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Ordered fluids of globular supermolecules†

Alexandros G. Vanakaras[a] **and Demetri J. Photinos***[b]

[a]*Department of Materials Science, University of Patras, Patras 26500, Greece*
[b]*Department of Physics, University of Patras, Patras 26500, Greece.*
E-mail: photinos@upatras.gr

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A molecular description of the mesomorphic behaviour of globular supermolecules of radial dendritic architecture is presented. It is based on coarse grained structural and conformational features, namely, anisometry of the overall shape, submolecular partitioning of the interactions and non-convexity of the supermolecular surface. The relevance of these features to conformational phase transitions, orientational ordering, layering and microsegregation phenomena in ordered fluid phases is studied using density functional theory of deformable bodies and Monte Carlo simulations of rigid fan molecules. Orientationally ordered and layered phases are found, both in theory and simulation, even in the absence of significant overall shape anisometry.

1. Introduction

Common, low molar mass, liquid crystals are made of molecules (mesogens) with highly directional interactions. The anisometry (inequality of dimensions) of the molecular shape, in essence the geometrical transcription of the directionality of steric interactions, is the feature most commonly used to differentiate mesogens (calamitic, discotic, sanidic, banana,...) in relation to the possible general types of self organisation they can produce in fluid phases.[1] The underlying physical justification is that self organisation is dictated primarily by steric restrictions on molecular packing. This picture is generally accepted and is not in contradiction with well known instances where other, weak, interactions such as hydrogen bonding, electrostatic *etc.*, could affect critically the ordering.

Low molar mass mesogens typically consist of a relatively rigid, shape-anisometric, core and one or more flexible end chains. The type of anisometry of the mesogenic core essentially determines the structural type of the phases that can be formed by the molecules. As a rule (notable exceptions being some interesting cases of core photoisomerisation),[2] molecular flexibility, whether associated with the end-chains or with internal motions of the mesogenic core, has limited effects on the overall molecular anisometry. Such effects could, nevertheless influence critically the stability of some mesophases relative to others. On the other hand, the molecular environment produced by the self organisation of the molecules influences the statistics of their conformations but not to the point of changing the type of molecular anisometry. Thus, for example, the statistical distribution of conformations of common calamitic mesogens in the isotropic phase differs from their distribution in the nematic phase but the average molecular shape appears only slightly more elongated in the nematic phase than in the isotropic.[3]

The situation is radically different for some classes of globular supermesogens of dendritic topology.[4–12] A usual molecular architecture for such systems consists of an inner scaffold, rigid or flexible, and a number of mesogenic units linked in branching configurations to the core by means of flexible spacer chains. An example of such a structure[8] is shown in Fig. 1. These supermolecules typically have a very large number of accessible conformations whose shapes can be very different. Furthermore, the dominant conformations in a bulk phase could be quite different from the dominant conformations of the isolated supermolecule. On the other hand, phase structure and thermodynamic stability depend sensitively on the packing properties and intrinsic probabilities of the supermolecular conformational states. This strong interdependence of phase organisation and dominant conformational structure is an important difference between the mesomorphic behaviour of the dendritic supermolecular mesogens and that of the low molar mass mesogens.

In this paper we present an attempt to rationalise the mesomorphic behaviour of the supermolecular systems in terms of basic structural features. The focus is on identifying the key topological and statistical ingredients for the description of their self organisation propensities. Naturally, this excludes cases where special interactions play an exceptionally important role in the determination of the mesomorphic behaviour. The obvious motivation for this low resolution approach is that an atomistic approach is in general computationally prohibitive in view of the huge number of internal degrees of freedom associated with the flexibility of the supermesogens. Moreover, the focus of the atomistic approach would necessarily be on structural and interaction details of specific supemolecular systems rather than on the possible unifying aspects of the behaviour of different types of systems.

The directionality of the supermolecular structure, more precisely of its various conformational states, could be produced in different ways, depending on the details of the architecture and the presence of site specific interactions. For example, directionality could be produced by deformations of the mass distribution of the supermolecule, leading to highly anisometric overall shapes,[4] or, in the other extreme, by mere alignment of the mesogenic units in the periphery,[11] leading to highly directional surface interactions among the supermolecules without necessarily producing a strong anisometry of their overall shapes.

