1 The model

- It allows to study the entropic effects on the wall as well as further studies using realistically modeled biopolymers.
- The model interpolates between the united atom model and the bead-spring model. In contrast to these two models it uses non-spherical force fields for the non-bonded. interaction
- The main idea of this approach with a more general form of the force field is to generalize the united atom model in a way that larger atom groups are combined to one construction unit, but the possible anisotropy of

these groups is still taken into account.

- As one wants the force field to degenerate into a sphere with increasing distance, we use a con-focal force field inside this interaction volume:

$$\mathcal{H}_{\text{inter}} = V_{\text{abs}} \left(\frac{d_1^{(p)} + d_2^{(p)}}{2} - c \right), \tag{1}$$

  where $d_1^{(p)}$ and $d_2^{(p)}$ denote the distance of the point $\mathbf{p}$ to the focal points of the ellipsoid and V_{abs} is the absolute potential.

- For convenience we use only a repulsive part

$$V_{\text{abs}}(r) \sim r^{-6} \quad . \tag{2}$$

- The mass of the building units is distributed between the focal points of the ellipsoids in the hard core region of the con-focal potential.
- The main ingredient of the model is the mass matrix of our rod-chains. In order to construct it we, must first calculate the Lagrangian of a single rod $\mathcal{L}_i = T_i - V_i$ with the kinetic energy T_i and the potential energy V_i. The subindex i marks the position of the rods in the chain. This one-dimensional homogeneous rod i has the length l_i starting at $\vec{a}_i$ and ending at $\vec{b}_i$.
- If we suppose that the rods all have the same mass m and that the velocity of the rod mass scales linearly with the position between the boundaries of the rod,

the kinetic energy can be written as

$$\begin{aligned} T_i &= \frac{1}{2}\int_0^{l_i} \frac{m}{l_i}\left(\frac{(l_i - x)\dot{\vec{a}}_i + x\dot{\vec{b}}_i}{l_i}\right)^2 dx \\ &= \frac{1}{6}m(\dot{\vec{a}}_i^{\,2} + \dot{\vec{a}}_i\dot{\vec{b}}_i + \dot{\vec{b}}_i^{\,2}). \end{aligned}$$

- Adding the single terms of the rods building the chain we get the Lagrangian $\mathcal{L}$ of the whole rod chain.
- The equations of motion of the chain can be calculated from the Lagrange equations of the second kind. Since the equations of motion separate in each direction, we have only to solve three tridiagonal $(N+1) \times (N+1)$ matrices per chain which consist of N rods per time

step of the form

$$\mathbf{W}\ddot{\vec{x}} = \vec{F} \tag{3}$$

$$\frac{m}{6}\begin{pmatrix} 2 & 1 & 0 & 0 & \dots \\ 1 & 4 & 1 & 0 & \dots \\ 0 & 1 & 4 & 1 & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}\begin{pmatrix} \ddot{x}_0 \\ \ddot{x}_1 \\ \ddot{x}_2 \\ \vdots \end{pmatrix} = \begin{pmatrix} F_{10} \\ F_{11}+F_{21} \\ F_{22}+F_{32} \\ \vdots \end{pmatrix} \tag{4}$$

with the force F_{ij} on the coordinate j of the flexible point i of the chain

$$F_{ij} = -\frac{\partial V_i}{\partial j} \tag{5}$$

and $\ddot{x}_i$ denote the accelerations of the flexible points of

the chain. The flexible points are the link points of the ellipsoids and the end points of the rod chain. The sub-indices mark the positions in the chain: 0 and $N+1$ are the end-points of the chain and the numbers between them denote the linking points of rods in the chain.

- The bonded interactions between neighboring units are given by harmonic length and angle potentials:

$$\mathcal{H}_{bond} = \frac{1}{2}k(r - r_0)^2 \tag{6}$$

$$\mathcal{H}_{angle} = \frac{1}{2}k_\theta(\cos\theta - \cos\theta_0)^2 \tag{7}$$

with the bond lengths r and the bending angles θ. Here

r_0 and θ_0 denote the mean values.

2 Mean-Field Theory for the Pressure that a Grafted Chain exerts on the Wall

- Consider a wall with a repulsive r^6 potential and a polymer grafted at the wall. The constraint that the polymer is grafted and that one half-space is excluded leads to a competition between the necessity to avoid the wall and the constraint to be fixed at the wall.
- Due to the entropy the monomers would like to stay as

far away from the wall as possible.

- In order to do so they exert a pressure on the wall.
- This pressure decreases radially from the grafting point.
- For a theoretical treatment of the pressure we shall regard an elastic wall.
- Let the surface of the wall be described by $h(x, y)$. The thermodynamic properties of the chain of length N grafted at the repulsive wall can be described by the propagator $G_N(\vec{r}, \vec{r}')$ resulting from the Edwards equation

$$\frac{\partial G_N(\vec{r}, \vec{r}')}{\partial N} = \frac{l^2}{6} \Delta G_N(\vec{r}, \vec{r}') \tag{8}$$

with the $G_N(\vec{r},\vec{r}') = 0$ at the wall and $\lim_{N\to 0} G_N(\vec{r},\vec{r}') = \delta(\vec{r},\vec{r}')$.

- The partition function is then given by

$$Z_N(l) = \int d\vec{r}' G_N(\vec{r},\vec{r}') \quad , \tag{9}$$

where the integral extends over all space that is available to the free end. The Greens-function for a planar wall $h(x,y) = 0$ can then be factorized as

$$G_N^{(0)}(\vec{r},\vec{r}') = \left(\frac{3}{2\pi N l^2}\right)^{3/2} \exp\left[-\frac{3(x-x')^2}{2Nl^2}\right] \exp\left[-\frac{3(y-y')^2}{2Nl^2}\right] \times \left(\exp\left[-\frac{3(z-z')^2}{2Nl^2}\right] \exp\left[-\frac{3(z+z')^2}{2Nl^2}\right]\right) \quad .$$

- The partition function is therefore

$$Z_N^{(0)}(l) = \int_{-\infty}^{+\infty} dx' \int_{-\infty}^{+\infty} dy' \int_0^{+\infty} dz' G_N^{(0)}(\vec{l}, \vec{r}') \quad (10)$$

$$= \mathrm{erf}(\frac{l}{2R_g}) \quad , \quad (11)$$

  where $R_g = \sqrt{Nl^2/6}$ is the radius of gyration of the free chain and erf the error function.

- To compute the pressure we introduce a small perturbation in h. We can write the partition function as $Z_N = Z_N^{(0)} + Z_N^{(1)} + Z_N^{(2)} + \ldots$, where $Z_N^{(i)}$ is of order h^i and Z_N^0 as in (10).

