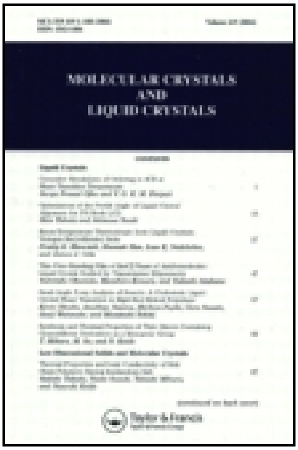

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Theory of Phase Transitions in the Assembly of Biaxial Molecules Interacting via Dispersion Forces

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Theory of Phase Transitions in the Assembly of Biaxial Molecules Interacting via Dispersion Forces

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The ordering in the assembly of biaxial molecules which interact pairwise via the dispersion force is investigated statistical-mechanically, where four kinds of liquid crystalline phase and phase transitions between some pairs of those phases are discussed in comparison with the existing theoretical results from the model of uniaxial molecules. There appear one uniaxial nematic phase, two kinds of biaxial nematic phase and one discotic phase. The phase diagram of temperature versus interaction strength are obtained, where the four phases mentioned above appear in different regions depending on the molecular shape. Some advantages of the present method in investigating the orientational ordering in biaxial liquid crystals, including the discotic phases, are discussed.

Keywords: biaxial molecules; induced dipole-dipole interaction

§ 1. INTRODUCTION

Some progress has been made in investigating liquid crystalline phases in the system of biaxial molecules during these two decades. That is, the disco-nematic phase was discovered in the assembly of discoid molecules by several authors[1] and further the biaxial nematic phase which manifests a biaxial symmetry macroscopically was discovered by many researchers in the assembly of long biaxial molecules.[2] Thus, it is significant to investigate theoretically what kinds of liquid crystal phase are exhibited by the assembly of biaxial molecules and the properties of those phases. Shih and Alben discussed first the biaxial nematic phase and the disco-nematic phase on the basis of a lattice model.[3] Straley investigated the assembly of molecules shaped as rectangular parallelepiped[4] for the purpose of

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discussing various phases including the two phases mentioned above. However, these attempts remain tentative and do not discuss the normal nematic, biaxial nematic and disco-nematic phases as a whole. In this respect, we attempt here to discuss such liquid crystal phases as mentioned above as a whole, by taking as a typical system the assembly of biaxial molecules which interact pairwise via the dispersion force proposed by one of the present authors previously.[5]

According to Priest and Lubensky[6] we need four order parameters to describe the ordering in the system of biaxial molecules with long principal axes whose orientations are defined in terms of the three Eulerian angles. One of these order parameters is concerned with the orientational ordering of the long axis and the other three with the biaxial orientational ordering. Although the energy term in the free energy of this system can be calculated as a function of the four order parameters without much trouble, the entropy term is rather troublesome. Thus, the model has been simplified so as to make the calculation tractable. Freiser[7] and some others[8] were confined only to the two order parameters, ignoring two biaxial order parameters, and Straley[4] divided the four order parameters into two sets of pairs, neglecting the correlation between the sets. On the basis of such simplified models we cannot understand well the phase transition in the system. In this respect, the method of Shih and Alben[3], who studied the system by restricting the molecular orientations to six possibilities, is noteworthy. We will use their model to derive the free energy, including the entropy term in the present investigation.

The statistical theory on the nematic, cholesteric and smecticA phases based on some appropriate models of the intermolecular dispersion force was developed for the system of uniaxial molecules or rod-like molecules with circular section by Maier and Saupe,[9] Goossens[10] and McMillan[11], respectively, who succeeded in explaining those phases. For the system of biaxial molecules Freiser[7] determined a certain appropriate form of the effective intermolecular interaction from the expansion into spherical harmonics based on the biaxial molecular symmetry and Straley[4] took into account the effect of molecular shape due to the hard core model. However, the intermolecular interactions proposed by these authors are not sufficient to clarify various possible phases exhibited by the system of biaxial molecules and discuss transitions between those phases.

We investigated the liquid crystal of chiral molecules previously by making use of the advantage of the method of symmetry-breaking potential[12] to successfully explain the temperature dependence of the cholesteric pitch, where we assumed a dispersion force to interact between a pair of molecules with hard cores.[13] Although we further intended to inquire into the case of the system of biaxial molecules interacting pairwise via a similar dispersion force, we did not succeed in obtaining the free energy as a function of the four relevant order parameters.[5] Therefore we were unable to discuss the influence of the biaxial orientational ordering on the temperature dependence of the cholesteric pitch and, of course, could not derive the biaxial liquid crystal phases exhibited in the system. Recently, however, we have succeeded in obtaining the free energy in terms of the four order parameters by using a six-configuration model. That is a generalization of Zwanzig's three-orientation model[14], where we substitute one of the biaxial order parameters introduced by Priest and Lubensky with a truncated one so as to make it tractable and physically reasonable.

In § 2, we derive the effective intermolecular interaction in the assembly of biaxial molecules from the induced dipole-dipole interaction in terms of the order variables and of the relative coordinate of a pair of molecules. In § 3, applying the method of symmetry-breaking potential[12] to this assembly, we obtain the free energy of the system as a function of the order parameters defined as thermal averages of the above four order variables. In § 4, on the basis of this free energy we investigate the biaxial liquid crystal phases which appear and the transitions between those phases. And, finally, we discuss the influence of the six-direction model and the substitution of one order variable on the reliability of the result.

§ 2. INTERMOLECULAR POTENTIAL AND ORDER VARIABLES

In order to investigate the intermolecular potential energy, according to Priest and Lubensky[6], we define a tensor

$$Q_{pq}{}^{ij}(I) = a_p{}^i(I)a_q{}^i(I) - \frac{\delta_{pq}\delta_{ij}}{3} \quad (p,q = 1,2,3;\ i,j = x,y,z) \qquad (1)$$

for the molecule I, where $a_p{}^i(I)$ denotes an orthogonal component of the unit vector $\mathbf{a}_p(I)$ parallel to the p-th principal axis of the molecule I, and δ_{pq} and δ_{ij} are Kronecker's delta symbols. In Table I we show the interrelation of the directions of the orthogonal coordinate system (ξ,η,ζ) in the molecular frame relative to the orthogonal coordinate system (x,y,z) in the laboratory frame, where the direction cosines between the two coordinate systems are shown in terms of the Eulerian angles θ_I, ϕ_I and ψ_I.