Here we concentrate on three basic aspects of directionality and we show that they could provide a consistent description of mesomorphism and related conformational phenomena in a wide class of supermolecular sytems. These aspects are:

(i) *anisometry of the overall shape* of the supermolecular state, which determines the packing properties of the system in the absence of extensive interdigitations among supermolecules;

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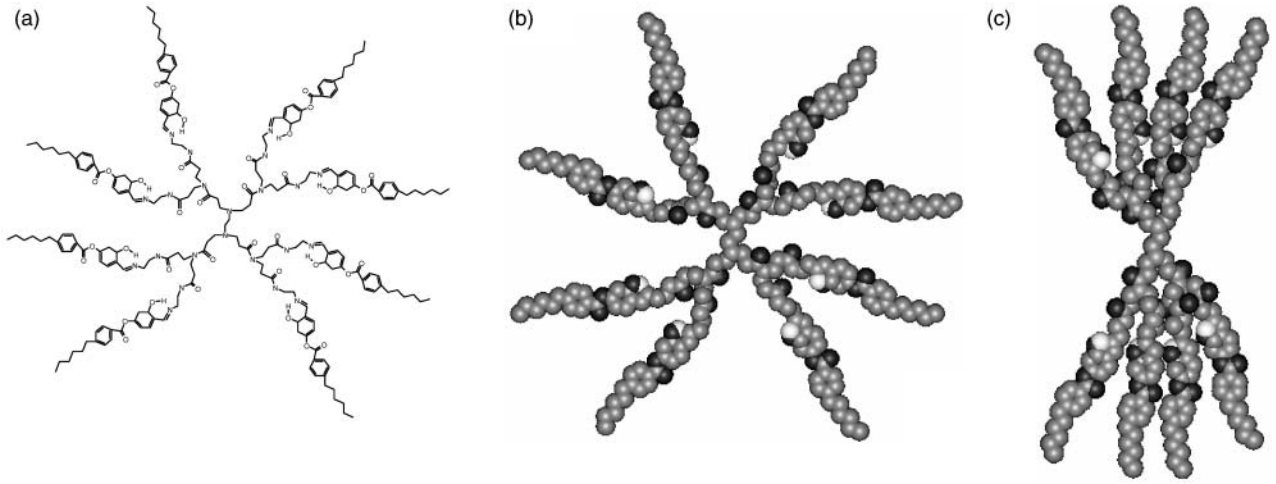

Fig. 1 Chemical structure (a) and space filling model of different conformations (b), (c), of a representative[8] globular dendritic supermesogen.

(ii) *submolecular partitioning* into regions with distinctly different interactions depending on their intra-molecular organization and on their chemical affinity. This type of partitioning underlies the mechanism of phase-microsegregation that is operative in low molar mass systems as well and is known to favour the formation of lamellar and columnar structures; (iii) *non-convexity of the shape*, describing in higher resolution the super-molecular surface topology. It becomes important when there is substantial interdigitation of the interacting supermolecules.

These three aspects are examined separately in this paper in order to identify their particular roles. In many real supermolecular systems of interest, however, all three aspects could be simultaneously present, to different extents, in mutually supplementing or counteracting roles, to promote or to suppress certain types of self organisation. Particular consideration is given to the possibility of orientationally ordered phases from supermolecular structures that are intrinsically globular or completely non-directional in a statistical sense.

The deformable convex body approximation, based on the anisometry of the overall molecular shape through the concept of the molecular envelope, is introduced in the next section. A primitive application of this approximation is presented in Section 3 for a dendritic supermesogen of radial topology whose conformations are assumed to be grouped in just two states of the enveloping shape, a spherical and cylindrical one. The molecular volumes and statistical weights associated with the enveloping states are estimated. A density functional theory of the isotropic, nematic and smectic A phases exhibited by the two state system is presented in Section 4. The statistical mechanical formulation is outlined in the Appendix. The limitations of the deformable body model and the necessity of including submolecular partitioning and shape non-convexity into the description are discussed in Section 5. In Section 6 we present results of Monte Carlo simulations on spherical fan molecules that form layered fluid phases, thus demonstrating that non-convexity of the shape could give rise to mesomorphic behaviour even in the absence of overall shape anisometry and submolecular partitioning. The conclusions are drawn in Section 7.

2. The deformable convex body approximation

Even if one ignores all but the steric interactions of highly flexible supermesogens, such as those of Fig. 1, one would still have to describe the shape of each conformation. A detailed description is in general rather difficult, involving a large number of geometrically complex objects. Many of these difficulties can of course be avoided at the expense of some crudeness in the representation of molecular shapes. Thus, as a first step towards a description of their steric interactions, one could imagine that each of the supermolecules is "wrapped" with some impenetrable but easily stretchable wrapping and treat them as impenetrable objects whose outer surface is defined by the wrapping. For brevity, these objects will be referred to as the "envelopes" of the supermolecular conformations. The wrapping is understood as the enclosure of the molecule within a convex volume of the smallest possible surface area. In this picture, conformational changes are perceived as deformations of the envelope, which is therefore considered to be an impenetrable but deformable convex body.

Convexity of the volume means that the linear segments connecting any two points on its outer surface are entirely contained with the volume. It is invoked in the present context primarily in order to provide a well defined meaning for the concept of "wrapping". Convex objects are also more convenient to handle mathematically[13] when evaluating their excluded volume. In more physical terms, convexity indicates the absence, or neglect, of interdigitations and/or entanglements among the supermolecules. In that sense, non-convex structures made by fusion of a small number of convex shapes (*e.g.* united-atom spheres) in a way that does not give rise to extensive molecular interdigitation could be adequately approximated by their convex envelopes.

