Distribution of genetic material inside a simple RNA virus

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A virus represents one of the most elegant self-assembling systems, made up of protein subunits which constitute the capsid, the envelop containing genetic material. This viral genome can consist of single-stranded or double-stranded RNA or DNA, which, through various specific and non-specific interaction, can self-assemble together with the capsid proteins to form a complete virus. One of the many aspects of the study of viruses has been the concentration profile inside the capsid, because of the interactions between genome polymer and capsid wall, this is not a homogeneous solution, as shown by experiments. These have shown that the genome polymer is very concentrated on the wall, theory on the subject, however, predicts the concentration profile to vary more slowly and gradually. Since these do not reconcile, the main objective of this project is to use a specific model and find out under what circumstances the genome polymer condensates on the wall.

The effects of a container compared to a single wall will be studied as well as the effect of curvature. It will be shown that under good solvent conditions, positive second virial coefficient, there is an optimal amount of material resulting in a lowest energy state for a given radius of the virus and attraction strength. For bad solvent conditions, negative second virial coefficient, it will be shown that there are many minima in the free energy. Typical concentration profiles for a negative virial coefficient exhibit oscillatory behaviour and can feature holes or bulges in the center.
My decision to work on this project was made when I followed a course named *Physics of Life*, I loved the way life worked on small scales and I was impressed and amazed beyond measure when I heard how viruses self-assemble and operate. I always believed the living nature to be the ultimate engineer, and this belief has only been strengthened. Life, however, has had millions of years to test and try and fail, trying to come up with something smarter than life is like playing bullet chess against an opponent who has unlimited time to think through every move. This project was about finding the right question to ask, for the answer we already know.

I’d like to thank Paul van der Schoot, my supervisor at Eindhoven university of technology, for always saying exactly what I needed to hear to stay motivated and always giving the answer I was looking for.

“The Answer to the Great Question, of Life, the Universe and Everything...
“Forty-two,” said Deep Thought, with infinite majesty and calm.”

- *The hitchhiker’s guide to the galaxy*

I’d like to thank Lily Sunna for all the love and support, and introducing me to the wonderful world of \LaTeX{}, this thesis would have looked unimaginably different otherwise. I’d like to thank Mathijs Vermeulen for helping me relax whenever I needed to, sometimes a bit more than necessary. Last I’d like to thank all my friends and all the other people I forgot to mention, their support can make the biggest mountain an anthill.

No coffee was consumed during the project or the writing of this report, it was all an act of pure willpower.
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A virus is a self-assembled structure consisting of protein subunits which make up the capsid, the envelop enclosing genetic material. This viral genome can be single-stranded or double-stranded RNA or DNA, and stored in one or more polynucleotide chains [1]. Many viruses are pathogenic to humans, like HIV or Hepatitis B, the second causes about 750,000 deaths a year [2]. A virus operates by infiltrating a host cell and inserting genetic material which contains the information to reproduce the virus, a process which repeats itself until the cell dies. Recent developments however, have tried harness the power of viruses to the benefit of human beings.

A major application of this virus technology is gene therapy, a medical technology which alters or inserts new or healthy genes into the DNA. Since naturally occurring viruses, and in particular retroviruses, already have this property, it seems an obvious choice of using these to perform this task [3]. One of the most interesting applications of gene therapy is in the treatment of cancer, advances in the understanding of the source of cancer shows it is a genetic disease resulting in the abnormal proliferation of cell clones [4]. In the last 50 years cancer-directed-therapy, be it radiation or chemical treatment, have targeted the dividing cells, recent research however, has shown that therapy may be more effective if it is directed at the mutated genes [5].

Other applications of gene therapy include chronic diseases, like rheumatoid arthritis, a group of conditions involving inflamed joints, which can lead to long-term damage [6]. Rheumatoid arthritis patients are currently treated with anti-TNF therapy, a treatment which injects antibodies to stop certain cytokines. The main disadvantage of this type of treatment is that it affects the entire body, causing heightened probability of infections, since that is what TNF is supposed to counter under normal circumstances. Gene therapy has the possibility to affect genes locally, thereby directing the treatment to very specific places in the body [7]. Another advantage is the fact that the body produces its own medicine, which makes frequent use of syringes or intravenous therapy unnecessary.

In order to perfect technologies like gene therapy, it is imperative to understand the processes of self-assembly and the resulting structures. This thesis deals with the internal
structure of a virus, and in particular the spatial distribution of genetic material.

1.1 Physical background

Viruses represent one of the most elegant self-assembling systems, they can be produced both in vivo and in vitro [9]. The basic constituents are designed in such a way that a complete virus is the lowest free energy state, which allows it to self-assemble. The actual process is governed by various specific and non specific interactions [10], among them the electrostatic interaction, since almost all components carry a net charge. Any approach to understanding the structure of a virus is done using thermodynamics, by finding or assuming a certain free energy functional and minimizing it.

1.2 Motivation

Recent developments in electron cryomicroscopy and image analysis combined with X-ray crystallography have made it possible to study the geometrical structure of a wide range of biological samples including viruses [8]. Using these techniques experimental work has shown that the genetic material seems tightly packed against the capsid wall [9], while theoretical work concluded the monomer density should decrease more gradual towards the center [11]. A model of polymer adsorption on a wall has been set up by Hone and Ji [12], which assumes a very simple free energy functional for the interaction of the polymer with the wall. Van der Schoot suggested that this condensation process may be due to bad solvent conditions, which could be implemented in the Hone and Ji model by assuming the second virial coefficient negative.

1.3 Objective

The main objective is to use the model set up by Hone and Ji, and explore the possibilities of solving it inside a spherical container, and in particular to find out under what circumstances the polymer adheres to the wall almost completely. In this light, the effect of a negative second virial coefficient will be studied. Other objectives include studying the effect of curvature of the wall of the container and studying the energetics of the concentration profile.
CHAPTER 2

Theory

2.1 Conformational free energy of a polymer solution

The RNA strand inside a virus is an example of a polymer solution, due to interactions between the polymer and the capsid wall, the concentration profile inside a virus is not homogeneously distributed. In order to find the monomer concentration profile, it is necessary to have some knowledge of the energetics of non-homogeneous polymer solutions, since a virus is in thermal equilibrium, the concentration profile inside is such that it minimises the free energy.

Consider a free Gaussian polymeric chain, were the size of the chain $R_G$ is proportional to $M^{1/2}a$, the square root of the number of monomers in the chain, which are assumed to be identical and structureless units with a Kuhn length $a$. $M$ is usually a large number, so the size of the chain is much greater than scales compared to the Kuhn length. Next, consider a virus, inside is a polymer which is for the main part adhered to the wall, this layer has to be thicker than the Kuhn length, but at the same time, the entire polymer is contained in a volume much smaller than $\frac{4}{3}\pi R_G^3$.