TABLE I Direction cosines between the molecular and laboratory frames

	x	y	z
ξ	$\cos\theta\cos\phi\cos\psi - \sin\phi\sin\psi$	$\cos\theta\sin\phi\cos\psi + \cos\phi\sin\psi$	$-\sin\theta\cos\psi$
η	$-\cos\theta\sin\phi\cos\psi - \sin\phi\cos\psi$	$-\cos\theta\sin\phi\sin\psi + \cos\phi\cos\psi$	$\sin\theta\sin\psi$
ζ	$\sin\theta\cos\phi$	$\sin\theta\sin\phi$	$\cos\theta$

(ξ,η,ζ): coordinate axes on the molecular frame.
(x,y,z): coordinate axes on the laboratory frame.

Thermal averages of the orthogonal components of the tensor (1) are expressed as

$$< Q_{pq}{}^{ij}(I) >_0 = 0, \quad (p \neq q) \tag{2}$$

$$< Q_{11}{}^{ij}(I) >_0 = \sigma_1(n_1^i n_1^j - \delta_{ij}/3) + \sigma_2(n_2^i n_2^j - n_3^i n_3^j)/2 \tag{3}$$

$$< Q_{22}{}^{ij}(I) >_0 = -(\sigma_1 - \sigma_3)(n_1^i n_1^j - \delta_{ij}/3)/2 + (\sigma_4{}' - \sigma_2/2)(n_2^i n_2^j - n_3^i n_3^j) \tag{4}$$

$$\langle Q_{33}{}^{ij}(I)\rangle_0 = -(\sigma_1 + \sigma_3)(n_1^i n_1^j - \delta_{ij}/3)/2 - (\sigma_4{}' + \sigma_2/2)(n_2^i n_2^j - n_3^i n_3^j) \tag{5}$$

in terms of the orthogonal i-component $n_p{}^i$ of the unit vector $\mathbf{n}_p$ directing the average p-th principal axis, of which $\boldsymbol{n}_1$ for the long axis denotes the director. The order parameters σ_1, σ_2, σ_3 and $\sigma_{4'}$ will be obtained as thermal averages of the order variables defined in terms of the Eulerian angles as

$$\hat{\sigma}_1 = \frac{3}{2}\cos^2\theta_I - \frac{1}{2}, \hat{\sigma}_2 = \sin^2\theta_I \cos 2\phi_I, \hat{\sigma}_3 = \frac{3}{2}\sin^2\theta_I \cos 2\psi_I, \tag{6}$$

$$\hat{\sigma}_4{}' = \frac{1}{4}(1 + \cos^2\theta_I)\cos(2\phi_I)\cos(2\psi_I) \tag{7}$$

whose thermal averages

$$\sigma_s = \langle\hat{\sigma}_s(I)\rangle_0 (s = 1,2,3), \quad \sigma_4{}' = \langle\hat{\sigma}_4{}'(I)\rangle_0 \tag{8}$$

which will be defined in the next section are the order parameters.

Assuming that the center of mass of each biaxial molecule is distributed at random in the whole space of the system in the multipole expansion of the intermolecular potential, we write the induced dipole-dipole interaction potential between biaxial molecules as

$$\begin{aligned} \Phi_{I,J} = &- U_1(r_{IJ}) \sum_{i=x,y,z} \sum_{j=x,y,z} Q_{11}^{ij}(I) Q_{11}^{ij}(J) \\ &- U_2(r_{IJ}) \sum_{i=x,y,z} \sum_{j=x,y,z} [Q_{11}^{ij}(I) R^{ij}(J) + R^{ij}(I) Q_{11}^{ij}(J)] \\ &- U_3(r_{IJ}) \sum_{i=x,y,z} \sum_{j=x,y,z} R^{ij}(I) R^{ij}(J), \end{aligned} \tag{9}$$

where we have defined.

$$R^{ij}(I) \boxminus Q_{22}^{ij}(I) - Q_{33}^{ij}(I) \tag{10}$$

and potential functions $U_1(r_{IJ})$, $U_2(r_{IJ})$ and $U_3(r_{IJ})$ of the distance r_{IJ} between the pair of molecules. The potential (9) which we have previously introduced to investigate the influence of the biaxial ordering on the temperature dependence of the cholesteric pitch is also useful here to discuss orientational orderings in various phases such as nematic, biaxial nematic and discotic phases. We derive

(9) from the model of induced dipole-dipole interacion between molecules in the Appendix.

§ 3. FORMULATION OF THE FREE ENERGY

TABLE II Euler angles and order variables in 6 configurations

Ω_n	θ_n	ϕ_n	ϕ_n	$\hat\sigma_1$	$\hat\sigma_2$	$\hat\sigma_3$	$\hat\sigma_4$	$\hat\sigma_4'$
Ω_1	0	0	0	1	0	0	1/2	1/2
Ω_2	0	0	π/2	1	0	0	−1/2	−1/2
Ω_3	π/2	0	0	−1/2	1	3/2	0	1/4
Ω_4	π/2	0	π/2	−1/2	1	−3/2	0	−1/4
Ω_5	π/2	π/2	0	−1/2	−1	3/2	0	1/4
Ω_6	π/2	π/2	π/2	−1/2	−1	−3/2	0	−1/4

In order to investigate the long-range ordering in the system of N biaxial molecules whose orientations are restricted to the six cases as shown in Table II, we apply the symmetry-breaking potential[12] using $\eta_s\hat\sigma_s$ as those potentials for the ordering s=1,2,3 and 4, respectively. Thus we write the partition function in terms of the order variables $\hat\sigma_s(I)$ for the molecule I which will be defined later in (13) and (14) explicitly as

$$Z(\{\eta_s\})=\frac{1}{N!}\prod_{I=1}^{N}\int d^3r_I\sum_{\Omega(I)=\Omega_1}^{\Omega_6}\exp\left[\sum_{I=1}^{N}\sum_{s=1}^{4}\eta_s\hat\sigma_s(I)-\beta\sum_{I=1}^{N}\sum_{J=1}^{N}(I\neq J)\Phi_{IJ}\right], \tag{11}$$

where β denotes the inverse temperature $1/k_BT$and Φ_{IJ} has been defined in (9). The integration over the spatial coordinates **r** run in the whole space of the system and the summation over the orientation $\Omega(I)$ of the molecule I in the six directions defined in Table II, where the values taken by the four order variables are also shown. We have substituted

