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Influence of dimerization on the nematic–isotropic phase transition in strongly polar liquid crystals

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A molecular theory of the nematic–isotropic phase transition is developed for the fluid composed of rod-like particles with large longitudinal dipoles. The equilibrium between the monomers and dimers with antiparallel dipoles is explicitly taken into account and the concentration of dimers is determined self-consistently together with the nematic order parameters. We show that for small central dipole moments the nematic–isotropic transition temperature increases with the increasing dipole. This is in accordance with the results of previous approaches. By contrast, for large values of the dipole the transition temperature decreases due to the growing concentration of dimers. This result enables one to explain the results of recent computer simulations that reveal a destabilization of the nematic phase in a system of hard rods with large central longitudinal dipoles. The temperature variation of the concentration of dimers is also analysed and the sign of the concentration discontinuity at the transition point is correlated with the qualitative influence of dimers on the transition temperature.

1. Introduction

Many nematic liquid crystals are composed of polar or even strongly polar molecules. Permanent dipoles are used to optimize the electro-optic and rheological properties of liquid crystalline materials and also to increase their chemical stability. Physical properties of polar liquid crystals are known to differ significantly from those of non-polar liquid crystals. In particular, strongly polar liquid crystals can form re-entrant, incommensurate and other complex smectic phases (see, for example, [1–6]).

In the nematic phase, the influence of molecular dipoles is not so pronounced. However, there exist some experimental data on the influence of molecular polarity on the nematic–isotropic transition temperature. For example, some experimental data indicate that the nematic–isotropic transition temperature is increased when a non-polar terminal group is substituted for a polar one [7]. Interesting effects are also observed in mixtures of polar and non-polar nematics, where the transition temperature appears to be a strongly non-linear function of the molar fractions of the components [8, 9]. Such behaviour of the transition temperatures is generally not observed in mixtures of non-polar nematics. Permanent molecular dipoles play a more important role in smectic phases. Strongly polar mesogens can form re-entrant nematic and smectic phases, ferroelectric tilted smectic phases and various modulated smectic structures.

On the microscopic level, strongly polar liquid crystals are characterized by a formation of dimers with antiparallel dipoles. The existence of dimers has been confirmed both by X-ray [10–12] and dielectric measurements [13, 14]. These dimers should not strictly speaking be considered as stable particles, of course, and one finds a dynamical equilibrium between dimers and monomers in the nematic phases. The coexistence of dimers and monomers is an important feature of strongly polar nematics and it should be taken into account in a consistent molecular theory of the nematic–isotropic phase transition.

Several theoretical studies of the influence of permanent molecular dipoles on the nematic–isotropic transition have been reported [15–18]. Most of them refer to a system of hard spherocylinders or ellipsoids with permanent dipoles. We note that in such systems the N–I phase

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transition is actually induced by a change of concentration of hard particles, while the temperature only scales the value of the reduced dipole. The results of the recent studies by Vanakaras and Photinos [16] and Vega and Lago [17] suggest that central dipoles stabilize the nematic phase. The same qualitative result has been obtained by Osipov and Simonov [18] in the study of polar thermotropic nematics. Within the two-particle cluster approximation, the N–I transition temperature rapidly grows with the increasing value of the molecular dipole [18]. These results, however, appear to be in contradiction with the results of recent computer simulations [19–21]. These simulations show some destabilization of the nematic phase [19, 20] or do not reveal any influence of central dipoles on the N–I transition [21]. In particular, McGrother *et al.* [19] have found that central longitudinal dipoles, added to non-polar hard spherocylinders, shift the N–I transition to higher densities at all temperatures. By contrast, the smectic A phase is stabilized with respect to the nematic phase for a system with central longitudinal dipoles.

The discrepancy between the statistical theory and computer simulations can be attributed to an insufficient accuracy of the theory. We note that there is no straightforward way to take into account dipole–dipole interactions consistently in the statistical theory of nematic liquid crystals. The nematic phase is non-polar and therefore the average dipole–dipole interaction potential must vanish. Thus, the dipole–dipole interaction does not contribute directly to the average molecular field in the nematic phase. On the other hand, large permanent dipoles promote strong short range dipole–dipole correlations that can affect thermodynamic parameters of the N–I transition.

The existing statistical theories of polar nematics are based on scaled [16] or unscaled [15] formulation of the Onsager theory or on the two-particle cluster approximation for a lattice model [17]. Thus some short range orientational correlations are taken into account in these approaches and the results are expected to be correct at least for small values of the dipole. However, in the case of large dipoles the situation can be qualitatively different because very strong correlations can lead to the formation of dimers.

In the Onsager theory, the free energy depends mainly on the second virial coefficient. In the case of large dipoles the value of this coefficient is approximately determined by the large factor $\exp(d^2/kTR_0^3) \gg 1$, where R_0 is the minimal approach for the two molecules. Higher order virial coefficients also contain this large factor. Moreover, with increasing dipole moment they grow faster than the second virial coefficient and, as a result, any series based on the virial expansion may diverge.

In general there are two ways to solve this problem. One is to use some resummation technique for the diverging series. This method, however, appears to be very complex in the case of anisotropic fluids. The second way is to take into account explicitly the dynamical equilibrium between monomers and dimers. In this way the minimum energy configurations (that actually cause formal difficulties) are accounted for separately by calculating the equilibrium concentration of dimers.

In this paper we follow the second strategy for the case of thermotropic nematics and analyse the dependence of the N–I transition temperature on the value of the dipole using a Maier–Saupe type model which accounts for an equilibrium between dimers and monomers. The attractive interaction between monomers and dimers is evaluated using the site–site interaction potential. We show that for small dipoles the transition temperature is indeed a growing function of the dipole strength. By contrast, in the case of large dipoles, the transition temperature decreases with increasing dipole because the dimers appear to be less mesogenic than the monomers.

The paper is arranged as follows. In §2 we develop the statistical theory of the nematic–isotropic transition taking into account the dimer–monomer equilibrium and obtain a system of equations for the order parameters and for the molar fraction of monomers. In §3 we consider the contributions from the dipole–dipole and dispersion interactions between monomers and dimers and in §4 we present the results and discussion. Finally, in Appendix A the effective bond energy of the dimer is estimated and in Appendix B the parameters of the dispersion interaction potential are calculated in the context of the site–site interaction model.

2. Statistical theory of nematic ordering in the fluid composed of monomers and dimers

In this paper we consider a nematic liquid crystal composed of strongly polar molecules, a mixture of monomers and dimers with the number densities ρ_1 and ρ_2, respectively. In the nematic phase the monomers and dimers are also characterized by the orientational distribution functions $f^{(1)}((\mathbf{an}))$ and $f^{(2)}((\mathbf{an}))$, where the unit vector $\mathbf{a}$ is in the direction of the molecular long axis.

The monomer particles are assumed to be uniaxial. At the same time, the dimers are biaxial and their orientation is specified both by the unit vector $\mathbf{a}$ in the direction of the long axis and by the unit vector $\mathbf{b}$ in the direction of the short axis; $(\mathbf{a}\ \ \mathbf{b}) = 0$.

The free energy of such mixture is a functional of the densities $\rho_i(\mathbf{a}) = f^{(i)}((\mathbf{an}))\rho_i$, where $i = 1, 2$. Taking into account only direct pair correlations between particles, the free energy of the mixture of monomers and dimers can be written as [22]:

$$\begin{aligned}\frac{\Phi}{NkTV}F = &\int \rho_1(\mathbf{a}_1)\{\ln[\rho_1(\mathbf{a}_1)\Lambda^3] - 1\}\,\mathrm{d}^2\mathbf{a}_1\\ &+\int \rho_2(\mathbf{a}_1)\{\ln[\rho_2(\mathbf{a}_1)\Lambda^3] - 1\}\,\mathrm{d}^2\mathbf{a}_1\\ &-\frac{1}{2}\int \rho_1(\mathbf{a}_1)\rho_1(\mathbf{a}_2)C_{11}(1,2)\,\mathrm{d}^2\mathbf{a}_1\,\mathrm{d}^3\mathbf{R}_{12}\,\mathrm{d}^2\mathbf{a}_2\\ &-\int \rho_1(\mathbf{a}_1)\rho_2(\mathbf{a}_2)C_{12}(1,2)\,\mathrm{d}^2\mathbf{a}_1\,\mathrm{d}^3\mathbf{R}_{12}\,\mathrm{d}^2\mathbf{a}_2\\ &-\frac{1}{2}\int \rho_2(\mathbf{a}_1)\rho_2(\mathbf{a}_2)C_{22}(1,2)\,\mathrm{d}^2\mathbf{a}_1\,\mathrm{d}^3\mathbf{R}_{12}\,\mathrm{d}^2\mathbf{a}_2\\ &-\rho_2\frac{E_0}{kT}\end{aligned} \tag{1}$$

where N is the number of molecules, V is the volume of a molecule, $\Phi = \rho_0 V$ is the volume fraction of molecules, Λ is the de Broglie thermal wavelength, $\mathbf{R}_{12}$ is the intermolecular vector and $C_{ij}(1,2)\,(i,j = 1,2)$ are the effective direct correlation functions, averaged over the orientations of molecular short axes. The function $C_{11}(1,2)$ describes the direct correlations between two monomer particles, the function $C_{22}(1,2)$ is the same for two dimers and finally the function $C_{12}(1,2)$ is the direct correlation function between monomers and dimers.

