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## Conformational Phase Transitions and Re-Entrance Phenomena in Dendromesogens

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We investigate theoretically the liquid crystalline phase behaviour of globular dendrimers consisting of a soft inner scaffold and peripheral mesogenic units attached to the scaffold by means of flexible chains. We use a generalised Onsager molecular theory to analyse model systems exhibiting conformational rod-sphere and rod-disc interconversions. Phase transitions normally not encountered in low molar mass mesogens are reported. For a system with spherical lowest energy conformation a thermotropic re-entrance to the isotropic phase is observed.

**Keywords:** molecular deformations; liquid crystal dendrimers; phase transitions; re-entrance phenomena; molecular theory

### INTRODUCTION

Liquid crystalline (LC) dendrimers, consisting of a soft inner core and a number of mesogenic units attached to the core by means of flexible chains, show novel mesophases<sup>[1-5]</sup>. Due to their extensive flexibility, these molecules exhibit a large number of anisometric conformations, the statistical weights of which are strongly coupled to the type of molecular organisation in the bulk phase. Such coupling can give rise to new phases and phase transition phenomena.

A realistic microscopic description that would include in detail the structural and conformational features of all the constituents of the dendrimer is not feasible with present computational resources. However, certain general features of self-organisation in relation to molecular structure can be studied by resorting to a less detailed description of the structural and conformational characteristics of the dendromesogens. To this end, we have recently developed a theoretical approach<sup>[6]</sup> whereby the entire dendritic molecule is treated as a deformable continuum that can assume different shapes. The major classes of conformations that are accessible to the real dendrimer are approximated by their "effective" shapes. An internal conformational energy is assigned to each effective shape of the deformable molecule. The intermolecular interactions are purely of the excluded-volume type.

The theory is outlined in the next section. It is then applied to simplified systems exhibiting interconversions between just two groups of conformations. Calculations on the nematic-isotropic phase transition of interconverting rod-sphere and rod-disc systems are presented in the third section. The fourth section concludes the paper.

## STATISTICAL MECHANICAL DESCRIPTION OF DEFORMABLE MOLECULES

The free energy of the dendrimer fluid phase is obtained by using a generalisation of the Onsager approach wherein the groups of conformations are treated as distinct states of a single, deformable, "effective molecule"<sup>[6]</sup>.

Each molecule is allowed to deform into a number of distinct conformations with conformational energy  $E_n$ . The intrinsic probability for the molecule to be found in a conformation with shape  $S_i$  is given by

$$p_i^0 = \sum_{n(S_i)} e^{-E_n(S_i)/kT} / \sum_n e^{-E_n/kT}, \quad (1)$$

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

The intermolecular potential for a pair of molecules in conformations  $n, n'$ , with relative position  $\bar{r}$  and orientations  $\omega, \omega'$  is denoted by  $u(\bar{r}; n, n', \omega, \omega')$ . 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:

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

where

$$q_{n, n'}(\omega, \omega') = (1 / v_0) \int d\bar{r} [1 - e^{-u(\bar{r}; n, n', \omega, \omega') / kT}], \quad (3)$$

$v_0$  is a fixed molecular volume. The orientational distribution for conformer  $n$  is denoted by  $f_n(\omega)$  and is obtained self-consistently. The density  $\rho = Nv_0 / V$  is expressed as a packing fraction. The effective density  $\rho^*$  is in general a function of  $\rho$  that coincides with  $\rho$  at low densities and diverges when  $\rho$  exceeds the maximal packing fraction.

Since the intermolecular potential is assumed to represent purely hard-body repulsive forces, the orientation dependent function  $q_{n, n'}(\omega, \omega')$  of Eq. (3) is completely determined from the shapes of the conformations  $n, n'$ .

The respective expression for the pressure, obtained within the two-site cluster approximation, is given by:

$$P^{(2)} / kT = \rho [1 + (\rho^* / 2) \sum_{n, n'} e^{-(E_n + E_{n'}) / kT} \int d\omega d\omega' f_n(\omega) f_{n'}(\omega') q_{n, n'}(\omega, \omega')], \quad (4)$$

The probability for a molecule in the bulk phase to be found in a conformation with shape  $S_i$  is given by:

$$P_i = \sum_{n(S_i)} e^{-E_{n(S_i)}/kT} \zeta_{n(S_i)} / \sum_n e^{-E_n/kT} \zeta_n, \quad (5)$$

where

$$\zeta_n = \int d\omega \exp[-\rho^* \sum_{n'} e^{-E_{n'}/kT} \int d\omega' f_{n'}(\omega') q_{n,n'}(\omega, \omega')], \quad (6)$$

Equations (1) to (6) can be used to describe deformable molecules exhibiting several conformations. 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).

