Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Roberto Berardi [a], Silvia Orlandi [a] & Claudio Zannoni [a]

[a] Dipartimento di Chimica Fisica ed Inorganica, Università Viale Risorgimento 4, Bologna, 40136, Italy

Version of record first published: 18 Oct 2010

To cite this article: Roberto Berardi, Silvia Orlandi & Claudio Zannoni (2003): Nonspontaneous Nematic Induction and other Field Effects in Model Mesogens, Molecular Crystals and Liquid Crystals, 394:1, 141-151

To link to this article: http://dx.doi.org/10.1080/15421400390193738

Mol. Cryst. Liq. Cryst., Vol. 394, pp. 141–151, 2003

ISSN 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400390193738

NONSPONTANEOUS NEMATIC INDUCTION AND OTHER FIELD EFFECTS IN MODEL MESOGENS

Roberto Berardi, Silvia Orlandi, and Claudio Zannoni
Dipartimento di Chimica Fisica ed Inorganica, Università
Viale Risorgimento 4, 40136 Bologna, Italy

We investigate the effect of an external field on transitions and structural organization in systems of Gay-Berne (GB) particles devoid of a nematic phase in zero field. We consider GB particles both without and with a transverse dipole and observe the induction of nonspontaneous nematic and other modifications of the orientational and positional order.

Keywords: smectics; induced order; Monte Carlo simulations; Gay-Berne

INTRODUCTION

One of the most interesting and technologically useful properties of liquid crystals is that of being easily aligned in an external field [1,2]. An immediately appreciable effect associated with the application of a sufficiently strong external field on a nematic is that of director alignment, which causes a decrease in the turbidity of the phase. More generally, an external field will make the isotropic phase an anisotropic, paranematic one, at least from the point of view of group theory, thus suppressing the symmetry difference with the nematic that guarantees that transforming from an isotropic to a nematic phase occurs with a first order transition [3]. This in turn suggests a first order paranematic-nematic transition below a certain critical point, which was indeed predicted by molecular field theory [4–9] and experimentally observed, e.g. by subjecting a virus suspension to a large magnetic field [10] or applying a strong electric field to nematogens in their isotropic phase [11,12]. Another very interesting effect, theoretically predicted by Rosenblatt [13], is that a sufficiently strong field should induce an intermediate, "nonspontaneous", nematic phase in a system that only undergoes an isotropic to smectic transition in the absence of a field. This

We wish to thank the EU TMR (CT970121) project, coordinated by Prof. P. L. Nordio until his untimely death, for support.

nematic induction was also experimentally observed in a thermotropic mixture of n-octyl and n-decyl cyanobiphenyls only exhibiting a direct isotropic to smectic transition in zero field [14].

Understanding the effects of an external field on the molecular organization, at a level beyond that of simple molecular field theory which, for instance, cannot yield pair properties and clustering effects, is an interesting problem that can in principle be tackled with computer simulations. Modelling field effects on the ordering and the phase transitions of realistic, atomistic level, models of liquid crystals is, however, still beyond current computational possibilities.

Field effects have thus been studied using Monte Carlo simulations of simple lattice models, e.g. of bulk [15] and confined [16,17] nematics. While this approach is useful for studying field effects on the orientational ordering, lattice models cannot intrinsically offer the possibility of studying clustering, the coupling of orientational and positional degrees of freedom, and the induction of nematic or positional order in competition with each other. Molecular resolution models, like the anisotropic Gay-Berne potential [18], have, however, shown to be capable of reproducing the main features of liquid crystal phases including smectics, nematics and their transitions [19]. To our knowledge there is only one study of field ordering effects on Gay-Berne systems, where Luckhurst and Saielli [20] have examined the effect of applying a field on a GB system showing isotropic, nematic and smectic phases and have found that a strong field at a temperature near the nematic-isotropic transition induces a smectic.

