Monte Carlo simulation of polymer systems with topological constraints
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Appendix A

Closed random walks

The purpose of this appendix is to calculate the radius of gyration of a closed random walk of \(N\) steps.

\[
R_g^2 = \frac{1}{N} \sum_{k=0}^{N-1} (\bar{r}_k - \bar{r}_{cm})^2 \quad (A.1)
\]

\[
\bar{r}_{cm} = \frac{1}{N} \sum_{k=0}^{N} \bar{r}_k \quad (A.2)
\]

**Lemma 1** *The expression for the radius of gyration can be rewritten as*

\[
R_g^2 = \frac{1}{2N^2} \sum_{k=0}^{N-1} \sum_{l=0}^{N-1} (\bar{r}_k - \bar{r}_l)^2 \quad (A.3)
\]

Proof: By expanding the square in (A.1) it is rather easy to show that

\[
R_g^2 = \frac{1}{N} \sum_{k=0}^{N-1} \bar{r}_k^2 - \left( \frac{1}{N} \sum_{k=0}^{N-1} \bar{r}_k \right)^2 \quad (A.4)
\]

In a similar way one can show that

\[
\sum_{k=0}^{N-1} \sum_{l=0}^{N-1} (\bar{r}_k - \bar{r}_l)^2 = 2N \sum_{k=0}^{N-1} \bar{r}_k^2 - 2 \left( \sum_{k=0}^{N-1} \bar{r}_k \right)^2 \quad (A.5)
\]

Combining equations (A.4) and (A.5) leads to (A.3).
Lemma 2  For an isotropically distributed set of points in d dimensions the following relation holds

\[ \langle e^{i\vec{q} \cdot (\vec{r}_k - \vec{r}_l)} \rangle = 1 - \frac{d}{2a^2} \langle (\vec{r}_k - \vec{r}_l)^2 \rangle + \cdots \]  \hspace{1cm} (A.6)

The right hand side should be read as a series expansion in \( \vec{q}^2 \).

Proof: Expanding the exponential function leads to

\[ e^{i\vec{q} \cdot (\vec{r}_k - \vec{r}_l)} = 1 + i\vec{q} \cdot (\vec{r}_k - \vec{r}_l) - \frac{1}{2} (\vec{q} \cdot (\vec{r}_k - \vec{r}_l))^2 + \cdots \]  \hspace{1cm} (A.7)

Now we use isotropy:

\[ \langle \vec{r}_k - \vec{r}_l \rangle = 0 \]  \hspace{1cm} (A.8)

\[ \langle (\vec{q} \cdot (\vec{r}_k - \vec{r}_l))^2 \rangle = \frac{d}{d} \langle (\vec{r}_k - \vec{r}_l)^2 \rangle \]  \hspace{1cm} (A.9)

Combining (A.7), (A.8) and (A.9) leads to (A.6).

Lemma 1 is true for any set of \( N \) points. Lemma 2 is true for any set of \( N \) points that is distributed isotropically. So these lemma’s have a general validity. The following lemma’s are specific for closed random walks.

Lemma 3  Consider a closed random walk of \( N \) steps. For the weight of a single step \( \vec{R} \) we take a Gaussian:

\[ \rho(\vec{R}) = \left( \frac{d}{2\pi a^2} \right)^d \exp \left( -\frac{d\vec{R}^2}{2a^2} \right) \]  \hspace{1cm} (A.10)

Then we have the following result:

\[ \langle e^{i\vec{q} \cdot (\vec{r}_k - \vec{r}_l)} \rangle = \exp \left( -\frac{|k - l|(N - |k - l|) a^2 \vec{q}^2}{N 2d} \right) \]  \hspace{1cm} (A.11)

