

Gaussian Chain Polymer in an External Field

Lutz Klaczynski

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Abstract

The continuous Gaussian chain model for a linear homopolymer is derived and extended to the case of a diblock copolymer. First, a Gaussian random walk whose paths represents the random monomer arrangement in space is introduced. Then, the continuum limit for infinitely small steps, known as *Brownian Motion*, is taken in the case of an external field that acts on the monomers. Finally, by calculating the path propagator functions and proving that they satisfy a diffusion equation, an expression for the monomer density field is derived for both the linear homopolymer and the copolymer.

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1 The Gaussian Chain

Polymers are long-stretched chain molecules whose subunits, named *monomers*, are themselves molecules. These long molecules can have various architectures, a simple example is a linear alkane shown in Figure 1. 'Linear' refers to the fact that the molecule has no branches but instead is solely made up of one single chain. These chemical species can for instance be found in crude oil. The monomers in this case are comprised of a carbon 'C' and two hydrogen atoms, denoted as 'H'. Polymers like this one consisting of only one type of monomer are called *homopolymers*, if they have more than one type incorporated into the chain, one speaks of *copolymers*.

A *linear homopolymer* can be described as a path of a *random walk*. We consider the following rather special but very important *Gaussian random walk*: let $\mathbf{b}_1, \dots, \mathbf{b}_N$ be a collection of N random vectors taking values in 3-dimensional space \mathbb{R}^3 , all independent and identically distributed according to a Gaussian distribution characterized by mean 0 and variance $a^2/3$, that is

$$p(\mathbf{b}) = \left(\frac{3}{2\pi a^2}\right)^{3/2} \exp\left(-\frac{3\mathbf{b}^2}{2a^2}\right) \quad (1)$$

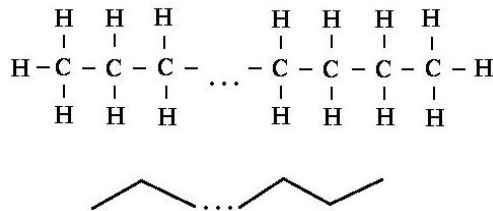


Figure 1: The chemical structure of a linear alkane (the lower picture is a simpler notation).

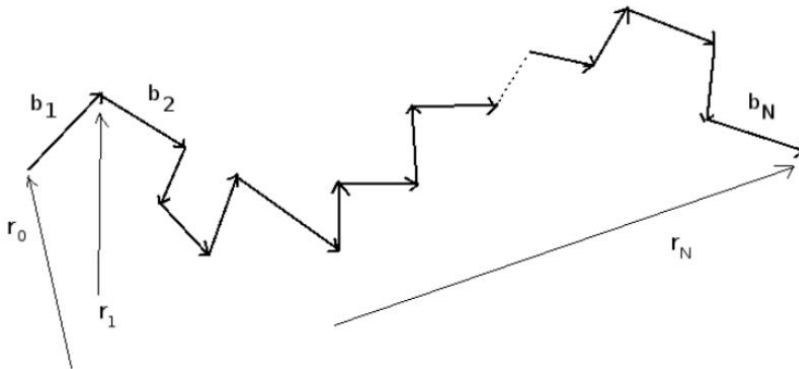


Figure 2: Step and position vectors for the construction of the random walk. Note that in this model the step length is Gaussian distributed.

is the probability density of one of the vectors. By means of these random vectors we define

$$\mathbf{r}_l := \mathbf{r}_0 + \sum_{i=1}^l \mathbf{b}_i \quad l = 0, 1, \dots, N$$

where \mathbf{r}_0 is a random or non-random starting 3-vector, pointing to where the walk starts (see Figure 2). The vectors $\mathbf{r}_0, \dots, \mathbf{r}_N$ represent the random walk, one particular realization $\{\mathbf{r}_j\} = \{\mathbf{r}_0, \dots, \mathbf{r}_N\}$ of which is called discrete *path* of the walk. 'Discrete' refers to the discreteness of the steps. We assign to it a probability density which is given by

$$P(\{\mathbf{r}_j\}) = \frac{1}{Z_N} \prod_{j=1}^N e^{-\frac{3}{2a^2}(\mathbf{r}_j - \mathbf{r}_{j-1})^2} = \frac{1}{Z_N} e^{-\frac{3}{2a^2} \sum_{j=1}^N (\mathbf{r}_j - \mathbf{r}_{j-1})^2}, \quad (2)$$

where the normalization factor

$$Z_N = \int d\mathbf{r}_0 \dots \int d\mathbf{r}_N e^{-\frac{3}{2a^2} \sum_{j=1}^N (\mathbf{r}_j - \mathbf{r}_{j-1})^2}$$

is an integral over all possible discrete paths. The integration is throughout this paper if not otherwise stated to be understood over some (large) box of size $V \subset \mathbb{R}^3$, outside of which the path density in (2) is supposed to vanish.

A path $\{\mathbf{r}_j\}$ of the random walk can be interpreted as the random arrangement of the monomers of a polymer, i.e. the different ways the polymer can be situated in space, its various *conformations*. The connecting step vectors $\{\mathbf{b}_j\}$ correspond to the bonds between the monomers. To see how their Gaussian distribution in (1) is motivated, the interested reader is referred to the standard polymer physics literature[3]. A polymer whose behaviour can be characterized by this model is called *Gaussian chain polymer*. Whether or not a polymer can be seen as a Gaussian chain depends on how *flexible* it is: unlike a Gaussian chain all polymers rupture when they are sufficiently overstretched. Therefore it is the imposed force regime that the validity of this simplification depends on.

A possible drawback of this model must be considered: the walk can go back to where it has been before. For the polymer this corresponds to an overlapping of monomers. Moreover, the most extreme case in which all monomers are merged into one point has the highest probability density. However, these configurations occupy a negligible part of the whole configuration space V^{N+1} , which is $(N + 1)$ -dimensional. As regards the other extreme case, one finds: though the majority of accessible states in V^{N+1} is occupied by extremely overstretched configurations they have vanishing probability weight. Consequently, this theory is not too bad an approximation as it may seem at first glance. Here, the considered Gaussian chain has $N + 1$ monomers. However, the polymer in question might have, chemically speaking, a number of real monomers that differs from this. The reason is that the bonds between the real monomers cannot move independently, especially the neighbouring ones correlate strongly. However, from a certain distance onwards that the real monomers are apart from each other, the correlations die out. This distance is generally in the polymer physics literature referred to as *Kuhn length* or *statistical segment length*. Here, this length scale enters the theory as the parameter $a > 0$ in the distribution (1)[5]. From experimental studies [2] it is known that the number of real monomers encompassed by the Kuhn length for carbon chains should for example be chosen as 4. Since the C-C bond length is in the range 0.13 ... 0.3 nm, the segment length is of order $a \sim 1\text{nm}$ [10]. Say the length of the polymer is L , then the number of (theoretical) monomers $N + 1$ is chosen such that $L = aN$.

Ignoring the finiteness of our volume V , we infer from (2) a *translational symmetry* for the polymer's position in space: the configurations of the polymer, i.e. the paths of the random walk, do not depend on where the polymer is but only on *how the monomers are arranged with respect to one another*. Note that due to this translational invariance of the density in (2) the starting vector \mathbf{r}_0 can be taken as a uniformly distributed random vector. The translational symmetry is broken if we introduce a non-constant external field $w(\mathbf{x})$ which acts on a monomer at position \mathbf{x} in the box: the probability density now reads

$$P(\{\mathbf{r}_j\}) = \frac{1}{Z_N[w]} e^{-\frac{3}{2a^2} \sum_{j=1}^N (\mathbf{r}_j - \mathbf{r}_{j-1})^2 - \sum_{i=0}^N w(\mathbf{r}_i)}. \quad (3)$$

The normalization factor

$$Z_N[w] = \int d\mathbf{r}_0 \dots \int d\mathbf{r}_N e^{-\frac{3}{2a^2} \sum_{j=1}^N (\mathbf{r}_j - \mathbf{r}_{j-1})^2 - \sum_{i=0}^N w(\mathbf{r}_i)} \quad (4)$$

turns out to be a functional of the field w . At positions where the values of w are large, the polymer is unlikely to have its monomers and the starting vector \mathbf{r}_0 clearly is no longer uniformly distributed but rather most likely to land where w has its minimum.

