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## Liquid Crystals

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### Liquid crystalline order in fluids with hydrogen bonds

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# Liquid crystalline order in fluids with hydrogen bonds

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A mean-field theory of liquid crystalline ordering in hydrogen bonded liquids is proposed. It is shown that hydrogen bonds may cause liquid crystalline ordering. For a simple example of spherical molecules containing hydrogen bonding functional groups the existence of a nematic phase is predicted and the thermodynamics of the phase transition is discussed.

## 1. Introduction

It is well known [1] that liquid crystalline ordering is caused by the microscopic anisotropy of molecular interactions. The most common examples are steric repulsion and dipole-dipole interaction. They cause liquid crystalline mesophases in liquids with molecules that have highly non-spherical shapes and large dipole (or higher order) moments. There are, however, other possible candidates for the role of a driving force for the liquid crystalline ordering. One of them is the hydrogen bonding. This interaction often leads to the formation of interesting structures, the famous complex structure of liquid water being an example. However neither water nor other liquids consisting of small hydrogen bonded molecules have liquid crystalline mesophases. One reason may be the complex geometry of the hydrogen bonded aggregates in most of liquids studied to date, which is unlikely to withstand a long range order. One is tempted to suppose that a simpler structure of aggregates may lead to the liquid crystalline ordering. The role of the geometry of hydrogen bonded aggregates in the liquid crystalline ordering was qualitatively discussed long ago [2]. It is known that phenolic compounds are not mesomorphic, but substituting of a phenolic hydrogen by an alkyl group may result in mesomorphic liquid. One of the reasons is that hydrogen bonds in phenols encourage a non-linear molecular arrangement, which prevents the liquid crystalline ordering. On the other hand, when aggregates have a simple geometry, the hydrogen bonds increase the tendency to the liquid crystalline ordering. For example, hydrogen bonded 4-*n*-alkoxybenzoic acids have liquid crystalline phases, but the corresponding alkyl esters have not [2]. In 1989 Kato and Fréchet found [3,4] that intermolecular hydrogen bonds between pyridine and carboxylic acid functional

groups can give rise to mesogenic structures. Since then a number of systems have been observed [5-15] where the hydrogen bonds supposedly play the major part in the mesophase formation. This effect may be important for liquid crystal science and technology. Indeed it is possible to synthesize molecules with a given number and distribution of the hydrogen bonding functional groups. Thus, one could design, in principle, fluids having a desired phase diagram. Moreover, the number of hydrogen bonds formed is sensitive to temperature, pH and other factors. Therefore, the phase diagram might be both interesting and easily controllable.

However up to now there is no theory of the hydrogen bonded liquid crystals that would predict their mesogenic properties basing on the microscopic parameters (shape, dipole moments, equilibrium constants of hydrogen bonds, etc.). An approach to such theory is discussed in the present paper.

In the next section we will introduce the general way of extending the mean-field theory of liquid crystals to account for the contribution of hydrogen bonds. The results of the application of this theory to various systems depend on the details of the molecular structure and interactions. They will be addressed in the subsequent publications. In this paper the general considerations will be illustrated in the third section by a simple example of isotropic molecules with highly anisotropic H-bonding. Besides illustrative purposes, this example is interesting because it predicts that hydrogen bonds *alone* may cause liquid crystalline ordering in otherwise isotropic liquids.

## 2. General theory

In the mean-field approximation the system's partition function can be factorized and the free energy can be written as the sum

$$f = -TS_{\text{orient}} + f_{\text{phys}} + f_{\text{H}}, \quad (1)$$

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where  $S_{\text{orient}}$  is the orientational entropy of molecules,  $f_{\text{phys}}$  includes ideal gas part and 'physical' interactions [16] (i.e. all interactions but hydrogen bonding), and  $f_{\text{H}}$  is the contribution of the network of hydrogen bonds. Equation (1) differs from the mean-field equations for the non-bonded crystals [1] by the extra term  $f_{\text{H}}$ .