$$\hat\sigma_4(I)=\frac{2\hat\sigma(I)+1}{3}\hat\sigma_4{}'(I)=\frac{1}{4}(\cos^2\theta_I+\cos^4\theta_I)\cos(2\phi_I)\cos(2\psi_I) \tag{12}$$

for $\hat\sigma_4{}'(I)$ which have been defined as (7) for the convenience of calculation. The order parameter σ_s is calculated from

$$\sigma_s=\frac{1}{N}\frac{\partial}{\partial\eta_s}\ln Z(\{\eta_s\}),(s=1,2,3,4) \tag{13}$$

where the difinition (8) of the order parameter is replaced with

$$\sigma_s=\langle\hat\sigma_s(I)\rangle_0.\quad(s=1,2,3,4) \tag{14}$$

Expanding (11) with respect to the intermolecular potential divided by temperature as

$$Z(\{\eta_s\}) =$$
$$\frac{1}{N!}\prod_{I=1}^{N}\int d^3\mathbf{r}_I \sum_{\Omega(I)=\Omega_1}^{\Omega_6} \exp\left(\sum_{I=1}^{N}\sum_{s=1}^{4}\eta_s\hat{\sigma}_s(I)\right)\left(1-\beta\sum_{I=1}^{N}\sum_{J=1(I<J)}^{N}\Phi_{IJ}+\dots\right), \tag{15}$$

we obtain

$$\frac{1}{N}\ln Z(\{\eta_s\}) = A - \ln\rho + \ln\Theta_0(\{\eta_s\}) - \frac{1}{2}\beta\Theta_2(\{\eta_s\}) + \cdots, \tag{16}$$

where A is an irrelevant constant and ρ denotes the number density N/V of molecules in terms of the total volume V of the system. We have defined Θ_0 and Θ_2 by

$$\Theta_0(\{\eta_s\}) = 2e^{\eta_1}\cosh\left(\frac{\eta_4}{2}\right) + 4e^{\frac{\eta_1}{2}}\cosh\eta_2\cosh\left(\frac{3\eta_3}{2}\right), \tag{17}$$

$$\Theta_2(\{\eta_s\}) = \tag{18}$$
$$\frac{\rho}{\Theta_0(\{\eta_s\})^2 V}\int d^3\mathbf{r}_I\int d^3\mathbf{r}_J \sum_{\Omega(I)=\Omega_1}^{\Omega_6}\sum_{\Omega(J)=\Omega_1}^{\Omega_6}\exp\left(\sum_{s=1}^{4}\eta_s\{\sigma_s(I)+\sigma_s(J)\}\right)\Phi_{IJ}$$

as functions of the symmetry breakers η_s. Substituting (16) into (13) with (17) and (18) being taken into account, we obtain

$$\sigma_s = \tau_s - \frac{1}{2}\beta\frac{\partial}{\partial\eta_s}\Theta_2(\{\eta_s\}) + \cdots, \tag{19}$$

where we have defined $\tau_s = \partial\ln\Theta_0/\partial\eta_s$ and obtain

$$\tau_1 = \Theta_0^{-1}\left[2e^{\eta_1}\cosh\left(\frac{\eta_4}{2}\right) - 2e^{-\frac{\eta_1}{2}}\cosh\eta_2\cosh\left(\frac{3\eta_3}{2}\right)\right], \tag{20}$$

$$\tau_2 = 4\Theta_0^{-1}e^{\frac{-\eta_1}{2}}\sinh\eta_2\cosh\left(\frac{3\eta_3}{2}\right), \tag{21}$$

$$\tau_3 = 6\Theta_0^{-1}e^{-\frac{\eta_1}{2}}\cosh\eta_2\sinh\left(\frac{3\eta_3}{2}\right), \tag{22}$$

$$\tau_4 = \Theta_0^{-1}e^{\eta_1}\sinh\left(\frac{\eta_4}{2}\right). \tag{23}$$

We rewrite Θ_2 in terms of $\tau_s$as

$$\Theta_2(\{\eta_s\}) = -U_1\left(\frac{2}{3}\tau_1^2 + \frac{1}{2}\tau_2^2\right) - U_2\left(\frac{4}{3}\tau_1\tau_3 + 4\tau_2\tau_4 + \frac{\tau_2^2\tau_3}{1-\tau_1}\right) - U_3\left[\frac{2}{3}\tau_3^2 + 8\left(\tau_4 + \frac{1}{4}\frac{\tau_2\tau_3}{1-\tau_1}\right)^2\right] \tag{24}$$

in terms of the integrals

$$U_n = \frac{4\pi}{3}\rho\int U_n(r)d^3r. \quad (n = 1,2,3) \tag{25}$$

Substituting (24) into (19), where τ_s are rewritten in terms of η_s, we obtain the order parameters $\sigma_s$as functions of the symmetry-breakers η_s. We solve these functional relations (19) with respect to the symmetry-breakers in the form

$$\eta_s = \eta_s^{(0)}(\{\sigma_s\}) + \frac{\beta}{2}\frac{\partial}{\partial\sigma_s}\Theta_2(\{\sigma_s\}), (s = 1,2,3,4) \tag{26}$$

where the zeroth order or the configuration terms are written as

$$\eta_1^{(0)}(\{\sigma_s\}) = \frac{2}{3}\ln\frac{1+2\sigma_1}{1-\sigma_1} + \frac{2}{3}\ln\frac{\cosh(\eta_2^{(0)})\cosh(3\eta_3^{(0)}/2)}{\cosh(\eta_4^{(0)}/2)}, \tag{27}$$

$$\eta_2^{(0)}(\{\sigma_s\}) = \frac{1}{2}\ln\frac{1-\sigma_1+(3/2)\sigma_2}{1-\sigma_1-(3/2)\sigma_2}, \tag{28}$$

$$\eta_3^{(0)}(\{\sigma_s\}) = \frac{1}{3}\ln\frac{1-\sigma_1+\sigma_3}{1-\sigma_1-\sigma_3}, \tag{29}$$

$$\eta_4^{(0)}(\{\sigma_s\}) = \ln\frac{1+2\sigma_1+6\sigma_4}{1+2\sigma_1-6\sigma_4}, \tag{30}$$

for the respective orderings, and the next term due to the intermolecular energy is obtained by substituting

$$\Theta_2(\{\sigma_s\}) = -U_1\left(\frac{2}{3}\sigma_1^2 + \frac{1}{2}\sigma_2^2\right) - U_2\left(\frac{4}{3}\sigma_1\sigma_3 + 4\sigma_2\sigma_4 + \frac{\sigma_2^2\sigma_3}{1-\sigma_1}\right) - U_3\left(\frac{2}{3}\sigma_3^2 + 8\left(\sigma_4 + \frac{1}{4}\frac{\sigma_2\sigma_3}{1-\sigma_1}\right)^2\right) \tag{31}$$

into (26).

