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## REVIEW ARTICLE

# Computer simulations of biaxial nematics

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**Abstract.** Biaxial nematic ( $N_b$ ) liquid crystals are a fascinating condensed matter phase that has baffled for more than thirty years scientists engaged in the challenge of demonstrating its actual existence, and which has only recently been experimentally found. During this period computer simulations of model  $N_b$  have played an important role, both in providing the basic physical properties to be expected from these systems, and in giving clues about the molecular features essential for the thermodynamic stability of  $N_b$  phases. However, simulations studies are expected to be even more crucial in the future for unravelling the structural features of biaxial mesogens at molecular level, and for helping in the design and optimisation of devices towards the technological deployment of  $N_b$  materials. This review article gives an overview of the simulation work performed so far, and relying on the recent experimental findings, focusses on the still unanswered questions which will determine the future challenges in the field.

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## Introduction

Biaxial nematic ( $N_b$ ) liquid crystals (LC) are nematics where the mesogenic molecules organise with two mutually orthogonal directions of preferential alignment (directors), while keeping a uniform distribution of centres of mass (see Figure 1). The principal director  $\mathbf{n}$  is typical of uniaxial nematics ( $N_u$ ), while the secondary director  $\mathbf{m}$  is specific to biaxial systems which then behave optically as macroscopic trirefringent materials, i.e. with three different refractive indexes.

The quest for a truly thermotropic  $N_b$  has been aptly named “*the holy grail*” [1] of LC since it has fuelled experimental and theoretical research for more than 30 years, starting from the seminal theoretical papers of Freiser [2] and Straley [3]. This is an interesting scientific case since by relying on idealised models the theoretical predictions first, and later on the computer simulations, have paved the way for the difficult task of actually synthesising molecules with the desired mesogenic behaviour. While theoretical investigations of LC usually lag behind the discoveries of clever and imaginative synthetic chemists, the specific case of  $N_b$  is quite remarkably the opposite. However, it should be pointed out that neither theory nor simulations have yielded a specific molecular design but rather have provided reassurance on the  $N_b$  not being a priori forbidden. The  $N_b$  phase was not the only “*missing link*” in the class of thermotropic LC organisations, and as a side comment we also quote the ferroelectric nematic among the elusive phases predicted by theory [4] and computer simulations [5] which is yet an open challenge on the experimental ground. As we shall discuss later, part of the elusivity of  $N_b$  may be due to the fact that many of the molecular features that favour a biaxial arrangement of the molecules in the fluid nematic also favour their packing in the competing smectic or crystalline biaxial phases.

The motivations for this search have been certainly widespread, ranging from purely academic interest in an unsolved scientific problem, to the potential usage of these materials in faster displays, where in principle the commutation of the secondary director should give lower response times compared to the conventional twisted nematic and ferroelectric smectic devices.

At the time of writing a few instances of stable thermotropic biaxial nematics and their characterisation [6, 7, 8, 9, 10] have been reported. The papers of Luckhurst [11] and Praefcke [12] and the book of Chandrasekhar [13] also give a critical account of the early synthetic attempts, while assessment of the more recent achievements can be found in [14]. These experimental findings are now fuelling a target oriented research towards other mesogenic compounds, and the implementation of envisaged technological applications. It should be noted anyway that the experimental identification of  $N_b$  phases is so difficult that an active debate that includes challenging published results [11, 15, 16] has taken place, and to some extent still is [17]. The role that confinement, external fields and boundaries [18], or sample preparation [19, 20] may play in determining the actual observed biaxial behaviour is also questioned. While ordinary  $N_u$  are typically formed by elongated (calamitic, or rod-like), or squashed

(discotic, or disc-like) mesogens, what molecular shape is more conducive towards  $N_b$  behaviour is far from obvious.

While the search of  $N_b$  formed by rod-like and bent-core (boomerang) molecules has been actively pursued, the actual existence of such phases also from disc-like mesogens as predicted by theoretical models [2, 3] and simulations [21, 22, 23] is still an open question, and has received little attention from the point of view of chemical synthesis. One possibility that has been suggested [24] is that of combining the properties of rods and discs. The simplest possibility is that of mixing them but it has been found by theories [25] and experiments [26] that these mixtures tend to phase separate. A recent experimental paper by Apreutesei and Mehl [27] challenges the past modelling work in view of considering the role of flexibility and attractive interactions. Even though LC phase transitions can be driven by entropic effects [4], the detailed balance of contributions leading to the formation of specific organisations also includes energetic factors arising from attractive-repulsive interactions between molecules.

The chemistry of synthesised mesogens has been even more far-reaching in scope than theories, and besides organic compounds with a rigid aromatic core and terminal flexible alkyl spacers, the ingenuity and rational design of synthetic chemists [28, 29, 30] has considered as candidate  $N_b$  mesogens also dendrimers, silicon organic, and metallo organic coordination compounds [31], to name a few.

This paper reviews computer simulations of  $N_b$ , and it is fair to say that the field of computer simulations of LC systems has now reached a well established state. Simulations allow to draw direct relations between specific molecular properties and macroscopic mesogenic behaviour, and to study the spontaneous formation of liquid crystalline phases, characterise their structure, and determine anisotropic properties and responses to external fields. Furthermore, computer simulations automatically account for the  $n$ -body correlations in condensed phases, and as such are useful for validating the predictions of theories. We should recall, for instance, that the original predictions for the existence of  $N_b$  [2, 3] were based on a simple mean field theory, which is known to make rather large errors in determining phase boundaries. The progresses in the field encompass all classes of lattice, coarse-grained, molecular, and atomistic models, and have been thoroughly reviewed in the last years [32, 33, 34, 35], and also presented in NATO schools [36] and workshops [37]. This manuscript relies on these general works and focuses on the specific aspects of simulating  $N_b$  systems, which have only partly discussed in the previous reviews. Section 1 contains a few highlights to the most recent synthetic and experimental findings related to the search of  $N_b$  phases. The order parameters used to characterise the biaxial ordering are presented in Section 2 along with theoretical models, while the principal potentials used for  $N_b$  systems are described in Section 3. The remaining Sections are specifically devoted to simulation results, and are organised according to the symmetry/structure of the simulation models. Section 4 deals with systems with spins and single-site particles of  $D_{2h}$  symmetry. Multi-site potentials for molecules with symmetry  $C_{2v}$  or lower, and atomistic models are treated instead in Section 5. The rod-disc mixtures, which are also candidates for  $N_b$  systems

but still lack conclusive confirmation or disproof, are discussed in Section 6. Some concluding remarks close the review.

## 1. Experiments

From a purely thermodynamical point of view, the most frequent experimental scenario with (virtually) biaxial mesogens is that upon cooling the  $N_u$  phase, the free energy of the underlying smectic/columnar becomes lower earlier than that of the  $N_b$  phase, which is consequently not observed [38] (see Figure 2). The quest for the  $N_b$  phase has been then a synthetic (and modelling) attempt of either destabilising smectic phases, or stabilising the  $N_b$  phase (or both), in such a way that the  $N_b$  becomes the equilibrium phase over a finite temperature range. In this respect theoretical models based on purely orientational potentials and lattice simulations are not haunted by the formation of a competing layered or crystal phase before a  $N_b$  becomes thermodynamically stable, since they do not consider positional degrees of freedom (see Ref. [38] for an exception). This has been turned into an advantage for the identification of the intrinsic molecular properties (e.g. shape anisotropy) relevant for the stabilisation of an overall  $N_b$  organisation, and for efficiently mapping phase diagrams.

It should be noted that our cartoon of  $N_b$  phases in terms of a locally uniform distribution of the secondary  $\mathbf{m}$  director might be an exception in real systems. Some evidences from experimental measurements and computer simulations [39], and theoretical models [18] are pushing forward a different picture of what the standard  $N_b$  phase might be. According to these sources, biaxial or even polar cybotactic clusters might be the most common motifs of  $N_b$  phases, and the long-range biaxial ordering would be induced by external perturbations (e.g. a field), or surface anchoring [40], or shear stress [31]. One of the questions which still awaits to be answered is therefore if the observed biaxiality is an intrinsic property of the nematic fluid or instead, as pointed out by Vanakaras and Photinos, a gigantic response of biaxial cybotactic clusters to the surface anchoring or external field [18]. According to this picture, the discordant measurements of phase structure for claimed  $N_b$  might also have been originated by the boundary conditions typical of each experiment, and the ensuing different degrees of alignment of biaxial clusters. These issues are also related to the observation of  $N_u$  phases with cybotactic clusters of Torgova *et al.* [41], or the spontaneous segregation into chiral domains reported by Görtz and Goodby [19] and Bruce and coworkers [20]. For this latter example, the formation of organised supramolecular structures seems to take place above the ordering transition, and it is also depending on the sample history, hinting to a kinetic rather than thermodynamic effect.

The experimental identification of biaxiality has always proved to be fairly difficult [16, 42, 43], and still does because of the small magnitude of the transversal orientational ordering, and the necessity of filtering out the possible perturbations arising from laboratory setup, and anchoring conditions [43]. Actually, this is an additional hurdle to cope with for those scientists trying to characterise potentially

$N_b$  systems. As a matter of fact, most claims of  $N_b$  phases published earlier than 2004 seem to have been caused by deceptive experimental evidences, later challenged by independent measurements of different anisotropic properties.