Let  $\mathbf{p}$  be a unit vector defining orientation of a chosen molecule. Let  $g(\mathbf{p})$  be the orientation distribution function, so the probability that a molecule has an orientation in a spherical angle  $d\Omega$  is  $g(\mathbf{p})d\Omega$ . Therefore

$$\int g(\mathbf{p})d\Omega = 1. \quad (2)$$

In the mean field approximation we express the right hand side of equation (1) in terms of the orientation distribution function. Minimizing then equation (1) with respect to  $g(\mathbf{p})$  we obtain both free energy and the equilibrium orientation distribution.

The orientation entropy of a molecule is [1, 17]

$$-k \int g(\mathbf{p}) \ln [4\pi g(\mathbf{p})] d\Omega,$$

where  $k$  is the Boltzmann constant. The dependence of the 'physical' part of the free energy can be obtained for dilute solutions in the framework of the Onsager's virial expansion [1, 17]. There are generalizations of the Onsager approach allowing one to estimate  $f_{\text{phys}}$  for more concentrated solutions [18].

Let us discuss now the contribution of hydrogen bonds  $f_{\text{H}}$ . Recently [19–22] a mean-field theory of H-bonded liquids was proposed. Its results are consistent with those of association models [16], but are more easily extended to the complicated case of a developed network. This theory displays rather unexpected success in predicting phase diagrams and thermodynamic properties of various fluids [22–24], and we will extend this approach to orientationally ordered liquids. It was shown in [19–22] that  $f_{\text{H}}$  can be expressed in terms of equilibrium constants describing H-bond formation, which are in turn, proportional to the probabilities that proton-donor and proton-acceptor groups are neighbours. For anisotropic liquids we must introduce the orientation dependence of these probabilities, which can be easily done in the mean field approximation.

Let  $K_{12}$  be the equilibrium constant describing the hydrogen bond formation between two neighbouring molecules 1 and 2 with orientation vectors  $\mathbf{p}_1$  and  $\mathbf{p}_2$ , and  $\mathbf{t}$  be the unit vector directed from the centre of the molecule 1 to the centre of the molecule 2. Let  $R(\mathbf{p}_1, \mathbf{p}_2, \mathbf{t})$  be the probability of hydrogen bond formation between them at the given orientation  $(\mathbf{p}_1, \mathbf{p}_2, \mathbf{t})$ . If  $g_{12}^{(2)}(\mathbf{p}_1, \mathbf{p}_2, \mathbf{t})$  is the pairwise correlation function (the probability that a

molecule has orientation  $\mathbf{p}_1$  if its neighbour has an orientation  $\mathbf{p}_2$ ) then  $K_{12}$  is proportional to

$$\int d\Omega_1 d\Omega_2 d\Omega_t R(\mathbf{p}_1, \mathbf{p}_2, \mathbf{t}) g_{12}^{(2)}(\mathbf{p}_1, \mathbf{p}_2, \mathbf{t}), \quad (3)$$

where  $d\Omega_1$ ,  $d\Omega_2$  and  $d\Omega_t$  are the spherical angles associated with the vectors  $\mathbf{p}_1$ ,  $\mathbf{p}_2$  and  $\mathbf{t}$ .

Now we will make some assumptions concerning  $R(\mathbf{p}_1, \mathbf{p}_2, \mathbf{t})$  and  $g_{12}^{(2)}(\mathbf{p}_1, \mathbf{p}_2, \mathbf{t})$ . First, in the spirit of the mean field theory, we will substitute the pairwise correlation function  $g_{12}^{(2)}(\mathbf{p}_1, \mathbf{p}_2, \mathbf{t})$  by the product of unary functions

$$g_{12}^{(2)}(\mathbf{p}_1, \mathbf{p}_2, \mathbf{t}) = g_1(\mathbf{p}_1)g_2(\mathbf{p}_2)h_{12}(\mathbf{t}). \quad (4)$$

