level of molecular order in the cluster, we constructed the order tensor $Q_{ij} = \langle 3 \cos \Theta_i \cos \Theta_j - \delta_{ij} \rangle / 2$ where $i, j = x, y, z$ are indices which refer to the laboratory frame [20]. The bracket $\langle \dots \rangle$ denotes spatial and temporal averaging

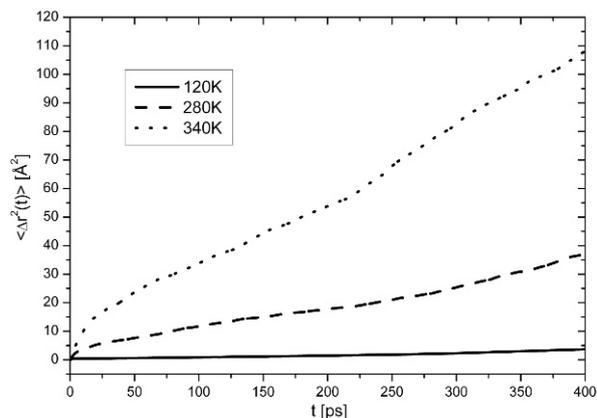


Fig. 6. The mean square displacement function of the center of mass of 9CB molecules at three temperatures.

over the whole sample and simulation time. Θ is the angle between the molecular long axis and the eigenvector \hat{n} of the order tensor Q_{ij} corresponding to the maximum eigenvalue. The vector \hat{n} is usually called the director of a sample (see Fig. 4). We calculated the distribution function $P(\beta)$ of the angle β between the long axis of the molecule and the director \hat{n} of the nanodroplet (Fig. 5). At a low temperature the majority of molecules are oriented almost parallel to the director, there are no molecules perpendicular to \hat{n} and only a few molecules oriented antiparallel to the director. The orientational distribution $P(\beta)$ at higher temperature becomes more symmetrical as a result of the increasing mobility of surface molecules. The largest eigenvalue of the order tensor Q_{ij} is the second-rank order parameter P_2 [21, 22] ($0 \leq P_2 \leq 1$), we obtained $P_2 = 0.90, 0.85, 0.68$ for $T = 120$ K, 200 K and 304 K, respectively. Such high values of P_2 indicate the liquid crystal ordering of a nanodroplet.

The plot of the mean square displacement $\langle |\Delta \vec{r}(t)|^2 \rangle$ of a 9CB molecule (Fig. 6), where $\Delta \vec{r}(t) = \vec{r}(t) - \vec{r}(0)$ and \vec{r} is the position of the center of mass of 9CB, indicates that for $T = 120$ K we are dealing with a solid phase of the cluster whereas at higher temperatures translational diffusion of molecules appears. Hence, at higher temperatures the cluster is not in the solid state. This is clear if we recall Einstein relation, which connects the slope of the linear part of the mean square

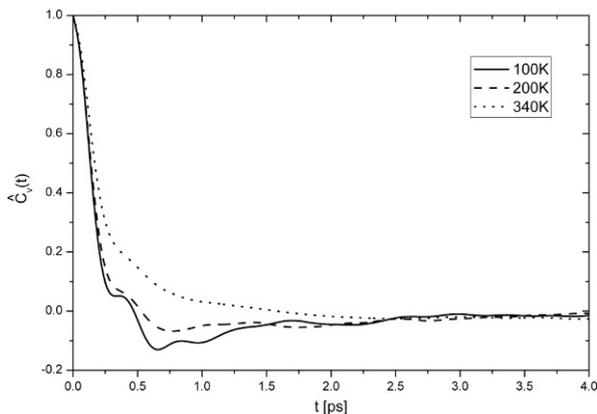


Fig. 7. The linear velocity autocorrelation function of the center of mass of 9CB molecules at several temperatures.

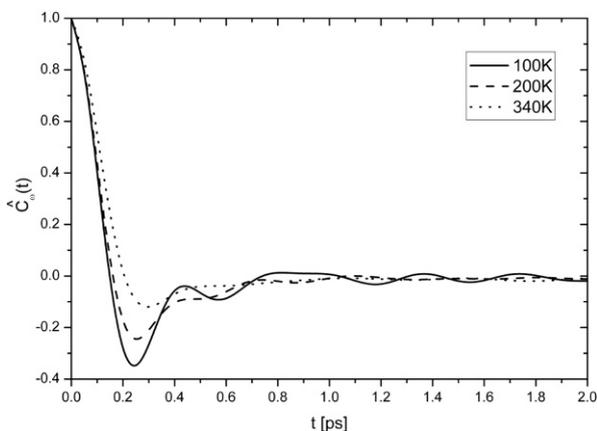


Fig. 8. The angular velocity autocorrelation function of 9CB molecules at several temperatures.

displacement with the translational diffusion coefficient D of a molecule: $\langle |\Delta\vec{r}(t)|^2 \rangle \gg 6Dt$. The calculated diffusion coefficients D increase with increasing temperature, for example $D = 1.28 \cdot 10^{-6} \text{ cm}^2/\text{s}$ for $T = 280 \text{ K}$ and $D = 4.06 \cdot 10^{-6} \text{ cm}^2/\text{s}$ for $T = 340 \text{ K}$. The soft, spatially ordered phase of mesogene molecules corresponds to a liquid crystal phase.

To obtain further insight into the mesogene dynamics we calculated the normalized velocity autocorrelation function $C_v(t) = \langle \vec{v}(t) \cdot \vec{v}(0) \rangle / \langle v(0)^2 \rangle^{-1}$, where \vec{v} is the translational velocity of the center of mass of 9CB. Fig. 7 shows that – in spite of the significant mass of the 9CB molecule – its velocity changes rapidly, being al-

most entirely decorrelated after 2 ps. The oscillations of $C_v(t)$, characteristic of a solid phase at low temperature, wash out at a higher temperature, $T = 340 \text{ K}$. The angular velocity autocorrelation function $C_\omega(t) = \langle \vec{\omega}(t) \cdot \vec{\omega}(0) \rangle / \langle \omega(0)^2 \rangle^{-1}$, presented in Fig. 8, decays even faster than $C_v(t)$. The negative dip of $C_\omega(t)$ at $t = 0.25 \text{ ps}$ ($T = 120 \text{ K}$) vanishes at $T = 340 \text{ K}$. In general, $C_\omega(t)$ changes with temperature, the lower the temperature, the deeper the dip of $C_\omega(t)$ becomes.

In conclusion, our atomistically detailed MD simulations show the existence of liquid crystal phase in a small mesogenous cluster (9CB)₂₀ for a temperature ranging between 280 K and 340 K. Note that even the presence of the surface (finite size) effect does not destroy the tendency of rod-like mesogenes 9CB to order spatially and orientationally.

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