Here we wish to continue our studies of nonpolar and dipolar GB systems [21,22] and investigate field effects in these more complex systems, studying the possibility of using a combination of molecular dipoles and field to influence the molecular organization and obtain new structures. In particular we are interested in testing the possibility of formation of nonspontaneous nematic phases [13] which, to the best of our knowledge, has not hitherto been observed in simulations. To investigate this phenomenon we shall need a system that, differently from that in [20], does not exhibit a nematic in the absence of the field and we shall show first how to prepare this by changing the pressure of a GB system with a certain [23] parameterization.

In the following sections we describe the model employed and the simulations performed and we then concentrate on the results.

MODEL AND SIMULATIONS

We consider a system of polar or nonpolar uniaxial rod-like ellipsoidal particles with axes σ_s and σ_e that interact between themselves through a Gay-Berne potential and that can be exposed to an external magnetic (or

electric) field. The total dimensionless potential is the sum of a Gay-Berne (GB) term, U^*_{GB} [18,23], a dipolar, U^*_{dd}, and a field coupling term, U^*_ξ.

The Gay-Berne term is a sum of pairwise repulsive and attractive contribution with a 12-6 inverse distance dependence form:

$$U^*_{GB}(\mathbf{u}_i, \mathbf{u}_j, \hat{\mathbf{r}}) = 4\varepsilon(\mathbf{u}_i, \mathbf{u}_j, \hat{\mathbf{r}}) \left[\left\{ \frac{\sigma_s}{r - \sigma(\mathbf{u}_i, \mathbf{u}_j, \hat{\mathbf{r}}) + \sigma_s} \right\}^{12} - \left\{ \frac{\sigma_s}{r - \sigma(\mathbf{u}_i, \mathbf{u}_j, \hat{\mathbf{r}}) + \sigma_s} \right\}^{6} \right] \tag{1}$$

with strength, ε, and range, σ, parameters dependent on the direction vectors $\mathbf{u}_i, \mathbf{u}_j$ of the two particles i,j and on their separation vector $\mathbf{r}$ (the cap indicates a unit vector) as discussed in [18]. The molecular orientation is defined here in terms of their principal axes, namely $\mathbf{u}_i \equiv \mathbf{z}_i$ and $\mathbf{u}_j \equiv \mathbf{z}_j$. We employ the same parameterization introduced by us in [23], with GB exponential coefficients $\mu = 1, \nu = 3$, shape anisotropy $\sigma_e/\sigma_s = 3$, interaction anisotropy $\varepsilon_s/\varepsilon_e = 5$ and a cut-off radius $r_c = 4\sigma_s$. We have shown elsewhere [23] that this has a wide nematic temperature range in canonical conditions for a number density $\rho^* \equiv N\sigma_s^3/V = 0.3$. The calculated pressure near the transition is in that case $\langle P^* \rangle \equiv \langle P \rangle \sigma_s^3/\varepsilon_s \approx 10.2$. However, if the pressure is reduced to $P^* = 1$ the model has no nematic phase and exhibits, as we shall show later on, only isotropic and smectic phases. This makes the system suitable for the purpose of investigating the occurrence or not of field induced, nonspontaneous nematics.

The pair dipolar term included when we intend to simulate polar molecules is:

$$U^*_{dd} = \frac{\mu^*_i \mu^*_j}{r^*_d} [\mathbf{x}_i \cdot \mathbf{x}_j - (\mathbf{x}_i \cdot \hat{\mathbf{r}}_d)(\mathbf{x}_j \cdot \hat{\mathbf{r}}_d)] \tag{2}$$

where $\mathbf{r}_d$ is the vector joining the two point dipoles at distance $r_d (r^*_d \equiv r_d/\sigma_s)$; we have considered transverse dipole moments $\boldsymbol{\mu}_i = \mu^*_i \mathbf{x}_i, \boldsymbol{\mu}_j = \mu^*_j \mathbf{x}_j$, where $\mu^*_i = \mu^*_j \equiv \boldsymbol{\mu}/(\varepsilon_s^{1/2} \sigma_s^{3/2})$ is the dimensionless dipole, positioned off-centre at a distance $d^* \equiv d/\sigma_s = 1$ along the $\mathbf{z}$ molecular axis. We use a value for the reduced dipole moment $\mu^* = 1.5$, that, assuming a molecular cross section $\sigma_s = 5$ Å and an energy scale $\varepsilon_s/k = 100$ K, would correspond to about 2 Debye.

