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## The isotropic-nematic transition in charged liquid crystals

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**Résumé.** — Nous étudions le diagramme de phase d'un système dense de particules allongées avec une interaction Coulombienne, et montrons l'existence d'une transition isotrope-nématique du premier ordre.

**Abstract.** — We discuss the phase diagram of a concentrated system of rods interacting *via* a Coulomb potential, and demonstrate the existence of a first-order isotropic-nematic transition.

1. **Introduction.** — There are several approaches to the statistical mechanics of liquid crystal systems [1]. For rods interacting *via* short range forces at low density, the virial expansion can be employed [2]. At high density, however, no such rigorous expansion has yet been devised for interactions which are strongly singular at the origin, such as hard-core or Lennard-Jones interactions.

In this paper, we show that for potentials less singular than  $r^{-3}$ , a high density expansion resembling the Debye-Hückel theory of electrolytes [3] may be performed, and that the results yield a first-order phase transition between an isotropic and a nematic phase. This class of potentials includes the Coulomb potential, which is of particular interest in the light of a recent experiment on DNA molecules [4].

2. **Theory.** — We consider a system with volume  $V$ , of  $N$  rods, of length  $l$  and charge per unit length  $\sigma$  suspended in a fluid of counterions, such that the system is electrically neutral. Points on the  $i$ th rod are described by three parameters:  $\mathbf{r}_i$ , the centre of mass of the rod;  $\hat{\mathbf{n}}_i$ , a unit vector in the direction of the rod, and  $s_i$ , the distance of the point from the centre of mass. The position of a point on the  $i$ th rod is thus

$$\mathbf{R}_i(\hat{\mathbf{n}}_i, s_i) = \mathbf{r}_i + \hat{\mathbf{n}}_i s_i \quad -\frac{l}{2} \leq s_i \leq \frac{l}{2}. \quad (1)$$

It should be made clear that the rods have no thickness, and interact solely *via* a pair potential between points on the rods,  $U(|\mathbf{R}_i(\hat{\mathbf{n}}_i, s_i) - \mathbf{R}_j(\hat{\mathbf{n}}_j, s_j)|)$ . We assume that the rods are highly overlapping, so that, if  $\rho = N/V$  is the density, then

$$\rho l^3 \gg 1. \quad (2)$$

The partition function satisfies

$$Z \propto \int \prod_i d^2 \hat{\mathbf{n}}_i d^3 \mathbf{r}_i \times \exp\left(-\frac{1}{2 k_B T} \sum_{ij} \int_{-\frac{l}{2}}^{\frac{l}{2}} ds ds' U(\mathbf{r}_i + \hat{\mathbf{n}}_i s - \mathbf{r}_j - \hat{\mathbf{n}}_j s')\right) \quad (3)$$

where  $k_B T$  has its usual meaning, and we have integrated over the kinetic degrees of freedom. To proceed, we introduce the collective coordinate transformation

$$\rho_{\mathbf{k}}(\{\hat{\mathbf{n}}_i\}) = \sum_{i=1}^N \int_{-\frac{l}{2}}^{\frac{l}{2}} ds e^{i\mathbf{k} \cdot (\mathbf{r}_i + \hat{\mathbf{n}}_i s)} \quad (4)$$

which is the Fourier transform of the microscopic density, and replace the integration over the centre of mass coordinates by an integration over the collective coordinates.

This makes the integrand of (3) particularly simple so that

$$Z \propto \int \prod_i d^2 \mathbf{n}_i \prod_{\mathbf{k}} d\rho_{\mathbf{k}} \frac{\partial(\{\mathbf{r}_i\})}{\partial(\{\rho_{\mathbf{k}}\})} \times \exp\left(-\frac{1}{2 V k_B T} \sum_{\mathbf{k}} \rho_{\mathbf{k}} \rho_{\mathbf{k}}^* U_{\mathbf{k}}\right) \quad (5)$$

where

$$U_{\mathbf{k}} = \int d^3 \mathbf{R} e^{i\mathbf{k} \cdot \mathbf{R}} U(\mathbf{R}). \quad (6)$$