The free energy F as a function of the order parameters is calculated in the unit of the thermal energy $k_BT=\beta^{-1}$ from the formula

$$\begin{aligned} F(\sigma_1,\sigma_2,\sigma_3,\sigma_4) = F_0 &+ \int_0^{\sigma_1} \eta_1(x,0,0,0)dx + \int_0^{\sigma_2} \eta_2(\sigma_1,y,0,0)dy \\ &+ \int_0^{\sigma_3} \eta_3(\sigma_1,\sigma_2,z,0)dz + \int_0^{\sigma_4} \eta_4(\sigma_1,\sigma_2,\sigma_3,u)du, \end{aligned} \tag{32}$$

where $F_0 \equiv F(0,0,0,0)$ represents the disordered phase. Thus we obtain

$$\begin{aligned} F_{(\sigma_1,\sigma_2,\sigma_3,\sigma_4)} =& S_1(\sigma_1) + S_2(\sigma_1,\sigma_2) + S_3(\sigma_1,\sigma_3) + S_4(\sigma_1,\sigma_4) \\ & - \frac{\beta}{2}\left[U_1\left(\frac{2}{3}{\sigma_1}^2 + \frac{1}{2}{\sigma_2}^2\right) + U_2\left(\frac{4}{3}\sigma_1\sigma_3 + 4\sigma_2\sigma_4 + \frac{{\sigma_2}^2\sigma_3}{1-\sigma_1}\right)\right. \\ & \left. + U_3\left\{\frac{2}{3}{\sigma_3}^2 + 8\left(\sigma_4 + \frac{1}{4}\frac{\sigma_2\sigma_3}{1-\sigma_1}\right)^2\right\}\right] \end{aligned} \tag{33}$$

where we have defined the entropy terms as

$$S_1(\sigma_1) = \frac{1}{3}[(1+2\sigma_1)\ln(1+2\sigma_1) + 2(1-\sigma_1)\ln(1-\sigma_1)], \tag{34}$$

$$\begin{aligned} S_2(\sigma_1,\sigma_2) =& \frac{1}{3}\left[\left(1-\sigma_1+\frac{3}{2}\sigma_2\right)\ln\left(1-\sigma_1+\frac{3}{2}\sigma_2\right)\right. \\ & \left. + \left(1-\sigma_1-\frac{3\sigma_2}{2}\right)\ln\left(1-\sigma_1-\frac{3\sigma_2}{2}\right)\right] \\ & - \frac{2}{3}(1-\sigma_1)\ln(1-\sigma_1), \end{aligned} \tag{35}$$

$$\begin{aligned} S_3(\sigma_1,\sigma_3) =& \frac{1}{3}(1-\sigma_1+\sigma_3)\ln(1-\sigma_1+\sigma_3) \\ & + \frac{1}{3}(1-\sigma_1-\sigma_3)\ln(1-\sigma_1-\sigma_3) \\ & - \frac{2}{3}(1-\sigma_1)\ln(1-\sigma_1), \end{aligned} \tag{36}$$

$$\begin{aligned} S_4(\sigma_1,\sigma_4) =& \frac{1}{6}(1+2\sigma_1+6\sigma_4)\ln(1+2\sigma_1+6\sigma_4) \\ & + \frac{1}{6}(1+2\sigma_1-6\sigma_4)\ln(1+2\sigma_1-6\sigma_4) \\ & - \frac{1}{3}(1+2\sigma_1)\ln(1+2\sigma_1). \end{aligned} \tag{37}$$

The equilibrium is determined from the condition

$$\frac{\partial}{\partial \sigma_s} F(\sigma_1, \sigma_2, \sigma_3, \sigma_4) = \eta(\sigma_1, \sigma_2, \sigma_3, \sigma_4) = 0 \quad (\mathrm{s} = 1, 2, 3, 4) \tag{38}$$

to minimize the free energy (33) with respect to the order parameters σ_s.

§ 4. RESULTS OF CALCULATION BASED ON A MODEL FOR THE POLARIZATION OF MOLECULAR DIPOLE

In the first place the relations between the interaction potentials U_1,U_2 and U_3 in (9) are investigated by assuming a simple model of the transition dipole moment of the molecule whose orthogonal components are given by

$$\langle n|P_{\mathrm{I},z}|0\rangle = p(\Delta E_{\mathrm{I}}^{n}) \cos\alpha_{\mathrm{I}}, \tag{39}$$

$$\langle n|P_{\mathrm{I},x}|0\rangle = \varepsilon_x p(\Delta E_{\mathrm{I}}^{n}) \sin\alpha_{\mathrm{I}} \cos\beta_{\mathrm{I}}, \tag{40}$$

$$\langle n|P_{\mathrm{I},y}|0\rangle = \varepsilon_y p(\Delta E_{\mathrm{I}}^{n}) \sin\alpha_{\mathrm{I}} \sin\beta_{\mathrm{I}}, \tag{41}$$

respectively, where the matrix elements of the orthogonal x, y and z components of the dipole moment operator $\mathbf{P}_I$ of the molecule I are taken between the ground state 0 and an excited state n, and where α_I and β_I denote the polar and azimuth angles in the molecular frame, respectively. The anisotropy parameters ε_x and ε_y are confined as

$$0 \le \varepsilon_y \le \varepsilon_x \le 1, \tag{42}$$

where they are specified by

$$\varepsilon_x = \varepsilon_y < 1, \quad \varepsilon_y < \varepsilon_x = 1, \quad \varepsilon_x = \varepsilon_y = 1, \tag{43}$$

for the rod-like, disc-like and spherical molecules, respectively.

