Phase behavior of colloidal rods and stiff biopolymers:
The effect of charge and linkers.

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Abstract

Within Onsager’s second virial theory we have studied the phase behavior of long colloidal rods as a model for stiff biopolymers. In particular we considered the effects of charge, ionic strength, bundle formation, and orthogonal cross linkers on the phase diagram. Phase diagrams for various situations are presented, revealing isotropic, nematic, cubatic and ring phases, with two-phase regions and triple points. In the low salt regime a novel nematic-nematic coexistence is found. The implications of our findings for understanding filamentous actin, a stiff biopolymer that forms either bundles or a ‘cubatic’ network in the cytoskeleton, will be discussed.
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Chapter 1

Introduction

Colloids in suspension are particles surrounded by much smaller solvent particles. For example oil drops in water or smoke particles in air. They should be so small that they still have Brownian motion. This Brownian motion makes them different from a heap of balls because the balls will just stay in one point in phase space when left undisturbed while colloids are constantly moving due to the Brownian motion. This constant motion makes colloids sample their phase space extensively. We assume that the colloids are so big that we can ignore all quantum effects and treat them purely classical. Colloids can have any form or be made from any material for example: silica spheres, protein molecules, oil drops, smoke particles and virus rods. In this report we will only look at the latter shape, the rod-shaped colloids.

Rod-shaped colloids have a very nice advantage and that is that if their aspect ratio is large enough we can terminate the virial expansion quickly. The virial expansion is an expansion of the ideal gas law to extend to non ideal gasses and is derived in [2, chapter 8]. For (nearly) spherical particles the virial expansion is a slowly converging series at high packings that needs to be evaluated nearly completely to get accurate results especially at higher densities. Onsager showed in 1949 [1] that for rod-like particles with a high aspect ratio the second order virial expansion becomes exact because the higher order terms go to zero in this limit.

Long colloidal hard rods have four phases as can be seen in figure [1.1] when there are no ions linkers or other disturbing effects present. The phase with the lowest density is the isotropic phase, in this phase the orientation and the position of the rods is isotropic. For higher densities we have the nematic phase where the position of the rods is still homogenous but all the rods are aligned in more or less the same direction. For higher densities we have what is called the smectic phases where the positions of the rods are ordered in the length direction but not in the perpendicular direction. When we increase the density further we reach a crystal phase where the position and orientation are fully ordered. The transition from isotropic to nematic will occur at very low number densities for
long rods. We will only be looking at phase transitions between phases without any positional ordering so we can describe them with Onsager’s theory.

We are going to use Onsager’s theory to study the effect of charge, screening ions and linkers on the phase diagram of long rods. This is interesting because nearly all colloidal rods carry some charge and so counter ions must be present to maintain global charge neutrality. Moreover in biological systems of rods like actin, DNA or microtubuli, there is a wide variety of proteins linking to these rods. The ions and linkers can attach/condensate to one or more rods and thereby cause some attraction between these rods. If the ions have a high charge and concentration they can even overcharge the rods and hence inverse the charge of the rods. In intermediate ion concentration the rods are nearly neutral and will attract each other such that they condensate into a dense state.
Chapter 2

Theory

2.1 The model

Our system consists of rods with length $L$ and diameter $D$ capped on each end point with half a sphere with the same diameter as the rod. There are $N$ of these rods dispersed in a solvent with volume $V$ giving a number density $\frac{N}{V} = \rho$. An important concept is the orientational distribution function $\Psi$ normalized in such a way that $\int du \, \Psi(u) = \rho$ with $u$ a vector on the unit sphere. The physical interpretation of this is that $\Psi(u)du$ is the density of the rods within the interval $du$ around $u$. So in an isotropic phase where the rods point in every direction $\Psi$ is independent of $u$ and is given by $\Psi = \frac{\rho}{4\pi}$ where the factor $4\pi$ comes from the surface of the unit sphere. We denote $\beta = 1/(k_B T)$, with $T$ the temperature and $k_B$ the Boltzmann constant.

2.2 The free energy

Onsager derived the free energy as functional of this orientational distribution function:

$$\frac{\beta F[\Psi]}{V} = -\rho + \int du \Psi(u) \ln \Psi(u) + \frac{1}{2} \int \int du du' \Psi(u) \Psi(u') B(u,u'),$$

(2.1)

where $\mathcal{V}$ is the thermal volume and $\mathcal{B}$ is the excluded volume containing all interaction terms, $\beta = (k_B T)^{-1}$ and $V$ is the volume. This equation is valid for rods with a high aspect ratio $\frac{L}{D}$.

To find the minimum of the free energy with respect to the orientational distribution we take the derivative with respect to this orientational distribution with lagrangian multiplier $\lambda$ to fix the normalization.

$$\frac{\partial}{\partial \Psi(u)} \left[ \frac{F[\Psi(w)]}{V} - \lambda \int dw \, \Psi(w) \right] = 0$$

(2.2)
2.3 Phase coexistence

By differentiating the free energy we get the chemical potential on the left side and the lagrangian multiplier on the right side:

$$\mu(u) = \lambda.$$  \hspace{1cm} (2.3)

This means that the chemical potentials for rods of all orientations should be identical. This is of course to be expected in equilibrium. So we can write the chemical potential as:

$$\beta \mu = \ln \mathcal{V} \Psi(u) + \int du' \mathcal{B}(u, u') \Psi(u').$$  \hspace{1cm} (2.4)

For fixed $\mu$ and $\mathcal{B}$ this is a nonlinear integral equations for $\Psi(u)$ which can be solved with the algorithm described in section 2.5. In the canonical ensemble one must then tune $\mu$ such that the imposed $\rho$ is obtained.

We are also interested in finding the pressure because it gives a nice way of finding the phase coexistence. The pressure is given by:

$$\beta P(\Psi(u)) = -\frac{\partial}{\partial V}(\beta F(\Psi(u)))$$  \hspace{1cm} (2.5)

Differentiating the free energy gives:

$$\beta P(\Psi(u)) = \rho + \frac{1}{2} \int \int du du' \mathcal{B}(u, u') \Psi(u) \Psi(u')$$  \hspace{1cm} (2.6)

2.3 Phase coexistence

We can calculate the free energy as a function of the chemical potential or the density. To find phase coexistence we use that the pressures and chemical potentials of the two coexisting phases must be identical, otherwise the system would not be in equilibrium. To find state points where $P$ and $\mu$ are the same we can solve two equations with two variables namely $P(\rho_1) = P(\rho_2)$ and $\mu(\rho_1) = \mu(\rho_2)$. An easier way is to calculate the grand potential as function of the chemical potential instead of the density. We then only have to solve $P_1(\mu) = P_2(\mu)$ which can be done quickly.

There is also a different way to find the phase coexistence: the common tangent method. If we plot the free energy density as function of the density we will see something like in figure 2.1. If we take two points with the same slope in the graph for the free energy density $f(\rho) = F(N, V)/V$ as function of the density we have two points for which the following equation holds:

$$\frac{\partial f(\rho)}{\partial \rho} \bigg|_{\rho_1} = \frac{\partial f(\rho)}{\partial \rho} \bigg|_{\rho_2}$$  \hspace{1cm} (2.7)

$$\mu(\rho_1) = \mu(\rho_2)$$  \hspace{1cm} (2.8)
2.4 Order parameters

There are many different possible orientational distributions, especially when one does not demand a specific orientational symmetry. Here I will describe a few phases some of which we will encounter later and one I did not encounter.

The isotropic phase is the phase with the lowest free energy of all the phases at low densities. The orientation of the rods is, as the name already suggests, isotropic. At higher densities this phase will become unfavorable because this isotropic orientation will limit the available volume of the other rods.

At higher densities the nematic phase has the lowest free energy. It is a phase where all the rods are oriented in a cone centered in one direction. This phase is favorable at high densities because the rods have more space to move.
although they have sacrificed some orientational freedom. The shape of the angular distribution as function of the angle resembles a gaussian. The width of this orientational distribution decreases for higher densities.