## RESULTS AND DISCUSSION

We restrict our consideration to nematic-isotropic phase diagrams of dendrimers with radial topology that can deform into spherical or uniaxial elongated or oblate structures. Calculations were carried out on a model system showing interconverting rod-like and disc-like conformations and a system exhibiting spherical lowest energy conformations that can deform into rod-like conformations of equal molecular volume.

In Figures 1 and 2 we present the phase diagrams of interconverting rod-like and disc-like conformations. It is assumed that both conformations have a spherical 'core' such that  $D_{rod} = L_{disc}$ . The packing fraction is determined relative to the volume  $v_0$  of a sphere of diameter equal to  $D_{rod}$  (volume of the 'core'). The volumes of the two conformations are similar ( $5.5 v_0$  and  $6.75 v_0$  for the rod-like and disc-like conformation respectively). For low values of the intrinsic probability of the rod-like conformation an isotropic to disc-like nematic ( $N_c$ ) phase transition is obtained. For higher intrinsic

probabilities we observe transition from the disc-like nematic phase to the rod-like nematic ( $N_+$ ) phase. The density for the isotropic to  $N_-$  transition appears to be insensitive to the intrinsic probability  $p_{rod}^0$  up to the  $I$ ,  $N_-$ ,  $N_+$  triple point. By contrast, on increasing the intrinsic probability of the rod-like conformations, either by lowering the conformational energy or by increasing the multiplicity of the rod-like conformation, the density for the  $N_-$  to  $N_+$  or for the direct isotropic to  $N_+$  transition is rapidly reduced.

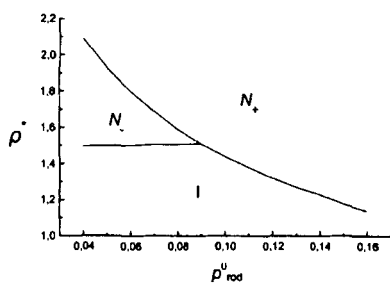


FIGURE 1 Phase diagram of effective density  $\rho^*$  vs. the intrinsic probability  $p_{rod}^0$  of the rod-like conformation for a system with interconverting rod-like and disc-like conformations with purely excluded volume interactions. Results are shown for fixed aspect ratios for the disc-like conformation at  $D_{disc}/L_{disc}=2.2$  and for the rod-like conformation at  $L_{rod}/D_{rod}=3.0$ .

Figure 2 shows plots of the effective density as a function of the temperature. The temperature dependence of the present (hard body) systems is introduced solely through the temperature dependence of the intrinsic probabilities of the (fixed-energy) conformations and is expressed in arbitrary energy units in all the diagrams.

When the rod conformation has lower energy and much smaller multiplicity than the disc, we observe that for low values of the

density and for high values of the temperature the isotropic phase is the most stable phase (upper diagram, Fig. 2). At higher densities we obtain on heating a transition from the rod nematic phase  $N_+$  (which is favored by the energetic preference of the rod-like conformation) to a disc nematic phase  $N_-$  (which is favored by the large multiplicity of the disc-like conformations).

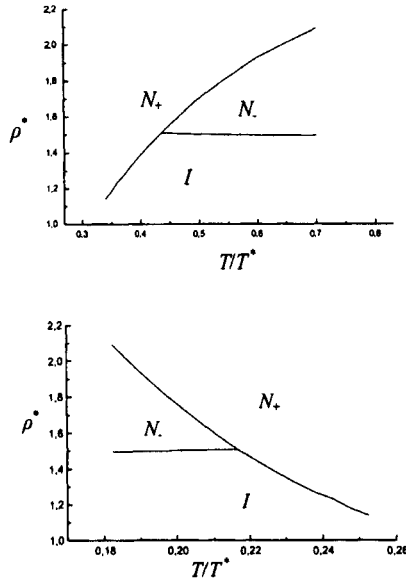


FIGURE 2 Phase diagrams of effective density .vs. temperature for a system with interconverting rod-like and disc-like conformations with purely excluded volume interactions. The upper diagram corresponds to energy difference  $E^{\text{disc}} - E^{\text{rod}} = kT^*$  and to multiplicity ratio  $m^{\text{rod}}/m^{\text{disc}} = 0.01$ . The lower diagram is obtained for  $E^{\text{rod}} - E^{\text{disc}} = kT^*$  and to multiplicity ratio  $m^{\text{rod}}/m^{\text{disc}} = 10.0$ .



