# Phase transitions in polyelectrolyte solutions

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December 13, 2005

### Abstract

Polyelectrolytes in solution present a fascinating field of study that has been under intense scrutiny for the last few decades, but because of inherent difficulties in handling long-range electrostatic interactions has not reached the level of development achieved for ordinary polymer solutions. Stiff charged polyelectrolytes exhibit two novel and interesting phase transitions: the counterion condensation transition, and the like-charge aggregation transition, neither of which has been fully understood. I present a brief review of work done towards understanding these transitions, which are closely related.

# 1 Introduction

Polymers in solution exhibit a surprisingly wide range of interesting behavior, including a veritable zoo of different phases and microstructures. As the experimental conditions are varied, changes can be observed not only in the global properties of the solution, but also in the properties of the molecules themselves—changes in the average conformational state, the mechanisms for molecular transport, and so on. As we consider molecules with more complicated internal structures, even more interesting phase behaviors become available, as is the case, for example, with block copolymers. In the extreme case we have biological macromolecules, where a single molecule can exhibit a wide range of structural "phases", which on their own push the limits of current understanding—consider the phenomenon of protein folding, or of the helix–coil transition.

Polymer solutions can also exhibit novel behavior as we consider systems were different kinds of inter-particle interactions are important. For example, if we allow for covalent bonds (or other strong interactions) between sites on different polymers, we can end up with gels or rubber networks. Another example, which we will focus on in this work, is that of polyelectrolyte solutions, were electrostatic interactions dominate. The key characteristic of electrostatic interactions is that they are long-ranged, dropping off as $1/r$ (where $r$ is the inter-particle distance), which makes it difficult to apply many of the standard treatments of polymer solutions. Despite a few decades of intense study, polyelectrolyte solutions remain relatively poorly understood.

If we restrict ourselves to solutions of stiff charged polymers, then there are two distinct but closely related phenomena which are highly interesting from the point of view of phase transitions. The first is the "counterion condensation transition", which separates two regimes of interaction between a polyelectrolyte and the surrounding free ions, and the second is the so-called "like-charge" attraction, wherein two or more polyelectrolytes with the same sign of charge will aggregate under certain conditions. This behavior is at first glance counterintuitive, because the like charges on the polymers would lead us to always expect repulsion. However, it turns out there are several possible mechanisms which can induce attraction between such molecules. These attractions can lead to the formation of ordered, macroscopic bundles of polyelectrolytes, but whether and when such bundles constitute a separate equilibrium phase of the system remains an open question.

Understanding both of these phenomena is essential to any theory of polyelectrolyte solutions, and therefore is of fundamental interest. Progress in this area has a wide range of potential applications, both theoretically (e.g. techniques for dealing with electrostatic interactions), and practically (e.g. techniques for water treatment). Furthermore, understanding the formation and properties of polyelectrolyte bundles is relevant to a wide range of biological systems in which such bundles occur (1).

Most of the theoretical work on solutions of stiff polyelectrolytes has focused on isolated rods (i.e. dilute solutions), or on the interaction between two rods. Many of the experimental results on like-charge attraction, on the other hand, are based (understandably) on macroscopic bundles. Extensive computational work has been done at both ends of the scale, and has played a prominent role in the last two decades, providing benchmark results for comparison with the two-rod theories, and illuminating the different contributions to the attractions.

# 2 Isolated Rods

Polyelectrolytes become charged via dissociation of certain functional groups, releasing ions into the surrounding solution. These mobile counterions, which maintain the electrouneutrality of the system, are usually monovalent. However, multivalent ions can easily be introduced to the system via the addition of salt to the solution (although this also introduces salt co-ions). Many important polyelectrolytes, such as the M13 and fd viruses, actin, and double-stranded DNA, are highly stiff, often having persistence lengths longer than the molecules themselves. The pioneering work on such charged, stiff rods is largely due to Manning, Onsager, and (independently) by Oosawa ((17), (21), (22)), and revolves around the idea of counterion condensation. Namely, that for sufficiently strong electrostatic rod-ion interactions, a fraction of the counterions will be strongly associated with the rod, or "condensed". Although condensed ions remain mobile in a region around the rod, they will not, for example, contribute as much to the osmotic pressure of the system. Thus, the extent of counterion condensation can strongly affect the equation of state and other properties.

