Counter-ion condensation and Kosterlitz–Thouless transition

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Abstract
The similarity between counter-ion condensations in polyelectrolyte rod
systems and Kosterlitz–Thouless phase transitions in two-dimensional systems
is discussed at the level of mean-field theory. Based on the similarity, the
renormalization group theory is applied to polyelectrolyte liquid systems
aligned in parallel. It is found that the critical separation between monovalent
charges for the counter-ion condensation is renormalized in polyelectrolyte
liquid systems and becomes shorter than the Bjerrum length which is the
critical separation predicted by the mean-field theory for a dilute solution of
polyelectrolyte rods.

1. Introduction

Macromolecules containing many ionizable groups are called polyelectrolytes. In solution
they dissociate into polyvalent macroions and a large number of small ions charged oppositely
(counter-ions). Polyelectrolytes have been studied for a long time.

Many biomaterials are made of polyelectrolytes (DNA, protein, etc). They play important
roles in the fields of biology, medicine, cosmetics, and the food industry. Therefore, the physics
of polyelectrolytes is important in applications. In particular, biopolymers are now under
extensive investigations. Their unique behaviours are mostly related to the polyelectrolyte
characters, and polyelectrolytes in solutions have drawn the attention of researchers in recent
years.

One of the characteristics of the polyelectrolyte solution is the complex behaviour of
counter-ions. In a dilute solution of weakly charged polyelectrolytes, counter-ions are free
from macroions. In a solution of strongly charged polyelectrolytes, on the other hand, a
fraction of counter-ions stays in the vicinity of the macroions. Between these two distinctive
regions, there is a threshold value in the average separation between neighbouring (monovalent)
charges, called the Bjerrum length $l_B = e^2/4\pi\epsilon kT$, which is about 7 Å in water at room
temperature. Below this separation (strongly charged polyelectrolyte), the counter-ions stay

near the macroions. Due to screening by the condensed counter-ions, the apparent charge of the macroion is reduced. The maximum linear density in apparent charge of the macroions is observed to be $\rho_c = e/l_B$. This phenomenon is called counter-ion condensation (CIC) after the analogy of gas–liquid phase transition. CIC occurs in many kinds of polyelectrolyte system.

The study on CIC was originated by Onsager [1], Oosawa [2], Manning [3], and followers. They focused on the simplest polyelectrolyte system, that is, a dilute solution of polyelectrolyte rods. Their explanation of CIC is associated with the logarithmic distribution of electric potential around a charged rod together with many-body effects of counter-ions. They assumed that the counter-ions screen the electrostatic potential of macroions and are subjected to the mean field of macroions and the other counter-ions. Most studies of counter-ion condensations are still within mean-field approximations. There are a few studies [4, 5] beyond the mean-field theory, but there is no exact theory even for a simple model. Recent experiments on polyelectrolytes such as polymer brushes [6, 7], however, demand improvements of the counter-ion condensation theory beyond mean-field approximations.

The Kosterlitz–Thouless (KT) transition [9, 11] in the two-dimensional (2D) classical Coulomb gas is also associated with the logarithmic distribution of electric potential and the many-body problem. The KT transition occurs in various systems, such as the 2D classical XY model, dislocations in crystal surfaces, vortices of superconductors, and superfluid helium. In these systems, the interactions between topological excitations depend logarithmically on the spatial separation and the entropy also has logarithmic dependence on the system sizes. Kosterlitz and Thouless [9] explained the phase transition observed in such systems by the bound–unbound transition of topological excitations. Kosterlitz [10] had further developed a renormalization group theory for the KT transition beyond the mean-field approximation. Due to the renormalization group theory, we now know the exact details of the KT transition, such as the order parameter, the correlation function, the transition temperature, and the critical exponents [12].

In this paper, based on the renormalization group theory, we discuss the exact results for CIC in homogeneously charged polyelectrolyte-rod systems.

2. Similarity in the mean-field theory

There is a wide variety of polyelectrolytes which bring up counter-ion condensation. They are different in charge, shape, stiffness, anisotropy, etc. Onsager, Oosawa, and Manning selected rodlike polyelectrolytes to develop a limiting (standard) theory of polyelectrolyte solutions in a dilute solution. First we follow the same track, and then we will step further beyond mean-field approximations. Most theories of polyelectrolyte solutions have dealt with mean-field approximations. Manning cited the exact solution of the Poisson–Boltzmann equation [8] in his paper [3]. However, even *the Poisson–Boltzmann equation itself is a result of mean-field theory*.

Let us first discuss a 2D Coulomb gas system and we get back to a single rod macroion with monovalent counter-ions in solution. We assume, for simplicity, that the size of all the systems is R, and that the 2D size of all the objects is a (radii of charged particles, charged rods, counter-ions, and macroions).