- Due to the linearity of (8), each term satisfies the

Edwards equation

$$\frac{\partial Z_N^{(i)}}{\partial N} = \frac{l^2}{6}\Delta Z_N^{(i)} \quad i = 0, 1, 2, \ldots \tag{12}$$

- The solutions of higher orders are coupled to the constraint. Now we have

$$\begin{aligned} 0 &= Z_N(x, y, h) \\ &= Z_N(x, y, 0) + h(x, y)\frac{\partial Z_N}{\partial z}(x, y, 0) + \frac{h^2(x, y)}{2}\frac{\partial^2 Z_N}{\partial z^2}(x, y, 0) + \ldots \quad . \end{aligned}$$

- For the linear contribution $Z_N^{(1)}$ we get

$$Z_N^{(1)}(x, y, 0) = -h(x, y)\frac{\partial Z_N^{(0)}}{\partial z}(x, y, 0) \quad , \tag{13}$$

yielding [?]

$$Z_N^{(1)}(\vec{l}) = \frac{l^2}{6}\int_0^N dn \int dS \frac{\partial G_{N-n}^0}{\partial z}(x,y,0;\vec{a}) Z_n^{(1)}(x,y,0) \quad . \qquad (14)$$

- Hence, the change in the height is, to first order, due to the work

$$\begin{aligned} \Delta W &= W[h] - W[0] \\ &= -k_B T \log\left[1 + \frac{Z_N^1}{Z_N^0}\right] \\ &= \int dS p(x,y) h(x,y) \quad , \end{aligned}$$

where $p(x,y)$ has the symmetric form

$$p(r) = \frac{k_B T}{2\pi(r^2+l^2)^{3/2}} \left(1 + \frac{r^2+l^2}{2R_g^2}\right) \exp\left[-\frac{r^2+l^2}{4R_g}\right] \tag{15}$$

with $r = \sqrt{x^2+y^2}$.

- To push at $\vec{r} = (x,y)$ an elementary volume of $dV(r) = h(r)dS$ we need the work $dW = p(r)h(r)dS$.
- The function $p(r)$ is the pressure.
- The entire entropic force which the chain exerts on the wall is then given by

$$F = \int_0^\infty dr 2\pi r p(r) = \frac{k_B T}{l} \exp\left[-\frac{l^2}{4R_g^2}\right] \tag{16}$$

$$= \frac{k_B T}{l} \exp\left[-\frac{3}{2N}\right] \quad . \tag{17}$$

3 Simulation Results

- 10 different chain lengths $N = 20, N = 40, N = 60, N = 80, N = 100, N = 125, N = 150, N = 175, N = 200$ and $N = 250$ to study the pressure and the corresponding finite effects.

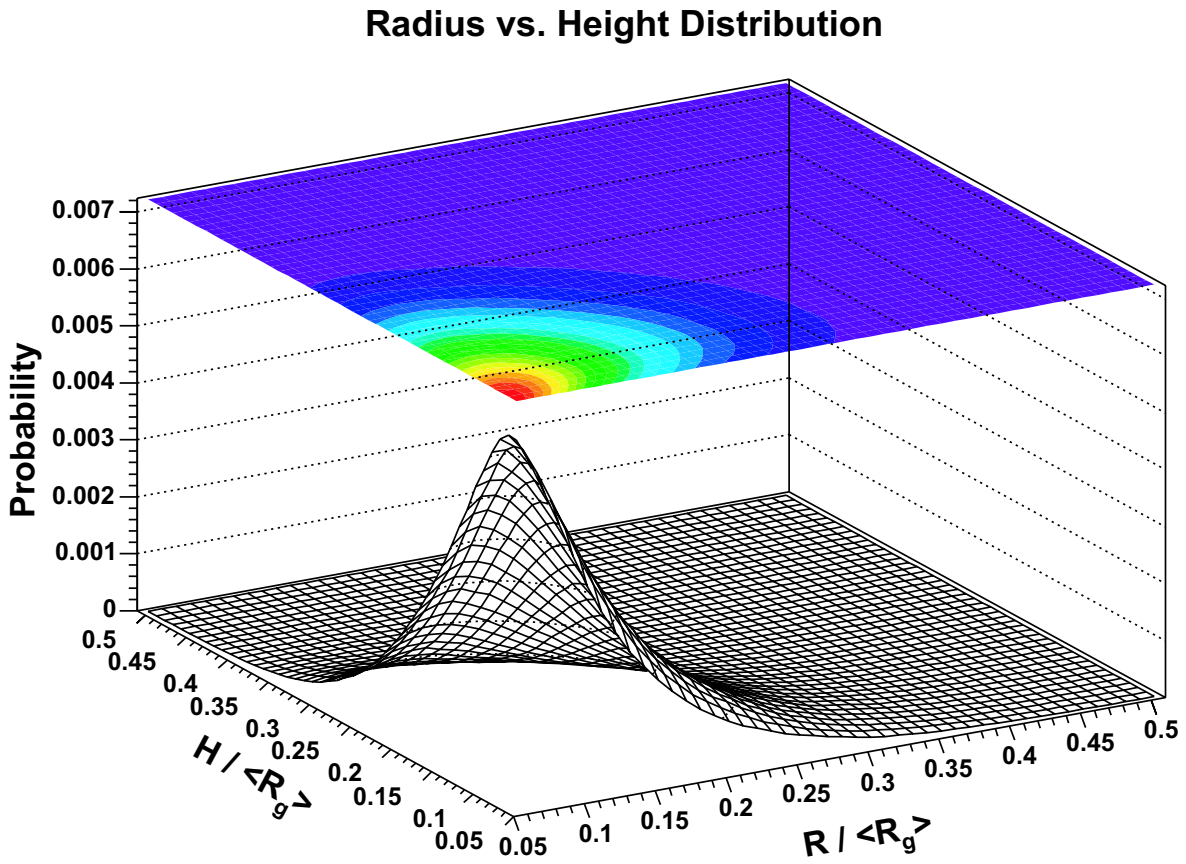

Abbildung 1: Shown is the distribution of the height with respect to the radius. The values are divided by their respective radii of gyration for reasons of finite-size scaling.