The original counterion condensation theory of polyelectrolyte solutions, proposed by Manning (17) is based on several simplifying assumptions. The solvent is treated implicitly as a dielectric medium with relative dielectric constant $\epsilon_r$ (thus ignoring hydration forces and other solvent-specific interactions). This mean-field-like treatment of the solvent is an assumption that we will make throughout the rest of this paper—the question of how to treat the solvent more accurately goes beyond the scope of this review. The rods are assumed dilute enough to ignore rod-rod interactions, and a single rod is treated as an infinitely long uniform line charge with charge density $-e/b$, where $e$ is an elementary charge, and therefore $b$ corresponds to the characteristic linear charge spacing on the rod[1]. The effect of the condensed counterions is limited to lowering the effective charge density on the rod. The uncondensed ions are treated in the Debye-Hückel approximation, which is a mean-field theory for electrostatic interactions[2]. A central result of the Debye-Hückel approximation is that the interaction between charges in a solution with free ions is a *screened* Coulomb interaction, in which the long-ranged $1/r$ term is multiplied with an exponential damping term of the form $\exp^{-\kappa r}$. The quantity $1/\kappa$ is called the Debye length and dictates the range of interactions, and is given by

$$\frac{1}{\kappa} = \left( \sum_i \frac{\rho_i q_i e^2}{\epsilon_r \epsilon_0 k_{\mathrm{B}} T} \right)^{-1/2} , \tag{1}$$

where the sum is over ionic species, and $\rho_i$ and $q_i$ give the concentration and valency of species $i$, respectively. Thus we see that the Debye length decreases with increasing ionic strength. The Debye-Hückel approximation considerably simplifies the analysis because we replace long-ranged interactions with effective short-ranged ones. As with any mean-field approximation for interactions, the predicted exponential form deviates significantly from the true interactions at short enough interparticle distances.

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[1] Following the majority of experimental systems of interest, I generally assume the polyelectrolytes to be negatively charged

[2] In fact, the Debye-Hückel theory is a linearized version of the more general Poisson–Boltzmann mean-field theory

Before going further into the model described above, it is interesting to point out that, at least in principle, the mean-field Debye-Hückel treatment could be applied to the polyelectrolyte solution itself, taking the rods to be a highly multivalent species. This approximation only becomes valid at impracticably low rod concentrations, however (17). The work done by Manning improves on Debye-Hückel theory by introducing a model (however crude) of the rod structure and of the interactions between rod and ions (i.e. condensed versus uncondensed), but otherwise retains the mean-field assumptions. We shall see that this approach of introducing specific corrections to the basic mean-field theory is quite common in this field. There has been considerable controversy, however, about how to do so *systematically*.

## 2.1 The Manning parameter

The motivation for thinking about ions as either ”condensed” or ”uncondensed” is provided in the context of the above model by an observation of Onsager's (17) about the configurational integral of the system. Consider the contribution to this integral from the region of phase space where the mobile ion $i$ is sufficiently close to the line charge (say, $r \leq r_0$, where $r$ is the distance from the line) to have an unscreened Coulomb interaction with it, and all the other ions are further from the rod ($r_j > r_0$, for $j \neq i$). The other ions contribute a finite factor $f(r_0)$ to the configurational integral, and the entire contribution from this region is given by

$$A(r_0) = f(r_0) \int_0^{r_0} e^{-\beta u_i(r)} 2\pi r \mathrm{d}r \ , \tag{2}$$

where $\beta = 1/k_\mathrm{B}T$, and $u_i$ is the rod-ion interaction, which we can obtain by integrating along the line charge to get

$$u_i(r) = \frac{2q_i e^2}{\epsilon_r \epsilon_0 b} \log r \ . \tag{3}$$

Thus, we can write

$$A(r_0) = 2\pi f(r_0) \int_0^{r_0} r^{(1-2q_i\xi)} \mathrm{d}r \ , p \tag{4}$$

where the Manning parameter $\xi$ is defined as

$$\xi \equiv \frac{e^2}{\epsilon_r \epsilon_0 k_\mathrm{B} T b} \ . \tag{5}$$

This is an important dimensionless parameter. If we recall that the Bjerrum length is given by $\ell_\mathrm{B} = e^2/\epsilon_r\epsilon_0 k_\mathrm{B}T$ we see that $\xi$ is the ratio of two important length scales in the model[3]. The Manning parameter can also be thought of as the ratio of electrostatic energy to thermal energy. Or it can be seen as playing the role of an inverse scaled temperature.