Assuming that the excitation energies of a molecule are not influenced by any neighbouring molecules and distributed with the energy distribution density $g(\Delta E_I)$, we can rewrite the expressions (A4), (A5), (A6) for the interaction potentials as

$$U_{\mathrm{I}} = \frac{4\pi^2}{9} u[2 - ({\varepsilon_x}^2 + {\varepsilon_y}^2)]^2, \tag{44}$$

$$U_2 = \frac{4\pi^2}{9} u[2 - ({\varepsilon_x}^2 + {\varepsilon_y}^2)]({\varepsilon_x}^2 - {\varepsilon_y}^2), \tag{45}$$

$$U_2 = \frac{4\pi^2}{9} u({\varepsilon_x}^2 - {\varepsilon_y}^2)^2, \tag{46}$$

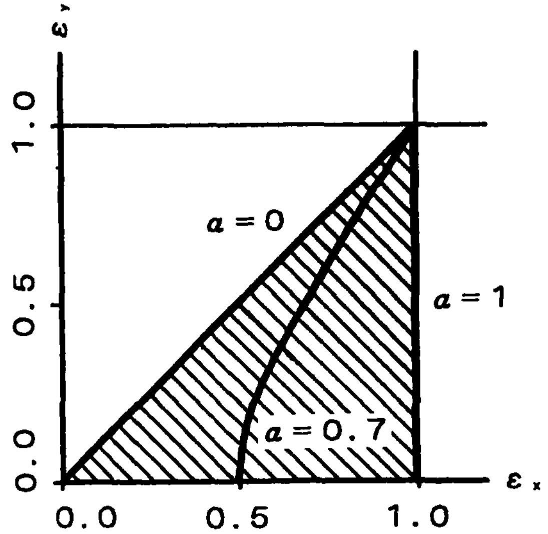

FIGURE 1 Diagram of the molecular shape parameters ε_x and ε_y. The region defined by eq. (42) in the main text is shaded and the lines defined by the relation (48) for α equal to 1, 1/7 and 0, respectively, are drawn. The cases where $\alpha = 0$ or $\varepsilon_x = \varepsilon_y = 0$ and $\varepsilon_y = 0$ with ε_x being finite represent a rod and a plate, respectively, both with vanishing thickness

defining u as an integral

$$u = \frac{1}{5R^6} \int dE \int dE' \frac{|p(E)|^2 |p(E')|^2}{E + E'} g(E) g(E') \tag{47}$$

which is a specific function of the mean distance R between molecules in the system. In terms of a parameter α defined as

$$\alpha \equiv \frac{{\varepsilon_x}^2 - {\varepsilon_y}^2}{2 - ({\varepsilon_x}^2 + {\varepsilon_y}^2)} \tag{48}$$

we can write the ratios of U_2 and U_3 to U_1 as

$$\frac{U_2}{U_1} = \alpha, \quad \frac{U_3}{U_1} = \alpha^2 \tag{49}$$

on the basis of (44), (45) and (46). Regarding α as a constant, the relation (48) gives a curve on the $(\varepsilon_x, \varepsilon_y)$-plane, as shown in Fig.1. The family of curves with different values of α covers the plane, where the phases and phase transitions appearing in the system represented by a point on a certain curve are specified by the value of α given to that curve. On each curve only the transition temperatures are different from one point to another. Taking into consideration (49) with the aid of (48), we compute for ε_x ranging from 0 to 1, keeping ε_y to be zero, in place of computing for all possible values of α from 0 to 1. Let us discuss the ordered phases appearing in the system and phase transitions between those phases by calculating the free energy (33) as a function of the order parameters. The results of calculation are described in terms of the reduced temperature and interaction strengths defined as

$$\tilde{T} \equiv \frac{k_B T}{u}, \quad \tilde{U}_n \equiv \frac{U_n}{u}, (n = 1, 2, 3) \tag{50}$$

in the unit u given by (47). The various phases are characterized by four kinds of order parameters and abbreviated symbolically, as displayed in Table III.

TABLE III Phases characterized by four order parameters with their symbols

Name of the Phase	σ_1	σ_2	σ_3	σ_4	*Symbol*
isotropic	0	0	0	0	I
nematic	finite	0	0	0	N
molecular biaxial nematic	finite	0	finite	0	N_{MB}
phase biaxial nematic	finite	finite	finite	finite	N_{PB}
disco-nematic	finite	finite	finite	finite	D_N

The ordering of the normal to molecular plane is assumed to be oriented to the y-axis. Replacing the y-axis with the z-axis, we can distinguish between N_{PB} and D_N, where σ_2 and $\sigma_4$vanish with σ_1 and σ_3 being finite and negative in D_N in contrast to N_{PB} with all order parameters being finite.

(I) In case $\varepsilon_x = 0$, there appear only the isotropic phase I and the nematic phase N. The transition temperature between these phases are estimated

$$\hat{T}_C = \frac{k_B \tilde{T}_C}{\tilde{U}_1} = \frac{k_B T_C}{U_1} = 0.365, \tag{51}$$

which are higher than the estimate 0.22 by Maier-Saupe as the result of confining the molecular orientation here.

(II) In case $0 < \varepsilon_x < 1$, we have the nematic phase N, two sorts of biaxial nematic phases and the disco-nematic phase $D_N$as the ordered phase displayed in the system. The two biaxial nematic phases were distinguished first by Priest and Lubensky[6] who named them the molecular and phase biaxial phases N_{MB}, N_{PB}, respectively. We comply with his naming here. In the presentation herein taking the direction of ordering of the normal to the molecular plane in parallel to the y-axis, only σ_1 and σ_3 are finite in N_{MB}, whereas the order parameters σ_1, σ_2, σ_3 and σ_4 are all finite in the phases N_{PB}, and D_N. In order to distinguish the characters of N_{PB}, and D_N, it is helpful to adopt the z-axis as the direction of ordering of the normal to the molecular plane. The expression (33) for the free energy can be

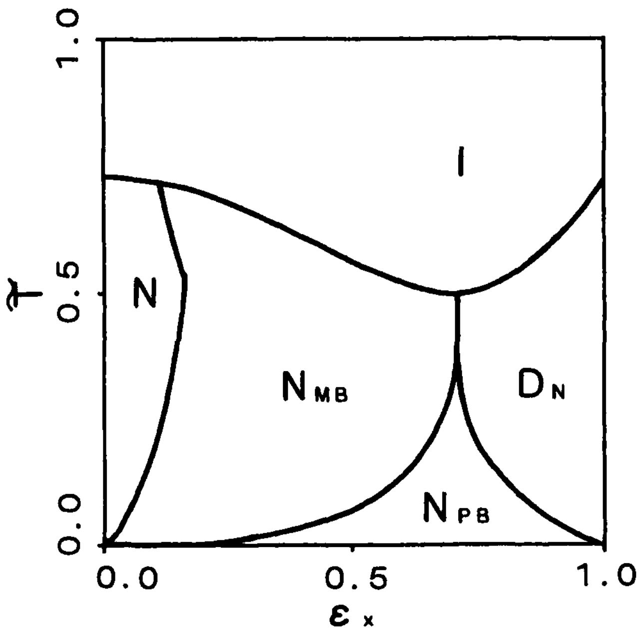

FIGURE 2 Phase diagram on the plane of temperature versus the form factor. The temperature is normalized to $\tilde{T} \equiv k_B T/u$ and the form factor ε_x is changed from 0 to 1 with ε_y being kept zero

used also for this presentation, where it is found that only σ_1 and σ_3 are finite and negative in D_N in contrast with N_{PB} where all order parameters are finite.