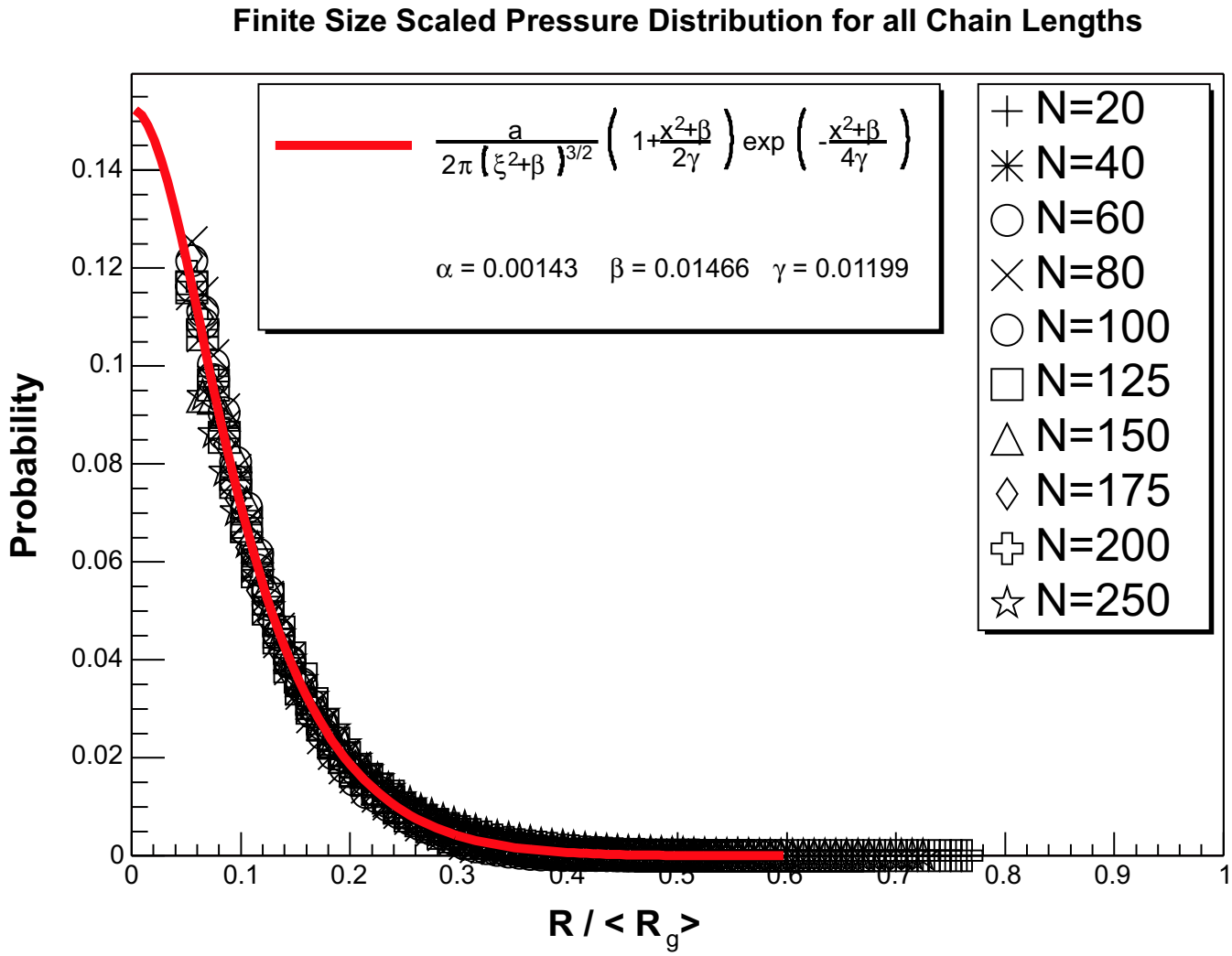

Abbildung 2: Finite-size scaling plot for the pressure distribution. The full curve is the fit using the predicted form of the distribution. The fit is very good over the entire region.

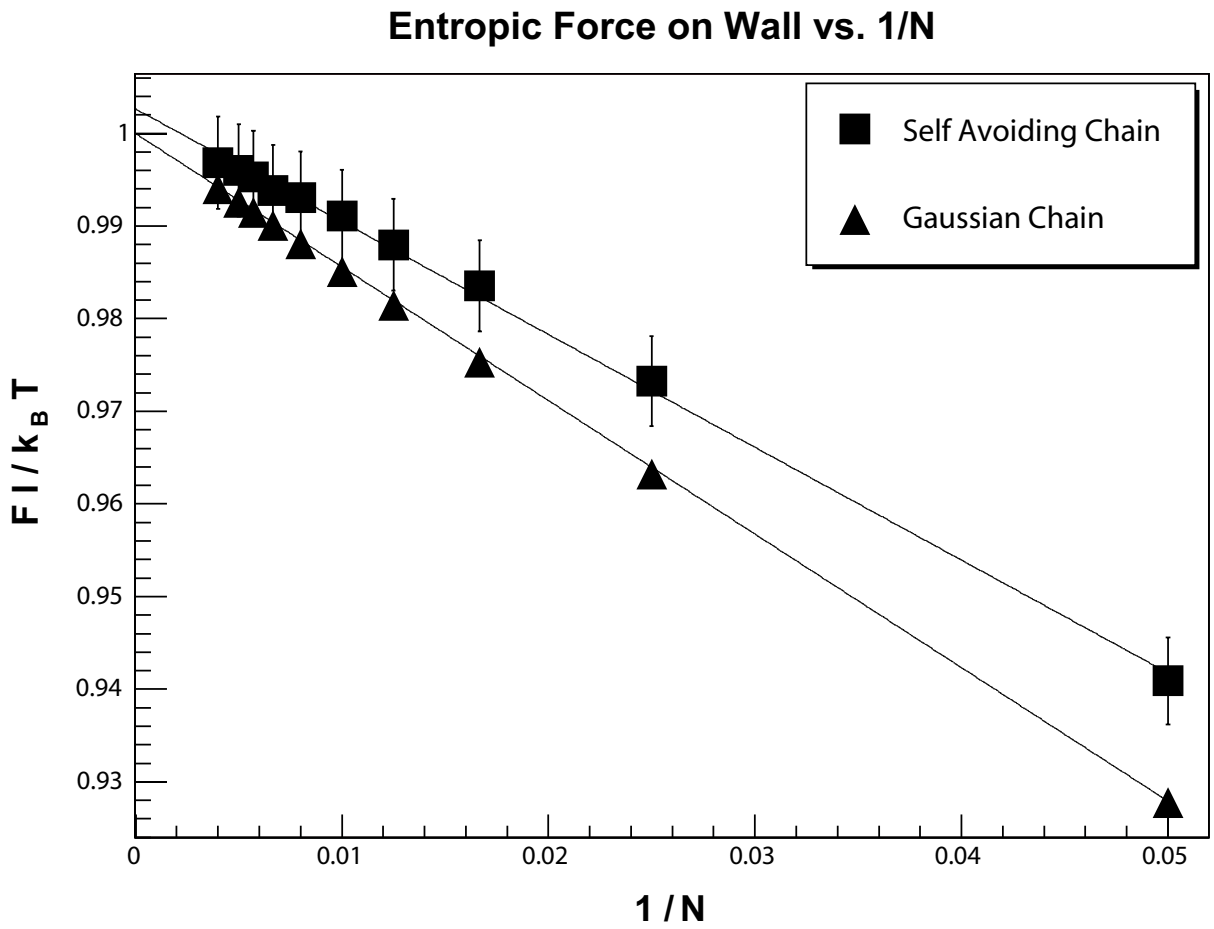

Abbildung 3: Shown is the entropic force exerted on the wall by the polymer. The figure gives the result for the Gaussian and for the chain with self-avoidance.

4 Force-elongation behavior

- Knowing the distribution function, we can calculate the partition function of the polymer with an external force:

$$Z = \int d\vec{r} p_N(\vec{r}) \exp\left(\frac{\vec{f}\cdot\vec{r}}{T}\right). \tag{18}$$

  But it is also possible to derive the desired results by fundamental reasoning.

- We only need to introduce the two characteristic lengths for the problem, $R_F \cong lN^{\nu}$ and $\xi_p = T/f$. In general, the norm of the mean end to end distance

vector can be written as:

$$\left|\left\langle \vec{r}(\vec{f}) \right\rangle\right| = R_F \varphi_r \left(\frac{R_F}{\xi_p} \right) = R_F \varphi_r(x), \qquad (19)$$

where $\varphi_r(x)$ is a dimensionless function.