Proof: We start with the following expression for \( \langle \exp(i\vec{q} \cdot (\vec{r}_k - \vec{r}_l)) \rangle \)

\[ \langle e^{i\vec{q} \cdot (\vec{r}_k - \vec{r}_l)} \rangle = \frac{\int d^d\vec{r}_0 \cdots d^d\vec{r}_N \delta^d(\vec{r}_N - \vec{r}_0) \rho(\vec{r}_0, \cdots, \vec{r}_N) e^{i\vec{q} \cdot (\vec{r}_k - \vec{r}_l)}}{\int d^d\vec{r}_0 \cdots d^d\vec{r}_N \delta^d(\vec{r}_N - \vec{r}_0) \rho(\vec{r}_0, \cdots, \vec{r}_N)} \]  \hspace{1cm} (A.12)
where \( \rho(\vec{r}_0, \cdots, \vec{r}_N) \) is the product of the weights of all the bonds:

\[
\rho(\vec{r}_0, \cdots, \vec{r}_N) = \left( \sqrt{\frac{d}{2\pi a^2}} \right)^{Nd} \exp \left( -\sum_{i=1}^{N} d(\vec{r}_i - \vec{r}_{i-1})^2 \right) \quad (A.13)
\]

We concentrate on the numerator of expression (A.12). The denominator follows automatically by putting \( k = l \). We perform a transformation of variables:

\[
\vec{R}_0 = \vec{r}_0 \\
\vec{R}_1 = \vec{r}_1 - \vec{r}_0 \\
\vdots \\
\vec{R}_i = \vec{r}_i - \vec{r}_{i-1} \\
\vdots \\
\vec{R}_N = \vec{r}_N - \vec{r}_{N-1}
\]

So \( \vec{R}_i \) is the bond vector from bead \( i-1 \) to bead \( i \). The Jacobian of the transformation is 1. Now we focus on the case \( l < k \):

\[
\vec{r}_k - \vec{r}_l = \vec{R}_{l+1} + \cdots + \vec{R}_k 
\]

So the numerator of (A.12) becomes:

\[
\int d^d \vec{R}_0 \cdots d^d \vec{R}_N \, \delta^d(\vec{R}_1 + \cdots + \vec{R}_N) \\
\times \left( \sqrt{\frac{d}{2\pi a^2}} \right)^{Nd} \exp \left( -\sum_{i=1}^{N} \frac{d(\vec{R}_i)^2}{2a^2} \right) e^{i\vec{q} \cdot (\vec{R}_{l+1} + \cdots + \vec{R}_k)} \quad (A.15)
\]

The integrand does not depend on \( \vec{R}_0 \) so the integration \( \int d^d \vec{R}_0 \) yields a factor \( V \) (the volume).

Now we use the Fourier representation of the delta function:

\[
\delta^d(\vec{r}) = \int \frac{d^d \vec{Q}}{(2\pi)^d} \exp(i\vec{Q} \cdot \vec{r}) \quad (A.16)
\]
Substituting this into (A.15) yields
\[
V \int \frac{d^d \vec{Q}}{(2\pi)^d} \int d^d \vec{R}_1 \cdots d^d \vec{R}_N \left( \sqrt{\frac{d}{2\pi a^2}} \right)^{Nd} \exp \left( -\sum_{i=1}^N \frac{d\vec{R}_i^2}{2a^2} \right) e^{i\vec{Q} \cdot (\vec{R}_1 + \cdots + \vec{R}_N)} e^{i\vec{q} \cdot (\vec{R}_{k+1} + \cdots + \vec{R}_N)}
\]
(A.17)

This can be factorized:
\[
V \int \frac{d^d \vec{Q}}{(2\pi)^d} \prod_{i=1}^l \int d^d \vec{R}_i \left( \sqrt{\frac{d}{2\pi a^2}} \right)^d \exp \left( -\frac{d\vec{R}_i^2}{2a^2} \right) \exp \left( i\vec{Q} \cdot \vec{R}_i \right)
\]
\[
\times \prod_{i=l+1}^k \int d^d \vec{R}_i \left( \sqrt{\frac{d}{2\pi a^2}} \right)^d \exp \left( -\frac{d\vec{R}_i^2}{2a^2} \right) \exp \left( i\vec{Q} + \vec{q} \cdot \vec{R}_i \right)
\]
\[
\times \prod_{i=k+1}^N \int d^d \vec{R}_i \left( \sqrt{\frac{d}{2\pi a^2}} \right)^d \exp \left( -\frac{d\vec{R}_i^2}{2a^2} \right) \exp \left( i\vec{Q} \cdot \vec{R}_i \right)
\]
(A.18)