The function  $R(\mathbf{p}_1, \mathbf{p}_2, \mathbf{t})$  describes the orientation dependence of the hydrogen bond. It is particularly simple if the H-bond is strongly orientation dependent, and forms only when the difference between the molecular orientations  $\mathbf{p}_1$ ,  $\mathbf{p}_2$  and the vector  $\mathbf{t}$  does not exceed some small spherical angle  $\omega$  ('stiff' bond). This is indeed the case for the carboxylic acid-like bonds [25]. If  $\omega \ll 4\pi$ , then

$$R(\mathbf{p}_1, \mathbf{p}_2, \mathbf{t}) = \omega^2 \delta(\mathbf{p}_1 - \mathbf{t}) \delta(\mathbf{t} - \mathbf{p}_2), \quad (5)$$

where  $\delta$  is the Dirac  $\delta$ -function. Therefore the constant of hydrogen bond formation is

$$K_{12} = K_{12}^{(1)}(4\pi)^2 \int g_1(\mathbf{t})g_2(\mathbf{t})h_{12}(\mathbf{t}) d\Omega, \quad (6)$$

where the coefficient is chosen in such a way that in the isotropic state the equilibrium constant of the bond formation equals its 'isotropic' value  $K_{12}^{(1)}$ .

The functions  $g_1(\mathbf{p})$  and  $g_2(\mathbf{p})$  describe the anisotropy of the molecular orientation, while the function  $h_{12}(\mathbf{t})$  describes anisotropy of their relative positions (for example, in smectics). For the simplest case of nematics  $h_{12}(\mathbf{t}) = \text{const.}$ , and equation (6) gives

$$K_{12} = K_{12}^{(1)}4\pi \int g_1(\mathbf{p})g_2(\mathbf{p}) d\Omega. \quad (7)$$

These general formulae will be illustrated by the following simple example.

### 3. Simple model

Let us consider non-polar roughly spherical molecules with a proton-donor group at the 'North pole' and a proton-acceptor group at the 'South pole'. These molecules will form rigid linear aggregates. At high temperatures the degree of hydrogen bonding is small. The aggregates are rare and short. The liquid is isotropic. As the temperature decreases, the number of aggregates and their length grows. Therefore at some temperature the transition to the ordered phase may occur. This transition is similar to the isotropic liquid–nematic transition in the

solution of rigid rods. The important feature of hydrogen bonded 'rods' is that their length is not constant, but depends on the temperature and environment.

The orientation entropy contribution to the free energy is [1, 17]

$$-TS_{\text{orient}} = nkT \int g(\mathbf{p}) \ln [4\pi g(\mathbf{p})] d\Omega, \quad (8)$$

where  $n$  is the number of molecules per unit volume,  $T$  is the temperature,  $k$  is Boltzmann's constant, and  $g(\mathbf{p})$  is the introduced above orientation distribution function. Now we shall use the simplifying assumption that the molecules are roughly spherical and non-polar. Thus the 'physical' part of their interaction does not depend on their orientation. So we can leave  $f_{\text{phys}}$  as it is: it will not affect our calculations.

### 3.1. Isotropic phase

To obtain  $f_{\text{H}}$  let us first recall the results for isotropic liquids [19]. For this case (one proton-donor and one proton-acceptor group per molecule), they are

$$f_{\text{H}} = kTn[v + 2 \ln(1 - v)], \quad (9)$$

where  $v$  is the fraction of H-bonds per unit volume. The value of  $v$  is determined by the equation

$$v = (1 - v)^2 K, \quad (10)$$

where  $K$  is the equilibrium constant describing H-bond formation.

It is easy to see that these results hold for ordered liquids, but now the equilibrium constant  $K$  depends on the relative orientation of the bonded molecules:

$$K = K_1 4\pi \int g^2(\mathbf{p}) d\Omega, \quad (11)$$

where  $K_1$  is the equilibrium constant for the isotropic liquid.

Let us recall that the equilibrium constant  $K_1$  is temperature dependent:

$$K_1 = \exp\left(-\frac{E_0}{kT} + \frac{S_0}{k}\right), \quad (12)$$

where  $E_0$  and  $S_0$  are energetic and entropic contributions to the free energy of H-bond formation (usually both are negative). At high temperatures  $K_1$  is small, and the isotropic liquid with  $g = 1/(4\pi)$  has the minimal free energy. At low temperatures  $K_1$  is large, and the state with broken orientation symmetry (nematic) has the minimal free energy.