For the statistical description of the supermolecular systems in the deformable convex body approximation,[14] each molecular envelope, or state s of the non-interacting deformable body, is assumed to have a certain intrinsic probability P_s^0. The latter can be determined from the intramolecular interactions, through the conformational energy E_s and from the number N_s (multiplicity) of distinct conformations that are described by the same envelope s (see eqn. (A1)). It should be noted here that, contrary to what is often assumed, the lowest energy state does not necessarily come with the largest intrinsic probability; a state of higher energy could be intrinsically more probable if its multiplicity N_s is sufficiently large. In the bulk phase, the state is obtained with a different probability, P_s, to be referred to as the bulk probability, which can be regarded as a modulation of the intrinsic probability P_s^0 by the intermolecular interactions (see eqn. (A6)). The two probabilities, P_s^0 and P_s, could differ dramatically in cases where, for example, a state with large intrinsic probability packs very inefficiently in the bulk phase.

3. A simplified two-state example

To illustrate the deformable convex body description we consider a supermolecular structure of radial topology consisting of an inner flexible dendritic scaffold and peripherally appended rod-like mesogenic units with flexible end-chains as in Fig. 2(a). Supermesogens of this structure are known to form layered mesophases for several generations of the dendritic scaffold.[8] Replacement of the single end chains of the mesogens with twin chains was found to favour the formation of columnar mesophases.[9]

Extended conformations such as the one shown in Fig. 2(a) would be very unlikely in any condensed fluid phase because of their large effective molecular volume. The exclusion of such conformations, however, still leaves a large number of more compact conformations in which the interacting supermolecule can be found. In extreme simplification, we assume that all the relevant conformations can be enclosed in just two envelopes, a sphere and a cylinder. Given the geometrical shapes of the two envelopes we estimate their volumes and their intrinsic probabilities. To this end we consider the accommodation of the supermolecule within a spherical envelope as shown in Fig. 2(b). The dendritic scaffold is contained within an inner sphere of diameter D_I and the cores "grow" radially from the surface of the inner sphere with average surface density $1/\sigma$. Ignoring the volume occupied by the end chains, the radius of the spherical envelope is $D_{sph} = D_I + 2L_R$, where L_R is the length of the mesogenic rod units. The accommodation of the same supermolecule in a cylindrical envelope is shown in Fig. 2(c). The mesogenic units are grouped in two cylindrical bundles and the dendritic scaffold is contained in the cylindrical volume between the two bundles. To compare quantitatively the total volumes of the two envelopes we assume that the surface density of the rods in the cylindrical bundles is also equal to $1/\sigma$ and that the dendritic scaffold occupies equal volumes in both types of envelopes. It then follows that the ratio of volumes of the two envelopes is given by eqn. (1).

$$V_{cyl}/V_{sph} = (1+3v)/(1+v)^3 \qquad (1)$$

with

$$v \equiv \sqrt{(8\pi/\sqrt{3})(L_R/D_R)}/\sqrt{N_R\sigma/\sigma_{cp}}$$

Here D_R is the diameter of the rod-like mesogenic units, N_R is their total number in a single supermolecule, σ is the average area per mesogenic unit and σ_{cp} is the area per mesogenic unit under conditions of hexagonal close packing.

Representative plots of the volume ratio in eqn. (1) as a function of the reduced grafting area σ/σ_{cp}, for different N_R corresponding to different generations of the dendritic scaffold, are shown in Fig. 3. It is apparent that the volume of the cylindrical envelope is substantially smaller than that of the spherical one in all cases of physical relevance. This result is simply the quantification of what can be seen qualitatively on comparing Figs 2(b) and (c), *i.e.* that the internal packing of the rod-like mesogenic units within the spherical envelope is not as efficient as in the cylindrical one. In turn, this implies that the cylindrical state is favoured by the gain in packing entropy, not only in the ordered phases but also in the isotropic. To estimate the relative probabilities for the two envelopes we assume that the number of configurations accessible to the scaffold is determined by the volume available to it, irrespectively of the shape (spherical or cylindrical) of that volume. It then follows that the multiplicity of the cylindrical envelope is essentially $N_R/2$ times that of the spherical one since there are that many ways to deform the configuration of Fig. 2(b) along two diametrically opposite rods in order to produce the configuration of Fig. 2(c).

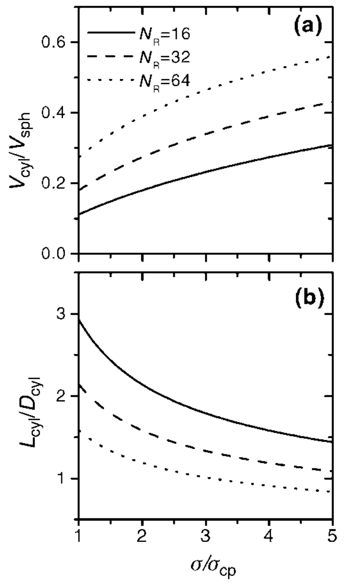

Fig. 3 (a) Plots of the ratio V_{cyl}/V_{sph} of the molecular volumes in eqn. (1) associated with the spherical and the cylindrical envelopes of Figs 2(b) and (c) as a function of the reduced area σ/σ_{cp} per rod-like mesogenic unit for different numbers N_R of such units, corresponding to different generations of the dendritic scaffold. (b) Plots of the aspect ratio L_{cyl}/D_{cyl} of the cylindrical envelope. The plotted results are obtained for rod-like mesogenic cores of aspect ratio $L_R/D_R = 4$.