(III) In case $\varepsilon_x = 1$, only the isotropic phase I and the disco-nematic phase D_N appear.

The phase diagram on the plane of the anisotropy parameter ε_x versus temperature with ε_y vanishing is shown schematically in Fig.2. The temperature dependence of the order parameters is displayed in Figs.3, 4, 5, 6, 7 and 8. Taking into consideration the competition between σ_1 denoting the order parameter for the long molecular axis and σ_4 representing the ordering of the normal to the plate of the plate-like molecule relative to the direction of the director, we can understand these figures.

In the case (II) the phase N_{PB}, which is stable at lowest temperatures, loses the ordering to zero with the rise of temperature and reduces to the isotropic phase. When $\varepsilon_x < 0.705$, σ_2 as well as σ_4 vanish earlier than σ_1. This is understandable for the biaxial or plate-like molecule we are concerned with, as follows. Because the long molecular axis which tends toward the director loses this tendency by

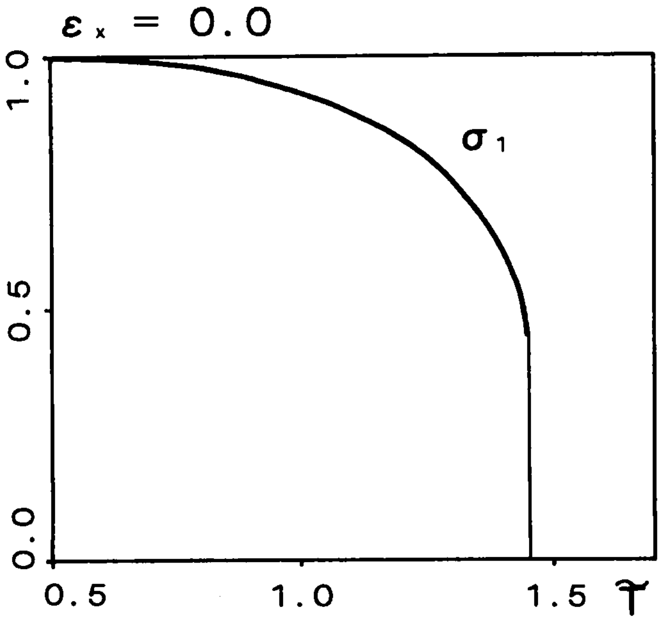

FIGURE 3 Temperature dependence of the order parameter σ_1 for the case $\varepsilon_x = \varepsilon_y = 0$ where only the isotropic and nematic phases appear

rotating around the normal to the molecular plate, when this normal of the molecule with the long molecular axis directed to the director is going to be oriented randomly around the long molecular axis and accordingly σ_4 vanishes, the long molecular axis is going to be distributed randomly around the director and thus σ_2 tends to vanish.

In this way the transition from N_{PB} to N_{MB} takes place first with the rising of temperature. When $\varepsilon_x < 0.165$, the nematic phase N comes about with a further rise of temperature. For the case where $0.115 < \varepsilon_x < 0.165$ the re-entrant transition occurs with N_{MB} reappearing at a higher temperature where long molecular axes of many molecules lose their tendency toward the director and their molecular plates tend to be more parallel to one another than otherwise.

When $\varepsilon_x > 0.705$, the long molecular axis is randomly oriented around the ordering direction of the normal to molecular plate which is taken as the *y*-axis, with σ_4 still being finite. Thus the phase $D_N$comes about. As mentioned above, by taking the direction of ordering of the normal to the molecular plate as the *z*-axis, the long molecular axis and the normal of the molecular plate of the molecule with the long axis directed to the *z*-axis tend to be randomly oriented

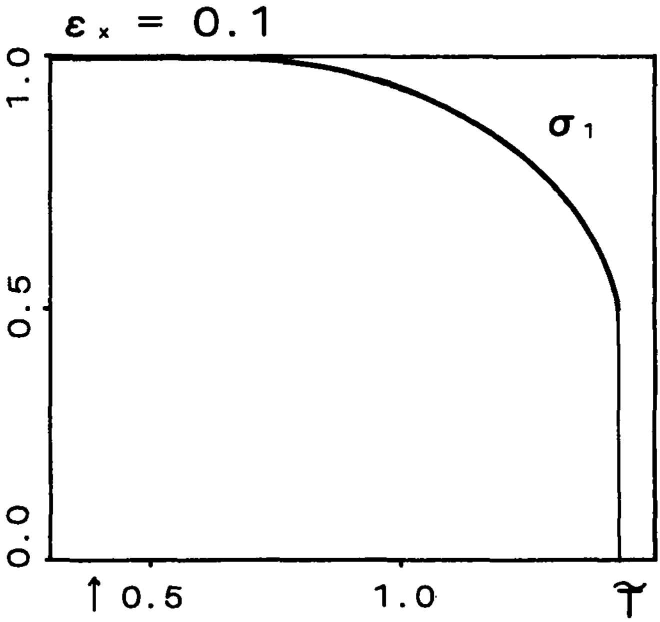

FIGURE 4 Temperature dependence of the order parameter σ_1 for the case $\varepsilon_x = 0.1$, $\varepsilon_y = 0$, where the phase N_{MB} comes about below the normalized temperature $\tilde{T} = 0.39$ accompanied by the order parameter σ_3 *which is too small to make obvious on the diagram*. The transition temperature between the N and N_{MB} is shown by an arrow. The phase N_{PB} also exists below N_{MB} at very low temperatures and the transition temperature cannot be shown in the diagram

around the z-axis. Thus both σ_2 and σ_4 vanish with σ_1 as well as σ_3 being finite and negative.