Let us explore this in detail. To check whether the isotropic state is stable let us consider a small deviation

from it

$$g(\mathbf{p}) = \frac{1}{4\pi} \left(1 + \sum_{l=1}^{\infty} a_l P_l(\cos \theta)\right), \quad (13)$$

where  $a_l$  are small coefficients,  $P_l$  are Legendre polynomials,  $\theta$  is the angle between the vector  $\mathbf{p}$  and the orientation axis. From equations (8) we have for small  $a_l$

$$-TS_{\text{orient}} = \frac{nkT}{2} \sum_{l=1}^{\infty} \frac{a_l^2}{2l+1} \quad (14)$$

and

$$K = K_1 \left(1 + \sum_{l=1}^{\infty} \frac{a_l^2}{2l+1}\right). \quad (15)$$

If the constant  $K$  depends on some parameter  $t$  then equation (10) gives

$$\frac{dv}{dt} = \frac{v(1-v)}{1+v} \frac{d \ln K(t)}{dt}. \quad (16)$$

Using equations (14)–(17) we can easily obtain the following expansion for the free energy

$$f = f_0 + \frac{nkT}{2} (1 - 2v) \sum_{l=1}^{\infty} \frac{a_l^2}{2l+1}, \quad (17)$$

where  $f_0$  does not depend on  $a_l$ . It is evident from equation (17) that the isotropic phase becomes unstable at  $v \geq \frac{1}{2}$ , i.e. at  $K_1 \geq 2$ .

This analysis checks the *local* stability of the isotropic phase. It does not answer the question, whether the ordering is a first order phase transition or a second order phase transition. Therefore we will explore anisotropic phase in more detail.

### 3.2. Anisotropic phase.

The direct minimization of the free energy using arbitrary  $g(\mathbf{p})$  is usually a very hard task. After Onsager [17] one usually picks a reasonable trial function depending on some adjustable parameters that are chosen to minimize the free energy. Evidently the trial function must reflect the symmetry of the given phase. If we assume that the ordered phase has the symmetry  $D_{\infty h}$ , that is typical for nematics, the reasonable trial function is the Onsager function

$$g(\mathbf{p}) = \frac{c}{4\pi \sinh c} \cosh(c \cos \theta), \quad (18)$$

where  $c = \text{const}$  is a free parameter. However, a numerical study reveals that the free energy with such trial function has no minima other than for  $c = 0$ . It means that the symmetry of the ordered phase is different from  $D_{\infty h}$ . As our molecules are highly anisotropic (donor site at one pole and acceptor site at another pole) it seems reasonable that the symmetry of the ordered phase is  $C_{\infty v}$ . It means that the molecules have both preferred axis and preferred

orientation along this axis. As the order parameter for such phase changes sign if the space coordinates change signs, the free energy can depend only on even powers of the order parameter. Therefore the ordering transition must be of the second order.

Let us seek the orientation distribution function in the form

$$g(\mathbf{p}) = \frac{c}{4\pi \sinh c} \exp(c \cos \theta). \tag{19}$$

It is easy to find that

$$-TS_{\text{orient}} = kTn \left( \ln \frac{c}{\sinh c} + c \coth c - 1 \right) \tag{20}$$

and

$$K = K_1 \frac{c \sinh 2c}{\sinh^2 c}. \tag{21}$$

The free energy as the function of the parameter  $c$  has a single minimum at some  $c^*(K_1)$ . At  $K_1 \leq 2$   $c^*(K_1) = 0$ , and at  $K_1 > 2$   $c^*(K_1) > 0$  (see figure 1). Therefore we indeed deal with the second order phase transition. In the vicinity of the transition point we can expand the free energy with respect to small parameters  $c$  and  $|K_1 - 2|$

$$\frac{f - f_{\text{phys}}}{nkT} = \frac{1}{2} - 2 \ln 2 - \frac{K_1 - 2}{4} - \frac{(K_1 - 2)^2}{36} - \frac{(K_1 - 2)c^2}{36} - \frac{7c^4}{540} + \dots \tag{22}$$