- In the case of small forces one expects a linear response of the polymer, so that we can write $\lim_{x \to 0} \varphi_r(x) \cong x$. Using this we get:

$$\left|\left\langle \vec{r}(\vec{f}) \right\rangle\right| \cong \frac{R_F^2}{T} f. \qquad (20)$$

- If the chain is stretched stronger, we expect deviations from the linear law. Let us assume that the stretched chain is composed of "blobs", i.e. small chain-balls.

Each of these blobs has a size of ξ_p. In such a blob the external force is just a small perturbation, so we can write for the number of monomers g_p in the blob:

$$\xi_p \cong l g_p^{\nu} \tag{21}$$

or:

$$g_p = \left(\frac{T}{lf}\right)^{1/\nu} . \tag{22}$$

- Considering that the number of the blobs must be N/g_p, one obtains for the three dimensional case:

$$\left|\left\langle \vec{r}(\vec{f}) \right\rangle\right| \cong \frac{N}{g_p}\xi_p \cong Nl\left(\frac{fl}{T}\right)^{0.689} . \tag{23}$$

- Hence for large forces the elongation behavior is not

linear. For the case of stretched polymers one can look again at the distribution function, which has the form $\exp(-(r/R_F)^\delta)$. The resulting entropy is:

$$S(r) = const + \ln p_N(r) = const - \left(\frac{r}{R_F}\right)^\delta . \qquad (24)$$

- In this case the corresponding elastic free energy amounts to:

$$F_{tot} = T\left(\frac{r}{R_F}\right)^\delta - fr. \qquad (25)$$

- If one minimizes this expression, one obtains the

wanted relation between force and end-to-end distance:

$$f \cong \delta \frac{T}{R_F} \left(\frac{r}{R_F} \right)^{\delta - 1} . \tag{26}$$

- We have seen how to calculate the relation between applied force and resulting elongation for long chains with self-avoiding as well as without self-avoiding. This result is important but not satisfactory. If one considers that the polymer cannot rupture, than the extension should be Nl for very large forces but in the results above it seems that the polymer chain can be stretched to infinite length. Furthermore, the case of a restricted geometry is not included. Both will be done in the next sections.

4.1 Large force-elongation behavior

- We now come back to the ideal polymer chain without self-avoidance. This seems to be a step back, but it gives the ability to calculate the exact force-elongation behavior for any force.

4.1.1 Force-elongation behavior for the ideal chain

- First we calculate the work that is performed by a force $\vec{f}$ if the polymer is elongated by $d\vec{R}$. This is:

$$\delta A = -\vec{f} \cdot \delta \vec{R} = -\sum_{i=1}^{N} \vec{f} \cdot d\vec{r_i} = -\sum_{i=1}^{N} d\varphi_i, \qquad (27)$$

where $\varphi_i = \vec{f} \cdot \vec{r_i} = f \cdot l \cdot \cos(\vartheta_i)$. So the partition function is

$$Z = \int \exp\left(\sum_{i=1}^{N} \left(\frac{f \cdot l}{T}\right) \cos(\vartheta_i)\right) \prod_{i=1}^{N} \sin(\vartheta_i) d\vartheta_i d\varphi_i. \tag{28}$$

- The multidimensional integral can be separated:

$$Z = \left(\int_0^{2\pi} \int_0^{\pi} \exp\left(\frac{f \cdot l}{T} \cos(\vartheta)\right) \sin(\vartheta) d\vartheta d\varphi\right)^N . \tag{29}$$

If one introduces $\beta = \frac{f \cdot l}{T}$, one gets:

$$Z = \left(\frac{4\pi \sinh(\beta)}{\beta}\right)^N . \tag{30}$$

- The exact force-elongation behavior is:

$$R = \left|\vec{R}\right| = N \cdot l \cdot (\coth(\beta) - \frac{1}{\beta}). \qquad (31)$$

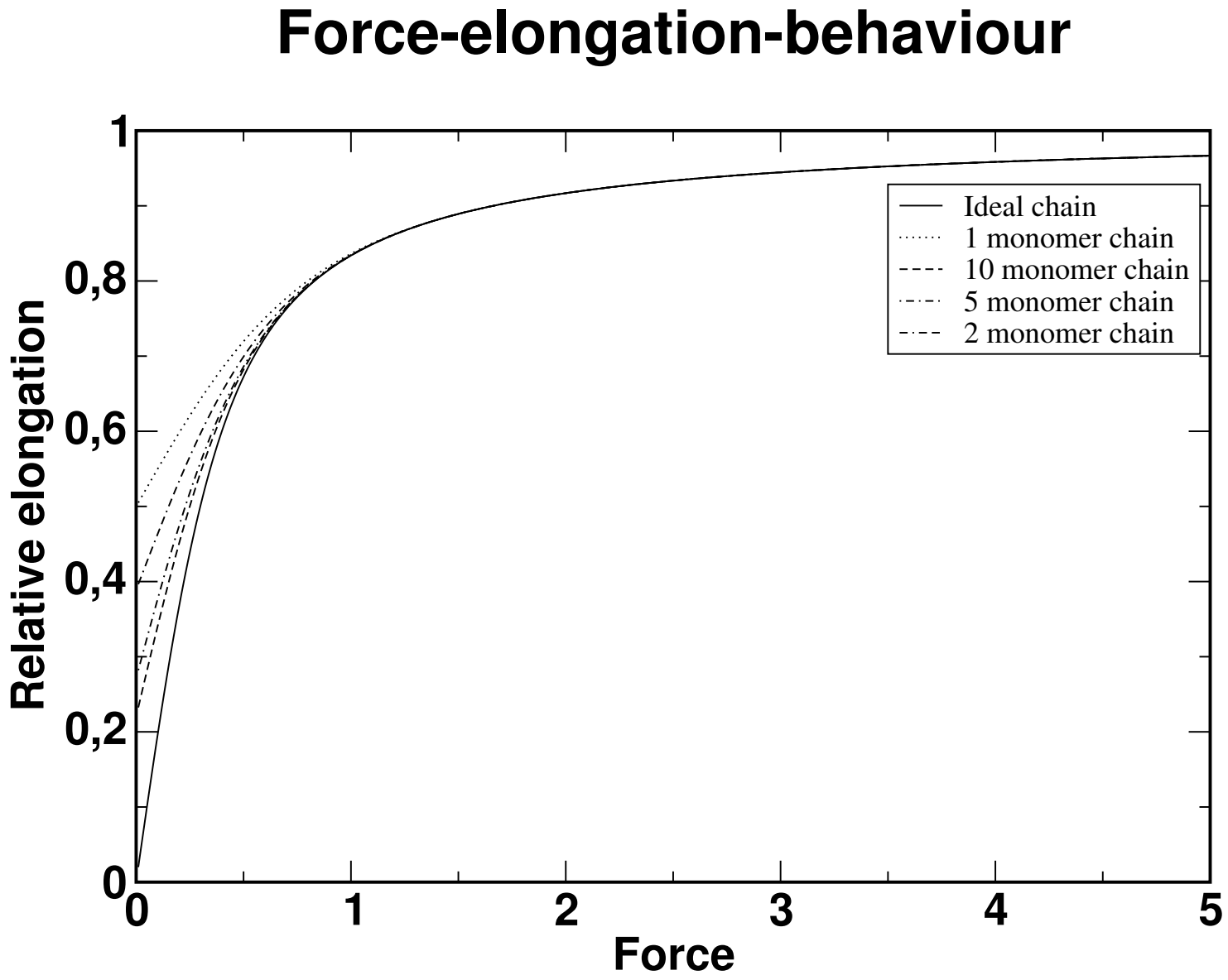

Abbildung 4: Shown is the force-elongation behavior for the ideal

- Now we restrict the geometry by a wall. Suppose that one monomer is attached to the wall. Starting with a single monomer, we will see what happens when we introduce the wall. The possible angle between the force f and the monomer of length l is restricted to a range of $[0; \frac{\pi}{2}]$. Because of the cylinder-symmetry of this problem, the angle φ is still arbitrary. For the one-monomer partition function we get