We introduce the microscopic monomer density $\hat{\rho}(\mathbf{x}; \{\mathbf{r}_j\}) := \sum_{j=0}^N \delta(\mathbf{x} - \mathbf{r}_j)$. We will henceforth suppress its path dependence in the notation and just write $\hat{\rho}(\mathbf{x})$. 'Microscopic' refers to the Dirac delta peaks that describe microscopic detail in the classical, that is, non-quantum mechanical sense. The normalization is

$$\int d\mathbf{x} \hat{\rho}(\mathbf{x}) = \sum_{j=0}^N \int d\mathbf{x} \delta(\mathbf{x} - \mathbf{r}_j) = \sum_{j=0}^N 1 = N + 1, \quad (5)$$

i.e. the number of monomers. Next, we abbreviate

$$\beta H_0(\{\mathbf{r}_j\}) := \frac{3}{2a^2} \sum_{j=1}^N (\mathbf{r}_j - \mathbf{r}_{j-1})^2 \quad (w, \hat{\rho}) := \int d\mathbf{x} w(\mathbf{x}) \hat{\rho}(\mathbf{x}), \quad (6)$$

where $\beta = 1/k_B T$ is the usual inverse temperature. The bracket notation for the second term is chosen to suggest what it is: an integral scalar product. So far without justification we name H_0 *Hamiltonian* of the free Gaussian chain. One can now write the functional $Z_N[w]$ in the form

$$Z_N[w] = \int d\mathbf{r}_0 \dots \int d\mathbf{r}_N e^{-\beta H_0(\{\mathbf{r}_j\}) - (w, \hat{\rho})}.$$

Suppose we want to consider a quantity $F(\{\mathbf{r}_j\})$ that depends on the path $\{\mathbf{r}_j\}$. We find its the average $\langle F \rangle$ with respect to all possible paths as the $P(\cdot)$ - weighted integral

$$\langle F \rangle := \int d\mathbf{r}_0 \dots \int d\mathbf{r}_N P(\{\mathbf{r}_j\}) F(\{\mathbf{r}_j\}) = \frac{1}{Z_N[w]} \int d\mathbf{r}_0 \dots \int d\mathbf{r}_N e^{-\beta H_0(\{\mathbf{r}_j\}) - (w, \hat{\rho})} F(\{\mathbf{r}_j\}). \quad (7)$$

An example that we will often be concerned with is the *local average monomer density* $\rho(\mathbf{x}) := \langle \hat{\rho}(\mathbf{x}) \rangle$. As we will show now, it can be calculated as the functional derivative of the logarithm of $Z_N[w]$ with respect to w .

Claim 1: The local average monomer density ρ is given by $\rho(\mathbf{x}) = -\frac{\delta \ln Z_N[w]}{\delta w(\mathbf{x})}$.

Proof. First note that formally we have

$$\begin{aligned} -\frac{\delta}{\delta w(\mathbf{x})} e^{-(w, \hat{\rho})} &= e^{-(w, \hat{\rho})} \frac{\delta(w, \hat{\rho})}{\delta w(\mathbf{x})} = e^{-(w, \hat{\rho})} \frac{\delta}{\delta w(\mathbf{x})} \int d\mathbf{x}' w(\mathbf{x}') \hat{\rho}(\mathbf{x}') \\ &= \int d\mathbf{x}' \hat{\rho}(\mathbf{x}') \frac{\delta w(\mathbf{x}')}{\delta w(\mathbf{x})} = \int d\mathbf{x}' \hat{\rho}(\mathbf{x}') \delta(\mathbf{x}' - \mathbf{x}) = \hat{\rho}(\mathbf{x}). \end{aligned}$$

A definition of the functional derivative $\delta/\delta(\mathbf{x})$ can be found in the Appendix A.1, equation (33). The claim follows from

$$\begin{aligned} \langle \hat{\rho}(\mathbf{x}) \rangle &= \frac{1}{Z_N[w]} \int d\mathbf{r}_0 \dots \int d\mathbf{r}_N e^{-\beta H_0(\{\mathbf{r}_j\}) - (w, \hat{\rho})} \hat{\rho}(\mathbf{x}) \\ &= -\frac{1}{Z_N[w]} \int d\mathbf{r}_0 \dots \int d\mathbf{r}_N \frac{\delta}{\delta w(\mathbf{x})} e^{-\beta H_0(\{\mathbf{r}_j\}) - (w, \hat{\rho})} \\ &= -\frac{1}{Z_N[w]} \frac{\delta}{\delta w(\mathbf{x})} \int d\mathbf{r}_0 \dots \int d\mathbf{r}_N e^{-\beta H_0(\{\mathbf{r}_j\}) - (w, \hat{\rho})} = -\frac{\delta}{\delta w(\mathbf{x})} \ln Z_N[w]. \quad \square \end{aligned}$$

For this reason one usually calls $Z_N[w]$ the *canonical partition function* and $H_0 + k_B T(w, \hat{\rho})$ or $\beta H_0 + (w, \hat{\rho})$ *Hamiltonian* of the Gaussian chain polymer[5]. The field w is seen as a 'thermodynamically conjugate' variable to the microscopic monomer density $\hat{\rho}$.

How can the Hamiltonian H_0 and scalar product $(w, \hat{\rho})$ be interpreted? The randomness of the polymer's monomer configuration as expressed by H_0 can be seen as caused by the incessant bombardment of the surrounding solvent molecules. In the framework of statistical mechanics, the Hamiltonian H_0 is therefore viewed as a *purely entropic* part of the energy that the polymer carries and βH_0 is in dimensionless units of the thermal energy $k_B T$.

The theory is considerably changed if one replaces βH_0 by H_0 in the definition (6) and still sets $\exp(-\beta H_0)$ for the Boltzmann weight: the distribution $P(\cdot)$ is in this case *temperature-dependent*. The chain is then more likely to be stretched at higher temperatures and thus more flexible. This is especially relevant if the polymer of interest is in some sense stiff and becomes more flexible as the temperature is raised: an established example is the semi-flexible harmonic chain(SHC) model which is applied to molecules such as DNA [8]. In this theory, the Gaussian chain is considered as a collection of particles that are connected by a 'harmonic' potential $u(x) = 3x^2/2a^2$ with spring constant $k = 3/a^2$. This can also be said about our Gaussian chain, except that the spring constant is $3k_B T/a^2$. It implies that for increasing temperature T the chain gets stiffer in such a way that the bond length's Boltzmann distribution is not temperature-dependent. Sometimes the monomer particles are seen as 'beads' and the bonds as 'springs' which is why some authors speak of the *bead-spring model* (Figure 3).

For the external field w different ways of integrating it into the theory are possible as well. If one wants temperature to play a role, one can replace w by βw so that for increasing temperature, i.e. decreasing β , the field w (which then is energy-valued) has less influence on the polymer's configuration.

2 Continuous Gaussian Chain Polymer

2.1 Edwards Hamiltonian

We now take a different, coarse-grained and hence more mesoscopic view on the polymer: we assume it to resemble a curve-like object that can be described as a random curve $\mathbf{r}(s)$ with

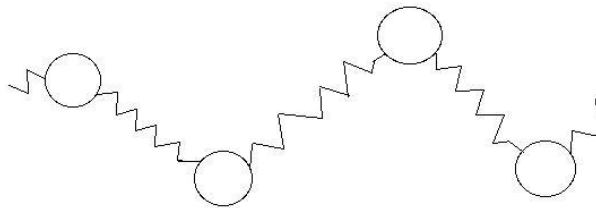


Figure 3: Monomers and bonds in the bead-spring view.