When the rods favor perpendicular alignment due to the presence of linkers other phases are possible. The cubatic phase is such a phase. In the cubatic phase one third of the rods is aligned in one direction (\( \hat{z} \)), an other third is aligned in a direction perpendicular to the first (\( \hat{y} \)), the third one third is perpendicular to the first and the second group (\( \hat{x} \)). This distribution is like three nematic-like phases arranged in a three dimensional cross. The width of the angular distribution again decreases at higher densities.

Then there is one other phase in between a nematic and an isotropic phase that shows up when the rods favor perpendicular arrangements. This I will call a "ring" phase because I do not know a better word for it. A fraction of the rods is aligned as in a nematic phase but the rest of the rods is arranged perpendicular to this nematic direction, in an azimuthally symmetric way. The total phase is therefore uniaxially symmetric around the nematic direction.

Then we have the cubatic phase with a broken symmetry. This is a phase where one of the cubatic directions is favored over the other two. This phase will appear for example when a cubatic phase is placed in a external field, for example an electric field. The opposite can also happen, where one direction becomes less favorable than the other directions, this can also happen in an external field but could also be caused by a wall.

To be able to distinguish all these different phases we need to define order parameters. For the isotropic and nematic phases the nematic order parameter \( S_z \) is used, it is defined in the \( z \) direction as:

\[
S_z \equiv \langle P_2(u \cdot \hat{z}) \rangle.
\]  

Here \( P_2 \) is the second Legendre polynomial and \( \hat{z} \) is the unit vector along the \( z \) axis. To get the order parameter in any direction we should calculate it for all directions and take the maximum, but because we always take the initial conditions of our iterations such that our system will align along the \( z \) axis, if it aligns, we do not have to worry about that. Introducing the polar angle \( \theta \) and the azimuthal angle \( \varphi \), such that \( u \cdot \hat{z} = \cos \theta \) we write:

\[
S_z = \langle P_2(\cos \theta) \rangle = \frac{1}{\rho} \int_0^\pi d\theta \sin(\theta) \int_0^{2\pi} d\varphi \frac{1}{2} \left( 3 \cos^2 \theta - 1 \right) \Psi(\theta, \varphi).
\]  

This order parameter is zero in the isotropic phase and unity for a perfectly aligned phase.

We need a similar order parameter for the cubatic phase. The cubatic phase is a phase where all rods are aligned in three directions perpendicular to each
other. For this we take the lowest spherical harmonic with the right symmetries:

\[ Q_{xyz} \equiv \left\langle \frac{2}{3} \sqrt{\pi} \text{Re} \left( Y_0^0(\theta, \phi) + \sqrt{\frac{10}{7}} Y_4^4(\theta, \phi) \right) \right\rangle, \] (2.14)

which is normalized to give unity in the case of a perfect cubatic phase or a nematic phase and zero in case of an isotropic phase. We again choose initial conditions for the iteration process such that the peaks in the orientational distribution nicely fall on the \( \hat{x}, \hat{y} \) and \( \hat{z} \) axes.

There is no difference in symmetry between the ring and the nematic phase, so we have to do something else to distinguish between these two phases. For the "ring" phase a fraction of the rods points to the equator. This fraction, combined with the two other order parameters, is enough to distinguish between all phases. In the isotropic phase both \( S \) and \( Q \) are zero. In the nematic phase both \( S \) and \( Q \) are high. In the cubatic phase \( S \) is zero and \( Q \) is high. In the "ring" phase both have an intermediate to high value, but now there is still a considerable fraction of the rods at the equator which is not the case in the nematic phase.

### 2.5 Algorithm

In order to solve the Euler-Lagrange equation\([2,4]\) we use the algorithm described by Herzfeld et al. in [4]. They start with an equation for the chemical potential which they write as:

\[ \mathcal{V}\Psi(u) = \exp \left( \beta \mu - \int du' \frac{B(u, u')}{L^2 D} L^2 D \Psi(u') \right). \] (2.15)

When we shift \( \mu \) by a constant independent of \( \rho \) and go over to a dimensionless concentration \( f(u) = \frac{e^4}{4} L^2 D \Psi(u) \) and to a dimensionless excluded volume \( B(u, u') = \frac{B(u, u')}{L^2 D} \) we arrive at:

\[ f(u) = \exp \left( \beta \mu - \frac{4}{\pi} \int du' B(u, u') f(u') \right) \] (2.16)

Now we can iterate this formula to get a numerical solution of the equation for the chemical potential

\[ f^{n+1}(u) = \exp \left( \beta \mu - \frac{4}{\pi} \int du' B(u, u') f^n(u') \right) \] (2.17)

Herzfeld et al. have shown that each of these iteration steps moves in a the direction of locally decreasing free energy. Although this does not mean that a whole step will decrease the free energy we can assume it will decrease our free energy if we make our steps small enough by mixing the previous with the next iteration.
Because $B(\mathbf{u}, \mathbf{u'})$ only depends on the angle between the two rods $\gamma = \arccos(\mathbf{u} \cdot \mathbf{u'})$ we can write $B(\mathbf{u}, \mathbf{u'}) = B(\gamma, \theta', \varphi - \varphi')$. In the case of an azimuthally symmetric solution around the $z$ axis this can be simplified further by taking the integration around the $z$ axis out of the iteration step:

$$f^{n+1}(\theta) = \exp \left( \beta \mu - \frac{4}{\pi} \int_0^\pi d\theta' K(\theta, \theta') f^n(\theta') \sin(\theta') \right),$$  \hspace{1cm} (2.18)

where the kernel is given by

$$K(\theta, \theta') = \int_0^{2\pi} d\varphi B(\gamma, \theta', \varphi))$$ \hspace{1cm} (2.19)

This is quite a reduction of the complexity of the problem, and it reduces the computation time enormously because this kernel needs to be calculated only once.

In the previous equations we fixed the chemical potential but when there is no bundle formation we can also fix the density. We can than use the following $\mu$ independent iteration scheme:

$$g^{n+1}(\mathbf{u}) = \frac{\exp \left[ -\frac{4c}{\pi} \int d\mathbf{u'} g^n(\mathbf{u'}) B(\mathbf{u}, \mathbf{u'}) \right]}{\int d\mathbf{u''} \exp \left[ -\frac{4c}{\pi} \int d\mathbf{u'} g^n(\mathbf{u'}) B(\mathbf{u''}, \mathbf{u'}) \right]}$$ \hspace{1cm} (2.20)

where $g$ is now a distribution function normalized to unity instead of $\frac{\pi}{4} L^2 D \rho$ and $c = \frac{\pi}{4} L^2 D \rho$. With this method it is easier to control the resulting phase because there is always only one stable phase at any given density. Moreover, often the coexistence densities are well separated, while in case of the chemical potential we have to finetune the initial conditions much more precisely. The disadvantage is that we need to solve two equations with two unknown variables to find the coexistence densities, instead of just one equation with one variable when we fix the chemical potential.

When we fix the chemical potential we have to calculate the dimensionless concentration $c$ of the rods:

$$c = \int d\mathbf{u} f(\mathbf{u}).$$ \hspace{1cm} (2.21)

We also need to compute the pressure which in dimensionless units then becomes:

$$p = c + \frac{2}{\pi} \int d\mathbf{u} \int d\mathbf{u'} B(\mathbf{u}, \mathbf{u'}) f(\mathbf{u}) f(\mathbf{u'}).$$ \hspace{1cm} (2.22)

When we fix the density we have to calculate the chemical potential which reads in dimensionless units

$$\mu = \ln f(\mathbf{u}) + \frac{4}{\pi} \int d\mathbf{u} B(\mathbf{u}, \mathbf{u'}) f(\mathbf{u'}).$$ \hspace{1cm} (2.23)
The free energy density is sometimes needed when one wants to use the common tangent method of finding phase coexistence, it is given by:

$$\frac{\beta F}{V} = \int \! du \, f(u) \ln f(u) - c + \frac{2}{\pi} \int \! du \int \! du' B(u, u') f(u) f(u'). \quad (2.24)$$

### 2.6 Hard rods

We will here show the phase behavior of hard rods, already obtained a long time ago by Onsager and others. In the later chapters we will add other effects: charge, bundles and linkers to this simple case. We will use this simple case to test our programs and use it here to illustrate how the procedure of calculating a phase diagram works.