In this section, the conformational free energy will be investigated following van der Schoot [13], using a Green’s function description. Consider a single Gaussian chain of $M$ segments contained in a volume $V$. The partition function of the polymer $Z_M$ can be written using the Green function $Z(r', r; M)$ of all possible configurations of the chain, starting at position $r'$ and ending at $r$:

$$
Z_M = \int_V \int_V Z(r', r; M) d\mathbf{r}' d\mathbf{r} \quad (2.1)
$$

This quantity obeys the operator equation [17]

$$
\frac{\partial}{\partial M} Z(r', r; M) = \exp \left(-\beta U(r) + \frac{1}{6}a^2 \nabla^2 \right) - 1 \right] \left[ Z(r', r; M) \quad (2.2)
$$
Provided $M \gg 1$ so the monomer ranking number can be taken as a continues parameter, $\beta$ is the reciprocal thermal energy $\frac{1}{k_B T}$ and $U(\mathbf{r})$ is a molecular field governing the interactions between monomers. The operator $\exp\left(\frac{1}{6}a^2\nabla^2\right)$ can be expanded giving

$$\exp\left(\frac{1}{6}a^2\nabla^2\right) = 1 + \frac{1}{6}a^2\nabla^2 + \frac{1}{2}\left(\frac{1}{6}a^2\nabla^2\right)^2 + \ldots \quad (2.3)$$

An 'initial' condition for the Green function can be found by considering a chain of length $M = 0$, which would mean formally it begins and ends at the same point in space, therefore the Green function is a Dirac-$\delta$.

$$\lim_{M \to 0} Z(\mathbf{r}', \mathbf{r}; M) = \delta (\mathbf{r}' - \mathbf{r}) \quad (2.4)$$

The standard expression for the free energy gives the free energy of the chain

$$\beta F = -\ln (Z_M) \quad (2.5)$$

Which is not what is sought for, so the internal energy of the system is subtracted, leaving only the conformational free energy of the chain.

$$\beta F_{\text{conf}} = \beta F - \int_V \beta U(\mathbf{r}) \rho(\mathbf{r}) \, d\mathbf{r} \quad (2.6)$$

Where the monomer number density $\rho(\mathbf{r})$ is given by

$$\rho(\mathbf{r}) = \frac{\int_0^M \int \int Z(\mathbf{r}', \mathbf{r}; s) Z(\mathbf{r}, \mathbf{r}''; M - s) \, dr'' \, dr' \, ds}{\int \int Z(\mathbf{r}', \mathbf{r}''; M) \, dr' \, dr''} \quad (2.7)$$

This definition looks rather complicated but is actually quite natural, the first Green function gives all possible configurations for a chain of length $s$ which start at point $\mathbf{r}'$ and end in point $\mathbf{r}$, the second Green function gives all possible configurations of a chain of length $M - s$ to start at point $\mathbf{r}$ and end at point $\mathbf{r}''$. This effectively gives the probability a chain of length $s$ to end at position $\mathbf{r}$ multiplied by the probability of a chain of length $M - s$ to begin at that point. Integrating this over all starting and ending points and all segment numbers and dividing by all possible configurations of chains that start in point $\mathbf{r}'$ and end in point $\mathbf{r}''$ gives the density at point $\mathbf{r}$. Figure 2.1 shows a visual interpretation of the integral.

Next, an eigenfunction expansion of the Green function is made

$$Z(\mathbf{r}', \mathbf{r}; M) = \sum_{n=0}^{\infty} \psi_n^*(\mathbf{r}') \psi_n(\mathbf{r}) \exp(-\lambda_n M) \quad (2.8)$$
2.1. Conformational free energy of a polymer solution

Figure 2.1: Visual interpretation of the density integral: some configurations of chains of lengths $s$ that start in point $r'$ and run to point $r$ and some configurations of chains of length $M - s$ that start in point $r$ and end in point $r''$.

This expansion assumes discrete eigenvalues, but the derivation would be the same for continuous eigenvalues with the sum replaced by an integral. The eigenfunctions and eigenvalues obey the operator equation 2.2.

$$\left[ \frac{1}{6} a^2 \nabla^2 - \beta U (r) \right] \psi_n (r) = -\lambda_n \psi_n (r) \quad (2.9)$$

The operator on the left hand side is self-adjoint, which means the eigenvalues $\lambda_n$ are real and the eigenfunctions $\psi_n (r)$ are orthogonal and can be made orthonormal by setting $\int \psi_n^* (r) \psi_n (r) \, dr = 1$. Now the ground-state approximation is made, which means the state with lowest eigenvalue, called $\lambda_0$, is assumed to dominate the behaviour of the Green function: $\lambda_0 \gg \lambda_m$ for $m \geq 1$, where the eigenvalues are ordered in a way that increasing $m$ mean smaller eigenvalues $\lambda_m$. In the continues case, the eigenvalue $\lambda (n)$ is assumed a rapidly increasing function of $n$, so that again, the smallest eigenvalue dominates the behaviour. This turns the Green function into

$$Z (r', r; M) = \psi_0^* (r') \psi_0 (r) \exp (-\lambda_0 M) \quad (2.10)$$

Which gives the following expression for the density

$$\rho (r) = M \psi_0^* (r) \psi_0 (r) \quad (2.11)$$

When the density is integrated over all space, the relation $\int \rho (r) \, dr = \bar{\rho} V = M$ holds. Using the argumentation previously presented, the interpretation of $\psi_0$ is recognized as the probability of a chain ending at point $r$, since probabilities are real, $\psi_0$ must be a real-valued function. By changing the normalization, one can pull any constant into the function $\psi_0$ and it becomes proportional to the probability of the chain ending in point
Inserting the truncated expansion for the Green function into the expression for the free energy, equation 2.5, gives

$$\beta F = \lambda_0 M - 2 \ln \left( \int \psi_0 (\mathbf{r}) \, d\mathbf{r} \right)$$  \hspace{1cm} (2.12)

Standard operator theory [14] gives the lowest eigenvalue $\lambda_0$ as

$$\lambda_0 = -\frac{1}{M} \int \rho^{\frac{1}{2}} (\mathbf{r}) \left[ \frac{1}{6} a^2 \nabla^2 - \beta U (\mathbf{r}) \right] \rho^{\frac{1}{2}} (\mathbf{r}) \, d\mathbf{r}$$  \hspace{1cm} (2.13)

Using this and equations 2.6 and 2.12 gives

$$\beta F_{\text{conf}} = -\frac{a^2}{6} \int \rho^{\frac{1}{2}} (\mathbf{r}) \nabla^2 \rho^{\frac{1}{2}} (\mathbf{r}) \, d\mathbf{r} - 2 \ln \left( \int \left( \frac{\rho (\mathbf{r})}{M} \right)^{\frac{1}{2}} \, d\mathbf{r} \right)$$  \hspace{1cm} (2.14)

The first term is the expression that was sought after, the second term is a finite-size correction, which is small compared to the first term, therefore it will be neglected from now on.

