LETTER TO THE EDITOR

Ordering in charged rod fluids

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Abstract. The statistical mechanics of a dense fluid of charged rods is considered, and the corresponding phase diagram is calculated, using a collective coordinate transformation. A first-order isotropic–nematic phase transition is found, as suggested by a recent experiment.

Collective coordinate transformations have been widely used in many different areas of physics. A well known example where they arise naturally is in the study of lattice vibrations, where such a transformation yields phonons. Some other fields where these transformations occur are plasma physics (Pines and Bohm 1952) and polymer physics (Edwards 1966). In general, they are useful for systems at high density with long-range interactions present. In this Letter we report on a new application of collective coordinates, namely to the statistical mechanics of a charged rod fluid. This is of interest for two reasons. Firstly our method is valid in the high-density limit where the rods are highly overlapping. This is the case that presents the greatest difficulty because the low-density limit can be dealt with correctly (in the mean field approximation) by using the virial expansion (Onsager 1949). Secondly, it is interesting because of an experiment on DNA persistence length fragments at high concentration (Brian *et al* 1981). These authors found an isotropic–nematic phase transition which they studied as a function of the salt concentration. At the lowest salt concentration (where the screening length is largest), they found that this phase transition occurred at a point that corresponded to an effective length-to-width ratio ten times smaller than in the case of a high salt concentration. This strongly suggests that at the lowest salt concentration, the system can be adequately described by line charges interacting via a screened Coulomb potential. A detailed comparison with experiment will be published elsewhere.

It should be stressed that our method is only applicable to line charges whose constituent points interact via a potential less singular than r^{-3}, and so is not applicable to hard-core interactions. Thus we cannot discuss the case of a high salt concentration in the DNA experiment, or any other system where steric effects are important. Full details of our calculation and its range of validity will be published elsewhere.

We start by writing down the partition function for the system of N line charges in a volume V interacting via a pair potential $U(r)$:

$$Z \propto \int \prod_i \mathrm{d}^2 \hat{n}_i \, \mathrm{d}^3 r_i \, \exp\left(-\frac{1}{2k_B T} \sum_{ij} \int_{-1/2}^{1/2} \mathrm{d}s \, \mathrm{d}s' U[R_{ij}(s, s')]\right). \tag{1}$$

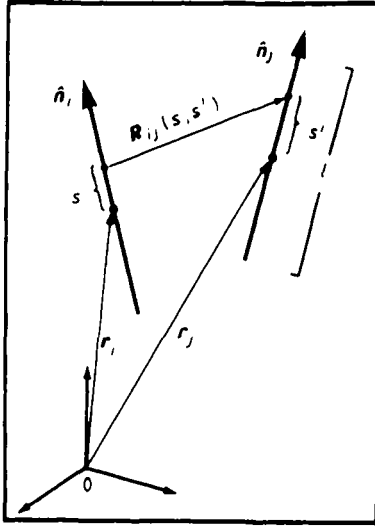$k_B T$ has its usual meaning, and the other symbols are defined in figure 1. The director $\hat{n}_i$

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Figure 1. Coordinate system used in equation (1).

is a unit vector. We introduce the collective coordinates

$$\rho_k(\{\hat{n}_i\}) = \sum_{i=1}^{N} \int_{-l/2}^{l/2} \mathrm{d}s \, \exp[\mathrm{i}k \cdot (r_i + \hat{n}_i s)] \tag{2}$$

which considerably simplify the integrand of (1). The Jacobian of this transformation is, in the first approximation,

$$\exp\left(-\tfrac{1}{2} \sum_{k \neq 0} \rho_k \rho_k^* / \Delta(k)\right) \delta(\rho_0 - Nl) / \prod_k [2\pi\Delta(k)]^{1/2},$$

$$\Delta(k) = 4 \sum_{i=1}^{N} \frac{\sin^2(k \cdot \hat{n}_i l/2)}{(k \cdot \hat{n}_i)^2}, \tag{3}$$

so that the integral over the ρ_k's becomes Gaussian. Once this has been performed, an integration over the directors remains. As usual, we introduce the orientational distribution function $f(\hat{n}) \, \mathrm{d}^2\hat{n}$ for the fraction of rods in the solid angle $\hat{n} \to \hat{n} + \mathrm{d}^2\hat{n}$, and evaluate the partition function by the saddle point method to obtain the free energy

$$\frac{F}{k_B T} = N \int \mathrm{d}^2\hat{n} \, \bar{f}(\hat{n}) \ln \bar{f}(\hat{n}) + \frac{V}{16\pi^3} \int \mathrm{d}^3k \, \ln\left(1 + \frac{4\rho U_k}{k_B T} \int \mathrm{d}^2 \hat{n} \, \bar{f}(\hat{n}) \frac{\sin^2(k \cdot \hat{n}l/2)}{(k \cdot \hat{n})^2}\right), \tag{4}$$

$$\rho = N/V,$$

where

$$\delta F[\bar{f}]/\delta f = 0. \tag{5}$$

Note that (5) is always satisfied in the isotropic case, where f is uniform.

We calculated (5) numerically by using a trial function

$$f(\hat{n}) = \alpha e^{\alpha|\cos\theta|} / 4\pi(e^\alpha - 1), \tag{6}$$

which is only a function of the angle θ between the axis of alignment and $\hat{n}$, and the

parameter α was varied so as to satisfy (5). In order to improve the convergence of (4), we replaced the oscillatory term in the integrand by a Gaussian, and found no qualitative difference between the results in the two cases.

The phase diagram when the interaction is Coulomb and screened-Coulomb is reproduced in figure 2. We find a strong first-order transition between the isotropic and nematic phases, with the value of the parameter α at the transition being about 60 for a Coulomb potential, and being somewhat higher when there is screening.
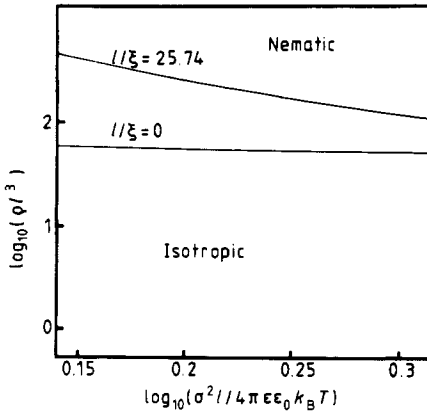

Figure 2. Phase diagram for charged rods with an interaction $U(k) = \sigma^2/\varepsilon\varepsilon_0(k^2 + \xi^{-2})$.

References

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Pines D and Bohm D 1952 *Phys. Rev.* **85** 338