#### 2.6.1 Potential

The pair potential $U$ as function of the distance $r$ is defined as the energy required to bring two objects at separation $r$ from infinity. For hard rods this energy is 0 if the rods do not overlap and $\infty$ when they do overlap so we get:

$$\beta U = \begin{cases} 0 & \text{No overlap} \\ \infty & \text{Overlap} \end{cases}, \quad (2.25)$$

with $\beta = k_b T$

#### 2.6.2 Excluded volume

If we assume that the rods are circular and their ends are capped by half a sphere, so they have the shape of a spherocylinder, the excluded volume of rods at an angle $\gamma$ is given by:

$$B(\gamma) = 2L^2 D \sin \gamma + 2\pi D^2 L + \frac{4}{3} \pi D^3 \quad (2.26)$$

Now if the spherocylinders have a large aspect ratio so $D/L \approx 0$ the first term dominates and we can write $B(\gamma) = 2L^2 D \sin \gamma$. When the rods have a slightly different shape at the end the excluded volume will differ only in the terms we just neglected so as long as the rods are straight, hard, more or less circular and have a large aspect ratio this equation holds.

Because we have no reason to expect non-rotational symmetric angular distribution profiles we can use the simplified iteration scheme for azimuthal around the $z$ axis. This will also ensure that a possible nematic phase will always line up with the $z$ axis. The azimuthally integrated kernel $2.19$ then becomes:

$$K(\theta, \theta') = \int_0^{2\pi} \! d\varphi \sqrt{1 - (\cos \theta \cos \theta' + \sin \theta \sin \theta' \cos \varphi)^2} \quad (2.27)$$
2.6 Hard rods

2.6.3 Phase behavior

The free energy depends only on one parameter, the density, so we have a very simple phase "diagram". Below a density of \( c = 3.290409 \) we have an isotropic phase, between \( c = 3.290409 \) and \( c = 4.191069 \) we have phase coexistence and above \( c = 4.191069 \) we have a nematic phase with order parameter \( S_z = 0.792201 \) as can be seen in figure [2.3]. For higher densities and rods with a finite aspect ratio there also will be a smectic phase, but this is beyond the scope of this project.
Chapter 3

Charged rods

Hard rods are very rare in the real world but charged rods are very common. Therefore I will discuss the effect of charging of the rods on the phase diagram. Stroobants et al. [7] already considered this but they made a simplification which made their approach only valid for intermediately charged rods in a solvent with a relatively high ion concentration. Because of the present-day computer power we need not make their approximation, and we find, perhaps surprisingly, an interesting phase diagram containing a coexistence between a low and a high density nematic phase.

3.1 Potential

We assume that the rods have a constant effective linear charge density \( v_{\text{eff}} = \frac{Z_{\text{eff}}}{L} \) (independent of their concentration) along their whole length, and that they are suspended in a solvent with screening length \( \kappa^{-1} \). The electrostatic part of the potential between the two charged rods at separation \( x \) and angle \( \gamma \) with an effective line charge density \( v_{\text{eff}} \) is then given by integrating the screened coulomb potential over both rods:

\[
\beta V(\gamma, x) = v_{\text{eff}}^2 Q \int_A da \int_B db \frac{e^{-\kappa|\mathbf{r}(a, b, x, \gamma)|}}{|\mathbf{r}(a, b, x, \gamma)|}. \tag{3.1}
\]

Here \( A \) and \( B \) are the integrations along the centers of rods, the Bjerrum length \( Q = \beta e^2/\epsilon_{\text{solvent}} \), and \( a \) and \( b \) are running along the rods. When we take \( a = 0 \) and \( b = 0 \) at the smallest separation of the rods the distance becomes \( r(a, b, x, \gamma) = \sqrt{a^2 + b^2 + x^2 - 2ab\cos\gamma} \). When we insert this in the integral we get:

\[
\beta V(\gamma, x) = v_{\text{eff}}^2 Q \int_A da \int_B db \frac{e^{-\kappa \sqrt{a^2 + b^2 + x^2 - 2ab\cos\gamma}}}{\sqrt{a^2 + b^2 + x^2 - 2ab\cos\gamma}}. \tag{3.2}
\]

The effective line charge density is chosen in such a way that the double layers outside the rod match that of a charge density on the surface of the rod. To
simplify this equation we will assume that the screening length is small compared
to the length of the rods so that we can ignore end effects. So now we integrate
along infinitely long rods so A and B become: $A = B = \{-\infty, \infty\}$. The integral
has now the following form:

$$
\beta V(\gamma, x) = v^2_{\text{eff}} Q \int_{-\infty}^{\infty} da \int_{-\infty}^{\infty} db \frac{e^{-\kappa \sqrt{a^2 + b^2 + x^2 - 2ab \cos \gamma}}}{\sqrt{a^2 + b^2 + x^2 - 2ab \cos \gamma}}.
$$

(3.3)

In this form we can now substitute polar coordinates $a = r \cos \phi$ and $b = r \sin \phi$.
With this trick we can now calculate the integral:

$$
\beta V(\gamma, x) = v^2_{\text{eff}} Q \int_0^{2\pi} d\phi \int_0^{\infty} dr \frac{r e^{-\kappa \sqrt{r^2 + x^2 - 2r^2 \sin \phi \cos \phi \cos \gamma}}}{\sqrt{r^2 + x^2 - 2r^2 \sin \phi \cos \phi \cos \gamma}}
$$

(3.4)

$$
= v^2_{\text{eff}} Q \int_0^{2\pi} d\phi \left[ -\frac{1}{\kappa} \frac{e^{-\kappa \sqrt{r^2 + x^2 - 2r^2 \sin \phi \cos \phi \cos \gamma}}}{1 - 2 \cos \phi \sin \phi \cos \gamma} \right]_{r=0}^{r=\infty}
$$

(3.5)

$$
= \frac{v^2_{\text{eff}} Q}{\kappa} e^{-\kappa x} \int_0^{\pi/4} d\phi \frac{8}{1 - \cos(\gamma) \sin^2(2\phi)}
$$

(3.6)

$$
= \frac{v^2_{\text{eff}} Q}{\kappa} e^{-\kappa x} \left[ \frac{4 \arctanh(\sin \gamma \tan 2\phi)}{\sin \gamma} \right]_{\phi=0}^{\phi=\pi/4}
$$

(3.7)

$$
= \frac{v^2_{\text{eff}} Q}{\kappa} e^{-\kappa x} \frac{2\pi}{\sin \gamma}.
$$

(3.8)

We see that when there are no ions present in the solvent the range of the potential
is infinite. We can also see that putting two rods parallel ($\gamma = 0$) costs an infinite
amount of energy. This is an effect of the infinite length of the rods for which
the extension of $A,B$ to $\infty$ leads to artefacts.