The last term in equation (1) describes the internal energy of the dimers. Here E_0 is the bond energy of the dimer formation that is related to the minimum value of the interaction energy between the molecules. The dimer energy is approximately given by:

$$\begin{aligned}E_0 = \ln\Bigg\{&\frac{1}{4\pi\Lambda^3}\int \Theta(\mathbf{R}_{12} - \xi_{12})\\ &\times\left[\exp\left(-\frac{U_{\mathrm{dd}}(1,2)}{kT}\right) - 1\right]\mathrm{d}^2\mathbf{a}_1\,\mathrm{d}^3\mathbf{R}_{12}\,\mathrm{d}^2\mathbf{a}_2\Bigg\}\end{aligned} \tag{2}$$

where $\Theta(\mathbf{R}_{12} - \xi)$ is a step-function that describes the steric cut-off. $\Theta(\mathbf{R}_{12} - \xi) = 0$ if the molecules penetrate each other and $\Theta(\mathbf{R}_{12} - \xi) = 1$ otherwise. The potential $U_{\mathrm{dd}}(1,2)$ is the dipole–dipole interaction energy:

$$U_{\mathrm{dd}}(1,2) = \frac{1}{R_{12}^3}\left[\mathbf{d}_1\mathbf{d}_2 - \frac{3(\mathbf{d}_1\mathbf{R}_{12})(\mathbf{d}_2\mathbf{R}_{12})}{R_{12}^2}\right] \tag{3}$$

where $\mathbf{d}$ is the molecular dipole.

For large values of the dipole, the effective bond energy E_0 is mainly determined by the energy of dipole–dipole interaction in the most probable configuration of the two polar molecules. In this paper we consider the simple model of a polar molecule [19, 20] that is represented by a spherocylinder with the central longitudinal dipole. For sufficiently long spherocylinders the dimer is composed of two parallel monomers, located side by side, with antiparallel dipoles. The bond energy of such a dimer is related to the value of the dipole–dipole interaction energy in this antiparallel configuration. This energy is equal to $-k(d^*)^2$, where $d^* = d/(kD^3)^{1/2}$ is the reduced molecular dipole. We note that the effective bond energy (2) includes also a contribution from thermal fluctuations [23]. The value of E_0 is calculated approximately in Appendix A. The result is:

$$E = \frac{2\pi^2\Phi D^3}{3V}\sqrt{\frac{\pi}{3}}(d^*/\sqrt{T})^{-5}\exp(d^*/\sqrt{T})^2 \tag{4}$$

where the dimensionless parameter E is related to the bond energy E_0 as

$$E \equiv \rho\Lambda^3\exp(E_0/kT).$$

The free energy (1) is a functional of the two densities ρ_1 and ρ_2. These densities, however, are not independent because the total density of molecules (which can exist independently as monomers or form dimers) is preserved. This is represented by the following conservation law:

$$\int [\rho_1(\mathbf{a}) + 2\rho_2(\mathbf{a})]\,\mathrm{d}^2\mathbf{a} = \rho_0 \tag{5}$$

where ρ_0 is the total number density.

Now we obtain the system of equations for ρ_1 and ρ_2 by minimization of the free energy (1) under the constraint (5):

$$\left\{\begin{aligned}&\ln\rho_1(\mathbf{a}_1) - \int \rho_1(\mathbf{a}_2)C_{11}(1,2)\,\mathrm{d}^3\mathbf{R}_{12}\,\mathrm{d}^2\mathbf{a}_2\\ &\quad-\int \rho_2(\mathbf{a}_2)C_{12}(1,2)\,\mathrm{d}^3\mathbf{R}_{12}\,\mathrm{d}^2\mathbf{a}_2 = \lambda^*\\ &\ln\rho_2(\mathbf{a}_1) - \int \rho_2(\mathbf{a}_2)C_{22}(1,2)\,\mathrm{d}^3\mathbf{R}_{12}\,\mathrm{d}^2\mathbf{a}_2\\ &\quad-\int \rho_1(\mathbf{a}_2)C_{12}(1,2)\,\mathrm{d}^3\mathbf{R}_{12}\,\mathrm{d}^2\mathbf{a}_2 - \ln\left[\frac{E}{\rho\Lambda^3}\right] = 2\lambda^*\end{aligned}\right. \tag{6}$$

where the parameter λ^* can be determined from equation (5).

From equations (6) one readily obtains the following equations for the orientational distribution functions $f^{(1)}(\mathbf{a}\ \mathbf{n})$ and $f^{(2)}(\mathbf{a}\ \mathbf{n})$ of monomers and dimers, respectively.

$$\begin{cases} p f^{(1)}(\mathbf{a}_1\ \mathbf{n}) \\ \quad = \lambda \exp\left\{ - pA_{11}((\mathbf{a}_1\ \mathbf{n})) - \dfrac{1-p}{2} A_{12}((\mathbf{a}_1\ \mathbf{n})) \right\} \\ \dfrac{1-p}{2} f^{(2)}(\mathbf{a}_1\ \mathbf{n}) \\ \quad = E\lambda^2 \exp\left\{ - pA_{12}((\mathbf{a}_1\ \mathbf{n})) - \dfrac{1-p}{2} A_{22}((\mathbf{a}_1\ \mathbf{n})) \right\} \end{cases} \tag{7}$$

where $p = \rho_1/\rho_0$ is the molar fraction of monomers, and the quantities $A_{ij}(i, j = 1, 2)$ are the effective one particle potentials:

$$A_{ij}((\mathbf{a}_1\ \mathbf{n})) = -\frac{\Phi}{V} \int f^{(j)}(\mathbf{a}_2\ \mathbf{n}) C_{ij}(\mathbf{a}_1, \mathbf{R}_{12}, \mathbf{a}_2)\, \mathrm{d}^3\mathbf{R}_{12}\, \mathrm{d}^2\mathbf{a}_2 \tag{8}$$

and where $\lambda = \exp \lambda^*/\rho\Lambda^3$.

Equations (7) depend on the parameter λ that is yet undetermined. The equation for λ can be obtained by integration of both equations (7) over $\mathbf{a}_1$. After summation of the integrated equations one obtains a quadratic equation:

$$I_1\lambda + 2I_2E\lambda^2 = 1 \tag{9}$$

where

$$\begin{aligned} I_1 &= \int \exp\left\{ - pA_{11} - \frac{1-p}{2} A_{12} \right\} \mathrm{d}^2\mathbf{a}_1 \\ I_2 &= \int \exp\left\{ - \frac{1-p}{2} A_{22} - pA_{21} \right\} \mathrm{d}^2\mathbf{a}_1 . \end{aligned} \tag{10}$$

We note that the parameter λ is simply related to the molar fraction of the monomers p. Integration of both sides of the first equation (7) yields the relation

$$p = \lambda I_1 . \tag{11}$$

The parameter λ is given by the positive root of equation (9):

$$\lambda = \frac{(I_1^2 + 8EI_2)^{1/2} - I_1}{4EI_2}$$

and therefore the monomer molar fraction can be expressed as

$$p = \frac{(I_1^2 + 8EI_2)^{1/2} - I_1}{4EI_2} I_1 . \tag{12}$$

We note that equations (7) represent a generalization of the Maier–Saupe theory to the case of a nematic with a monomer–dimer equilibrium. The familiar Maier–Saupe equation for the one particle orientation distribution function can be obtained from equations (7) by simultaneously putting $p = 1$ and $E_0 = 0$ and using (11).

