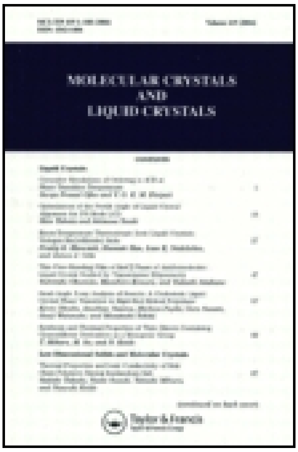

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Orientational Ordering in Anisotropic Fullerides

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ORIENTATIONAL ORDERING IN ANISOTROPIC FULLERIDES

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Absract A microscopic description of structural and orientational ordering of the high–symmetry anisotropic fullerides (AF) condensed state is presented. It is shown that the formed translational ordering removes degeneracy in the direction of preferred molecular orientation axis and leads to the appearance of the cross terms in pseudopotential inducing orientational ordering. Numerical calculations of the order parameters were carried out and phase transition temperature dependencies from molecular parameters were obtained. Using model parameters corresponding to C_{70} molecule the estimation of the structure phase transition temperature was obtained $T_{PC-I} \approx 50K$.

INTRODUCTION

One of the most essential restrictions of the commonly–accepted approaches in the description of ordering in molecular systems lies in the fact that instead of real organic compounds with rather intricate stereochemical configuration the utterly simplified model structures reflecting only the basic symmetry features of molecular structure are considered. Naturally, such assumptions yield some ambiguity: firstly, no unique interpretation of statistical description can be provided, and, secondly, the value of such theoretical treatment predictions for the synthesis of new compounds is rather questionable.

A new objects which exactly satisfy the approximations of statistical theory of structure ordering in molecular systems with universal Van–der–Waals' type of intermolecular interactions are recently synthesized fullerenes[1, 2, 3]. These molecules are of particular interest because of a combination of unique macroscopic properties and simple stereochemical and electronic structure in comparison to those of usual organic molecules[2, 3]. It is necessary to make an accent on the structural rigidity of the fullerene molecules, so the effects of conformational mobility can be neglected, and also to note the high symmetry of the molecules that confines the physically essential set of order parameters.

Recently descriptions of the structure and properties of several types of anisometric fullerenes such as C_{70},(D_{5h}), C_{84} (D_{6h}) and some other have appeared[2, 4, 5, 6]. Peculiarity of these molecules is the lower symmetry in comparison to that of C_{60} molecules, but still higher than usual organic molecules symmetry, and also the obvious anisotropy of intermolecular interaction.

An analogy between molecular mechanism of structural ordering and in a number of cases the similarity of spatial and orientational ordering of anisotropic fullerides (AF) and SmA liquid crystals (LC)[7] is obvious. But at the same time there is an essential difference – in the case of AF the isotropic component of intermolecular interaction is dominating, thus the effects of interaction anisotropy are weak and possible orientational phase transition occurs under the condition that translational order has been formed, hence, with corresponding symmetry restrictions.

The subject of the present work is the statistical description of spatial and orientational ordering in condensed state formed by anisometric van–der–Waals molecules for which the second–rank tensor molecular anisotropy is assumed. For a simplicity, we shall confine ourselves to the consideration of the states with one–dimensional translational order. But even such essential confinement of molecular symmetry (for a number of high–symmetry fullerenes anisotropy can be expressed only in terms of higher rank ($l \geq 6$) tensors)[8] and condensed state allows us to study some common features of widely spread states of organic molecules such as plastic and liquid crystals.

