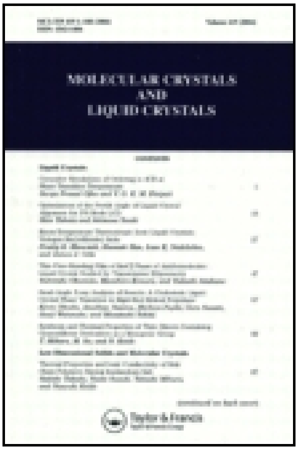

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Theory of Molecular Deformations and Mesomorphic Behavior of Dendrimers

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We present a simple statistical theory of anisotropic fluid phases consisting of deformable molecules and we use it to describe the self-organization of liquid crystalline dendrimers in the limit of very densely attached mesogenic units. We perform calculations for model-systems of spherical molecules that can deform into rod-like or disc-like states and we determine their mesomorphic range as a function of molecular shape parameters and intrinsic conformational probability

Keywords: molecular deformations; liquid crystal dendrimers; phase transitions; molecular theory

INTRODUCTION

The self-organization of supermolecular mesogens with dendritic topology is attracting increasing interest[1-4] because of the novel mesophases formed by these systems and of their potential applications. Typically such supermolecular mesogens, or liquid crystalline (LC) dendrimers, consist of an inner core or scaffold, which could be rigid or soft, and a number of mesogenic units linked in branching configuration to the core by means of flexible spacer chains. The dependence of the size, the shape and the rigidity LC dendrimers on the degree of branching combined with the huge number of accessible molecular conformations gives rise to unique physico-chemical phenomena. For example, dendrimers of radially symmetric topology can form anisotropic fluid phases[2,3], quite unlike low molar mass and LC polymers for which anisometry in the «average molecular shape» is a prerequisite for mesogenicity.

The extensive molecular flexibility normally exhibited by LC dendrimers is believed to be a key feature for understanding their macroscopic properties in relation to their molecular structure. To our knowledge, however, no molecular theory has been developed to that end. Undoubtedly, a realistic microscopic description should include in some detail the structural and conformational features of all the constituents of the dendrimer. Nevertheless, some general insight into the influence of extensive flexibility on phase behavior could be gained from a description at a lower level of resolution. With this in mind, we present here the first step towards a theoretical study of LC dendrimer self-organization. We develop a description wherein the entire dendritic molecule is treated as a deformable continuum. We model the interactions of such idealized molecules, we analyze their propensity to form ordered fluids and we discuss the relevance of the entire scheme to actual LC dendrimers.

INTERACTION MODELING

Depending on the density of mesogenic units in the dendritic periphery, two extreme situations can be distinguished in which the interactions underlying the mesomorphic behavior can be formulated in qualitatively different ways:

(a)Very low density of mesogenic units, high flexibility of spacers. In this case (see Fig. 1(a)) the anisotropic *inter*-dendrimer interactions can be treated as a superposition of interactions between pairs of mesogenic units belonging to different dendrimers. Interactions among mesogenic units belonging to the same dendrimer have negligible contribution to the ordering and their primary function is to generate conformational correlations among the constituents of the dendrimer. In practice, these correlations can be treated by straightforward extension of the rotational isomeric state method that has been used successfully on linear LC dimers and trimers[5].

(b) Very high density of mesogenic units. In this limit the correlations among mesogenic units belonging to the same dendrimer are very strong, irrespectively of the intrinsic flexibility of the spacers(see Fig. 1(c)). Furthermore, the extent of interdigitation among mesogenic units belonging to different dendrimers is limited, as a result of their high surface-density. Accordingly, the dendrimers, rather than the mesogenic units, can be used as the elementary interacting entities and the «effective shape» of the dendrimer becomes a meaningful property to use for modeling the *inter*-dendrimer potential. The deformability of the dendrimer depends primarily on the «softness» of the dendritic core.