The electrostatic potential between charges in the 2D Coulomb gas system is expressed as

$$U(\vec{r}_i, \vec{r}_j) = -\frac{q_i q_j}{2\pi \epsilon} \ln |\vec{r}_i - \vec{r}_j|, \tag{1}$$

where q_i and q_j are charges and $\vec{r}_i$ and $\vec{r}_j$ are positions of 2D particles. At low temperatures, positive and negative charges are attracted to each other and bound together. The system

becomes electrically neutral at low temperatures. At high temperatures, the kinetic energy (entropy) prevents the binding of charges.

The energy required to separate a pair of oppositely charged particles against the electrostatic interaction is

$$\delta E \approx \frac{q^2}{2\pi\epsilon} \ln\left(\frac{R}{a}\right). \tag{2}$$

The entropy is attributed to the movement of a pair of unbound particles. The entropy difference between the bound and unbound states is

$$\delta S \approx 2k \ln\left(\frac{R^2}{a^2}\right), \tag{3}$$

where k is the Boltzmann factor. The free energy difference between the bound and unbound states is

$$\delta F = \left(\frac{q^2}{2\pi\epsilon} - 4kT\right) \ln\left(\frac{R}{a}\right). \tag{4}$$

Therefore, the phase transition temperature of the bound–unbound transition is

$$kT_K = \frac{q^2}{8\pi\epsilon}. \tag{5}$$

Similar arguments can be applied to a single polyelectrolyte rod in solution. When a macroion is considered as a homogeneously charged rod with linear charge density ρ, the system is essentially two dimensional. The electrostatic potential around a linear macroion (rod) is

$$U(\vec{r}_i) = -\frac{\rho q_i}{2\pi\epsilon} \ln|\vec{R} - \vec{r}_i|, \tag{6}$$

where q_i and $\vec{r}_i$ are the charge and the position in 2D space of the ith counter-ion respectively, and $\vec{R}$ is the position of the macroion in 2D space. For simplicity, we assume $q_i = q$.

In solutions, macroions are usually treated as non-movable objects. We ignore the entropy of macroions since macroions are large and move slowly compared with counter-ions in solution. This is justified by the fact that CIC temperature is usually low compared to the temperature where the entropy of macroions is activated. For the rod system, only the entropy of counter-ions is, then, considered. The entropy difference between bound and unbound counter-ions is given in the mean-field approximation by

$$\delta S \approx Nk \ln\left(\frac{R^2}{a^2}\right), \tag{7}$$

where N is the number of counter-ions. The free energy, therefore, is

$$\delta F = N\left(\frac{\rho q}{2\pi\epsilon} - 2kT\right) \ln\left(\frac{R}{a}\right). \tag{8}$$

This gives us the transition temperature as

$$kT_c = \frac{\rho q}{4\pi\epsilon}. \tag{9}$$

The transition temperatures of KT transition and CIC are different by a factor of two in the mean-field level arguments [14] which corresponds to ignoring the entropy of macroions. This similarity has been discussed by a few physicists [13–15].

3. Renormalization group theory—beyond mean-field approximations

In the above section, we neglected the many-body problem, how the other particles affect the movement of a particle. In the mean-field approximations, we treat the potential for a particle as the average potential screened by the other particles. There is another fundamental problem. In 2D systems, according to the Mermin–Wagner theorem, there is no spatial long-range order. In the 2D systems described above, however, certain critical phenomena are observed at characteristic temperatures.

Kosterlitz and Thouless introduce the idea of condensation (bound–unbound transition) of topological excitations. In 2D systems, Kosterlitz and Thouless pointed out that there is no spatial long-range order, but there could be a phase transition (divergence of correlations below the transition temperature). At the transition temperature, there is no finite difference (jump) in specific heat or order parameters.

Let us consider the system described by the Hamiltonian

$$H = -\sum_{i,j}^{2N} p_i p_j \ln\left(\frac{|\vec{r_i} - \vec{r_j}|}{a}\right) + 2N\mu, \tag{10}$$

where p_i and p_j are 'charges' of particles, $2N$ is the total number of particles, and μ is the chemical potential. The partition function is

$$Z = \text{Tr}[\exp(-\beta H)], \tag{11}$$

which determines all the physical quantities. The procedure described here is a real space renormalization programme in statistical physics applied to the system near critical temperatures. The idea is to rescale the system based on a Kadanoff-type construction. At critical points, fluctuation increases in the system and characteristic lengths disappear. The system looks the same on all length scales. Then, the physics should not change under the following renormalization transformation [10, 12]:

$$a \rightarrow a + \mathrm{d}a. \tag{12}$$

In other words, the partition function should have the same functional form under the transformation but with rescaled interactions. The rescaled interaction parameters described by the original interaction parameters determine a flow diagram. The diagram allows us to study the critical behaviour. A point where the flow stops is called a fixed point. It was found that there is a fixed line rather than a fixed point for the Hamiltonian (20).