## 2.2 Modelling a virus

The RNA strand inside the virus is modelled as a non-branching polymer which has an interaction with a perfectly smooth wall. The interaction energy per unit area is assumed to be linear with the local volume fraction of monomers $\phi$ [15]. The strength of this interaction is accounted for by the parameter $\gamma_1$, this parameter is positive when the interaction is attractive, so a minus sign is put in front of the surface integral. The bulk energy is taken as the sum of the free energy in a homogeneous solution plus the conformational free energy of the polymer. In mean-field theory, the Flory-Huggins free energy density $f(\phi)$ for a homogeneous semidilute polymer solution is given by [12]

$$f(\phi) = \left( \frac{1}{\beta a^3} \right) \left[ \frac{\phi}{N} \ln \phi + \frac{1}{2} \nu \phi^2 + \frac{1}{6} \omega \phi^3 + \ldots \right]$$  \hspace{1cm} (2.15)

Where $a$ is the Kuhn length, $N$ is the molecular weight and $\beta$ is the reciprocal thermal energy $\frac{1}{k_B T}$, the first term represents translational entropy, $\nu$ is the second virial coefficient scaled with the monomer volume $a^3$ and $\omega$ is the third scaled with $a^6$. For semidilute polymer solutions, $\phi \ll 1$, the first term is neglected, since $N$ is large. In this thesis, the assumption is made that the behaviour of the chain is dominated by two-body interactions between monomers, hence the third virial coefficient is neglected. The conformational free energy was derived in the previous section, scaling to volume fraction $\phi = a^3 \rho$ and inserting these into the expression for the free energy gives

$$U - U_0 = -\gamma_1 \oint \oint \phi dS + \frac{1}{\beta a^3} \iiint \iiint \frac{1}{2} \nu \phi^2 - \frac{a^2}{6} \phi^{\frac{1}{2}} \nabla^2 \phi^{\frac{1}{2}} \, dV$$  \hspace{1cm} (2.16)
Where $U_0$ is the free energy of the pure solvent. Writing this in terms of the mean-field order parameter defined as

\[ \psi^2 \equiv \phi \]

The subscript 0 has been dropped and the the function is normalized to $a^3M$, this gives

\[ U - U_0 = -\gamma_1 \int \int \int \phi^2 dS + \frac{1}{\beta a^3} \int \int \int \frac{1}{2} \mu \psi^4 - \frac{a^2}{6} \psi \nabla^2 \psi dV \quad (2.17) \]

Furthermore, the normalization requirement gives a constraint that the total number of monomers be conserved:

\[ \int \int \int \psi^2 dV = a^3M = \text{constant} \]

**Minimization of the free energy**

In order to minimize the free energy, the function $\psi$ is taken to be the function that minimizes the free energy plus a small perturbation.

\[ \psi \to \psi + \delta \psi \]

The free energy will be varied by inserting the new expression for $\psi$ into the integral, subtracting the original and neglecting higher orders of $\delta \psi$

\[ \delta \left[ U - \mu \int \int \int \phi^2 dV \right] = \frac{1}{\beta a^3} \int \int \int \frac{2 \mu \psi^3 \delta \psi}{6} \left( \delta \psi \nabla^2 \psi + \psi \nabla^2 \delta \psi \right) - 2 \beta \mu a^3 \psi \delta \psi dV \]

\[ -\gamma_1 \int \int \int 2 \psi \delta \psi dS \quad (2.18) \]

Where $\mu$ is the Lagrange multiplier introduced by the constraint. The term involving $\psi \nabla^2 \delta \psi$ is integrated by parts twice using Gauss’s theorem.

\[ \int \int \int \psi \nabla^2 \delta \psi dV = \int \int \int \psi \nabla \delta \psi \cdot n dS - \int \int \int \delta \psi \nabla \psi \cdot n dS + \int \int \int \delta \psi \nabla^2 \psi dV \]

And the first term is again integrated by parts since it will be involved in the boundary condition on the wall

\[ \int \int \int \psi \nabla \delta \psi \cdot n dS = \oint \delta \psi \nabla \psi \cdot n \cdot d l - \int \int \int \delta \psi \left( \nabla \psi \cdot n + \psi \nabla \cdot n \right) dS \]

\[ = - \int \int \int \delta \psi \nabla \psi \cdot n dS \]
Where the loop integral is a line integral over the surface of the volume, it is zero because the normal perpendicular is perpendicular to the line element running along the surface. The divergence of the normal vector is a priori zero since it is not a real vector field but only defined on the boundary of the surface. Putting all this into the expression for $\delta U$ gives

$$
\delta \left[ U - \mu \int \int \int_{V} \psi^{2} dV \right] = \frac{1}{\beta a^{3}} \int \int \int_{V} 2\nu \psi^{3} \delta \psi - \frac{a^{2}}{3} \psi \nabla^{2} \psi - 2\beta \mu a^{3} \psi \delta \psi dV
$$

$$
+ \int_{\partial V} \frac{2}{6a\beta} \delta \psi \nabla \psi \cdot \mathbf{n} - 2\gamma_{1} \psi \delta \psi dS
$$

(2.19)

This integral must be stationary for all small variations of $\delta \psi$, the volume integral gives the bulk equation

$$
\nabla^{2} \psi - \frac{6\nu}{a^{2}} \psi^{3} + 6a\beta \mu \psi = 0
$$

(2.20)

The surface integral gives the boundary condition on the wall

$$
\nabla \psi \cdot \mathbf{n} - 6a\beta \gamma_{1} \psi = \frac{d\psi}{dn} - 6a\beta \gamma_{1} \psi = 0
$$

(2.21)

Where $\mathbf{n}$ is the normal vector to the surface, the operator $\frac{d}{dn}$ is the normal derivative at the surface. The sign in front of the second term is dependant on where the wall is, if the wall is in the direction of an increasing coordinate, it is a minus sign, otherwise a plus sign, figure 2.2 shows this visually. A second boundary condition is necessary due to the symmetry: there cannot be a gradient at the center of the volume.

$$
\nabla \psi (0) = 0
$$

(2.22)

Where the origin is chosen as the center of the volume.

Figure 2.2: Visual explanation of the boundary conditions at the wall, where $k \equiv 6a\beta \gamma_{1}$ and the attraction is positive.
Dimensionless equations

The next step is to turn these equations in dimensionless form, by scaling the order parameter and length scales with suitable factors, which will be chosen to make the governing equation as simple as possible. The order parameter will be scaled using $\psi = \psi_\ast \theta$ and the Laplacian term will be scaled with $\nabla^2 = \frac{1}{\xi^2} \tilde{\nabla}^2$.

$$\frac{1}{\xi^2} \psi_\ast \tilde{\nabla}^2 \theta - \frac{6\nu}{a^2} \psi^3 \theta^3 + 6a\beta \mu \psi \theta = 0$$

$$\tilde{\nabla}^2 \theta - \frac{6\nu}{a^2} \psi_\ast^2 \xi^2 \theta^3 + 6a\beta \mu \xi^2 \theta = 0$$

Choosing the constants to be one gives the scaling factors as

$$\xi^2 \equiv \frac{1}{6a \beta \mu}$$

$$\psi^2_\ast \equiv \frac{\beta \mu a^3}{\nu}$$

From these definitions, one can see that $\psi_\ast$ is the value of $\psi$ where $\nabla^2 \psi$ is zero. These scaling factors change the differential equation and the boundary conditions into

$$\tilde{\nabla}^2 \theta - \theta^3 + \theta = 0$$

$$\frac{d\theta}{d\tilde{n}} - k \xi \theta = 0$$

$$\tilde{\nabla} \theta (0) = 0$$

Where the first boundary condition, equation 2.26, must hold at the wall, $k$ is defined as $k \equiv 6a \beta \gamma_1$ and tildes mean dimensionless length scales. After solving these equations, a relation between the average volume fraction $\bar{\phi}$ and $\psi_\ast$ can be found since

$$\bar{\theta}^2 = \frac{\bar{\psi}^2}{\psi^2_\ast} = \frac{\bar{\phi}}{\psi^2_\ast}$$
CHAPTER 3