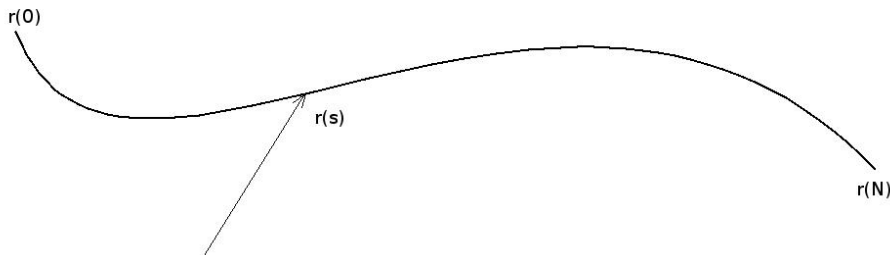


Figure 4: A homopolymer as a continuous Gaussian chain. The individual monomers are not depicted.

contour parameter $s \in [0, N]$. N is the number of monomers that the appropriately scaled curve $\mathbf{r}(s)$ runs through (see Figure 4). This model is generally known as *Gaussian thread* or *continuous Gaussian chain* model. The *microscopic monomer density* $\hat{\varrho}$ is defined as

$$\hat{\varrho}(\mathbf{x}) := \int_0^N ds \delta(\mathbf{x} - \mathbf{r}(s)). \quad (8)$$

In the polymer literature one very often finds that $\hat{\varrho}$ is called *microscopic segment density*. 'Segments' of the polymer are in the discrete theory of section 1 strictly speaking the links connecting the monomers. Nevertheless, in the continuous theory, the distinction is generally not made due to the somewhat model-dependent choice of the number of monomers. We will now justify that $\hat{\varrho}$ is indeed a good definition of a monomer density. First note that since $\mathbf{r}(s)$ is a random object, so is the density field $\hat{\varrho}$. Integrating over the whole box yields

$$\int d\mathbf{x} \hat{\varrho}(\mathbf{x}) = \int d\mathbf{x} \int_0^N ds \delta(\mathbf{x} - \mathbf{r}(s)) = \int_0^N ds \int d\mathbf{x} \delta(\mathbf{x} - \mathbf{r}(s)) = \int_0^N ds = N,$$

since for every single contour parameter $s \in [0, N]$ the point $\mathbf{r}(s)$ must be somewhere in the considered box. Assume now that one part of the polymer lies outside an integration area $X \subset V$, say a fraction $z \in (0, 1)$ of zN monomers are in $X \subset V$ and the rest not¹, i.e. for all $s \in [zN, N]$ we have $\mathbf{r}(s) \notin X$. We find

$$\begin{aligned} \int_X d\mathbf{x} \hat{\varrho}(\mathbf{x}) &= \int_X d\mathbf{x} \int_0^N ds \delta(\mathbf{x} - \mathbf{r}(s)) = \int_0^{zN} ds \int_X d\mathbf{x} \delta(\mathbf{x} - \mathbf{r}(s)) + \int_{zN}^N ds \underbrace{\int_X d\mathbf{x} \delta(\mathbf{x} - \mathbf{r}(s))}_{=0, \mathbf{r}(s) \notin X} \\ &= \int_0^{zN} ds \int_X d\mathbf{x} \delta(\mathbf{x} - \mathbf{r}(s)) = \int_0^{zN} ds = zN. \end{aligned}$$

Thus $\hat{\varrho}$ in (8) turns out to be a good choice for the monomer density. The energy contribution resulting from the external field is again the scalar product $(w, \hat{\rho}) = \int d\mathbf{x} w(\mathbf{x}) \hat{\rho}(\mathbf{x}) =$

¹Since the real number of monomers often differs from the number in the model and real monomers are spatially extended objects, we allow the fraction z to be any number between 0 and 1.

$\int d\mathbf{x} \int_0^N ds w(\mathbf{x})\delta(\mathbf{x} - \mathbf{r}(s)) = \int_0^N ds \int d\mathbf{x} w(\mathbf{x})\delta(\mathbf{x} - \mathbf{r}(s)) = \int_0^N ds w(\mathbf{r}(s))$. To find the entropic part of the Hamiltonian, we recall the Hamiltonian of the free Gaussian chain $\beta H_0(\{\mathbf{r}_j\})$ in (6) and translate the discrete into the continuous language by the following 'dictionary'

$$j \longleftrightarrow s \quad \sum_{j=0}^N \longleftrightarrow \int_0^N ds \quad \mathbf{r}_j \longleftrightarrow \mathbf{r}(s) \quad \frac{\mathbf{r}_j - \mathbf{r}_{j-1}}{1} \longleftrightarrow \mathbf{r}'(s). \quad (9)$$

The continuous version of the Hamiltonian H_0 is the so-called *Edwards Hamiltonian* or *Edwards-Helfand Hamiltonian* $\mathcal{H}_0[\mathbf{r}]$; using our dictionary we understand

$$\beta H_0\{\mathbf{r}_j\} = \frac{3}{2a^2} \sum_{j=1}^N (\mathbf{r}_j - \mathbf{r}_{j-1})^2 \quad \longleftrightarrow \quad \beta \mathcal{H}_0[\mathbf{r}] = \frac{3}{2a^2} \int_0^N ds |\mathbf{r}'(s)|^2, \quad (10)$$

and see that it is a functional of the curve. It is interpreted as *entropic stretching energy* in dimensionless units of the thermal energy $k_B T$. This can also be said about the discrete version: a situation in which the step vectors \mathbf{r}_j are further apart from one another corresponds to a more strongly stretched polymeric molecule. For the curve this is no different. The larger the values of the tangent vector $|\mathbf{r}'(s)|$, the longer the curve gets: as is known from elementary differential geometry the integral $\int_0^N ds |\mathbf{r}'(s)| ds$ represents its length [6].

The total Hamiltonian \mathcal{H} of the continuous Gaussian chain is finally given by

$$\beta \mathcal{H}[\mathbf{r}] = \frac{3}{2a^2} \int_0^N ds |\mathbf{r}'(s)|^2 - \int_0^N ds w(\mathbf{r}(s)). \quad (11)$$

2.2 Polymer Path Integral

We aim at finding a continuous version of the canonical partition function in (4) for the continuous Gaussian chain. We will denote it by $Q[w]$. In mathematically sloppy terms it should be of the form

$$Q[w] = \sum_{\mathbf{r}(s) \in \text{all paths}} e^{-\frac{3}{2a^2} \int_0^N ds |\mathbf{r}'(s)|^2 - \int_0^N ds w(\mathbf{r}(s))}. \quad (12)$$

As a definition, however, this is of no use. Since the space of paths cannot be a countable set, the sum must be some kind of integral.

We will now define the 'path integral' rigorously. To this end, we must *discretize* the continuous theory, a procedure that will be presented next. Note that what we are discussing here is the Gaussian thread model which must be clearly distinguished from the discrete Gaussian chain model as introduced in section 1. There is no way to avoid the dictionary in (9). We cannot just let the number of position vectors in the distribution of the discrete Gaussian chain $P \propto \exp(-\sum \dots)$ in (2) go to infinity without scaling the summands in the sums. We will come back to this point when we encounter the appropriate scaling factor.

To get an idea of where a path of a curve $\mathbf{r}(s)$ is situated in space, one can for an approximative description evaluate the curve at a finite set of parameter points $0 = s_0 < s_1 < \dots < s_n = N$ to construct a collection of positions $\mathbf{r}_k := \mathbf{r}(s_k)$, $k = 0, 1, \dots, n$ along the contour line.

Functionals of the curve $\mathbf{r}(s)$ like the Edwards-Hamiltonian $\mathcal{H}_0[\mathbf{r}]$ are mostly encountered in the form of integrals. These integrals can then be approximated by Riemann sums as follows: in technical terms, the integration line $[0, N]$ is partitioned into a uniform grid $G_n := \{s_k = k\varepsilon_n : k = 0, \dots, n\}$ with mesh size $\varepsilon_n := N/n$, see Figure 5.