5. DISCUSSION

We have investigated phase transitions exhibited in the assembly of long plate-like molecules interacting pairwise with one another via the intermolecular coupling Φ_{IJ} given in (9). By adjusting the form parameters of this model, we can discuss the thermal properties of not only the system of rod-like molecules but also the system of flat molecules such as discotic liquid crystals simultaneously. There exists only the coupling $U_1$for the system of rod-like molecules, where the long molecular axes tend to be parallel with one another. As the molecule is so shortened as the shape changes from rod to disc and the parameter α

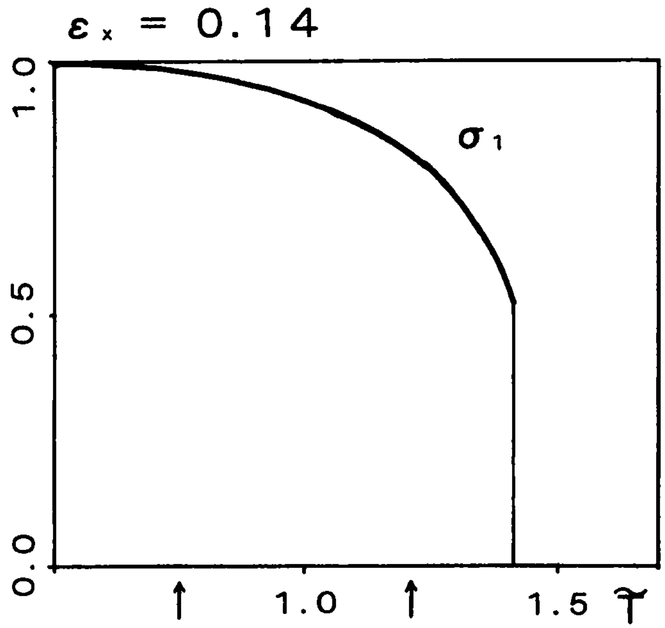

FIGURE 5 Temperature dependence of the order parameter σ_1 and for the case $\varepsilon_x = 0.14$, $\varepsilon_y = 0$, where the re-entrant transition occurs and σ_3 is too small to show on the diagram. The two arrows indicate the temperatures of N_{MB} -N and N-N_{MB} transitions, respectively

increases from zero, the ordering due to the alignment of molecular plates indicated by the order parameter σ_3 comes about first, where the phase N is transformed into the phase N_{MB}. Furthermore, as the molecule becomes as flat as the disc where α approaches 1, the phase D_N appears.

We have restricted the molecular orientations by adopting the six-direction model, which is regarded to give a little higher estimate of the transition temperature.[5]We have further used a substitute $\hat{\sigma}_4$ defined as (12) for $\hat{\sigma}_4{}'$ in the last expression in (8), by which the result is somewhat influenced quantitatively but unchanged qualitatively to describe the orientation of the molecular plate relative to the long axis oriented toward the director. Moreover, we have used $\hat{\sigma}_4$ as a substitute of $\hat{\sigma}_4{}'$ which is rather more helpful than $\hat{\sigma}_4{}'$ to grasp the relation of the phase transition with the molecular shape.

It is also worthwhile to investigate the system of rigid-body molecules in order to explain the dependence of the phase transition on the molecular shape. Shih and Alben[3] investigated the phase transition in the system of biaxial liquid crystal on the basis of the rigid-body model of the molecules arranged on a lattice. They did not introduce the four order parameters and their result is unsatisfac-

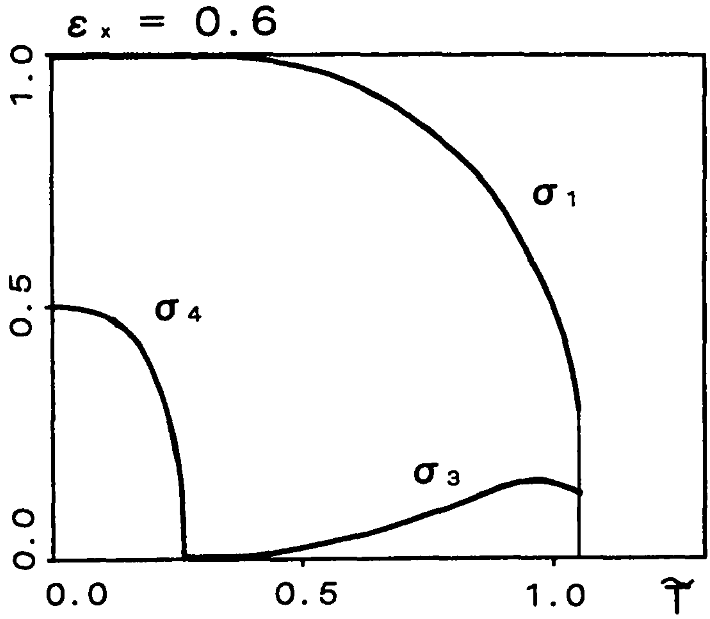

FIGURE 6 Temperature dependence of the order parameters for the case ε_x= 0.6, ε_y = 0. There exists the phase N_{PB}at temperatures below 0.27, where σ_2 and σ_3 are too small to show on the diagram

tory. The present method can be applied to the rigid molecule model by introducing four order parameters. In consequence the free energy of the form (33) is obtained, where the molecular density substitutes the temperature and the coupling parameters U_n are replaced with the shape-dependent parameters, say I_n, constituted of f-functions which were defined in Mayer's statistical-mechanical theory of condensation.

We hope further to apply the method to liquid crystals accompanied with ferroelectricity[15] and antiferroelectricity[16] where the biaxial ordering will play a significant role to clarify phase transitions in those systems.

APPENDIX

The expression (9) for the effective interaction potential is derived from the potential energy

$$\Phi_{IJ} = -\frac{1}{R_{IJ}{}^6}\sum_{n_I,n_J}\frac{\langle 0_I,0_J|a_{IJ}|n_I,n_J\rangle\langle n_I,n_J|a_{IJ}|0_I,0_J\rangle}{(E_{n_I,n_J}-E_{0_I,0_J})}, \qquad \text{(A1)}$$

