



Nanoparticles Effects in Liquid Crystals (NELC) -AFRL/RX ST Dr. Bunning

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14. ABSTRACT In this project, we focus on the understanding of the effects on order, dynamics and molecular organization of a host nematic caused by the introduction of nanoparticles through a modelling/computer simulation approach. We have modelled the nanoparticles and the oleic acid covering as berry-like clusters of spherical Lennard-Jones sites ('united atoms'), each of which can be endowed with specific features like size, charges, dispersion interactions, while the mesogen with a rodlike Gay-Berne ellipsoid. The results of our Monte Carlo simulations assess the influence of nanoparticles ferroelectricity and surfactant coating on the changes in order of the host nematic.						
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Summary

In this project, we focus on the understanding of the effects on order, dynamics and molecular organization of a host nematic caused by the introduction of nanoparticles through a modelling/computer simulation approach.

We have modelled the nanoparticles and the oleic acid covering as berry-like clusters of spherical Lennard-Jones sites (“united atoms”), each of which can be endowed with specific features like size, charge, dispersion, while the mesogen with a rod-like Gay-Berne ellipsoid.

The results of our Monte Carlo simulations assess the influence of nanoparticles ferroelectricity and surfactant coatings on the changes in order of the host nematic.

Introduction

The understanding of the effects of nanoparticles on the properties of a liquid crystal (LC) they are dispersed in, is a problem simple to state and important to solve for practical applications, but difficult to set up in detail and to tackle [1-7]. One of the main reasons resides in the difficulty to define the key features of the nanoparticle amongst the many existing ones: chemical nature, size, shape, polarity or ferroelectricity, ferromagnetism, polydispersity and the effect of surfactant coatings, like oleic acid, that are nearly always used to stabilize the suspension.

The problem of the effects of nanoparticles on solvents in general is also of great current interest even for isotropic solvents where a “universal structuring” of the solvent surrounding the NP has been recently proposed [8] and should be more manifest in LC. Much of the current modelling has drastically ignored most of these items, considering lattice models or off-lattice models based on a one-site representation of the nanoparticle, often just spherical.

Here we continue the work started in [8] adding some more realism to the system by reproducing the essential features and specific polarity of 5CB and BaTiO₃ nanoparticles.

This report is organized in five main parts:

(MOD1) Coarse-grained modelling of mesogenic (M) 5CB molecules and assessment of the specific Gay-Berne and electrostatic parametrization.

(MOD2a) Modelling of polar BaTiO₃ nanoparticles (N) and assessment of the specific Gay-Berne and electrostatic parametrization.

(MOD2b) Modelling of oleic acid covering and assessment of the specific Gay-Berne parametrization.

(SIM1) Simulations of a pure mesogenic system.

(SIM2) Preliminary simulations of a large system of a dispersion of BaTiO₃ nanoparticles covered with oleic acid in 5CB.

Methods, Assumptions, and Procedures

(MOD1) Coarse-grained modelling of 5CB molecules

We have chosen to model the mesogens as elongated ellipsoidal particles decorated with two charges (see Figure 1).

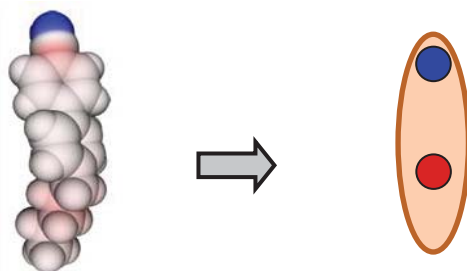


Figure 1: Schematic drawing of the proposed model for the 5CB mesogen

The dimensions $\sigma_x, \sigma_y, \sigma_z$ are adjusted in order to simultaneously obtain: (a) the atomistic value for the density in the nematic ($T=310$ K) phase (i.e. $N/V=2.427 \cdot 10^{-3} \text{ \AA}^{-3}$ or equivalently $V_{mol}=412 \text{ \AA}^3$); (b) the conditions $\sigma_x=\sigma_y$ and $\sigma_z=3.1 \sigma_x$ [9].