One-dimensional solutions

3.1 Exact solution

The differential equation derived in the previous chapter has known solutions when subject to a certain set of boundary conditions. These conditions correspond to an infinite wall with an infinite reservoir of polymer solution on one side, which therefore also contains an infinite amount of monomers. This is probably not comparable to the inside of a virus, but still it makes an interesting problem to study. In order to solve this problem the wall is set at the origin and because of translational symmetry only one dimension needs to be considered. The boundary condition at the wall remains unaffected, but the second boundary condition becomes

\[ \theta' (\tilde{x} \to \infty) = 0 \] (3.1)

Where \( \tilde{x} \) is now the only dimensionless variable considered, perpendicular to the wall, with the length scale adjusted to \( \sqrt{2}\xi \). The relation between the volume fraction in the bulk \( \phi_{bulk} \) and the correlation length \( \xi \) can be found by taking \( \tilde{x} \to \infty \) where there is no influence of the wall, hence \( \tilde{\nabla}^2 \theta = 0 \) giving \( \theta = 1 \). Since the container is infinite, \( \bar{\theta} = 1 \) and \( \psi^2 = \tilde{\psi}^2 = \phi = \phi_{bulk} \), using equations 2.23 and 2.24 gives

\[ \xi = \frac{a}{\sqrt{6\nu\phi}} = \frac{a}{\sqrt{6\nu\phi_{bulk}}} \] (3.2)

With the new length scale the differential equation turns into the familiar one for the hyperbolic (co)tangent.

\[ \frac{1}{2} \phi'' = \phi^3 - \phi \] (3.3)

The only remaining problem is that the hyperbolic cotangent diverges at the origin, but because of the boundary condition at the origin, the singularity is shifted towards the left, which is outside the infinite container. The dimensionless parameter \( b \) shifts the
function $\theta$ by setting $\theta(\tilde{x}) = \coth(\tilde{x} + b)$. From the boundary condition at the wall it can be determined as

$$b = \text{arccoth}\left(\frac{1}{2} \left(\sqrt{k^2\xi^2 + 4} + k\xi\right)\right)$$

(3.4)

This expression shows that the $b$ is always real for $k > 0$ and for $k \to 0$, $b \to \infty$ which causes the concentration profile to become constant.

Figure 3.1: Plot of the exact solution to the problem, the concentration near the wall is high and it drops rapidly to the bulk concentration where $\xi = 1a$ and $k = 0.5a^{-1}$.

Figure 3.1 shows how a polymer solution is attracted to a flat wall when the reservoir is much greater than the correlation length $\xi$. The concentration near the wall is high and drops rapidly to the bulk concentration, the value of a regular hyperbolic cotangent, with a singularity at the origin, drops to one in about two length units. But here the singularity is shifted with an amount $b\sqrt{2}\xi$, so the length over which the concentration drops is $\Delta x \approx \sqrt{2}\xi (2 - b)$, where $b$ is given by equation 3.4.

3.2 One-dimensional container

To achieve a better understanding of the internal structure of a virus, but still keep the mathematics fairly easy, the virus is now modelled as a one dimensional container. The problem is almost the same as the previous one, but instead of the boundary condition $\theta'(\tilde{x} \to \infty) = 0$ the zero gradient is set at a finite distance from wall, at $x = \frac{h}{2}$, which would be the same as placing a second wall at $x = h$. The scaling length used is the
correlation length \( \xi \), which reduces the differential equation with boundary conditions to

\[
\theta'' - \theta^3 + \theta = 0 \quad (3.5)
\]

\[
\theta'(0) + k\xi \theta(0) = 0 \quad (3.6)
\]

\[
\theta'\left(\frac{h}{2\xi}\right) = 0 \quad (3.7)
\]

### 3.2.1 Linearised equation

For this set of equations, there is no known solution, one way to gain information is to linearise the differential equation by setting \( \theta \) to unity plus a small disturbance \( \delta \ll 1 \).

\[
\theta = 1 + \delta \quad (3.8)
\]

This is inserted into the differential equation, expanded and higher order terms of \( \delta \) will be neglected.

\[
\delta'' - 1 - 3\delta + 1 + O(\delta^2) = \delta'' - 2\delta + O(\delta^2) = 0 \quad (3.9)
\]

The general solution to the linearised equation is a superposition of exponentials, the zero gradient boundary condition implies a relation between the constants. The solution is given by

\[
\delta(\tilde{x}) = C_1 \left( e^{\sqrt{2}\tilde{x}} + e^{\sqrt{2}\left(\frac{\tilde{x}}{\xi} - \tilde{z}\right)} \right) \quad (3.10)
\]

\( C_1 \) is found by applying the boundary condition at the wall, it is given by

\[
C_1 = -\frac{k\xi}{k\xi \left(1 + e^{\frac{\sqrt{2}\xi}{\tilde{z}}}ight) + \sqrt{2} \left(1 - e^{\frac{2\sqrt{2}\xi}{\tilde{z}}}ight)} \quad (3.11)
\]

With the solution known, the relation between the scaling factor \( \psi_\ast \) and the average volume fraction \( \bar{\phi} \) can be calculated. Using equation 2.28 and expanding theta to first order in \( \delta \) gives

\[
\bar{\theta}^2 = \frac{\xi}{h} \int_0^\frac{h}{\xi} \theta^2 d\tilde{x} = 1 + \frac{2\xi}{h} \int_0^\frac{h}{\xi} \delta d\tilde{x} + O(\delta^2) = \frac{\bar{\phi}}{\psi_\ast^2} \quad (3.12)
\]

Using the solution obtained previously, an exact expression can be found. Ignoring the higher order terms gives

\[
\bar{\theta}^2 = 1 + \frac{4k\xi^2}{h \left(2 - \sqrt{2}k\xi \coth\left(\frac{h}{\sqrt{2}\xi}\right)\right)} \quad (3.13)
\]

Which gives an implicit relation between the average volume fraction \( \bar{\phi} \) and the correlation length \( \xi \). To plot concentration profiles for various different values of the correlation
length $\xi$, the order parameter $\psi$ will be rescaled to have an squared average of 1, using the expression previously obtained for $\bar{\theta}$. A new length scale will be introduced which is defined as $x = a \rho$.

$$\frac{\psi}{\bar{\psi}} = \frac{\bar{\theta}}{\theta} = \frac{1}{\bar{\theta}} (1 + \delta (\rho)) = \frac{1}{\bar{\theta}} \left( 1 + C_1 \left( e^{\sqrt{2} \frac{a \rho}{\xi}} + e^{\sqrt{2} (h-a \rho)} \right) \right)$$

(3.14)

The error in the solution can be estimated by looking at a characteristic value of $\delta$, here the value for $\delta$ on the wall will be taken. When this becomes too great, $\delta^2$ can no longer be neglected and the linearisation scheme breaks down, a good value for a threshold is $\delta \left( \frac{R}{\xi} \right) = 0.25$.

One can see from figure 3.2 that as the correlation length increases, the concentration on the wall also increases, while the concentration in the center drops. From the graphs it can be seen that for small $\xi$ the concentration drops to a constant in about three times the correlation length $\xi$. This is completely comparable to the length scales involved in a single wall, since the concentration at a single wall drops to a constant in about $2\sqrt{2} \xi \approx 3 \xi$. The behaviour changes when three times the correlation length becomes comparable to half the width of the gap, $3 \xi \approx \frac{h}{2}$, in that case there is no region of constant concentration, as can be seen from the dotted curve in figure 3.2. For $\xi \approx \frac{h}{6}$, the concentration on the wall becomes relatively high giving $\delta \approx 0.25$, at this point the linearisation scheme starts to break down.