## 3.2 Excluded volume

The excluded volume due to the charge is given by:

$$
B_c(\gamma) = 2L^2 \sin \gamma \int_{D}^{\infty} dx \left( 1 - \exp \left( -\beta V(\gamma, x) \right) \right).
$$

(3.9)

The $L^2 \sin \gamma$ comes from the integration over the $y$ and $z$ directions and the 2
from the negative $x$. Here we ignored end effects of order $O(LD, D^2)$ as we did
before. Filling in the potential we found in the previous section gives an integral
of the form:

$$
\int_{D}^{\infty} dx \left( 1 - e^{-\beta V(\gamma, x)} \right) = \int_{D}^{\infty} dx \left( 1 - \exp \left( -\frac{A}{\sin \gamma} \exp(-\kappa x) \right) \right),
$$

(3.10)
where \( \frac{A}{\sin \gamma} = (v_{\text{eff}}^2 Q 2\pi)/((\kappa \sin \gamma)) \). We now substitute \(-y = -\kappa x + \ln(\frac{A}{\sin \gamma})\) and get:

\[
B_c(\gamma) = \frac{2L^2 \sin \gamma}{\kappa} \int_{\kappa D - \ln(\frac{A}{\sin \gamma})}^{\infty} (1 - e^{-e^{-y}})
\]

\[
= \frac{2L^2 \sin \gamma}{\kappa} \left( -\kappa D + \ln(\frac{A}{\sin \gamma}) + \gamma_E - \text{ExpIntegralEi}(-\frac{A e^{-\kappa D}}{\sin \gamma}) \right)
\]

\[
= \frac{2L^2 \sin \gamma}{\kappa} \left( \ln(\frac{A e^{-\kappa D}}{\sin \gamma}) + \gamma_E - \text{ExpIntegralEi}(-\frac{A e^{-\kappa D}}{\sin \gamma}) \right)
\]

Where \( \gamma_E \approx 0.5772 \) is Euler’s constant and \( \text{ExpIntegralEi}(z) = -\int_{z}^{\infty} \exp(-t)/t \, dt \).

Stroobants et al. made the assumption that \( \text{ExpIntegralEi}(-\frac{A e^{-\kappa D}}{\sin \gamma}) \approx 0 \) which is valid for \( A e^{-\kappa D} \equiv A' > 2 \) but because there are very efficient algorithms to calculate exponential integrals available we will simply keep the full expression \( 3.11 \).

**Figure 3.1:** The excluded volume of charged rods as function of the angle between the rods for different values of \( \kappa D \) and \( A' \).

It is convenient to scale the excluded volume as

\[
B(\gamma) = 2L^2 D \sin \gamma \left( 1 + \frac{\ln(\frac{A e^{-\kappa D}}{\sin \gamma}) + \gamma_E - \text{ExpIntegralEi}(-\frac{A e^{-\kappa D}}{\sin \gamma})}{\kappa D} \right)
\]

(3.12)

where the \( 2L^2 D \sin \gamma \) is the hard core part and the rest is due to the electrostatics.

Stroobants et al. proceeded as follows. They defined an effective diameter such that the isotropic behavior of the rods can be described by hard rods with this diameter. They also defined a parameter \( h \) which describes the deviation from the hard rod behavior. They get the following excluded volume:

\[
B(\gamma) = 2L^2 D_{\text{eff}} \sin \gamma \left( 1 + h(- \ln \sin \gamma - \ln 2 + \frac{1}{2}) \right)
\]

(3.13)

where

\[
D_{\text{eff}} \equiv D(1 + \delta),
\]

\[
\delta(A', \kappa D) = \frac{\ln A' + \gamma_E + \frac{2}{\pi} \langle (- \sin \gamma \ln(\sin \gamma)) \rangle_i}{\kappa D},
\]

\[
h(A', \kappa D) \equiv \frac{1}{\kappa D_{\text{eff}}} = \frac{1}{\kappa D(1 + \delta(A', \kappa D))}.
\]
This is valid for $A' > 2$ but leads to artifacts when one tries to let the charge of the rods go to zero.

Now in analogy with Stroobants et al. we choose an effective diameter $D_{\text{eff}}$. We define it in exactly the same way by demanding that the isotropic solution of the charged rods must be identical to the isotropic solution of uncharged rods with that diameter. This yields the following equations:

\[ B(\gamma) = 2L^2 D_{\text{eff}} \sin \gamma \left( 1 + h \left( - \ln \sin \gamma - \frac{4}{\pi} \langle \langle - \sin \gamma \ln(\sin(\gamma)) \rangle \rangle_i - \text{ExpIntegralEi} \left( -\frac{Ae^{-\kappa D}}{\sin(\gamma)} \right) - \frac{4}{\pi} \langle \langle - \sin \gamma \text{ExpIntegralEi} \left( -\frac{Ae^{-\kappa D}}{\sin(\gamma)} \right) \rangle \rangle_i \right) \]  

\[ D_{\text{eff}} \equiv D(1 + \delta) \]

\[ \delta(A', \kappa D) = \ln A' + \gamma_E + \frac{4}{\pi} \langle \langle - \sin \gamma \ln(\sin(\gamma)) \rangle \rangle_i + \frac{4}{\pi} \langle \langle - \sin \gamma \text{ExpIntegralEi} \left( -\frac{Ae^{-\kappa D}}{\sin(\gamma)} \right) \rangle \rangle_i \]

\[ h(A', \kappa D) \equiv \frac{1}{\kappa D_{\text{eff}}} = \frac{1}{\kappa D(1 + \delta(A', \kappa D))} \]

Here the $\langle \langle \rangle \rangle$ is an average over a double integral over the surface of a sphere with unit surface: $\langle \langle \sin \gamma \rangle \rangle = \frac{\pi}{2}$ and $\langle \langle - \sin \gamma \ln(\sin(\gamma)) \rangle \rangle_i = (\frac{\pi}{2})(\ln 2 - 1/2)$. The average over the ExpIntegralEi can’t be performed analytically so it has to be done numerically. This yields the following equation for
the dimensionless excluded volume:

\[
B(\gamma) = 2 \sin \gamma \left( 1 + h \left( -\ln \sin \gamma - \ln 2 + \frac{1}{2} - \text{ExpIntegralEi}\left( -\frac{Ae^{-\kappa D}}{\sin \gamma} \right) \right) - \frac{4}{\pi} \left\langle \left\langle -\sin \gamma \text{ExpIntegralEi}\left( -\frac{Ae^{-\kappa D}}{\sin \gamma} \right) \right\rangle \right\rangle \right) \tag{3.15}
\]

Note that we now used \( L^2 D_{\text{eff}} \) to make the excluded volume dimensionless so we also use a dimensionless concentration that is made dimensionless with the effective diameter: \( c = \rho L^2 D_{\text{eff}} \frac{\pi}{4} \).

As we can see in figure \( \text{3.2} \) the effective diameter increases linearly with the charge of the rods for low screening and increases more slowly for higher screening. The twisting parameter \( h \) diverges for zero screening and falls off for higher screening. When we look at the change of \( h \) with constant screening we see that it decreases with increasing charge. So a higher charge results in a higher effective diameter and in a lower twisting parameter, while a higher \( \kappa \) will decrease the twisting and the effective diameter. This breaks down however for low charge where the exponential integrals start becoming important. These exponential integrals will cancel the effect of the increase of \( h \) and cause the excluded volume to convert to the hard rods excluded volume when \( A' \to 0 \).

### 3.3 Phase behavior

Here we present the phase diagram of the charged rods. The phase coexistence has been calculated using a fixed \( \mu \) approach. So we looked at the pressure difference between two different phases with identical chemical potential and then iterated and shifted \( \mu \) towards the zero pressure difference. The lines in the phase diagram were constructed by starting at a known solution for \( \Psi(u) \) and following the lines from there. This speeds up the calculations because in this way we do not have to scan over the whole phase diagram. One can use a very good initial guess by using the end result of the previous step. All these calculations were done on a one-dimensional grid and with a precalculated kernel. This means we did not allow for any non-azimuthal symmetry breaking phases, since we have no reason to expect such phases. All calculations were done on a non equidistant grid of 100 points \( \theta \in (0, \pi/2) \) or more. The non equidistant grid was necessary in the high density nematic regions where the distribution is very sharply peaked. To check if our results were independent of the grid size we recalculated some lines with grids of 1000 points or more, and they gave the same results within four to five significant digits.

Apart form the dimensionless density the phase diagram depends on two parameters \( \kappa D \) and \( A' \). To get some feeling of the shape we plot the phase diagram with \( \kappa D \) fixed and then vary \( h \) by varying the charge \( A' \) (a change of
3.3 Phase behavior

Figure 3.3: The phase diagram of charged Onsager rods in the high salt concentration regime. The twisting parameter is for $A' > 2$ the same as the one used by Stroobants et al. and the same holds for the effective diameter.