We mimic the effect of the external field, assumed to be directed along the $\mathbf{Z}$ laboratory axis and to be homogeneous across the sample, by the additional second rank contribution to the total energy [17]:

$$U^*_\xi = \xi \sum_{i=1}^{N} P_2(\cos \beta_i) \tag{3}$$

Here β_i is the angle between the field direction and the molecular $\mathbf{z}_i$ axis, P_2 is a second rank Legendre polynomial and ξ determines the strength of coupling with the field. The parameter ξ depends on the anisotropy of the susceptivity and on the field intensity. For a magnetic field:

$$\xi = \Delta\kappa/(3\mu_0)B^{*2}, \tag{4}$$

where $\Delta\kappa$ is the magnetic susceptivity anisotropy and $B^* \equiv (B/\varepsilon_s)^{1/2}$ the field intensity [2]. An analogous expression holds for an external electric field acting on a non-ferroelectric system, and in that case:

$$\xi = \varepsilon_0\Delta\varepsilon/3E^{*2}, \tag{5}$$

with $\Delta\varepsilon$ the dielectric anisotropy and $E^* \equiv (E/\varepsilon_s)^{1/2}$. μ_0, ε_0 in Eqs. 4, 5 are the vacuum permittivities. In practice, because of the higher susceptivities it is much easier to reach field strengths high enough to produce observable effects with an electric rather than a magnetic field [24]. In any case, here we have considered a positive coupling term ξ, so that the field has the effect of favouring alignment of the particles parallel to its direction.

We have first performed isothermal-isobaric ensemble (constant number of molecules N, pressure P and temperature T) Monte Carlo (MC) simulations [25], without field, on samples of $N = 1000$ apolar GB particles, at pressure $P^* = 1$, studying several temperatures $T^* \equiv kT/\varepsilon_s$ in the range 1–8, in order to investigate phases with a different degree of orientational order. We have then explored for each temperature the behaviour of the system for different values of the field coupling strength: $\xi = 1, 3, 5$.

In a second set of simulations we have concentrated on dipolar GB systems. A preliminary randomization of the dipole orientations (sign of the molecular $\mathbf{x}$ axis) was performed on the initial configurations to ensure starting from a non ferroelectric phase ($\langle P_1 \rangle = \langle \cos\beta \rangle = 0$). Once again, we have first performed extensive NPT simulations without external fields and then we have considered the application of external fields of different strength. Each sample was equilibrated from a minimum of 100 kcycles to a maximum of 400 kcycles, where a cycle corresponds to N attempted MC moves. The production runs were typically 200 kcycles long. In order to speed up the equilibration process we have allowed the dipoles to flip of 180 degrees; in practice flip moves are attempted with 20% probability. The dipolar energy has been computed using the Reaction Field [26,27] method, with cut-off $r_{\mathrm{RF}} = 6\sigma_s$ and dielectric constant of the surrounding medium $\varepsilon_{\mathrm{RF}} = 1.5$. This method has proved to be adequate in treating liquid crystalline systems as large as the present ones in alternative to the more demanding Ewald method [27].

RESULTS

We report in Figure 1 our results for the molecular **z** axis order parameter $\langle P_2 \rangle = (3\langle \cos^2 \beta \rangle - 1)/2$ and the number density $\rho^* = N/V^*$ for the different phases. We see that, as long as the field is off, both the apolar and dipolar systems undergo at this pressure only a sharp, first order, transition to smectic when cooling from the isotropic phase. This provides then a suitable model system for studying the formation of the non-spontaneous nematic phases upon applying the field.