The specific GB well depths are adjusted in order to obtain a system of 1000 mesogenic molecules interacting through GB and charges interactions which gives a nematic-isotropic transition at the atomistic value of T_{NI} (i.e. 307 K).

σ_x (Å)	σ_y (Å)	σ_z (Å)	ϵ_x (kcal/mol)	ϵ_y (kcal/mol)	ϵ_z (kcal/mol)	σ_c (Å)
5	5	15.5	0.475	0.475	0.095	5

Table 1: Dimensions and interaction parameters of the mesogenic interaction sites

For the modeling of the electrostatic interaction, a Genetic Algorithm [10] is used to calculate the best set of effective point charges that mimic the electrostatic field around the molecule; in practice two charges are founded and mapped on the GB ellipsoid, that is, are shifted/scaled assuming the centre of mass of the GB ellipsoid located in the middle of the bond between the two phenyl groups. The coordinates and the magnitude of the two charges are:

i	x (Å)	y (Å)	z (Å)	q (e)
1	0	0	-7.52	-0.11562
2	0	0	3.875	0.11562

Table 2: Positions and intensities of the reduced set of mesogenic charges obtained by a Genetic Algorithm minimization.

(MOD2a) Modelling of polar BaTiO₃ nanoparticles

The BaTiO₃ nanoparticles are modelled as tightly-packed spherical clusters of 32 identical LJ spheres, rigidly connected with each other and slightly overlapping (see Figure 2, left plate).

Concerning the nanoparticle size, we have chosen the minimal dimension compatible with the milling procedure [3], while the ϵ value of each LJ sphere is adjusted in order to reproduce the Hamaker interaction between two BaTiO₃ nanoparticles (i.e. $A_H=5 \cdot 10^{-20} \text{ J}=7.2 \text{ kcal/mol}$) [11], via the GB potential (Figure 2, right plate).

For the modeling of the electrostatic interaction, we have assumed a reference polarization for BaTiO₃ of 0.26 C m^{-2} , which for our $r \approx 1.6 \text{ nm}$ nanoparticle, can be rendered with 4 positives charges ($q_1 = q_2 = q_3 = q_4 = 3e$) charges, positioned in the centers of LJ sites at the nanoparticle top, and with 4 negative ($q_5 = q_6 = q_7 = q_8 = -3e$) charges positioned in the centers of LJ sites at the bottom (see Figure 2, left plate).

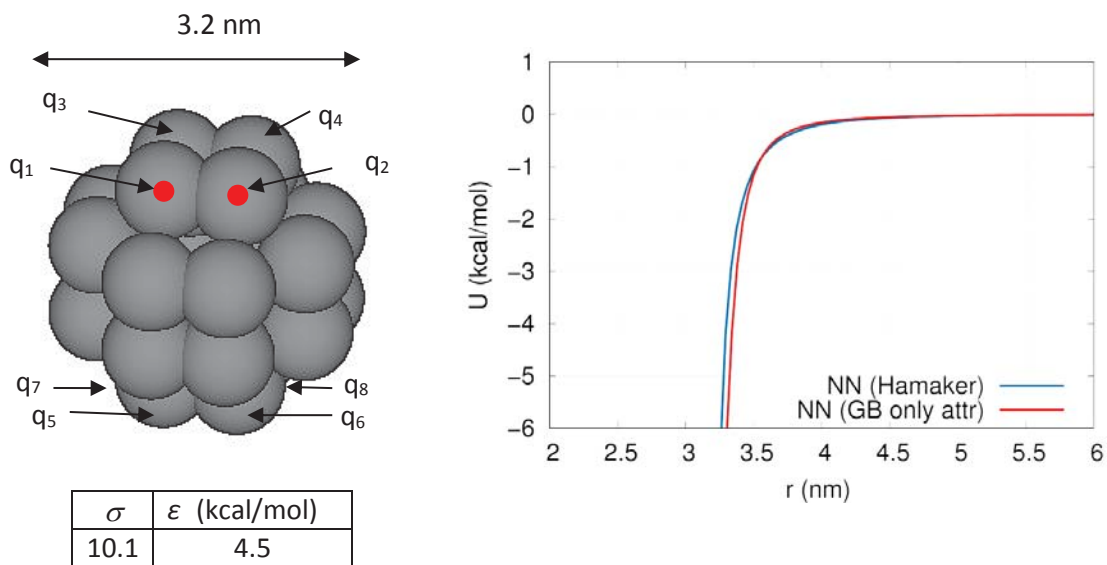


Figure 2: (left) Schematic drawing of the proposed model for the BaTiO₃ and corresponding parametrization; (right) Comparison between the pair potential profiles of Hamaker interaction between BaTiO₃ nanoparticles as calculated in [11] and as obtained through our spherical cluster of LJ particles.