INTERMOLECULAR POTENTIAL

The most general $O(3)$ – invariant expansion of anisotropic intermo–

lecular potential can be written in a form[9]:

$$\Phi_{12}(\mathbf{r}, o_1, o_2) = \sum_{\lambda_1} \sum_{\lambda_2} \sum_{\lambda} \sum_{\mu_1} \sum_{\mu_2} R^{\lambda_1\,\lambda_2\,\lambda}_{\mu_1\,\mu_2}(r)\, \Theta^{\lambda_1\,\lambda_2\,\lambda}_{\mu_1\,\mu_2\,0}(o_1,\, o_2,\, \mathbf{e}_{\mathbf{r}}), \tag{1}$$

where $\mathbf{r} = \mathbf{R}_2 - \mathbf{R}_1$ is an intermolecular vector, $o = \alpha, \beta, \gamma$ are the Eighler angles denoting molecular orientation in laboratory frame, $\Theta^{\lambda_1\,\lambda_2\,\lambda}_{\mu_1\,\mu_2\,\mu}(o_1,\, o_2,\, o)$ is the spherical invariant. Peculiarities of different types of intermolecular interaction are accounted in the expressions for expansion coefficients $R^{\lambda_1\,\lambda_2\,\lambda}_{\mu_1\,\mu_2}(r)$, the latter can be calculated in corresponding approximations[11, 12, 13].

Analysis of possible types of intermolecular interactions and their relative contribution to intermolecular potential for the molecules of the discussed type on the typical distances in condensed state shows that only dispersive and steric interactions are to be taken into account. Besides that, in order to simplify further consideration we assume that molecules possess an axial symmetry. For mesogenic molecules such assumption bases on the fact that thermal excitation of the rotational degrees of freedom leads to the degeneracy of the molecular biaxiality[14], and for AF with D_{nh} symmetry this assumption is fully correct because of condition $n \geq 5$.

For the purposes of the present work an account of dipole−dipole term of polarizability is sufficient. Expressions for isotropic and anisotropic components of intermolecular potential in approximation of static polarizability are given by[13]:

$$\begin{aligned} R^{000\ disp}_{00}(r) &= -\frac{3\hbar\omega_0}{\pi}\,\frac{\overline{\alpha}^2}{r^6}, \\ R^{220\ disp}_{00}(r) &= -\frac{\hbar\omega_0}{3\pi}\left(\frac{1}{5}\right)^{1/2}\frac{(\Delta\alpha)^2}{r^6}, \end{aligned} \tag{2}$$

where $\overline{\alpha}$ is the average dipole polarizability, $\Delta\alpha$ is the anisotropy of dipole polarizability, ω_0 is the typical frequency of the molecular electron spectrum.

Steric repulsion is in fact a phenomenological equivalent of exchange and Coulomb interactions at short distances and can be calculated in one of the known empiric approximations[10]. Anisotropic $SO(3)$ − invariant expansion of "soft"($\sim r^{-n}$, $n \geq 12$) steric component and calculations of the coefficients $R_{0\,0}^{\lambda_1\,\lambda_2\,\lambda\; ster(n)}(r)$ are given in[12, 15]. "Hard" component corresponds to the infinite repulsive potential

$$\Phi_{12}^{ster,h.c.}(\mathbf{r}, o_1, o_2) = \begin{cases} \infty, & \text{if particles 1,2 overlap,} \\ 0, & \text{otherwise} \end{cases} \tag{3}$$

and by means of the pair correlations forms an entropy contribution to free energy; this component can be found after calculation of the excluded volume $(\Omega_{excl.})$[16, 17]. Corresponding calculations are presented below.

ONE-PARTICLE DISTRIBUTION FUNCTION APPROACH

For further statistical description we adopt a structure with orientational and one-dimensional translational order as a model of condensed state of anisotropic fullerenes. This assumption is rather general and allows us to use the formalism developed for the SmA liquid crystals for several types of weakly ordered anisotropic plastic crystals such as AF. It should be noted that the X-ray experimental data for AF formed by C_{70} molecules demonstrate weak translational ordering at room temperatures[18].