In Eq. 4 above we see immediately that the configurational integral diverges at the lower limit if $\xi \leq q_i^{-1}$. A system where this condition occurs is therefore unstable, and it is predicted that

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[3] The Bjerrum length is the length scale at which two unscreened monovalent charges have an interaction energy comparable to $k_\mathrm{B}T$, and is therefore a measure of the strength of electrostatic interactions

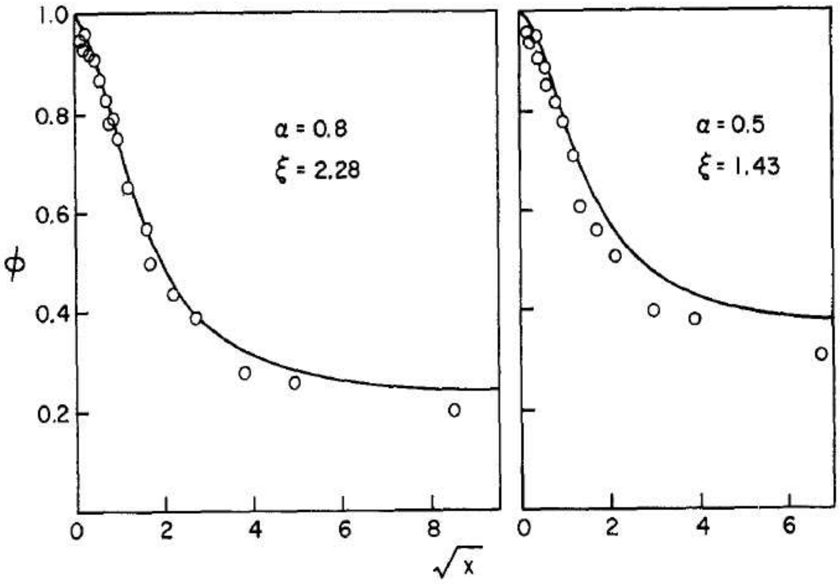

Figure 1: Osmotic pressure coefficient of a dilute polyelectrolyte solution. The quantity $x$ is the ratio of counterion concentration to monovalent salt concentration in the solution. The solid lines are the Manning result, and points are experimental data (17)

a fraction of the available counterions will ”condense” onto the rod until they reduce the *effective* value of $\xi$ below $q_i^{-1}$. Because of the divergence of the phase integral, this condensation persists even as we let the volume containing the rod grow to infinity—the divergent logarithmic gain in entropy of a free ion is offset by the divergent logarithmic rod-ion interaction (Eq. 3). The critical temperature (or, equivalently, critical charge density) $\xi_c = q_i^{-1}$ marks the transition between condensed and uncondensed states.

Although the comments in the previous paragraph are strictly true only for a single mobile ion, and moreover only in the context of this admittedly crude model, they provide all the essential clues about the counterion condensation transition[4]. Treating the two regimes separately Manning was able to obtain estimates for the excess free energy and osmotic pressure coefficients of dilute solutions, which compared favorably to experiments, as shown in Fig. 1.

## 2.2 Improving condensation theory

As mentioned earlier, improvements to the Manning theory can be made by modeling specific aspects of the problem more accurately, within the context of the mean-field theory. This is illustrated nicely by the two-zone model developed by Rubinstein et al ((7), (8)). In this model, the polyelectrolyte is modeled as a finite charged cylinder of length $L$, total charge $Q_0$ (in units of $e$) and radius

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[4] In the last two months Netz published an interesting paper (19) discussing the criticality of the counterion condensation transition, based on a model very similar to Manning’s. An order parameter for the system is proposed and critical exponents are computed. Unfortunately I became aware of this paper too late to include the results here.

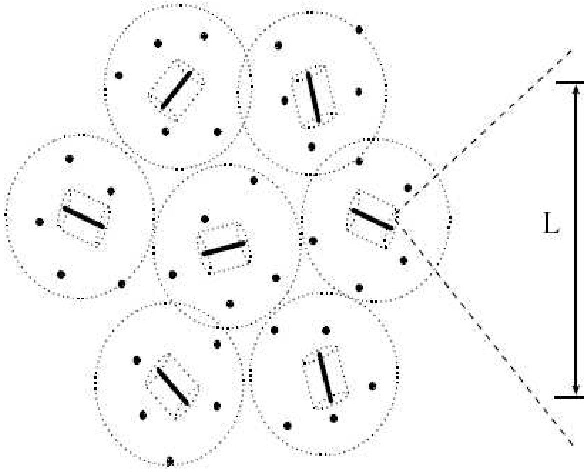

Figure 2: Illustration of the two-zone model proposed by Rubinstein et al.