The first convincing thermotropic biaxial nematic phase has been jointly reported in year 2004 by Kumar, Samulski and coworkers [6, 7, 8] from bent-core mesogens based on a mesogenic oxadiazole core [6] with lateral substituents. The phase has been further characterised by X-ray [7, 44], and polarised microscopy, conoscopy, and deuterium NMR spectroscopy [8] with more stringent experimental evidences. The interpretation of these experiments has anyway been questioned [17], but an answer from the authors [45] dismissed the doubts raised. Even if the  $N_b$  for these mesogens occurs at high temperature ( $\approx 200$  °C) these molecules have opened the search of other systems forming  $N_b$  phases under operating conditions closer to room temperature as needed for standard technological applications. Kumar and coworkers have reported another class of rigid bent-core mesogens with aperture angle of 90 degrees [46] which appear to also form  $N_b$  phases.

This thermotropic  $N_b$  behaviour is far from being the common one for bent-core mesogens which are often devoid of a  $N_u$  phase. Even molecules with a chemical structure very similar to that of the compounds studied by Kumar and Samulski do not have a  $N_b$  phase but display other interesting properties, like the formation of nematic phases with cybotactic clusters [41] stable over a quite wide range of temperatures.

Besides the bent-core shaped mesogens, in the same 2004 year, a novel class of  $N_b$  based on organo-siloxane tetrapodes has been found by Mehl, Vij and coworkers [9]. These thermotropic systems have been thoroughly characterised by measuring the anisotropy of infrared absorbance, with the addition of conoscopic and textural imaging under polarised light [9], and the temperature dependence of the averaged quadrupolar coupling constant of a deuterated 8CB solute probe by deuterium NMR [10]. Such tetrapodes are quite complex and for the time being represent a challenge for a computer simulation aimed at understanding the molecular origin of their  $N_b$  phase, especially in relation to their high flexibility which makes difficult to define their shape and interaction anisotropies in terms of simple models.

Severing and Saalwächter [47] have also given evidence of a new class of  $N_b$  LC polymers with lateral mesogens. This is a subsequent development after the seminal paper of Hessel and Finkelmann [48]. Also new asymmetric bent-core mesogenic compounds forming  $N_u$  and  $N_b$  phases have been reported [49, 19]. The differential scanning calorimetry measurements for these systems support the theoretical [50] and computer simulation [51, 52] prediction of a second-order transition from  $N_u$  to  $N_b$ .

$N_b$  phases open the possibility of designing new bistable devices with faster response than those based on  $N_u$ , because the characteristic switching times of the principal and secondary directors are expected to be very different. The dynamics for the electro-optical commutation processes of a  $N_b$  phases when confined between planar plates has been measured by Lee *et al.* [53], and this is the first experimental investigation studying the issues related to switching experiments of  $N_b$  phases. Other experimental

studies probing biaxial bistability have been performed, for instance the time resolved characterisation of the commutation of a nematic LC cell submitted to a strong electric field (to induce biaxiality) between two topologically distinct textures [54], or with covalently bonded rod- and disc-like mesogens [40]. In spite of these results, the devising of an efficient bistable  $N_b$  devices relying on the switching of the secondary director might not be easy, and a relevant amount of experimental and computer modelling work still has to be done.

## 2. Order parameters and theories

The anisotropic properties of  $N_b$  phases are expected to arise from a long-range degree of orientational ordering along two orthogonal directions, the principal  $\mathbf{n}$  and the secondary  $\mathbf{m}$  directors, while molecular centres of mass have a random distribution in space. The quantitative assessment of this organisation is conventionally made by measuring (or computing) suitable orientational order parameters. The symmetry analysis of the  $D_{2h}$   $N_b$  phases identifies a set of four different second rank order parameters that can be used to fulfil the task.

Unfortunately, there is not a universally adopted convention about the definition and notation of such order parameters. Over the years a number of equivalent sets have been used, and the paper of Rosso [55] gives quite a complete list of the notations employed for these order parameters, and is certainly useful in decoding the various conventions and comparing the published findings. The two most popular definitions are those based on a cartesian representation of the order matrices [22, 56], and those using symmetrised Wigner matrices [21]. The first set arises from a purely mathematical modelling of the alignment process, and has the (nice) feature that all order parameters range between 0 (no ordering) and 1 (complete ordering). The second definition originates from the formal description of static physical observables (e.g. from NMR, Raman, or fluorescence depolarisation measurements) obtained from the experimental characterisation of LC phases. This formulation relies on an irreducible tensors approach [57] where the order parameters are averages values of the Wigner rotation matrices transforming from laboratory to director frame (and vice versa). The two sets of order parameters are equivalent and mathematical relations convert from one to the other. We quote here the second kind of definitions, using the scalar products between molecular and director frame axes to identify rotations. The equivalent definition in terms of Euler angles can be found in Ref. [21]. The Wigner matrices symmetrised for the  $D_{2h}$  group of a  $N_b$  phase are

$$R_{m,n}^L = \frac{1}{4} \delta_{m,\text{even}} \delta_{n,\text{even}} \left[ D_{m,n}^{L*} + D_{-m,n}^{L*} + D_{m,-n}^{L*} + D_{-m,-n}^{L*} \right]. \quad (1)$$

The order in a  $N_b$  phase, and the mean values of second rank tensorial observables, can be characterised with the following ensemble averages

$$\langle R_{0,0}^2 \rangle = \left\langle \frac{3}{2} (\mathbf{z} \cdot \mathbf{n})^2 - \frac{1}{2} \right\rangle, \quad (2)$$

$$\langle R_{2,0}^2 \rangle = \left\langle \sqrt{\frac{3}{8}} [(\mathbf{z} \cdot \mathbf{l})^2 - (\mathbf{z} \cdot \mathbf{m})^2] \right\rangle, \quad (3)$$

$$\langle R_{0,2}^2 \rangle = \left\langle \sqrt{\frac{3}{8}} [(\mathbf{x} \cdot \mathbf{n})^2 - (\mathbf{y} \cdot \mathbf{n})^2] \right\rangle, \quad (4)$$

$$\langle R_{2,2}^2 \rangle = \left\langle \frac{1}{4} [(\mathbf{x} \cdot \mathbf{l})^2 - (\mathbf{x} \cdot \mathbf{m})^2 - (\mathbf{y} \cdot \mathbf{l})^2 + (\mathbf{y} \cdot \mathbf{m})^2] \right\rangle, \quad (5)$$

where  $\mathbf{l}$  is the third axis of a (right-handed) cartesian frame defined by the first two. The molecular axes are instead  $\mathbf{x}$ ,  $\mathbf{y}$ , and  $\mathbf{z}$ .

Typical ranges for these order parameters in models and simulations of  $N_u$  and  $N_b$  phases are approximatively  $[0.4, 0.8]$  for  $\langle R_{0,0}^2 \rangle$  and  $[0.1, 0.3]$  for  $\langle R_{2,2}^2 \rangle$  (see ref. [23] and Figure 9 for an exception). An example of temperature dependence of such order parameters from a lattice simulation of a  $N_b$  is given in Figure 4. It should be noted that molecular models (both hard and soft attractive-repulsive) usually overestimate these values, especially at the ordering transitions. Experimental values are usually much smaller, in particular for the observed biaxialities  $\langle R_{2,2}^2 \rangle$ . Differently from molecular models which offer at most semi-quantitative results, the atomistic simulations with predictive capabilities [58, 34, 59] can provide reliable estimates of such order parameters as well as other macroscopic properties.

While widely adopted, the sets of second rank order parameters are not sufficient to characterise all LC phases, either known or theoretically envisaged. For instance, bent-core mesogens can form an extremely rich class of LC and their proper characterisation also requires third rank tensors [4]. Another counterexample is that of ferroelectric phases where also first rank order parameters are relevant [60, 61].

Prior to computer simulations, laboratory syntheses and experiments, the theoretical models have provided the general framework background information for all subsequent studies on  $N_b$  systems. The fundamental proof of principle for the possible existence of a thermotropic nematic phase with three orthogonal optical axes, was given by Freiser [2] first, and Straley [3] a few years later. By considering mesogens as rigid board-like particles (sometimes called sanidic) it was found that shape biaxiality  $\lambda$  (which is zero for cylindrical  $D_{\infty h}$  symmetry, i.e. rod-like and disc-like particles) is the physically relevant parameter connected to the excluded volume

$$\lambda = \sqrt{3/2} \frac{\sigma_x - \sigma_y}{2\sigma_z - \sigma_x - \sigma_y}, \quad (6)$$

where  $\sigma_x$ ,  $\sigma_y$ , and  $\sigma_z$  are the particle dimensions. The mean field models have phase diagrams where both rod- and disc-like parameterisations show a transition from isotropic to  $N_u$  (conventionally labelled  $N_+$  for calamitic, and  $N_-$  for discotic nematics, also see Figure 3), followed by a second one to  $N_b$  [62]. At the crossover point (also named Landau point) the molecular biaxiality  $\lambda$  becomes maximum, and the ordering transition from isotropic leads directly to the  $N_b$  phase (see Figure 3). Since this state point is the one where the  $N_b$  phases was expected to appear at the highest temperature, the synthetic chemists focussed toward assembling mesogenic molecules with an effective

shape biaxiality falling within this region. At the Landau point biaxiality identifies the particles as rod-like and disc-like at the same time. However, by using scaled particle theory and taking into account also translational order Taylor and Herzfeld [38] have shown how in a fluid of rigid spheroplatelets the range of existence for the  $N_b$  phase becomes extremely narrow (see Figure 2), or even vanishes, when a smectic organisation can form (as usually observed).