Equations (7) are the integral equations for the orientational distribution functions of the monomers and dimers. In the spirit of the generalized Maier–Saupe theory [22], one can obtain approximate expressions for the nematic order parameters S_1 and S_2 of monomers and dimers. For this purpose we expand the effective one particle potentials $A_{ij}((\mathbf{a}\mathbf{n}))$ in Legendre polynomials and retain the first two terms:

$$A_{ij}((\mathbf{a}_1\mathbf{n})) = A_0^{ij} + A_2^{ij} S_j P_2((\mathbf{a}_1\mathbf{n})) + \ldots \tag{13}$$

Multiplying equations (7) by $P_2((\mathbf{a}_1\ \mathbf{n}))$, integrating over $\mathbf{a}_1$ and $\mathbf{b}_1$ and using the approximation (13) one obtains the final equations for the order parameters S_1 and S_2 and the monomer molar fraction p:

$$\begin{cases} S_1 = \dfrac{1}{I_1^{\mathrm{a}}} \displaystyle\int_{-1}^{1} P_2(x) \\ \quad \times \exp\left\{ - \left[A_2^{11} pS_1 + A_2^{12} \dfrac{1-p}{2} S_2 \right] P_2(x) \right\} \mathrm{d}x \\ S_2 = \dfrac{1}{I_2^{\mathrm{a}}} \displaystyle\int_{-1}^{1} P_2(x) \\ \quad \times \exp\left\{ - \left[A_2^{12} pS_1 + A_2^{22} \dfrac{1-p}{2} S_2 \right] P_2(x) \right\} \mathrm{d}x \\ p = \dfrac{(I_1^2 + 8EI_2)^{1/2} - I_1}{4EI_2} I_1 \end{cases} \tag{14}$$

where

$$I_1^{\mathrm{a}} = \int_{-1}^{1} \exp\left\{ - \left[A_2^{11} pS_1 + A_2^{12} \frac{1-p}{2} S_2 \right] P_2(x) \right\} \mathrm{d}x \tag{15}$$

$$I_2^{\mathrm{a}} = \int_{-1}^{1} \exp\left\{ - \left[A_2^{12} pS_1 + A_2^{22} \frac{1-p}{2} S_2 \right] P_2(x) \right\} \mathrm{d}x \tag{16}$$

$$\begin{aligned} I_1 &= I_1^{\mathrm{a}} \exp\left\{ - A_0^{11} p - A_0^{12} \frac{1-p}{2} \right\} \\ I_2 &= I_2^{\mathrm{a}} \exp\left\{ - A_0^{12} p - A_0^{22} \frac{1-p}{2} \right\} . \end{aligned} \tag{17}$$

The coupled system of equations (14) describe the temperature dependence of the order parameters and the monomer molar fraction in the nematic phase with monomer–dimer equilibrium. The temperature T_c of the first order nematic–isotropic transition can be found using an explicit expression for the free energy of the system. The general expression for the free energy is given by equation (1). Substituting equations (7) into (1) and using the approximation (13), one obtains the following expression for the free energy density of the nematic phase:

$$\begin{aligned}\frac{F}{NkT} &= \frac{1}{2}(A_0^{11} + A_2^{11} S_1^2)p^2 \Phi \\ &+ \frac{1}{2}(A_0^{22} + A_2^{22} S_1^2)\left(\frac{1-p}{2}\right)^2 \Phi \\ &+ (A_0^{12} + A_2^{12} S_1 S_2)p\frac{1-p}{2}\Phi \\ &+ p \ln\frac{p}{I_1} + \frac{1-p}{2}\ln\frac{\left(\frac{1-p}{2}\right)}{EI_2} - \frac{1+p}{2} + \ln\frac{\Lambda^3 \Phi}{V}.\end{aligned} \tag{18}$$

We note that equations (14) can also be obtained by a direct minimization of the free energy (18) with respect to S_1, S_2 and p.

The free energy (18) and the equations (14) contain the parameters $A_{0,2}^{ij}$ which depend on temperature and on the molecular structure. These coefficients are the corresponding moments of the direct correlation functions $C_{ij}(1,2)$ and remain undetermined in the context of the general theory presented in this section. Further progress can be achieved by using some approximation for the direct correlation functions that enables one to separate the effects of the non-polar dispersion interaction and the dipole–dipole interaction between molecules. This development is performed in the following section.

3. Dipole–dipole and dispersion interactions between monomers and dimers

The equations for the order parameters S_1 and S_2 and the monomer fraction p can be solved numerically provided the coefficients A_0^{ij} and A_2^{ij} are known. As mentioned in the previous section, these coefficients are the moments of the effective direct correlation function $C_{ij}(1,2)$.

The function $C_{ij}(1,2)$ has a simple analytical form in the generalized mean-field approximation:

$$C_{ij}(1,2) = -\Theta(\mathbf{R}_{12} - \xi_{12})\frac{U_{ij}(1,2)}{kT} \tag{19}$$

where $U_{ij}(1,2)$ is the intermolecular interaction potential and the step-function $\Theta(\mathbf{R}_{12} - \xi_{12})$ represents the excluded volume effects. The function $\Theta(\mathbf{R}_{12} - \xi_{12}) = 0$ if the two molecules penetrate each other and $\Theta(\mathbf{R}_{12} - \xi_{12}) = 1$ otherwise.

In this paper we consider anisotropic dispersion and dipole–dipole electrostatic interactions between monomers. A dimer composed of two monomers possesses also an effective quadrupole and thus dipole–quadrupole and quadrupole–quadrupole interactions are also present in the system. However, these interactions are too short range and relatively weak, and we will not take them into account in the first approximation.

Thus the interaction between monomers can be written in the form:

$$U_{11}(1,2) = U_{11}^{\mathrm{disp}}(1,2) + U_{11}^{\mathrm{dd}}(1,2) \tag{20}$$

where $U_{11}^{\mathrm{disp}}(1,2)$ is the dispersion interaction energy and $U_{11}^{\mathrm{dd}}(1,2)$ is the dipole–dipole potential.

We note that the electrostatic interaction potential vanishes after averaging in equations (8) because the nematic phase is non-polar. Thus the dipole–dipole interaction does not contribute to the free energy in the mean-field approximation. This approximation can be improved by taking the dipole–dipole interaction into account in the framework of the second order perturbation theory. In this case the three direct correlation functions between monomers and dimers are approximated as:

$$\begin{cases} C_{11}(1,2) = -\Theta(\mathbf{R}_{12} - \xi_{12}) \\ \qquad \times\left[\dfrac{1}{kT}U_{11}(1,2) - \dfrac{1}{2}\left(\dfrac{1}{kT}U_{11}^{\mathrm{dd}}\right)^2\right] \\ C_{12}(1,2) = -\Theta(\mathbf{R}_{12} - \xi_{12})\dfrac{1}{kT}U_{12}(1,2) \\ C_{22}(1,2) = -\Theta(\mathbf{R}_{12} - \xi_{12})\dfrac{1}{kT}U_{22}(1,2) \end{cases} \tag{21}$$

In the equations (21) the dispersion interaction is taken into account in the mean-field approximation and the dipole–dipole interaction between monomers is treated by a second order perturbation theory. We have also neglected the dipole–quadrupole and quadrupole–quadrupole interactions betweeen a monomer and a dimer and between dimers, respectively.

The quantity A_{11} separates into the dispersion and dipole–dipole contributions:

$$A_{11} = A_{11}^{\mathrm{disp}} + A_{11}^{\mathrm{es}} \tag{22}$$

where the quantities A_{ij}^{disp} are expanded in a Legendre series similar to equation (13):

$$A_{ij}^{\mathrm{disp}} = J_0^{ij} + J_2^{\mathrm{ij}} S_j P_2((\mathbf{a}_1 \ \ \mathbf{n})) + \ldots \tag{23}$$

In this paper we are mainly interested in the influence of molecular dipoles on the nematic–isotropic phase transition. Thus, we start with the explicit evaluation of the contribution from the dipole–dipole interaction to the coefficient A_{11}^{es}. We now start to expand the dipole–dipole contribution in Legendre polynomials [similar to equation (13)] and retain the first two terms:

$$
\begin{aligned}
A_{11}^{\mathrm{es}} = -\frac{\Phi}{2V(kT)^2}\int f^{(1)}(\mathbf{a}_2)\Theta(\mathbf{R}_{12}-\xi_{12}) \\
\times [U_{ij}^{\mathrm{dd}}(1,2)]^2\,\mathrm{d}^3\mathbf{R}_{12}\,\mathrm{d}^2\mathbf{a}_2 \\
= J_0^{\mathrm{es}} + J_2^{\mathrm{es}} S_1 P_2((\mathbf{a}_1\;\mathbf{n})) + \ldots
\end{aligned}
\tag{24}
$$

where the dipole–dipole potential is given by equation (3).