Figure 3.4: The phase diagram of charged Onsager rods in the low salt concentration regime. The excluded volume plotted on the right has developed a sharper bend and low angles. This causes a separation of the nematic phase in a high and a low density nematic phase.
3.3 Phase behavior

$A'$ at constant $\kappa D$ is a change in the charge. The phase diagrams are plotted for the dimensionless concentration that depends on the effective diameter, and hence also on $A'$ and $\kappa D$. In figure 3.3, we have plotted the phase diagrams for high salt concentrations. It is visible that the lines of constant $\kappa D$ convert to the line calculated by Stroobants for values of $A' > 2$. For lower values of $A'$ the lines deviate from the results of Stroobants and as the charge is lowered ($h$ increases) the binodals turn back to the well known isotropic nematic coexistence. In the phase diagram 3.4, for low screening, we see that interesting phenomena occur in this region where the exponential integrals cause the convergence to the hard rod. The phase behavior differs greatly from that in the high salt regime. The bump in the excluded volume is now so sharp that the nematic phase splits up in a high density and a low density nematic phase. The phase diagram also shows a triple point where $I$, $N$ and $N$ coexist.

![Figure 3.5: The low salt regime. Lines are for $\kappa D = 0.3$ and the charge is changed by changing $A'$.](image)

The shape of these phase diagrams is obscured by plotting them as function of $h$ when $h$ is countered by the exponential integrals. We can also plot the phase diagram as a function of $A'$ and $\kappa D$, as in figures 3.7, 3.6 and 3.5. This gives rise to graphs that are not as easy to compare with the results of Stroobants et al. but they give a clearer overview of the phase behavior. Here we also plotted them as function of the dimensionless concentration that is made dimensionless with $D$ instead of $D_{\text{eff}}$. It can be seen that at zero charge the rods behave as hard rods and that then with a really small increase in charge the rods develop
3.3 Phase behavior

Figure 3.6: The low salt regime. Lines are for $\kappa D = 0.2$ and the charge is changed by changing $A'$.

Figure 3.7: The low salt regime. Lines are for $\kappa D = 0.1$ and the charge is changed by changing $A'$. 
a huge twisting. Then for higher charges the rods just increase their effective
diameter and the twisting effect lessens. It is in these figures more obvious that
the nematic-nematic coexistence is only present in a very small region of the
phase diagram for really low salt concentrations.

So although the results of Stroobants et al. are not valid for a big parameter
range (namely the low charge high screening regime), in the largest part of this
regime the rods behave as expected: they just convert to hard rods. But for a
very small part of the parameter regime something unexpected happens and there
is a nematic-nematic coexistence. But it is only in a very small part of the big
parameter regime and this makes it probably difficult to observe experimentally.
Chapter 4

Linking rods

Experiments show a very drastic change in the phase behavior when there are linkers added who pull orthogonal neighboring rods closer together. These linkers can have very different shapes and natures: in biological systems like microtubules, actin and DNA there are many different proteins present all in their own way linking and interacting with the rods (see section 6.2).

4.1 Potential and Excluded Volume

We define a pair potential $w$ between two rods at distance $x$ and angle $\theta$ in a suspension with linkers in the following way:

$$w(\gamma, x) = \begin{cases} -\alpha e^{-\eta(\frac{\pi}{2} - \gamma)^2} & D < x < \sigma \\ \frac{2e^{-\kappa x}}{\sin \gamma} & x > \sigma \end{cases}$$  \hspace{1cm} (4.1)

where $\alpha$, $\eta$ and $\sigma$ are the strength, the angular width and the range of the attraction caused by the linkers. When we plot the excluded volume corresponding to a typical potential, as shown in figure 4.1 we see that it looks very similar to an excluded volume already discussed in this report namely that of Stroobants et al.:

$$B(\gamma) = 2L^2D_{\text{eff}} \sin \gamma (1 + h(- \ln \sin \gamma - \ln 2 + \frac{1}{2}))$$  \hspace{1cm} (4.2)
but now for high values of the twisting parameter $h$ that can not be reached by charging.

![Figure 4.2: A potentially interesting excluded volume shape we miss because of our simplification. Here we expect it to be possible to have coexistence between two different cubic phases. In this case we have picked a low salt concentration and a rather narrow angle for attraction.](image)

On the basis of the shape of the excluded volume we can expect a cubic phase so we need to do the calculations on a two dimensional ($\theta, \varphi$) grid. This system with three extra parameters is very interesting but has a huge parameter range and the calculations on a two dimensional grid are time consuming. Therefore I will limit my calculations to the excluded volume as used by Stroobants et al., for high twisting parameters that can not be reached by charge alone. This is reasonable because with this assumption we will cover most interesting shapes of the excluded volume while keeping the phase diagram dependent on the single parameter $h$ and the density.

4.2 Linkers without preferred linking angle

Here we consider the possibility of linking rods perpendicular, with linkers that can bind to one or to two rods without any preferred direction in the angle between the rods. To do so we look at a pair of rods in a volume $V$ in contact with a bath of linkers with chemical potential $\mu_l$. We first write down the partition sums for three different cases: the unlinked rods, the perpendicular linked rods and the parallel linked rods:

$$Z_{\text{unlinked}} = \frac{(4\pi)^2 V (V - \langle B(\theta) \rangle)}{2V^2} \exp(-\beta u_0)$$  \hspace{1cm} (4.3)

$$Z_\perp = \frac{8\pi^2 V}{2V^2} v_\perp \exp(-\beta u_\perp)$$  \hspace{1cm} (4.4)

$$Z_\parallel = \frac{8\pi^2 V}{2V^2} v_\parallel \exp(-\beta u_\parallel)$$  \hspace{1cm} (4.5)

where $u_0, u_\perp, u_\parallel$ are the free energies of the linkers in the cases of separated, perpendicular and parallel rods and $v_\perp$ and $v_\parallel$ are small volumes in which we call the rods perpendicular and parallel linked, $v_\perp, v_\parallel \ll V$ and $v_\perp \approx v_\parallel$. The linked rods have a factor of $8\pi^2$ instead of $16\pi^2$ because they have one rotational degree of freedom less. We now look at the free energy difference between the linked
and the unlinked cases:

\[ \beta(F_\perp - F_{\text{unlinked}}) = -\ln \left( \frac{v_\perp}{2V - 2\langle B(\theta) \rangle} \right) + \beta(u_\perp - u_0) \]  

\[ \beta(F_\parallel - F_{\text{unlinked}}) = -\ln \left( \frac{v_\parallel}{2V - 2\langle B(\theta) \rangle} \right) + \beta(u_\parallel - u_0) \]

We want to calculate the free energy difference of the linkers in the case of perpendicular, parallel and un-linked rods. To do this we use an adsorption model. We assume that the rods can be divided into a number \( \frac{L}{d} \) of independent binding sites for the linkers with \( d \) the size of such a site. We have a two state model for the free rods. At a certain place on a rod there can be two possible situations: a bound linker (energy \( e_1 \)) or no linker (energy 0). The places where two rods are close together we treat differently. Where the rods are close together we have five possible situations: a linker bound to rod one (energy \( e_{01} \)), a linker bound to rod two (energy \( e_{02} \)), a linker bound to rod one and two (energy \( e_{00} \)), no linkers bound (energy \( e_{00} \)), and a linker bound to rod one and another linker bound to rod two (energy \( e_{11} \)). Depending on the kind of linker, different situations contribute to the linking. There are proteins like (like scruin) where \( e_{11} \) is very low and causes the binding, but for example in the case of ions \( e_2 \) has the lowest energy and contributes most to the linking. Further we assume that the binding energy of the linkers does not depend on the angle between the rods. This gives the following partition sums:

\[ Z_{\text{free}} = (e^{-\beta e_{00}} + e^{-\beta(e_1 - \mu I)})^2 \]  

\[ Z_{\text{link}} = e^{-\beta e_{00}} + e^{-\beta(e_{10} - \mu I)} + e^{-\beta(e_{01} - \mu I)} + e^{-\beta(e_2 - \mu I)} + e^{-\beta(e_{11} - 2\mu I)} \]

where \( Z_{\text{free}} \) is the partition sum for two places where the rods are far away and \( Z_{\text{link}} \) the sum for two places close enough together to allow linking. This gives then the following free energies:

\[ \beta u_0 = -\frac{L}{d} \ln (Z_{\text{free}}) \]  

\[ \beta u_\perp = -\frac{L - d}{d} \ln (Z_{\text{free}}) - \ln (Z_{\text{link}}) \]  

\[ \beta u_\parallel = -\frac{L}{d} \ln (Z_{\text{link}}) \]