The effect of polydispersity or variable shape in model single-component systems have been accounted for by either considering a frequency-dependent polarisability anisotropy [63], or with a gaussian distribution of shape biaxiality modelled as quadrupolar mass distribution [64]. For two-component systems this effect is also quite relevant since it may be a pathway for the stabilisation of  $N_b$  phases by preventing demixing in mixtures, and it has been studied theoretically by Ratón and Cuesta [65] (see Fig. 6), and experimentally by van der Kooij and Lekkerkerker [26]. Another interesting result is the paper of Biscari *et al.* [66] which discusses the possibility of inducing a  $N_b$  phase by using curved surfaces with homeotropic anchoring. The recent analysis of Vanakaras and Photinos [18] suggests us that our view of  $N_b$  phases should be widened to include macroscopic uniaxial systems with large transversal response where a field-induced biaxiality could be used for bistable devices. From this point of view, earlier mesogens which have been dismissed as forming  $N_b$  phases might still have interesting response properties due to the presence of locally biaxial cybotactic clusters, especially if they possess a negative dielectric anisotropy [18]. Over the last few years other theoretical models and studies of  $N_b$  have been published [67, 68, 69, 70, 71] showing how the field of  $N_b$  is quite lively within the scientific community.

Models (and simulations) have been extensively used to study distributions of the nematic directors and topological defects [13, 72, 73, 74, 42, 75] in  $N_b$ . Theories for the elastic [76, 77, 78, 79, 80, 81, 82, 83, 41], flexoelectric [84, 85], and rheological [86] behaviour of  $N_b$  have also been proposed. However, computer simulations of the associated mesoscopic coefficients (e.g. elastic constants, viscosities) for  $N_b$  have not been performed systematically. These coefficients are also necessary for the description of  $N_b$  fluids using mesoscopic models, or finite elements methods and further work is required in the future for the reliable prediction of these relevant quantities.

### 3. Model potentials

Several classes of potentials have been used in the attempt of modelling samples of biaxial particles, and it is somewhat mystifying that while most  $N_b$  computer simulations have considered single-site  $D_{2h}$  models it has been instead the class of bent-core mesogens to provide the first experimental evidence of a thermotropic  $N_b$  phase. In this section we review the principal types of potentials in order of increasing complexity, from lattice to atomistic models, postponing the discussion of the simulation results to the following sections.

Due to their computational cheapness, lattice models were among the first ones to



be used by using suitable anisotropic orientational potentials between neighbouring sites. Among the many lattice models which have been considered in computer simulations, the most studied so far is the biaxial generalisation to  $D_{2h}$  symmetry of the Lebwohl–Lasher potential [62]

$$U(\boldsymbol{\omega}_{12}) = -\epsilon_0 \left( R_{0,0}^2(\boldsymbol{\omega}_{12}) + 2\lambda_{0,2} \left[ R_{0,2}^2(\boldsymbol{\omega}_{12}) + R_{2,0}^2(\boldsymbol{\omega}_{12}) \right] + 4\lambda_{2,2} R_{2,2}^2(\boldsymbol{\omega}_{12}) \right), \quad (7)$$

where  $\boldsymbol{\omega}_{12}$  is the relative orientation of neighbouring sites on a cubic lattice. An equivalent expression can be cast in cartesian form as [51]

$$U(\boldsymbol{\omega}_{12}) = -\epsilon_0 \left( \frac{3}{2} V_{z,z} - \sqrt{6} \lambda_{0,2} [V_{x,x} - V_{y,y}] + 2\lambda_{2,2}^2 [V_{x,x} + V_{y,x} - V_{x,y} - V_{y,x}] - \frac{1}{2} \right), \quad (8)$$

where  $V_{a,b} = (\mathbf{a}_1 \cdot \mathbf{b}_2)^2$ , and the unit vectors  $\mathbf{a}_1$ ,  $\mathbf{b}_2$  are the axes  $\mathbf{x}_i$ ,  $\mathbf{y}_i$ , and  $\mathbf{z}_i$  of two neighbouring lattice sites. In the case of dispersive interactions the model parameters  $\lambda_{0,2} = \lambda$ , and  $\lambda_{2,2} = \lambda^2$  are both defined in terms of a biaxiality parameter  $\lambda$ . Furthermore, both  $\lambda$  and  $\epsilon_0$  are related to the anisotropy of the polarisability tensor [62, 51]. This is a particular case of the archetypal formulation of Straley [3], where the parameters  $\lambda_{m,n}$  are independent and can be chosen to model more general interaction schemes. For instance, the mesogenic properties for a different choice  $\lambda_{0,2} = \lambda$ , and  $\lambda_{2,2} = 0$  have been studied theoretically and with MC simulations in Refs. [63, 71]. Lattice models have been thoroughly studied and are now mostly useful for investigating mesoscopic properties of fairly large samples, like topological defect distributions and optical properties [87].

A second broad class of potentials used in simulations is that of molecular models, either purely repulsive (e.g. hard–ellipsoids [88, 22], or hard–spherocylinders [89, 90, 91]), or attractive–repulsive (e.g. Gay–Berne [92]). These potentials allow to draw a clear link between specific molecular properties, in particular shape and interaction anisotropies, and collective mesogenic behaviour. For instance since the work of Allen [22], the hard–ellipsoid fluid has been thoroughly studied considering how the semiaxes  $a$ ,  $b$ , and  $c$ , and the aspect ratios  $a : b : c$  determine the phase diagram. Several off–lattice soft potentials have been derived from the gaussian overlap model due to Berne and Pechukas [93]. The first one was that of Ayton and Patey [94] who proposed a generalisation for describing purely repulsive soft biaxial ellipsoidal particles. By reducing the thickness of a uniaxial 1 : 1 : 3 ellipsoid (which as a hard particle was known to be devoid of a nematic phase) to a 0.8 : 1 : 3, and then to a 0.4 : 1 : 3 aspect ratio, first a  $N_u$  and then a  $N_b$  were found (although for a single state point). Unfortunately the study of this model has been discontinued.

The most studied molecular systems are those belonging to the class of attractive–repulsive off–lattice potentials obtained by generalising the Lennard–Jones (LJ) potential to ellipsoidal shape. The standard model of this class is the Gay–Berne (GB) [92]. The interaction between unlike biaxial particles can be written as [95, 96]

$$U(\mathbf{r}, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2) = 4\epsilon_0 \epsilon(\mathbf{r}, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2) \left[ u^{12}(\mathbf{r}, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2) - u^6(\mathbf{r}, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2) \right], \quad (9)$$

where  $u(\mathbf{r}, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2) \equiv \sigma_c / (r - \sigma(\mathbf{r}, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2) + \sigma_c)$ , depends on the anisotropic contact term  $\sigma(\mathbf{r}, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2)$  parameterised in terms of the three axes  $\sigma_x$ ,  $\sigma_y$ , and  $\sigma_z$  of the ellipsoid, and the orientations  $\boldsymbol{\omega}_1$ ,  $\boldsymbol{\omega}_2$  for the molecules, and the intermolecular vector  $\mathbf{r}$ . The anisotropic interaction term  $\epsilon(\mathbf{r}, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2)$  defines the potential well depth and it is parameterised in terms of the three axes  $\sigma_i$ , and three interaction coefficients  $\epsilon_x$ ,  $\epsilon_y$ , and  $\epsilon_z$  defining the relative energy for the *side-by-side*, *face-to-face*, and *end-to-end* configurations of a pair of particles [96] (see Figure 7). Three additional empirical parameters  $\sigma_c$ ,  $\mu$ , and  $\nu$  can be tuned to modify the width and depth of the interaction wells. The constant  $\epsilon_0$  defines the energy scale. The contact term  $\sigma(\mathbf{r}, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2)$  approximates the geometrical “*contact distance*” between two ellipsoids (see Refs. [97, 98] for a discussion). A similar generalisation of the GB potential to non-homogeneous biaxial interactions is that of Cleaver *et al.* [99]. The issues concerning the approximation of the contact distance for ellipsoids using the recipe of Ref. [93] (i.e.  $\sigma(\mathbf{r}, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2)$ ) have stimulated the proposal of additional generalisations of the biaxial GB model like the RE-squared potential of Ejtehadi and Everaers [97, 100, 101], which is based on Hamaker theory, and that of Paramonov and Yaliraki [102] who have used the elliptic function approach due to Perram and Wertheim [103]. Both biaxial [95, 96] and RE-squared [97] versions of the GB potential have recently escaped the realm of in-house simulation codes to be included into the popular molecular dynamics engine LAMMPS [104, 105] released under the open-source licensing scheme.

These single-site potentials were initially used to simulate mesogens with board-like symmetry, but were also combined to model lower symmetry molecules (e.g. boomerang shaped) in terms of multi-site objects as described later on. In this class of molecular potentials small attention has been given to including and understanding the role of flexibility, probably to keep models as computationally cheap as possible. We now recognise that these neglected contributions when taken into account may also compensate for the unrealistic density changes across ordering transitions which curse most simulations of both hard and soft molecular models, and which are not observed experimentally.