Now we use the following result concerning the Fourier transform of the bond weight \(\rho(\vec{R})\)
\[
\hat{\rho}(\vec{q}) = \int d^d \vec{R} \rho(\vec{R}) \exp(i\vec{q} \cdot \vec{R}) = \exp \left( -\frac{a^2\vec{q}^2}{2d} \right)
\]
(A.19)

using this result (A.18) becomes
\[
V \int \frac{d^d \vec{Q}}{(2\pi)^d} \prod_{i=1}^l \exp \left( -\frac{a^2\vec{Q}^2}{2d} \right)
\]
\[
\times \prod_{i=l+1}^k \exp \left( -\frac{a^2(\vec{Q} + \vec{q})^2}{2d} \right) \prod_{i=k+1}^N \exp \left( -\frac{a^2\vec{Q}^2}{2d} \right)
\]
(A.20)

which equals
\[
V \int \frac{d^d \vec{Q}}{(2\pi)^d} \exp \left( -\frac{(N-k+l)a^2\vec{Q}^2}{2d} \right) \exp \left( -\frac{(k-l)a^2(\vec{Q} + \vec{q})^2}{2d} \right)
\]
(A.21)

The integral \(\int d^d \vec{Q}\) can be evaluated analytically. This leads to
\[
V \left( \sqrt{\frac{d}{2\pi Na^2}} \right)^d \exp \left( -\frac{(k-l)(N-k+l)a^2\vec{q}^2}{2d} \right)
\]
(A.22)
The denominator of (A.12) equals:

\[ V \left( \sqrt{\frac{d}{2\pi Na^2}} \right)^d \]  

(A.23)

So we have

\[ \langle e^{i\vec{q} \cdot (\vec{r}_k - \vec{r}_l)} \rangle = \exp \left( -\frac{(k-l)(N-k+l) a^2 \bar{q}^2}{2d} \right) \]  

(A.24)

This was derived under the assumption \( l < k \). In general we have

\[ \langle e^{i\vec{q} \cdot (\vec{r}_k - \vec{r}_l)} \rangle = \exp \left( -\frac{|k-l|(N-|k-l|) a^2 \bar{q}^2}{2d} \right) \]  

(A.25)

which completes the derivation of lemma 3.

**Lemma 4**  For a closed random walk (as specified in lemma 3) we have the following result:

\[ \langle (\vec{r}_k - \vec{r}_l)^2 \rangle = \frac{|k-l|(N-|k-l|)a^2}{N} \]  

(A.26)

Proof: Expand the right hand side of (A.11) in powers of \( \bar{q}^2 \). Compare the linear term in the expansion with the linear term in (A.6). Equating both terms leads to (A.26).

**Lemma 5**  For a closed random walk (as specified in lemma 3) the radius of gyration is given by

\[ \langle R_g^2 \rangle = \frac{(N-1)(N+1)a^2}{12N} \]  

(A.27)

Proof: Combining (A.3) and (A.26) leads to

\[ \langle R_g^2 \rangle = \frac{1}{2N^2} \sum_{k=0}^{N-1} \sum_{l=0}^{N-1} \frac{|k-l|(N-|k-l|)a^2}{N} \]

\[ = \frac{a^2}{N^2} \sum_{k=0}^{N-1} \sum_{l=0}^{k-1} (k-l)(N-k+l) \]  

(A.28)
The sum can be calculated analytically:

\[
\sum_{k=0}^{N-1} \sum_{l=0}^{k-1} (k - l)(N - k + l) = \frac{(N - 1)N^2(N + 1)}{12}
\] (A.29)

Combining (A.28) and (A.29) results in (A.27).

**Lemma 6** For a closed random walk (as specified in lemma 3) the root mean square bond length is given by:

\[
\langle (\vec{r}_i - \vec{r}_{i-1})^2 \rangle = \frac{(N - 1)a^2}{N}
\] (A.30)

Proof: Simply use (A.26) taking \( k = i \) and \( l = i - 1 \).