(MOD2b) Modelling of oleic acid covering

In current theoretical modelling, including our previous one [8], nanoparticles dispersed in LC are normally assumed as “naked”, while in reality a stabilizing coating, typically of oleic acid, is added and has proved to be essential. We have now tried to model this effect by covering our nanoparticles with a concentric shell of identical 48 LJ neutral spheres, rigidly connected with each other and slightly overlapping (see Figure 3):

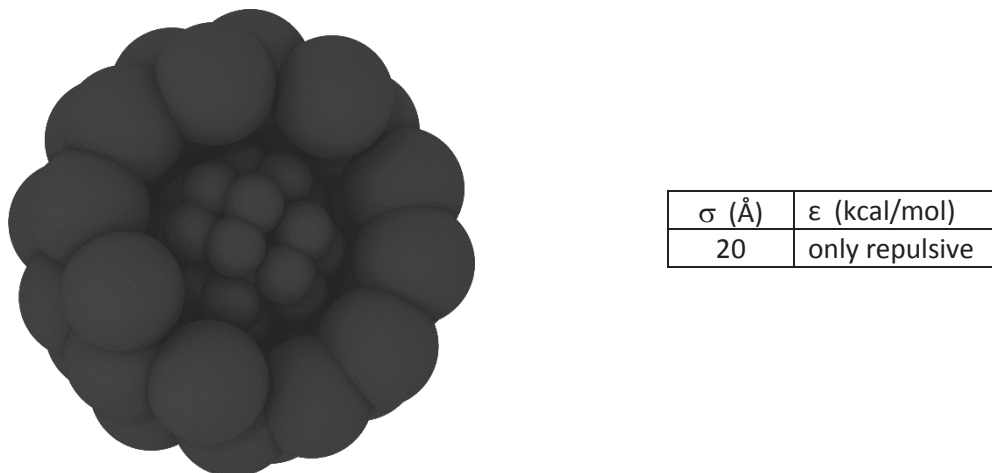


Figure 3: Schematic drawing of the proposed model for the oleic acid covering and corresponding parametrization.

The effect of the oleic acid covering on electrostatic/GB/total interactions is shown in Figure 4:

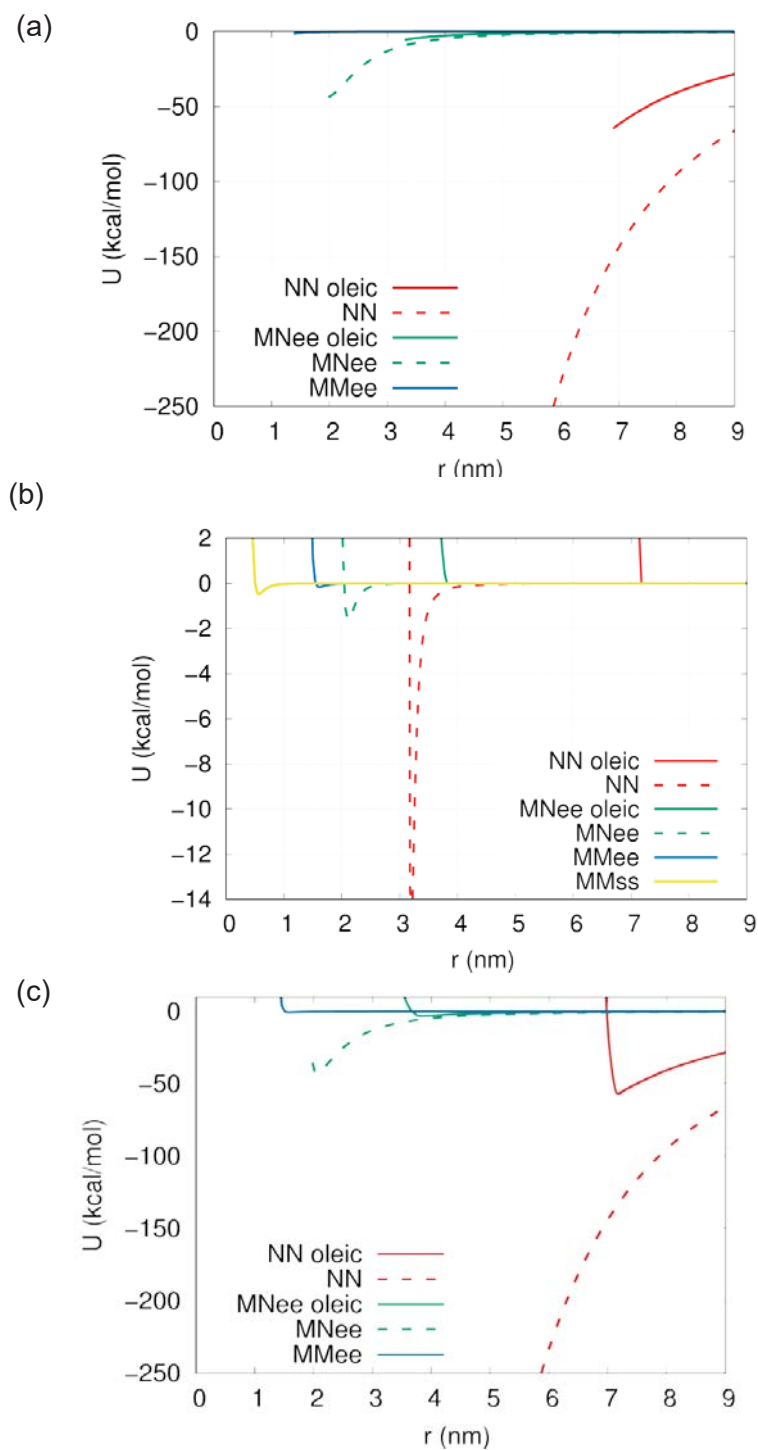


Figure 4. Representative pair potential profiles relative to BaTiO_3 - BaTiO_3 (NN), BaTiO_3 -5CB (NM) and 5CB-5CB (MM) interactions with or without oleic acid covering.

