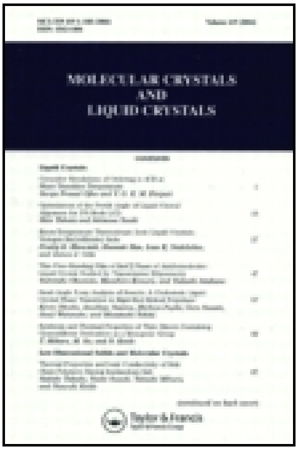

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

The Lyotropic Smectic Phase on the Flory Lattice

Maciej Wneka [a] & Jozef K. Moscicki [b]

[a] ABB Corporate Research, ul. Starowislna 13A, 31-038, Krakow, Poland

[b] Smoluchowski Institute of Physics, Jagellonian University, ul. Reymonta 4, 30-059, Krakow, Poland

Version of record first published: 27 Oct 2006

To cite this article: Maciej Wneka & Jozef K. Moscicki (2001): The Lyotropic Smectic Phase on the Flory Lattice, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 365:1, 789-802

To link to this article: http://dx.doi.org/10.1080/10587250108025358

Mol. Cryst. and Liq. Cryst., 2001, Vol. 365, pp. 789-802
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint,
a member of the Taylor & Francis Group.
Printed in the USA

The Lyotropic Smectic Phase on the Flory Lattice

MACIEJ WNEK[a] and JOZEF K. MOSCICKI[b]

[a]*ABB Corporate Research, ul. Starowislna 13A, 31–038 Krakow, Poland and*
[b]*Smoluchowski Institute of Physics, Jagellonian University, ul. Reymonta 4, 30–059 Krakow, Poland*

The Flory lattice approach for rod-like molecules is extended to encompass the position-restricted (smectic-A) phase. The phase equilibria conditions are obtained from equity of relevant chemical potentials, together with minimization conditions of the Gibbs potential with respect to the system orientational (Flory disorder index, y) and positional (translational disorder index, ξ in the smectic phase) order.

Keywords: phase transition; smectic phase; lattice model

THEORY

The model of phase equilibria developed here describes rod-like molecules dispersed in a solvent. The solution is modeled by a cubic lattice filling out the space with molecules approximated by trains of subsequent cuboids. The molecule elongation equals to the number of cuboids in the train, x (Fig.1). Generally, the phase equilibrium between two phases (1) and (2) requires equality of chemical potentials in both phases for all components:

$$\frac{(\mu_i-\mu_i^0)}{kT}\Big|_1=\frac{(\mu_i-\mu_i^0)}{kT}\Big|_2 ;1,2 = iso, nem, sm; i = slovent, solute \quad (1)$$

where *i* denotes solvent or solute, respectively, and *1,2* stand for isotropic, nematic or the smectic phase. By definition, the chemical potentials are[1,2]:

$$\begin{aligned}\frac{\mu_s-\mu_s^0}{RT}\Big|_a&=\frac{\partial G_{eq}}{\partial n_s}\Big|_a=\frac{\partial(-\ln(Z))_{eq}}{\partial n_s}\Big|_a ;\\ \frac{\mu_x-\mu_x^0}{RT}\Big|_a&=\frac{\partial G_{eq}}{\partial n_x}\Big|_a=\frac{\partial(-\ln(Z))_{eq}}{\partial n_x}\Big|_a ;\end{aligned} \quad (2)$$

where *G* is the Gibbs free energy, *Z* is the partition function, and *T* denote the absolute temperature . The subscript "*eq*" signifies the orientational equilibrium of rods in the nematic or orientational and positional equilibrium in the smectic phase, *a* denotes isotropc, nematic or an smectic phase. The partition function, *Z*, can be factorized [1,3,4]:

$$Z = Z_{comb}\, Z_{or}\, Z_{int} \;;. \quad (3)$$

where the three factors are: the combinatory or steric factor Z_{comb}, the orientational factor Z_{or}, and the factor introducing the exchange free energies of interaction between the solvent and rods, Z_{int}.

The essential for this model is the Z_{comb} term. For nematic and isotropic phases the model was solved by Flory and followers [1,2]. Here we present only the modifications introduced by the smectic phase, i.e., by layers formation whereas all the basic assumptions concerning the lattice, rod-like molecules, solvent molecules remain unchanged [1,2].

The smectic layer is introduced into the lattice model as two impenetrable infinite planes, perpendicular to the nematic order axis, Z (Fig.1).