Figure 3.3 shows that larger correlation lengths and attractions result in higher concentrations on the wall as can be seen in figure 3.3, both graphs are approximately linear in
3.2. One-dimensional container

Figure 3.3: Plot of the normalized order parameter on the wall $\frac{\psi(R)}{\psi}$. Left plot as a function of $\xi$ with $k = 0.1a^{-1}$ and right as a function of $k$ with $\xi = a$, $h = 22a$ in both graphs.

the area of interest.

3.2.2 Perturbation expansion approach

Another approach to gaining information is the perturbation expansion approach [18][19], the interaction with the wall is assumed to be very weak. This changes the boundary condition at the wall to

$$\theta'(0) - \epsilon \theta(0) = 0$$  \hspace{1cm} (3.15)

Where $\epsilon \equiv k\xi$ and $|\epsilon| \ll 1$, this allows for a perturbation expansion of $\theta$, a power series of the form

$$\theta = 1 + \epsilon \theta_1 + \epsilon^2 \theta_2 + \epsilon^3 \theta_3 + O(\epsilon^4)$$  \hspace{1cm} (3.16)

This expansion, called a Poincaré expansion, is inserted into the equations and by collecting like powers of $\epsilon$ a system of differential equations is obtained.

$$\epsilon (\theta_1'' - 2 \theta_1) + \epsilon^2 (\theta_2'' - 2 \theta_2 - 3 \theta_1^2) + \epsilon^3 (\theta_3'' - 2 \theta_3 - \theta_1^3 - 6 \theta_1 \theta_2) + O(\epsilon^4) = 0$$

By setting all terms to zero, the differential equations for the first three orders are obtained.

$$\theta_1'' - 2 \theta_1 = 0$$  \hspace{1cm} (3.17)

$$\theta_2'' - 2 \theta_2 = 3 \theta_1^2$$  \hspace{1cm} (3.18)

$$\theta_3'' - 2 \theta_3 = \theta_1^3 + 6 \theta_1 \theta_2$$  \hspace{1cm} (3.19)

The same expansion 3.16 is inserted into the boundary conditions, first at $\tilde{x} = \frac{h}{2k}$.

$$\epsilon \theta_1' + \epsilon^2 \theta_2' + \epsilon^3 \theta_3' + O(\epsilon^4) = 0$$
Equating all terms again to zero gives the boundary condition at the center for all orders as
\[ \theta_i' \left( \frac{h}{2\xi} \right) = 0 \] (3.20)
Substituting the expansion 3.16 into the wall boundary condition gives
\[ \epsilon (\theta_0' - 1) + \epsilon^2 (\theta_1' - \theta_0) + \epsilon^3 (\theta_2' - \theta_1) = 0 \]
Again equating all orders of \( \epsilon \) to zero gives the boundary condition in a general form.
\[ \theta_i' - \theta_{i-1} = 0, \quad i \geq 0 \] (3.21)
The boundary condition takes on a pleasant form, it connects each order to the previous one, since \( \theta_0 \equiv 1 \).
The single most attractive feature of this approach is the structure of the equations, one can solve the first order perturbation quite easily and use this solution as the particular differential equation to the next order perturbation. This way, it is possible to attain any desired order of accuracy by sequentially solving the differential equations. The homogeneous part of every order differential equation is exactly the same as the linearised equation, but the boundary condition at the wall is different, which gives different constants in the solution. The first order solution is given by
\[ \theta_1 (\tilde{x}) = C_1 \left( e^{\sqrt{2} \tilde{x}} + e^{\sqrt{2} (\tilde{x} - \tilde{x})} \right) \] (3.22)
Where \( C_1 \) is given by
\[ C_1 = \frac{-1}{\sqrt{2} \left( 1 - e^{\sqrt{2} \tilde{x}} \right)} \] (3.23)
Again expressing the function \( \theta_1 \) in terms of the dimensionless variable \( \rho \) defined by \( x = a \rho \) gives
\[ \theta_1 (\rho) = C_1 \left( e^{\frac{\sqrt{2} \rho}{1}} + e^{\frac{\sqrt{2} (h-a \rho)}} \right) \] (3.24)
The difference between a linearised solution and a perturbation solution is made in the particular solutions of higher order perturbations. The mathematics involved in finding higher order solutions is fairly straightforward, since all homogeneous solutions are the same, it all becomes a matter of finding the particular solutions. The second order perturbation, for example, must involve exponentials of the form \( e^{2\sqrt{2} \tilde{x}} \) since the right hand side of equation 3.18 is the square of exponentials involving \( e^{\sqrt{2} \tilde{x}} \). Getting a particular solution is a matter of substituting the right exponentials into the equation and comparing coefficients. Therefore, the equations will not be reproduced here, only the results. All particular solutions inherently obey the center boundary condition, so all homogeneous solutions are of the form of equation 3.22. The solutions and coefficients can be found in appendix A.
As in the previous section, the solutions will be normalized with respect to the average value of $\theta$ to give $\bar{\psi}$. For the first order solution, $\bar{\theta}^2$ is given by

$$\bar{\theta}^2 = 1 + \frac{2k\xi^2}{h}$$  \hspace{1cm} (3.25)

The choice to calculate everything up to third order was made because the desired level of accuracy was higher than first order, since this was expected to be similar to the linearisation scheme and the third order is only a small correction on the second order. Surprisingly, the perturbation expansion seems to work increasingly better for larger correlation lengths $\xi$ when considering the criterion that the value of $\psi$ on the wall needs to be small. The left side of figure 3.4 shows the three truncated perturbation expansions for the same values, showing that the corrections on previous orders are increasingly smaller. The right side of the same figure shows the linearised solution together with the first order perturbation solution, showing that they are practically the same for $\epsilon < 0.1$, shown here is the relatively large value of $\epsilon = 0.11$, where the methods begin to part.

### 3.2.3 Negative virial coefficient

Now the case is examined where the second virial coefficient is negative, which corresponds to bad solvent conditions. The dimensional equation 2.20 is modified by using the absolute values of $\nu$ and $\mu$. This is necessary since $\psi_*$ is the value of $\psi$ where $\nabla^2 \psi$ is
zero, this is in many cases in the middle of the sphere, especially when three times the
correlation length is smaller than the radius of the sphere $3\xi < R$. Since $\psi$ is real due to
the interpretation given in section 2.1, it follows that $\mu$ and $\nu$ must have the same sign.

$$\nabla^2 \psi + \frac{6|\nu|}{a^2} \psi^3 - 6a\beta |\mu| \psi = 0$$  \hspace{1cm} (3.26)

Scaling the equation gives slightly different definitions $\psi^*$ and $\xi$.

$$\xi^2 \equiv \frac{1}{6a\beta |\mu|}$$  \hspace{1cm} (3.27)

$$\psi^2 \equiv \frac{\beta |\mu| a^3}{|\nu|}$$  \hspace{1cm} (3.28)

Note that $\psi^*$ stays the same. This will change the differential equations and boundary
conditions to

$$\theta'' + \theta^3 - \theta = 0$$

$$\theta' (0) + k\xi \theta (0) = 0$$  \hspace{1cm} (3.29)

$$\theta' \left( \frac{h}{2\xi} \right) = 0$$

On linearising this equation using the same method as in section 3.2.1 one finds

$$\delta'' + 1 + 3\delta - 1 - \delta + O(\delta^2) = \delta'' + 2\delta + O(\delta^2) = 0$$  \hspace{1cm} (3.30)