It is apparent from the curves corresponding to the results at different values of the field strength ξ that applying the external field has the effect of inducing order over a large temperature range. We also observe a softening of the disorder-order transition, which becomes progressively

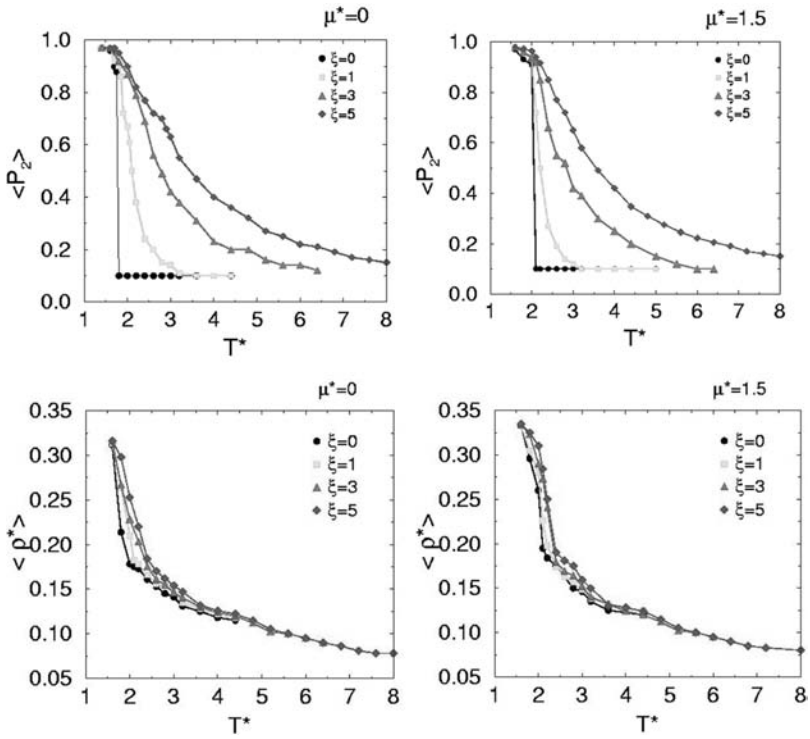

FIGURE 1 Average orientational order parameter $\langle P_2 \rangle$ and number density $\langle \rho^* \rangle$ for the system of $N = 1000$ GB apolar ($\mu^* = 0$) and dipolar ($\mu^* = 1.5$) rod-like particles as a function of temperature T^* at dimensionless pressure $P^* = 1$ and for various field coupling strengths ξ as obtained from NPT MC simulations.

smoother as the isotropic phase is itself ordered by the field. More specifically, when a weak field (i.e. $\xi = 1$) is applied, the system increases its local paranematic orientational order in the temperature range far above the zero-field transition, while at a temperature in proximity of $T^* = 3$, the system undergoes what seems to be an isotropic-nematic transition.

We can check the phase assignment by examining the radial distribution $g_0(r) = \langle \delta(r - r_{12}) \rangle_{12} / (4\pi r^2 \rho)$ and the centre of mass density along the director $g(z) = \langle \delta(z - z_{12}) \rangle_{12} / (\pi R^2 \rho)$ (R is the radius of a cylindrical sampling region and $z_{12} = \mathbf{r}_{12} \cdot \mathbf{n}$ is measured with respect to the director $\mathbf{n}$ frame) at two selected temperatures (see Fig. 2). These show that the