For this purpose let us first consider the integral over the intermolecular vector $\mathbf{R}_{12}$ in equation (24). The integral over the absolute value R_{12} can be taken explicitly and one obtains:

$$
\begin{aligned}
A_{11}^{\mathrm{es}} = \frac{\Phi d^4}{6V(kT)^2}\int f^{(1)}(\mathbf{a}_2\;\mathbf{n})[(\mathbf{a}_1\;\mathbf{a}_2) - 3(\mathbf{a}_1\;\mathbf{u})(\mathbf{a}_2\;\mathbf{u})]^2 \\
\times \xi_{12}^{-3}(\mathbf{a}_1,\mathbf{u},\mathbf{a}_2)\,\mathrm{d}^2\mathbf{u}\,\mathrm{d}^2\mathbf{a}_2
\end{aligned}
\tag{25}
$$

where $\mathbf{u} = \mathbf{R}_{12}/|R_{12}|$.

In equation (25) the distance of minimum approach for the centres of the two molecules $\xi_{12}^{-3}(\mathbf{a}_1,\mathbf{u},\mathbf{a}_2)$ depends on the relative orientation of the molecules in contact. The function ξ_{12} cannot be calculated analytically for spherocylinders but it is possible to evaluate it using an interpolation expression following the idea of van der Meer and Vertogen [24]. The corresponding interpolation expression can be obtained in the following way.

Firstly we expand the quantity ξ_{12}^{-3} in a complete set of spherical invariants [25] and retain the first few terms:

$$
\begin{aligned}
\xi^{-3} = D_{\mathrm{eff}}^{-3}\Bigg[\alpha + \beta_1 P_2(\mathbf{a}_1\mathbf{u}) + \beta_2 P_2(\mathbf{a}_2\mathbf{u}) + \gamma P_2(\mathbf{a}_1\mathbf{a}_2) \\
+ \delta\bigg(\frac{9}{2}(\mathbf{a}_1\mathbf{u})(\mathbf{a}_2\mathbf{u})(\mathbf{a}_1\mathbf{a}_2) - \frac{3}{2}(\mathbf{a}_1\mathbf{u})^2 - \frac{3}{2}(\mathbf{a}_2\mathbf{u})^2 \\
- \frac{3}{2}(\mathbf{a}_1\mathbf{a}_2)^2 + 1\bigg)\Bigg].
\end{aligned}
\tag{26}
$$

Substituting equation (26) into (25) one obtains the following expression for the coefficients J_0^{es} and J_2^{es}.

$$
J_0^{\mathrm{es}} = \frac{4}{9}\pi\frac{\Phi D_{\mathrm{eff}}^3}{V}\frac{(d^*)^4}{T^2}\left(\alpha + \frac{1}{5}\beta_1 + \frac{1}{5}\beta_2 + \frac{1}{25}\gamma - \frac{1}{25}\delta\right)
\tag{27}
$$

$$
J_2^{\mathrm{es}} = \frac{4}{9}\pi\frac{\Phi D_{\mathrm{eff}}^3}{V}\frac{(d^*)^4}{T^2}\left(\frac{1}{5}\alpha + \frac{1}{7}\beta_1 + \frac{1}{7}\beta_2 + \frac{37}{35}\gamma + \frac{101}{245}\delta\right).
\tag{28}
$$

Here D_{eff} is the effective diameter of the spherocylinder which is taken to be slightly larger then the actual diameter D in order to exclude the close configuration in which the two monomers already form a dimer. In actual calculations we put $D_{\mathrm{eff}} = 1.62D$.

Now we consider the five coefficients α, β_1, β_2, γ and δ in equations (27), (28) as free parameters and require that equation (26) for ξ_{12}^{-3} should yield the exact result for the following five relative orientations and positions of the two molecules, presented in figure 1.

The explicit expressions for the dimensionless quantity $X_n = \xi_{12}^{-3}D^3$ in these five cases are presented in table 1, where $q = L/D_{\mathrm{eff}}$ is the effective axial ratio. Using the values of X_n presented in table 1, one obtains the following expressions for the coefficients in equations (27), (28):

$$
\left\{
\begin{aligned}
\alpha &= \frac{2}{9}\left\{2 + \frac{1}{2}q^{-3} + 2[(q+1)/2]^{-3}\right\} \\
\beta_1 &= \frac{2}{9}\{-2 + q^{-3} + [(q+1)/2]^{-3}\} \\
\beta_2 &= \frac{2}{9}\{-2 + q^{-3} + [(q+1)/2]^{-3}\} \\
\gamma &= \frac{2}{9}\{1 + q^{-3} - 2[(q+1)/2]^{-3}\} \\
\delta &= \frac{2}{9}\{1 + q^{-3} - 2[(q+1)/2]^{-3}\}
\end{aligned}
\right.
\tag{29}
$$

Equations (24) and (27)–(29) specify the contribution from the electrostatic dipole–dipole interaction

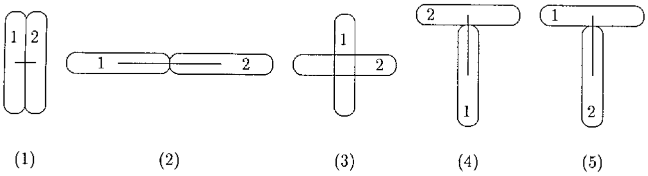

Figure 1. Five relative orientations of the two spherocylinders used in the calculation of the coefficients in equation (27).

Table 1. Explicit expressions for the dimensionless quantities $X_n = \xi_{12}^{-3}D^3$ [see equation (25)] calculated for the five relative orientations of the two spherocylinders presented in figure 1. Here q is the effective axial ratio of the spherocylinder.

Position (n)	X_i
1	1
2	q^{-3}
3	1
4	$[(q+1)/2]^{-3}$
5	$[(q+1)/2]^{-3}$

between monomers to the effective one particle potentials $A^{ij}((\mathbf{a}\ \mathbf{n}))$. The corresponding contribution from the dispersion interaction is given by the expansion (23) where the parameters J_0^{11} and J_2^{11} can be determined using a model for the dispersion interaction between monomers. We note that the dispersion interaction between two particles can be parametrized in several different ways. At the same time it is much more difficult to estimate the dispersion interaction between a monomer and a dimer or between two dimers without using additional model parameters. In this paper we address this problem in the following way. We consider a simple model of the rod-like molecule composed of five interaction sites of diameter D. Any two interaction sites that belong to different molecules are assumed to interact via the Lennard–Jones potential with the energy constant ε_0. Now the dimer is composed of 10 interaction sites (see figure 2) and thus the total interaction between the dimer and a monomer can be calculated in a straightforward way. The actual calculations can be performed only numerically and the corresponding results are obtained in Appendix B. The numerical values of the parameters J_0^{12} and J_2^{12} of the interaction potential between a monomer and a dimer and the corresponding parameters J_0^{22} and J_2^{22} for the pair of dimers are presented in table 2 for $\varepsilon_0/k = 5350$ K, where ε_0 is the energy constant in the Lennard–Jones potential.

Now we have determined all coefficients A_0^{ij} and A_2^{ij} in equations (14)–(17) in terms of the dipole strength, molecular axial ratio, volume fraction and temperature. These coefficients can finally be written as:

$$\begin{cases} A_{0,2}^{11} = J_{0,2}^{11} + J_{0,2}^{\mathrm{es}} \\ A_{0,2}^{12} = J_{0,2}^{12} \\ A_{0,2}^{22} = J_{0,2}^{22} \end{cases} \tag{30}$$

Figure 2. Simple model for a monomer and a dimer composed of several interaction sites.

Table 2. Numerical values of the dimensionless coefficients $\tilde{J}_0^{ij} = TJ_0^{ij}$ and $\tilde{J}_2^{ij} = TJ_2^{ij}$ which determine the dispersion interaction potential between a monomer and a dimer and between two dimers in the context of the site–site interaction model.

$\tilde{J}_0^{11}$	$\tilde{J}_0^{12}$	$\tilde{J}_0^{22}$	$\tilde{J}_2^{11}$	$\tilde{J}_2^{12}$	$\tilde{J}_2^{22}$
2100	4130	6580	1230	1990	2690

where the parameters J_0^{es}, J_2^{es} are given by equations (27)–(29) and the numerical values of the parameters J_0^{ij}, J_2^{ij} are presented in table 2. The results of a numerical solution of equations (14) are discussed in the following section.