For a fine enough grid G_n , i.e. large enough $n \gg N$, we have

$$\begin{aligned} \beta \mathcal{H}_0[\mathbf{r}] &= \frac{3}{2a^2} \int_0^N ds |\mathbf{r}'(s)|^2 \approx \frac{3}{2a^2} \sum_{k=1}^n \left(\frac{\mathbf{r}(k\varepsilon_n) - \mathbf{r}((k-1)\varepsilon_n)}{\varepsilon_n} \right)^2 \varepsilon_n \\ &= \frac{3}{2a^2} \sum_{k=1}^n \left(\frac{\mathbf{r}_k - \mathbf{r}_{k-1}}{\varepsilon_n} \right)^2 \varepsilon_n = \frac{3}{2a^2 \varepsilon_n} \sum_{k=1}^n (\mathbf{r}_k - \mathbf{r}_{k-1})^2. \end{aligned}$$

For the external field contribution this procedure leads to the approximation

$$\int_0^N ds w(\mathbf{r}(s)) \approx \sum_{k=0}^n w(\mathbf{r}_k) \varepsilon_n.$$

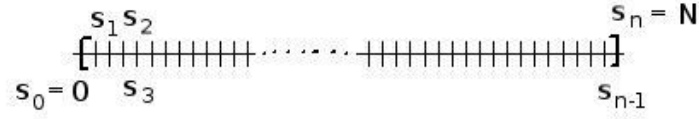


Figure 5: The parameter interval $[0, N]$ is partitioned into a grid G_n with $n + 1$ gridpoints.

The afore-mentioned scaling factor is ε_n and it is crucial. Without it, the sums would in the limit $n \rightarrow \infty$ have little sense.

For a finer grid G_n one can expect the path of the curve $\mathbf{r}(s)$ to be better approximated by the position vectors $\{\mathbf{r}_k\}$. Taken to the limit $n \rightarrow \infty$, the path should be sufficiently determined². With this in mind, we define the canonical partition function $Q[w]$ as

$$Q[w] = \int \mathcal{D}\mathbf{r} e^{-\frac{3}{2a^2} \int_0^N ds |\mathbf{r}'(s)|^2 - \int_0^N ds w(\mathbf{r}(s))} \quad (13)$$

$$:= \lim_{n \rightarrow \infty} \frac{1}{V} \int d\mathbf{r}_0 \dots \int d\mathbf{r}_n \left(\frac{3}{2\pi a^2 \varepsilon_n} \right)^{3n/2} e^{-\frac{3}{2a^2 \varepsilon_n} \sum_{k=1}^n (\mathbf{r}_k - \mathbf{r}_{k-1})^2 - \sum_{k=0}^n w(\mathbf{r}_k) \varepsilon_n}. \quad (14)$$

We refer to it as *polymer path integral* as to distinguish it from *Feynman's path integral* whose paths are those that a quantum particle can take through space[4]. It is the limit of a sequence of usual integrals over $V^{n+1} \subset \mathbb{R}^{3n+3}$ with Gaussian normalization factors that guarantee convergence. The factor $1/V$ is somewhat arbitrary but conventionally used to normalize the path integral for a zero field $w = 0$ to $Q[0] = 1$. The integral measure in (13), that we write formally as $\mathcal{D}\mathbf{r} e^{-\beta \mathcal{H}_0[\mathbf{r}]}$ is in probability theory called *Wiener measure* which measures volume elements in the space of continuous curves $\mathcal{C}([0, N], V)$. It is named after Austrian mathematician *Norbert Wiener* (1894-1964), who first derived it.

2.3 Chain Propagators

There is a more convenient representation of the canonical partition function in (13) that makes use of so-called *propagators*. To get there, we need some preparation. First, we consider the n -th approximation of the path integral

$$Q_n[w] := \frac{1}{V} \int d\mathbf{r}_0 \dots \int d\mathbf{r}_n \left(\frac{3}{2\pi a^2 \varepsilon_n} \right)^{3n/2} e^{-\frac{3}{2a^2 \varepsilon_n} \sum_{k=1}^n (\mathbf{r}_k - \mathbf{r}_{k-1})^2 - \sum_{k=0}^n w(\mathbf{r}_k) \varepsilon_n}.$$

Next, we define the normalized Gaussian function

$$\Phi_n(x) := \left(\frac{3}{2\pi a^2 \varepsilon_n} \right)^{3/2} \exp\left(-\frac{3x^2}{2a^2 \varepsilon_n}\right)$$

and realize that we can now rewrite $Q_n[w]$ as follows:

$$\begin{aligned} Q_n[w] &= \frac{1}{V} \int d\mathbf{r}_0 \dots \int d\mathbf{r}_n \left(\prod_{i=1}^n \Phi_n(\mathbf{r}_i - \mathbf{r}_{i-1}) \right) \left(\prod_{j=0}^n e^{-\varepsilon_n w(\mathbf{r}_j)} \right) \\ &= \frac{1}{V} \int d\mathbf{r}_n e^{-\varepsilon_n w(\mathbf{r}_n)} \int d\mathbf{r}_{n-1} \Phi_n(\mathbf{r}_n - \mathbf{r}_{n-1}) e^{-\varepsilon_n w(\mathbf{r}_{n-1})} \\ &\dots e^{-\varepsilon_n w(\mathbf{r}_1)} \int d\mathbf{r}_0 \Phi_n(\mathbf{r}_1 - \mathbf{r}_0) e^{-\varepsilon_n w(\mathbf{r}_0)}. \end{aligned}$$

²Mathematical remark: One must understand that the grid sequence G_n does *not* converge to the interval $[0, N]$. The limit $G_\infty = \lim_{n \rightarrow \infty} G_n$ is a countable set, whereas $[0, N]$ is not. Therefore, there is an overcountable number of different curves $\mathbf{r}(s)$ that agree on G_∞ . In physics, we shall not be concerned by this.

We now define the *propagator* $q(\mathbf{r}, s)$, a function that depends on points $\mathbf{r} \in V$ in space and the contour parameter $s \in G_n$, where G_n is the already introduced grid. The *starting value* of the propagator is given by $q(\mathbf{r}, 0) := e^{-\varepsilon_n w(\mathbf{r})}$. It can up to a normalization be interpreted as the probability density of the starting position to be at \mathbf{r} . For the following points on the contour grid G_n , the propagator is defined recursively by the integral equation

$$q(\mathbf{r}, s + \varepsilon_n) := e^{-\varepsilon_n w(\mathbf{r})} \int d\mathbf{r}' \Phi_n(\mathbf{r} - \mathbf{r}') q(\mathbf{r}', s) \quad s \in G_n \setminus \{n\varepsilon_n\}. \quad (15)$$

$q(\mathbf{r}, s)$ is interpreted (up to a normalization) as the probability density for the polymer's contour at s to be at position \mathbf{r} in space, in signs $\mathbf{r}(s) = \mathbf{r}$.

The integral equation in this picture describes how this probability density on the RHS for the polymer's path to fulfil $\mathbf{r}(s + \varepsilon_n) = \mathbf{r}$ is calculated: ignoring normalization requirements, the integrand $e^{-\varepsilon_n w(\mathbf{r})} \Phi_n(\mathbf{r} - \mathbf{r}') q(\mathbf{r}', s)$ has the following meaning: $\Phi_n(\mathbf{r} - \mathbf{r}')$ is the Gaussian transition probability density for the path to go from \mathbf{r}' to \mathbf{r} in a parameter step of length ε_n . It is weighted by the density $e^{-\varepsilon_n w(\mathbf{r})}$ to land in \mathbf{r} given the field w at that point and by the probability density $q(\mathbf{r}', s)$ that the path is at \mathbf{r}' for parameter s . Finally, the integration over \mathbf{r}' takes into account all such starting points \mathbf{r}' .