We are now interested in the free energy differences:

\[ \beta(u_\perp - u_0) = -\ln (Z_{\text{link}}) + \ln (Z_{\text{free}}) \]  

\[ \beta(u_\parallel - u_0) = -\frac{L}{d} (\ln (Z_{\text{link}}) - \ln (Z_{\text{free}})) \]
A perpendicular linked arrangement becomes favorable above a free arrangement when the free energy of the linked rods is lower than that of the free rods so $F_\perp - F_{\text{unlinked}} < 0$. This only happens when:

$$\ln \left( \frac{v_\perp}{2V - 2\langle B(\theta) \rangle} \right) > \beta(u_\perp - u_0)$$ \hspace{1cm} (4.16)

The left side of this is negative because $v_\perp < 2V - 2\langle B(\theta) \rangle$ and the logarithm of something smaller than one is negative. From this follows that:

$$-\ln (Z_{\text{link}}) + \ln (Z_{\text{free}}) < 0$$ \hspace{1cm} (4.17)

which means that also

$$-\frac{L}{d} \left( \ln (Z_{\text{link}}) - \ln (Z_{\text{free}}) \right) < -\ln (Z_{\text{link}}) - \ln (Z_{\text{free}})$$ \hspace{1cm} (4.18)

$$\beta(u_\parallel - u_0) < \beta(u_\perp - u_0)$$ \hspace{1cm} (4.19)

from this follows that:

$$\beta(F_\parallel - F_\perp) = \beta(F_\parallel - F_{\text{unlinked}}) - \beta(F_\perp - F_{\text{unlinked}})$$ \hspace{1cm} (4.20)

$$= -\ln \frac{v_\parallel}{v_\perp} + \beta(u_\parallel - u_0) - \beta(u_\perp - u_0)$$ \hspace{1cm} (4.21)

$$< 0$$ \hspace{1cm} (4.22)

So $F_\parallel < F_\perp$ for rods with $L/d \gg 0$. So we can conclude that parallel linking is always favorable over perpendicular linking when the linkers in question do not have a strong preference for perpendicular linking. This also holds for charged rods because we can incorporate the effect of the charge in $\varepsilon_{00}$.

This can be explained in the following way: When one linker gains enough energy to bind one rod to a neighboring rod to pay the price of entropy, and in the case of charged rods the charge repulsion to keep the two rods together, more linkers will follow. When one linker has paid this price it becomes easier for other linkers to bind to the same pair of rods because they already are close together, they have to pay a lower price to bind the two rods together while gaining the same amount of energy. So even in the case of charged rods isotropically linking linkers can never cause perpendicularly linked rods. This shows that the mechanism of ion bridges as described by Bruinsma [6] can not link rods perpendicularly and so cannot cause the twisting observed in experiments on actin as performed by Wong et al. [19].

### 4.3 Phase behavior

We performed all calculations for $h > 3.0$ on a non equidistant two dimensional grid. The grids we used had 1000 to 2000 points. The grid we used in the cubic...
4.3 Phase behavior

The phase diagram of twisting or orthogonally linking long rods is shown in Figure 4.3. The phase diagram starts with the well-known widening caused by the increasing slope of the excluded volume at zero angle. This slow widening continues up to \( h \approx 3.5 \) where two new phases appear as can be seen in the plot of the free energy in Figure 4.4. The ratio of the rods in the ring varies slowly from around 30 percent for low concentrations to zero where the ring disappears and the phase becomes a nematic phase for high concentrations. This uniaxial phase has only a
slightly lower free energy than the cubic phase appearing at slightly higher values of $h$. For higher values of $h$ the cubic phase becomes much more favorable than the nematic and ring phases. At $h \approx 3.8$ the ring phase has disappeared completely and at $h \approx 5$ the nematic phase disappears. At this point the dip in the excluded volume at $\gamma = \pi/2$ reaches zero. When this happens the free energy cost of the cubic phase compared with the nematic phase has completely disappeared, making the cubic phase more favorable at all densities. In figure 4.5 the order parameters and the fraction of the rods near the equator is plotted. Here one can see that the fraction of the rods decreases with increasing chemical potential.

We have searched for different phases by starting with different initial conditions but we could not find a stable tetratic phase like the phase mentioned by Bruinsma [6]. And we expect that any such phase would disappear when the dip in the excluded volume close to $\gamma = \pi/2$ degrees reaches zero. In this case there is no energetic or entropic gain from breaking the symmetry of the cubic phase.

We have found two additional phases in the case of linkers. The cubic and the ring phase: the ring phase has only a very small stable region in the phase diagram but because these results where obtained with just the one parameter model it is possible that this region is much bigger for different parameters. The cubic phase has completely pushed the nematic phase away when the dip in the excluded volume at $\gamma = \pi/2$ reaches zero. This phase should be easy to observe because the parameter regime for it is big. We can not let $h$ go to higher values because a negative excluded volume is unphysical. To study this case we would have to include higher order virial coefficients.
Figure 4.6: Logarithmic spherical plots of the density distribution. We have added 1 to the density distribution to avoid negative values.
Figure 4.7: Logarithmic plots of the density distribution. We have added 1 to the density distribution to avoid negative values.
Chapter 5

Bundling rods

Bundling caused by an angle independent attraction is difficult to describe with pure Onsager theory because a negative excluded volume is unphysical. To get around this problem we extend Onsager theory to handle bundles of different numbers of rods. So we now have not only different species with different angles (as Onsager describes the rods) but also different thicknesses.

5.1 Onsager for bundles

We want to know the free energy as function of the distribution of rods among bundles and the orientational distribution of the bundles. We will start by calculating the free energy of a bundle with $k$ rods, where all rods are assumed to be parallel to each other:

$$F_b(k) = -\frac{1}{\beta} \ln(Z_b(k)) \quad (5.1)$$

$$Z_b(k) = \frac{1}{V_{k-1} k!} \int_{\mathbf{r}_{SM}=0} d\mathbf{r}_1 \cdots d\mathbf{r}_k e^{-\beta E(r_1, \ldots, r_k)} \quad (5.2)$$

here the integral is over all coordinates $r$ with the center of mass fixed and

$$\frac{1}{V} = \int e^{-\beta p^2/2m} dp.$$ 

Now we make a few assumptions:

$$Z_b(k) \approx \frac{v^{k-1}}{V_{k-1}} e^{-\beta E(k)} \quad (5.3)$$

where $v$ is the volume of the area where the colloids attract each other, and $E(k)$ is the internal energy to be specified later. Then

$$\beta F_b(k) = (k-1) \ln \frac{V}{v} + \beta E(k). \quad (5.4)$$
5.2 Minimizing the free energy

We now can add the bundling term to the free energy and add summations over the bundles to the free energy and we get the free energy of the rod system:

\[
\frac{\beta F[\Psi_l]}{V} = -\rho + \sum_k \int \Psi_k(u) \ln V \Psi_k(u) \quad \text{Entropic term}
\]

\[
+ \sum_k \rho_k \beta F_b(k) + \frac{1}{2} \sum_{k,l} \int \int d u' B_{kl} (u, u') \Psi_k(u) \Psi_l(u') \frac{1}{L^2 D} \Psi_l(u') + \beta \mu_k
\]

where \( \int d u \Psi_k(u) = \rho_k \) is the density of the \( k \)-bundles.