4. Results and discussion

The equations (14) can be solved numerically to obtain the temperature variation of the order parameters S_1 and S_2 and of the monomer fraction p. From these equations one can also determine the dependence of the nematic–isotropic phase transition temperature on the absolute value of the molecular dipole. The dependence T_{NI} on the reduced dipole d^* is plotted in figure 3. One can see that for small dipoles the transition temperature is a growing function of the dipole moment d^*. This result is in accordance with the results of the previous study [18]. The growth of the transition temperature in this domain is mainly determined by the increasing effective orientational interaction between monomers due to the growing effective attraction caused by dipole–dipole interaction.

At the same time, one can see that for large dipoles the transition temperature decreases with the increasing dipole moment. This tendency is obviously related to the increase in the concentration of dimers. We note that for the case of molecules with central longitudinal dipoles, dimers possess a lower axial ratio than monomers and the remaining electrostatic interaction between dimers is also weak. Therefore the dimers are expected to be less mesogenic than monomers when dipole–dipole interaction between monomers becomes large enough.

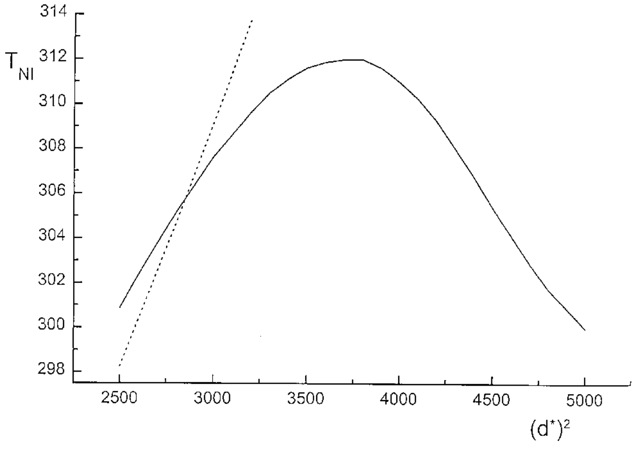

Figure 3. Variation of the nematic–isotropic transition temperature with the growing dimensionless molecular dipole moment d^*. The dashed curve presents the variation of the transition temperature obtained in the context of the same model but with zero concentration of dimers.

As a result, the transition temperature is indeed expected to decrease with increasing molar fraction of dimers. For intermediate values of dipole d^* both tendencies balance each other and the transition temperature reaches a maximum.

The dotted curve on figure 3 presents the dependence of the transition temperature on the value of the dipole moment calculated in the context of the same model but with zero concentration of dimers. In this case the transition temperature grows monotonically with the increasing dipole moment for all values of the dipole. This behaviour is similar to that obtained earlier by one of the authors [18] using the two particle cluster approximation. We note that for small dipoles the existence of dimers does not influence the qualitative behaviour of the transition temperature. At the same time, some quantitative difference exists. In particular, the formation of dimers results in an increase of the transition temperature in this domain. We will return to this interesting point below.

The decrease of the nematic–isotropic transition temperature with the increasing dipole obtained in the present model in the case of large dipoles, enables one to understand why a destabilization of the nematic phase has been observed in computer simulations of the nematic phase composed of hard spherocylinders with central longitudinal dipoles [19]. This tendency contradicts the results of early theories [16–18] and is related to the increasing concentration of dimers. For sufficiently large monomer dipole moments, the dimers appear to be less mesogenic then monomers. More exactly, the artificial nematic phase composed of pure monomers should have a higher transition temperature compared with that for the phase composed of pure dimers (provided the total volume fraction of particles is the same in both phases). We note also that the two tendencies, i.e. a growth of T_{NI} for small dipoles and a decrease of T_{NI} for large ones, partially compensate each other. As a result one can see in figure 3 that the absolute change of the transition temperature appears to be relatively small. This explains

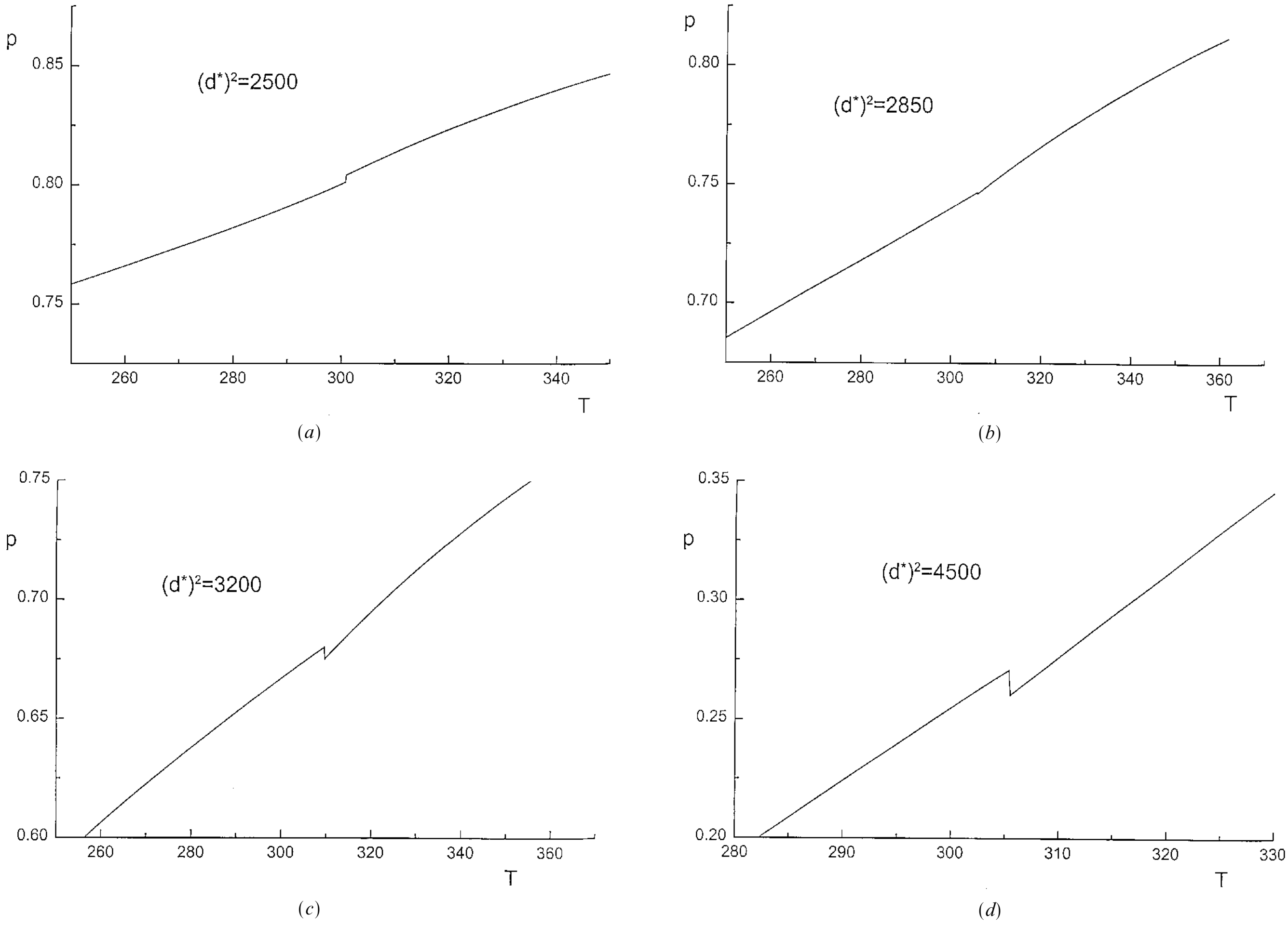

Figure 4. Temperature variation of the monomer fraction p in the vicinity of the nematic–isotropic phase transition for different values of the dimensionless molecular dipole d^*.

why practically no effect of the molecular dipoles on T_{NI} has been observed in a computer simulation of the polar Gay–Berne nematic [21].

The temperature variation of the relative number density of monomers p is presented in figure 4 for different values of the reduced dipole moment. The number densities of monomers and dimers change discontinuously at the nematic–isotropic transition point and one can readily see that for relatively small dipoles, figure 4 (*a*), the concentration of monomers at the transition temperature is large in the isotropic phase. This means that it is energetically favourable for the dimers to be in the nematic phase. This explains why in this regime the transition temperature is decreased when the formation of dimers is not taken into account (see the dotted curve in figure 3). By contrast, for high values of the reduced dipole the concentration of monomers is higher in the *nematic* phase and therefore the dimers prefer to be in the isotropic phase, see figures 4 (*c*) and 4 (*d*). In this domain the dimers appear to be less mesogenic than monomers.