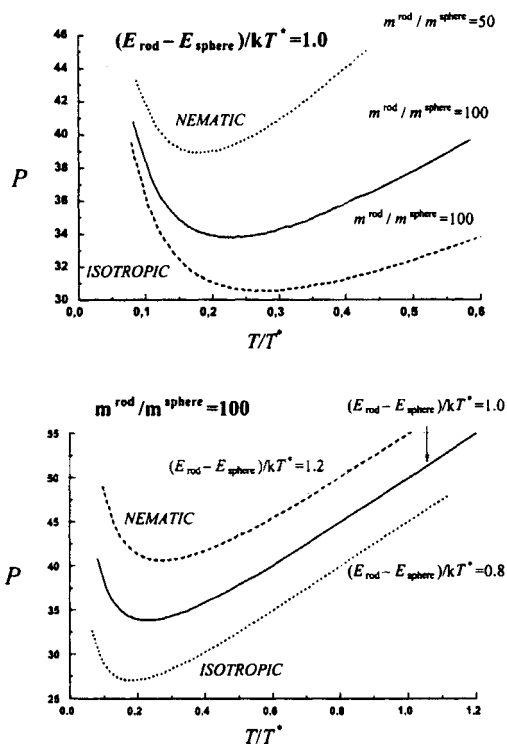


FIGURE 3 Phase diagrams of pressure .vs. effective temperature for a system with interconverting rod-like and spherical conformations with purely excluded volume interactions. Results are shown for fixed aspect ratio for the rod-like conformation at 5.0. The rod-like and spherical conformations have the same molecular volume.

The lower diagram of Figure 2 corresponds to a system for which the disc-like conformation is energetically favored but the rod-like conformations exhibit a larger set of conformations of equivalent

shapes. In this case, the most stable phase at high temperatures is the rod-like nematic, being favored by the large multiplicity of the rod-like conformations.

In addition we study dendrimers which show spherical lowest energy conformation and rod-like conformation of equal molecular volume. The upper graphs in Figure 3 show phase diagrams for fixed conformational energy difference and various multiplicity ratios of the two conformations. It is observed that for sufficiently large values of the multiplicity of the rod-like conformations a re-entrance of the isotropic phase is obtained on cooling at constant pressure. This behavior can be rationalized by considering the molecular organization at the low and high temperature regions of the diagrams. At low temperature the isotropic phase is the most stable as practically exclusively spherical conformations exist (i.e. the intrinsic probability of the spherical conformation is much larger compared to the rod-like conformation which comes with a higher energy). Very high temperatures are equivalent to very low densities, where independently of which conformation is more abundant the isotropic phase is more stable.

The upper plots of Figure 3 show that the low temperature re-entrance of the isotropic phase can occur at lower pressure as the multiplicity ratio is increased. This is to be expected as increasing the multiplicity of the rod-like conformation (i.e. occurrence of a larger set of conformations of equivalent rod-like shape) stabilizes the nematic phase over a larger pressure-temperature range.

The lower plots of Figure 3 confirm that decreasing the conformational energy difference between the two conformations, at fixed multiplicity ratio, moves towards lower temperatures and

pressures both the onset of the nematic region and the low temperature isotropic re-entrance.

The change of the conformational probabilities of the molecule in the bulk phase at the nematic-isotropic transition is depicted on the phase diagram of the probabilities as a function of the effective temperature shown in Figure 4. A notable feature of this diagram is the jump of the rod probability across the phase transition. For  $T/T^* < 0.2$  this jump corresponds to practically total conversion into the rod conformation.

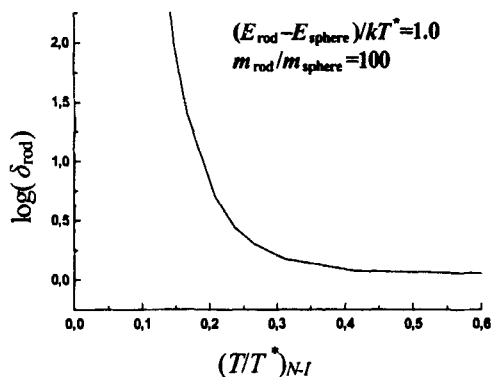


FIGURE 4 Phase diagram of the relative change of probabilities  $\delta_{rod} = [(p_{rod})_N - (p_{rod})_I]/p_{rod}^0$  across the nematic-isotropic phase transition as a function of the transition temperature  $(T/T^*)_{N-I}$  for the system of Fig. 3.

## CONCLUSIONS

Our simple modeling of transitions from the disordered to the orientationally ordered fluid phase of dendromesogens with radial

topology suggest the possibility of phase transitions with novel features. In particular:

Interconverting rod-disc systems exhibit nematic(discotic)-nematic (kalamitic) phase transitions. Depending on the energies and the multiplicities of the rod and disc conformations the higher temperature phase could be either the discotic or the kalamitic. The phenomenon is analogous to the recently observed<sup>[3]</sup> lamellar-to-columnar thermotropic transitions, although partial positional ordering was not explicitly considered in the present study.

Interconverting rod-sphere systems can exhibit thermotropic re-entrance of the isotropic phase on decreasing the temperature at constant pressure.

The transition into the ordered phase is marked by abrupt changes in the conformation probabilities. In particular, the type of the dominant conformation can change across the transition.

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