Université Paris Cité

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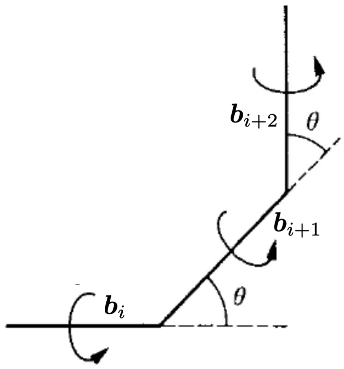
M2 PCS — Statistical field theory and soft matter
TD n°4 : Polymers

1 The freely rotating chain

We consider a polymer chain with no large loop interactions (ideal), consisting of N segments $\boldsymbol{b}_i$ of length b that are forced to make a bond angle θ between them while being free to rotate in the azimuthal direction:



We recall that if x and y are two random variables, the average $\langle f(x,y)\rangle_{x,y}$ over all realisations of x and y can be computed by first averaging over y at constant x, then averaging the result over x:

$$\langle f(x,y)\rangle_{x,y} = \langle\, \langle f(x,y)\rangle_y \,\rangle_x. \tag{1}$$

1. Show that, at fixed $\boldsymbol{b}_i$, the average $\langle \boldsymbol{b}_{i+1}\rangle$ is equal to $\boldsymbol{b}_i \cos\theta$.
2. Deduce that $\langle \boldsymbol{b}_i \cdot \boldsymbol{b}_{i+1}\rangle_{i,i+1} = b^2 \cos\theta$.
3. Decuce that $\langle \boldsymbol{b}_i \cdot \boldsymbol{b}_{i+2}\rangle_{i,i+1,i+2} = b^2 \cos^2\theta$.
4. By generalizing, calculate $\langle \boldsymbol{b}_i \cdot \boldsymbol{b}_j\rangle$.
5. Deduce that the persistence length, i.e., the length along the chain over which correlation are negligible, is given by

$$\ell_p = \frac{b}{\ln\left(\dfrac{1}{\cos\theta}\right)}. \tag{2}$$

6. The radius of giration, i.e., the typical size of the polymer, is given by $R_g = \langle R^2 \rangle$, where $R = \sum_{i=1}^{N} \boldsymbol{b}_i$ is the end-to-end vector. Show that in the thermodynamic limit (i.e., for very long chains) it is given by

$$R_g^2 = Nb^2 \frac{1+\cos\theta}{1-\cos\theta}, \tag{3}$$

7. What is the value of the exponent ν?

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2 Giration radius of a Gaussian polymer

Let us consider a Gaussian polymer in d dimension. Its shape is described by a coarse-grained field $\boldsymbol{r}(s)$, $s \in [0, N]$, with effective dimensionless Hamiltonian:

$$\mathcal{H}[\boldsymbol{r}] = \int_0^N ds \, \frac{1}{2a^2} \, \dot{\boldsymbol{r}}^2. \tag{4}$$

The giration radius $R_g = \langle (\boldsymbol{r}(N) - \boldsymbol{r}(0))^2 \rangle^{1/2}$ of the polymer (i.e., its size), can be deduced from the moments generating function:

$$G(\boldsymbol{k}) = \langle e^{i\boldsymbol{k}\cdot(\boldsymbol{r}(N)-\boldsymbol{r}(0))} \rangle = \int \mathcal{D}\boldsymbol{r} \, e^{i\boldsymbol{k}\cdot(\boldsymbol{r}(N)-\boldsymbol{r}(0))} \, e^{-\mathcal{H}[\boldsymbol{r}]}. \tag{5}$$

1. Show that

$$G(\boldsymbol{k}) = 1 - \frac{R_g^2}{2d} \, k^2 + O(k^4). \tag{6}$$

2. Compute $G(\boldsymbol{k})$ using the change of variable $\boldsymbol{r}'(s) = \boldsymbol{r}(s) - ia^2\boldsymbol{k}\, s$.