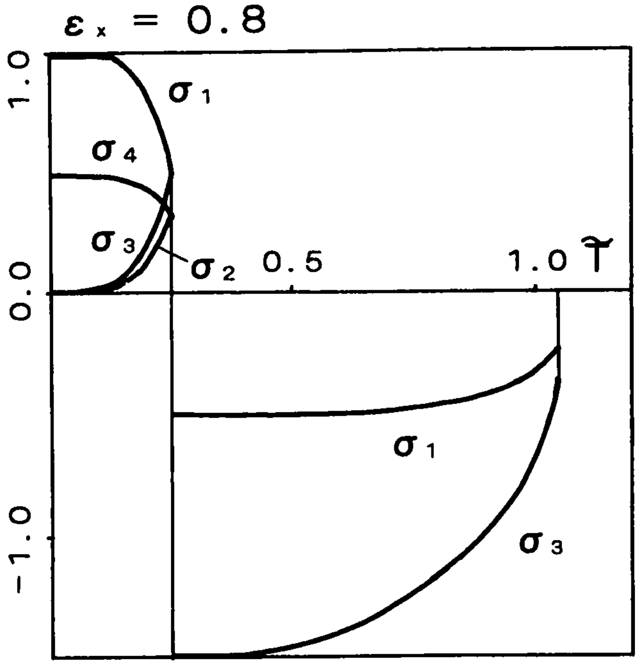

FIGURE 7 Temperature dependence of the order parameters in the case $\varepsilon_x = 0.8$, $\varepsilon_y = 0$. The phases N_{PB} and D_N are exhibited at temperatures $\tilde{T} \leq 0.25$ and $\tilde{T} \geq 0.25$, where the direction of alignment of the normal to the molecular plane is taken as the *y*- and the *z*-axes, respectively, to define the order parameters

due to the dispersion force between induced dipoles of the electrically neutral molecules *I* and *J* which possess the biaxial symmetry around the principal axis of molecule, where R_{IJ} denotes the distance between the molecules *I* and *J*, E_{n_I,n_J} is the energy of the pair of molecular *I* and *J* when they are in the excited states n_I and n_J, respectively, and $E_{0_I,0_J}$ is the energy of the pair whose component molecules are both in the ground state denoted as 0_I and 0_J. The quantity a_{IJ} is defined as

$$a_{IJ} = \sum_{i,j}[3(\rho_{I,j}\cdot \mathbf{u}_{I,J})(\rho_{J,i}\cdot \mathbf{u}_{I,J}) - \rho_{I,i}\cdot \rho_{J,j}]e_{I,i}e_{J,j}, \qquad (A2)$$

where $\rho_{I,i}$ and $\mathbf{u}_{I,J}$ denote the vector extending from the centre of gravity of the molecule *I* to the *i*-th electric charge in that molecule and the unit vector between the molecules *I* and *J*, respectively, and $e_{I,i}$, $e_{J,j}$ are the *i*-th electric charge in the molecule *I*and the *j*-th electric charge in the molecule *J*, respectively. The summation with *i,j* is carried out over the electric charges in the molecules *I* and *J*, respectively.

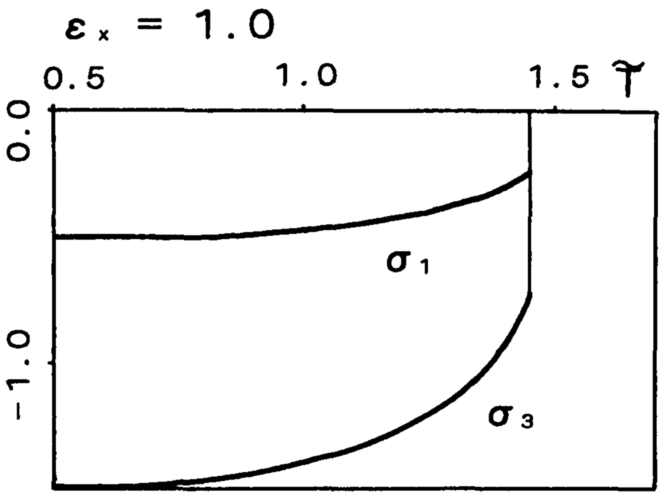

FIGURE 8 Temperature dependence of the order parameters in the case ε_x= 1.0, ε_y = 0, where only the isotropic phase and the phase D_N appear. To define the order parameter for the phase $D_N$the direction of alignment of the normal to the molecular plane is taken as the *z*-axis

We can readily rewrite (A1) as

$$\Phi_{IJ} = -\frac{1}{R_{IJ}{}^6}\sum_{\alpha,\beta}[\mathbf{a}_I{}^\alpha\cdot\mathbf{a}_J{}^\beta - 3(\mathbf{a}_I{}^\alpha\cdot\mathbf{u}_{I,J})(\mathbf{a}_J{}^\beta\cdot\mathbf{u}_{I,J})] \cdot\sum_{n_I,n_J}\frac{|\langle 0_I|p_{I,\alpha}|n_I\rangle|^2|\langle 0_J|p_{J,\beta}|n_J\rangle|^2}{(E_{n_I,n_J}-E_{0_I,0_J})}, \tag{A3}$$

where the first summation is taken over all principal axes of the pair of molecules concerned, $a_I{}^\alpha$ denotes the unit vector along the principal axes forming the molecular orthogonal coordinate axes ($\alpha,\beta = x,y,z$). The matrix elements of the operators $p_{J,\beta}$ and $p_{I,\alpha}$ for orthogonal components of dipole moments of the molecular pair between the ground state 0 and any excited state *n* are involved in the second summation. Assuming that the relative distribution of the centres of mass of the molecular pair is invariant by changing signs of any orthogonal components, we can obtain the expression (9) in the main text, where we have defined

$$U_1 = \frac{1}{5R_{IJ}{}^6}\sum_{n_I,n_J}\frac{9}{E_{n_I,n_J}-E_{0_I,0_J}}D_{0_I,n_I}D_{0_J,n_J}, \tag{A4}$$

$$U_2 = \frac{1}{5R_{IJ}{}^6}\sum_{n_I,n_J}\frac{3}{E_{n_I,n_J}-E_{0_I,0_J}}D_{0_I,n_I}P_{0_J,n_J}, \tag{A5}$$

$$U_3 = \frac{1}{5R_{IJ}{}^6}\sum_{n_I,n_J}\frac{1}{E_{n_I,n_J}-E_{0_I,0_J}}P_{0_I,n_I}P_{0_J,n_J} \tag{A6}$$

in terms of

$$D_{0_I,n_I} = \frac{1}{3}\left(|\langle 0_I|p_{I,z}|n_I\rangle|^2 - \frac{1}{2}|\langle 0_I|p_{I,x}|n_I\rangle|^2 - \frac{1}{2}|\langle 0_I|p_{I,y}|n_I\rangle|^2\right), \tag{A7}$$

$$P_{0_I,n_I} = \frac{1}{2}(|\langle 0_I|p_{I,x}|n_I\rangle|^2 - |\langle 0_I|p_{I,y}|n_I\rangle|^2) \tag{A8}$$

for the molecule I and similarly for the molecule J.

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