The edge of the fixed line corresponds to a phase transition point. It determines the transition temperature as [10, 12]

$$\frac{p^2}{2kT_c} - 2 = 4\pi \exp\left(-\frac{\mu}{kT_c}\right). \tag{13}$$

Below this temperature, the correlation length becomes infinite.

Applying this argument to the 2D Coulomb gas Hamiltonian,

$$H = -\sum_{i,j}^{2n} \frac{q_i q_j}{2\pi\epsilon} \ln\left(\frac{|r_i - r_j|}{a}\right) + 2N\mu, \tag{14}$$

where $q_i = q_j = q$ is the charge of the particles. The transition temperature of the 2D Coulomb gas system is determined by

$$\frac{q^2}{4\pi\epsilon kT_c} = 2 + 4\pi \exp\left(-\frac{\mu}{kT_c}\right). \tag{15}$$

The original motivation of Kosterlitz and Thouless analysing the above model is to understand the phase transition of the 2D XY model. The XY model is described by the Hamiltonian

$$H = -J \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j$$
$$= -J \sum_{\langle i,j \rangle} \left(S_i^x S_j^x + S_i^y S_j^y \right), \tag{16}$$

where the spins are unit vectors confined to rotate in a plane

$$|\vec{S}_i| = S = 1, \tag{17}$$

and

$$\vec{S}_i \cdot \vec{S}_j = \cos(\phi_i - \phi_j). \tag{18}$$

The vortex-type topological excitation of this spin system is described by

$$\phi(r) = \bar{\phi}(r) + \psi(r), \tag{19}$$

where $\bar{\phi}(r)$ denotes the pure winding configuration given by vortices (topological excitation), and $\psi(r)$ is the local deviations from it (spin wave). The XY Hamiltonian can be converted into

$$H = J \int \mathrm{d}^2 r \, (\nabla \psi)^2 - \sum_{n=1}^{\infty} \left[\sum_{i,j}^{2n} p_i p_j \ln \left(\frac{|r_i - r_j|}{a} \right) + 2n\mu \right], \tag{20}$$

where p_i and p_j are the vortex winding numbers. The parameters of the XY model and 2D Coulomb gas system are connected with the Euler constant γ by

$$p_i p_j = p^2 = 2\pi J, \tag{21}$$
$$\mu = \pi^2 J \left(\tfrac{3}{2} \ln 2 + \gamma \right). \tag{22}$$

Then, we can apply the scaling argument to the Hamiltonian (20) and find the transition point as [12]

$$\frac{\pi J}{kT_c} = 1 + 2\pi \exp \left[\left(-\frac{\pi^2 J}{kT_c} \right) \left(\frac{3}{2} \ln 2 + \gamma \right) \right]. \tag{23}$$

Therefore, the transition temperature of the XY model is approximately

$$kT_c \approx \pi J. \tag{24}$$

Based on the renormalization group theory, the singularity and the universality class of the phase transition was determined [9, 10, 12]. The free energy has the essential singularity at the critical line. The correlation length diverges below the transition temperature. The details of the KT transition are written in review articles [12].

4. Homogeneously charged parallel rods

Beyond the limiting theory of a single-rod system in solution established by Onsager, Oosawa, and Manning, we consider a many-rod system (many-centre problem) aligned in parallel (liquid crystal). The analysis by the renormalization group theory can be applied to this polyelectrolyte rod system. Electrostatic attractive interactions between homogeneously charged rods and counter-ions in the liquid crystal systems can be described as

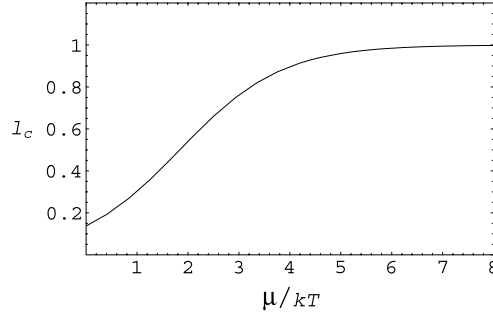$$U(\vec{R}_i, \vec{r}_j) = -\frac{\rho_i q_j}{2\pi \epsilon} \ln |\vec{R}_i - \vec{r}_j|, \tag{25}$$

Figure 1. Critical charge separation of homogeneously charged polyelectrolyte rods plotted in the unit of Bjerrum length.

where $\vec{R}_i$ and ρ_i are the position and the linear charge density of the ith rod respectively, and $\vec{r}_j$ and q_j are the position and the charge of the jth counter-ion. For simplicity, we consider each rod has the same linear charge density $\rho_i = \rho$. In the case of monovalent counter-ions, all the charge is $q_j = e$.