3. Deduce that

$$R_g^2 = Na^2 d, \qquad \nu = \frac{1}{2}.$$

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3 Renormalization of a polymer under tension

A polymer in a good solvent, described by Edwards' model with a field $\boldsymbol{r}(s)$ of cutoff Λ in reciprocal space, with $s \in [0, N]$, is stretched by a pair of opposite forces of modulus f acting on both extremities of the chain. Its effective Hamiltonian is given by

$$\mathcal{H}[\boldsymbol{r}] = \int_0^N ds \, \frac{1}{2a^2} \dot{\boldsymbol{r}}^2 + \iint_0^N ds_1 \, ds_2 \, v \, \delta(\boldsymbol{r}(s_1) - \boldsymbol{r}(s_2)) \; + \mathcal{H}_{\text{ext}}, \tag{7}$$

$$\mathcal{H}_{\text{ext}} = -\beta \boldsymbol{f} \cdot (\boldsymbol{r}(N) - \boldsymbol{r}(0)) \,, \tag{8}$$

where β is the inverse temperature. We apply renormalization group transformations:

$$\boldsymbol{r}(s) \longrightarrow \boldsymbol{r}'(s') = g^D \bar{\boldsymbol{r}}(gs'), \tag{9}$$

with coarse-graining $\boldsymbol{r}(s) = \bar{\boldsymbol{r}}(s) + \tilde{\boldsymbol{r}}(s) \longrightarrow \bar{\boldsymbol{r}}(s)$ performed by removing the Fourier modes of wavevector within Λ/g and Λ.

1. Show that $\mathcal{H}_{\text{ext}}$ corresponds to a force $\boldsymbol{f}$ acting on the last monomer and a force $-\boldsymbol{f}$ acting on the first one.
2. Explain without calculations why $\mathcal{H}_{\text{ext}}[\boldsymbol{r}] \simeq \mathcal{H}_{\text{ext}}[\bar{\boldsymbol{r}}]$. Under which condition is that correct?
3. Infer that that the parameter f is not affected by the coarse-graining, i.e., $\bar{f} = f$, while de Gennes' relations $\bar{a} = a[1 + h(u)]$ and $\bar{v} = v[1 - k(u)]$ still hold.
4. Deduce the renormalization step transformation (d is the space dimension):

$$\begin{cases} a_{n+1} = a_n \left[1 + h(u_n, g)\right] g^{\frac{1}{2}+D}, \\ v_{n+1} = v_n \left[1 - k(u_n, g)\right] g^{2+Dd}, \\ f_{n+1} = f_n \, g^{-D}. \end{cases} \tag{10}$$

5. Show, by using the π theorem, that the elongation $L = \langle |\boldsymbol{r}(N) - \boldsymbol{r}(0)| \rangle$ of the polymer can be written as

$$L = a\, \phi(u, N, \beta a f), \tag{11}$$

where ϕ is a dimensionless function (g and d implicit).

6. By renormalizing down to a fixed $N/g = N_0$, deduce the scaling law

$$\frac{L}{R_g} = \Phi_d \left(\frac{f}{k_{\text{B}} T / R_g} \right), \tag{12}$$

where Φ_d is a universal function[1] and $R_g \sim N^\nu$ is the giration radius.

7. Picture two identical polymers under tension chained together. What relation between L and N is expected in the regime of large forces?
8. Deduce that the elongation obeys the nontrivial power-law:

$$L \sim f^{\frac{1-\nu}{\nu}}. \tag{13}$$

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[1]Remember we showed in the course that $R_g = C a^\star N^{-D}$ with C a universal constant.

4 Polymers and the O(n) models in the limit $n \to 0$

P.-G. de Gennes, laureate of the 1991 Nobel Prize, proved that the exponent $\nu(d)$ of real polymers is equal to the analytic continuation to $n \to 0$ of the exponent $\nu(n,d)$ of the correlation length in the $O(n)$ magnets models.

Consider in d dimensions a polymer in a good solvent, described by Edwards' model with a field $\boldsymbol{r}(s)$, $s \in [0,N]$, of effective Hamiltonian

$$\mathcal{H}[\boldsymbol{r}] = \int_0^N ds\, \frac{1}{4}\dot{\boldsymbol{r}}^2 + \iint_0^N ds\, ds'\, u\, \delta(\boldsymbol{r}(s) - \boldsymbol{r}(s')). \tag{14}$$

Note that $\boldsymbol{r}(s)$ has been normalized by $a/\sqrt{2}$ so that it is now dimensionless.