$r_0$, and the surrounding bulk solution is split into two zones (as opposed to the single region implicit in the Manning model). The two zones are illustrated in Fig. 2: a cylindrical zone with radius $R$ (on the order of the size $L$ of the rod) surrounding the polyion, and a spherical shell surrounding the smaller cylinder, with an outer radius determined by the overall polyelectrolyte concentration. Counterions can distribute themselves freely, so that the total charge of the cylindrical region, $Q_R$, may be nonzero.

Within this setup, the distribution of counterions around the polyelectrolyte (within the cylindrical region) can be determined from mean-field theory by solving the Poisson-Boltzmann (PB) equation, subject to the boundary conditions at the polyion and cylindrical surfaces (this is a separate refinement over the Manning treatment, which used the simpler Debye-Hückel approximation). This was done analytically, to yield the counterion concentration

$$c(r) = \frac{2}{\pi}\frac{\alpha^2}{r^2\ell_{\mathrm{B}}}\left[\left(\frac{r}{\zeta}\right)^{\alpha} - \left(\frac{r}{\zeta}\right)^{-\alpha}\right]^{-2}, \tag{6}$$

where $\alpha$ and $\zeta$ are defined by the relations

$$\zeta^{2\alpha} = r_0^{2\alpha}\frac{\xi_0 - 1 - \alpha}{\xi_0 - +\alpha} \tag{7}$$

$$\zeta^{2\alpha} = R^{2\alpha}\frac{\xi_R - 1 - \alpha}{\xi_R - +\alpha}. \tag{8}$$

Here $\xi_0 = -Q_0\ell_{\mathrm{B}}/L$ is the Manning parameter defined previously, and $\xi_R = -Q_r\ell_{\mathrm{B}}/L$ is a "Manning parameter" for the cylindrical region as a whole. The solution is determined by a particular choice of the parameters $\xi_0$, $\xi_R$, $R$, and $r_0$. By exploring this parameter space the authors found the phase diagram depicted in Fig. 3 with three distinct phases corresponding to qualitatively

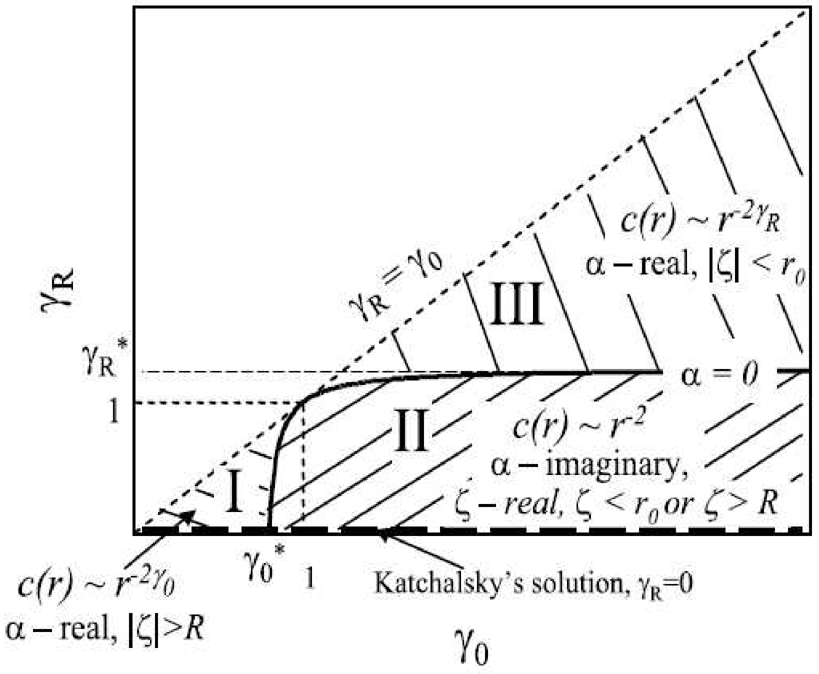

Figure 3: Phase diagram obtained from the model proposed by Rubinstein et al. The parameters $\gamma_0$ and $\gamma_R$ correspond to $\xi_0$ and $\xi_R$ as defined in the text. The different phases are divided by different regimes of the parameters $\zeta$ and $\alpha$, as shown. Phase I corresponds to weakly condensed rods, Phase II to saturated condensation, and Phase III to unsaturated condensation.

different $c(r)$'s. In (8) the authors also computed the osmotic pressure coefficient $\phi$, and found data collapse for the quantity $\xi_0\phi/\xi_R$. Although the results were found to agree well with simulations (14), I know of no direct comparison to experiment.