Both of the above ways of formulating dendrimer interactions become inefficient at intermediate densities (see Fig. 1(b)). The low density formulation grows computationally very demanding on increasing the number of mesogenic units per dendritic core since this (i) causes very rapid increase of the number of conformations and (ii) renders the interactions among the mesogenic units of the same dendrimer increasingly important to the collective alignment. On the other hand, the high density scheme becomes impractical at lower densities because of the increasing extent of interdigitation among dendrimers, which makes it necessary to use large numbers of increasingly complicated shapes.

In this work we restrict our consideration to the high mesogenic density limit. The entire dendritic unit is treaded as a deformable molecule that can assume different shapes. The effective shapes of the deformable molecule and their respective internal (conformational) energies are modeled to approximate the major classes of conformations that are accessible to the actual dendrimer. The *inter*-dendrimer forces are assumed to be simply hard-body repulsions and are therefore completely determined by the shapes of the molecular conformations. Results of calculations performed with less primitive forms of the interaction potential are presented elsewhere.

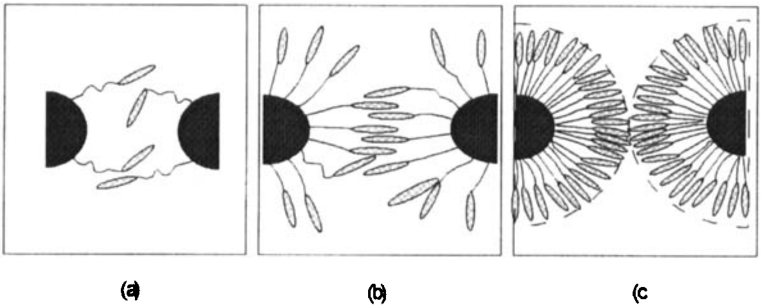

FIGURE 1 Schematic representation of interacting LC dendrimer for low(a) , intermediate(b) and high(c) surface density of the mesogenic units.

GENERALIZED ONSAGER THEORY FOR DEFORMABLE MOLECULES

We have used the variational cluster expansion method[6] to derive the generalization of the Onsager free energy[7] for the order-disorder transition in spatially uniform fluids consisting of deformable molecules. Each molecule is allowed to deform into a number of distinct conformations with *intra*-molecular energy E_n. The *inter*-molecular potential for a pair of molecules in conformations n,n', with relative position $\vec{r}$ and orientations ω,ω' is denoted by $u(\vec{r};n,n';\omega,\omega')$. The appropriate expression for the NVT free energy, denoted by $F^{(2)}$, is obtained by retaining only up to two-molecule anisotropic contributions in the cluster expansion and is given by:

$$F^{(2)}/NkT = -1 + \ln\rho - \ln\zeta \\ -(\rho^{*}/2)\sum_{n,n'} e^{-(E_n+E_{n'})/kT} \int d\omega d\omega' f_n(\omega) f_{n'}(\omega') q_{n,n'}(\omega,\omega') , \tag{1}$$

where

$$q_{n,n'}(\omega,\omega') = (1/v_0)\int d\mathbf{r}\,[1 - e^{-u(\mathbf{r};n,n';\omega,\omega')/kT}\,], \tag{2}$$

v_0 is a fixed molecular volume, $f_n(\omega)$ is the orientational distribution for conformer n and is obtained self-consistently from the relation

$$f_n(\omega) = (1/\zeta)\exp\left[-\rho^{*}\sum_{n'} e^{-E_{n'}/kT}\int d\omega' f_{n'}(\omega') q_{n,n'}(\omega,\omega')\;\right], \tag{3}$$

with

$$\zeta = \sum_{n} e^{-E_n/kT}\zeta_n, \tag{4}$$

and

$$\zeta_n = \int d\omega \exp\left[-\rho^{*}\sum_{n'} e^{-E_{n'}/kT}\int d\omega' f_{n'}(\omega') q_{n,n'}(\omega,\omega')\;\right], \tag{5}$$

The density $\rho = Nv_0/V$ is expressed as a packing fraction. The effective density $\rho^{*} = \rho^{*}(\rho)$ is a function of the actual density such that $\rho^{*} \to \rho$ at low densities and $\rho^{*} \to \infty$ as ρ approaches the maximal packing value. The precise form of $\rho^{*}(\rho)$ depends on how the effects of higher virial terms are approximated[8] but is not of particular significance to the results of the present study. It readily follows from Eqs. (1)-(5) that they reduce to the usual rigid-molecule Onsager formulation[7] on restricting all the molecules to a single conformation and setting $\rho^{*} = \rho$.