$$Z_1 = \int_0^{2\pi} \int_0^{\frac{\pi}{2}} \exp(\beta \cos(\vartheta)) \sin(\vartheta) d\vartheta d\varphi. \qquad (32)$$

- For the partition functions of the longer chains the

φ-integration will also range over 2π, so we define:

$$Z_N = (2\pi)^N \cdot \hat{Z}_N. \tag{33}$$

For $\hat{Z}_1$ we get:

$$\hat{Z}_1 = \frac{e^\beta - 1}{\beta}. \tag{34}$$

Now assume two monomers attached to a wall. If the chain is appended by a further monomer the first one will not be influenced by the second. But the possible angles between the new monomer and the force are dependent on the position of the first monomer.

- We have two different cases to consider. The first case is that the distance of the end of the first monomer to the

wall is large enough that all angles between the second monomer and the force are possible. In the other case the end of the first monomer is situated closer to the wall. This means the possible angles between the force and the second monomer have to be calculated.

- If we call the integration-angle of the two monomers ϑ_1 and ϑ_2 we get for the possible angles:

$$0 \leq \vartheta_2 \leq \pi - \vartheta_1. \tag{35}$$

So, we get for $\hat{Z}_2$:

$$\hat{Z}_2 = \int_0^{\frac{\pi}{2}} \int_0^{\pi-\vartheta_1} exp(\beta(\cos(\vartheta_1)+\cos(\vartheta_2)))\sin(\vartheta_1)\sin(\vartheta_2)d\vartheta_2\vartheta_1. \tag{36}$$

- With the substitution $x_i = \cos(\vartheta_i)$ we have

$$\hat{Z}_2 = \int_0^1 \int_{-x_1}^1 exp(\beta(x_1 + x_2))dx_2 dx_1. \qquad (37)$$

- Therefore, we obtain:

$$\hat{Z}_2 = \int_0^1 \frac{e^\beta}{\beta}(e^{x_1} - e^{-\beta})dx_1 = \frac{e^\beta}{\beta}\hat{Z}_1 - \frac{1}{\beta}$$

.

- From now on, we define

$$I_1 = \int_0^1 dx_1. \qquad (38)$$

- Let us look now at the case of three and more monomers. By taking more monomers into our chain,

we increase the number of configurations for the polymer. At each step we know that the already existing monomers are not influenced by the new one. So we must find out how the possible angle for the last monomer is restricted.

- We see that in a chain with N monomers, the position for the last one does only depend on the position of the ending point of the $(N-1)$th monomer. If this monomer ends in a distance from the wall that is larger than a monomer length, then the last monomer can take place in any position.
- But if the end of the $(N-1)$th monomer is closer to the wall than one monomer length, the possible angles

for ϑ_N are restricted. In this case we get for the three-monomer-chain an upper integration limit of $\vartheta_{3,max} = \pi - \vartheta = \pi - \arccos(\cos(\vartheta_1) + \cos(\vartheta_2))$. The partition function is now:

$$\hat{Z}_3 = \int_0^{\frac{\pi}{2}} \int_0^{\pi-\vartheta_1} \int_0^{\pi-a(\vartheta_1,\vartheta_2)} \exp(\beta(\cos(\vartheta_1) + \cos(\vartheta_2) + \cos(\vartheta_3)) \cdot \sin(\vartheta_1)\sin(\vartheta_2)\sin(\vartheta_3) d\vartheta_3 d\vartheta_2 d\vartheta_1, \tag{39}$$

where we used $a(\vartheta_1, \vartheta_2)$

$$a(\vartheta_1, \vartheta_2) = \begin{cases} \arccos(\cos(\vartheta_1) + \cos(\vartheta_2)) & 0 \leq \cos(\vartheta_1) + \cos(\vartheta_2) \leq \\ 0 & 1 < \cos(\vartheta_1) + \cos(\vartheta_2) \end{cases} \tag{40}$$

- With the substitution for $a(\vartheta_1, \vartheta_2)$ and $b(x_1, x_2) = \cos(a(\vartheta_1, \vartheta_2))$ we obtain

$$\hat{Z}_3 = \int_0^1 \int_{-x_1}^1 \int_{-b(x_1,x_2)}^1 exp(\beta(x_1 + x_2 + x_3))dx_1dx_2dx_3. \tag{41}$$

$b(x_1, x_2)$ can be written as

$$b(x_1, x_2) = \sum_{i=1}^{2} x_i \Theta(\sum_{i=1}^{2} x_i)\Theta(1 - \sum_{i01}^{2} x_i) + \Theta(\sum_{i=1}^{2} x_i - 1), \tag{42}$$

from which we obtain the integral:

$$\hat{Z}_3 = \int_0^1 \int_{-x_1}^1 \frac{exp(\beta(x_1 + x_2))}{\beta}(e^{\beta} - e^{-\beta b(x_1,x_2)})dx_2dx_1 \tag{43}$$

$$= \frac{e^\beta}{\beta}\hat{Z}_2 - \frac{1}{\beta}\int_0^1 \int_{-x1}^1 e^{\beta(x_1+x_2-b(x_1,x_2))}. \quad (44)$$

- We can write:

$$I_2 = \int_0^1 \int_{-x_1}^1 exp(\beta(x_1 + x_2 - b(x_1, x_2)))dx_2dx_1. \quad (45)$$

- Now we can generalize the formulae for N monomers in the following way:

$$Z_N = (2\pi)^N \hat{Z}_N = (2\pi)^N \int_0^1 ... \int_{-b_N(x_1,...,x_{N-1})}^1 exp(\beta \sum_{i=1}^N x_i)dx_N...dx \quad (46)$$

With the integrals I_N:

$$I_N = \int_0^1 ... \int_{-b_N(x_1,...,x_{N-1})}^1 exp\left(\beta(\sum_{i=1}^{N} x_i - b_{N+1}(x_1, ..., x_N))\right) dx_N \quad (47)$$

and the b_N

$$b_N(x_1, ..., x_{N-1}) = \sum_{i=1}^{N-1} x_i \Theta(\sum_{i=1}^{N-1} x_i)\Theta(1-\sum_{i=1}^{N-1} x_i)+\Theta(\sum_{i=1}^{N-1} x_i - 1) \quad (48)$$

one obtains by recursive insertion the following

partition function

$$Z_N = (2\pi)^N \left(\left(\frac{e^\beta}{\beta} \right)^N - e^{-\beta} \sum_{i=0}^{N-1} \left(\frac{e^\beta}{\beta} \right)^{N-i} I_i \right) . \quad (49)$$