Minimizing this equation we see that the equilibrium value of  $c$  at  $|K_1 - 2| \ll 1$  is

$$c^*(K_1) = \begin{cases} 0, & K_1 \leq 2 \\ \sqrt{\left[ \frac{15(K_1 - 2)}{14} \right]}, & K_1 > 2 \end{cases} \tag{23}$$

and the corresponding free energy is

$$\frac{f - f_{\text{phys}}}{nkT} = \begin{cases} \frac{1}{2} - 2 \ln 2 - \frac{K_1 - 2}{4} - \frac{(K_1 - 2)^2}{36} + \dots, & K_1 \leq 2 \\ \frac{1}{2} - 2 \ln 2 - \frac{K_1 - 2}{4} - \frac{43(K_1 - 2)^2}{1008} + \dots, & K_1 > 2. \end{cases} \tag{24}$$

When  $K_1$  goes through the value  $K_1 = 2$ , the second derivative ( $d^2f/dK_1^2$ ) has a jump equal to  $-\frac{5}{168}nkT$ . It corresponds to a jump in the molar heat capacity equal to  $0.03R$ . Orientation properties are usually described by the

set of order parameters  $p_l = \langle P_l(\cos \theta) \rangle$ . The first two of them in the region  $|K_1 - 2| \ll 1$  are

$$p_1 = \langle \cos \theta \rangle = \begin{cases} 0, & K_1 \leq 2 \\ \frac{1}{3} \sqrt{\left[ \frac{15(K_1 - 2)}{14} \right]}, & K_1 > 2 \end{cases} \tag{25}$$