The volume ratio in the plots Fig. 3(a) assumes its smallest value at close packing. Practically, however, this corresponds to thermodynamically inaccessible conditions as the close packed states, spherical or cylindrical, are normally associated with low intrinsic probabilities. This is so because such states, aside from their energies, which could be rather high, have low multiplicities compared to respective envelopes of larger volume, where a much larger number of configurations of the rods and of the dendritic scaffold could be accommodated. The

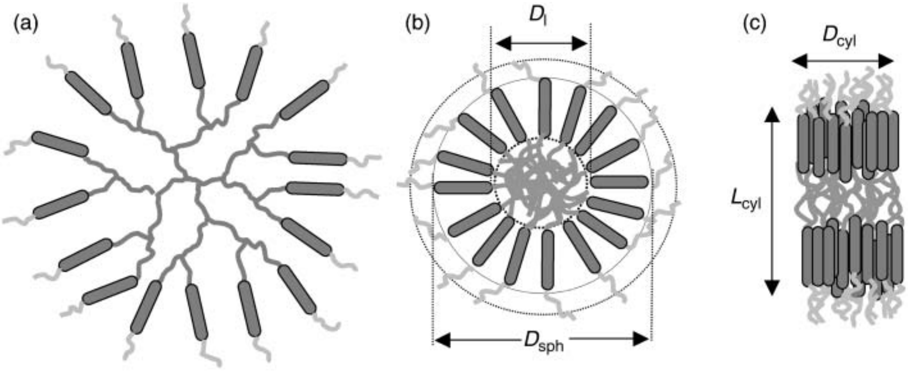

Fig. 2 (a) Extended configuration of a dendritic supermesogen with flexible scaffold and rod-like mesogenic units attached longitudinally in the outer periphery of the scaffold. (b) Average configuration of the supermesogen within a spherical envelope. (c) The same within a cylindrical envelope.

physically relevant value of the area per rod, σ/σ_{cp}, can be estimated by noting that the optimisation of the internal entropy of the supermolecules *versus* their packing entropy in the bulk requires that the density of mesogenic units within the envelope be nearly equal to their average density in the bulk phase. In other words, the supermolecules in, say, the layered phase are packed with uniform rod density as shown in Fig. 4(a) rather than as shown in Fig. 4(b) where the rods are densely packed within the envelopes leaving more free volume between envelopes. Accordingly, representative values of the reduced area are in the vicinity of $\sigma/\sigma_{cp} \approx 2$.

Fig. 3(b) shows the calculated aspect ratio L_{cyl}/D_{cyl} of the cylindrical envelope as a function of the reduced rod area. As expected, it decreases with increasing rod area and with generation number of the dendritic scaffold. In fact, the aspect ratio for the high generation cases turns out to be too low (<3) to produce orientational ordering by anisometry of the overall shape. We shall return to this point in Section 5.

4. Structural and conformational phase transitions

Having established that the cylindrical envelope is in general of lower volume and possibly of higher multiplicity than the spherical one, we now consider the transitions among fluid phases for a system that can exist in these two types of interconverting molecular envelopes with specified intrinsic probabilities. The free energy is formulated according to the density functional approach for a system of interconverting[14] spherical and spherocylindrical states of the molecular envelope interacting *via* hard-body forces. The fluid phases considered are the isotropic, the nematic and the smectic A phase. The procedure is outlined in the appendix. The spherocylindrical shape (a cylinder with two hemispherical caps in its ends) is chosen to represent the shape of the cylindrical envelope in these calculations mainly in order to avoid certain mathematical complications associated with the excluded volume of simple cylinders.

The results of calculated phase transitions as a function of the intrinsic probability of the cylindrical envelope are shown in Figs. 5(a)–(c) for a system where the (sphero)cylinder aspect ratio is set at $L_{cyl}/D_{cyl} = 4$ and the molecular volume ratio of the two envelopes is $V_{cyl}/V_{sph} = 0.5$. As shown in Fig. 5(a), an isotropic and a smectic A phase are always present. At high intrinsic probabilities of the cylinder, a nematic phase appears between the isotropic and the smectic. Fig. 5(b) shows that the bulk probability of the cylindrical envelope in the ordered phases is nearly equal to unity, independently of its intrinsic probability. This is in accordance with the packing efficiency considerations discussed earlier. The discontinuous increase of the bulk probability across the phase transition is large, particularly at low intrinsic probabilities. Interestingly, near the phase transition the bulk probability of the cylindrical envelope is found to be higher than its intrinsic probability, even in the isotropic phase. The layer spacing is determined exclusively from the size of the rod like conformation.