To calculate the propagator q from (15), one needs the whole field w . Therefore, q is functionally dependent on w which is why conventionally the propagator is in the literature written $q(\mathbf{r}, s; [w])$ to indicate this. We will suppress w and stick to the notation $q(\mathbf{r}, s)$ whenever there is no danger of confusion. By means of the propagator, the canonical partition function $Q_n[w]$ can be written simply as

$$Q_n[w] = \frac{1}{V} \int d\mathbf{r}_n q(\mathbf{r}_n, N) = \frac{1}{V} \int d\mathbf{r} q(\mathbf{r}, N), \quad (16)$$

where it should be understood that for $Q_n[w]$ the propagator q is the one defined on the grid G_n via the integrals. It is for a physically relevant field w clearly difficult, to calculate the propagator q by using its definition, especially when aiming at the limit $n \rightarrow \infty$ to find the propagator for $Q[w]$. Since the computational effort increases to the untractable for ever finer becoming grids G_n , one should try and look for different approach to circumvent these difficulties.

Diffusion Equation for the Propagator

In fact, there an easy way to find the propagator $q(\mathbf{r}, s)$ for the whole intervall $[0, N]$.

Claim 2. The propagator q satisfies a *damped diffusion equation* with damping function w .

Proof. The objective is to find a propagator function $q(\mathbf{r}, s)$ that would satisfy the integral equation (15) for all possible grids G_n . This corresponds to satisfying

$$q(\mathbf{r}, s + \varepsilon) = e^{-\varepsilon w(\mathbf{r})} \int d\mathbf{r}' \Phi_\varepsilon(\mathbf{r} - \mathbf{r}') q(\mathbf{r}', s) \quad \forall \varepsilon > 0, \quad (17)$$

where

$$\Phi_\varepsilon(x) := \left(\frac{3}{2\pi a^2 \varepsilon} \right)^{3/2} \exp\left(-\frac{3x^2}{2a^2 \varepsilon} \right)$$

is a Gaussian density. We will show now that this integral equation is equivalent to a diffusion equation with a damping function w . For small enough ε the 'probability mass' of the Gaussian Φ_ε is strongly concentrated around 0. This makes it sufficiently localized such that contributions from areas faraway from \mathbf{r} are small and vanish in the limit $\varepsilon \rightarrow 0$. We can therefore Taylor-expand $q(\mathbf{r}', s)$ in the above integral equation around a fixed point $\mathbf{r} \in \mathbb{R}^3$:

$$q(\mathbf{r}, s + \varepsilon) = e^{-\varepsilon w(\mathbf{r})} \int d\mathbf{r}' \Phi_\varepsilon(\mathbf{r} - \mathbf{r}') \left(q(\mathbf{r}, s) + \Delta x_j \partial_j q(\mathbf{r}, s) + \frac{1}{2} \Delta x_j \Delta x_i \partial_{ij} q(\mathbf{r}, s) + \dots \right),$$

where we have used Einstein's summation convention and the abbreviation $\Delta x_j = (\mathbf{r} - \mathbf{r}')_j$ for the j -th component of the step vector. For symmetry reasons only terms containing $(\Delta x_j)^n$ with even n survive after the integration. We can use the one-dimensional integral formula for $n \geq 1$, $c > 0$

$$\int_{\mathbb{R}} \frac{dx}{\sqrt{2\pi c}} e^{-x^2/2c} x^n = \begin{cases} (n-1)!c^{n/2} & n \text{ even} \\ 0 & n \text{ odd} \end{cases} \quad (18)$$

and $\int d\mathbf{r}' \Phi_\varepsilon(\mathbf{r} - \mathbf{r}') = 1$ to find

$$q(\mathbf{r}, s + \varepsilon) = e^{-\varepsilon w(\mathbf{r})} \left(q(\mathbf{r}, s) + \varepsilon \frac{a^2}{6} \nabla^2 q(\mathbf{r}, s) + o(\varepsilon^2) \right)$$

where due to (18) all unmentioned integrals exist for small enough $c > 0$ and depend on the mesh size ε , since $c = \varepsilon a^2/3$. Further we write

$$\begin{aligned} q(\mathbf{r}, s + \varepsilon) &= e^{-\varepsilon w(\mathbf{r})} \left(q(\mathbf{r}, s) + \varepsilon \frac{a^2}{6} \nabla^2 q(\mathbf{r}, s) + o(\varepsilon^2) \right) \\ &= (1 - \varepsilon w(\mathbf{r}) + \mathcal{O}(\varepsilon^2)) \left(q(\mathbf{r}, s) + \varepsilon \frac{a^2}{6} \nabla^2 q(\mathbf{r}, s) + o(\varepsilon^2) \right) \\ &= q(\mathbf{r}, s) + \varepsilon \left(\frac{a^2}{6} \nabla^2 q(\mathbf{r}, s) - w(\mathbf{r}) q(\mathbf{r}, s) \right) + o(\varepsilon^2) \end{aligned}$$

and finally sending $\varepsilon \rightarrow 0$ in

$$\frac{q(\mathbf{r}, s + \varepsilon) - q(\mathbf{r}, s)}{\varepsilon} = \frac{a^2}{6} \nabla^2 q(\mathbf{r}, s) - w(\mathbf{r}) q(\mathbf{r}, s) + o(\varepsilon)$$

yields the damped diffusion equation

$$\frac{\partial}{\partial s} q(\mathbf{r}, s) = \frac{a^2}{6} \nabla^2 q(\mathbf{r}, s) - w(\mathbf{r}) q(\mathbf{r}, s). \quad \square \quad (19)$$

Consequently, to find the propagator $q(\mathbf{r}, s)$, one must solve this diffusion equation. The initial condition is given by $q(\mathbf{r}, 0) = 1$, which is the limit of the starting value: $q(\mathbf{r}, 0) = e^{-\varepsilon_n w(\mathbf{r})} \rightarrow 1$ for $n \rightarrow \infty$ since $\lim_{n \rightarrow \infty} \varepsilon_n = 0$. The boundary conditions depend on the way the theory is constructed: Dirichlet boundary conditions $q(\mathbf{r}, s) = 0$ for $\mathbf{r} \in \partial V$ are a typical choice. A vanishing propagator means that the polymer cannot be on the boundary ∂V of the considered volume V .

3 Monomer Densities

3.1 Homopolymer

In the continuous theory we define canonical ensemble averages of functionals $F[\mathbf{r}]$ that depend on the random Gaussian thread $\mathbf{r}(s)$ in path integral terms as

$$\langle F \rangle := \frac{1}{Q[w]} \int \mathcal{D}\mathbf{r} e^{-\beta \mathcal{H}[\mathbf{r}]} F[\mathbf{r}],$$

where $\mathcal{H}[\mathbf{r}] \equiv 3/(2a^2) \int_0^N ds |\mathbf{r}'(s)|^2 + \int_0^N ds w(\mathbf{r}(s))$ is the Hamiltonian. Recall that like in the discrete theory, the coupling term can be expressed as a scalar product $\int_0^N ds w(\mathbf{r}(s)) = (w, \hat{\varrho})$. Again, as in the discrete theory (8) the *average local monomer density* $\varrho(\mathbf{x}) := \langle \hat{\varrho}(\mathbf{x}) \rangle$ is the functional derivative of $\ln Q[w]$ with respect to the external field $w(\mathbf{x})$:

$$\langle \hat{\varrho}(\mathbf{x}) \rangle = \frac{1}{Q[w]} \int \mathcal{D}\mathbf{r} e^{-\beta \mathcal{H}_0[\mathbf{r}] - (w, \hat{\varrho})} \hat{\varrho}(\mathbf{x}) = -\frac{1}{Q[w]} \int \mathcal{D}\mathbf{r} \frac{\delta}{\delta w(\mathbf{x})} e^{-\beta \mathcal{H}_0[\mathbf{r}] - (w, \hat{\varrho})} \quad (20)$$

$$= -\frac{1}{Q[w]} \frac{\delta}{\delta w(\mathbf{x})} \int \mathcal{D}\mathbf{r} e^{-\beta \mathcal{H}_0[\mathbf{r}] - (w, \hat{\varrho})} = -\frac{\delta}{\delta w(\mathbf{x})} \ln \int \mathcal{D}\mathbf{r} e^{-\beta \mathcal{H}_0[\mathbf{r}] - (w, \hat{\varrho})} \quad (21)$$

$$= -\frac{\delta \ln Q[w]}{\delta w(\mathbf{x})} \quad (22)$$

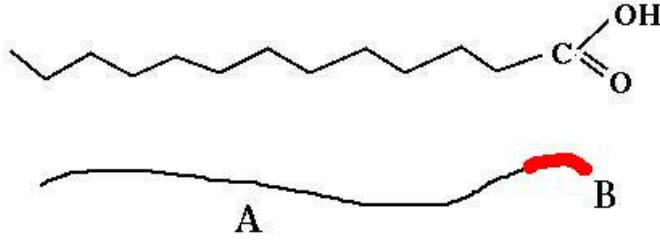


Figure 6: Diblock copolymer: a carbonic acid, also known as fatty acid and its continuous Gaussian chain representation. The carbonic acid end group -COOH (monomer type B) interacts differently with solvent water molecules than the rest of the chain (type A monomer).