- We use $I_0 = 1$. Now we must calculate the I_i's, or we must find a way to simplify them. As an alternative to the preceding, we can use for the case of three or more monomers

$$Z = \left(\int_0^{2\pi} \int_0^{\pi} \exp\left(\frac{f \cdot l}{T} \cos(\vartheta) \right) \sin(\vartheta) d\vartheta d\varphi \right)^N . \quad (50)$$

- Here any angle between the monomers and the force is allowed. In the case with the wall this is not always true for all monomers, hence we introduce an effective

angle for all monomers. If we do this, we get:

$$Z = \left(\int_0^{2\pi} \int_0^{\vartheta_0} \exp\left(\frac{f \cdot l}{T} \cos(\vartheta) \right) \sin(\vartheta) d\vartheta d\varphi \right)^N \quad (51)$$

- The calculation of this integral gives:

$$Z = \left(\frac{2\pi}{\beta} (\exp(\beta) - \exp(\beta \cos(\vartheta_0))) \right)^N \quad (52)$$

- For the average end-to-end distance we obtain

$$R = N \cdot l \cdot \left(\frac{1 + \alpha \exp(\beta(\alpha - 1))}{1 - \exp(\beta(\alpha - 1))} - \frac{1}{\beta} \right), \quad (53)$$

with $\alpha = \cos(\vartheta_0)$.

- For $\vartheta_0 \to \pi$, what means $\alpha \to -1$ we get the well-known formula:

$$R = N \cdot l \cdot (\coth(\beta) - \frac{1}{\beta}). \tag{54}$$

- With $\beta \to 0$ we get: $R = \frac{Nl}{2}(\alpha + 1)$. And for $\beta \to \infty$ we get: $R = Nl$. This gives us now an approximation for the end-to-end distance if we have the effective angle ϑ_0.

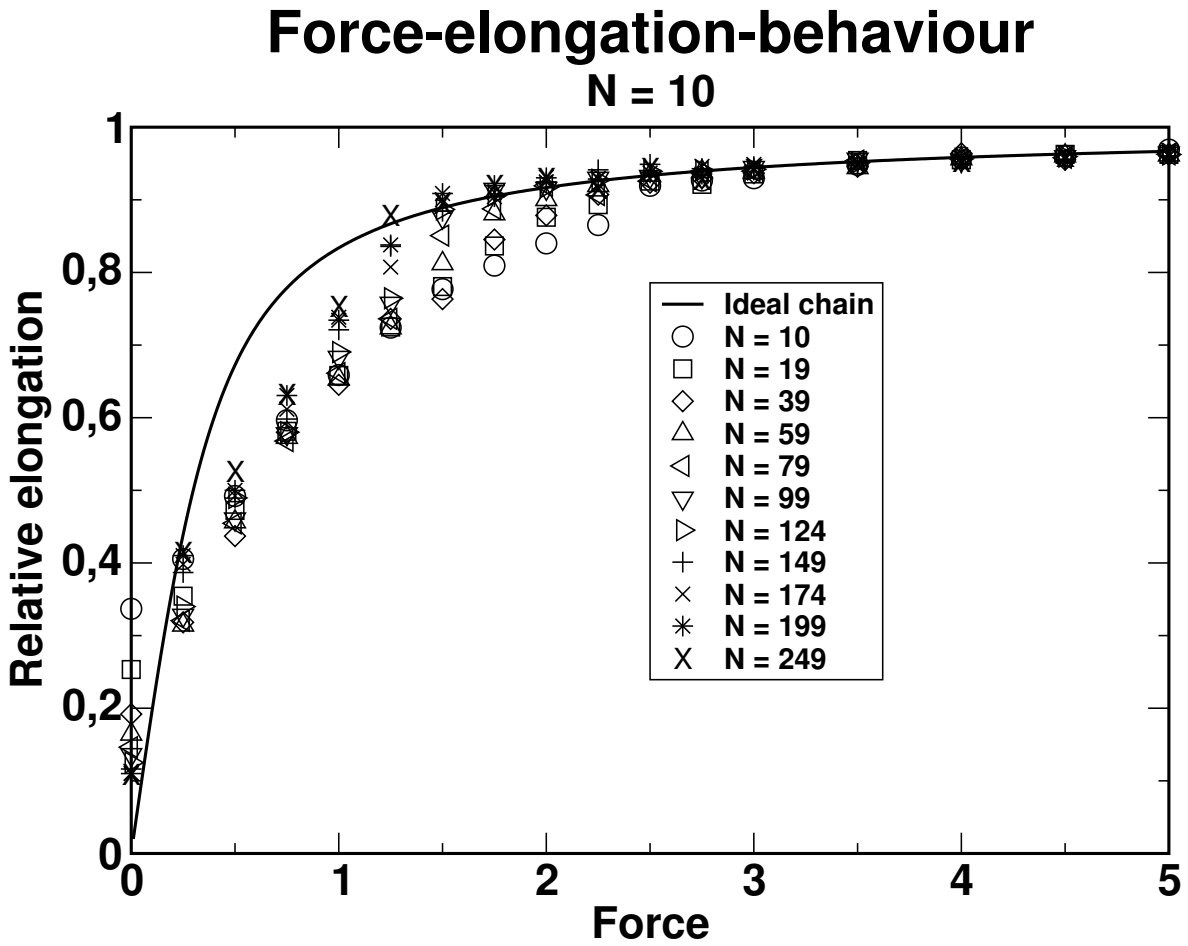

Abbildung 5: Shown are the force-elongation simulation results for all simulated chain lengths compared to the ideal chain behavior.