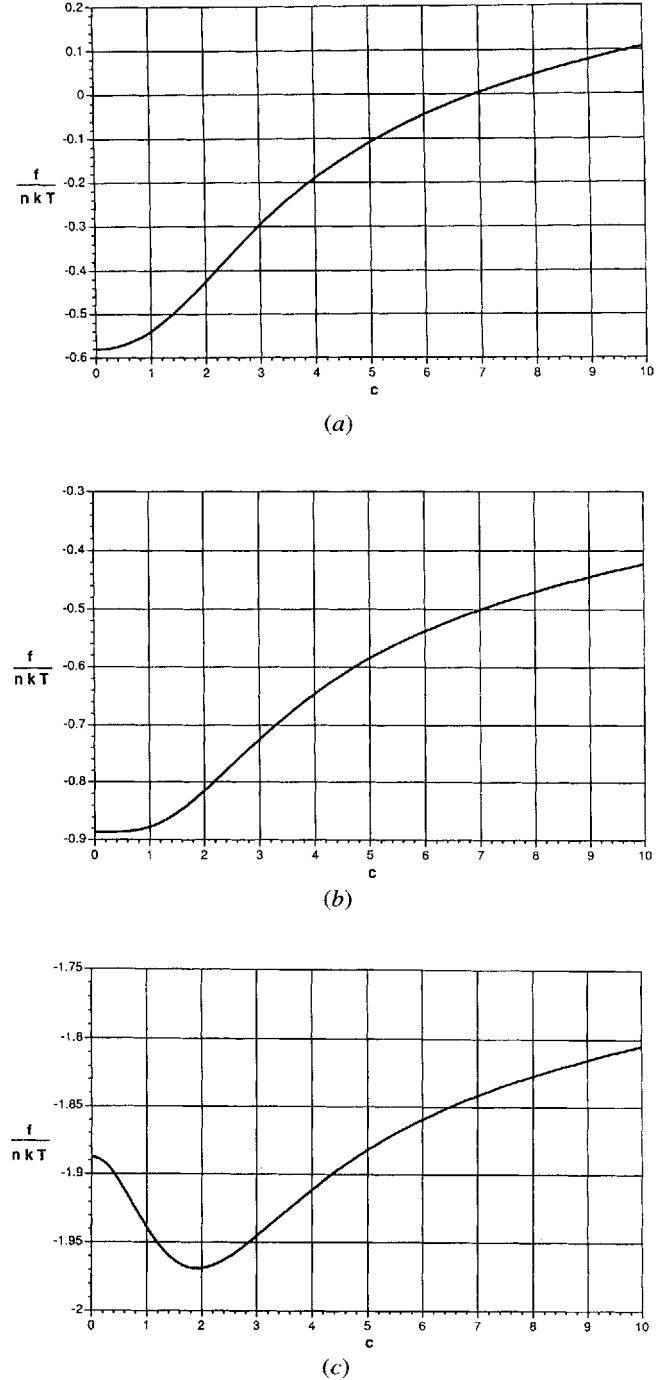
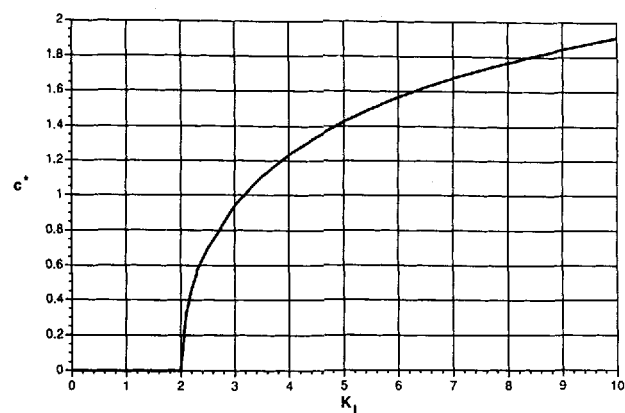
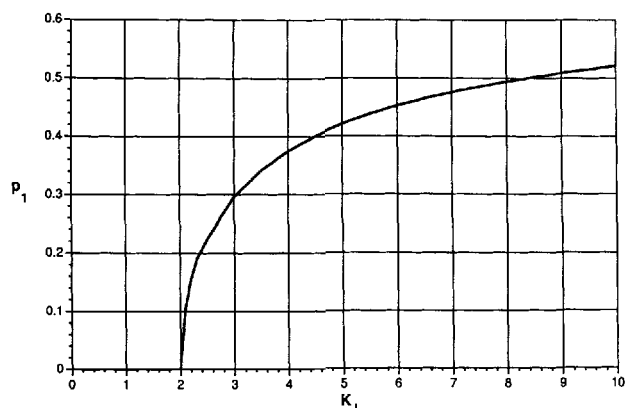


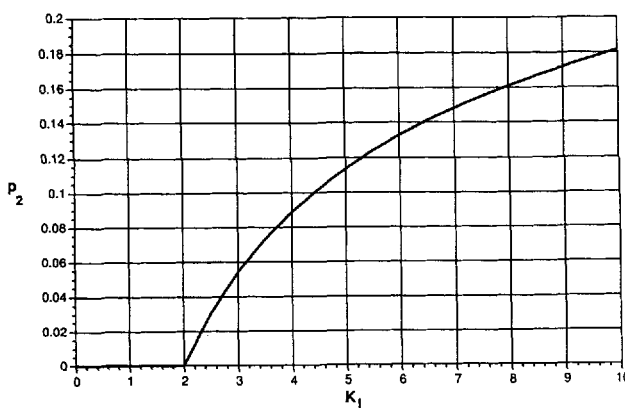
Figure 1. Free energy as a function of  $c$  for (a)  $K_1 = 1$ ; (b)  $K_1 = 2$ ; (c)  $K_1 = 10$ .



(a)



(b)



(c)

 Figure 2. Orientation ordering for (a)  $c^*(K_1)$ ; (b)  $p_1(K_1)$ ; (c)  $p_2(K_1)$ .

and

$$p_2 = \left\langle \frac{3 \cos^2 \theta - 1}{2} \right\rangle = \begin{cases} 0, & K_1 \leq 2 \\ \frac{K_1 - 2}{14}, & K_1 > 2. \end{cases} \quad (26)$$

 The values of  $c^*$ ,  $p_1$  and  $p_2$ , computed in a wider region

 of  $K_1$ , are presented on figure 2.