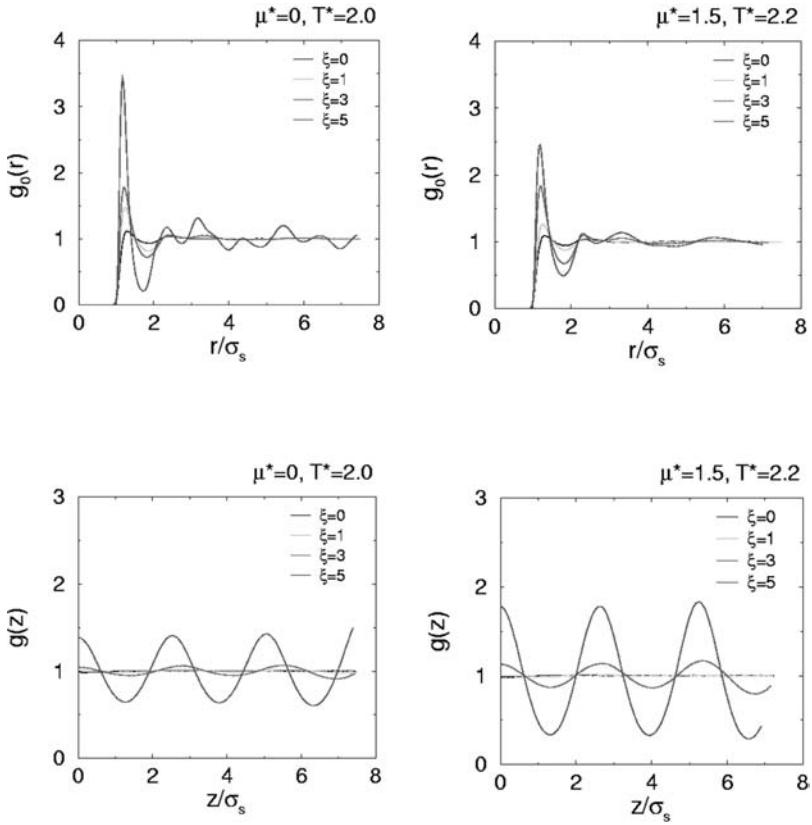

FIGURE 2 Radial correlation function $g_0(r)$ and density along the director $g(z)$ for NPT systems of $N = 1000$ apolar ($\mu^* = 0$) and polar ($\mu^* = 1.5$) rod-like GB particles without external field ($\xi = 0$) and for field strengths $\xi = 1, 3, 5$. Dimensionless pressure is $P^* = 1$.

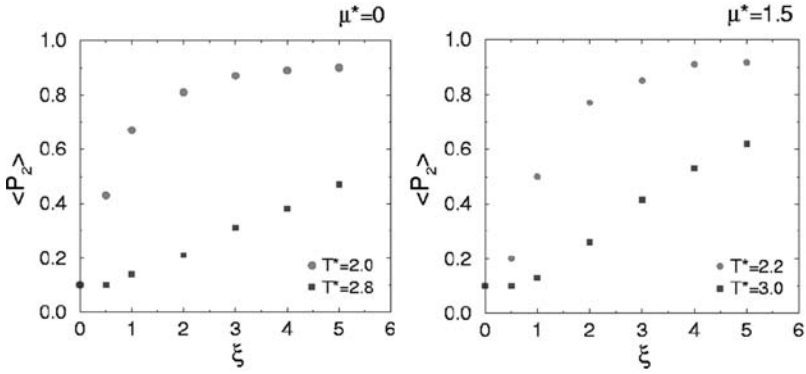

FIGURE 3 Orientational order parameter $\langle P_2 \rangle$ for the system of $N = 1000$ GB apolar ($\mu^* = 0$) and dipolar ($\mu^* = 1.5$) rod-like particles, as a function of the field coupling strength ξ. Dimensionless pressure is $P^* = 1$.

ordered phase induced by fields of strength up to $\xi = 3$ for no dipole and $\xi = 1$ for $\mu^* = 1.5$ are translationally uniform, and thus that the corresponding phases are nematic. As the field strength increases at the same temperature, we see that $g(z)$ becomes periodic, corresponding to a layered, smectic structure.