Atomistic potentials account flexibility implicitly, however, the complexity of candidate mesogens poses a challenge since this modelling requires computational resources which have become available only in the past few years. In this class of models the total potential energy is broken down into a sum of intra-molecular terms describing how the energy changes upon variations in bond angles and lengths, conformational motions, and atomic positions, with the addition of inter-molecular terms giving non-bonding and electrostatic interactions. A generic atomistic potential can be written as

$$U_{\text{total}} = \sum_{\text{bonds}} K_r (r - r_{\text{eq}})^2 + \sum_{\text{angles}} K_\theta (\theta - \theta_{\text{eq}})^2 + \sum_{\text{dihed}} \sum_{n=0}^6 V_n [1 + \cos(n\phi + \gamma)] +$$

$$\sum_{\text{atoms}}^{i < j} \left\{ \sqrt{\epsilon_i \epsilon_j} \left[ \left( \frac{\sigma_i + \sigma_j}{2r_{ij}} \right)^{12} - \left( \frac{\sigma_i + \sigma_j}{2r_{ij}} \right)^6 \right] + \frac{q_i q_j}{r_{ij}} \right\}. \quad (10)$$

The specific mathematical formulation of the additive terms and the complete collection of coefficients  $K$ ,  $V$ ,  $\sigma$ ,  $\epsilon$ , and atomic charges  $q$  define the force field.

Even if atomistic simulations can provide invaluable details on specific systems, often hardly or not accessible at all by experimental techniques, the task of correctly reproducing phase transition temperatures for a given mesogen is to date not trivial, and this is mainly due to the absence of force fields specifically parameterised for the purpose. Therefore, prior to performing atomistic simulations, a necessary step is that of testing if the chosen force field is adequate: for instance dihedral potentials should be checked as the full conformational space often determines the phase behaviour [106]. In addition, other force field terms may need to be tuned to match relevant experimental observables (e.g. density). If these optimisations are not sufficient (see e.g. [107, 108, 109, 110]), a long and computationally demanding re-parameterisation procedure is needed [111, 110]. We should also notice that atomistic potentials have been successfully used only recently [59] even because no convincing  $N_b$  had been reported earlier and molecular structures to start with were not available. From this point of view computer simulations of lattice and molecular models have been invaluable for studying the fundamental properties of  $N_b$  systems prior to their experimental discovery.

#### 4. Single-site models

The simplest computer simulation models for  $N_b$  are the single-site ones where the mesogenic system is described by a collection of weakly interacting potential centres with orientational degrees of freedom. The interaction sites can be either fixed on a lattice or free to move (off-lattice), and can thus represent an uniformly oriented molecular domain or a single molecule.

Lattice simulations have been the first ones to provide evidences of a spontaneous thermotropic  $N_b$  ordering, starting from the MC computer simulations of Luckhurst and Romano [112] who used the potential of eqn. 7. The complete phase diagram and the temperature dependence of the four second rank biaxial order parameters has been obtained by Biscarini *et al.* [21] (see Figure 3). These results have been compared against theoretical mean field predictions to find a semi-quantitative agreement between the two (see Figure 4). The transition from  $N_u$  to  $N_b$  has been predicted [50] and simulated [51] with dispersive models to be of second order. There are anyway theoretical predictions by Virga and coworkers based on a mean field model that this behaviour is not universal. Relaxing the parameterisation constraints of eqn. 7 two narrow regions of weak first order transitions between  $N_u$  and  $N_b$ , and between isotropic to  $N_b$  have been found in correspondence of a nematic-nematic tricritical point [63, 113, 68] in proximity of the Landau point (see Fig. 5). Recent dynamic light scattering measurements based on organo-siloxane tetrapodes [114], and lattice computer simulations [115], support these theoretical models. Bates and Luckhurst [116, 117], and Romano [115, 118, 119, 120]

have further simulated several generalisations of the model potential of eqn. 7. Lattice models are computationally cheap, and taking advantage of this, it is possible to simulate extensively samples with (sub)–mesoscopic size, and large enough to compute director fluctuations, topological defects structure, and schlieren textures of confined systems or free standing films. These are interesting properties because optical microscopy (either orthoscopy and conoscopy) is often used as a screening technique for quickly identifying LC phases, Chandrasekhar [13, 72] predicted the two–brushes defects to be a signature of  $N_b$  phases, differently from  $N_u$  LC which are characterised instead by four–brushes defects. Chiccoli *et al.* [74, 42] have theoretically computed the free energy difference between two– and four–brushes defects, and produced optical images from MC computer simulations of a  $N_b$  lattice model. Such studies have outlined that the presence of topologically stable two–brushes defects is not a universal fingerprint of  $N_b$  phases because their appearance is related not only to the degree of biaxial orientational ordering but also to the magnitude of elastic constants. This is a clear example of the usefulness of computer simulations in providing a possible explanation for the earlier claims of  $N_b$  mesogens based on deceptive optical measurements.

Moving to off–lattice potentials we quote the seminal MC simulation of Allen [22] who mapped the phase diagram of a model fluid formed by hard ellipsoids with three different axes (aspect ratios ranging from 1 : 1 : 10 to 1 : 10 : 10). This was the first simulation with full translational and rotational degrees of freedom to compare against the results of theoretical models, and it was a proof of principle that a  $N_b$  phase might be thermodynamically more favourable than a smectic, or solid one. For such hard particle model the formation of a  $N_b$  phase is based on an entropic driving force related to the excluded volume of ellipsoidal particles. Allen was able to trace the phase diagram with respect to the shape biaxiality finding calamitic  $N_+$ , and discotic  $N_-$  nematic phases, and also conducted detailed simulations for the Landau crossover shape. In a later work Camp and Allen [121] studied with higher accuracy the phase diagram locating the transition points for the prolate parameterisation. The range of shape anisotropies leading to biaxial nematic phases was found to be very narrow, supporting the elusive character of this mesophase. Recently McBride *et al.* [122] performed additional Monte Carlo simulations of the hard biaxial ellipsoids fluid studying the reliability of the theoretical equation of state in predicting the isotropic–nematic transition and finding fairly good agreement.

Repulsive off–lattice simulations have been useful for studying the entropic effects stabilising  $N_b$  phases. However, hard particle models do not consider attractive interactions which are expected to be important in real  $N_b$  [59], and which have been found to stabilise the  $N_b$  phase for aspect ratios closer to those of conventional mesogens. For instance, uniaxial hard ellipsoids and hard spherocylinders with aspect ratio equal or smaller than respectively 1 : 1 : 3 and 1 : 1 : 5 do not form nematic phases upon compression, while soft attractive–repulsive ones do [32].

The effect of attractive interactions have been first considered in a MC simulations of biaxial ellipsoids [52] modelled with the generalised GB potential [95,

96]. These simulations have given hints about the competing role of shape and interaction anisotropies in stabilising the  $N_b$  phase, and have shown that a suitably parameterised off-lattice system with attractive–repulsive soft particles with aspect ratios  $1.4 : 0.714 : 3$ , and interactions  $1.7 : 1 : 0.2$ , might form a stable thermotropic  $N_b$  phase (see Figure 8). The choice of opposite shape and interaction biaxialities destabilises the smectic phase which is normally observed below the uniaxial nematic phase whenever both shape and interaction anisotropies are positive [13, 123]. The usage of *side-by-side* interactions stronger than those *face-to-face*, i.e. giving a negative interaction biaxiality, produces particles with a dual nature: rod-like from the point of view of shape, and disc-like with respect to interactions [13] (see Figure 7). Virtual MD experiments [124] have been used to estimate the switching times of the principal and secondary director of this model  $N_b$  [125]. The reorientation of the secondary director  $\mathbf{m}$  has been found to be, on average, an order of magnitude faster than that of  $\mathbf{n}$ . This kind of direct measurement of a response might be useful for screening the technological suitability of  $N_b$  phases in displays and other devices since in virtual experiment the setup such as sample shape, pair potential, anchoring geometry and strength, and coupling to an external field can be controlled by design without a prior knowledge of mesoscopic response coefficients.

A drawback of all molecular models is that it is not easy to map an idealised potential with specific parameters into a real molecular structure. For instance, in the case of the biaxial ellipsoidal particles of Ref. [52], the stronger lateral interactions may be obtained by synthesising a mesogen with suitable lateral substituents [28] giving weak bonding (e.g. hydrogen bonding groups), or with a specific electrostatic charge distribution. The practical realisation of this prescription is anyway not straightforward. For instance Bruce and coworkers [126] have ingeniously tailored metallorganic mesogens, although without obtaining  $N_b$  mesogens.

Very limited experimental and theoretical work has been done so far for disc-like  $N_b$  mesogens, possibly because only a few systems have been experimentally found to date to form a thermotropic nematic phase, being the columnar one their most common anisotropic organisation. In Ref. [23] a first attempt of studying with MC computer simulations the competition of shape and interaction anisotropies for biaxial GB discs has been presented. A discotic  $N_b$  phase was found for GB particles with opposite shape and interaction biaxialities, i.e. having *face-to-face* pair interactions much weaker than those *side-by-side* (see Figure 9). The most striking result of these MC simulations was that the columnar phase was completely suppressed in favour of a nematic fluid stable over a quite wide range of temperature, and for order parameter values much higher ( $\langle R_{0,0}^2 \rangle > 0.9$ ) than those typical of a calamitic nematic phase.

