Single Chain Partition Function

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This article will focus on the single chain partition function and why it can be computed through a solution to a modified diffusion equation. If one looks at a paper in the literature, the single chain partition function is defined by the functional integral

$$Q[w] = \frac{\int \mathcal{D}\mathbf{R} e^{-(3/2b^2)\int_0^N |d\mathbf{R}/ds|^2 ds - \int w(r)\rho(x)dx}}{\mathcal{D}\mathbf{R} e^{-(3/2b^2)\int_0^N |d\mathbf{R}/ds|^2 ds}} \tag{1}$$

Here, $w(r)$ is the external field that could in general depend on the contour variable s, $\mathbf{R}$ is the space curve that represents a single polymer, and the density is

$$\rho(x) = \int_0^N \delta(x - \mathbf{R}(s))ds \tag{2}$$

I've written this expression in one dimension, consistent with the calculations that we're interested in doing. Let's express the contour variable s in units of N by defining $t = s/N$, so then the stretching energy becomes

$$-\left(\frac{3}{2Nb^2}\right)\int_0^1 \left|\frac{d\mathbf{R}}{dt}\right|^2 dt = -\left(\frac{1}{4R_{g0}}\right)\int_0^1 \left|\frac{d\mathbf{R}}{dt}\right|^2 dt \tag{3}$$

and the field term is

$$-\int w(r)\int_0^N \delta(x - \mathbf{R}(s)dsdr = -\int_0^1 Nw(\mathbf{R}(t))dt \tag{4}$$

After expressing the space curve in units of R_{g0} through $\tilde{\mathbf{R}} = \mathbf{R}/R_{g0}$, the single chain partition function becomes

$$Q[W] = \frac{\int \mathcal{D}\tilde{\mathbf{R}} e^{-(1/4)\int_0^1 |d\tilde{\mathbf{R}}/dt|^2 dt - \int_0^1 W(\tilde{\mathbf{R}}(t))dt}}{\mathcal{D}\tilde{\mathbf{R}} e^{-(1/4)\int_0^1 |d\tilde{\mathbf{R}}/dt|^2 dt}} \tag{5}$$

where we've used the definition of the density and performed the integration over x and defined the scaled field $W(x) = Nw(x)$.

Suppose that one changed the field from $W(x)$ to $W_0 + W(x)$ where W_0 is a constant. How would the value of $Q[W]$ change? It is straightforward to evaluate this effect from the previous equation.

$$Q[W_0 + W(x)] = \frac{\int \mathcal{D}\tilde{\mathbf{R}} e^{-(1/4)\int_0^1 |d\tilde{\mathbf{R}}/dt|^2 dt - \int_0^1 [W_0 + W(\tilde{\mathbf{R}}(t))]dt}}{\mathcal{D}\tilde{\mathbf{R}} e^{-(1/4)\int_0^1 |d\tilde{\mathbf{R}}/dt|^2 dt}} = e^{-W_0} Q[W(x)] \tag{6}$$

The constant shift in the field multiplies the single chain partition function by a factor of e^{-W_0}. In general, one multiplies the single chain partition function by a factor of $e^{-W_0 g}$ where g is the range of the integration for the scaled contour variable t. This analytic results gives us a check on our code that solves the modified diffusion equation and calculates the single chain partition function. If we add a constant to the field, the single chain partition function value should change appropriately. If our code does not give the correct value, then there's something wrong with the code.

Now we will derive how the single chain partition function is related to the propagator $q(x,t)$ defined previously. To do this, we discretize the integrals over contour variable t, defining an arbitrarily small interval Δt. Also, we discretize the functional integral over the space curve into $N+1$ discrete points or beads[1] x_i where $N = (\Delta t)^{-1}$ is the number of intervals between the points.

$$\int_0^1 \left| \frac{d\tilde{\mathbf{R}}}{dt} \right|^2 dt \longrightarrow \sum_{i=1}^{N} \frac{(x_i - x_{i-1})^2}{\Delta t^2} \Delta t \tag{7}$$

$$\int_0^1 W(\tilde{\mathbf{R}}(t)) dt \longrightarrow \sum_{i=0}^{N} W(x_i) \Delta t \tag{8}$$

[2] Then the single chain partition function becomes

$$Q[W]$$

[1]We use the terminology beads here since this is closely related to bead-spring models for polymers.