Again higher order terms of $\delta$ are neglected. Since the boundary conditions are independent of $\mu$ and $\nu$, they remain unchanged. The solutions to the linearised problem are
sines and cosines

$$\delta = C_1 \cos \left( \sqrt{2} \tilde{x} \right) + C_2 \sin \left( \sqrt{2} \tilde{x} \right)$$  \hspace{1cm} (3.31)

The boundary condition at the wall gives a relation between the constants

$$C_2 = \frac{k\sqrt{|\lambda|}}{\sqrt{2}} C_1$$  \hspace{1cm} (3.32)

The second boundary condition gives the equation

$$C_1 \left[ -\sqrt{2} \sin \left( h \sqrt{\frac{|\lambda|}{2}} \right) + k \sqrt{|\lambda|} \cos \left( h \sqrt{\frac{|\lambda|}{2}} \right) \right] = 0$$  \hspace{1cm} (3.33)

Since $\lambda$ must be a continuously varying parameter and the term in brackets is generally
not zero, this means $C_1$ must be zero, hence there is no physically acceptable solution to
the linearised equation.
In this chapter, the problem set in chapter 2 will be treated in three dimensions, in a spherical symmetry, this means that only \( \frac{\partial}{\partial r} \) can be non-zero. The resulting differential equation and boundary equations become

\[
\begin{align*}
\theta'' + \frac{2}{\tilde{r}} \theta' - \theta^3 + \theta &= 0 \\
\theta'(\frac{R}{\xi}) - k\xi \theta\left(\frac{R}{\xi}\right) &= 0 \\
\theta'(0) &= 0
\end{align*}
\]  

Where \( \tilde{r} \) is the dimensionless radial coordinate and accents represent differentiation with respect to it. As with the one dimensional case, first the equation will be linearised and later the second virial coefficient is assumed negative again. No perturbation expansions are made, since section 3.2.2 showed that linearising the governing equation yields a far greater range of parameters for which the relative error is acceptable.

### 4.1 Linearised equation

#### 4.1.1 Solution, error and plot

The same approach as in section 3.2.1 is used, so \( \theta \) is again assumed to be unity plus something small, \( \delta \).

\[ \theta = 1 + \delta \]
This is inserted into the differential equation and higher orders of \( \delta \) are neglected since \( \delta \ll 1 \). The resulting equation and boundary conditions becomes

\[
\delta'' + \frac{2}{\tilde{r}} \delta' - 2 \delta = 0 \quad (4.4)
\]

\[
\delta' \left( \frac{R}{\xi} \right) - k \xi \left[ \delta \left( \frac{R}{\xi} \right) + 1 \right] = 0 \quad (4.5)
\]

\[
\delta'(0) = 0 \quad (4.6)
\]

In order to solve this equation, the substitution \( \delta = \frac{f(\tilde{r})}{\tilde{r}} \) is made, this transforms the differential equation into

\[
f'' - 2f = 0 \quad (4.7)
\]

The general solution is a superposition of exponentials

\[
f (\tilde{r}) = C_1 e^{\sqrt{2} \tilde{r}} + C_2 e^{-\sqrt{2} \tilde{r}} \quad (4.8)
\]

The boundary condition at the center of the sphere gives a relation between the constants, since the solution cannot straightforwardly be substituted into the equation, a Taylor expansion is made.

\[
\frac{f'(\tilde{r})}{\tilde{r}} - \frac{f(\tilde{r})}{\tilde{r}^2} = \frac{C_1 + C_2}{\tilde{r}^2} + (C_1 + C_2) + O(\tilde{r}) = 0 \quad (4.9)
\]

Both terms must be equal to zero in order to satisfy the equation, so \( C_1 = -C_2 \). Substituting the solution into the boundary condition at the wall gives a rather complicated expression for \( C_1 \) as

\[
C_1 = \frac{kR}{\sinh \left( \frac{\sqrt{2} R}{\xi} \right) + k \xi \left[ \sqrt{2} \cosh \left( \frac{\sqrt{2} R}{\xi} \right) \right]} \quad (4.10)
\]

The resulting function is the same as Hone and Ji found [12] for the inside of a sphere, although different scaling is used and they only calculated to constant to first order in \( k \) while here it has been calculated exactly.

An equivalent of equation 3.12 can be found for the spherical case, the same strategy of expanding to first order in \( \delta \) is used.

\[
\tilde{\theta}^2 = 1 + \frac{3 \xi}{R} - \frac{3 \xi \sinh \left( \frac{\sqrt{2} R}{\xi} \right)}{\sqrt{2} k R \xi \cosh \left( \frac{\sqrt{2} R}{\xi} \right) + (R - k \xi^2) \sinh \left( \frac{\sqrt{2} R}{\xi} \right)} \quad (4.11)
\]

Here too, the function \( \theta \) will be plotted against a dimensionless variable defined by \( r = a \rho \). The resulting function becomes

\[
\frac{\psi(\rho)}{\psi} = 1 + C_1 \frac{\xi}{a \rho} \sinh \left( \frac{\sqrt{2} a}{\xi} \rho \right) \quad (4.12)
\]
4.1. Linearised equation

Figure 4.1 shows the concentration profile inside the sphere for three different values of $\xi$. The basic properties of the graphs are the same as for the one-dimensional case, the concentration drops to the average concentration in approximately three times the correlation length $\xi$. Larger correlation lengths result in higher concentration on the wall, but the concentration on the wall seems to reach a more-or-less constant value within the confidence interval of $\xi$, as can be seen in figure 4.2. The concentration on the wall is less than in the one-dimensional case. In section 3.2.1 the error was estimated by the value of $\delta$ on the wall and it was found that the linearisation scheme started to break down at the point where three times the correlation length $\xi$ was about half the distance between the plates $h$. In the spherical case, a similar thing happens when three times the correlation length $\xi$ becomes comparable to the radius $R$, but here, the concentration on the wall does not increase further, the concentration in the center does increase however, indicating violation of mass conservation.

Figure 4.2 shows how the concentration on the wall depends on both $\xi$ and $k$. The left graph is comparable to the one-dimensional case, a monotonically increasing function of $k$ which can be approximated by a straight line. The right graph however, is completely different from the one-dimensional case, the concentration seems to saturate and even decrease slightly after a maximum has been reached.