Results and Discussion

(SIM1) Simulations of a pure mesogenic system

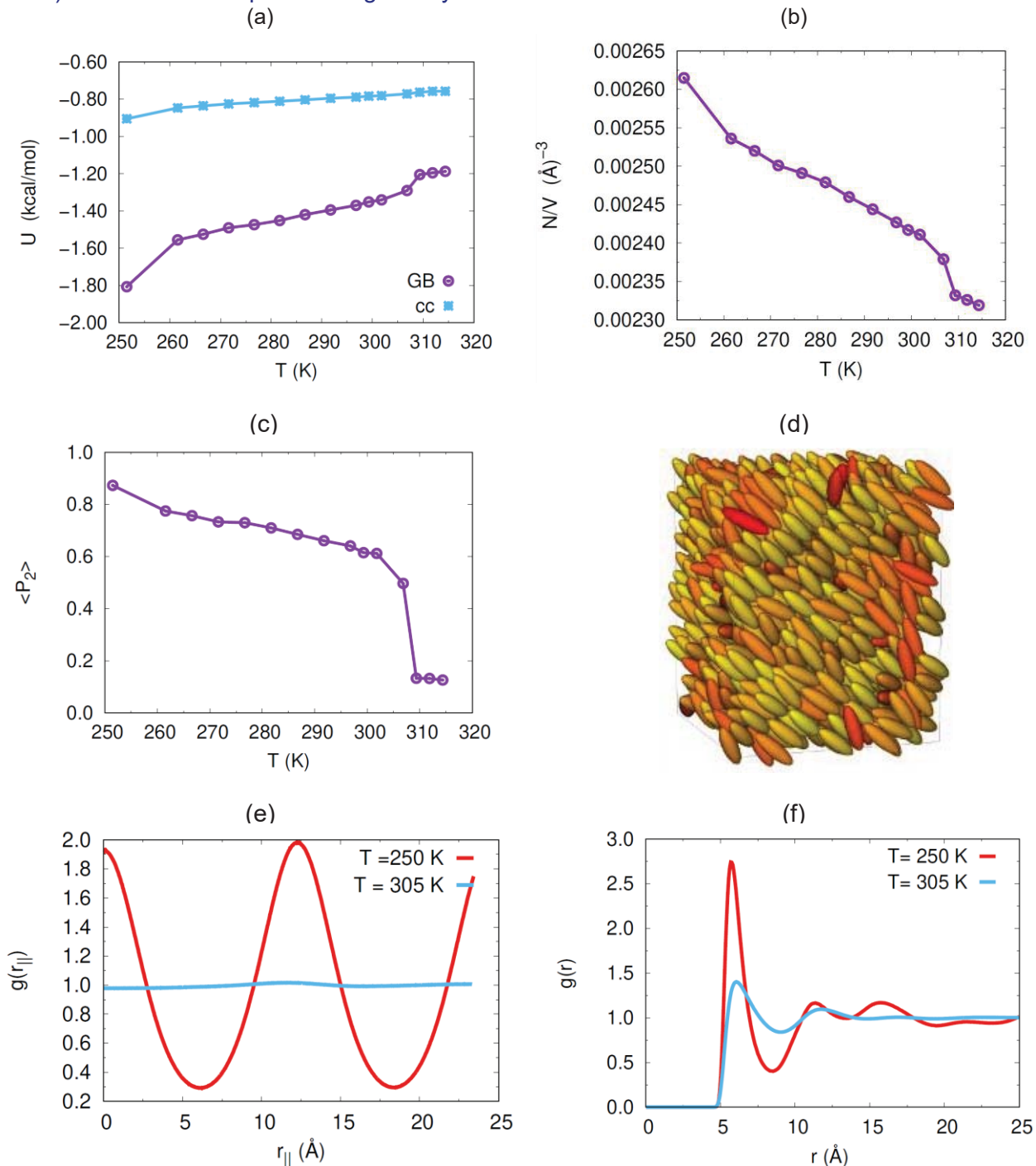


Figure 5. Plots against temperature of the average values of (a) electrostatic and GB energy, (b) density and (c) orientational order parameter for a system of $N_M=1000$ pure 5CB mesogenic molecules. (d) Snapshot of an equilibrium configuration in nematic phase; here the GB mesogens are colour coded according to their orientation with respect to the phase director (yellow for parallel, blue for orthogonal). (e) Density correlation function along the director and (f) radial correlation function in nematic ($T=305$ K) and crystal phase ($T=250$ K).

Monte Carlo (MC) simulations have been first performed on a pure mesogenic system that has been the reference for the dispersions of embedded nanoparticles. We have considered systems of $N_M = 1000$ GB rods modelled as above, in the isobaric-isothermal (NPT) ensemble, using 3D periodic boundary conditions, in a range of temperatures wide enough to observe both isotropic–nematic and nematic–crystal transitions of the pure mesogen. The MC experiments were run in a cooling sequence starting from isotropic configurations. From the equilibrium configurations, we have computed the average values of both GB and electrostatic energy (Fig. 5a), density (Fig. 5b), orientational order parameter $\langle P_2 \rangle = (3 \langle \cos^2 \beta \rangle - 1)/2$ (Fig. 5c), where β is the angle between mesogen long axis and director, which shows a steep increase at $T=308$ K, corresponding to the first order isotropic–nematic transition, and a further jump at $T=255$ K denoting the nematic–crystal transition.

(SIM2) Preliminary simulations of a large system of a dispersion of BaTiO₃ nanoparticles covered with oleic acid in 5CB.