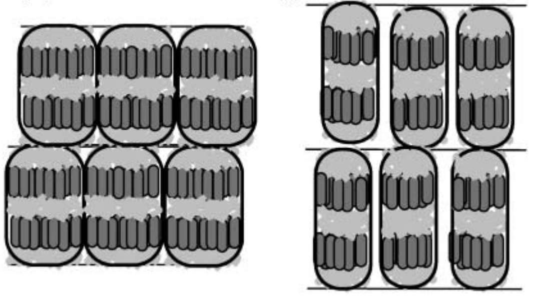

Fig. 4 (a) Optimal packing in the ordered, layered, phase. The density of the mesogenic cores within the cylindrical envelopes does not differ from the average density in the phase. (b) High packing density within the envelopes, resulting in increased translational and rotational freedom of the individual envelopes within the phase, albeit at the expense of the internal freedom of the mesogenic cores within each envelope.

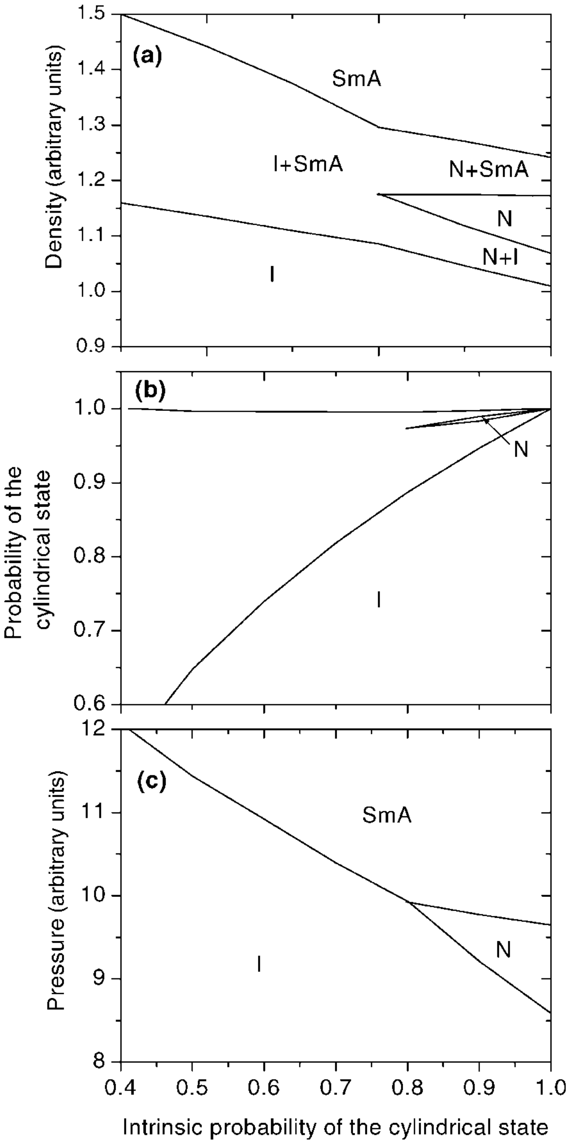

Fig. 5 Results of density functional calculations for the phase diagrams of the system of interconverting cylindrical–spherical envelope states as a function of the intrinsic probability of the cylindrical state. The cylinder aspect ratio is $L_{cyl}/D_{cyl} = 4$ and the cylinder to sphere molecular volume ratio is $V_{cyl}/V_{sph} = 0.5$. The fluid phases in these calculations are isotropic (I), nematic (N) and smectic A (SmA). (a) Phase coexistence densities (in arbitrary units). (b) Probability of the rod like deformation at the phase transition. (c) Transition pressure (in arbitrary units).

The results obtained in this section obviously involve too many simplifications to be quantitatively realistic. Nevertheless, these results could be quite relevant to real systems in the sense that they clearly demonstrate the selection and statistical enhancement of the supermolecular conformations according to their packing properties in the ordered phase. It might be useful at this point to stress that supermolecules of the type considered here cannot be strictly impenetrable and deformable: as the dendritic generations grows, conditions of peripheral steric congestion (packing catastrophe) could be reached. In that case the dendrimers would become impenetrable but also highly unlikely to deform due to lack of space. For generations below the congestion limit, the dendrimers are quite deformable but only some of their relatively compact conformations can be considered as reasonably impenetrable whereas the more extended conformations can produce many highly interdigitating configurations. The applicability of both impenetrability and deformability to the interacting objects rests in this case on the assumption that the bulk probabilities of such extended conformations are negligible. But even so, the approximate validity of impenetrability does not of course imply that the relatively compact conformations are adequately represented by convex objects. In fact, as discussed in the next two sections, a description based on shape could accommodate a certain extent of peripheral interdigitation of the interacting supermolecules by relaxing the convexity restriction.