Applying the strongest field, $\xi = 5$ (apolar case) the smectic phase is stabilized while the nematic one is broadened to the detriment of the

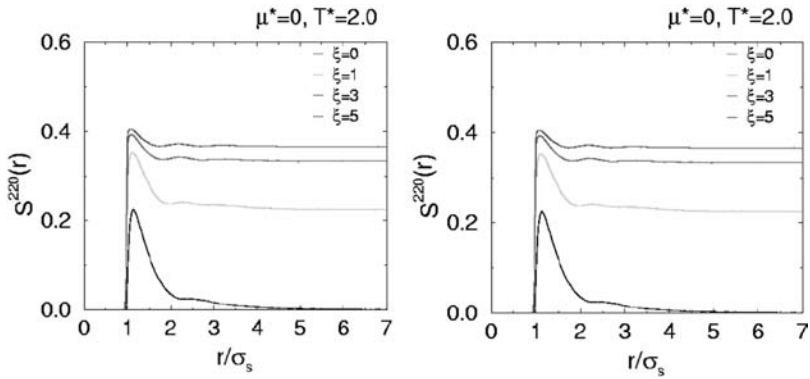

FIGURE 4 Orientational correlation function $S^{220}(r)$ for the system of $N = 1000$ GB rod particles at the selected temperatures $T^* = 2.0 (\mu^* = 0)$ and $T^* = 2.2$ ($\mu^* = 1.5$). Dimensionless pressure is $P^* = 1$.

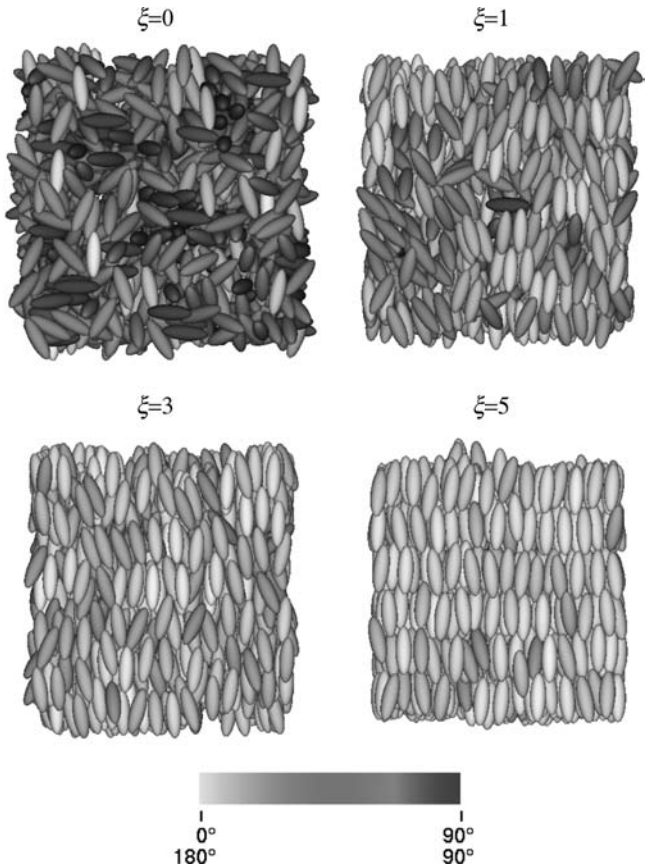

FIGURE 5 Snapshots of configurations for $NPT(N = 1000, P^* = 1, T^* = 2)$ systems of apolar ($\mu^* = 0$) rod-like GB particles without external field ($\xi = 0$) and for field strengths $\xi = 1, 3, 5$. The colour coding indicates the orientation of the molecular axis with respect to the director, ranging from parallel (yellow) to perpendicular (blue) [23].

isotropic phase, which is now found only for very high temperatures (i.e. $T^* > 5$). The smectic character is clearly shown by the periodic density wave Figure 2. At lower temperature a nematic-smectic transition is observed.