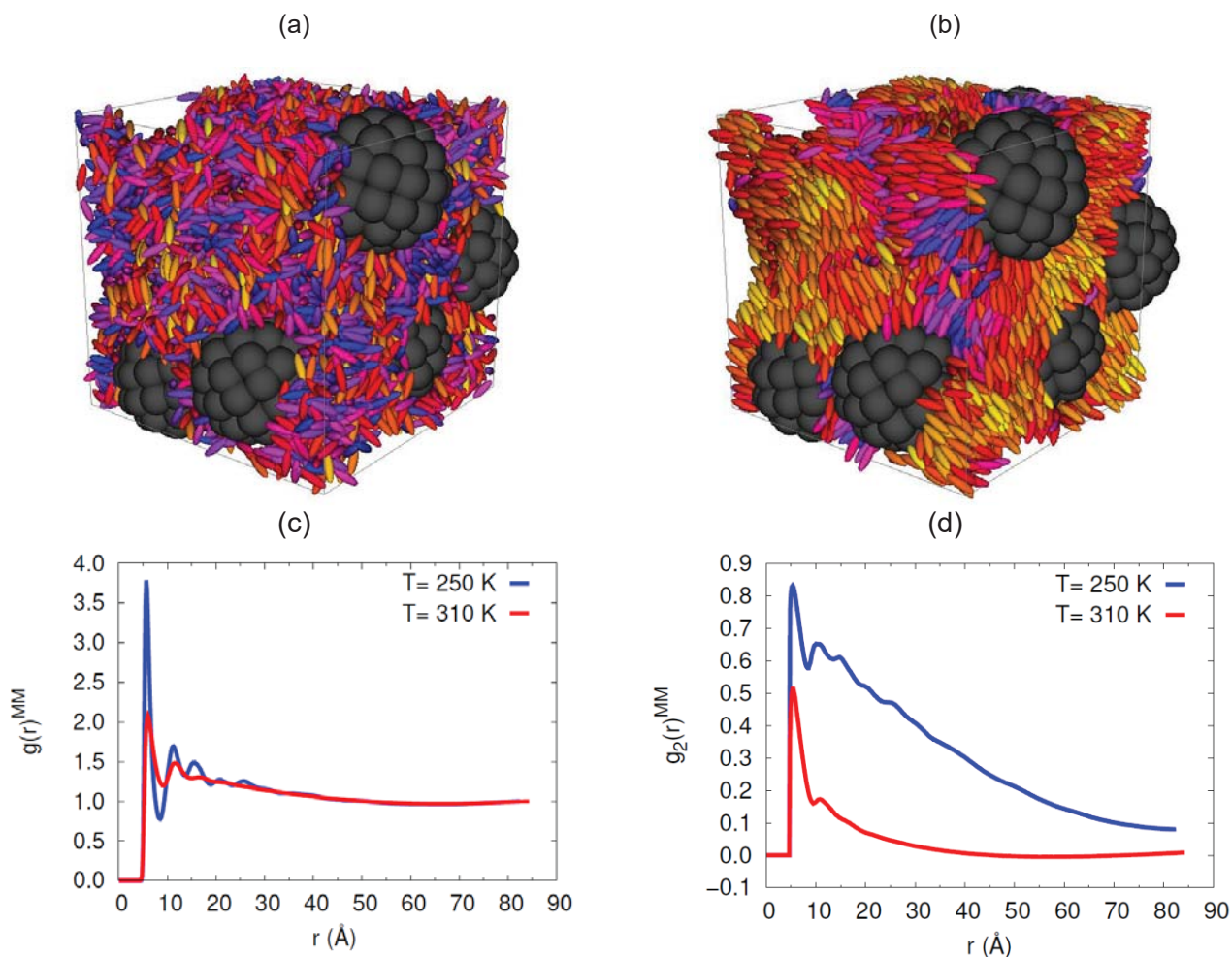


Figure 6. Snapshots of 6% nanoparticles dispersion in 5CB, in isotropic (a) and nematic (b) phase; profiles of the $g(r)^{MM}$ (c) and $g_2(r)^{MM}$ (d) correlation functions at the two reference temperatures.