Combining (A.27) and (A.30) leads to the final result:

**Lemma 7** For a closed random walk of \( N \) steps the radius of gyration is related to the bond length in the following way:

\[
\langle R_g^2 \rangle = \frac{N + 1}{12} \langle (\vec{r}_i - \vec{r}_{i-1})^2 \rangle
\] (A.31)
Appendix B

Persistent ring polymers

In this appendix we consider the correlation between the tangential vectors $\vec{n}(0)$ and $\vec{n}(s)$ of a persistence ring polymer characterized by a persistence length $\lambda$. It is well known that for a linear persistence chain

$$\langle \vec{n}(0) \cdot \vec{n}(s) \rangle = \langle \cos \theta(s) \rangle = \exp(-s/\lambda)$$

(B.1)

where $\theta(s)$ is the angle between $\vec{n}(s = 0)$ and $\vec{n}(s)$. Generally, for a ring polymer the problem is very complicated. Therefore, we will restrict the analysis to the case where the persistence length $\lambda$ is much larger than the contour length $L_c$, $\lambda \gg L_c$. Obviously, the situation of minimal elastic free energy corresponds to a circular shape of the ring (we ignore complications due to twisting). We will consider the two-dimensional situation where the tangential vector $\vec{n}(s) = (\cos \theta(s), \sin \theta(s))$. The circular shape implies that in the 0th approximation $\theta_0(s) = 2\pi s/L_c$ and hence that for the ideal ring

$$\langle \cos \theta(s) \rangle = \cos \theta_0(s) = \cos \frac{2\pi s}{L_c}$$

(B.2)

In order to calculate corrections to Eq. (B.2), we have to take fluctuations into account based on the increase in elastic energy $U_{el}$ of the deformed circle,

$$U_{el} = k_BT \frac{\lambda^2}{4} \int_0^{L_c} \left( \frac{d\vec{n}(s)}{ds} \right)^2 ds$$

(B.3)

We will fix two angles $\theta(0) = 0$ and $\theta(s = s^*) = \theta^*$ and calculate the probability that the chain trajectory actually passes through these points. To this
end we will determine the chain trajectory passing through these points and having the minimal elastic energy. Hence, this elastic energy will be a function of $s^*$ and $\theta^*$, $U_{el} = U_{el}(s^*, \theta^*)$. In the zeroth approximation,

$$U_{el}^0 = k_BT \frac{\pi^2 \lambda}{L_c}$$

(B.4)

and the distribution function $p(s^*, \theta^*)$ of the deformed circle with fixed angle $\theta(s = 0) = 0$ and $\theta(s = s^*) = \theta^*$ can be written in the Boltzmann form,

$$p(s^*, \theta^*) = C \exp \left[ -\frac{(U_{el}(s^*, \theta^*) - U_{el}^0)}{k_BT} \right]$$

(B.5)

where $C$ is the normalization constant.

To find the trajectory with the minimal elastic energy passing through these points the following constraints have to be satisfied:

$$\theta(s = L_c) = 2\pi$$  

$$\int_0^{L_c} \sin \theta(s)ds = 0$$  

$$\int_0^{L_c} \cos \theta(s)ds = 0$$

(B.6)

Minimization of Eq. (B.3) under these constraints results in

$$\frac{\lambda}{2} \frac{d^2 \theta(s)}{ds^2} = \mu_2 \cos \theta(s) - \mu_1 \sin \theta(s)$$  

where $\lambda_1$ and $\lambda_2$ are Lagrange multipliers. To solve our problem Eq. (B.7) has to be considered for two different parts, $0 \leq s \leq s^*$ and $s^* \leq s \leq L_c$, which results in the following integral equations for $\theta = \theta(s)$:

$$\frac{2s}{\sqrt{\lambda}} = \int_0^\theta \frac{d\theta'}{\sqrt{C_1 + \mu_1 \cos \theta' + \mu_2 \sin \theta'}}; \quad 0 \leq s \leq s^*$$

(B.8)

$$\frac{2(s - s^*)}{\sqrt{\lambda}} = \int_{\theta^*}^\theta \frac{d\theta'}{\sqrt{C_2 + \mu_1 \cos \theta' + \mu_2 \sin \theta'}}; \quad s^* \leq s \leq L_c$$  

(B.9)

where the parameters $C_1$, $C_2$, $\mu_1$, $\mu_2$ can be found from Eq. (B.6) and the condition $\theta(s = s^*) = \theta^*$.