## 5. Multi-site models

Multi-site potentials allow to model more specifically the effects of molecular shape and interaction anisotropy of mesogenic molecules. The range of simulated systems is fairly

large and goes from rigidly connected hard particles to molecular models with charges, dipoles, and quadrupoles, to fully atomistic models with internal degrees of freedom. Asymmetric models have received little attention, even though experimentally have been reported to widen the  $N_u$  temperature range [19].

Among board-like models, the papers of Sarman [127, 128] report MD simulations of systems formed by rigid objects obtained by embedding from 8 to 11 repulsive GB discs along a line, with aspect ratios similar to those of the hard ellipsoids of Allen [22]. The compression of isotropic samples of all four model particles gave a first order transition to  $N_u$  phase (either calamitic  $N_+$ , or discotic  $N_-$ ), followed by transitions to  $N_b$ . Sarman [129, 130] has also estimated some viscosities using Green-Kubo relations and linear response theory. This is the only computer simulation of multi-site molecular model reported so far to yield a  $N_b$ . In spite of that, multi-site models have been extensively used to study bent-core mesogens, but generally speaking most of the simulations reported in literature do not provide  $N_b$  (actually nematic phases are rather exceptional for such class of molecules, and smectic LC are the typical organisations observed experimentally and in simulations). Since more  $N_b$  mesogens with bent-core shape may be found in the future, it is nonetheless interesting to overview some of the published simulation results.

The majority of published simulations for bent-core mesogens are based on rigid models with two anisotropic sites joined at one end. For instance, Camp *et al.* [131], and Lansac *et al.* [132] have reported MC results for hard-core dimers formed by two spherocylinders with aspect ratios 1 : 1 : 2, and 1 : 1 : 5. Both papers studied the phase diagram for various apex (or aperture angles) finding  $N_u$  organisations for the larger angles, and isotropic fluids of interlocked dimers for smaller apertures.

Moving to attractive-repulsive potentials, similar results have been obtained with the GB models simulated by Memmer [133] and Neal and coworkers [134, 135] who performed NPT MC simulations of rigid bent-core dimers with aspect ratio 1 : 1 : 3 and various apex angles. The isotropic to  $N_u$  transition temperature was found to decrease reducing the aperture angles. Even for this GB model, the  $N_u$  phase disappeared for an intermediate 170 degrees apex angle. Interestingly, close to the nematic-smectic phase transition a spontaneous chirality symmetry breaking [136] was reported [133, 134, 137] to produce organisations related to those predicted by Lubensky and Radzihovsky [4], or observed by Görtz and Goodby [19]. The presence of a central transverse dipole [135] suppresses the  $N_u$  phase to give transitions from isotropic to smectic phases, and this is at variance with results from atomistic simulations (see later on). However, two terminal tilted dipoles embedded into the arms of a three GB bent-core model have been found with MC simulations to stabilise the  $N_u$  phase with respect to smectic ordering [138] (see Figure 10). No  $N_b$  organisations were observed for any of these systems. Interestingly, Clark and coworkers [139] have studied a three-site zig-zag model observing a rich polymorphism reminding that of dipolar bent-core models.

The multi-site models of rigidly connected LJ spherical sites simulated by Dewar and Camp [140, 84] produce results comparable the other bent-core models, but in this

case the effect of a central transversal dipole seems to favour the  $N_u$  phase [84]. A five-site bent model with terminal flexible chains was also studied [84] to find that both smectic and  $N_u$  phases disappear. The effect of flexibility on the phase diagram, even though for linear chains, has been thoroughly studied instead by Galindo *et al.* [141] with Gibbs ensemble MC simulations finding that the polymorphism is strongly affected by the non-rigid model.

To date, the most relevant simulation of multi-site bent-core mesogens has been that of Peláez and Wilson [59] who have performed the first MD simulation of a real  $N_b$  molecule [7, 8] using a full-atomistic potential including electrostatic interactions (see Figure 11). In particular, the spontaneous ordering was observed cooling-down an isotropic sample, and Peláez and Wilson have given evidences regarding the formation of local ferroelectric domains in the  $N_b$ . Atomistic computer simulations are invaluable since they can help in studying some issues (e.g. flexibility), and the detailed effect of electrostatic charges as computed from ab-initio calculations on specific molecules (see e.g. [142]) that would be difficult to tackle with theory or simpler potentials. For instance, in [59] the same atomistic model devoid of electrostatic charges (e.g. an overall transversal dipole moment) does not give a  $N_b$  phase but, upon cooling-down, a smectic one. This is again a confirmation that the subtle balance of anisotropic shape and interaction anisotropy is necessary in mesogenic molecules to stabilise the  $N_b$  phase.

The picture resulting from the published simulation work is that there is no general agreement regarding the optimal apex angle of bent-core mesogens for the stabilisation of  $N_u$  phases, since the results also depend on other specific model features. A certain bend seems to be necessary to observe a  $N_u$ , but the useful range of apertures may be fairly broad. A large apex angle generally favours the  $N_u$  with respect to layered organisations, while small values have given interlocked dimers (even though Ref. [46] reports  $N_b$  mesogens with 90 degrees aperture). Certain intermediate apex angles destroy the  $N_u$  [131, 134, 135]. To provide a  $N_b$  phase a bent molecular shape is not sufficient, and other interactions terms (e.g. a suitable transverse dipole), or a certain amount of flexibility may be necessary to lower the symmetry, and/or the propensity to form ordered layers. To summarise, only atomistic simulations have been successful so far, and the lack of multi-site molecular models of  $N_b$  is a sign that we still do not know what are the minimal molecular features for obtaining these phases.

## 6. Mixtures

One of the possible pathways early recognised by Alben [24] as a candidate for finding  $N_b$  systems has been that of using a suitable mixture of rod- and disc-like mesogens fully miscible over the whole phase diagram. The rationale behind this strategy was that of creating a mixed nematic system where molecular symmetries would promote the independent self-alignment of the mesogens along two mutually orthogonal principal directors (one for the rods, and the other for the discs) producing a  $N_b$  system. This apparently simple picture is deceiving as to date the only published

example of  $N_b$  mixture is not thermotropic but lyotropic [143], and even these findings have been subject to discussion and challenges [144, 145]. To our knowledge, no computer simulations have been conducted on lyotropic systems, possibly due to their complexity, but theoretical models strongly hint polydispersity [65], and rod–disc shape interconversion [146] as possible mechanisms underlying the  $N_b$  behaviour even for thermotropic mesogens. In particular, the paper of Ratón and Cuesta [65] reports theoretical phase diagrams showing stable  $N_b$  mixtures of uniaxial board–like mesogens with a 1 : 1 : 5, and 5 : 5 : 1 aspect ratios (see Fig. 6), and a gaussian distribution of shape.

In spite of the neatness of the suggestion of Alben [24], the practical realisation of a thermotropic  $N_b$  phase of mixed rod– and disc–like molecules has always proved to be difficult both on the experimental [26] and modelling grounds [147, 148, 149, 150, 151, 152, 153, 154, 155]. The common reason behind this failure is that when both orientational and positional degrees of freedom are considered the ordered phases show a thermodynamic tendency to demix.

It is not surprising that one of the few computer simulation successes has been that of lattice models, like those of Hashim *et al.* [156] where phase separation could not take place by design. It should be noted anyway that when particle exchange moves between the two distinct interpenetrated sub–lattices were included, a phase separation did take place also in this model system.

Similarly, almost all attempts made to simulate a biaxial rod–disc mixtures with off–lattice models have lead to phase separations as long as an ordering transition from the isotropic (mixed) phase set in. The majority of studies have been performed with hard particles, like the Gibbs MC simulations of Allen, Frenkel and coworkers [25], where only extreme aspect ratios ( 1 : 1 : 15 with 15 : 15 : 1, and 1 : 1 : 20 with 20 : 20 : 1) appeared to be compatible with a mixed phase of rod– and disc–like particles. Camp and Allen [157] have also simulated fluid mixtures of hard uniaxial ellipsoids with smaller aspect ratios 1 : 1 : 10 and 10 : 10 : 1 and composition 0.5 and 0.6. They have observed I, N, and  $N_b$ , and but have not explored higher density regions of the phase diagram to address the competition between a  $N_b$  phase and demixing. One possibility to overcome these difficulties would be that of enhancing specific rod–disc interactions [147, 149]. The aspect ratios typical of standard mesogens, when considered as hard rigid particles, are predicted by all theoretical models to produce demixing. This behaviour has been explained in terms of entropic effects related to the excluded volume of the mesogens, and their ratio [158, 159]. The mixed ordered state has higher mixing and orientational entropies, while the separated phases gain in translational entropy. As it comes out, for systems with not extremely large aspect ratios, the latter contribution is dominant.

By using a theoretical model Camp and Allen [157] predict a symmetric phase diagram with respect to mole fraction, but forecast that using additional virial coefficients this may become asymmetrical. This has been specifically addressed by Vanakaras, Bates, and Photinos [160] which have studied by MC simulations and theory phase separation in mixtures of perfectly aligned hard boards with rod–like shape but



different aspect ratios. The idea the three authors propose is that of disfavouring the smectic and crystal phases by mixing particles with similar breadth and width, but incommensurable lengths. This strategy also enhances miscibility and lowers the minimum aspect ratio necessary to stabilise a  $N_b$ . Another relevant result is that the most favourable concentration for observing a  $N_b$  system is not the standard equimolar, but instead a 0.3 mole fraction of the longer mesogen (see Figure 12).