It is useful for the subsequent analysis to group the various conformations according to their effective shape. For simplicity it is assumed that all the conformations of the system can be grouped into a small number of distinct shapes S_i that possess at least one axis of full rotational symmetry (uniaxial objects). The intrinsic probabilities for the <u>isolated</u> molecule to be found in a conformation with shape S_i is given by

$$p_i^{0} = \sum_{n(S_i)} e^{-E_{n(S_i)}/kT} \;\Big/\; \sum_{n} e^{-E_n/kT} , \tag{6}$$

where the index $n(S_i)$ runs over the set of conformations that correspond to the shape S_i.

The probability for the interacting molecule to be found in a conformation with shape S_i is given by

$$p_i = \sum_{n(S_i)} e^{-E_{n(S_i)}/kT}\zeta_{n(S_i)} \Big/ \sum_n e^{-E_n/kT}\zeta_n \quad , \tag{7}$$

The orientation dependent function $q_{n,n'}(\omega,\omega')$ of Eq. (2) is tensor-expanded with respect to the relative orientation θ of the symmetry axes of the uniaxial conformations according to

$$q_{n,n'}(\omega,\omega') = q_{n,n'}(\theta) = \sum_l q^l_{n,n'} P_l(\cos\theta) \quad . \tag{8}$$

Since the intermolecular potential is assumed to represent purely hard-body repulsion, the $q_{n,n'}(\theta)$ functions, and their respective tensor coefficients $q^l_{n,n'}$, are completely determined from the shapes of the conformations n,n'. Normally, tensor coefficients $q^l_{n,n'}$ above a certain rank can be ignored in the expansion of the right hand side of Eq. (8) without appreciably affecting the accuracy of the tensor decomposition.

RESULTS AND DISCUSSION

We present results of calculations on model systems whose conformations can be grouped into just two distinct shapes S_1, S_2. As a crude model of LC dendrimers with radially symmetric lowest energy conformation, we have considered spherical molecules of diameter D_{sphere} that can deform into a number of rod-like conformations of equal molecular volume.

For simplicity, all the rod-like conformations are taken to be of the same spherocylindrical shape (a cylinder of length L_{rod} and diameter D_{rod} capped on both ends with hemispheres of the same diameter). The tensor coefficients in Eq. (8) are evaluated, up to rank $l = 6$, as a function of the geometrical parameters of the sphere and rod conformations. These coefficients are then used in Eq. (1) and (3) to evaluate the density ρ^*_{N-I} at which the nematic-isotropic transition takes place for given intrinsic probability of the spherical conformation p^0_{sphere}, or, equivalently, of the intrinsic probability $p^0_{rod}(= 1 - p^0_{sphere})$ of deformation into a rod like shape. According to Eq. (6), these intrinsic probabilities depend on the relative conformational energies and on the multiplicity of ways in which the spherical conformation can be deformed into energetically equivalent rod-like conformations.

The dependence of the transition density ρ^*_{N-I} on the aspect ratio L_{rod}/D_{rod} of the rod shaped conformations is shown in Fig. 2 for two different values of the intrinsic probability p^0_{rod}.