According to the renormalization group theory [12] discussed in the previous section, the separation of charges in the macroions being fixed, the transition temperature is given by an edge of the fixed line as

$$\rho e = (4\pi\epsilon kT_c)\left[1 + 2\pi \exp\left(-\frac{\mu}{kT_c}\right)\right]. \tag{26}$$

The free energy of the system has an essential singularity at the CIC point. CIC falls in the same universality class as the KT phase transition. It could be called an infinite-order phase transition, since even higher-order physical quantities do not have discontinuities at the phase transition point.

We can describe the critical charge density of a rod at a temperature T as

$$\rho_c e = (4\pi\epsilon kT)\left[1 + 2\pi \exp\left(-\frac{\mu}{kT}\right)\right]. \tag{27}$$

With the definition of critical separation l_c as $\rho_c = e/l_c$, the critical separation for CIC in the rod system is given by

$$l_c = \frac{l_B}{1 + 2\pi \exp\left(-\frac{\mu}{kT}\right)}, \tag{28}$$

where $l_B = e^2/4\pi\epsilon kT$ is the Bjerrum length which is approximately 7 Å in water. In the dilute limit ($\mu \to \infty$), $l_c = l_B$, the critical separation becomes the Bjerrum length, and the mean-field result for a single rod is recovered. This function is plotted in figure 1.

5. Summary

CIC of the homogeneously charged rod systems is more like a bound–unbound transition rather than 'condensation'. There is no spatial long-range order in the system, unlike gas–liquid transition, even below the CIC temperature. The free energy and physical quantities have an essential singularity below the transition temperature. There is no finite jump in any physical quantities at the CIC point (infinite-order phase transition) unlike ordinary first- and second-order phase transitions. The correlation function diverges throughout the counter-ion

condensation phase. The universality class of CIC for polyelectrolyte rod systems is same as the KT transition.

Although our results for the homogeneously charged polyelectrolyte rods are exact, applications of our model are limited. We have ignored the entropy of macroions. It could be justified from the temperature considered that we can ignore the movement of the centre of gravity of the macroions, but we cannot ignore the shape fluctuation of the macroions. This fluctuation leads polyelectrolytes to self-contraction which is important in protein systems. We assume that the parallel rods are homogeneously charged, ignoring charge discreteness along the rods. This might leads to a charge density wave of counter-ions along the rods. The most promising systems which our theory is applicable to are liquid crystals of polyelectrolyte rods and polyelectrolyte-brush systems if the effect from the surface can be ignored.

Our main result for polyelectrolyte liquid crystal systems is that CIC belongs to the same universality class as the KT transition and that the condensation point depends on the density of rods. The critical separation l_c is renormalized due to many-body effects and gets shorter following equation (28). Note, however, that the condensation point (the critical separation) is related to the separation of charges along the rods following equation (28) not along the polymer back-bone.

References

[1] Onsager 1949 *Nuovo Cimento* **9** 279–87
[2] Oosawa F 1971 *Polyelectrolytes* (New York: Dekker)
[3] Manning G S 1969 *J. Chem. Phys.* **51** 924–33
[4] Lozada-Cassou M *et al* 1983 *J. Phys. Chem.* **87** 2821–4
[5] Gonzales-Tovar E *et al* 1985 *J. Chem. Phys.* **83** 361–72
[6] Csajka F S and Seidel C 2000 *Macromolecules* **33** 2728–39
[7] Balastre M *et al* 2002 *Macromolecules* **35** 9480–6
[8] Fuoss R *et al* 1951 *Proc. Natl Acad. Sci. USA* **37** 579
[9] Kosterlitz J M and Thouless D J 1973 *J. Phys. C: Solid State Phys.* **6** 1181–203
[10] Kosterlitz J M 1974 *J. Phys. C: Solid State Phys.* **7** 1046–60
[11] Berezinskii V L 1972 *Sov. Phys.—JETP* **34** 610–6
[12] Gulácsi Z and Gulácsi M 1998 *Adv. Phys.* **47** 1–89
[13] Kholodenko A L and Beyerlein A L 1995 *Phys. Rev. Lett.* **74** 4679–81
[14] Levin Y 1998 *Physica* A **157** 408–12
[15] Levin Y 2002 *Rep. Prog. Phys.* **65** 1577–632