Account of the first term in pair correlation function virial expansion gives the following expression for one-particle distribution function:

$$F^{(1)}(1) = N\,\frac{\exp[(-kT)^{-1}\,U(1)]}{\int \exp[(-kT)^{-1}\,U(1)]\,d1}\,. \tag{4}$$

Taking into consideration short-range steric repulsive interactions and long-range dispersive interactions we transform the expression for the pseudopotential to the form:

$$U(1) = -kT\int \mathrm{f}_{\mathrm{M}}^{ster}(1,2)\,F^{(1)}(2)\,d2 + \int \left[\mathrm{f}_{\mathrm{M}}^{ster}(1,2) + 1\right]\,\Phi_{12}^{disp}(1,2)\,F^{(1)}(2)\,d2, \tag{5}$$

where

$$\mathrm{f}_{\mathrm{M}}^{ster}(1,2) = \exp[(-kT)^{-1}\,\Phi_{12}^{ster}(1,2)] - 1 \tag{6}$$

is the Mayer function for "hard" steric component. Account of the "soft" component in (5) leads only to renormalization of an energy contribution to free energy and will be omitted further.

In accordance with the above assumptions we take the symmetry of condensed state to be uniaxial ($R^2 \otimes Z^1 \wedge D_{\infty h}$), so one−particle distribution function is given by $F^{(1)}(1) = \rho\frac{1}{4\pi^2} f(z,\beta)$, where β is the angle denoting molecular polar axis orientation. Distribution function $f(z,\beta)$ satisfies the condition of translational symmetry $f(z+d,\beta) = f(z,\beta)$, where d is the layer period, ρ is the molecular density.

Taking into account only axially symmetric part of "hard" steric correlations we transform the second term in (5) to the form:

$$U^{disp}(z,\beta) = \sum_{\lambda_1}\sum_{\lambda_2}\sum_{\nu} V^{\lambda_1\,\lambda_2\;disp}_{0\,0,\,\nu}\,\eta_{\lambda_2\,0,\,\nu}\,\exp(2\pi i\nu z/d) D^{\lambda_1}_{0\,0}(\beta)\;, \tag{7}$$

where

$$\eta_{\lambda\,0,\,\nu} \;=\; \frac{1}{d}\int\!\!\int \exp(2\pi i\nu z/d)\; D^{\lambda}_{0\,0}(\beta)\, f(z,\beta)\, dz\, d(\cos\beta) \tag{8}$$

are the structural order parameters.

Using (2), after obvious calculations we obtain isotropic and anisotropic energy parameters of the dispersive pseudopotential $V^{\lambda_1\,\lambda_2\;disp}_{0\,0,\,\nu}$ ($\lambda_1 = \lambda_2 = 0, 2,\ \lambda = 0, 2,\ \nu = 0, 1$):

$$\begin{aligned}
V^{0\,0\;disp}_{0\,0,\,1} &= -\frac{3\pi}{4}\,\hbar\omega_0\,\rho\,(\overline{\alpha})^2\,\frac{1}{r^3_{\perp_0}}\,e^{-\xi}(1+\xi), \\
V^{2\,0\;disp}_{0\,0,\,1} &= -\frac{\pi}{16}\,\hbar\omega_0\,\rho\,\overline{\alpha}\,\Delta\alpha\,\frac{1}{r^3_{\perp_0}}\,e^{-\xi}\left(1+\xi+\xi^2\right), \\
V^{2\,2\;disp}_{0\,0,\,0} &= -\frac{\pi}{60}\,\hbar\omega_0\,\rho(\Delta\alpha)^2\,\frac{1}{r^3_{\perp_0}}\,, \\
V^{2\,2\;disp}_{0\,0,\,1} &= -\frac{\pi}{60}\,\hbar\omega_0\,\rho\,(\Delta\alpha)^2\,\frac{1}{r^3_{\perp_0}}\,e^{-\xi},
\end{aligned} \tag{9}$$

where $\xi = 2\pi r_{\perp_0}/d$, $r_{\perp_0}$ is the spatial parameter of steric correlations in the layer plane.

It is necessary to mention that parameters corresponding to the axially symmetrical translationally disordered state ($\lambda \neq 0$, $\lambda_1 \neq \lambda_2$, and $|\nu| = 0$), are absent in above expressions because we assume isotropic distribution of the molecular mass centers when there is no translational order. Besides that for the sake of simplicity we omitted parameters with $\lambda_1 = \lambda_2 = 2$, $\lambda = 2, 4$, $|\nu| = 0, 1$, because account of these terms leads only to the numeral renormalization of the coefficients while the structure of expressions remains unchanged.