Besides using specific rod–disc interactions, another strategy for overcoming phase separation in mixtures may be that of using molecules with both rod– and disc–like mesogenic units joined by a flexible alkyl spacer (the so–called shape amphiphiles [161]). After the work of Fletcher and Luckhurst [162], other molecular design concepts have been explored [162, 163, 161, 164, 165, 166] obtaining  $N_u$  but not  $N_b$ . So far, the mesogen with closest resemblance to the theoretical cartoon of joined mesogens is the one of Kouwer and Mehl [164]. Relying on this picture Bates and Luckhurst [167] have characterised extensively a lattice model with rods and discs at the same sites (completely overlapped sub–lattices) by using MC simulations. The effect of a flexible spacer has been modelled via a coupling between the rod and the disc at the same lattice site, to find from the simulations that the shape of the two–component phase diagram is quite modified by the strength of this interaction. Unfortunately, this lattice model with overlapped sites can not account for the segregation effects of rod and disc moieties observed experimentally [166, 165] and which may be interesting for other nanotechnological applications (although not for  $N_b$ ). Rod–disc dimeric systems have also been studied with theoretical models [168], and experiments in presence of an electric [40] or magnetic [169] field. In the case of Ref. [169] a uniaxial discotic nematic was induced, while in [40] a field–induced  $N_b$  phase was achieved.

Considering all the previous modelling work, the findings of Apreutesei and Mehl [27] of completely miscible disc– and rod–shaped mesogens in the nematic phase are quite important since they are at variance with the theoretical predictions which always doom the mixed phase with the nemesis of demixing.

Attractive–repulsive off–lattice models have received small attention, and the question which choice of shape and interaction biaxialites can prevent demixing still has no answer. Also the effect of weak bonds between unlike particles [149], and flexibility have not been studied in detail by theories, and a model of miscible rod– and disc–like mesogens with monodisperse shape distributions has never been put forward.

## Concluding remarks

The field of  $N_b$  phases still poses many unanswered theoretical and practical questions, and besides experimental investigations there is large scope for modelling and computer simulations. Taking into account recent experimental results, our current view of the  $N_b$  phase, mostly derived from early theoretical and simulation models, might be too narrow and idealised. Rather than considering as  $N_b$  only nematic LC systems with spontaneous macroscopic biaxial ordering, we might broaden the classification to also

include overall uniaxial systems with local biaxial or polar cybotactic clusters which could be converted into a  $N_b$  by a suitable weak perturbation, like a surface treatment or an external field.

If the nature of  $N_b$  organisations is still not completely unravelled, on the molecular side we still do not know exactly what are the minimal features necessary to be accounted for in model potentials for obtaining a  $N_b$  phase. Electrostatic interactions, flexibility, and polydispersity are important ingredients which, along with shape anisotropy, may help in stabilising  $N_b$  phases against freezing, or layering, or demixing.

Besides contributing in clarifying these issues, the future impact of  $N_b$  computer simulations relies on their ability in helping chemists in designing candidate mesogens (e.g. by using atomistic models) to predict LC properties prior to the actual synthesis, and in contributing to the design of model devices (e.g. with lattice and molecular models) in view of a technological deployment of  $N_b$  materials. The achievement of these ambitious goals will require improving model potentials, predicting mesoscopic coefficients in bulk and confined environments, and devising efficient procedures for virtual computer experiments of responses.

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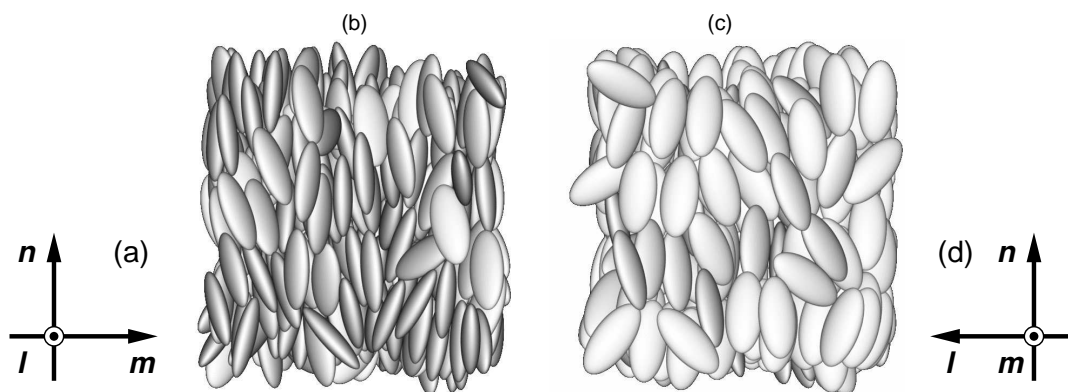
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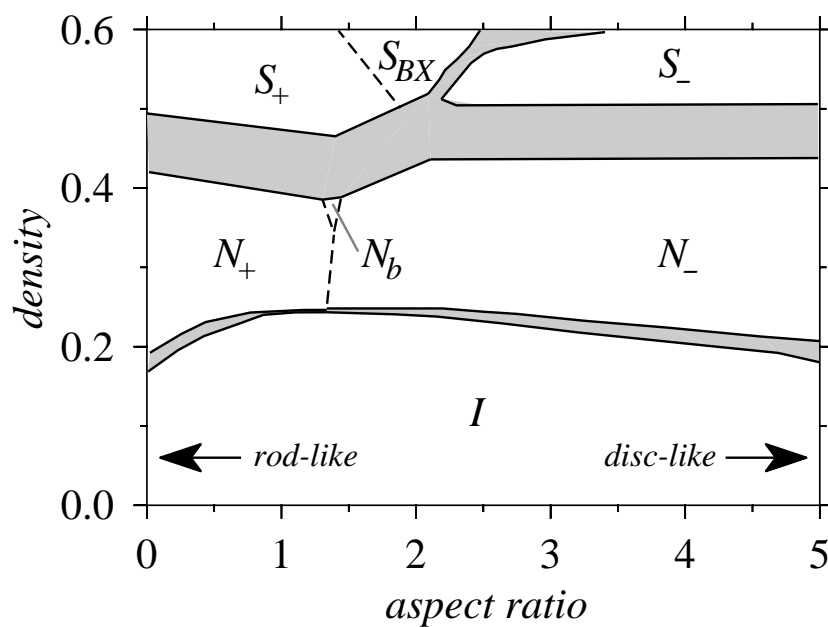
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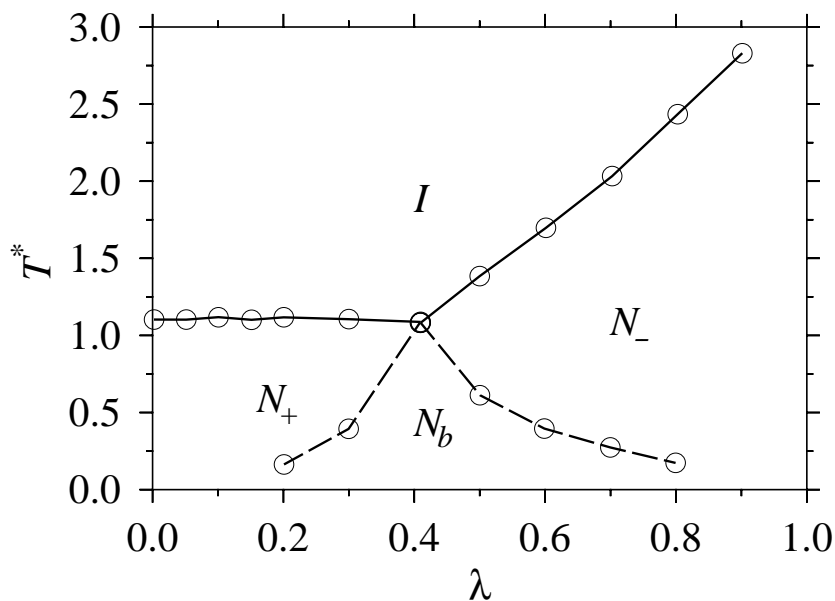
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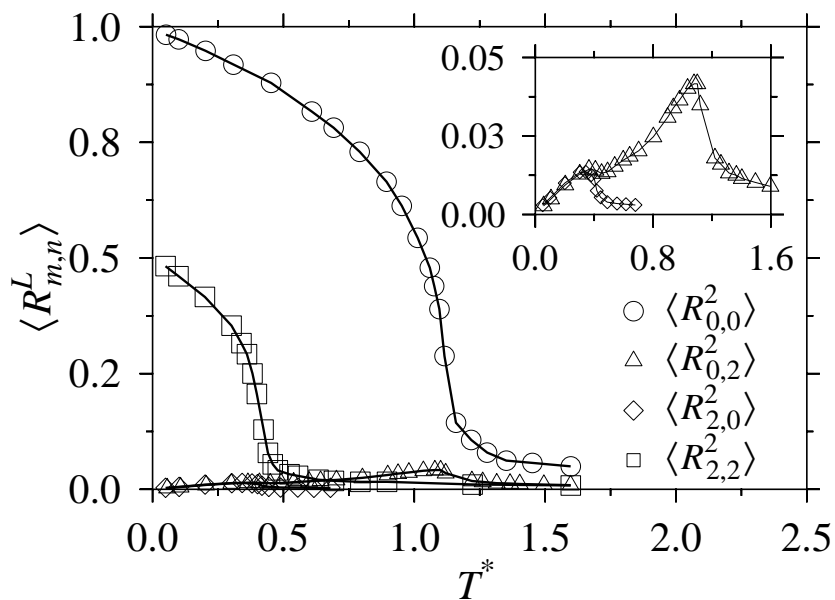
**Figure 1.** Detail of a  $N_b$  phase obtained from the MC simulations of biaxial GB ellipsoids of Ref. [52], and showing the principal  $\mathbf{n}$  and secondary  $\mathbf{m}$  directors. The two snapshots are relative to the same sample observed along  $l$  [plates (a), and (b)], and along  $m$  [plates (c), and (d)].