4.1.2 Free energy

The free energy can be calculated using equations 2.17 and 2.20, it will be scaled using the zero-attraction solution $\theta = 1$ as a reference, all length scales are scaled with the
Figure 4.2: Plot of the normalized order parameter on the wall $\psi(\frac{R}{a})$. Left as a function of $\xi$, with $k = 0.1a^{-1}$ and right as a function of $k$ with $\xi = a$ and in both cases $R = 11a$.

correlation length $\xi$.

$$U - U_0 = -\gamma_1 \xi^2 \psi^2 \int \frac{\theta^2 dS}{\hat{V}} - \frac{\xi^3}{\beta a^3} \int \int \int \frac{a^2}{6\xi^2} \psi^2 \theta^2 d\hat{V}$$

$$= \frac{a}{36\beta \nu \xi} \left[ -k \xi \int \frac{\theta^2 d\hat{S}}{\hat{V}} + \int \int \int \theta^2 - \frac{1}{2} \theta^4 d\hat{V} \right]$$

Where tildes mean differentiation and integration with respect to dimensional coordinates. Inserting the expression $\theta = 1 + \delta$ and expanding to leading order gives

$$36\beta \nu \Delta U = \frac{a}{\xi} \left[ \frac{2\pi R^3}{\xi^3} - \frac{4\pi k R^2}{\xi^2} \left( 1 + 2\delta \left( \frac{R}{\xi} \right) \right) - 8\pi \int_0^{\frac{R}{\xi}} \delta^2 \hat{r}^2 d\hat{r} \right]$$  (4.13)

Figure 4.3 shows that for a sphere of a given radius $R$ there is an optimal correlation length $\xi$ which is roughly of the same magnitude with some dependence on the attraction parameter $k$. Since the correlation length and the average volume fraction are related, there is an optimal volume fraction and hence chain length for which the free energy is at a minimum. There is no optimal value for $k$ since increasing $k$ gives lower and lower free energies, shifting the minimum in free energy towards smaller correlation lengths. A consequence of this is that given a radius, any correlation length smaller or equal to the radius of the sphere can be made a minimum in free energy by adjusting the attraction parameter.

### 4.2 Negative virial coefficient

In this section, the virial coefficient is assumed negative, just as in section 3.2.3, but this time the geometry is spherical. The equations used are almost the same as the one
4.2. Negative virial coefficient

Figure 4.3: Plot of the free energy as a function of $\xi$ (left), the solid line represents the case for $k = 0.1a$, the dashed line represents $k = 0.2a$ and the dotted line represents $k = 0.4a$. There is a minimum in the free energy around $\xi = R$, depending on $k$. Higher values of $k$ shifts minimum to the left and also makes it deeper. The right plot shows the free energy as a function of $k$ for $\xi = 11a$ (solid), $\xi = 15a$ (dashed) and $\xi = 18a$. There is no minimum in the free energy as a function of $k$, the radius of the sphere is $R = 11a$.

dimensional case, equations 3.29, with the exception of the differential equation, an extra term is added to accommodate the spherical geometry.

\[
\theta'' + \frac{2}{r}\theta' + \theta^3 - \theta = 0
\]
\[
\theta'(0) - k\xi\theta(0) = 0
\]
\[
\theta'\left(\frac{h}{2\xi}\right) = 0
\] (4.14)

In order to solve it, it is first linearised using the familiar expression $\theta = 1 + \delta$ where $\delta \ll 1$. This is once again inserted into the differential equation and higher order terms of $\delta$ are neglected. The resulting differential equation becomes

\[
\delta'' + \frac{2}{r}\delta' + 2\delta = 0
\] (4.15)

This differential equation is transformed using the familiar $\delta (\tilde{r}) = \frac{f(\tilde{r})}{\tilde{r}}$ into the simpler differential equation

\[
f'' + 2f = 0
\] (4.16)

The general solution to this equation is a superposition of sines and cosines, however, the boundary condition at the center of the sphere does not allow for the cosine, since $\frac{\cos(x)}{x}$ diverges at $x = 0$. The solution is given by

\[
\delta (\tilde{r}) = C \sin \left(\sqrt{2}\tilde{r}\right)
\] (4.17)
Where the constant $C$ can be determined by applying the boundary condition at the wall, it is found to be

$$C = \frac{kR^2}{\sqrt{2}R \cos\left(\sqrt{\frac{2R}{\xi}}\right) - \xi \sin\left(\sqrt{\frac{2R}{\xi}}\right) - kR\xi \sin\left(\sqrt{\frac{2R}{\xi}}\right)}$$  \hspace{1cm} (4.18)

The denominator in this equation is generally non-negative, as opposed to the one-dimensional case where the solution yielded very specific values of $\xi$. The function $\delta$ is again plotted against a dimensionless variable defined by $r = a \rho$. Giving $\delta$ as a function of $\rho$

$$\delta(\rho) = C\frac{\xi \sin\left(\sqrt{\frac{2a}{\xi}}\rho\right)}{a \rho}$$  \hspace{1cm} (4.19)

Some characteristic solutions to the problem with the negative virial coefficient are shown in figure 4.4, because of the sine in $\delta$, the general behaviour of the solutions is oscillatory. The left plot shows solutions which feature holes in the center together with maxima that are not at the wall. The right plot shows a higher concentration in the center, which means the polymer is collapsed onto itself there. Whether a profile features a hole or a bulge at the center is determined by the sign of the denominator in equation 4.18, positive sign means a hole, negative sign means a bulge.

### 4.2.1 Free energy

As in the previous section, the free energy will be calculated using equation 4.13, to see if there is an optimal amount of material given a certain interaction strength $k$ and radius $R$. When the second virial coefficient was positive, there was one minimum in the free
4.2. **Negative virial coefficient**

energy as a function of $\xi$ corresponding to an optimal amount of material, while there was no minimum as a function of the interaction strength $k$.

![Image of graphs](image)

*Figure 4.5: Plot of the free energy when the second virial coefficient is negative, the left plot shows the free energy as a function of $\xi$ with $k = 0.005$ (solid) and $k = 0.1$ (dashed). The right plot shows the free energy as a function of $k$ with $\xi = 3a$."

Figure 4.5 shows that the free energy has a minimum at a certain value of $\xi$ for a given $k$ but this minimum need not be finite, in the graph a value of $k$ was chosen to make the minimum finite in order to show the resemblance with the positive virial coefficient case. The free energy as a function of $k$ shows many minima that run all the way down to minus infinity. These points might be where the chain collapses onto itself in a volume of size zero, due to the neglect of the third virial coefficient, like what happens in Flory theory when the third virial coefficient is neglected.
In chapter 2, a differential equation with boundary conditions was derived from a Green function description of a polymer chain, Flory-Huggins theory and a simple assumption about the interaction with a wall. This differential equation governed the behaviour of a mean-field order parameter defined as $\psi^2 \equiv \phi$, where $\phi$ is the volume fraction. It was found that this mean-field order parameter $\psi(r)$ must be real by interpreting it as proportional to the probability of the chain ending at point $r$, depending on the normalization used. The boundary condition, equation 2.21 and figure 2.2, show the tangent of the concentration profile must carry the same or the opposite sign as the attraction parameter $k$, depending on the position of the wall, since the volume fraction cannot be negative. This enables one to judge with a single glance if a solution obeys the boundary conditions.

Using equation 2.20, it was found that the chemical potential $\mu$ is proportional to the monomer volume fraction where there is no gradient, usually in the center. Together with the demand that $\psi$ is real, this produced the condition that the second virial coefficient $\nu$ must carry the same sign as $\mu$. Out of these parameters a correlation length $\xi$ could be constructed which is very prominent in all solutions.

The exact solution to the governing equation 2.20 in a one-dimensional geometry is a hyperbolic cotangent, when the interaction is attractive the concentration is higher on the wall than in the bulk and it drops rapidly to the bulk concentration. Both the length over which the concentration drops and the concentration on the wall depend on $k$ and $\xi$. The length over which the concentration drops is $\Delta x \approx \sqrt{2} \xi (2 - b)$, where $b$ is given by equation 3.4.