Quite a similar procedure gives us an expression for steric component of the pseudopotential in the form analogous to (7). Employment of the standard procedure for the calculations of steric pseudopotential faces some difficulties arising from the non-analyticity of Mayer function (6) in the range of integration (5).

Following a method from[17] we consider the integral

$$I_\nu(o_1, o_2) = \int \mathrm{f}_{\mathrm{M}}^{ster}\,(\mathbf{r}, o_1, o_2)\, \exp(2\pi i\nu z/d)\, d\mathbf{r} = -\int_{\Omega_{excl.}} \exp(2\pi i\nu z/d)\, d\mathbf{r}. \quad (10)$$

Direct calculations show that steric energy parameters coincide up to a constant with the coefficients of $I_\nu(o_1, o_2)$ expansion into bipolar spheric harmonics. Using uniaxial ellipsoids as a model approximation of the real molecules share, after the calculations of the first terms in the expansion of $I_\nu(o_1, o_2)$ ($\lambda_1 = \lambda_2 = 0, 2,\ \nu = 0, 1$) under fixed molecular orientations we obtain the following expressions for isotropic and anisotropic energy parameters:

$$\begin{aligned}
V^{00\,ster}_{00,1} &= \frac{4}{3}\rho v^*\, kT\left[2\Delta\, u(4\pi a/d,\, 0) + (1+\Delta)^2\, u\big((\Delta+1)2\pi a/d,\, 0\big)\right] \\
V^{20\,ster}_{00,1} &= -\frac{4}{3}\rho v^*\, kT\,(1+\Delta)^2\left[u(4\pi a/d,\, 0) - u\big((\Delta+1)2\pi a/d,\, 0\big)\right] \\
V^{22\,ster}_{00,0} &= -\frac{4}{3}\rho v^*\, kT\,(\Delta-1)^2\,, \\
V^{22\,ster}_{00,1} &= -\frac{4}{3}\rho v^*\, kT\,(\Delta-1)^2\, u(4\pi a/d,\, 0)\,, \qquad (11)
\end{aligned}$$

where introduced are: $\Delta = \frac{c}{a}$ is the anisometry of molecular shape ($a < c$ are the molecular ellipsoid semi-axis), $v^* = \frac{4}{3}\pi a^3$ and

$$u(x, 0) = \frac{3\,(\sin x - x\cos x)}{x^3}\,. \quad (12)$$

So, proceeding to the real order parameters $S_{\lambda 0,\nu} = Re\,\eta_{\lambda 0,\nu}$, pseudopotential (5) can be presented as:

$$\begin{aligned}
-\frac{U(z,\,\beta)}{kT} &= \frac{1}{t}\left[S_{20,0}D^2_{00}(\beta) + 2\big(\delta_{tr}\, S_{00,1} + \delta_{cr}\, S_{20,1}\big)\cos\frac{2\pi z}{d} + \right. \\
&\left. + \ 2\big(\delta_{mix}\, S_{20,1} + \delta_{cr}\, S_{00,1}\big)\cos\frac{2\pi z}{d}\, D^2_{00}(\beta)\right]\,, \qquad (13)
\end{aligned}$$

where introduced are:

$$t = \frac{kT_{\hbar\omega_0}}{\frac{\pi}{60}\,\rho\,\frac{1}{r^3_{\perp_0}}\,(\Delta\alpha)^2 + \frac{4}{3}\,\rho v^*\,kT_{\hbar\omega_0}\,(\Delta - 1)^2} \tag{14}$$

is the reduced temperature, $kT_{\hbar\omega_0} = kT/\hbar\omega_0$, $\delta_{tr} = V^{00}_{00,1}/V^{22}_{00,0}$, $\delta_{cr} = V^{20}_{00,1}/V^{22}_{00,0} = V^{02}_{00,1}/V^{22}_{00,0}$ and $\delta_{mix} = V^{22}_{00,1}/V^{22}_{00,0}$ are the pseudopotential parameters, $V^{\lambda_1\lambda_2}_{0\,0,\,\nu} = V^{\lambda_1\lambda_2\,disp}_{0\,0,\,\nu} + V^{\lambda_1\lambda_2\,ster}_{0\,0,\,\nu}$ are defined in accordance with (9), (11).