5.2 Minimizing the free energy

To find the minimum of the free energy with respect to the orientational distribution we take the derivative with respect to this orientational distribution again with lagrangian multiplier \( \mu \) to conserve the number of rods and the normalization.

\[
\frac{\partial}{\partial \Psi_k(u)} \left[ \frac{F[\Psi_l]}{V} - \mu \sum_l \int d w \ln \Psi_l(w) \right] = 0
\]

By differentiating the free energy we get the chemical potential on the left side and the \( k \) times the lagrangian multiplier on the right side:

\[
\mu_k - \mu_k = 0
\]

So the \( k \) dependance of \( \mu(k) \) is as expected for bundles made out of \( k \) identical rods. So now we can calculate the chemical potential:

\[
\beta \mu_k = \ln V \Psi_k(u) + \beta F_b(k) + \sum_l \int d u' B_{kl}(u, u') \Psi_l(u')
\]

We also want to calculate the pressure and this is in analogy with the normal non bundling case:

\[
\beta P(\Psi_k(u)) = \rho + \frac{1}{2} \sum_{k,l} \int \int d u' B_{kl}(u, u') \Psi_k(u) \Psi_l(u')
\]

5.3 Algorithm

\[
\Psi_k(u) = \exp \left( (k-1) \ln \frac{V}{V} - \beta E(k) - L^2 D \sum_l \int d u' \frac{B_{kl}(u, u')}{L^2 D} \Psi_l(u') + \beta \mu_k \right)
\]
We can now write \( E(k) = \xi(k) \cdot k \) with \( \xi(k) \) the energy per rod in a bundle of \( k \) rods. When we also shifting \( \mu \) by a constant independent of \( k \) or \( \rho \) and go to dimensionless concentration \( f_k(u) = \frac{\pi}{4} L^2 D_{\text{eff}} \Psi_k(u) \), dimensionless volume \( v = \frac{v}{L^2 D_{\text{eff}}} \) and dimensionless excluded volume \( B_{kl}(u, u') = \frac{B_{kl}(u, u')}{L^2 D_{\text{eff}}} \) we arrive at:

\[
f_k(u) = \frac{\pi}{4v} \exp \left( -\beta k\xi(k) - \frac{4}{\pi} \sum_l \int \! \! d\mathbf{u}' B_{kl}(u, u') f_l(u') + \beta \mu k \right)
\]  \hspace{1cm} (5.11)

Now we can iterate this equation to get a numerical solution of the equation for the chemical potential:

\[
f_{k+1}^{n+1}(u) = \frac{\pi}{4v} \exp \left( -\beta k\xi(k) - \frac{4}{\pi} \sum_l \int \! \! d\mathbf{u}' B_{kl}(u, u') f_{l}^{n}(u') + \beta \mu k \right)
\]  \hspace{1cm} (5.12)

Because \( B(u, u') = B(\gamma(\theta, \theta', \varphi - \varphi')) \) only depends on the angle between the two rods, we can, in the case of a rotational symmetric solution around the \( z \) axis, simplify this further by taking out the integration around the \( z \) axis:

\[
f_{k+1}(\theta) = \frac{\pi}{4v} \exp \left( -\beta E(k) - \frac{4}{\pi} \sum_l \int_0^{\pi} \! \! d\theta' K_{kl}(\theta, \theta') f_{l}^{n}(\theta') \sin(\theta') + \beta \mu k \right)
\]  \hspace{1cm} (5.13)

where the kernel is given by:

\[
K_{kl}(\theta, \theta') = \int_0^{2\pi} \! \! d\varphi B_{kl}(\gamma(\theta, \theta', \varphi)).
\]  \hspace{1cm} (5.14)

When we fix the chemical potential we have to calculate the dimensionless concentration of the bundles and the rods. They are given by:

\[
c = \sum_k \int \! \! d\mathbf{u} \ f_k(u)
\]  \hspace{1cm} (5.15)

\[
c_{\text{rod}} = \sum_k \int \! \! d\mathbf{u} \ k f_k(u)
\]  \hspace{1cm} (5.16)

We also need to compute the pressure which in dimensionless units then becomes:

\[
p = c + \frac{2}{\pi} \sum_k \sum_l \int \! \! d\mathbf{u} \int \! \! d\mathbf{u}' \ B_{kl}(u, u') f_k(u) f_l(u')
\]  \hspace{1cm} (5.17)

When we fix the density we have to calculate the chemical potential in dimensionless units. This is then:

\[
\mu_k(u) = \frac{1}{k} \left( \ln c + \ln \frac{4V}{\pi} + E(k) + \frac{4}{\pi} \sum_l \int \! \! d\mathbf{u} \ B_{kl}(u, u') f_l(u') \right)
\]  \hspace{1cm} (5.18)
The dimensionless free energy density is sometimes needed when you want to use
the common tangent method of finding phase coexistence. It is given by:

\[
\frac{F}{V} = c \ln v - c + \sum_k \int du \ f_k(u) \ln f_k(u) + \\
\sum_k E(k) \int du \ f_k(u) + \frac{2}{\pi} \sum_k \sum_l \int du \int du' B_{kl}(u, u') f_k(u) f_l(u')
\]  (5.19)

## 5.4 Potential Energy and Excluded volume

We will assume now that the interaction between the bundles themselves can be
described by the previously described hard and charged rod interactions for rods
with a different diameter. What we want to know is the energy of a rod in a
bundle with \( k \) rods. We assume that the rods inside a bundle arrange themselves
closepacked and perfectly parallel. So the length of a bundle is the length of a
rod and the thickness of a bundle is determined by the thickness of the rods and
the number of rods. So every rod in the center of the bundle has 6 neighbors
while rods on the sides have on average 3 neighbors. When we assume a purely
attractive potential with a minimum \( B \) the energy of a bundle is given by:

\[
E(k) \approx 3B(k - \sqrt{k})
\]  (5.20)

But as we have seen the important thing is not the energy per bundle but the
energy per rod in a bundle and that is given by:

\[
\xi(k) \approx 3B(1 - \frac{\sqrt{k}}{k})
\]  (5.21)

Where we now see that we can drop the the 3\( B \) factor because it is just a shift
of the potential and we remain with:

\[
\xi(k) \approx -3B\frac{\sqrt{k}}{k}
\]  (5.22)

which leads to the counter intuitive result that for higher bundling energy we
only limit the number of small bundles. This is naturally not the case when we
look at situations with a fixed chemical potential, since then increasing \( B \) will
cause more bundles to form. The chemical potential for this case of rods with
different sizes is given by:

\[
c\Psi_k(u) = \frac{\pi}{4v} \exp \left( -\beta k \xi(k) - c \frac{4}{\pi} \sum_l (\sqrt{k} + \sqrt{l}) \int \int du' B(u, u') \Psi_l(u') + \beta \mu k \right)
\]  (5.23)
The distribution of bundle thicknesses must be a solution of this equation. If we look carefully at this we see that with the energy per bundle we introduced there will be either an exponentially decaying or an exponentially growing number of bundles with thickness \( k \). The excluded volume only goes with the square root of the bundle thickness which means that for high \( k \) the linear terms in \( k \) in the chemical potential or the potential will always dominate. So the prefactor of this linear term is dominant.

Because we want to look at more interesting situations where there is a well defined bundle size we have to go to charged rods with a long range repulsion on top of the short ranged attraction. We still assume that the rods in a single bundle will be close packed and that the length of a bundle is the same as the length of a rod. This close packing will not happen for very weak attraction and strong long range repulsion. In this case the "living necklaces" observed by Needleman et al. 9 will form.

**Figure 5.1:** The energy per rod of a bundle of \( k \) rods for different repulsive force strength. The higher the line the stronger the repulsion.