The Jacobian  $\partial(\{\mathbf{r}_i\})/\partial(\{\rho_{\mathbf{k}}\})$  cannot be calculated exactly, but becomes a Gaussian in the high density limit

$$\frac{\partial(\{\mathbf{r}_i\})}{\partial(\{\rho_{\mathbf{k}}\})} \rightarrow \frac{\exp\left(-\frac{1}{2} \sum_{\mathbf{k} \neq 0} \rho_{\mathbf{k}} \rho_{\mathbf{k}}^* / \Delta(\mathbf{k})\right)}{\prod_{\mathbf{k}} [2\pi \Delta(\mathbf{k})]^{1/2}} \delta(\rho_0 - Nl). \quad (7)$$

To see this, we consider the quantities  $\langle \rho_{\mathbf{k}} \rho_{\mathbf{k}'} \rangle$ ,  $\langle \rho_{\mathbf{k}} \rho_{\mathbf{k}'} \rho_{\mathbf{k}''} \rangle$  etc. where  $\langle \dots \rangle$  means

$$\frac{1}{V^N} \int \prod_i d^3\mathbf{r}_i \dots$$

The average over an even number of  $\rho_{\mathbf{k}}$ 's is dominated by the terms obtained from the distribution (7), namely products of terms like  $\langle \rho_{\mathbf{k}_1} \rho_{\mathbf{k}_2} \rangle$ , and in the high density limit the remaining terms are negligible. This result also holds in the Debye-Hückel theory of electrolytes [3], and in polymer solution theory [5]. From the definition of  $\rho_{\mathbf{k}}$ , we find that

$$\Delta(\mathbf{k}) = \langle \rho_{\mathbf{k}} \rho_{\mathbf{k}}^* \rangle = 4 \sum_{i=1}^N \frac{\sin^2\left(\mathbf{k} \cdot \hat{\mathbf{n}}_i \frac{l}{2}\right)}{(\mathbf{k} \cdot \hat{\mathbf{n}})^2} \quad (8)$$

so that (5) becomes

$$\int \prod_{\mathbf{k}} d\rho_{\mathbf{k}} \prod_i d^2\hat{\mathbf{n}}_i \exp\left(-\frac{1}{2} \sum_{\mathbf{k}} \rho_{\mathbf{k}} \rho_{\mathbf{k}}^* \left[\frac{U_{\mathbf{k}}}{k_B T V} + \frac{1}{\Delta(\mathbf{k})}\right] - \frac{1}{2} \sum_{\mathbf{k}} \ln \Delta(\mathbf{k})\right). \quad (9)$$

At this point, we introduce the orientational distribution function  $f(\hat{\mathbf{n}})$   $\delta^2\hat{\mathbf{n}}$  which is the fraction of rods pointing within a small solid angle  $\delta^2\hat{\mathbf{n}}$  about the unit vector  $\hat{\mathbf{n}}$ , for a given set of  $\mathbf{r}_i$ . The change of variables

$$\prod_i d^2\hat{\mathbf{n}}_i \rightarrow \prod_{\mathbf{n}} df(\mathbf{n}) \equiv \mathcal{D}f$$

in (9) then leads to

$$e^{-F/k_B T} = \int \mathcal{D}f \exp\left(-N \int d^2\hat{\mathbf{n}} f(\hat{\mathbf{n}}) \ln f(\hat{\mathbf{n}})\right) \times \exp\left[-\frac{V}{16\pi^3} \int d^3\mathbf{k} \ln \left(1 + \frac{4\rho U_{\mathbf{k}}}{k_B T} \int d^2\hat{\mathbf{n}} f(\hat{\mathbf{n}}) \frac{\sin^2\left(\mathbf{k} \cdot \hat{\mathbf{n}} \frac{l}{2}\right)}{(\mathbf{k} \cdot \hat{\mathbf{n}})^2}\right)\right]. \quad (10)$$