The expression for the pseudopotential (13) differs from the well known results[17, 19, 20, 21] because of the presence of cross terms that in ranks of phenomenological theory describe the interaction between orientational and translational order parameters. This terms appear in microscopical description when a phase axial symmetry is accounted, in our model this symmetry is caused by one-dimensional translational mode (see also[22]).

Minimization of the ordered state free energy

$$g = \frac{G}{NkT} = \frac{1}{2t}\left(S^2_{20,0} + 2\,\delta_{tr}\,S^2_{00,1} + 4\,\delta_{cr}\,S_{00,1}\,S_{20,1} + 2\,\delta_{mix}\,S^2_{20,1}\right) -$$

$$- \ln\left(\frac{1}{d}\int_0^d\int_0^1 \exp(-\mathrm{U}(z,\,\beta)/kT)\,dz\;d\cos\beta\right) \tag{15}$$

on the order parameters $S_{\lambda 0,\nu}$ gives us a set of self-consistency equations

$$\left\{\frac{\partial g}{\partial S_{\lambda 0,\nu}}\right\}_{\lambda 0,\nu} = 0\,, \tag{16}$$

that defines the equilibrium values of order parameters.

RESULTS AND DISCUSSIONS

The typical results of the numerical solutions of the self-consistency equations (16) are shown in the Fig.1,2. In the first case (Fig.1, a-c) the obtained dependences describe a variety of well known phase transitions in liquid crystals. The second case (Fig.2,a-b) corresponds to the ordering of plastic crystals' type. Peculiarity of this result is that degeneracy on the primary axis orientation is removed after translational order has been formed, thus non-zero orientational order

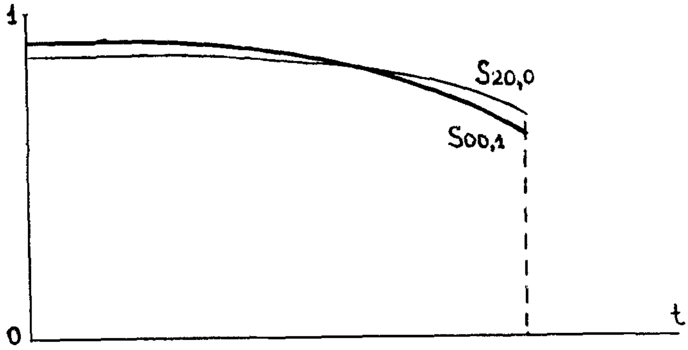

FIGURE 1a Temperature dependences of $S_{00,1}$ and $S_{20,0}$ for LC ρ =0.108, d/c=1.4, Δ=5, $\overline{\alpha}/\Delta\alpha$=0.05

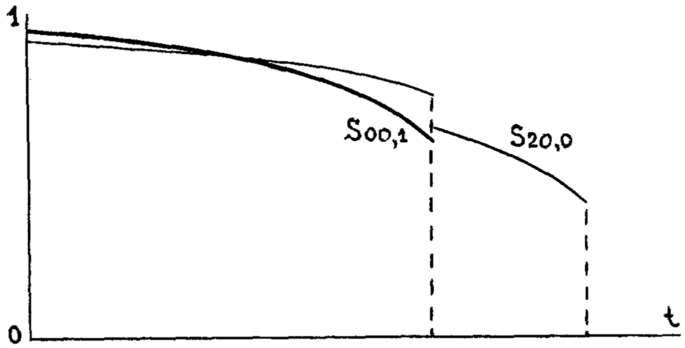

FIGURE 1b Temperature dependences of $S_{00,1}$ and $S_{20,0}$ for LC ρ =0.1, d/c=1.2, Δ=7, $\overline{\alpha}/\Delta\alpha$ =1.0