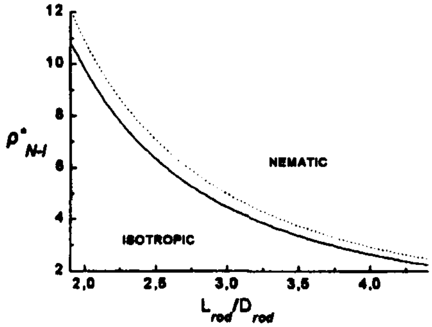

FIGURE 2 Plots of the transition density ρ^*_{N-I} as a function of the aspect ratio L_{rod}/D_{rod} for a system with interconverting rod-sphere conformations. The solid line is obtained for $p^0_{rod} = 0.91$ and the dotted line for $p^0_{rod} = 0.50$.

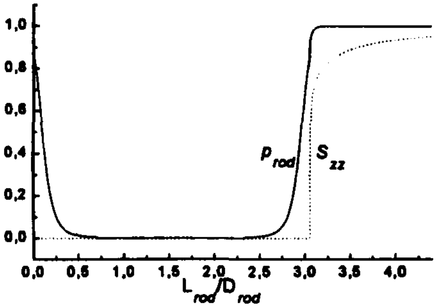

FIGURE 3 Plots of probability for interacting rod-shaped conformations p_{rod} (solid line) and of their principal order parameter S_{zz} (dotted line) as a function of rod aspect ration, at fixed effective density $\rho^* = 3$ and $p^0_{rod} = 0.91$, for a system with interconverting rod-sphere conformations.

Figure 3 shows plots of: (i) the principal order parameter $S_{zz} = <(3\cos^2\theta_{rod} - 1)/2>$, where θ_{rod} denotes the angle between the nematic director and the molecular rod axis, and (ii) the probability p_{rod} of the rod shaped conformations in the bulk phase, as a function of the aspect ratio at constant density and fixed intrinsic probability p^0_{rod}. The dramatic variation p_{rod} with aspect ratio is noteworthy. The rod population practically disappears in the disordered phase but begins to grow very rapidly as the transition to the ordered phase is approached. Above the transition practically all the molecules deform into the rod-shaped state. This behavior can be rationalized in terms of packing considerations: In the ordered phase, spherocylindrical rods can be packed more efficiently (they leave less «empty space») than spheres of the same volume. By contrast, the rod conformations lead to more extensive molecular intersections than the spherical ones in the isotropic phase, hence the probability of the rods diminishes as their aspect ratio grows.

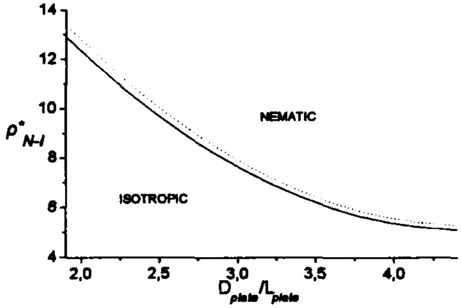

FIGURE 4 Plots of the transition density ρ^*_{N-I} as a function of the aspect ratio D_{plate}/L_{plate} for a system with interconverting plate-sphere conformations. The solid and dotted lines are obtained with $p^0_{plate} = 0.99$ and $p^0_{plate} = 0.50$ respectively. Packing fractions are determined relative to the molecular volume v_0 of the spherical conformations.

Analogous results are obtained for systems exhibiting interconverting spherical and plate-like conformations. The shapes of the latter are represented by cut spheres of diameter D_{plate} and thickness L_{plate}. The dependence of the nematic-isotropic transition density ρ^{*}_{N-I} on the aspect ratio D_{plate}/L_{plate} of the plate-like conformartions is shown in Fig. (3) for two values of the intrinsic probability p^{0}_{plate}.

CONCLUSIONS

We have presented a simple molecular theory of deformable molecules and used it to describe order-disorder transitions in fluids of dendrimers with high surface-density of mesogenic units. We have studied model systems that exhibit conformational sphere-rod and sphere-plate interconversions. Our results clearly indicate that orientationally ordered fluid phases can be obtained even if the lowest energy conformation is of radial symmetry, provided that the higher energy conformations are sufficiently anisometric and abundant. The ordering is accompanied by dramatic shifts in the conformational probabilities and can be attributed entirely to packing restrictions.

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