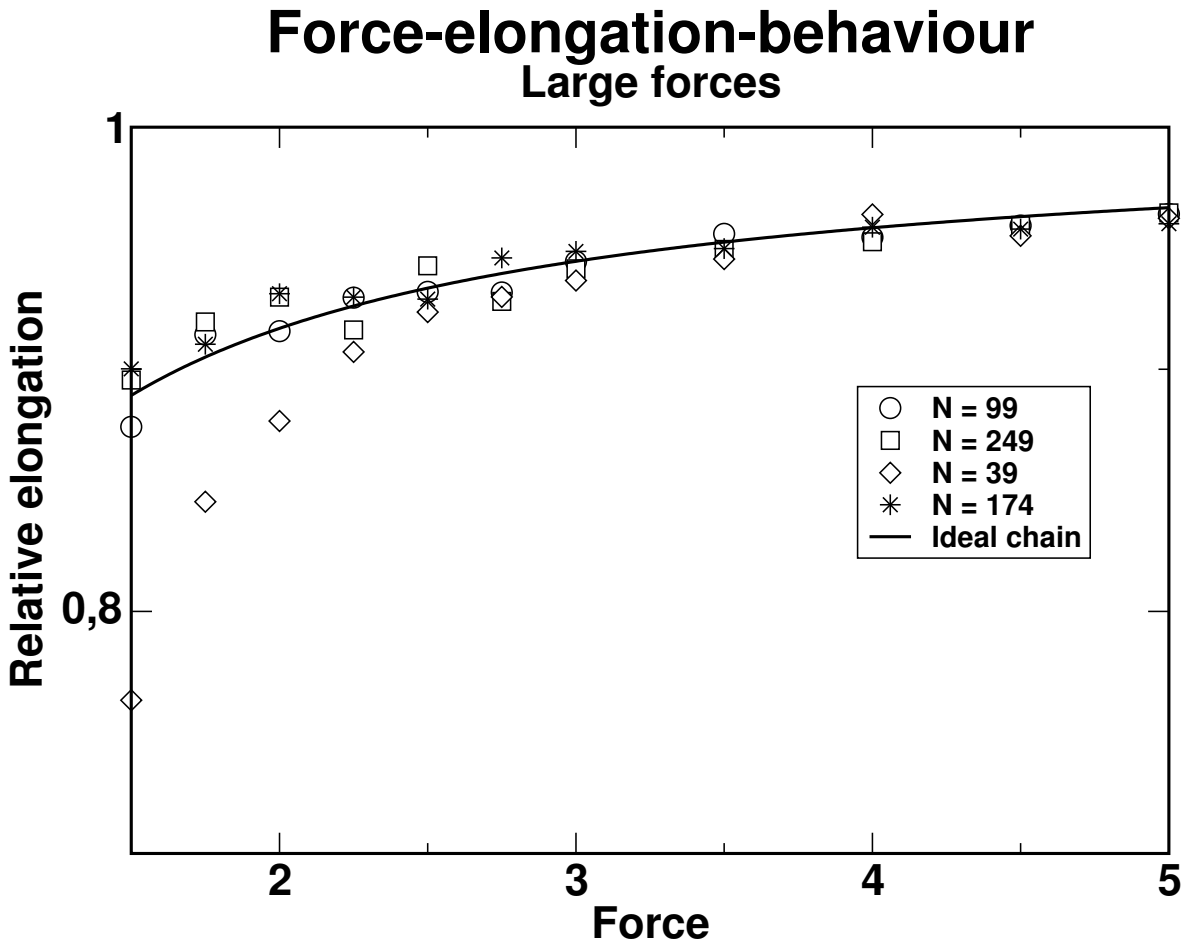

Abbildung 6: End-to-end-distance for large forces

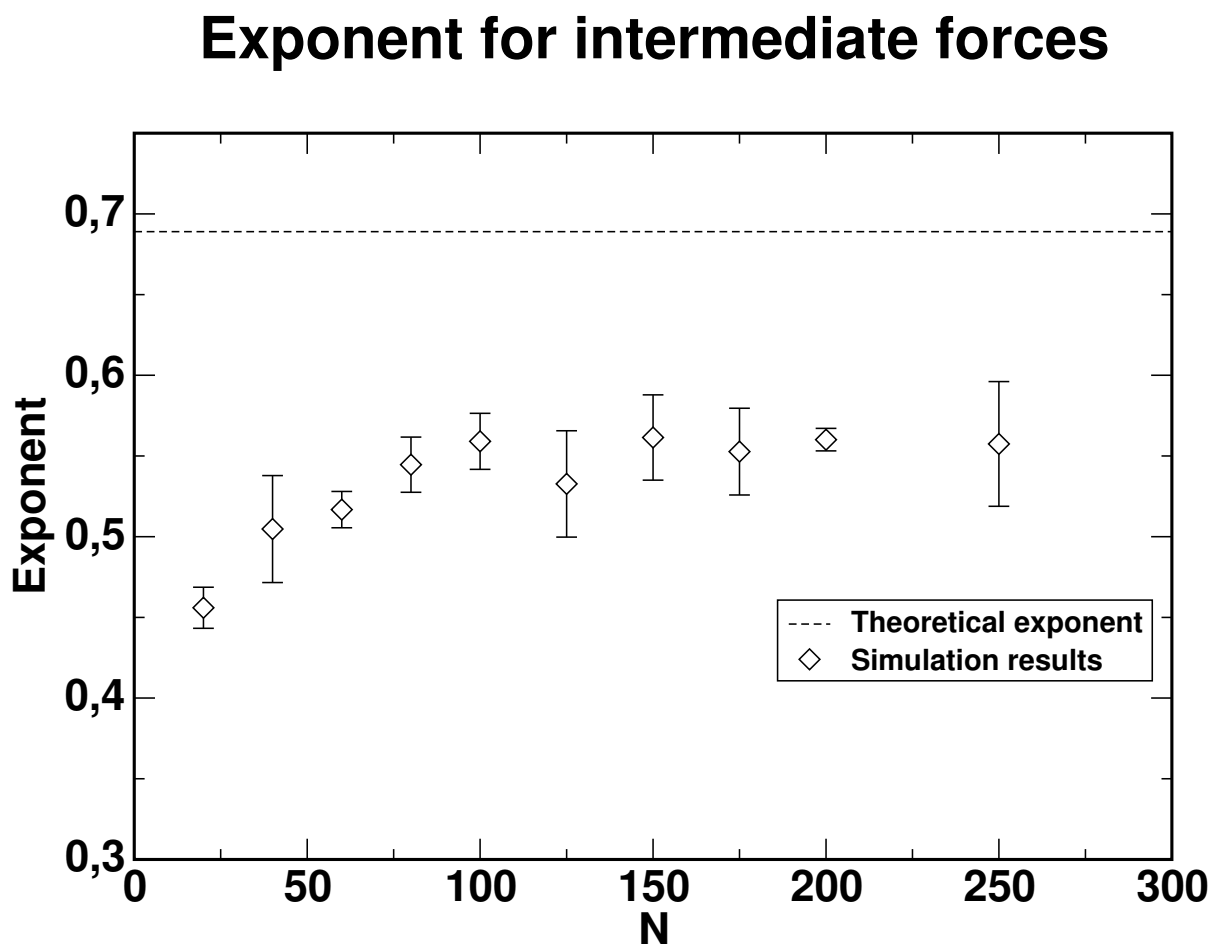

Abbildung 7: Elongation exponent for intermediate forces

In the small-force range we have two predictions for the force-elongation behavior, one for simple random walks and the other for the self-avoiding walks. In both cases a linear behavior is predicted. In the ideal case we expect a fix spring constant for any polymer length, but in the self-avoiding case the spring constant depends of the chain length. Now we will investigate if this dependence is reproduced by the simulations. But first the theoretical spring constants

$$k_{id} = \frac{l}{3T} \tag{55}$$

$$k_{sa} = \frac{lN^{0.184}}{T} \tag{56}$$

(here "id" means ideal and "sa" means self-avoiding). The

fit to the data is shown in figure (8), where we can see the spring constant for the different polymer length.