5. Direct segmental interactions and microsegregation

The impenetrable deformable convex body model provides an interpretation of self organisation and conformational phase transitions in terms of the interplay between extensive flexibility and packing entropy. Its applicability is of course restricted to supermolecular structures that can be reasonably approximated by the shapes of their envelopes. The model, however, does not constitute a complete description of real dendritic supermolecular systems, not even on the qualitative level. It fails, for example, to explain why dendromesogens of the structure shown in Fig. (2) do produce smectic phases for high generation[8] in spite of the fact that the aspect ratio of the cylindrical envelope decreases with increasing generation (see Fig. 3(b)) and eventually goes below the value required for the formation of a smectic phase of cylindrical objects. The failure is partly due to not accounting for submolecular partitioning that can give rise to strongly microsegregated ordering. Such partitioning is obviously present in the cylindrical states of Fig. 2(c), which show two clearly separated core regions, two end chain regions and a central region containing the scaffold part. This kind of microsegregation is thought to be the primary driving mechanism for the formation of the layered phases of poly(amidoamine) dendrimer derivatives[8,9] of the general structure shown in Fig. 2. Another reason for the failure is the underestimation of the anisotropic interactions of the supermolecular structures as a result ignoring direct interactions of individual mesogenic units belonging to different supermolecules.

Indeed, cylindrical envelopes with densely packed contents and high aspect ratio, such as the ones shown in Fig. 4(b), could be sufficiently directional objects to produce an ordered phase. Their aspect ratio, however, decreases with increasing generation number and, furthermore, such states of dense internal packing are intrinsically far less probable than states of lower internal packing densities, such as shown in Fig. 4(a). The latter states are clearly of smaller aspect ratio and eventually not sufficiently directional by virtue of their shape, but the mesogenic units contained in them have more freedom to interact individually with the mesogenic units of neighbouring supermolecules. Such interactions are further facilitated in the presence of microsegregation and promote the mutual alignment of the mesogenic units. However, it is the aspect ratio of the mesogenic units that is relevant to these interactions and not the aspect ratio of the overall cylindrical envelope.

The explicit consideration of direct interactions among the supermolecular constituents is, in general, hard to accommodate within the conceptual framework of the deformable body model. Nevertheless, in many cases of interest where the relevant conformations are more or less compact and preclude extensive entanglements, the intermolecular interactions involve only the constituents that are near the surface of the supermolecule. In such cases the deformable body model can be extended to account for direct interactions among constituents by relaxing the hard convex body restriction. This can be accomplished, for example, by using soft potentials to describe the interaction among the deformable states of the envelopes and/or by allowing for non-convexity of their shapes, thus accounting for the steric interactions that are generated by the interdigitation the superficial constituents in neighbouring supermolecules. As shown in the next section, non-convexity of the shape could give rise to directional interdigitations of the molecules, sufficiently strong to produce both orientational ordering and layering. It should be noted here that the layered configurations of the supermolecules, such as the one shown in Fig. 4(a), exhibit two kinds of interdigitation. One kind takes place across the layer interface and involves the flexible end chains. The effect of these interdigitations on the supermolecular alignment is marginal and will not be considered further. The other kind of interdigitation takes place laterally, within the layers, and involves the mesogenic units in side-by-side neighbouring supermolecules. These interdigitations obviously have a direct effect on the long-range supermolecular alignment.

Finally, by relaxing the hard body restriction it becomes readily possible to introduce submolecular partitioning into the model, simply by assigning different interactions to different parts of the deformable envelopes, in correspondence with the structure of the respective conformations. The elongated states exhibiting submolecular partitioning generally promote the formation of layered phases. As demonstrated in ref. 12 the lateral attachment of the mesogenic units to the scaffold (as opposed to the longitudinal attachment of the systems in Fig. 2) has the effect of stabilizing the nematic ordering. In the present context this can be interpreted as the removal of the submolecular partitioning from the conformational structure through the lateral substitution, while still maintaining the other factors, global shape anisometry and shape non-convexity, that promote orientational ordering.

6. Highly interdigitating non-convex shapes: spherical fans

In this section we consider the contribution of shape non-convexity to the anisotropy of the effective intermolecular interaction, in isolation from any contributions of overall shape anisometry or submolecular partitioning, by studying the ordering of rigid fan-like structures[15] of the spherical envelope. An idealised, and computationally convenient, representation of a spherical fan molecule is shown in Fig. 6. It consists of a number of thin discs symmetrically fused along a common diameter, to be identified with the z molecular axis in what follows. The molecular envelope of these structures is obviously a sphere of diameter equal to the disc diameter. It is apparent that the closest distance of approach of two such objects is

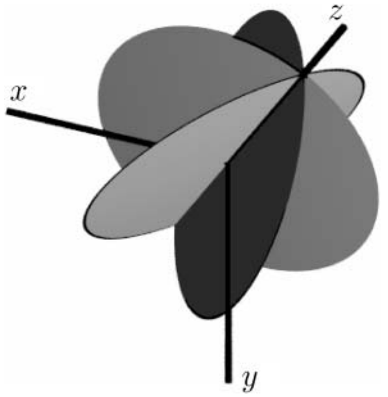

Fig. 6 Diagram of a spherical fan molecule consisting of three symmetrically fused thin discs.

achieved when their z axes are side-by-side parallel. Assuming therefore that the spherical fan molecules interact only *via* hard body interactions, they would be expected to form layered phases with orientational ordering of the z-axes. This kind of phase organization should appear at densities near or above the density that corresponds to the close packing of the spherical envelope. Such behaviour is indeed observed in isobaric-isothermal (NPT) Monte Carlo (MC) simulations, the details of which can be found in ref. 16.

