The Nature of Attraction between Like-Charged Rods

The origin of attractive interactions in polyelectrolyte solutions has provoked a lot of attention. In recent Letters Ha and Liu [1] attempted to study this interesting problem using a two-state model originally introduced by Oosawa and Manning. In the context of this model the counterions are treated as either free or condensed.

To calculate the free energy of interaction between two rodlike polyions the authors performed the Hubbard-Stratonovich transformation to map the Hamiltonian of the interacting charged rods onto an effective field theory. The authors proceeded to linearize the resulting action, finishing up with the so-called Gaussian approximation. The attraction between two charged rods, within this approximation, arises as a result of correlations in *thermal* fluctuations. Although nowhere stated explicitly, the Gaussian approximation, being a form of high-temperature expansion (weak coupling), is *only* valid for $\alpha^2\xi \ll 1$, where ξ is the Manning parameter, $\xi = \beta q^2/Db$, and α is the valence of the counterions [2]. However, in order to have a significant counterion condensation, it is necessary to have $\xi > 1/\alpha$. Thus, the inequality above is strongly violated for multivalent counterions. We must, therefore, conclude that the Gaussian approximation is inapplicable to the problem of attraction between like-charged polyions. An analogy with a two-component plasma (TCP) is perhaps worthwhile. It is well known that the TCP is isomorphic to the sine-Gordon field theory. If a Gaussian approximation is applied to study this field theory, a lot of important physics associated with the strong coupling limit would be lost. In particular, no account could be taken of ionic association which becomes prevalent as soon as the electrostatic energy of interaction becomes comparable to the thermal energy. Thus, although the Gaussian approximation is sufficient to capture the physics leading to Debye-Hückel limiting laws, it is insufficient to go beyond this point.

To further explore the extent of validity of the Gaussian approximation as it applies to rigid polyions, we study a simple model of interaction between two charged rods with Z negative sites (separated by b) and n condensed multivalent counterions [2]. The Hamiltonian for this system takes a particularly simple form which can be studied exactly. We find that the attraction is produced by the structure of the ground state and *not* by the thermal fluctuations. In fact, for values of Manning parameter relevant for real polyelectrolytes such as DNA, the attractive force between the two rods is almost exactly the same as at zero temperature, $\xi = \infty$ (Fig. 1). The mechanism of attraction at zero temperature is quite straightforward. To minimize the *electrostatic* energy, the condensed counterions on the two rods arrange themselves in a staggered configuration so that, if the site of one polyion is occupied by a counterion, a parallel site of the second polyion stays empty. At

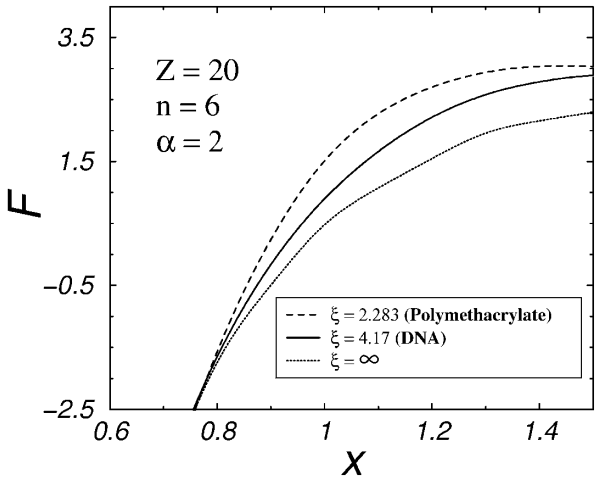

FIG. 1. Force between polyions as a function of distance (in units of b) for various temperatures; attraction when $F < 0$.

short distances, this results in attraction if the number of condensed counterions is sufficiently large, $2n\alpha > Z$, i.e., the number of favorable counterion-monomer interactions is larger than the number of unfavorable bare monomer-monomer interactions. We find that the same mechanism persists to finite temperature and is not captured in the high-temperature Gaussian approximation as applied by Ha and Liu. Finally, we would like to stress that the formation of an ionic crystal is not necessary for the appearance of attraction, the correlations in positions of condensed counterions on the two rods are sufficient. As an example, let us consider two rods of length Z(even) with $n = Z/2$ divalent condensed counterions. Clearly, the ground state configuration is $(\cdots + - + - + \cdots)$ on one polyion and $(\cdots - + - + - \cdots)$ on the other, i.e., the counterions at zero temperature form a crystal. Obviously, the Hamiltonian in this example is invariant under the transformation $+ \rightleftharpoons -$. For a finite system this symmetry cannot be broken, so that for any nonzero temperature the average charge on any site is zero and no crystal is possible. The correlations, however, persist and result in attraction. The attractive force is purely correlational, and to a good approximation arises from the structure of the ground state. The thermal fluctuations serve only to *diminish* this attraction.

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