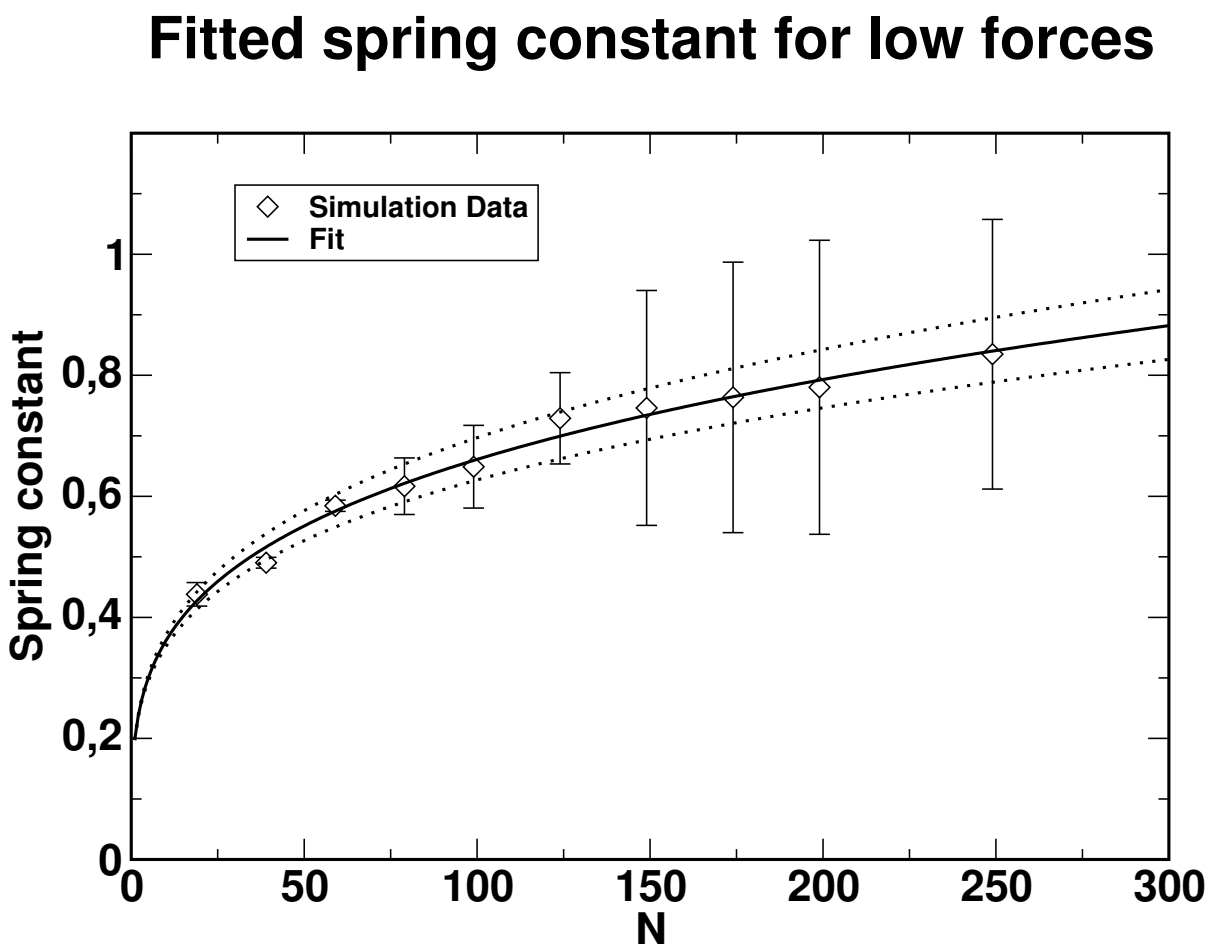

Abbildung 8: Spring constants for the low force range

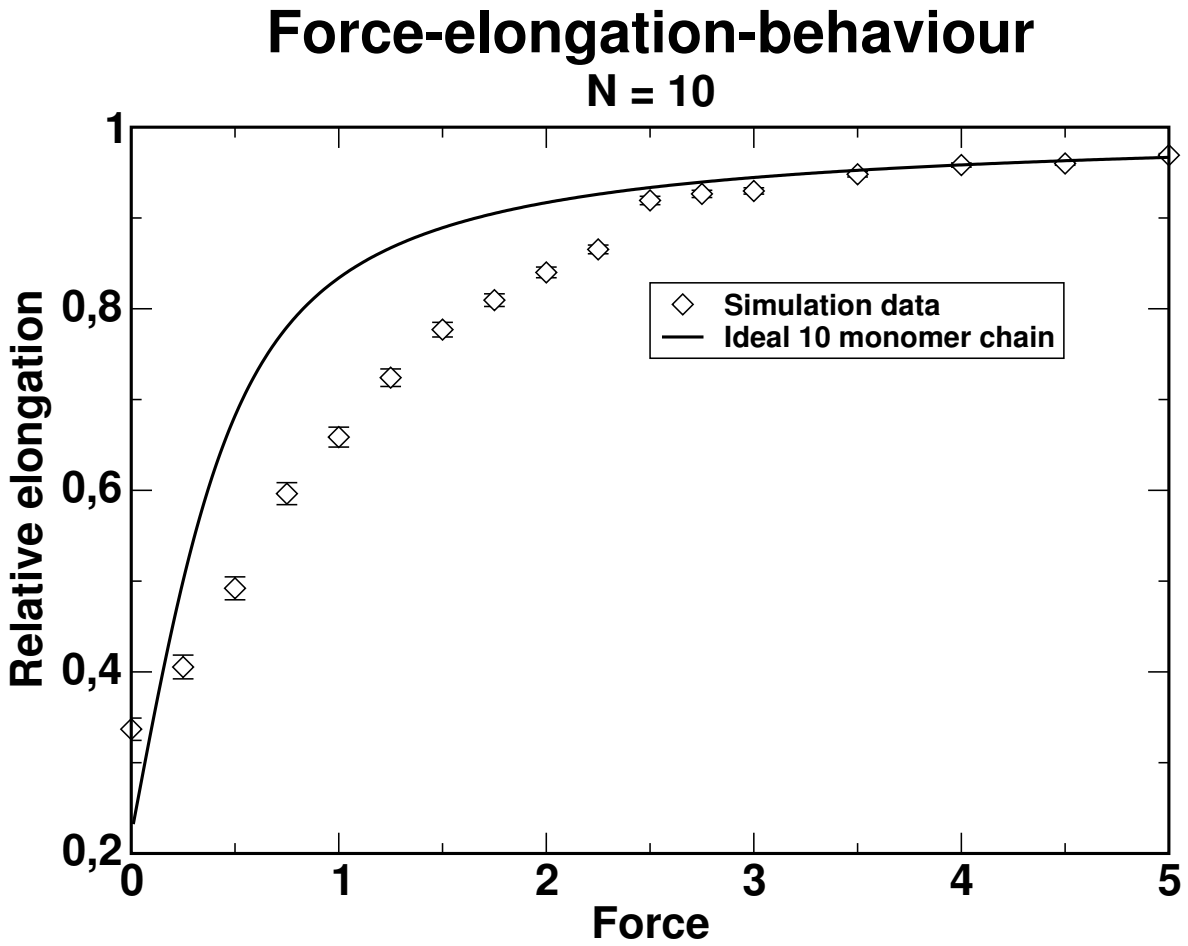

Abbildung 9: Force-elongation behavior for 10 monomer chains