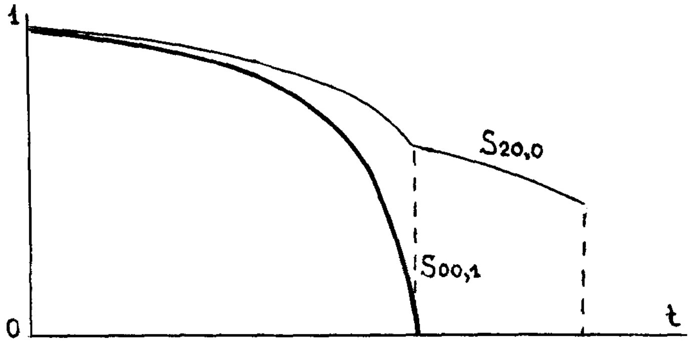

FIGURE 1c Temperature dependences of $S_{00,1}$ and $S_{20,0}$ for LC ρ =0.28, d/c=1.4, Δ=7, $\overline{\alpha}/\Delta\alpha$=0.05

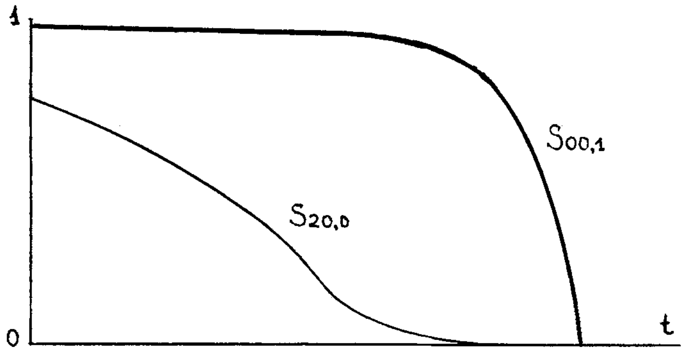

FIGURE 2a Temperature dependences of $S_{00,1}$ and $S_{20,0}$ for AF $\rho = 0.7$, $d/c = 1.08$, $\Delta = 1.18$, $\overline{\alpha}/\Delta\alpha = 1$

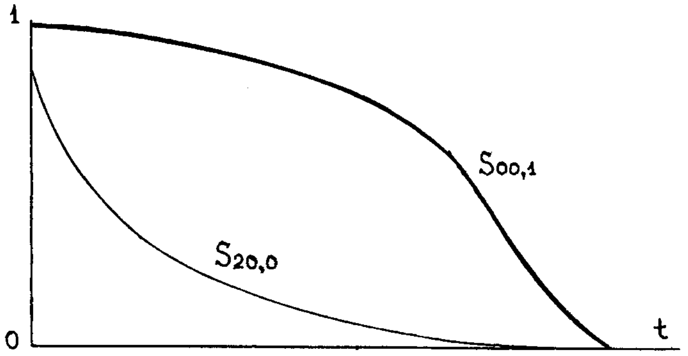

FIGURE 2b Temperature dependences of $S_{00,1}$ and $S_{20,0}$ for AF $\rho = 0.7$, $d/c = 1.08$, $\Delta = 2$, $\overline{\alpha}/\Delta\alpha = 2$

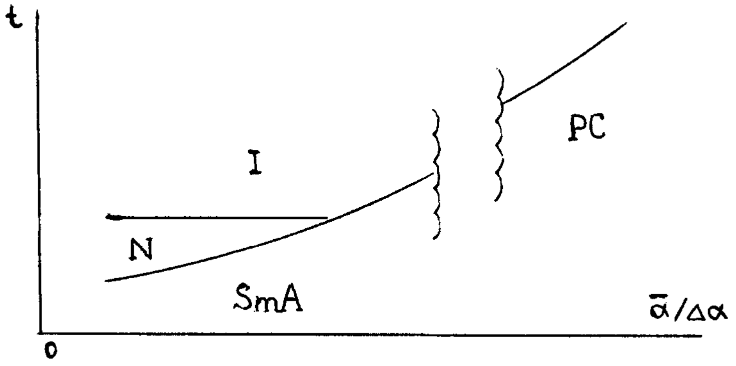

FIGURE 3a Phase diagram for mesogenic compounds $\rho = 0.28$, $d/c = 1.4$, $\Delta = 7$