To investigate the field dependence of the orientational order parameter $\langle P_2 \rangle$, we have analysed in detail the results at two selected temperatures, $T^* = 2.0$ and $T^* = 2.8$ for $\mu^* = 0$ and $T^* = 2.2$ and $T^* = 3.0$ for $\mu^* = 1.5$ see Figure 3. At the lower temperatures we can observe a rapid

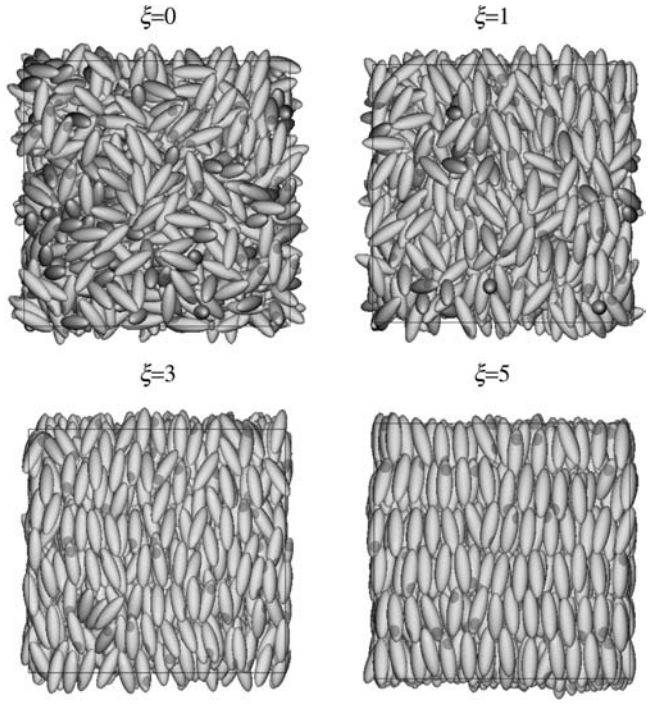

FIGURE 6 Snapshots of configurations for $NPT(N = 1000, P^* = 1, T^* = 2.2)$ systems of dipolar ($\mu^* = 1.5$) rod-like GB particles without external field ($\xi = 0$) and for field strengths $\xi = 1, 3, 5$. The red and cyan spots on each particle represent the head and tail of the transverse dipole.

saturation of the order with the field strength, while at the higher temperature the order increases linearly except possibly for the very low fields values ($\xi = 0.5$).

The non linear behaviour is a clear indication of nematic formation and it is very similar to what was observed experimentally by Fraden [10] using magnetic fields up to 20 T. Essentially the same behaviour is obtained both with polar and apolar molecules.

The growth of the single particle order $\langle P_2 \rangle$ with applied field takes place through a progressive increase of the orientational pair correlation length. Figure 4 shows the induced changes in the orientational correlation function between two molecules at distance r, $S^{220}(r)$, defined as:

$$S^{220}(r) = \langle \delta(r - r_{12})(-1 + 3(\mathbf{z}_1 \cdot \mathbf{z}_2)^2 \rangle_{12} / 2\sqrt{5} \tag{6}$$

We see that in absence of the field the correlation extends only for a few molecular diameters, while for $\xi \geq 1$ for both apolar and dipolar system a long- range order tail exists.

All the field induced ordering effects are reversible and the samples relax back to the corresponding state of the $\xi = 0$ systems, upon switching off the external field.

It is also instructive to examine snapshots of configurations of the system at the selected temperatures $T^*= 2.0$ (case $\mu^*= 0$) and $T^*= 2.2$ (case $\mu^*= 1.5$) and in Figure 5 and Figure 6 these are shown for different field strengths. Here the molecules are represented with ellipsoids and for the apolar case their orientation is given by a colour code ranging from yellow to blue, providing an immediate visualization of the existing short-range and long-range order.

It is clear that, as the field strength increases up to the highest value $\xi = 5$, the majority of particles becomes aligned with the field direction. For the $\mu^*= 1.5$ systems, we focus on dipolar positions and orientations: the molecules are coloured in grey, while the red and cyan spots label head and tail of the transverse dipoles.

In summary, we have shown that the application of an external field of suitable strength can induce the formation of a nonspontaneous nematic phase in systems of Gay-Berne particles showing only an isotropic and a smectic phase when the field is absent. Apolar and polar mesogens with transverse dipoles are found to behave very similarly from this point of view.

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