Kosterlitz–Thouless and Manning condensation

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Abstract

A comparison between the Kosterlitz–Thouless theory of metal–insulator transition in a two dimensional plasma and a counterion condensation in a polyelectrolyte solution is made. It is demonstrated that, unlike some of the recent suggestions, the counterion condensation and the Kosterlitz–Thouless transition are distinct. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The polyelectrolyte solutions present one of the outstanding problems in the field of physical chemistry. Although the work of Debye and Hückel [1] shed some light on the unusual behavior of simple symmetric electrolytes, the properties of the polyelectrolyte solutions still remain to large extent ununderstood. In general a polyion can be a flexible polymer chain or a rigid molecule of specific shape some of whose monomers are ionized. For now, we shall confine our discussion to rigid polyelectrolytes whose polyions can be modeled as cylinders or spheres, since as the reader will see, even these significantly simpler systems already present more than enough complications. In particular even such basic question, as what is the form of electrostatic interaction between two polyions, still remains controversial. A prototypical molecule whose shape can be modeled as a cylinder is a DNA. It should be noted, however, that even in this case the approximation of replacing a long molecule by an infinite cylinder will only be valid if the persistence length is sufficiently greater than the Debye screening length inside the solution. As an example of spherical polyions, one can consider various colloidal suspensions, for example the ones made of latex or polystyrene particles.

In this note we shall confine our attention to the case of rigid cylindrical polyions. In particular, our discussion is motivated by the recent observation of Kholodenko and Beyerlein [2] that the commonly observed counterion condensation during which a finite fraction of disassociated counterions recondenses onto polyions, is a "special case of

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the Kosterlitz–Thouless [3] (KT)-like phase transition" [2]. Here we shall demonstrate that the KT transition and the Manning's counterion condensation [4] have nothing in common. The erroneous conclusion reached by the above authors can be attributed to the confusion over the system of units used in the original KT theory.

To begin our discussion let us first define the Primitive Model of Polyelectrolyte (PMP) [5]. It consists of N cylindrical polyions of a cross-sectional diameter a_p and length L, each carrying P ionized groups of charge $-q$ spaced uniformly, with a separation b, along the axis of a cylinder. A total of PN counterions are present to preserve the overall charge neutrality of the system. The counterions are assumed to be spherical in shape with a diameter a_c, each carrying a charge q. The whole system is confined inside a region of volume V. It will prove convenient to define the distance of closest approach between the centers of a polyion and a counterion, $a = (a_p + a_c)/2$. The solvent is modeled as a uniform medium of a dielectric constant D. The bare interaction between a sufficiently long polyion and a counterion can then be approximated by

$$\phi(r) = \begin{cases} +\infty, & r < a, \\ -2q(\sigma/D)\ln(r/a), & r \geqslant a, \end{cases} \tag{1}$$

where $\sigma = -Pq/L = -q/b$. If we make the replacement $\sigma \to -q$ (or $b \to 1$), the logarithmic potential which appears in the above expression is exactly the same as for two oppositely charged hard disks in two dimensions (assuming we keep the same Poisson equation, $\nabla^2 \phi = -4\pi\rho_q/D$, as in three dimensions). Furthermore, it is well known that when the temperature of a two dimensional plasma is lowered below a certain value, all the ions associate into dipolar pairs, changing the properties of plasma from being a conductor to an insulator [3]. This is a continuous thermodynamic transition, which happens to be of infinite order. Is it possible that the counterion condensation observed in polyelectrolytes is a realization of this transition? In order to answer this question we shall present two simple mean-field theories, one for a two dimensional Coulomb gas and another for a polyelectrolyte solution in three dimensions.