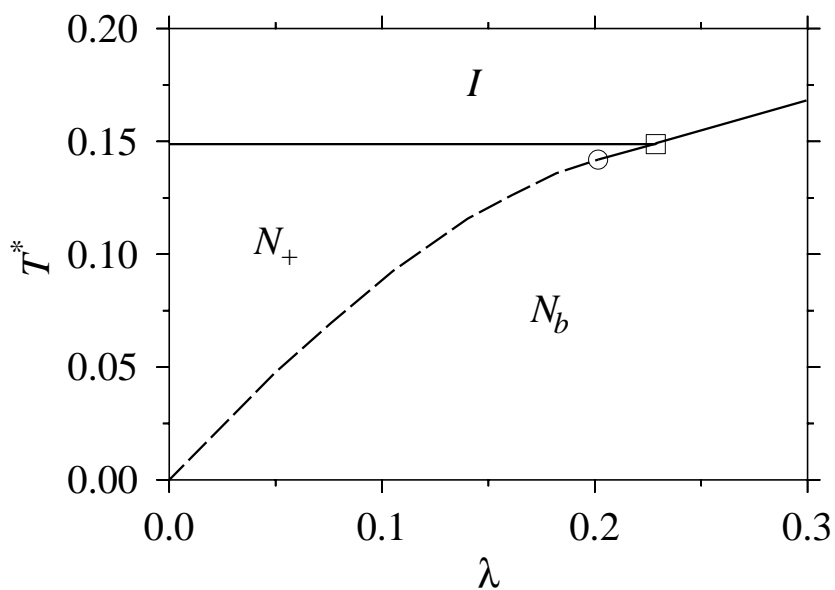
**Figure 2.** Phase diagram, with respect to the dimensionless density and aspect ratio, from the theoretical spheroplatelets model of Ref. [38]. First and second order equilibrium curves are plotted as continuous and dashed lines. Coexistence regions are shaded. (adapted from Figure 4 of Ref. [38].)



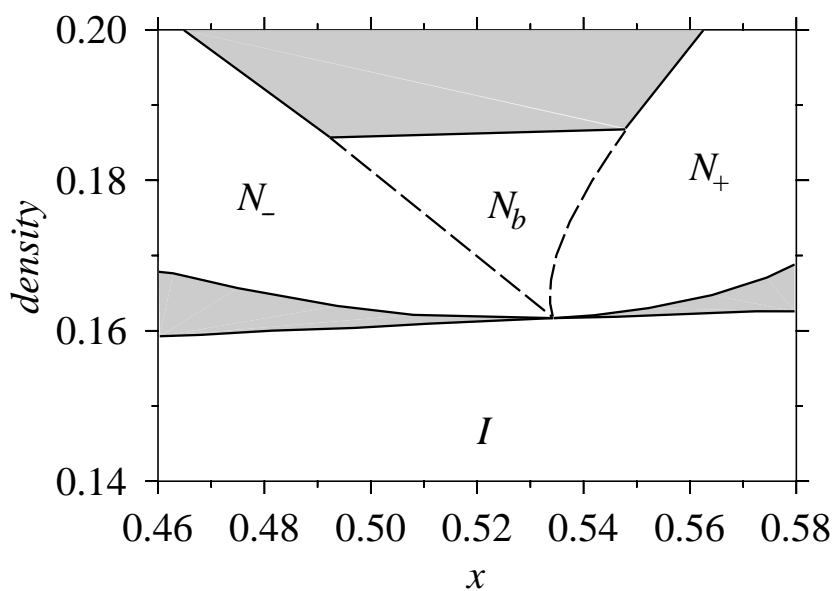
**Figure 3.** Phase diagram, with respect to dimensionless temperature  $T^*$  and shape biaxiality  $\lambda$  (see eqn. 6), from the MC simulations of Ref. [21] using a  $10 \times 10 \times 10$  square lattice and the potential of eqn. 7. First and second order equilibrium curves are plotted as continuous and dashed lines. (adapted from Figure 2 of Ref. [21].)



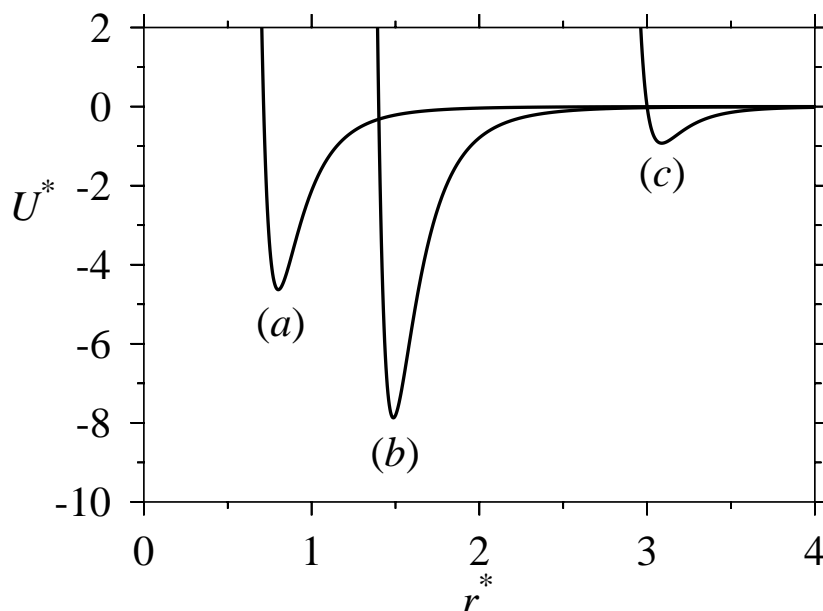
**Figure 4.** The average order parameters  $\langle R_{m,n}^L \rangle$  (see eqns. 2–5), plotted against dimensionless temperature  $T^*$ , for a shape biaxiality  $\lambda = 0.3$  of Figure 3 (adapted from Figures 3 and 4 of Ref. [21].)



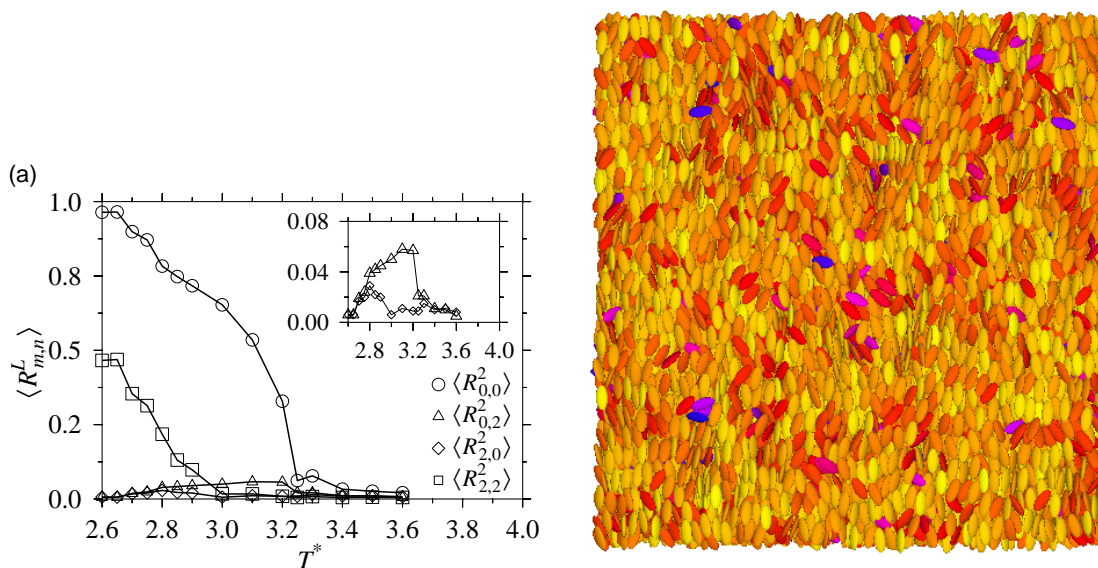
**Figure 5.** Phase diagram, with respect to the dimensionless temperature  $T^*$  and shape biaxiality  $\lambda$  (see eqn. 6), from the theoretical model of Ref. [113]. First and second order equilibrium curves are plotted as continuous and dashed lines. The tricritical and triple points are indicated as a circle and a square. (adapted from Figure 2 of Ref. [113].)