To calculate the energy of a bundle of \( k \) rods I use a little mathematica program that places \( k \) rods on a hexagonal lattice. It places the rods as close to the center of the bundle as possible. The resulting graphs are seen in figure 5.1. We must make sure that we are not in the regime where necklaces are formed instead of hexagonal bundles. We assume that the charge of the bundle is proportional the the surface of the bundle and not to the volume so the excluded volume of the charged rods scales in the same way with the radius as the excluded volume of hard rods.
5.5 Phase behavior

The phase behavior we have observed is rather featureless. No new phases or phase coexistence have shown up although all densities shift to higher values. We hoped for a coexistence between a phase with and a phase without any bundles but the change from no bundles to a lot of bundles seems to be very smooth and is not accompanied by a phase change. We have not yet explored the whole parameter range and can not show any definite results yet. It is possible that we have been looking in the wrong regime to observe interesting behavior. Further analysis remains to be done.
Chapter 6

Experiments

Our efforts to look at charged and linking rods are motivated by experiments done on viruses, actin and other rod like particles like DNA or microtubules. Here I will discuss a few of the most interesting experimental results.

6.1 Viruses

Viruses such as the Tobacco Mosaic Virus (TMV) are one of the best model systems for long rod systems. They are stiff, monodisperse and have a long aspect ratio. However it is difficult to obtain large quantities of TMV, most of the recent studies are therefore carried out on different viruses such as the fd bacteriophage. The fd virus however is semi flexible which affects the phase behavior.

The experiments done with the fd virus at different ionic strength come quite close to the interesting regime where we would expect the nematic nematic coexistence. The flexibility is reduced by the higher repulsion within the rod caused by the lower ionic strength, called electrostatic stiffening. The problem in the low ionic strength regime is that $L/D_{\text{eff}} \approx 15$ for fd, at this point the second virial approximation starts to break down even combined with scaled particle theory [10]. To verify our results experimentally the rods should even in a solution with a very low ionic strength be well in the large $L/D_{\text{eff}}$ regime.

The depletion interaction is caused by the addition of more or less spherical polymers with a diameter in the order of the diameter of the rods. The center of mass of these polymers can not come closer to the edge of the rods than half their diameter and exclude in this way part of the volume for the polymer. When rods come close together these excluded volumes start to overlap giving the polymers more space to move around causing attraction. This effective attraction between the rods is easy to tune because the concentration of polymers and the average size of the polymer can be controlled in experiments. Experiments as well as simulations on these systems give a phase diagram where the isotropic-nematic
coexistence widens considerably when the attraction or polymer concentration is increased. Theory by Lekkerkerker et al. [11] describes this widening by the inclusion of higher order correction terms of the virial expansion.

There are experiments done by Purdy et al. [15] on rods with different diameters made by coating the fd viruses with a polymer shell. The nematic-nematic coexistence in this system is at such densities that with the aspect ratio of these thickened rods the higher order virial coefficients and end effects start to play an important role and need to be taken into account.

6.2 Actin filaments

![Schematic figure of some common actin linking proteins and the binding of filamin on two actin filaments.](image)

Figure 6.1: At the left a schematic figure of some common actin linking proteins. The actin binding domains have been colored red. At the right a schematic representation of the binding of filamin (green) on two actin filaments (red). Both come from Alberts et al. [16].

Actin is a much more complex rod than the fd virus. Actin filaments are polymers made out of actin monomers. To polymerize the actin monomers requires high ionic strength and a high \(Mg^{2+}\) concentration. This already puts a bottom limit on the ion concentration. The filaments are asymmetrical, they have a barbed and a pointed end. It is a semi flexible polymer and highly charged in normal solvents. In most normal cells the actin is very dynamic: it polymerizes and depolymerizes constantly. To study actin properties this is stopped by adding capping proteins that cap the end points and thereby stop the dynamics of the actin itself but this results in a very wide length distribution of filaments.

The required concentration of ions for the actin to polymerize and especially the required multivalent ions complicate things. The multivalent ions can cause attraction between the filaments as described by Tang et al. [12] [13]. Nearly all images of actin filaments show some bundling and although the actin is semi flexible it is still quite flexible at large enough \(L/D\). This makes actin difficult to compare with stiff rods, the flexibility or the finite aspect ratio should be taken into account together with the attraction between filaments to form an accurate description.
Network formation or gelation due to linkers takes place when the linker concentration reaches a certain threshold \[18\]. This threshold depends on the kind of linkers in question but also on the pH, the concentration of ions and the presence of other actin binding proteins. Also different kinds of networks have been observed like a lamellar network where we would have expected filaments perpendicular to the plane, and it remains an interesting question why they are not there.

### 6.3 Microtubules

**Figure 6.3:** A figure from Needleman et al. \[9\] where he shows schematically the effect of different multivalent counter ions.
Microtubules are just as actin made out of monomers and form a dynamic part of the cytoskeleton. They just like actin have two different ends, a plus end and a minus end. They normally grow from the plus end but can also shrink very fast from the plus end. They are thicker and much stiffer than actin. The aspect ratio that can be obtained while maintaining enough rigidity to be treated as hard rods is higher than that of actin. Microtubules also need $Mg^{2+}$ and GTP to polymerize. Just as with actin there is a wide variety of proteins binding to the filaments. As far as we know there are not yet any known proteins linking microtubules to other microtubules.

Microtubules also form bundles at high counter ion concentrations as shown very nicely by Needleman et al. \cite{9} and in figure 6.3. It is shown that multivalent ions of 3+ or more cause hexagonal bundles while 2+ ions cause the formation of more open structures called necklaces. In this case the attraction of the ions is not strong enough to overcome the long range repulsion of multiple rods.

6.4 DNA

Also studied heavily in the presence of multivalent counter ions is DNA, it is like actin and microtubules a long semi flexible bio polymer. In cells most DNA is compacted in a dense form. This compact form is possible by the condensation of multivalent counter ions on the DNA causing attraction instead of repulsion between the highly charged DNA strands. Here also the effect of over-charging has been observed. When the counter ion concentration reaches a certain threshold, the DNA strand comes loose again. Computer simulations on these systems have also been done by Allahyarov et al. \cite{17} showing a complex pair potential with two minima. These simulations take the complex shape of the DNA strands and the charge distribution along these strands into account. The results are far from trivial and show that the exact pair potential depends strongly on the microscopic details of the surface of the rods.
Chapter 7

Conclusion

We have calculated phase diagrams of infinitely long straight charged rods. In this limit our theory is exact and we find new phase coexistence’s at low ion concentrations and a new phase for the linking rods. The guess we made for the linkers is very restricted but does cover the most interesting shapes of the excluded volume.

We also looked at the formation of bundles. We did not find what is found in experiments and simulations done on systems with a depletion interaction but further analysis is needed.

We are still far away from describing experiments. Or put differently the experiments are still far from testing these theories. The main problem is the length and stiffness of the rods. Really long rods are not Brownian and really thin rods are never stiff. Especially the charging and the bundling will require rods with a really large aspect ratio because these effects will make them ”look thicker”.

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Chapter 8

Outlook

What can we do to come closer to describing real experiments?

• Look at the effect of flexibility in the phase behavior.
• Look at the effects of finite size.
• Further study the phase space of the bundling rods.
Appendix A

A.1 The angle between two spherical vectors


We have three vectors A, B and C. All three have length one and originate in (0, 0, 0). We will choose A to be (0, 0, 1). Now we will give names to some of the angles: the angle between B and C we call $\alpha$, between A and C we call $\beta$ and between C and B we call $\delta$. The angle ACB we will call $c$, between ABC we will call $b$ and between CAB we will call $a$.

\[
(A \times B) \cdot (A \times C) = (|A||B| \sin \delta) (|A||C| \sin \beta) \cos a
\]

but also:

\[
(A \times B) \cdot (A \times C) = A \cdot [B \times (A \times C)]
\]
\[
= A \left[ A (B \cdot C) - C (A \cdot B) \right]
\]
\[
= (B \cdot C) - (A \cdot C)(A \cdot B)
\]
\[
= \cos \alpha - \cos \delta \cos \beta
\]

Since both must be equal we get:

\[
\cos \alpha = \cos \beta \cos \delta + \sin \beta \sin \delta \cos a \quad \text{(A.1)}
\]
Bibliography