It is also interesting to consider the temperature variation of the concentration of monomers at the point where the dotted curve crosses the solid one in figure 3. At this point the transition temperature is insensitive to the existence or otherwise of the dimers. One can also see from figure 4 (*b*) that the concentration of monomers is practically the same in the coexisting nematic and isotropic phases. Thus, for the corresponding value of the dipole moment, the dimers do not have any preference and as a result they do not influence the nematic–isotropic transition temperature.

Finally in figure 5 we show the temperature variation of the nematic order parameter S_1 for monomers, figure 5 (*a*), and the order parameter S_2 for dimers, figure 5 (*b*). We note that the absolute value and the temperature dependence of the monomer order parameter do not differ significantly from that obtained in the usual Maier–Saupe theory. At the same time the order parameter of dimers is slightly higher (for this value of the effective dipole).

The results of this paper indicate that the properties of strongly polar nematics can at least qualitatively be described in the context of the present model that accounts for the monomer–dimer equilibrium. The advantage of this model lies in its simplicity. The strongest short range dipole–dipole correlations between monomers are accounted for by assuming the nematic phase to be a mixture of monomers and dimers. The concentration of dimers is then determined self-consistently and strongly depends on the value of the dipole. In this model, reasonable results can be obtained without going too far beyond the mean-field approximation and performing complicated resummations of the diverging expansion series. We expect that the same model can also be used to calculate the coexisting densities of the nematic and isotropic phases in the athermal system of hard dipolar rods that actually has been simulated by McGrother *et al.* [19, 20]. The corresponding work is in progress.

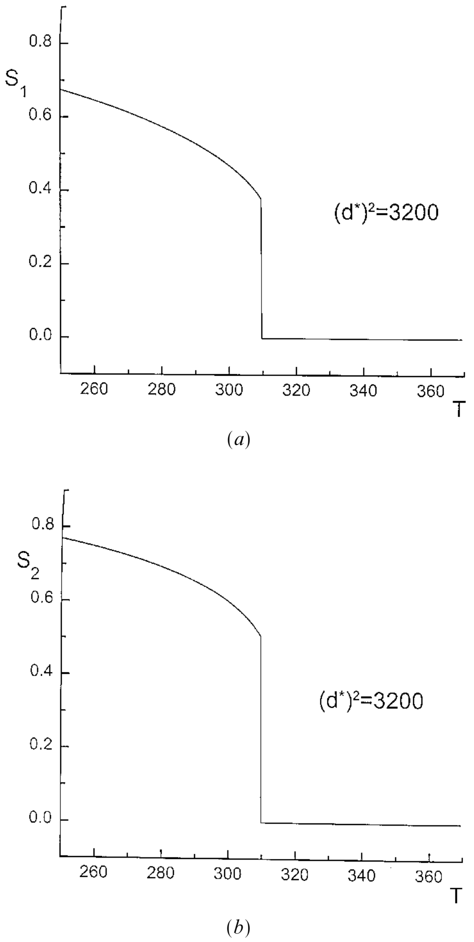

Figure 5. Temperature variation of the nematic order parameter S_1 for monomers (*a*) and S_2 for dimers (*b*).

Permanent molecular dipoles are known to have a strong effect on the properties of smectic phases. In particular, the formation of dimers is known to be very important in the phase transition from the smectic A to the re-entrant nematic phase [26]. The present model can be generalized to include the nematic–smectic A phase transition; the concentration of dimers can then be independently calculated in the smectic and re-entrant phases.

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Appendix A

The dimer bond energy

In the case of hard spherocylinders with central longitudinal dipoles the dimer is composed of two spherocylinders with antiparallel dipoles located side by side, in their minimum energy configuration. The effective bond energy E of N dimers in the volume V (see §2) is expressed as:

$$E = \frac{1}{4\pi}\rho \int \Theta(\mathbf{R}_{12} - \xi_{12})\left[\exp\left(-\frac{U_{\mathrm{dd}}(1,2)}{kT}\right) - 1\right] \times \mathrm{d}^2\mathbf{a}_1\, \mathrm{d}^3\mathbf{R}_{12}\, \mathrm{d}^2\mathbf{a}_2 \qquad \text{(A1)}$$

where

$$U_{\mathrm{dd}}(1,2) = \frac{1}{R_{12}^3}\left[\mathbf{d}_1\mathbf{d}_2 - \frac{3(\mathbf{d}_1\mathbf{R}_{12})(\mathbf{d}_2\mathbf{R}_{12})}{R_{12}^2}\right]. \qquad \text{(A2)}$$

In the case of large dipoles, the exponent under the integral in equation (A1) has a sharp maximum at the minimum energy configuration that corresponds to $\mathbf{a}_1 = -\mathbf{a}_2$, $(\mathbf{R}_{12}\ \mathbf{a}_1) = (\mathbf{R}_{12}\ \mathbf{a}_2) = 0$ and $R_{12} = D$. Taking this into account, we estimate the integral in equation (A1) by the saddle point method.

Let us define the molecular coordinate system with the z-axis parallel to the dipole moment of the first molecule as shown in figure 6:

$$\mathbf{d}_1 = d\begin{pmatrix}0\\0\\1\end{pmatrix} \qquad \mathbf{d}_2 = d\begin{pmatrix}\sin\theta_{12}\cos\varphi_{12}\\ \sin\theta_{12}\sin\varphi_{12}\\ \cos\theta_{12}\end{pmatrix}$$

$$\mathbf{R}_{12} = R_{12}\begin{pmatrix}\sin\theta\cos\varphi\\ \sin\theta\sin\varphi\\ \cos\theta\end{pmatrix}.$$

Nearby the minimum energy configuration one can use the following approximations:

$$\sin\theta_{12} \approx (\pi - \theta_{12}) \qquad \cos\theta_{12} \approx -1 + (\theta_{12} - \pi)^2$$

$$\sin\theta \approx 1 - \left(\theta - \frac{\pi}{2}\right)^2 \qquad \cos\theta \approx \left(\frac{\pi}{2} - \theta\right)$$

$$R_{12} \approx D(1 + \xi)$$

where $\theta_{12} \to \pi$, $\theta \to \pi/2$, $\xi \to 0$.

Let us keep only terms $\sim(\theta_{12} - \pi)^i(\theta - \pi/2)^j\xi^k$ in $U_{\mathrm{dd}}(1,2)$, where $i + j + 2k \leqslant 2$. Then one obtains from equation (A2) the following simplified expression for the dipole-dipole interaction potential:

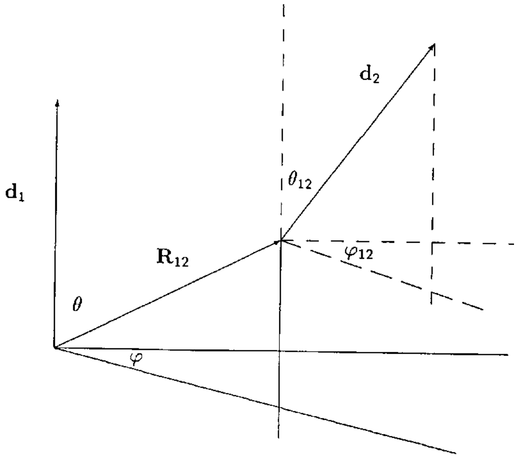

Figure 6. Local coordinate system with the z-axis parallel to the dipole moment $\mathbf{d}_1$ of the first spherocylinder in the dimer pair.

$$U_{\mathrm{dd}} \approx -\frac{d^2}{D^3}\left[1 - 3\xi - (\theta_{12} - \pi)^2 - 3\left(\theta - \frac{\pi}{2}\right)^2 + 3(\theta_{12} - \pi)\left(\theta - \frac{\pi}{2}\right)\cos(\varphi_{12} - \varphi)\right]. \qquad \text{(A3)}$$