# 3 Two interacting rods

So far, we have considered only dilute solutions were the rods do not interact, and have focused on the counterion condensation transition. When considering stiff interacting rods, and a possible attractive interaction, however, the idea of counterion condensation has played a key role in the theoretical developments, especially on the work done by Ha and Liu (10), which we will focus on here. I should point out, though, that dozens of authors have contributed to this field, with approaches that go far beyond the scope of this paper. A good source of references can be found in (18). What is common to all these approaches is that they somehow go beyond the PB mean-field approximation, since it has been shown rigorously((20)) that mean-field approaches can never predict attraction between like-charged objects. The attractive interactions are thus thought to originate from correlations between the ions that are neglected by the mean-field approximation. These correlations may lead to van der Waals-like attractions between polyions, or they may

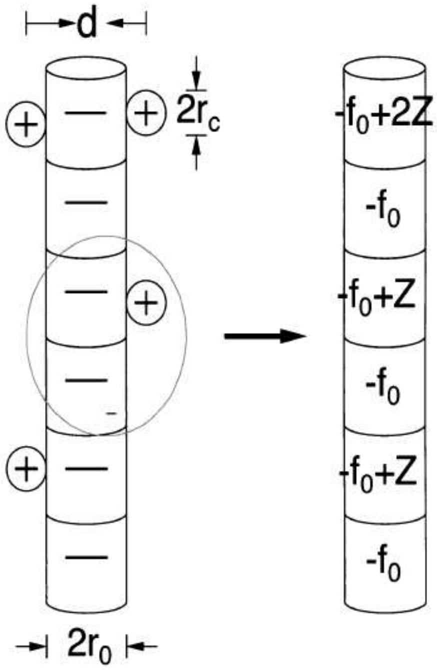

Figure 4: Illustration of the model for a single rod used by Ha and Liu in (10). (a) A negatively charged rod with condensed counterions. (b) The corresponding configuration of fluctuating charge variables, according to the model.

induce neighboring polyelectrolytes to share their counterions so as to maximize entropy (27). Alternatively, we might think of a low temperature "ionic crystal" picture in which attractions arise from the complementary positions of ions on neighboring rods (10). Other mechanisms are also possible. In what follows, I will discuss an approach based on the van der Waals idea.

### 3.1 Fluctuating charge variables

Ha and Liu (10) have described a simple model for two rods that yields an attractive regime. This model is illustrated in Fig. 4. The rods are modeled as stacks of $N$ charged cylindrical monomers of length $a$ and radius $r_0$ (with total length $L \equiv Na$). Both rods are enclosed in a larger cylinder of length $L$ and radius $L_\perp$. Counterions are divided into condensed and uncondensed. The condensed ions lie *on* the rod, and as in the Manning theory effectively reduce the charge on the monomer. Uncondensed counterions move freely in the larger cylindrical region. If we let $m$ denote the number of condensed counterions on monomer $s$ of rod $i$, then the effective charge on the monomer (in units of $e$) is $q_i(s) = -f_0 + mz$, where $-f_0$ is the bare charge on the monomer, and $z$ is the counterion valency. Having defined this charge variable, we can write the Hamiltonian for rod-rod electrostatic interactions:

$$\beta\mathcal{H} = \frac{\ell_\mathrm{B}}{2} \sum_{ij}^{2} \sum_{ss'}^{N} \frac{q_i(s)q_j(s')}{|\mathbf{r}_i(s) - \mathbf{r}_j(s')|} \tag{9}$$

The partition function (ignoring momentarily the free counterions) is then given by a sum over all possible realizations of the charge variables

$$Z = \sum_{i}^{2} \sum_{s}^{N} \int \mathrm{d}q_j(s) e^{-\beta \mathcal{H}} \ . \tag{10}$$