2. 2D Coulomb gas

Our system will consist of hard disks of diameter a, half of which carry the charge $+q$, while the other half carry the charge $-q$. As is usual for the restricted primitive model (RPM), the solvent is modeled as a uniform medium of a dielectric constant D. Due to strong electrostatic interactions we expect that some of the ions will associate forming dipolar pairs [6]. The total density of hard spheres is $\rho = \rho_+ + \rho_- + 2\rho_2$, where $\rho_+ = \rho_- \equiv \rho_1/2$ is the density of free unassociated ions, while the ρ_2 is the density of dipolar pairs. In order to explore the thermodynamic properties of this plasma, we need the free energy for the system. We shall construct this free energy out of two parts: the entropic free energy associated with the momentum degrees of freedom in the partition function, and the electrostatic free energy due to the interactions between the ions. It is a simple matter to write the expression for the entropic part of the free

energy, since it corresponds to that of an ideal gas. Defining the Helmholtz free energy density as $f = -F/V$ we have

$$\beta f^{\text{ent}} = \sum_s \rho_s [1 - \ln(\rho_s \Lambda_s^{d|s|}/\zeta_s)] \,, \tag{2}$$

where d is the dimensionality, $\beta = 1/k_B T$, Λ_s is the de Broglie thermal wavelength, ζ_s is the internal partition function for species $s = +, -, 2$, and $|s|$ is how many particles constitute a specie, i.e. $|+| = |-| = 1, |2| = 2$. The electrostatic free energy is easily calculated in the spirit of the original Debye-Hückel theory [6]. We find

$$\beta f^{el} = \frac{1}{2\pi a^2} \ln[\kappa a K_1(\kappa a)] \,, \tag{3}$$

where K_1 is the modified Bessel function of first order, $(\kappa a)^2 = 4\pi \rho_1^*/T^*$, and the reduced density and temperature are respectively $\rho^* = \rho a^2$ and $T^* = k_B T/q^2$. The densities of the free and the associated ions are related through the law of mass action $\mu_+ = \mu_- = \mu_2$, where the chemical potentials are determined from the free energy $\mu_s = -\partial f/\partial \rho_s$. We find

$$\rho_2 = \frac{1}{4} K(T) \rho_1^2 e^{2\mu^{ex}} \,, \tag{4}$$

where the excess chemical potential is $\mu^{ex} = -\partial f^{el}/\partial \rho_1$ and the equilibrium constant $K(T) = \zeta_2(T)/\zeta_+ \zeta_-$. For the purpose of the present exposition it is sufficient to know that the equilibrium constant remains finite in the limit $\rho_1 \to 0$, for further discussion we refer the interested reader to [6]. In the limit of small densities the excess chemical potential can be expanded in powers of ρ_1, $\mu^{ex} = -[\gamma_E + \ln(\kappa a/2)]/T^* + O(\rho_1)$. Substituting this expression into Eq. (4), we observe that $\rho_2^* \approx \rho_1^{*2} e^{-\ln(\rho_1^*)/T^*} = \rho_1^{*(2-1/T^*)}$ [6,7]. In particular, we see that for a *fixed* density ρ, as the temperature is reduced to $T^* \to T_{KT}^* = 1/2$ the density of free ions, $\rho_1 \to 0$. This is exactly the Kosterlitz–Thouless metal insulator transition. Since the Debye screening length is inversely proportional to $\sqrt{\rho_1}$, we see that it will diverge as $T \to T_{KT}^+$.

Let us now take a look at what happens in the case of cylindrical polyelectrolytes [5].

3. Polyelectrolyte solution

We shall work in the context of the PMP defined above. Just as in the case of simple electrolyte addressed in the previous section, we expect that the strong electrostatic interaction between the polyions and the counterions will result in formation of clusters composed of one polyion and $1 \leqslant n \leqslant Z$ condensed counterions. We are then lead to two conservation laws:

$$\rho = \sum_{n=0}^{P} \rho_n \,, \tag{5}$$

$$Pp = \rho_+ + \sum_{n=0}^{P} n\rho_n , \tag{6}$$

where ρ is the total density of the polyions, ρ_0 is the density of free polyions, ρ_n is the density of the clusters of size n, and ρ_+ is the density of free, unassociated, counterions. In order to explore the thermodynamic properties of the PMP we require the free energy. As in the case of simple electrolyte, this can be constructed as a sum of the entropic and the electrostatic contributions. The entropic part of the free energy is given by the Eq. (2) with $s = \{+, 0 \leqslant n \leqslant Z\}$. The electrostatic contribution, however, is significantly more complex than for simple electrolyte. It consists of the free energies due to the polyion–counterion, polyion–polyion, and the counterion–counterion interactions. In general it is quite difficult to take a full account of all these effects. The condensation phenomena that we are interested in studying, however, already occurs in the limit of vanishingly small densities, $\rho \to 0$. In this limit, it is possible to show that the polyion–polyion and the counterion–counterion interactions are small and the main contribution to the electrostatic free energy comes from the polyion–counterion interaction [5]. This contribution can be calculated in the spirit of the Debye–Hückel theory and we find [5]

$$\beta f^{el} = \sum_{n=0}^{P} \frac{\rho_n^*(P-n)^2}{La^2 T^*} \left[\ln\left(\frac{\kappa a}{2}\right) + O(\rho_+^0) \right] , \tag{7}$$

where $(\kappa a)^2 = 4\pi \rho_+^* / T^*$ and the reduced density and temperature are now $\rho^* = \rho a^3$ and $T^* = k_B T D a / q^2$, respectively. The distribution of cluster sizes can be found from the law of mass-action, $\mu_n = \mu_0 + n\mu_+$, which reduces to

$$\rho_n^* = K_n(T)\rho_0^*(\rho_+^*)^n e^{\beta\mu_0^{ex} + n\beta\mu_+^{ex} - \beta\mu_n^{ex}} , \tag{8}$$

where the excess chemical potentials, $\mu_s^{ex} = -\partial f^{el}/\partial \rho_s$, are $\beta\mu_s^{ex} = -\frac{(P-n)^2 a}{PT^* b}[\ln(\frac{\kappa a}{2}) + O(\rho_+^0)]$ and $\beta\mu_+^{ex} = O(\rho_+^0)$. The equilibrium constant, $K(T) = \zeta_s(T)/\zeta_+^n$, as in the case of simple electrolyte will remain finite in the limit $\rho \to 0$. Substituting the expressions for the excess chemical potential into Eq. (8) we find that $\rho_n^* \approx \rho_0^* \rho_+^{*g(n)}$, where $g(n) = n - na/T^* b + n^2 a/2PT^* b$. In the limit $\rho \to 0$ the only possible cluster has the size n^*, for which the function $g(n)$ attains its minimum. In particular we see that for $T^* < T_M^* \equiv a/b$ the minimum is attained when $n^* = P(1 - T^* b/a)$ counterions are associated with a polyion, while for $T^* > T_M^*$ no clusters form and the minimum is at $n^* = 0$. In the limit $\rho \to 0$, the formation of clusters is a continuous transition which occurs when the temperature is lowered below $T^* = T_M^* = a/b$.

4. Conclusion

As was discussed following Eq. (1) the isomorphism between 2D Coulomb law and the interaction potential between a polyion and a counterion is valid if $b \to 1$ ($\sigma \to -q$).

In these units $T_M = q^2/k_B D$, while the Kosterlitz–Thouless transition occurs at $T_{KT} = q^2/2k_B D$, which is half the value of the equivalent Manning temperature. Furthermore, we would like to stress that while at KT transition *all* the ions associate into dipolar pairs, thus leading to a divergent Debye screening length, nothing like this happens in the case of polyelectrolytes. Quite on the contrary, all the way down to zero temperature there remain some free counterions, producing a finite screening length. Finally, while the KT transition is found at non-zero density, the sharpness (discontinuity in slope as a function of temperature) of the counterion condensation transition will disappear with an increase of density [8].

Acknowledgements

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