The distance between planes which equals to thickness of the smectic layer, *d*.

$$d=m+x=x(1+m/x)=x\xi; \quad (4)$$

where x is the model molecule elongation and m denotes number of XY slices along the Z axis where the molecule (its center) can be placed.

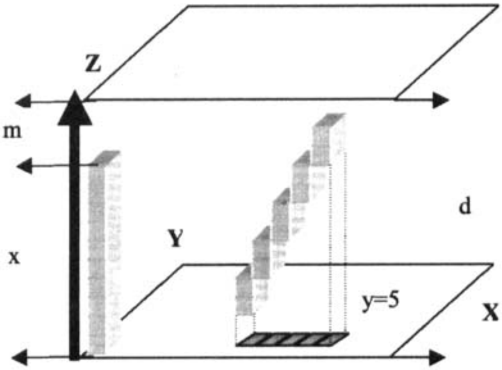

FIGURE 1

The model smectic layer. The layer thickness, $d = x + m$. Note the orientational disorder described by the projection of the model rod onto the *XY* plane, $y=5$ [1,2].

In other words if one plots the molecules center of mass distribution function (σ) along the **Z** axis one obtains a square wave function with a period d which is a non-zero constant on distance m and zero otherwise (Fig.2).

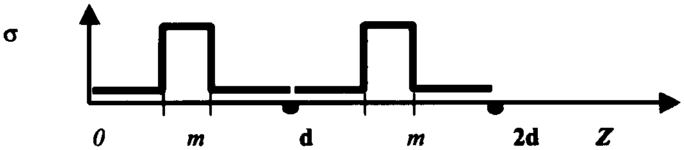

FIGURE 2.

Density distribution of centers of mass of the model molecules along the Z axis.

Index ξ can be thus understood as a positional disorder index. The higher values of ξ (*m*) the more diffusional freedom the molecule has. On the other side, for $\xi=1$,i.e., $m=0$, along the **Z** axis the system transfers into a positionally perfectly ordered solute like a 1D crystal phase.

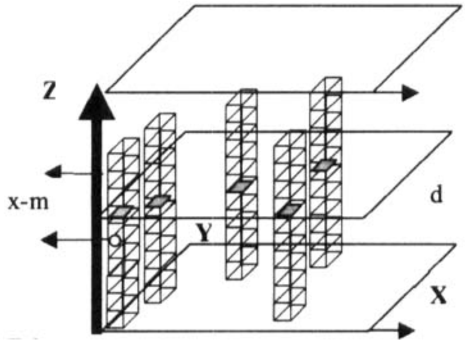

FIGURE 3.

In-plane **XY** density. The *x-m* **XY** slices in the middle of the layer are penetrated by all molecules.

As it was done by Flory also here the molecules distorted from the ideal orientation are broken into *y* segments (Fig.1) thus *y* describes orientational disorder of the system (a disorder parameter). All of the segments are parallel to the **Z** axis. One can evaluate also the segment (sub-molecule) distribution function along the **Z** axis. There are two different regions within the layer . The middle region of thickness *x-m* that is penetrated by all the molecules and two symmetric border regions of thickness *m*, with the density decreasing linearly towards the layer wall and reaching zero value at the walls. This linear decreasing from ρ_{max} to 0 is a consequence of uniform distribution of centers of mass between *m* middle **XY** layers and in the model is approximated by the average density (Fig.4):

$$\rho_{av} = 1/2\rho_{max} \tag{5}$$

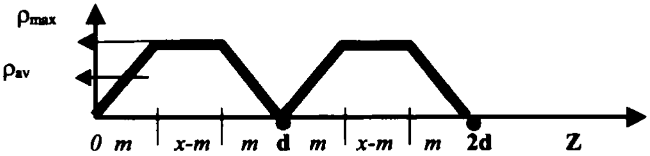

FIGURE 4.

In-plane density wave (a number of sites in a XY plane occupied by molecules divided by the total number of sites in a XY plane):

Now one can proceed with the Flory procedure remembering that we have now two different in plane density regions along the **Z** axis Fig.3,4 [1,2]:

$$x\text{-}m \text{ slices with } \rho_{max} \qquad (6)$$

$$2m \text{ slices of } \rho_{av} = 1/2\rho_{max}$$

Additionally one has to take into account that the centers of mass of all molecules have to lay in one of the middle *m* XY planes.

Combinatory or "steric" factor, Z_{comb}.