Introducing the parameter $\mu = d^2/kTD^3$ we obtain

$$\begin{aligned}
E &\approx \rho D^3 \int_0^\infty \mathrm{d}\xi \int_0^\pi \mathrm{d}\theta\sin\theta \int_0^\pi \mathrm{d}\theta_{12}\sin\theta_{12} \int_0^{2\pi}\mathrm{d}\varphi \\
&\quad\times \int_0^{2\pi}\mathrm{d}\varphi_{12}\exp\left\{\mu\left[1 - 3\xi - (\theta_{12} - \pi)^2 - 3\left(\theta - \frac{\pi}{2}\right)^2 + 3(\theta_{12} - \pi)\left(\theta - \frac{\pi}{2}\right)\cos(\varphi_{12} - \varphi)\right]\right\} \\
&\approx 2\pi\rho D^3\frac{1}{3\mu}\exp(\mu)\int_0^\pi \mathrm{d}\theta\sin\theta\int_0^\pi \mathrm{d}\theta_{12}\sin\theta_{12} \\
&\quad\times \int_0^{2\pi}\mathrm{d}\varphi\exp\left\{\mu\left[-(\theta_{12} - \pi)^2 - 3\left(\theta - \frac{\pi}{2}\right)^2 + 3(\theta_{12} - \pi)\left(\theta - \frac{\pi}{2}\right)\cos\varphi\right]\right\} \\
&= 4\pi^2\rho D^3\frac{1}{3\mu}\exp(\mu)\int_0^\pi \mathrm{d}\theta\sin\theta\int_0^\pi \mathrm{d}\theta_{12}\sin\theta_{12} \\
&\quad\times \exp\left\{\mu\left[-(\theta_{12} - \pi)^2 - 3\left(\theta - \frac{\pi}{2}\right)^2\right]\right\} \\
&\quad\times J_0\left[3\mathrm{i}\mu(\theta_{12} - \pi)\left(\theta - \frac{\pi}{2}\right)\right]
\end{aligned}$$

where J_0 is the Bessel function of zero order. In our case $J_0[3\mathrm{i}\mu(\theta_{12}-\pi)(\theta-\pi/2)]\approx 1$ and therefore we obtain the following estimate for the effective bond energy

$$\begin{aligned}
E &\approx 4\pi^2\rho D^3\frac{1}{3\mu}\exp(\mu)\int_0^{\pi}\mathrm{d}\theta_{12}\sin\theta_{12}\exp[-\mu(\theta_{12}-\pi)^2]\\
&\quad\times\int_0^{\pi}\mathrm{d}\theta\sin\theta\exp\left[-3\mu\left(\theta-\frac{\pi}{2}\right)^2\right]\\
&\approx \pi^2\rho D^3\frac{4}{3\mu}\exp(\mu)\int_0^{\pi}\mathrm{d}\theta_{12}[\pi-\theta_{12}]\exp[-\mu(\theta_{12}-\pi)^2]\\
&\quad\times\int_0^{\pi}\mathrm{d}\theta\left[1-\left(\theta-\frac{\pi}{2}\right)^2\right]\exp\left[-3\mu\left(\theta-\frac{\pi}{2}\right)^2\right]\\
&\approx \pi^2\rho D^3\frac{4}{3\mu}\exp(\mu)\int_0^{\infty}x\exp[-\mu x^2]\,\mathrm{d}x\\
&\quad\times\int_{-\infty}^{\infty}\exp[-3\mu y^2]\,\mathrm{d}y\\
&=\frac{2\pi^2\Phi D^3}{3\mu^2 V}\left(\frac{\pi}{3\mu}\right)^{1/2}\exp(\mu). \qquad (A4)
\end{aligned}$$

The expression (A4) is expected to be correct when $\mu=(d^*)^2/T>1$. We note that this condition is satisfied for strongly polar mesogenic molecules.

Appendix B

Dispersion interaction between monomers and dimers in the context of the site–site interaction model

The coupling constants J_0^{ij}, J_2^{ij} for an interaction potential between a monomer and a dimer and between two dimers can be calculated using the simple site–site interaction model, where a monomer is composed of 5 spherical sites, figure 2 (*a*). The dimer is then composed of 10 interaction sites, figure 2 (*b*). Each interaction centre of a particle (monomer or dimer) interacts with each site of another particle via the Lennard–Jones potential $\varepsilon_0[(D/r)^{12}-(D/r)^6]$, where D is the diameter of the site. The total interaction potential $U_{ij}^{\mathrm{disp}}(i,j=1,2)$ is a double sum over all corresponding sites of the two particles.

We now expand the effective dispersion one particle potentials A_{ij}^{disp} in Legendre polynomials and retain the first two terms:

$$\begin{aligned}
A_{ij}^{\mathrm{disp}} &= \frac{\Phi}{4\pi VkT}\int f^{(j)}(\mathbf{a}_2\;\mathbf{n})\Theta(\mathbf{R}_{12}-\xi_{12})\\
&\quad\times U_{ij}^{\mathrm{disp}}(1,2)\,\mathrm{d}^3\mathbf{R}_{12}\,\mathrm{d}^2\mathbf{a}_2\,\mathrm{d}^2\mathbf{b}_2\\
&= J_0^{ij}+J_2^{ij}S_jP_2((\mathbf{a}_1\;\mathbf{n}))+\dots \qquad (B1)
\end{aligned}$$

where we have taken into account that the dispersion interaction potential between a dimer and a monomer and between two dimers depends on the short axis $\mathbf{b}$ of the dimer.

We actually have to obtain some expressions for the coefficients J_0^{ij} and J_2^{ij}. For this purpose let us first consider the integral over the absolute value R_{12} and $\mathbf{b}_2$ in equation (B1). It is convenient to define the following functions:

$$\begin{aligned}
Y_{ij}(\mathbf{a}_1,\mathbf{u},\mathbf{a}_2) &\equiv \frac{1}{4\pi D^3k}\int\Theta(\mathbf{R}_{12}-\xi_{12})\\
&\quad\times U_{ij}^{\mathrm{disp}}(1,2)R_{12}^2\,\mathrm{d}\mathrm{R}_{12}\,\mathrm{d}^2\mathbf{b}_2. \qquad (B2)
\end{aligned}$$

Now one can express the coefficients A_{ij}^{disp} as

$$A_{ij}^{\mathrm{disp}}=\frac{\Phi D^3}{VT}\int f^{(j)}(\mathbf{a}_2\;\mathbf{n})Y_{ij}(\mathbf{a}_1,\mathbf{u},\mathbf{a}_2)\,\mathrm{d}^2\mathbf{u}\,\mathrm{d}^2\mathbf{a}_2. \qquad (B3)$$

The functions $Y_{ij}(\mathbf{a}_1,\mathbf{u},\mathbf{a}_2)$ depend on the orientations of the long axes of the particles and on the orientation of the intermolecular vector. We use the same interpolation expression for Y_{ij} as in equation (26):

$$\begin{aligned}
Y_{ij} &= \alpha'_{ij}+(\beta'_1)_{ij}P_2(\mathbf{a}_1\;\mathbf{u})+(\beta'_2)_{ij}P_2(\mathbf{a}_2\;\mathbf{u})\\
&\quad+\gamma'_{ij}P_2(\mathbf{a}_1\;\mathbf{a}_2)+\delta'_{ij}\left[\frac{9}{2}(\mathbf{a}_1\;\mathbf{u})(\mathbf{a}_2\;\mathbf{u})(\mathbf{a}_1\;\mathbf{a}_2)\right.\\
&\quad\left.-\frac{3}{2}(\mathbf{a}_1\;\mathbf{u})^2-\frac{3}{2}(\mathbf{a}_2\;\mathbf{u})^2-\frac{3}{2}(\mathbf{a}_1\;\mathbf{a}_2)^2+1\right]. \qquad (B4)
\end{aligned}$$

Substituting equation (B4) into (B3) one obtains the following expression for the coefficients J_0^{ij} and J_2^{ij}:

$$J_0^{ij}=4\pi\frac{\Phi D^3}{V}\frac{1}{T}\alpha'_{ij} \qquad (B5)$$

$$J_2^{ij}=4\pi\frac{\Phi D^3}{V}\frac{1}{T}\gamma'_{ij}. \qquad (B6)$$

Now we consider the coefficients α'_{ij} and γ'_{ij} in equations (B5) and (B6) as free parameters and require that equation (B4) for Y_{ij} should yield exact results for the five orientations of the long axes $\mathbf{a}_1$ and $\mathbf{a}_2$ with respect to the vector $\mathbf{u}$, presented in figure 1. After some algebra one obtains the following result for α'_{ij} and γ'_{ij}:

$$\left[\begin{array}{l}
\alpha'_{ij}=\dfrac{2}{9}\left(Y_1^{ij}+\dfrac{1}{2}Y_2^{ij}+Y_3^{ij}+Y_4^{ij}+Y_5^{ij}\right)\\[2ex]
\gamma'_{ij}=\dfrac{2}{9}(2Y_1^{ij}+Y_2^{ij}-Y_3^{ij}-Y_4^{ij}-Y_5^{ij}).
\end{array}\right. \qquad (B7)$$

The parameters Y_n^{ij} (where index n specifies the number of orientations of the long axes—see figure 1 can be determined if one considers the integral over the short axis $\mathbf{b}_2$ for a dimer in, for example, equation (B2). The integral is to be evaluated separately for all 5 fixed orientations. It is again convenient to define the functions:

$$Z_n^{ij}(\mathbf{b}_1, \mathbf{u}, \mathbf{b}_2) \equiv \frac{1}{D^3 k}\int \Theta(\mathbf{R}_{12} - \xi_{12}) U_{ij}^{\mathrm{disp}}(1, 2) R_{12}^2 \,\mathrm{d}R_{12} \tag{B8}$$

for n orientations of long axes.