At low pressures an isotropic fluid phase is stable. On increasing the pressure, a layered fluid phase appears with uniaxial ordering of the fan z-axes along the layer normal. The uniaxial layered phase (see Fig. 7) has the same symmetries with the usual smectic A phase of common calamitic mesogens. An additional, unique, feature of this phase, that distinguishes it from the usual smectic A, is the very strong correlation of the rotations of neighbouring molecules about their z-axes.

The pressure at the transition to the ordered phase depends strongly on the number of blades (twice the number of fused discs) in the fan molecule. Pressure–density phase diagrams obtained from the MC simulation for different numbers of blades are shown in Fig. 8. As the number of blades increases, the pressure of the transition to the layered phase is elevated and the pressure–density relation tends to that of hard spheres corresponding to the envelopes of the fans. As seen in Fig. 8, fans made of 10 discs behave practically as their hard sphere envelopes. On the other extreme, fans with a small number of thin blades (four or less) do not show fluid ordering tendencies in the simulations since they can interdigitate substantially for any relative orientation.

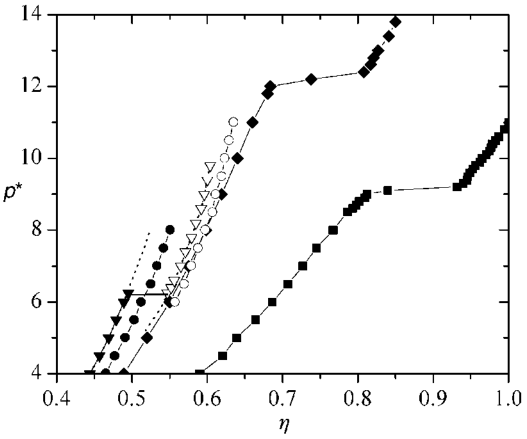

Fig. 8 Phase diagrams of pressure *vs.* packing fraction calculated from Monte Carlo simulations of fan molecules with different numbers of blades. The fans are made of fused discs as in Fig. 6. ■ 3-disc fans, ◆ 6-disc fans, 10-disc fans in expansion (○) and in compression (●) sequences. Hard spheres (of equal diameter with the discs) in expansion (▽) and in compression (▼) sequences. The line connecting the two sequences corresponds to the melting transition of the hard sphere system.

7. Conclusions

We have presented a low-resolution molecular theory in which the microscopic properties giving rise to the directionality of the supermolecular interactions are identified with overall shape anisometry, submolecular partitioning of the interactions and non-convexity of the molecular surface. The theory can provide a consistent description of the basic features of the mesomorphic behaviour of supermolecular systems. Since the primary interacting objects are the supermolecules, and not their submolecular constituents, the theory is not applicable to systems exhibiting extensive intermolecular entanglements.

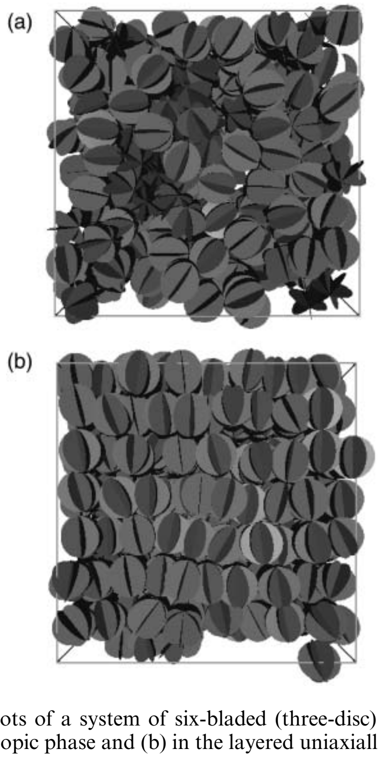

Fig. 7 Snapshots of a system of six-bladed (three-disc) spherical fans (a) in the isotropic phase and (b) in the layered uniaxially ordered fluid phase.

We have studied a simple model of convex deformable hard body supermolecules that can interconvert between spherical and cylindrical states. The model exhibits an isotropic, a nematic and smectic A phase and strong thermodynamic selection of the conformations according to their packing efficiency in each of the phases. The ordered fluid phases in this model are stabilised solely by the anisometry of the enveloping shape of the dominant supermolecular conformations. It is argued, however, that phase microsegregation and intermolecular surface interactions could give rise to ordering even in the absence of substantial shape anisometry of the dominant conformations.