We can apply the Hubbard-Stratonovich transformation to this partition function to replace the two-body interactions between charge variables with one-body interactions between a charge variable and an electrostatic field. If we then assume Gaussian fluctuations in $q_i(s)$, the partition function can be expressed in terms of Bessel functions. This is a non-trivial approximation: it neglects higher-order correlations between condensed counterions *along* the rods, and is only valid at high temperatures, and indeed it sparked some debate ((13), (12)). However, the approximation retains all correlations of the charge variables *between* the two rods. This is important for two reasons. First of all, consider the two-monomer unit that is circled in Fig. 4. This is effectively a dipole, which can interact with similar structures on the neighboring rod. If the charge distributions along the two rods become correlated, we can see how this would lead to a van der Waals-like attraction between the two rods. And indeed it is the term describing such correlations which gives rise to the attraction, in this model. Secondly, *all* such correlations are considered, which means interactions between dipoles, quadrapoles, and higher-order multipoles are included. This is important because the authors find that the multipole expansion is divergent when the attractions dominate. In previous studies ((9)) the multipole expansion had also been truncated.

To construct the rest of the free energy, the authors follow a strategy similar to that of Oosawa in (21). The condensed ions have an entropic contribution proportional to the volume of a cylinder with radius $(r_0 + r_c)$, the free counterions contribute a similar term, taking the volume of the larger cylinder, and the electrostatic interaction between the rods and the free ions is obtained via a Debye-Hückel approximation. Using this free energy the authors compute the effective force between the rods, which agrees very well with results from simulations (with no adjustable parameters), as shown in Fig. 5.

## 4 Bundled phase

Theoretical treatment of the bundled phase is considerably more difficult than the other topics described in this paper, and has so far eluded a solid, systematic framework. There are several complicating factors. For one thing, effective interactions between the rods have been shown to be non-pairwise additive ((24), (11)). There is also the possibility of the bundle building up a net charge. Additionally, if we consider the bundle to be a bulk phase, then there are questions of mechanical and chemical equilibrium between the rod and the surrounding bulk solution, which may lead, for example, to redistribution of salt between the two phases (much computational work has been done on salt-free solutions, but this is of limited relevance to experimentally realizable bundles). Finally, although in the majority of experimental system—and in the rest of this paper—the polyelectrolyte bundles have a parallel, hexagonally-coordinated, close-packed structure, other microstructures have also been observed to occur.

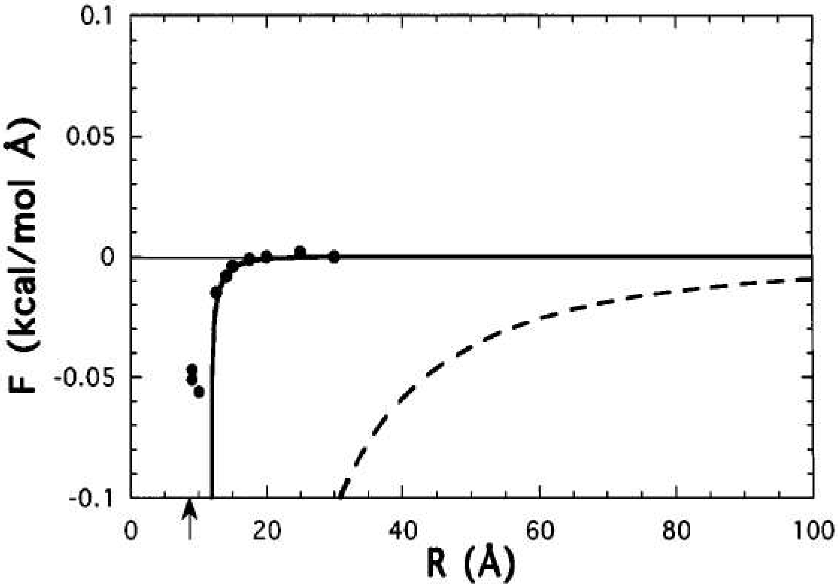

Figure 5: The solid curve is the force between two rods as a function of rod-rod separation, computed using the model described in (10). The dashed curve is the solution to the same model, truncating the multipole expansion. The dots are values obtained from simulations in (9). The repulsive regime at short distances $R$ found in simulation is absent in the analytical results because excluded volume interactions were not included in the model.