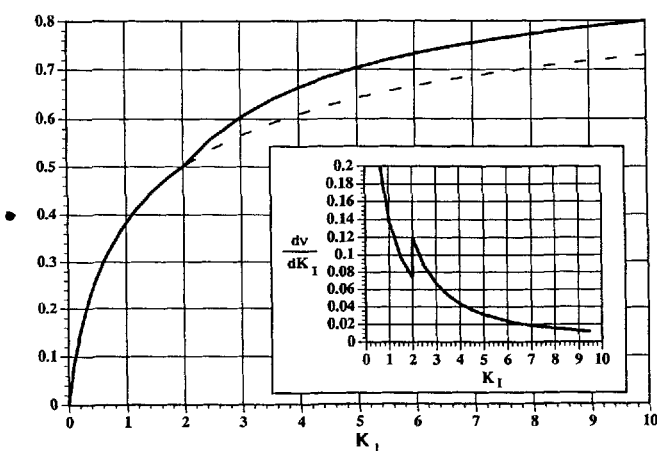
 The most interesting feature of this phase transition is its effect on the fraction of hydrogen bonded groups  $n$ . In the vicinity of the transition point we have

$$v = \begin{cases} \frac{1}{2} + \frac{K_1 - 2}{12}, & K_1 \leq 2 \\ \frac{1}{2} + \frac{K_1 - 2}{7}, & K_1 > 2. \end{cases} \quad (27)$$

We see that while the fraction of hydrogen bonded groups is continuous at the point of phase transition, its derivative is not (see figure 3). Such behaviour may be observed by IR spectroscopy [16].

#### 4. Conclusions

In this paper we proposed an approach for a general theory of liquid crystalline ordering in the hydrogen bonded fluids. It is based on the coupling between the orientation order and the equilibrium constants of the hydrogen bonds formation. This approach was illustrated on a simple example of the nematic–isotropic transition caused by the anisotropy of hydrogen bonds.

 The results for our simple model seem to be interesting. There exists an isotropic liquid–nematic phase transition, and the value of the equilibrium constant at the transition point is not too large. The fraction of hydrogen bonds at the transition temperature turns out to be independent of the details of the molecular interaction and is universal for all molecules of spherical shape having two opposite (or complementary) functional groups. The phase transition in this system, unlike the classical rigid rods solution, is of the second order. The ordered state is ferroelectric,  $g(\mathbf{p}) \neq g(-\mathbf{p})$ . Such anisotropy is caused by the high anisotropy of the molecules. The ordering transition

 Figure 3. Fraction of hydrogen bonded functional groups. Solid line represents actual values of  $v(K_1)$  and the dashed line the analytical continuation of the function  $v(K_1)$  from the isotropic phase. Insert: the derivative  $[dv(K_1)]/(dK_1)$ .

influences the system thermodynamics and the number of hydrogen bonds formed.

It is interesting to note that the phase transition in this system occurs at  $\nu = \frac{1}{2}$ . This fact has a simple intuitive meaning. The average length of an aggregate in this system is  $1/(1 - \nu)$  units. At  $\nu > \frac{1}{2}$  the solution has mostly monomers and dimers. The values  $\nu < \frac{1}{2}$  correspond to the situation when an average aggregate has more than 2 units thus ensuring a sort of many-particle interaction (I am grateful to the reviewer of *Liquid Crystals* whose comment stimulated my interest to this fact).

We explored the simplest situation when all anisotropic interactions but hydrogen bonding are neglected. The separation of free energy equation (1) makes it possible to account for other contributions in a more realistic model. Such a model should depend on the details of the molecular structure (polarizability, dipole moments, etc.). We will address these matters in the future works. It is prudent to say, however, that the main feature of the explored system, the sensitivity of the fraction of formed hydrogen bonds to the phase transition, will be imminent to the more complex systems. It makes the described phenomena especially interesting for IR study.

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