Following the Flory approach we abandon correlation between segments when considering their placement on the lattice. Let us assume further that there are n_x molecules placed on the n_0 available sites (the layer volume). All of the remaining space, n_s:

$$n_s = n_0 - n_x x, \qquad (7)$$

is filled by cuboid solvent molecules, occupying one lattice site each. The volume concentration of the species are defined as follows:

$$v_x = \frac{n_x \cdot x}{n_0}; \qquad v_s = \frac{n_s}{n_0}; \qquad (8)$$

for rods and solvent respectively. The Z_{comb} is then defined as a product over j of a number (ν_{j+1}) of ways how the "$j+1$"th molecule can located on the lattice provided that j molecules are already positioned there.

$$Z_{comb} = \frac{1}{n_x!} \prod_{j+1=1}^{n_x} v_{j+1} \tag{9}$$

The structure of the molecules and their positional restrictions are described by index y and parameter m (ξ). As we have mentioned, the rod is divided into y segments located in neighboring elementary columns parallel to **Z**-axis (Fig.1).

Since all of the rods penetrate the middle high density region and also stick out of it, the rod is partitioned into the two density regions. k_1x sites of the rod will be located in the high density region(Fig.3,4):

$$k_1=(x-m)/x \tag{10}$$

whereas the remaining sites will be located in the lower density region:

$$k_2=x-k_1=m/x \tag{11}$$

The scaling factors k_1,, k_2 describe also the distribution of the segments, i.e.,k_1y out of y segments are located in high density region and k_2y in thelower density one. The first site of the $j+1^{\text{th}}$ molecule – one of its ends, lays in the low density region (Fig.1). The number of potential free sites where the $j+1^{\text{th}}$ rod can be started is:

$$2m\left(\frac{n_0}{d} - \frac{j}{2}\right) = \frac{2m}{d}\left(n_0 - jd/2\right) \tag{12}$$

Since the rod can be constructed upwards or downwards, the factor $2\ m$ in Eq.12 denotes the number of layers where the molecule can start and the second factor gives the number of free sites in **XY** plane in the lower density region.

Similarly, probabilities of finding a free site for the starting cuboid of other segments of the $j+1^{\text{th}}$ molecule are [1,3]:

$$\begin{aligned} p_1 &= \left(n_0 - jd\right)/n_0; \\ p_2 &= \left(n_0 - jd/2\right)/n_0; \end{aligned} \tag{13}$$

for regions of high (p_1) and low (p_2) density respectively. Possibility of adding on next cuboids to the first one in order to build-up the whole segment is given by the conditional probabilities of finding an empty site directly in contact with the cuboid already placed [1,2]:

$$p_{c1} = \frac{(n_0 - jd)}{(n_0 - jd(1-\bar{y}/x))}; \qquad p_{c2} = \frac{(n_0 - jd/2)}{(n_0 - jd/2(1-\bar{y}/x))}; \tag{14}$$

where indexes *1,2* again number the two distinctive density regions.

The distribution of the segments between the two density regions (1,2) is given by Eq.10,11 thus the v_{j+1} can be written as follows(Eq.13,14):

$$\frac{v_{j+1}}{n_0} = \frac{2m}{d}\frac{(n_0 - jd/2)}{n_0}\left(\frac{(n_0 - jd/2)}{n_0}\right)^{(y-1)m/x}\left(\frac{(n_0 - jd)}{n_0}\right)^{y(x-m)/x} \cdot \left(\frac{(n_0 - jd/2)}{(n_0 - jd/2(1-\bar{y}/x))}\right)^{(x-y)m/x}\left(\frac{(n_0 - jd)}{(n_0 - jd(1-\bar{y}/x))}\right)^{(x-y)(x-m)/x} \tag{15}$$

Applying Eq.15 to Eq.9 and expanding the factorials within the Stirling approximation leads to final formula for the Z_{comb}:

$$\begin{aligned} \frac{-\ln(Z_{comb})}{n_0} = {} & \frac{v_x}{x}\left[(\bar{y}-1) + \ln\left(\frac{v_x}{x}\right) - \ln\left(\frac{2m}{d}\right)\right] + \\ & + \frac{x-m}{d}\left(1-\frac{v_x}{x}d\right)\ln\left(1-\frac{v_x}{x}d\right) + \frac{2m}{d}\left(1-\frac{v_x}{2x}d\right)\ln\left(1-\frac{v_x}{2x}d\right) - \\ & - \frac{2m}{d}\left(1-\frac{v_x}{2x}d(1-\bar{y}/x)\right)\ln\left(1-\frac{v_x}{2x}d(1-\bar{y}/x)\right) - \\ & - \frac{x-m}{d}\left(1-\frac{v_x}{x}d(1-\bar{y}/x)\right)\ln\left(1-\frac{v_x}{x}d(1-\bar{y}/x)\right); \quad d = x+m; \end{aligned} \tag{16}$$

Eq.16 reduces to the Z_{comb} of the nematic phase for m=x [1].