We make the saddle-point approximation to obtain

$$\frac{F}{k_B T} = N \int d^2\hat{\mathbf{n}} \bar{f}(\hat{\mathbf{n}}) \ln \bar{f}(\hat{\mathbf{n}}) + \frac{V}{16\pi^3} \int d^3\mathbf{k} \ln \left(1 + \frac{4\rho U_{\mathbf{k}}}{k_B T} \int d^2\hat{\mathbf{n}} \bar{f}(\hat{\mathbf{n}}) \frac{\sin^2\left(\mathbf{k} \cdot \hat{\mathbf{n}} \frac{l}{2}\right)}{(\mathbf{k} \cdot \hat{\mathbf{n}})^2}\right) \quad (11)$$

where

$$\frac{\delta F}{\delta \bar{f}} [\bar{f}] = 0. \quad (12)$$

We note that, as in Onsager's theory, the isotropic phase always satisfies (12). In practice, it is best to choose a suitable trial distribution function, and then minimize (11) numerically. Such a function is

$$\frac{\alpha e^{\alpha |\cos \theta|}}{4\pi(e^{\alpha} - 1)} \quad (13)$$

which only depends on the angle,  $\theta$ , between the axis of alignment and the director  $\hat{\mathbf{n}}$ , and is peaked around  $\theta = 0$  and  $\theta = \pi$ . The axial symmetry of  $f(\hat{\mathbf{n}})$  allows one of the  $\mathbf{k}$  integrals to be performed trivially, leaving four nested integrations. Unfortunately, the integral inside the logarithm in (11) is badly behaved for large values of  $|\mathbf{k}|$ , and we were unable to obtain satisfactory convergence, even using a Gaussian quadrature method with  $2^{20}$  integration points. This

oscillatory behaviour arises from the sharp cut-off in the charge density distribution along each rod. We replace the charge distribution

$$Q(s) = \begin{cases} \sigma & -\frac{l}{2} \leq s \leq \frac{l}{2} \\ 0 & \text{otherwise} \end{cases} \quad (14)$$

by

$$Q(s) = \frac{\sigma \cdot 2}{\sqrt{2\pi}} e^{-2s^2/l^2} \quad (15)$$

and in fact the results obtained from both distributions do not differ qualitatively, although the convergence using (14) is inferior to that of (15).

We are mainly interested in the cases of a Coulomb or a screened-Coulomb potential and the corresponding phase diagrams are reproduced in figure 1. We find a strong first-order transition between the isotropic and the nematic phases, with the parameter

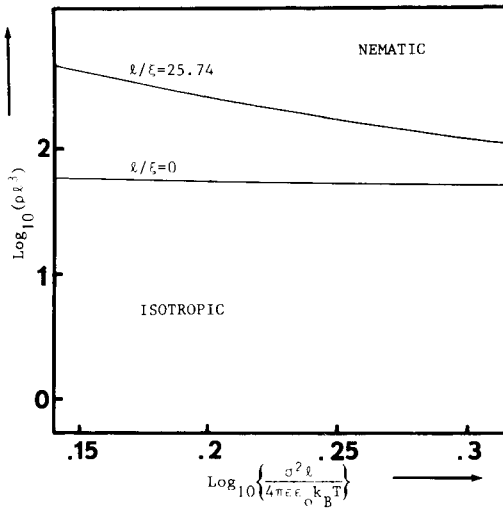


Fig. 1. — Phase diagram for charged rods with an interaction  $U(\mathbf{k}) = \sigma^2/\epsilon\epsilon_0(k^2 + \xi^{-2})$ .

$\alpha$  jumping from 0 to about 60 in the case of a bare Coulomb potential, and to a higher value when there is screening.

**3. Discussion.** — We have seen in the preceding section that for a certain class of potentials it is possible to construct a theory valid for high densities, and it would be interesting to extend this to the case of hard-core interactions. The theory however, requires that the Fourier transform of the potential  $U(r)$  exists. This requirement arises from the fact that we have replaced an integration over all possible positions of  $N$  rods (3) by an integration over all possible functions (9). This is because the Jacobian in (5) is discontinuous and we have approximated it by a continuous distribution (7). Hence, we have replaced an integral over a set of discrete lines of charge by a continuous charge distribution  $\rho(\mathbf{r})$ . The energy of a particular configuration in this case is

$$\int \rho(\mathbf{r}) \rho(\mathbf{r}') U(\mathbf{r} - \mathbf{r}') d^3\mathbf{r} d^3\mathbf{r}' = \int \rho_{\mathbf{k}} \rho_{\mathbf{k}}^* U_{\mathbf{k}} d^3\mathbf{k}$$

which only exists if  $U(r)$  is less singular than  $r^{-3}$ . On the other hand, the correct energy of a configuration of line charges is well defined, as long as none of the lines intersect one another.