Because of these complications, most of the progress towards understanding these bundled phases has taken place via simulations, with significant contributions from Lyubartsev and Nordenskiöld ((15), (16)), Deserno and Holm ((6), (5)), Bloomfield ((2), (3)), and many others. On the experimental side there have also been many contributors, such as, Tang and Janmey ((16), (29)), Wong ((1), (4)), and Parsegian and Rau ((23), (26), (24)).

Relative to the two-rod case there is a wealth of experimental data, based on measurements of colligative properties, as well as small angle x-ray scattering and light scattering to measure order properties of the bundles. Several other experimental approaches are also used. Bundles have been shown to form with filamentous actin, DNA, M13 and fd viruses, and microtubules, thus spanning a relatively wide range of rod radii and linear charge densities. In all cases multivalent ions are an essential ingredient to induce aggregation, highlighting the importance of electrostatic interactions and of going beyond the mean-field theories (which become less accurate with increasing ion valency). Bundles have also been induced with the help of an externally imposed pressure (via addition of an osmotically active species to the bulk solution which cannot penetrate the bundle (25), and with the presence of more complex "counterions" such as short chain molecules (4) or highly-charged proteins (28).

A range of salt concentrations, from salt-free to about one molar, have also been explored for different salt valencies. Often a redissolution of the bundle is observed upon addition of sufficiently high salt concentration increasing ionic strength, this is further evidence of the driving role of electrostatics in bundle formation. However, at lower concentrations the addition of salt can also have a stabilizing effect on the system, since the salt surrounding the bundled phase exerts an osmotic pressure on the bundle, and the concentration of salt inside the bundle might be lower than in the bulk solution ((15), (28)).

Simulations generally reproduce, qualitatively and sometimes quantitatively, the key experimental features. This includes the shape of osmotic pressure curves, the trends with changing the polymer charge density, rod radius, and Although the simulation methods vary widely, it is often the case that the simulated bundle phase has infinite extent via periodic boundary conditions. There is strong (simulational) evidence to indicate that such an infinite phase is stable at equilibrium, or at the very least resides in a free energy minimum that is tens of $k_{\mathrm{B}}T$ deep *per rod*. However, experiments usually show a finite bundle size. It has been hypothesized that the finite size is due to net charge buildup in the bundle, or simply to kinetic effects (11).

The only fundamental theoretical treatment I found of the full bundle was an extension by Ha and Liu of their two-rod work, based on essentially the same model of fluctuating charge variables in the Gaussian approximation, with free mean-field counterions. A key result of this work is shown in Fig. 6, which shows how the free energy varies with bundle size. Their treatment clearly predicts an infinite bundle size.

# 5 Conclusions

In conclusion, I have discussed several aspects of two interesting transitions in solutions of charged, stiff, polymers. Much work needs to be done before the bundling transition is properly understood, but there are powerful experimental, computational, and theoretical tools that have become avail-

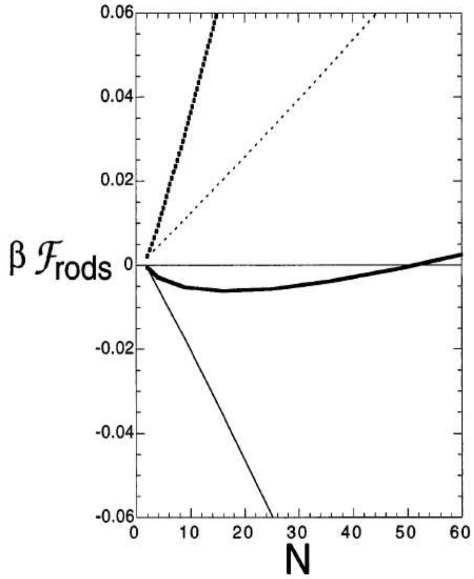

Figure 6: The electrostatic rod free energy (per monomer) for bundles with $N$ rods, obtained via the model described in (11). The bold curves are based on the two-rod results of (10), assuming pairwise additivity of rod-rod interactions. The thin curves are the results of the full $N$-rod analysis. The solid and dashed curves correspond to different values of the Debye length.

able over the years for this work. The counterion condensation transition has been explored much more fully, but there still remain questions of how to systematically improve the PB mean-field theory, and indeed it was not until recently that this transition was addressed as a phase transition *per se* with the toolkit that we have been learning throughout this semester. Despite many years of intense activity, this remains an interesting field full of possibilities.

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