[2]So I'm pulling a fast one on you here since the contour integrals of the stretching term contain N factors of Δt and the integrals of the field contain $N+1$ factors of Δt. Since this difference doesn't matter as $\Delta t \to 0$, this quirk in the derivation won't affect our final results.

$$= \frac{\int dx_0 \dots dx_N e^{W(x_0)\Delta t - (4\Delta t)^{-1}(x_1-x_0)^2 - W(x_1)\Delta t - (4\Delta t)^{-1}(x_2-x_1)^2 - \dots}}{\int dx_0 \dots dx_N e^{-(4\Delta t)^{-1}(x_1-x_0)^2 - (4\Delta t)^{-1}(x_2-x_1)^2 - \dots}}$$

$$= \frac{\int dx_0 d\Delta x_1 \dots d\Delta t x_N e^{W(x_0)\Delta t - (4\Delta t)^{-1}\Delta x_1^2 - W(x_1)\Delta t - (4\Delta t)^{-1}\Delta x_2^2 - \dots}}{L \int d\Delta x_1 \dots d\Delta x_N e^{-(4\Delta t)^{-1}\sum_{i=1}^{N}\Delta x_i^2}}$$

After the second equality, we have made the change of variable $\Delta x_i = x_i - x_{i-1}$ for $i = 1 \dots N$ but kept the integration over x_0. In the denominator, we've explicitly done the integration over x_0, which provides the L. The numerator becomes integrals over the field terms with a Gaussian distribution $e^{-(4\Delta t)^{-1}\Delta x_i^2}$ for the distance between the discrete beads, and the product of constant terms in the denominator serve as normalization. In fact, it's straightforward to check that $Q[0] = 1$ with this normalization. Now if we define

$$q(x, 0) = e^{-W(x)\Delta t} \tag{9}$$

as an "initial condition" and then "propagate" this along the polymer contour

$$q(x, \Delta t) = e^{-W(x)\Delta t} \int d\Delta x \Phi(\Delta x) q(x - \Delta x, 0) \tag{10}$$

where

$$\Phi(\Delta x) = \frac{1}{\sqrt{4\pi\Delta t}} e^{-\Delta x^2/(4\Delta t)} \tag{11}$$

is a normalized Gaussian in one dimension. In general, we have the relation

$$q(x, t + \Delta t) = e^{-W(x)\Delta t} \int d\Delta x \Phi(\Delta x) q(x - \Delta x, t) \tag{12}$$

Once we get to the end of the polymer contour, we get the partition function as

$$Q[W] = L^{-1} \int dx q(x, 1) \tag{13}$$

It is not a coincidence that $q(x, t)$ has the same function name as the propagator that satisfies the modified diffusion equation. They are the same function. To see this, consider the relation

$$q(x, t + \Delta t) = e^{-W(x)\Delta t} \int d\Delta x \Phi(\Delta x) q(x - \Delta x, t) \tag{14}$$

and expand the propagator to second order in Δx and first order in Δt.

$$q(x, t + \Delta t) = q(x, t) + \Delta t \frac{\partial}{\partial t} q(x, t) + O(\Delta t^2) \tag{15}$$

$$q(x-\Delta x,t) = q(x,t) - \Delta x \frac{\partial}{\partial x} q(x,t) + \frac{1}{2}\Delta x^2 \frac{\partial^2}{\partial x^2} q(x,t) + O(\Delta x^3). \quad (16)$$

Then, using $e^{-W(x)\Delta t} = 1 - W(x)\Delta t$ we obtain

$$\begin{aligned}
& q(x,t) + \Delta t \frac{\partial}{\partial t} q(x,t) \\
= & \Big(1 - W(x)\Delta t\Big) \int d\Delta x \Phi(\Delta x) \left(1 - \Delta x \frac{\partial}{\partial x} + \frac{1}{2}\Delta x^2 \frac{\partial^2}{\partial x^2}\right) q(x,t) \\
= & q(x,t) - \langle \Delta x \rangle \frac{\partial}{\partial x} q(x,t) + \frac{1}{2}\langle \Delta x^2 \rangle \frac{\partial^2}{\partial x^2} q(x,t) - W(x)\Delta t q(x,t) \\
& + W(x)\Delta t \langle \Delta x \rangle \frac{\partial}{\partial x} q(x,t) - W(x)\Delta t \frac{1}{2} \langle \Delta x^2 \rangle \frac{\partial^2}{\partial x^2} q(x,t)
\end{aligned}$$

where the brackets denote averages over a Gaussian distribution

$$\langle \cdots \rangle \equiv \int \cdots \Phi(\Delta x) d\Delta x \quad (17)$$

By symmetry, $\langle \Delta x \rangle = 0$ and one can calculate that $\langle \Delta x^2 \rangle = 2\Delta t$. With these relations, the terms to order Δt give the equation

$$\frac{\partial}{\partial t} q(x,t) = \frac{\partial^2}{\partial x^2} q(x,t) - W(x) q(x,t). \quad (18)$$

This is exactly the diffusion equation that we've been solving. It's straightforward to extend this derivation to three dimensions.