1. Show that the second term $\mathcal{H}_2$ in the Hamiltonian can be rewritten as $\mathcal{H}_2 = \int d^dx\, u\rho^2$, where $\rho(\boldsymbol{r}) = \int_0^N ds\, \delta(\boldsymbol{r} - \boldsymbol{r}(s)$ is the polymer chain density.
2. The density ρ appears as a square in the Boltzmann factor $e^{-\mathcal{H}_2}$. Show that we can make ρ appear only linearly by performing a Hubbard-Stratonovich transformation through the introduction of a new field $V(\boldsymbol{x})$:

$$e^{-\mathcal{H}_2} \propto \int \mathcal{D}V\, e^{-\int d^dx \left[\frac{V^2}{4u} + iV\rho\right]}. \tag{15}$$

3. Deduce that the generating function $G(\boldsymbol{k};N) = \langle e^{i\boldsymbol{k}\cdot(\boldsymbol{r}(N)-\boldsymbol{r}(0))}\rangle$ of the moments of the end-to-end vector can be expressed as

$$G(\boldsymbol{k};N) \propto \int \mathcal{D}V\, e^{-\int d^dx\, \frac{V^2}{4u}} \int \mathcal{D}\boldsymbol{r}\, e^{i\boldsymbol{k}\cdot(\boldsymbol{r}(N)-\boldsymbol{r}(0))}\, e^{-\int_0^N ds\, [\frac{1}{4}\dot{\boldsymbol{r}}^2 + iV(\boldsymbol{r}(s))]}. \tag{16}$$

Analogy with a quantum mechanics path integral.—It follows that

$$G(\boldsymbol{k};N) = \int \mathcal{D}V\, e^{-\int d^dx\, \frac{V^2}{4u}} \int d^d\boldsymbol{r}'\, d^d\boldsymbol{r}'' e^{i\boldsymbol{k}\cdot(\boldsymbol{r}''-\boldsymbol{r}')}\, \Gamma(\boldsymbol{r}',\boldsymbol{r}'';N), \tag{17}$$

with

$$\Gamma(\boldsymbol{r}-\boldsymbol{r}';N) = \int_{\boldsymbol{r}(0)=\boldsymbol{r}}^{\boldsymbol{r}(N)=\boldsymbol{r}'} \mathcal{D}\boldsymbol{r}\, e^{-\int_0^N ds \left[\frac{1}{4}\dot{\boldsymbol{r}}(s)^2 + iV(\boldsymbol{r}(s))\right]}, \tag{18}$$

the partition function of an *ideal* polymer with fixed extremities, interacting with an imaginary external field $iV(\boldsymbol{r})$. This quantity ressembles the path integral of a quantum particle of Hamiltonian $\hat{H} = \hat{\boldsymbol{p}}^2/(2m) + \mathcal{V}(\hat{\boldsymbol{r}})$. Indeed, the probability amplitude for detecting the particle at time T in $\boldsymbol{r}'$, knowing that it was at time 0 in $\boldsymbol{r}$, is given by

$$\psi(\boldsymbol{r}',T) = \int_{\boldsymbol{r}(0)=\boldsymbol{r}}^{\boldsymbol{r}(T)=\boldsymbol{r}'} \mathcal{D}\boldsymbol{r}\, e^{\frac{i}{\hbar}\int_0^T dt \left[\frac{1}{2}m\dot{\boldsymbol{r}}(t)^2 - \mathcal{V}(\boldsymbol{r}(t))\right]}. \tag{19}$$

4. Using this quantum analogy and the evolution operator $e^{-i\hat{H}T/\hbar}$ acting on the initial state $|\boldsymbol{r}\rangle$, show that $\Gamma(\boldsymbol{r};N)$ is the Green function of the operator $e^{N\left(-\boldsymbol{\nabla}^2 + iV\right)}$.

5. Show (without seeking rigor), that its Laplace transform[2] $\hat{\Gamma}(\boldsymbol{r};t)$ is the Green function of $-\boldsymbol{\nabla}^2 + iV(\boldsymbol{r}) + t$.