We have performed a preliminary simulation of a dispersion of $N_M + N_N = 8000$ particles, with $N_N = 8$, corresponding to a nanoparticle volume concentration of 6%. The simulation has been started from an isotropic configuration generated by replacing with the appropriate number of nanoparticles some mesogens of a pure LC sample, previously equilibrated at the same pressure and temperature, and slightly increasing the sample volume to accommodate more easily the nanoparticles.

As in the pure 5CB system, decreasing the temperature causes an increasing of the mesogenic orientational order, as evident from the snapshots of typical configurations at $T = 310$ K (Figure 6a) and 250 K (Figure 6b).

We have found that the addition of oleic acid is essential in simulation to avoid aggregation, which would otherwise be inevitable for this strong polar nanoparticle.

Additional insights into the local structure of the phases can be gained by examining the pair correlation functions for both MM (Figures 6c and 6d) and MN pairs (Figure 7).

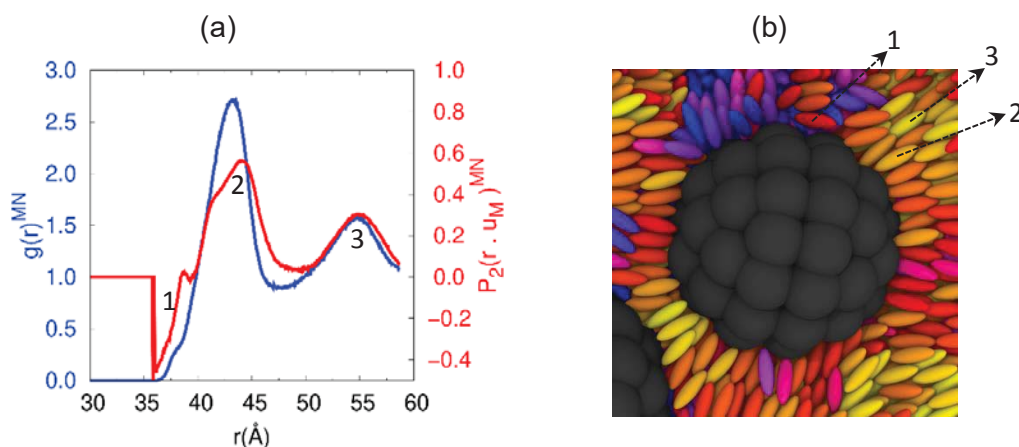


Figure 7: Mesogenic-nanoparticle correlation functions $g(r)^{MN}$ and $P_2(r \cdot u_M)^{MN}$ in nematic phase (a); close up of a nanoparticle environment in a typical instantaneous configuration (b).

In particular, in order to evaluate the nanoparticle–mesogen reciprocal arrangement at the nanoparticle surface, we have examined the anisotropic radial distribution functions $g(r)^{MN}$ and $P_2(r \cdot u_M)^{MN}$ (see Figure 7a), where r is the vector connecting their centers of mass of NM pair and u_M is the mesogen long axis. The correlations indicate a small number of NM pairs with parallel orientations (i.e. $P_2(r \cdot u)^{MN} \approx -0.5$) in the range 35-38 Å; at larger distances two pronounced peaks arise at $r \approx 40$ Å and $r \approx 55$ Å, suggesting instead a radial arrangement of mesogens around the nanoparticle as evident from the close up of the nanoparticle environment in Figure 7b.

Conclusions

We have reported the results of MC computer simulation studies on systems of mesogens doped with nanoparticles. The modelling and simulation work performed in this project has considerable advanced realism of the system by introducing:

- (1) LC polarity and reproduction of essential features of 5CB (order and T_{NI})
- (2) NP polarity modelled on BaTiO_3
- (3) Oleic acid coating

The results clearly show that even a simple model based on a multi-site Gay–Berne potential and polar interaction can help to figure out the features which favors the enhancement of the LC order. We reckon that the work could be fruitfully pursued by (i) applying an electric field and study the response, (ii) comparing with experiments.

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List of Symbols, Abbreviations, and Acronyms

N: nanoparticles
M: mesogen
LC: liquid crystal
GB: Gay-Berne
LJ: Lennard-Jones
MC: Monte Carlo