We note that the functions Z_n^{ij} do not depend on $\mathbf{a}_1$ and $\mathbf{a}_2$ because the orientation of the long axes is fixed. The coefficients Y_n^{ij} can be expressed as integrals over the functions $Z^{ij}(\mathbf{b}_1, \mathbf{u}, \mathbf{b}_2)$:

$$Y_n^{ij} = \frac{1}{4\pi}\int Z_n^{ij}(\mathbf{b}_1, \mathbf{u}, \mathbf{b}_2)\,\mathrm{d}^2\mathbf{b}_2. \tag{B9}$$

If the interaction particles are monomers ($i = 1, j = 1$), the integration in equation (B9) yields a simple relation:

$$Y_n^{11} = Z_n^{11}. \tag{B10}$$

The quantities Z_n^{11} can now be determined by integrating numerically the site–site potential over the absolute value R_{12}, equation (B8), for every orientation n, presented in figure 1.

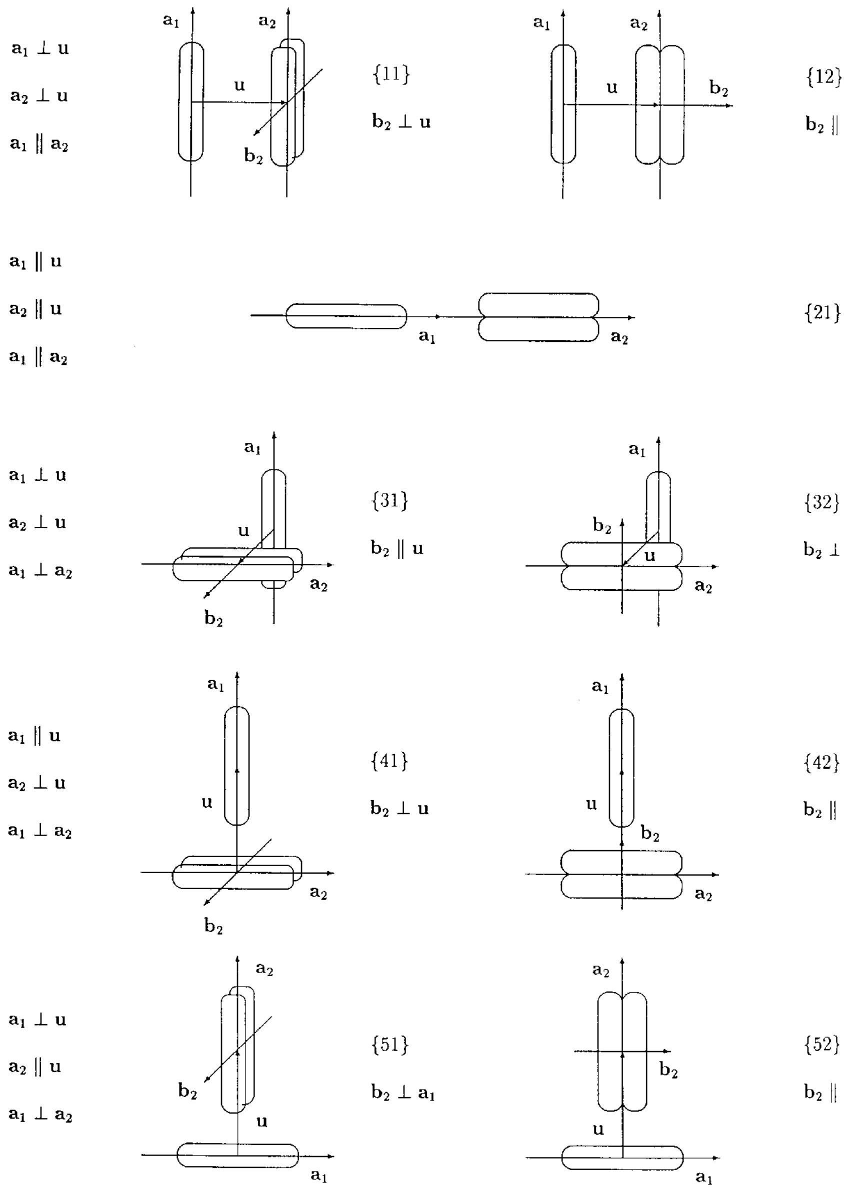

Figure 7. The set of relative orientations of a monomer and a biaxial dimer used in the calculations of the coefficients in equation (B11).

For a monomer and a dimer ($i = 1, j = 2$) the functions Z_n^{12} depend on the short axis of dimer $\mathbf{b}_2$. We approximate $Z_n^{12}(\mathbf{b}_1, \mathbf{u}, \mathbf{b}_2)$ by the following simple polynomials:

$$\left\{\begin{aligned} Z_1^{12} &= \alpha_1 + \beta_1 P_2(\mathbf{b}_2\ \ \mathbf{u}) \\ Z_2^{12} &= \alpha_2 \\ Z_3^{12} &= \alpha_3 + \beta_3 P_2(\mathbf{b}_2\ \ \mathbf{u}) \\ Z_4^{12} &= \alpha_4 + \beta_4 P_2(\mathbf{b}_2\ \ \mathbf{u}) \\ Z_5^{12} &= \alpha_5 + \beta_5 P_2(\mathbf{b}_2\ \ \mathbf{a}_1). \end{aligned}\right. \tag{B11}$$

Substituting equation (B11) into (B9) one obtains:

$$Y_n^{12} = \alpha_n. \tag{B12}$$

We again require that equations (B11) for Z_n^{12} should yield exact results for all relative orientations of a monomer and a dimer, presented in figure 7. Then one obtains the following expressions for the coefficients α_n:

$$\left\{\begin{aligned} \alpha_1 &= \frac{1}{3}(2Z_{11}^{12} + Z_{12}^{12}) \\ \alpha_2 &= Z_{21}^{12} \\ \alpha_3 &= \frac{1}{3}(Z_{31}^{12} + 2Z_{32}^{12}) \\ \alpha_4 &= \frac{1}{3}(2Z_{41}^{12} + Z_{42}^{12}) \\ \alpha_5 &= \frac{1}{3}(2Z_{51}^{12} + Z_{52}^{12}). \end{aligned}\right. \tag{B13}$$

The quantities Z_{nm}^{12} (where the double index $\{nm\}$ specifies one of the orientations presented in figure 7) have also been obtained by the numerical integration of the site–site potential over the absolute value R_{12} for every orientation $\{nm\}$, presented in figure 7:

$$Z_{nm}^{12} = \frac{1}{D^3 k} \int \Theta(\mathbf{R}_{12} - \xi_{12}) U_{ij}^{\mathrm{disp}}(1, 2) R_{12}^2 \, \mathrm{d}R_{12} \tag{B14}$$

for $\{nm\}$ orientations of particles.

The same procedure has been used to determine the coefficients of the dispersion interaction potential between two dimers ($i = 2, j = 2$). The only difference is that in this case new polynomials, for example $P_2(\mathbf{b}_1\ \ \mathbf{u})$, $P_2(\mathbf{b}_1\ \ \mathbf{b}_2)$, are to be included in the interpolation expressions for $Z_n^{22}(\mathbf{b}_1, \mathbf{u}, \mathbf{b}_2)$, and some new orientations of the two dimers are to be considered to obtain the coefficients in these expressions.

The resulting values of Y_n^{11}, Y_n^{12} and Y_n^{22} were substituted into equations (B7). The coefficients J_0^{ij}, J_2^{ij}, obtained for $\varepsilon_0/k = 5350$ K, are presented in table 2.

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