Orientational factor, Z_{or}

The inclined rod is described by the independent disorder index, y, defined as surface occupied by the rod projection on the XY expressed in the lattice units (Fig.1). For perfectly ordered rod we have:

$$\bar{y} = y = 1; \tag{17}$$

where the bar denotes the ensemble average. For the isotropic phase the molecules orientations are uniformly distributed over the unit sphere and the condition y=x is fulfilled [1].

Since the layer formation does not influence directly the orientational distribution of the model rods, the Z_{or} remains the same is for the model nematic phase and can be expressed as follows [1,3]:

$$-\ln(Z_{or}) \cong -2n_x \ln(\bar{y} - 1)\,; \tag{18}$$

The above approximated expression is equivalent to assuming a uniform orientational distribution of rods over a solid angle defined by the average value of y [1].

Solute-Solvent interactions, Z_{int}.

The interactions between the rods and solvent molecules are introduced in order to follow temperature dependence of the phase situation and are based basing on the usual van Laar model [1,3]:

$$Z_{int} = \exp(-\theta n_0 v_x v_s);\, \theta = \frac{\chi}{kT}\,; \tag{19}$$

where v_i are the concentrations of solute (i=x) and solvent (i=s), θ is the model temperature and χ the interactions constants.

Phase Equilibria Conditions.

The conditions for any biphasic equilibrium are stipulated by simultaneous equity of the chemical potentials of the same component in both phases, Eq.2. The Gibbs potential (Eq.2) is obtained by combining Eq.17,18,19 with Eq.3. At the same time in the nematic phase there must be the orientational equilibrium of rods, which requires [1]:

$$\left.\frac{\partial(G/kT)}{\partial \bar{y}}\right|_{nem} = 0\,; \tag{20}$$

with the second derivative being greater than zero. Solution of Eq.19 provides the equilibrium value of $\bar{y}$ for the nematic phase.

For the smectic phase we have the orientational and positional equilibria, respectively:

$$\left.\frac{\partial(G/kT)}{\partial \bar{y}}\right|_{sm} = 0; \quad \left.\frac{\partial(G/kT)}{\partial m}\right|_{sm} = 0; \tag{21}$$

It remains to solve numerically the set of equations Eq.1,20,21 in the various cases of interest.

RESULTS.

Firstly we evaluated behaviour of the model Gibbs potential as functions of, ξ (m) and y to verify conditions required by existence of the smectic phase (suitable minima of the Gibbs function, Eq.20,21. In Fig.5 plots of $G=G(\xi;x,v_x,\theta,y)$ vs. ξ for $x=16$, $v_x=0.75$, 0.6 and 0.55 at $\theta=0$ are shown (athermal conditions). The phase is at orientational equlibrium, $\left.\frac{\partial(G/kT)}{\partial y}\right|_{sm} = 0$ is fulfilled along the curves..

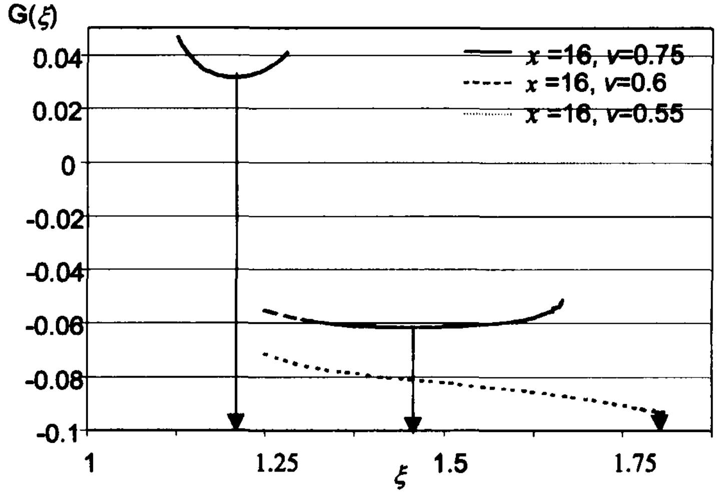

FIGURE 5.