This functional derivative can be expressed more conveniently using the propagator $q(\mathbf{r}, s)$: in section A.1 of the appendix, the functional derivative of the canonical partition function $Q[w]$ with respect to the field is shown to be

$$-\frac{\delta Q[w]}{\delta w(\mathbf{x})} = \frac{1}{V} \int_0^N ds q(\mathbf{x}, N-s)q(\mathbf{x}, s) = \frac{1}{V} \int_0^N ds q^\dagger(\mathbf{x}, s)q(\mathbf{x}, s),$$

where the function $q^\dagger(\mathbf{x}, s) := q(\mathbf{x}, N-s)$ is called *backward propagator*. The density ϱ is then given by the propagator integral

$$\varrho(\mathbf{x}) = -\frac{1}{Q} \frac{\delta Q[w]}{\delta w(\mathbf{x})} = \frac{1}{QV} \int_0^N ds q^\dagger(\mathbf{x}, s)q(\mathbf{x}, s). \quad (23)$$

3.2 Copolymer

In what follows we will extend the continuous Gaussian chain theory to a *diblock copolymer*, consisting of two types of monomers labelled A and B as in the example shown in Figure 6.

Let $f \in (0, 1)$ be the fraction of type A monomers. Since the choice of where one block ends and the next starts depends on the model, we let this number be any between 0 and 1. The diblock arrangement is such that the first section of the contour line, say from $s = 0$ to $s = fN$ carries A-monomers and the rest, namely from $s = fN$ to $s = N$ B-monomers.

The A- and B-monomers can be different in various ways: their chains can have a different Kuhn length parameter $a > 0$ and respond differently to the external field that acts on them. For simplicity, we assume only the latter. To account for that, we introduce two different fields w_A and w_B , where w_K acts only on monomers of type $K (K = A, B)$. The external field could be generated by the surrounding solvent that, for example, interacts favourably with A-monomers and unfavourably with B-monomers. The potential energy contribution takes the form

$$V_{AB}[\mathbf{r}] = \int d\mathbf{x} (w_A(\mathbf{x})\hat{\varrho}_A(\mathbf{x}) + w_B(\mathbf{x})\hat{\varrho}_B(\mathbf{x})) = (w_A, \hat{\varrho}_A) + (w_B, \hat{\varrho}_B), \quad (24)$$

where $\hat{\varrho}_A(\mathbf{x}) := \int_0^{fN} ds \delta(\mathbf{x} - \mathbf{r}(s))$ and $\hat{\varrho}_B(\mathbf{x}) := \int_{fN}^N ds \delta(\mathbf{x} - \mathbf{r}(s))$ are the corresponding monomer densities. The Hamiltonian \mathcal{H}_0 of the free copolymer chain is the same as that for the homopolymer since we assume both parts of the chain to have the same Kuhn length. The canonical partition function now is given by

$$Q[w_A, w_B] := \int \mathcal{D}\mathbf{r} e^{-\beta\mathcal{H}_0[\mathbf{r}] - (w_A, \hat{\varrho}_A) - (w_B, \hat{\varrho}_B)}. \quad (25)$$

The canonical average of a functional $F[\mathbf{r}]$ that depends on the Gaussian copolymer thread is calculated according to

$$\langle F \rangle := \frac{1}{Q} \int \mathcal{D}\mathbf{r} e^{-\beta\mathcal{H}_{AB}[\mathbf{r}]} F[\mathbf{r}],$$

where $\mathcal{H}_{AB} = \mathcal{H}_0 + V_{AB}$ is the copolymer's Hamiltonian.

The *local average monomer densities* can be calculated as functional derivatives just as before in (20): $\varrho_K(\mathbf{x}) = \delta \ln Q[w_A, w_B] / \delta w_K(\mathbf{x})$, $K = A, B$. To find an expression for these functional derivatives of $Q[w_A, w_B]$ in terms of propagators, there are *two different propagators* that need to be defined as opposed to just *one* in the homopolymer theory: solutions of the two diffusion equations

$$\frac{\partial}{\partial s} q(\mathbf{r}, s) = \left(\frac{a^2}{6} \nabla^2 - w(\mathbf{r}, s) \right) q(\mathbf{r}, s) \quad w(\mathbf{r}, s) := \begin{cases} w_A(\mathbf{r}) & s \in [0, fN] \\ w_B(\mathbf{r}) & s \in (fN, N]. \end{cases} \quad (26)$$

and

$$\frac{\partial}{\partial s} q_c(\mathbf{r}, s) = \left(\frac{a^2}{6} \nabla^2 - w_c(\mathbf{r}, s) \right) q_c(\mathbf{r}, s) \quad w_c(\mathbf{r}, s) := \begin{cases} w_B(\mathbf{r}) & s \in [0, (1-f)N] \\ w_A(\mathbf{r}) & s \in [(1-f)N, N]. \end{cases} \quad (27)$$

The function $q_c(\mathbf{x}, s)$ is called *complementary propagator*. The canonical partition function can then be expressed as $Q[w_A, w_B] = \frac{1}{V} \int d\mathbf{r} q(\mathbf{r}, N) = \frac{1}{V} \int d\mathbf{r} q_c(\mathbf{r}, N)$. In the appendix it is shown that the functional derivatives of $Q[w_A, w_B]$ can be written in terms of q and q_c as

$$\frac{\delta Q[w_A, w_B]}{\delta w_A(\mathbf{x})} = \frac{1}{V} \int_0^{fN} ds q(\mathbf{x}, s) q_c(\mathbf{x}, N-s) \quad (28)$$

and

$$\frac{\delta Q[w_A, w_B]}{\delta w_B(\mathbf{x})} = \frac{1}{V} \int_{fN}^N ds q(\mathbf{x}, s) q_c(\mathbf{x}, N-s). \quad (29)$$

The local average monomer densities for the two monomer types are

$$\varrho_A(\mathbf{x}) = -\frac{\delta \ln Q[w_A, w_B]}{\delta w_A(\mathbf{x})} = -\frac{1}{Q} \frac{\delta Q[w_A, w_B]}{\delta w_A(\mathbf{x})} = \frac{1}{QV} \int_0^{fN} ds q(\mathbf{x}, s) q_c(\mathbf{x}, N-s).$$

and

$$\varrho_B(\mathbf{x}) = -\frac{\delta \ln Q[w_A, w_B]}{\delta w_B(\mathbf{x})} = -\frac{1}{Q} \frac{\delta Q[w_A, w_B]}{\delta w_B(\mathbf{x})} = \frac{1}{QV} \int_{fN}^N ds q(\mathbf{x}, s) q_c(\mathbf{x}, N-s).$$

In case one wants to mandate different Kuhn lengths a for the A and B segments, one introduces a piecewise constant contour function $a(s)$ that takes different but constant values on the intervals $[0, fN]$ and $(fN, N]$.