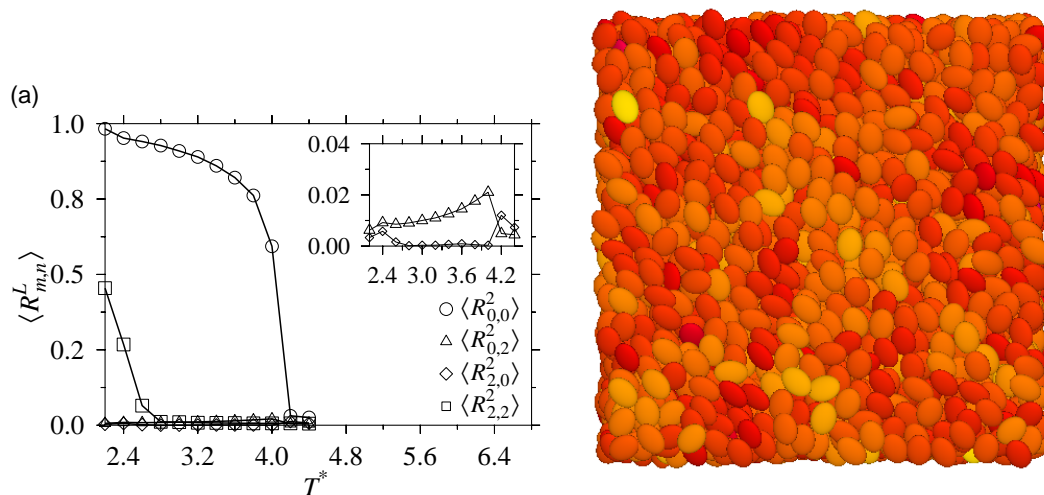
**Figure 6.** Phase diagram, with respect to the dimensionless number density and mole fraction  $x$  of the rod-like mesogen, for a mixture of polydispersed uniaxial rod- and disc-like boards with aspect ratios 1 : 1 : 5 and 5 : 5 : 1 from the theoretical model of Ref. [65]. First and second order equilibrium curves are plotted as continuous and dashed lines. Coexistence regions are shaded. (adapted from Figure 2 of Ref. [65].)



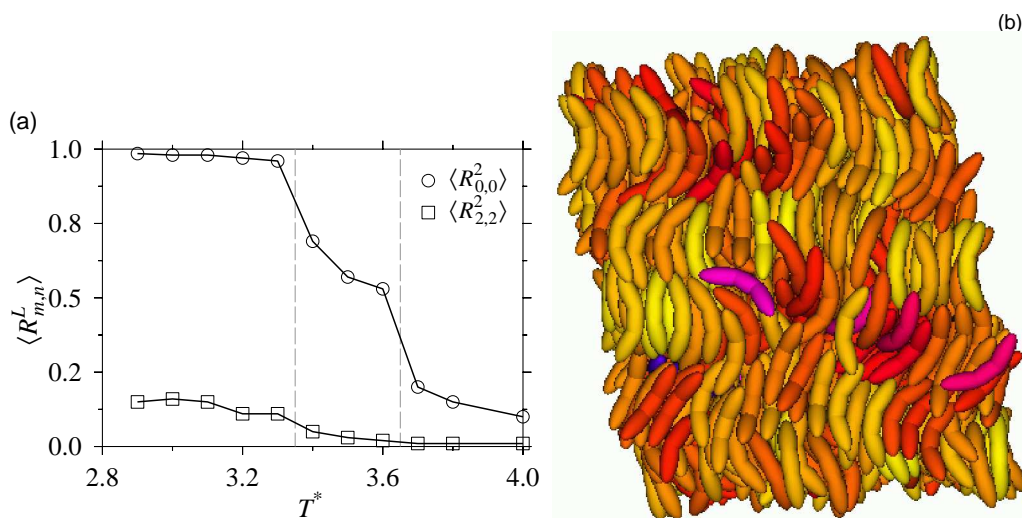
**Figure 7.** The dimensionless  $U^* = U/\epsilon_0$  GB potential profiles for a pair of biaxial ellipsoids in the *face-to-face* (curve a), *side-by-side* (curve b), and *end-to-end* (curve c) configurations [95]. The parameters  $\sigma_x = 1.4$ ,  $\sigma_y = 0.714$  and  $\sigma_z = 3$  (all in  $\sigma_0$  units), and  $\epsilon_x = 1.7$ ,  $\epsilon_y = 1$  and  $\epsilon_z = 0.2$  (all in  $\epsilon_0$  units) are those of Ref. [52]. Empirical parameters  $\mu = 1$ ,  $\nu = 3$ , and  $\sigma_c = \sigma_y$ . Dimensionless distance  $r^* = r/\sigma_0$ . (adapted from Figure 2 of Ref. [52]; we note that the value  $\epsilon_y = 1.2$  given at page 5975 of Ref. [52] was misprinted, and should be instead  $\epsilon_y = 1$ .)



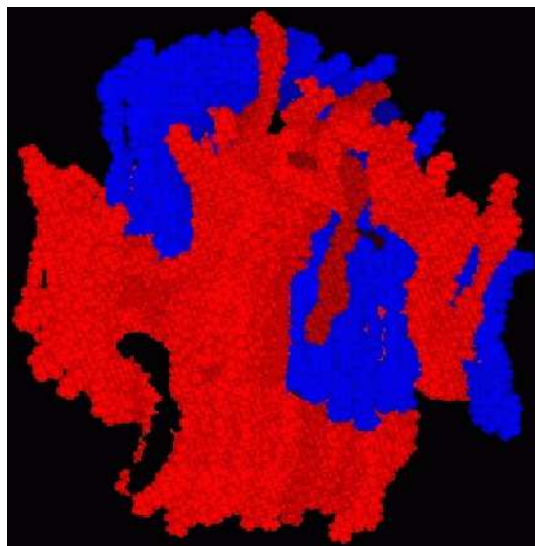
**Figure 8.** Average order parameters  $\langle R_{m,n}^L \rangle$  [plate (a)] from the NPT MD simulations of the model biaxial rod-like GB mesogen of Ref. [95, 96], and snapshot [plate (b)] of a  $N_b$  phase formed by 65536 elongated biaxial GB ellipsoids at  $T^* = 2.8$  and  $P^* = 8$ , with  $\langle R_{0,0}^2 \rangle = 0.78$ , and  $\langle R_{2,2}^2 \rangle = 0.22$ . Sample viewed along the  $\mathbf{m}$  mesophase director.



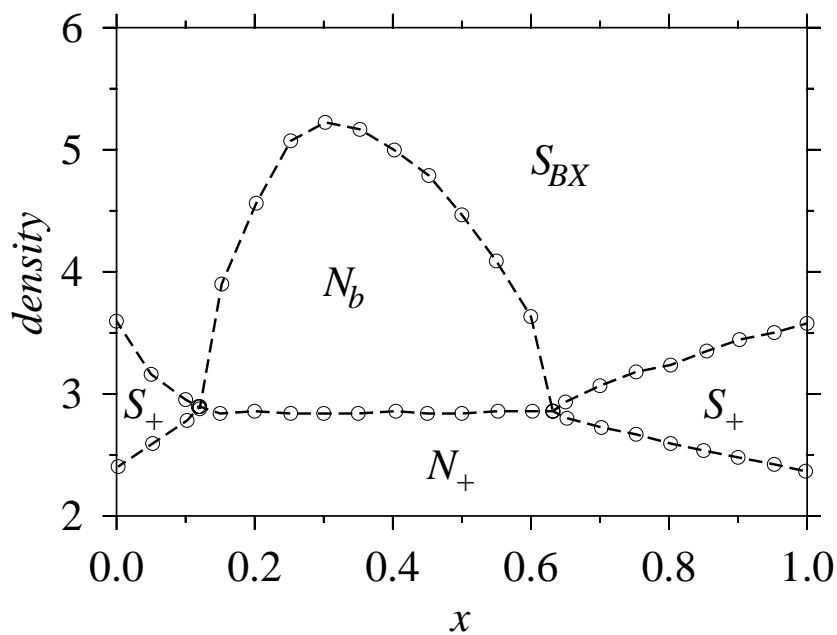
**Figure 9.** Average order parameters  $\langle R_{m,n}^2 \rangle$  [plate (a)] from the NPT MD simulations of the model biaxial disc-like GB mesogen of Ref. [23], and snapshot [plate (b)] of a  $N_b$  phase formed by 8192 squashed biaxial GB ellipsoids at  $T^* = 2.4$  and  $P^* = 8$  with  $\langle R_{0,0}^2 \rangle = 0.95$ , and  $\langle R_{2,2}^2 \rangle = 0.27$ . Sample viewed along  $\mathbf{n}$  mesophase director.



**Figure 10.** Average order parameters  $\langle R_{m,n}^2 \rangle$  [plate (a)] from the NPT MC simulations of the model bent-core GB mesogen of Ref. [138], and snapshot [plate (b)] of a  $N_u$  phase formed by 1000 three-site GB particles with two terminal dipoles at dimensionless temperature  $T^* = 3.5$  and pressure  $P^* = 10$  and  $\langle R_{0,0}^2 \rangle = 0.57$ , and  $\langle R_{2,2}^2 \rangle = 0.03$ . Sample viewed from a direction perpendicular to the  $\mathbf{n}$  mesophase director.



**Figure 11.** Snapshot of a bent-core  $N_b$  phase from the MD atomistic simulations of Ref. [59] showing the formation of ferroelectric domains with opposite polarity. (Image courtesy of Prof. Mark Wilson.)



**Figure 12.** Phase diagram, with respect to the dimensionless reduced density and mole fraction  $x$  of the longer mesogen, for a two-component mixture of hard-body biaxial board-like particles from the theoretical model of Ref. [160]. All equilibrium curves correspond to second order transitions. (adapted from Figure 3 of Ref. [160].)