Monte Carlo simulation of rigid spherical fan molecules produce layered, uniaxially ordered fluid phases. The self organisation in these systems is driven by the high non-convexity of the molecular shapes which strongly couples the distance of intermolecular approach to the relative molecular orientation.

Acknowledgements

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Appendix

Here we outline a density-functional formulation of the free energy for the fluid phases of deformable molecules with predetermined interconverting shapes. Further details can be found in ref. 14.

The conformations of the molecule are grouped according to their shape into a number of distinct "envelope" state s. The intrinsic probability P_s^0 for the isolated molecule to be found in the state s is defined by:

$$P_s^0 = \frac{N_s e^{-\beta E_s}}{\sum_{s'} e^{-\beta E_{s'}}} \tag{A1}$$

where E_s is the intra-molecular energy of the state s and N_s is the multiplicity of that state, *i.e.* the number of distinct ways (conformations) in which it can be obtained. Consider N deformable molecules in a volume V and at temperature T and denote by $u(\boldsymbol{r}_{1,2},\omega_{1,2},s_1,s_2)$ the intermolecular potential for a pair of molecules in states s_1 and s_2, with relative position $\boldsymbol{r}_{1,2}$ and orientation $\omega_{1,2}$. In order to derive an approximation for the *NVT* free energy of the system in terms of the intermolecular potential we use the variational cluster expansion method. The resulting form of the free energy is a generalization of the Onsager free energy and is appropriate for describing order–disorder transitions, including isotropic, nematic and smectic A phase symmetries, in fluids consisting of deformable molecules:

$$\beta F = \ln \rho - \ln \zeta - \frac{\rho *}{2} \sum_{s_1,s_2} e^{-\beta(E_{s_1}+E_{s_2})} \tag{A2}$$

$$\int \mathrm{d}\omega_1 \mathrm{d}\omega_2 \mathrm{d}Z_1 \mathrm{d}Z_2 q_{s_1,s_2}(\omega_{1,2},Z_{1,2}) f_{s_1}(\omega_1,Z_1) f_{s_2}(\omega_2,Z_2)$$

Here, $q_{s_1},s_2(\omega_{1,2},Z_{1,2})$ is the orientational–positional integral of the Meyer function of the intermolecular potential:

$$q_{s_1,s_2}(\omega_{1,2},Z_{1,2}) = \int \mathrm{d}X_{1,2} \mathrm{d}Y_{1,2} (1 - \exp[-\beta u(1r_{1,2},\omega_{1,2};s_1,s_2)]) \tag{A3}$$

and $f_s(\omega,Z)$ is the orientational–positional distribution function for the state s. This distribution is obtained from the self-consistency relation:

$$f_{s_1}(\omega_1,z_1) = \frac{\exp[-\rho^* \sum_{s_2} P^0_{s_2} \int \mathrm{d}\omega_2 \mathrm{d}z_2 q_{s_1,s_2}(\omega_{1,2},z_{1,2}) f_{s_2}(\omega_2,z_2)]}{\zeta}$$

where (A4)

$$\zeta = \sum_s P^0_s \zeta_s$$

and

$$\zeta_{s_1} = \int \mathrm{d}\omega_1 \exp[-\rho * \sum_{s_2} P^0_{s_2} \int \mathrm{d}\omega_2 \mathrm{d}Z_2 q_{s_1,s_2}(\omega_{1,2},Z_{1,2}) f_{s_2}(\omega_2,Z_2)] \tag{A5}$$

and ρ^* is renormalized effective density that tends to the actual particle density ρ when the latter is small.

For given thermodynamic variables (ρ,T), eqn. (A4) has, in principle, several solutions which correspond to phases of different symmetry. The solution associated with lower free energy is the thermodynamically stable one. The phase boundaries are calculated by solving the coexistence conditions obtained from equating the pressures and the chemical potentials of the coexisting phases.

The probability for a molecule in the bulk phase to be found in state s is given by:

$$P_s = N_s e^{-\beta E_s} \zeta_s \Big/ \sum_{s'} e^{-\beta E_{s'}} \zeta_{s'} = P^0_s \frac{\zeta_s}{\zeta} \tag{A6}$$

If the envelope states are uniaxial objects, *i.e.* if they posses at least one axis of full rotational symmetry, then the ordering and other structural information of the phases can be fully described in terms of the following ensemble averages: $<((3\cos^2\theta - 1)/2>$, representing the principal order parameter of the orientations θ of the molecular symmetry axes relative to the symmetry axis of the ordered phase, nematic or smectic A, $<\cos(2\pi Z/d)>$, describing the strength of the positional modulation (layering of thickness d) of the molecular density along the layer normal in the smectic A phase and $<\cos(2\pi z/d)(3\cos^2\theta - 1)/2>$, giving a measure of the strength of the coupling between orientational ordering and layering in the smectic A phase.

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