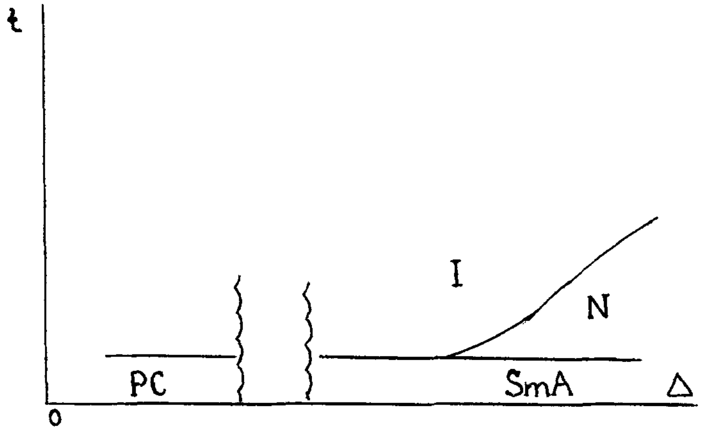

FIGURE 3b Phase diagram for mesogenic compounds ρ=0.1, d/c=1.4, $\bar{\alpha}/\Delta\alpha$=0.05

parameters occur. This is formal consequence of the presence of cross terms in (13), which in phenomenological models are considered as order parameter generators and can cause a number of abnormal effects in the sequence of phase transitions (e.g, reentrant smectic polymorphism in LC[23, 24]). It is necessary to mention that while in liquid crystals only first order orientational phase transitions can occur, the presence of the one–dimensional translational order changes situation.

For model parameters corresponding to C_{70} and "calamitic" fullerenes the temperature dependences of $S_{20,0}$ are rather different. For some types of fullerides that difference could yields to ambiguities in experimental investigation of the phase transition characteristics.

The more detailed analysis of the results obtained permits us to note a significant influence of interaction anisotropy on the phase diagram (Fig.3,a,b). When intermolecular potential anisotropy is strong the LC type of ordering occurs, and the area of translationally disordered state existence depends from the ratio of isotropic and anisotropic energy parameters. This ratio is a factor that determines the type of mesogenic state. When the interaction anisotropy is weak, the ordering of PC type occurs in molecular system.

Phase diagrams are in qualitative agreement with experimental tendencies found for SmA LC[17, 19, 20, 21], and allow us to introduce molecular level factors which determine mesogenic characteristics of van–der–Waals molecules. It is important to note that employment of the results obtained for predictions of real compounds' mesogenic properties is to be complemented with effects of conformational mobility that is usual for mesogenic molecules and sometimes drastically change the phase diagrams (see, e.g.,[14, 25, 26]).

Using the expression (14) we obtain phase diagrams in real temperature scale and the results of phase transition temperature calculations for various values of model parameters.

In particular, for model parameters corresponding to C_{70} $kT_{\hbar\omega_0 PC-I} = 14,6 \cdot 10^{-5}$. Assuming in accordance with[27, 28] estimates for ionization potential $\hbar\omega_0 \approx 8\,\mathrm{eV}$, polarizability tensor components $\overline{\alpha} \approx 383\mathrm{a.u.}$ and $\Delta\alpha \approx 27\mathrm{a.u.}$, we obtained $T_{PC-I} \approx 50\mathrm{K}$, that is much lower than the experimental result for thermal stability of condensed C_{70} state. In the framework of the presented model for C_{70} fullerene condensed state this result can be interpreted as thermal instability of one–dimensional ordered structure under $T \geq 50\,K$. For real 3–dimensional crystals this result means that "defective closely packed layers with high degree of stacking disorder" can appear as it was stated in the experimental work[18*]. It is necessary to mention that quantitative estimations can be improved to the considerable degree provided the additional information on the C_{70} fullerene appear. Also, molecular model employed can be improved, particularly by the account of 3–dimensional structure of C_{70} fullerene.

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[*] Here we shall not provide any analysis of physical reasons for such an unusual result, note only a probable influence of the impurities including those left after the process of synthesis (see, for instance[29]).

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