One might think that a way of extending this method to deal with more singular potentials would be to include higher powers of  $\rho_{\mathbf{k}}$  in (7), for example

$$\exp\left(-\frac{1}{2} \sum_{\mathbf{k}} \rho_{\mathbf{k}} \rho_{\mathbf{k}}^* / \Delta(\mathbf{k}) + \sum_{\mathbf{k}, \mathbf{k}', \mathbf{k}'', \mathbf{k}'''} \rho_{\mathbf{k}} \rho_{\mathbf{k}'} \rho_{\mathbf{k}''} \rho_{\mathbf{k}'''} / \Delta_4(\mathbf{k}, \mathbf{k}', \mathbf{k}'', \mathbf{k}''')\right). \quad (16)$$

However, by the argument of the preceding paragraph, such attempts must fail.

Another approach might be to replace  $U(r)$  by a delta function pseudo-potential

$$U(\mathbf{R}) \rightarrow D\delta(\mathbf{R}) \quad (17)$$

with  $D$  being the hard-core diameter. This yields a first-order transition as well, but the method can be criticized on the following grounds. Since the delta function does not exclude a non-zero volume of phase space, the use of the exact Jacobian in the partition function cannot lead to any deviations from the ideal gas terms in the free energy. The fortuitous result is merely an artifact of the approximation (7).

The above objections do not apply to the Coulomb potential since the predominant contributions to the energy

$$\int \rho_{\mathbf{k}} \rho_{\mathbf{k}}^* \frac{1}{k^2} d^3\mathbf{k} \quad (18)$$

are from long-wavelength modes which are unaffected by the approximation (7). Note that as the singularity of the potential approaches  $r^{-3}$ , the short-wavelength modes become more important, leading to the divergence discussed above.

It is of interest to discuss qualitatively the effect of these short-wavelength modes, and here we offer some speculations on the behaviour of the system. The most ordered phase we envisage is the Smectic B phase, that is ordered positionally inside each layer. As the temperature is raised, we expect a transition to the Smectic A phase at a temperature

$$T \sim \sigma^2 l / k_B \epsilon \epsilon_0$$

which is roughly the melting temperature of a two dimensional gas interacting *via* a logarithmic potential. The stability of the Smectic layer can be estimated by considering small displacements,  $x_i$ , of the centre of mass of the  $i$ th rod from its mean position. The decrease in energy due to distant rods is

$$\frac{\sigma^2 l}{2} \sum_{ij} \frac{(x_i - x_j)^2}{R_{ij}^3}$$

where  $R_{ij}$  is the distance between the  $i$ th and the  $j$ th rod. But the increase in energy due to overlap between layers is proportional to the overlap, so the maximum contribution to the energy must come from neighbouring rods. In order to estimate the energy needed to disassociate a Smectic layer, we calculate the energy needed to transfer a rod from one layer to the next. This energy is of the order

$$\frac{\sigma^2 l}{\epsilon \epsilon_0} \ln\left(\frac{l}{a}\right)$$

where  $a$  is the average separation of the rods inside each layer. Thus we expect a transition to a different phase at a temperature given by

$$T \sim \frac{\sigma^2 l}{\epsilon \epsilon_0 k_B} \cdot \ln(\rho l^3).$$

Whether this phase is isotropic or nematic depends on the strength of the coupling between the orientational and positional ordering, which can only be ascertained by a detailed theory.

An experimental realization of the system we have discussed has been recently reported [4]. It consists of DNA persistence length fragments at high concentration in an ultracentrifuge. The authors find that the interactions are purely repulsive and observe an isotropic-nematic phase transition. They interpret their results in terms of an effective hard core radius, which is about 100 Å in the case of the lowest salt concentration used. The consequent reduction in the effective length to width ratio by a factor of 10, stron-

gly suggests that the interaction is dominated by a screened Coulomb potential rather than by steric effects. A detailed comparison with experiment will be published elsewhere.

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