Next, a one-dimensional container was considered by moving two walls within a finite distance of each other, for this situation there are no exact solutions, so the governing equation was linearised and a perturbation expansion was made. Both solution types showed that the length over which the concentration drops to the average concentration is slightly more than in the infinite container, approximately three times the correlation length $\xi$. The two methods seemed to complement each other as the linearisation method
worked well for small values of $\xi$ while the perturbation method became better for larger values of $\xi$. The first order perturbation solution is equivalent with linearisation for small values of the perturbation parameter $\epsilon \equiv k\xi$, the two methods coincide when $\epsilon \leq 0.1$. Perturbation methods were also considered for spherical geometry, but the resulting equations proved very hard to solve above first order, therefore this approach was abandoned and attention was focussed on linearisation since that is equivalent with first order perturbation.

In a one-dimensional geometry, there is no physically acceptable solution to the linearised equation when the second virial coefficient is assumed negative. There are solutions, but these have very specific values for $\xi$ and since the average volume fraction must be a continues parameter, these solutions are non physical. The correlation length $\xi$ contains the chemical potential $\mu$ which must be able to be freely chosen. In spherical geometry the concentration drops over the same length as in the one-dimensional case, approximately three times correlation length $\xi$. Curvature causes less material to adhere to the wall, since the concentration on the wall saturates as a function of both $\xi$ and $k$, while this is not the case in one-dimensional geometry.

For a given radius and attraction strength, there is an optimal correlation length corresponding to an optimal amount of material which has the lowest free energy. This minimum in free energy starts around $\xi = R$ but shifts to shorter correlation lengths for higher attraction strength and also becomes deeper. The free energy has no minimum as a function of the attraction parameter $k$, this means that for a given radius any amount of material can be made the minimum in free energy by adjusting the attraction strength accordingly provided $\xi \leq R$.

The solution to the linearised equation becomes very unstable when the second virial coefficient is chosen negative, the free energy as a function of $k$ shows many singularities going to minus infinity. This might be due to the neglect of the third virial coefficient, like when the third virial coefficient is neglected in Flory theory. The free energy as a function of $\xi$ shows one minima which can be either finite or infinite depending on $k$. The solutions show oscillatory behaviour and maxima that are not on the wall, furthermore there are either holes or bulges in the center.
In chapter 2, the conclusion was drawn that when the second virial coefficient \( \nu \) is negative, the chemical potential \( \mu \) must be negative too. This only holds if the order parameter is chosen as \( \phi = \psi^2 \), which was due to the interpretation of the function \( \psi \) as the probability of the chain ending at position \( r \). There are studies of the subject where the order parameter is chosen as \( \phi = |\psi|^2 \), for instance [15], in which case \( \psi \) does not have to be real meaning \( \mu \) and \( \nu \) are not required to have the same sign. If the order parameter is chosen as stated, the solutions to positive and negative virial coefficients become the same, the difference is made by \( \xi \), which will be imaginary for a negative virial coefficient. If \( \xi \) is allowed to become any complex number, the solutions could also include damped oscillations.

One reason the perturbation expansion becomes better with increasing correlation length \( \xi \), resulting in increasing perturbation parameter \( \epsilon \), could be that it is usually applied when the highest order derivative is multiplied by a small parameter. Here the small parameter was in the boundary conditions, so the method was not applied in the conventional way.

It might be beneficial to investigate the possibility of different types of perturbation methods since here only the Poincaré expansion was used. Also different approaches to the governing equation might be used such as investigating the behaviour of dominant terms in regions of interest. Close to the wall the gradient squared term and possibly the third power term dominate the behaviour while in the center the gradient term is much smaller.

The reliability of the free energy curve needs to be investigated, the reliability of solutions was estimated by the size of the small perturbation \( \delta \), but in the free energy it is not such a simple matter since it is integrated over the boundary and in the volume the square is integrated. Integration always gives an order of accuracy and taking the square of \( \delta \) makes it smaller as long as \( \delta < 1 \).

The solutions found with the negative virial coefficient are not very stable, which can be seen from the plot of the free energy as a function of \( k \). There are many singularities.
where the free energy becomes minus infinity, but it is suspected that when the third virial coefficient is taken into account, these will become finite minima. These minima probably correspond to a state where the chain collapses onto itself or the wall, by neglecting the third virial coefficient, the chain is allowed to collapse into a volume of size zero. It is therefore suggested that future research do take the third virial coefficient into account in the Flory volume exclusion free energy.
Perturbation solutions and coefficients

The first order perturbation solution is given by
\[ \theta_1 (\tilde{x}) = C_1 \left( e^{\sqrt{2} \tilde{x}} + e^{\sqrt{2} \left( \frac{h}{\xi} - \tilde{x} \right)} \right) \] (A.1)

The second order perturbation solution is given by
\[ \theta_2 = C_2 \left( e^{\sqrt{2} \tilde{x}} + e^{\sqrt{2} \left( \frac{h}{\xi} - \tilde{x} \right)} \right) + \frac{1}{6} C_1^2 \left[ e^{2\sqrt{2} \tilde{x}} + e^{2\sqrt{2} \left( \frac{h}{\xi} - \tilde{x} \right)} \right] - C_1^2 e^{\sqrt{2} h} \] (A.2)

And the third order perturbation solution is given by
\[ \theta_3 = C_3 \left( e^{\sqrt{2} \tilde{x}} + e^{\sqrt{2} \left( \frac{h}{\xi} - \tilde{x} \right)} \right) + 6C_1 C_2 \left( \frac{1}{7} e^{2\sqrt{2} \tilde{x}} + \frac{1}{7} e^{2\sqrt{2} \left( \frac{h}{\xi} - \tilde{x} \right)} - 2e^{\sqrt{2} h} \right) \]
\[ + 2C_1^3 \left( 5e^{\frac{2h\sqrt{2}}{\xi}} + \sqrt{2} \tilde{x} + 5e^{\frac{2h\sqrt{2}}{\xi}} - \sqrt{2} \tilde{x} \right) + \frac{1}{17} e^{3\sqrt{2} \tilde{x}} + \frac{1}{17} e^{3\sqrt{2} \left( \frac{h}{\xi} - \tilde{x} \right)} \] (A.3)

The coefficient \( C_1 \) is given by
\[ C_1 = \frac{-1}{\sqrt{2} \left( 1 - e^{\frac{2h}{\xi}} \right)} \] (A.4)

The coefficient \( C_2 \) is given by
\[ C_2 = -\frac{1}{3} C_1^3 \left( 1 - e^{\frac{2h\sqrt{2}}{\xi}} \right) - \frac{C_1^2}{\sqrt{2}} \left( 1 + e^{\frac{h\sqrt{2}}{\xi}} \right) \] (A.5)

and the coefficient \( C_3 \) is given by
\[ C_3 = C_1 C_2 \left( 1 + e^{\frac{h\sqrt{2}}{\xi}} \right) + \frac{1}{6} C_1^3 \left( 1 + e^{2h\sqrt{2} \tilde{x}} - 6e^{\frac{h\sqrt{2}}{\xi}} \right) \]
\[ - \frac{12}{7} C_1 C_2 - 10C_1^3 e^{\frac{h\sqrt{2}}{\xi}} - \frac{3\sqrt{2}}{17} C_1^4 \left( 1 - e^{\frac{h\sqrt{2}}{\xi}} \right) \] (A.6)
Bibliography