3.3 Summary

Using the notation introduced in the preceding sections, the following two boxes summarize the main characters of the Gaussian thread theory.

$$\begin{aligned} \left[\frac{\partial}{\partial s} - \frac{a^2}{6} \nabla^2 + w(\mathbf{x}) \right] q(\mathbf{x}, s) &= 0 \\ Q[w] &= \frac{1}{V} \int d\mathbf{x} q(\mathbf{x}, s) \quad \varrho(\mathbf{x}) = \frac{1}{QV} \int_0^N ds q(\mathbf{x}, s) q(\mathbf{x}, N-s) \end{aligned}$$

homopolymer in an external field

$$\begin{aligned} \left[\frac{\partial}{\partial s} - \frac{a^2}{6} \nabla^2 + w(\mathbf{x}, s) \right] q(\mathbf{x}, s) &= 0 & \left[\frac{\partial}{\partial s} - \frac{a^2}{6} \nabla^2 + w_c(\mathbf{x}, s) \right] q_c(\mathbf{x}, s) &= 0 \\ Q[w_A, w_B] &= \frac{1}{V} \int d\mathbf{x} q(\mathbf{x}, s) = \frac{1}{V} \int d\mathbf{x} q_c(\mathbf{x}, s) \\ \varrho_A(\mathbf{x}) &= \frac{1}{QV} \int_0^{fN} ds q(\mathbf{x}, s) q_c(\mathbf{x}, N-s) & \varrho_B(\mathbf{x}) &= \frac{1}{QV} \int_{fN}^N ds q(\mathbf{x}, s) q_c(\mathbf{x}, N-s) \end{aligned}$$

AB copolymer in an external field

A Propagator Integrals

It is the aim of this Appendix section to derive computationally tractable expressions for functional derivatives of the path integral functionals $Q[w]$ and $Q[w_A, w_B]$ in terms of the propagators. We will refer to the resulting integral expressions as *propagator integrals*.

A.1 Homopolymers

We will show now that

$$-\frac{\delta Q[w]}{\delta w(\mathbf{x})} = -\frac{\delta}{\delta w(\mathbf{x})} \int \mathcal{D}\mathbf{r} e^{-\beta\mathcal{H}_0[\mathbf{r}] - (w, \widehat{\rho})} = \frac{1}{V} \int_0^N ds q^\dagger(\mathbf{x}, s) q(\mathbf{x}, s), \quad (30)$$

where $q^\dagger(\mathbf{x}, s) := q(\mathbf{x}, N-s)$ is the *backward propagator*. First we will take the functional derivative of

$$Q_n[w] = \frac{1}{V} \int d\mathbf{r}_n \dots \int d\mathbf{r}_0 \Phi_n(\mathbf{r}_n - \mathbf{r}_{n-1}) \dots \Phi_n(\mathbf{r}_1 - \mathbf{r}_0) \left(\prod_{j=0}^n e^{-\varepsilon_n w(\mathbf{r}_j)} \right). \quad (31)$$

and then take the limit $\lim_{n \rightarrow \infty} Q_n[w]$ afterwards. We thus assume the interchangeability

$$\frac{\delta Q[w]}{\delta w(\mathbf{x})} = \frac{\delta}{\delta w(\mathbf{x})} Q[w] = \frac{\delta}{\delta w(\mathbf{x})} \lim_{n \rightarrow \infty} Q_n[w] = \lim_{n \rightarrow \infty} \frac{\delta Q_n[w]}{\delta w(\mathbf{x})}. \quad (32)$$

Due to the definition of the functional derivative[7]

$$\frac{\delta Q[w]}{\delta w(\mathbf{x})} := \lim_{\varepsilon \rightarrow 0} \frac{1}{\varepsilon} (Q[w + \varepsilon \delta_{\mathbf{x}}] - Q[w]), \quad (33)$$

where $\delta_{\mathbf{x}}$ is a delta Dirac function concentrated at \mathbf{x} , this is a non-trivial interchange of two limiting processes. However, we will not investigate into the mathematical intricacies of this. In taking the functional derivative of (31) we will use

$$\begin{aligned} -\frac{\delta}{\delta w(\mathbf{x})} \prod_{j=0}^n e^{-\varepsilon_n w(\mathbf{r}_j)} &= \sum_{j=0}^n \varepsilon_n \frac{\delta w(\mathbf{r}_j)}{\delta w(\mathbf{x})} \prod_{l=0}^n e^{-\varepsilon_n w(\mathbf{r}_l)} = \sum_{j=0}^n \varepsilon_n \delta(\mathbf{r}_j - \mathbf{x}) \prod_{l=0}^n e^{-\varepsilon_n w(\mathbf{r}_l)} \\ &= \sum_{j=0}^n \varepsilon_n \delta(\mathbf{r}_j - \mathbf{x}) e^{-\varepsilon_n w(\mathbf{x})} \prod_{l \neq j} e^{-\varepsilon_n w(\mathbf{r}_l)} \end{aligned}$$

which arises from the that the functional derivative obeys a product rule. Thus, when the functional derivative of Q_n is taken, a sum of n summands is created. The first and the last summand take a form that differs from that of the others. We will write therefore single them out and write them explicitly:

$$\begin{aligned} -\frac{\delta Q_n[w]}{\delta w(\mathbf{x})} &= \frac{\varepsilon_n}{V} \int \prod_{\alpha=1}^n d\mathbf{r}_\alpha \Phi_n(\mathbf{r}_n - \mathbf{r}_{n-1}) \dots \Phi_n(\mathbf{r}_1 - \mathbf{x}) e^{-\varepsilon_n w(\mathbf{x})} \prod_{j \neq 0} e^{-\varepsilon_n w(\mathbf{r}_j)} \\ &+ \frac{\varepsilon_n}{V} \sum_{l=1}^{n-1} \int \prod_{\alpha=0, \dots, n}^{\alpha \neq l} d\mathbf{r}_\alpha \Phi_n(\mathbf{r}_n - \mathbf{r}_{n-1}) \dots \Phi_n(\mathbf{r}_{l+1} - \mathbf{x}) \Phi_n(\mathbf{x} - \mathbf{r}_{l-1}) \dots \\ &\dots \Phi_n(\mathbf{r}_1 - \mathbf{r}_0) e^{-\varepsilon_n w(\mathbf{x})} \prod_{j \neq l} e^{-\varepsilon_n w(\mathbf{r}_j)} \\ &+ \frac{\varepsilon_n}{V} \int \prod_{\alpha=0}^{n-1} d\mathbf{r}_\alpha \Phi_n(\mathbf{x} - \mathbf{r}_{n-1}) \dots \Phi_n(\mathbf{r}_1 - \mathbf{r}_0) e^{-\varepsilon_n w(\mathbf{x})} \prod_{j \neq n} e^{-\varepsilon_n w(\mathbf{r}_j)}. \end{aligned}$$

In every integral one integration has broken down due to the delta function that occurred as a result of the differentiation. We now replace the integrals by the corresponding propagators, for the following reason: the first integral in the sum can be interpreted as an integral over all paths

starting from any \mathbf{r}_n and then stepping all the way to some fixed \mathbf{x} in exactly n steps, since every integration stands for one step. The last integral is seen as an integral over all paths starting from any \mathbf{r}_0 and then stepping all the way to some fixed \mathbf{x} in exactly n steps, both the first and the last integral give the same result:

$$\begin{aligned} q(\mathbf{x}, n\varepsilon_n) &= \int d\mathbf{r}_n \dots \int d\mathbf{r}_1 \Phi_n(\mathbf{r}_n - \mathbf{r}_{n-1}) \dots \Phi_n(\mathbf{r}_1 - \mathbf{x}) e^{-\varepsilon_n w(\mathbf{x})} \prod_{j \neq 0} e^{-\varepsilon_n w(\mathbf{r}_j)} \\ &= \int d\mathbf{r}_{n-1} \dots \int d\mathbf{r}_0 \Phi_n(\mathbf{x} - \mathbf{r}_{n-1}) \dots \Phi_n(\mathbf{r}_1 - \mathbf{r}_0) e^{-\varepsilon_n w(\mathbf{x})} \prod_{j \neq n} e^{-\varepsilon_n w(\mathbf{r}_j)}. \end{aligned}$$