6. Deduce that $\hat{\Gamma}(\boldsymbol{r},\boldsymbol{r}';t)$ coincides with the correlation function $\langle\phi(\boldsymbol{r})\phi(\boldsymbol{r}')\rangle$ of the Gaussian statistical field theory with Hamiltonian (normalized by $k_{\mathrm{B}}T$):
$$F[\phi] = \frac{1}{2}\int d^d r\left[t\phi^2 + iV(\boldsymbol{r})\phi^2 + (\boldsymbol{\nabla}\phi)^2\right]. \tag{20}$$

7. Deduce that the Laplace transform of $G(\boldsymbol{k};N)$ can be expressed as
$$\hat{G}(\boldsymbol{k};t) = \int\mathcal{D}V\, e^{-\int d^dx\,\frac{V^2}{4u}}\int\mathcal{D}\phi\,\phi(\boldsymbol{k})\phi(-\boldsymbol{k})\,\frac{e^{-F[\phi]}}{Z}, \tag{21}$$
with Z the partition function of ϕ. We have now matched the polymer to a field theory with two coupled fields, with a cubic term $\propto V\phi^2$.

The replica trick and the $n\to 0$ limit.—To get around a difficulty that will appear, we now replicate n times the field ϕ. We introduce a vectorial field $\vec{\phi}(\boldsymbol{x})$ with n components, $\vec{\phi} = (\phi_1,\dots,\phi_n)^t$, and $O(n)$ Hamiltonian:
$$F_n[\vec{\phi}\,] = \sum_{i=1}^{N} F[\phi_i] = \frac{1}{2}\int d^dx\left[t\vec{\phi}^{\,2} + iV(\boldsymbol{x})\vec{\phi}^{\,2} + \sum_{i=1}^{n}(\boldsymbol{\nabla}\phi_i)^2\right]. \tag{22}$$

8. Show that
$$\hat{G}(\boldsymbol{k};t) = \lim_{n\to 0}\int\mathcal{D}\vec{\phi}\,\phi_1(\boldsymbol{k})\phi_1(-\boldsymbol{k})e^{-\int d^dx\left[\frac{1}{2}t\vec{\phi}^{\,2}+\frac{1}{2}\sum_{i=1}^{n}(\boldsymbol{\nabla}\phi_i)^2+\frac{u}{4}\left(\vec{\phi}^{\,2}\right)^2\right]} \tag{23}$$
$$\propto \lim_{n\to 0}\langle\phi_1(\boldsymbol{k})\phi_1(-\boldsymbol{k})\rangle_4. \tag{24}$$
The correlation function $\langle\phi_1(\boldsymbol{k})\phi_1(-\boldsymbol{k})\rangle_4$ of the ϕ^4 model is therefore related, in the limit $n\to 0$, to the generating function of the moments of the size of a real polymer

9. In the $O(n)$ models, the scaling law for the correlation function close to the critical point is $\langle\phi_1(\boldsymbol{x})\phi_1(\boldsymbol{x}')\rangle_4 \sim |\boldsymbol{x}-\boldsymbol{x}'|^{-(d-2+\eta)}f(|\boldsymbol{x}-\boldsymbol{x}'|/(t-t_c)^{-\nu})$. Show that in Fourier space it corresponds to
$$\langle\phi_1(\boldsymbol{k})\phi_1(-\boldsymbol{k})\rangle_4 \sim (t-t_c)^{-\gamma}\tilde{f}(k(t-t_c)^{-\nu}), \tag{25}$$
with $\gamma = \nu(2-\eta)$.

10. Show that expanding $\hat{G}(\boldsymbol{k};t)$ in power series to second-order in $\boldsymbol{k}$ gives
$$\hat{G}(\boldsymbol{k};t) \propto a(t-t_c)^{-\gamma_0} + b(t-t_c)^{-(\gamma_0+2\nu_0)}k^2 + \dots \tag{26}$$
where $\gamma_0 = \lim_{n\to 0}\gamma(n)$ and $\nu_0 = \lim_{n\to 0}\nu(n)$.

11. Using the inverse Laplace transform, show that
$$G(\boldsymbol{k},N) \sim 1 + c\,k^2N^{2\nu_0} + O(k^4), \qquad (N\to\infty), \tag{27}$$
and deduce that $R_g \sim N^{\nu_0}$.

[2] The Laplace transform of $f(N)$ is $\hat{f}(t) = \int_0^\infty dN\,f(N)\,e^{-Nt}$.