The Gibbs potential, G, as a function of ξ for model rods $x=15$ and three different concentrations.

One can observe dramatic shift of the minimum of G in ξ with decreasing concentration of rods in the system. The lower the concentration the lower the positional order in the phase (higher ξ values). At a certain critical concentration, $v^{cr}{}_x$, the minimum in ξ does not appear any more thus the smectic phase cannot exist.

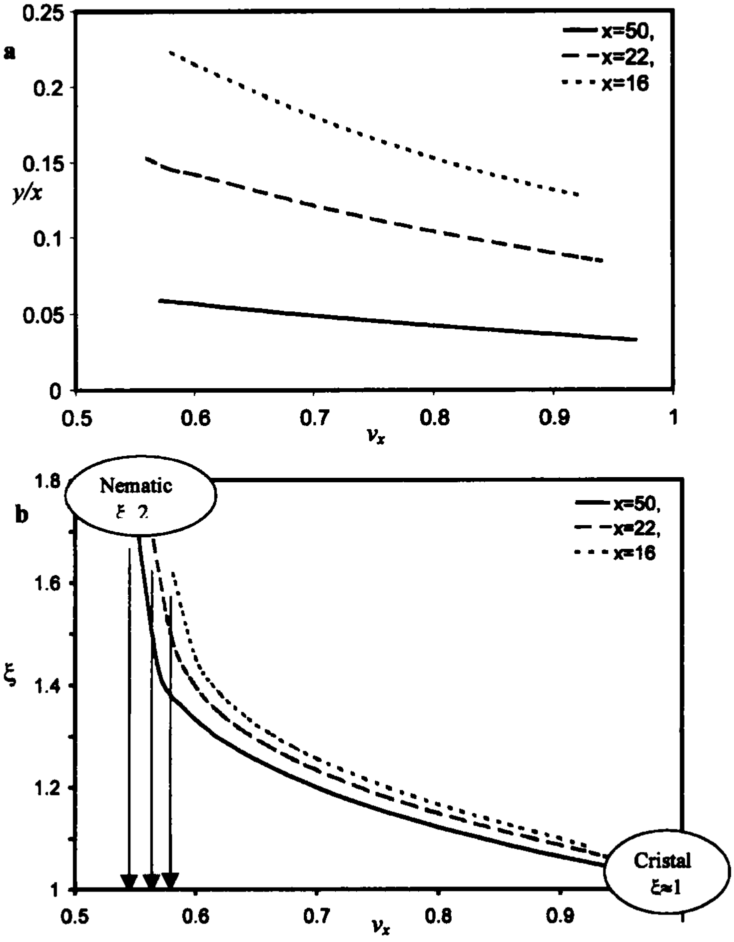

FIGURE 6.

(a) orientational disorder parameter, y/x and (b) positional order parameter, ξ, vs. v_x for different rods elongation, x = 16, 22, and 50. Arrows indicate v_x^{cr} at which the smectic phase disappears.

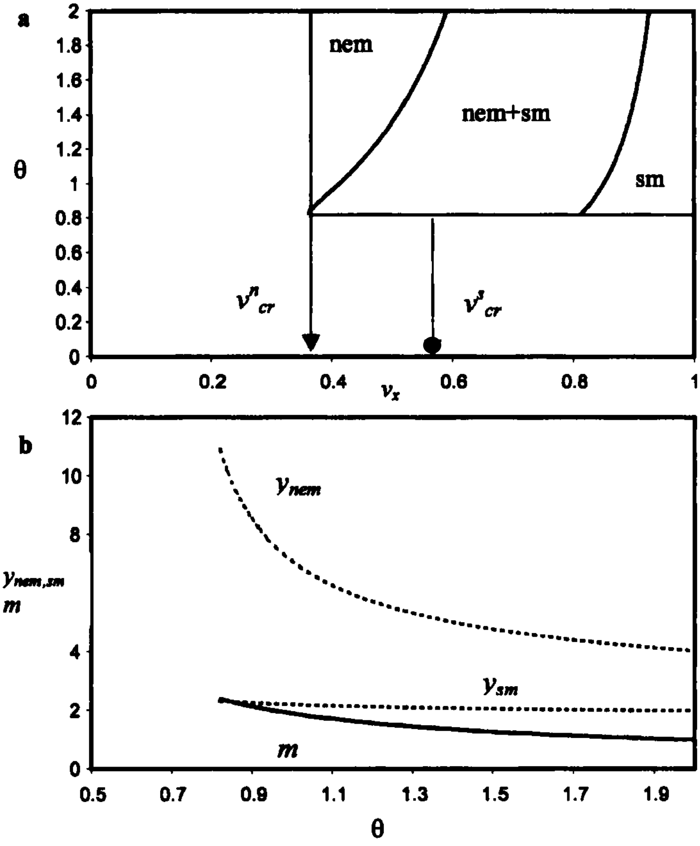

FIGURE 7.