The inbetween summands can be rewritten in a similiar way: we devide the multiple integral into two chunks, one for the path of $n - l$ and one for l steps towards \mathbf{x} :

$$\begin{aligned} &\int \prod_{\alpha=0, \dots, n}^{\alpha \neq l} d\mathbf{r}_\alpha \Phi_n(\mathbf{r}_n - \mathbf{r}_{n-1}) \dots \Phi_n(\mathbf{r}_{l+1} - \mathbf{x}) \Phi_n(\mathbf{x} - \mathbf{r}_{l-1}) \dots \Phi_n(\mathbf{r}_1 - \mathbf{r}_0) \\ \times &e^{-\varepsilon_n w(\mathbf{x})} \prod_{j \neq l} e^{-\varepsilon_n w(\mathbf{r}_j)} \\ &= e^{\varepsilon_n w(\mathbf{x})} \int d\mathbf{r}_n \dots \int d\mathbf{r}_{l+1} \Phi_n(\mathbf{r}_n - \mathbf{r}_{n-1}) \dots \Phi_n(\mathbf{r}_{l+1} - \mathbf{x}) e^{-\varepsilon_n w(\mathbf{x})} \prod_{j=l+1}^n e^{-\varepsilon_n w(\mathbf{r}_j)} \\ \times &e^{-\varepsilon_n w(\mathbf{x})} \int d\mathbf{r}_{l-1} \dots \int d\mathbf{r}_0 \Phi_n(\mathbf{x} - \mathbf{r}_{l-1}) \dots \Phi_n(\mathbf{r}_1 - \mathbf{r}_0) \prod_{j=0}^{l-1} e^{-\varepsilon_n w(\mathbf{r}_j)} \\ &= e^{\varepsilon_n w(\mathbf{x})} q(\mathbf{x}, (n-l)\varepsilon_n) q(\mathbf{x}, l\varepsilon_n) \end{aligned}$$

where a neutral factor $e^{\varepsilon_n w(\mathbf{x})} e^{-\varepsilon_n w(\mathbf{x})} = 1$ had to be inserted to satisfy the definition of the propagator for both integrals. Finally, we have

$$-\frac{\delta Q_n[w]}{\delta w(\mathbf{x})} = \frac{\varepsilon_n}{V} q(\mathbf{x}, n\varepsilon_n) + \frac{e^{\varepsilon_n w(\mathbf{x})}}{V} \sum_{l=1}^{n-1} \varepsilon_n q(\mathbf{x}, (n-l)\varepsilon_n) q(\mathbf{x}, l\varepsilon_n) + \frac{\varepsilon_n}{V} q(\mathbf{x}, n\varepsilon_n)$$

because $q(\mathbf{x}, 0) = e^{-\varepsilon_n w(\mathbf{x})}$ we can supplement the first and the last summand by a neutral factor $1 = q(\mathbf{x}, 0) e^{\varepsilon_n w(\mathbf{x})}$ to get

$$-\frac{\delta Q_n[w]}{\delta w(\mathbf{x})} = \frac{e^{\varepsilon_n w(\mathbf{x})}}{V} \sum_{l=0}^n \varepsilon_n q(\mathbf{x}, (n-l)\varepsilon_n) q(\mathbf{x}, l\varepsilon_n)$$

Taking the limit $n \rightarrow \infty$ where the mesh size $\varepsilon_n \rightarrow 0$, we find

$$-\frac{\delta Q[w]}{\delta w(\mathbf{x})} = \lim_{n \rightarrow \infty} \frac{e^{\varepsilon_n w(\mathbf{x})}}{V} \sum_{l=0}^n \varepsilon_n q(\mathbf{x}, (n-l)\varepsilon_n) q(\mathbf{x}, l\varepsilon_n) = \frac{1}{V} \int_0^N ds q(\mathbf{x}, N-s) q(\mathbf{x}, s).$$

A.2 Copolymers

The propagator integral for the copolymer's monomer density is derived along the same lines as that in Appendix section A.1. First, we recall the interaction potential in (24) and write it in the form

$$V_{AB}[\mathbf{r}] = \int_0^{fN} ds w_A(\mathbf{r}(s)) + \int_{fN}^N ds w_B(\mathbf{r}(s)). \quad (34)$$

Discretizing it by the same procedure as in section 2.2 yields

$$V(\{\mathbf{r}_i\}) = \sum_{k=0}^{\lfloor fn \rfloor} \varepsilon_n w_A(\mathbf{r}_k) + \sum_{k=\lfloor fn \rfloor + 1}^n \varepsilon_n w_B(\mathbf{r}_k),$$

where $\lfloor x \rfloor := \max\{z \in \mathbb{Z} : z \leq x\}$ denotes the 'floor function' which yields the largest possible integer that is smaller or equal to $x \in \mathbb{R}$. ε_n is the mesh size just as before. The discretized path integral now reads

$$Q_n[w_A, w_B] = \frac{1}{V} \int d\mathbf{r}_n \dots \int d\mathbf{r}_0 \left(\prod_{k=1}^n \Phi_n(\mathbf{r}_k - \mathbf{r}_{k-1}) \right) \left(\prod_{k=0}^{\lfloor fn \rfloor} e^{-\varepsilon_n w_A(\mathbf{r}_k)} \right) \left(\prod_{k=\lfloor fn \rfloor+1}^n e^{-\varepsilon_n w_B(\mathbf{r}_k)} \right). \quad (35)$$

We take the functional derivative of $Q[w_A, w_B]$ with respect to $w_A(\mathbf{x})$:

$$\begin{aligned} -\frac{\delta}{\delta w_A(\mathbf{x})} Q_n[w_A, w_B] &= \frac{1}{V} \int d\mathbf{r}_n \dots \int d\mathbf{r}_0 \left(\prod_{k=1}^n \Phi_n(\mathbf{r}_k - \mathbf{r}_{k-1}) \right) \\ &\times \left(\sum_{j=0}^{\lfloor fn \rfloor} \varepsilon_n \delta(\mathbf{x} - \mathbf{r}_j) e^{-\varepsilon_n w_A(\mathbf{x})} \prod_{\substack{k \neq j \\ k=0, \dots, \lfloor fn \rfloor}} e^{-\varepsilon_n w_A(\mathbf{r}_k)} \right) \left(\prod_{k=\lfloor fn \rfloor+1}^n e^{-\varepsilon_n w_B(\mathbf{r}_k)} \right). \end{aligned}$$

What is different now from the propagator integral in the previous Appendix section A.1 is that in order to express it in terms of the propagator q , one additionally needs the *complementary propagator* q_c . Then,

$$-\frac{\delta}{\delta w_A(\mathbf{x})} Q_n[w_A, w_B] = \frac{1}{V} \sum_{k=0}^{\lfloor fn \rfloor} \varepsilon_n q(\mathbf{x}, k\varepsilon_n) q_c(\mathbf{x}, N - k\varepsilon_n),$$

follows. Taking the limit $n \rightarrow \infty$ we obtain

$$-\frac{\delta}{\delta w_A(\mathbf{x})} Q[w_A, w_B] = \frac{1}{V} \int_0^{fN} ds q(\mathbf{x}, s) q_c(\mathbf{x}, N - s) = \frac{1}{V} \int_0^{fN} ds q(\mathbf{x}, s) q_c(\mathbf{x}, N - s).$$

The functional derivative with respect to $w_B(\mathbf{x})$ is along the same line of argumentation found to be

$$-\frac{\delta}{\delta w_B(\mathbf{x})} Q[w_A, w_B] = \frac{1}{V} \int_{fN}^N ds q(\mathbf{x}, s) q_c(\mathbf{x}, N - s) = \frac{1}{V} \int_{fN}^N ds q(\mathbf{x}, s) q_c(\mathbf{x}, N - s).$$

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