We will now use a perturbation scheme to calculate these parameters assuming that $|\theta_1' | = |\theta^* - 2\pi s^*/L_c | \ll 1$, i.e., $\theta^*$ is close to $2\pi s^*/L_c$ and the
fluctuations are small. The zeroth approximation implies that \( C_1 = C_2 = C_0 = \pi^2 \lambda / L_c \) and \( \mu_1 = \mu_2 = 0 \). Assuming therefore that \( C_1 = C_0 + C_1', \quad |C_1'| \ll 1; \quad C_2 = C_0 + C_2', \quad |C_2'| \ll 1, \) and \( |\mu_1| \ll 1, \ |\mu_2| \ll 1, \) we can find the chain trajectory as well as the elastic energy using a simple perturbation scheme. Without presenting the details, this leads to an elastic energy given by

\[
U_{el}(s^*, \theta^*) = U_{el}^0 + \frac{\lambda}{4 s^*(L_c - s^*)} \frac{\theta^2}{1 - \frac{2L_c^2 \sin^2(s^*/L_c)}{\pi^2 s^*(L_c - s^*)}} \tag{B.10}
\]

After substitution of this energy in Eq. (B.5) for the distribution function we obtain a Gaussian function for which the average \( \langle \cos \theta(s^*) \rangle = \langle \cos \theta^* \rangle \) can be easily calculated,

\[
\langle \cos \theta(s^*) \rangle = \cos \left[ \frac{2\pi s^*}{L_c} \left[ 1 - \frac{L_c}{\lambda} \left\{ \frac{s^*(L_c - s^*)}{L_c^2} - \frac{2}{\pi^2} \sin \left( \frac{\pi s^*}{L_c} \right) \right\} \right] \right] \tag{B.11}
\]

which is the functional form used in the test to compare with the numerical results.
Appendix B. Persistent ring polymers
Appendix C

Wall theorem

In this appendix we give a derivation of the wall theorem. Consider a system of $N$ particles. The energy of the system is denoted by $U$. If we are dealing with a polymer system $U$ also contains bond potentials to enforce the connectivity. Now consider a box of size $L_x \times L_y \times L_z$. The $x$-coordinate runs from $x = 0$ to $x = L_x$ and so on for $y$ and $z$. We will show that

$$\frac{p}{kT} = \rho(L_x)$$  \hspace{1cm} (C.1)

where $\rho(L_x)$ is the average density at the wall:

$$\rho(L_x) = \lim_{\epsilon \to 0} \frac{1}{L_y L_z} \int_0^{L_y} dy \int_0^{L_z} dz \rho(L_x - \epsilon, y, z)$$  \hspace{1cm} (C.2)

and because of symmetry we have $\rho(L_x) = \rho(0)$. The thermodynamic definition of the pressure is

$$p = -\frac{\partial F}{\partial V}$$  \hspace{1cm} (C.3)

where $F$ is the free energy defined in (1.5):

$$F = -kT \log Q$$  \hspace{1cm} (C.4)

where $Q$ is the partition function. Combining these definitions we get

$$\frac{p}{kT} = \frac{1}{Q} \frac{\partial Q}{\partial V}$$  \hspace{1cm} (C.5)
Appendix C. Wall theorem

Now consider a change in volume which consists of varying $L_x$:

$$\frac{p}{kT} = \frac{1}{L_y L_z Q} \frac{\partial Q}{\partial L_x}$$ \hspace{1cm} (C.6)

The partition function $Q$ can be represented in the following way

$$Q = \int \left[ \prod_{i=1}^{N} dx_i dy_i dz_i \right] \left[ \prod_{i=1}^{N} \theta(x_i) \theta(y_i) \theta(z_i) \theta(L_x - x_i) \theta(L_y - y_i) \theta(L_z - z_i) \right] \exp(-\beta U)$$ \hspace{1cm} (C.7)

where the boundary conditions (i.e. hard walls) are represented by Heaviside step functions $\theta(x)$.