(a) θ vs. v_x phase diagram for $x = 22$, and (b) the system equilibrium order parameters as a function of θ in the nematic and smectic phases.

The equilibrium values of y/x and ξ vs. concentration for different rods elongation are shown in Fig.6. The plots show that for more elongated rods the smectic phase appears at lower concentrations (v_x^{cr}) and is more ordered positionally and orientationally (Fig.6). The translational equilibrium condition in the model is possible only for v_x□0.5.

We also found the critical minimum value of x for formation of the stable smectic phase is $x^s_{cr}=8.57$, in case of the nematic phase $x^n_{cr}=7.76$ [1,2]. The rod elongation required by the smectic phase is about 10% bigger than for the nematic phase.

Finally we calculated the phase diagrams for coexistance of the nematic and smectic phase. A sample diagram for $x=22$ is shown in Fig.7.

First observation led to a conclusion that the nematic-smectic phase transition occurs only in presence of strong solute-solvent interactions (θ) or low temperature (Eq.19). Note the very high level of ordering (Fig.7b) in the smectic system. The nematic-smectic A phase transition occurs only for the highly ordered nematic phase (N', [1,2]) within the high θ range. In Fig.7 arrows indicate the critical concentration for existence of the nematic phase $v^n_{cr}=0.3525$, and $v^s_{cr}=0.566$ for the smectic phase.

CONCLUSIONS AND MODEL LIMITATIONS.

The lyotropic smectic phase can be generated within the Flory lattice framework, given that solution is sufficiently concentrated, and that rods are sufficiently long The model of the lyotropic Smectic A phase is consistent and fulfills assumed boundary conditions:

$\xi=1$ ($m=0$) -> 1-D cystal

$\xi=2$ ($m=x$) -> the nematic phase

already for the partition function, which confirms its consistency. Within the model we were able to calculate the critical alongation required to obtain the smectic phase: $x_{cr}=8.57$. One can also calculate desired phase diagrams within the three phases: isotropic, nematic smectic A. The model, however, bases on very severe restrictions on the density distribution function of rods (Fig.2) which induce certain limitations. The (x-m) fraction of all XY planes are penetrated by all n_x molecules. Thus the in-XY plane maximum density (Fig.4) is:

$$\rho_{\max} = \frac{n_x}{n_0 /(x+m)} = v_x \xi < 1$$

so

$$v_x < \frac{x}{x+m} = \xi^{-1}$$

$$\xi_{\max} < v_x^{-1} \quad or \quad m_{\max} < \frac{x}{v_x} - x$$

These conditions play a role for very high concentrations and disables possibility of considering thermotropic systems (v_x~1). "Smoothening" of the density distribution function (sine wave) should improve the results. One has to note that the phase transitions obtained in the model result only from steric interactions between molecules (plus isotropic solute-solvent ones). In real systems the soft type interactions play a big role and one may try to introduce them in a similar way as Flory and Ronca did for nematic phase [5,6].

Summarizing, the Flory can be extended on the position restricted phases and enables to estimate the steric interactions between the model molecules which are usually very difficult to calculate in other way [6,7].

References

[1] P, J. *Flory, Proc. Roy. Soc. (London),* **A234**, 73 (1956).
[2] P.J. Flory and G. Ronca, *Mol. Cryst. Liq. Cryst.*, **54**, 289 (79).
[3] Maciej Wnek and Jozef K. Moscicki, *Phys. Rev. E,* **56**, 1666 (96).
[4] Maciej Wnek and Jozef K. Moscicki, *Phys. Rev. E,* **59**, 535 (99).
[5] P.J. Flory and G. Ronca, *Mol. Cryst. Liq. Cryst.*, **54**, 311 (79).
[6] W.L. McMillan, *Phys. Rev. A,* **4**, 1238 (71).
[7] G. F. Kventsel, G.R. Luckhurst, H.B. Zewdie, *Mol. Phys.*, **56**, 589 (85).