We will prove (C.1) by showing that the left-hand-side and the right-hand-side reduce to the same expression. We start with the left-hand-side:

$$\frac{p}{kT} = \frac{1}{L_y L_z Q} \frac{\partial Q}{\partial L_x}$$

$$= \frac{1}{L_y L_z Q} \int \left[ \prod_{i=1}^{N} dx_i dy_i dz_i \ \theta(x_i) \theta(y_i) \theta(z_i) \right] \exp(-\beta U)$$

$$\times \left[ \prod_{i=1}^{N} \theta(L_y - y_i) \theta(L_z - z_i) \right]$$

$$\times \frac{\partial}{\partial L_x} \left[ \prod_{i=1}^{N} \theta(L_x - x_i) \right]$$ \hspace{1cm} (C.8)

The last factor can be evaluated using the product rule for differentiation:

$$\frac{\partial}{\partial L_x} \left[ \prod_{i=1}^{N} \theta(L_x - x_i) \right] = \sum_{k=1}^{N} \left[ \prod_{i \neq k} \theta(L_x - x_i) \right] \delta(L_x - x_k)$$ \hspace{1cm} (C.9)
So we arrive at:

\[
\frac{P}{kT} = \frac{1}{L_y L_z Q} \int \left[ \prod_{i=1}^{N} dx_i dy_i dz_i \theta(x_i)\theta(y_i)\theta(z_i) \right] \exp(-\beta U) \\
\times \left[ \prod_{i=1}^{N} \theta(L_y - y_i)\theta(L_z - z_i) \right] \\
\times \sum_{k=1}^{N} \left[ \prod_{i \neq k} \theta(L_x - x_i) \right] \delta(L_x - x_k)
\]

(C.10)

Now we turn to the right-hand-side of (C.1). The particle density \(\rho(x, y, z)\) is defined as:

\[
\rho(x, y, z) = \frac{1}{Q} \int \left[ \prod_{i=1}^{N} dx_i dy_i dz_i \right] \exp(-\beta U) \\
\times \left[ \prod_{i=1}^{N} \theta(x_i)\theta(y_i)\theta(z_i)\theta(L_x - x_i)\theta(L_y - y_i)\theta(L_z - z_i) \right] \\
\times \sum_{k=1}^{N} \delta(x_k - x)\delta(y_k - y)\delta(z_k - z)
\]

(C.11)

So

\[
\rho(L_x - \epsilon) = \frac{1}{L_y L_z} \int_{0}^{L_y} dy \int_{0}^{L_z} dz \rho(L_x - \epsilon, y, z) \\
= \frac{1}{L_y L_z Q} \int_{0}^{L_y} dy \int_{0}^{L_z} dz \left[ \prod_{i=1}^{N} dx_i dy_i dz_i \right] \exp(-\beta U) \\
\times \left[ \prod_{i=1}^{N} \theta(x_i)\theta(y_i)\theta(z_i)\theta(L_x - x_i)\theta(L_y - y_i)\theta(L_z - z_i) \right] \\
\times \sum_{k=1}^{N} \delta(x_k - L_x + \epsilon)\delta(y_k - y)\delta(z_k - z)
\]

(C.12)

The integrations over \(y\) and \(z\) and the delta functions \(\delta(y_k - y), \delta(z_k - z)\)
cancel, so we have

\[ \rho(L_x - \epsilon) = \frac{1}{L_y L_z Q} \int \left[ \prod_{i=1}^{N} dx_idy_idz_i \right] \exp(-\beta U) \]
\[ \times \left[ \prod_{i=1}^{N} \theta(x_i) \theta(y_i) \theta(z_i) \theta(L_x - x_i) \theta(L_y - y_i) \theta(L_z - z_i) \right] \]
\[ \times \sum_{k=1}^{N} \delta(x_k - L_x + \epsilon) \]

(C.13)

The factor \( \theta(L_x - x_k) \) in the product can be ignored since it is 1 anyway. (This is because of the delta function \( \delta(x_k - L_x + \epsilon) \), where \( \epsilon > 0 \).) So we arrive at

\[ \rho(L_x - \epsilon) = \frac{1}{L_y L_z Q} \int \left[ \prod_{i=1}^{N} dx_idy_idz_i \theta(x_i) \theta(y_i) \theta(z_i) \right] \exp(-\beta U) \]
\[ \times \left[ \prod_{i=1}^{N} \theta(L_y - y_i) \theta(L_z - z_i) \right] \]
\[ \times \sum_{k=1}^{N} \left[ \prod_{i \neq k} \theta(L_x - x_i) \right] \delta(x_k - L_x + \epsilon) \]

(C.14)

So after taking the limit \( \epsilon \downarrow 0 \) (C.14) reduces to (C.10) and this proves the wall-theorem.