The statistical mechanics of an interacting freely jointed chain

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January 27, 2025

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1 The spherical cow joke

Milk production at a dairy farm was low, so the farmer wrote to the local university, asking for help from academia. A multidisciplinary team of professors was assembled, headed by a theoretical physicist, and two weeks of intensive on-site investigation took place. The scholars then returned to the university, notebooks crammed with data, where the task of writing the report was left to the team leader. Shortly thereafter the physicist returned to the farm, saying to the farmer, "I have the solution, but it works only in the case of spherical cows in a vacuum."

2 End-to-end distance of a linear polymer

A simple way of distinguishing between a folded and an unfolded state is to measure the end-to-end distance of the polymer. For N connected monomers we have $M = N - 1$ links of length d and the end-to end distance reads,

$$\mathbf{R}_{ee} = d \sum_{l=1}^{M} \hat{\Omega}_l$$

where

$$\hat{\Omega}_l = \begin{pmatrix} \cos\phi_l \sin\theta_l \\ \sin\phi_l \sin\theta_l \\ \cos\theta_l \end{pmatrix}$$

is the unit direction of a single link in space. It is easier to work with the dimensionless order parameter,

$$r = \frac{1}{M}\sqrt{\mathbf{R}_{ee} \cdot \mathbf{R}_{ee}} = \frac{R_{ee}}{Md}$$

where Md is the maximum extension of the polymer. Now we have,

$$r \to 0 \quad \text{coil}$$

$$r \to 1 \quad \text{globule}$$

We are interested in the probability distribution $P(\mathbf{R}_{ee})$. It can be extracted from the theory we have developed for orientational order in finite liquid crystal samples in the isotropic phase.

3 Uncorrelated polymer - 3D random flight

3.1 Exact answer - Direct evaluation

In the case of a non-interacting polymer we have I.I.D. random variables and we can calculate the exact answer directly,

$$\begin{aligned} P(\mathbf{R}_{ee}) &= \left\langle \delta(\mathbf{R}_{ee} - d\sum_{l=1}^{M}\hat{\Omega}_l) \right\rangle \\ &= \left\langle \delta\left(R_1 - d\sum_{l=1}^{M}\cos\phi_l \sin\theta_l\right)\delta\left(R_2 - d\sum_{l=1}^{M}\sin\phi_l\sin\theta_l\right)\delta\left(R_3 - d\sum_{l=1}^{M}\cos\theta_l\right)\right\rangle \end{aligned}$$

With the use of the Fourier representation of the delta function we get,

$$P(\mathbf{R}_{ee}) = \frac{1}{(2\pi)^3}\int d\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{R}_{ee}} G_1^M(\mathbf{k})$$

$$G_1(\mathbf{k}) = \frac{\sin(kd)}{(kd)}$$

where $G_1(\mathbf{k})$ is the single molecule generating function in the Fourier space. After a straightforward manipulation and multiplying with the surface element of a hyper-sphere,

$$P(R_{ee}) = \frac{2\pi^{D/2}R_{ee}^{D-1}}{\Gamma(D/2)}P(\mathbf{R}_{ee}), \quad D = 3 \quad \text{for us}$$

we end up with the following exact answer for the probability density,

$$P(R_{ee}) = \frac{2}{\pi}\int_0^\infty (kR_{ee})\sin(kR_{ee})\left(\frac{\sin(kd)}{(kd)}\right)^M dk$$

This is the 3D random flight with individual flight length d and with the number of wing flaps being $M = N - 1$. We can play with the low k limit of the integral and recover the central limit theory answer where the bird stays on average at the origin after many wing flaps. Notice how we solved for the extensive variable. It is straightforward to solve for the intensive variable r if needed. I solved for the extensive variable R_{ee} in order to compare with the mathematics literature.

3.2 Large deviations theory

Our analysis is based on the intensive/extensive relation between γ and $\mathbf{R}_{ee}$. More specifically we recall,

$$e^{M\lambda(\gamma)} = \left\langle e^{\gamma\cdot\mathbf{R}_{ee}}\right\rangle$$

$$\mathbf{R}_{ee} = M\nabla_\gamma\lambda(\gamma)$$

$$P(\mathbf{R}_{ee}) \sim e^{-MI(\mathbf{R}_{ee})}$$

$$I(\mathbf{R}_{ee}) = \gamma\cdot\frac{\mathbf{R}_{ee}}{M} - \lambda(\gamma)$$

And for isotropic probability distributions we can write everything in terms of the modulus of $\mathbf{R}_{ee}$. More specifically, we have,

$$r = \frac{R_{ee}}{Md}$$

and

$$g = \gamma d$$

which leads to the drastic simplification of our formulas,

$$r = \frac{d\lambda(g)}{dg}$$

$$I(\mathbf{R}_{ee}) = r(g)g - \ln\left(\frac{\sinh g}{g}\right), \qquad r(g) = \coth g - \frac{1}{g}$$

$$P(\mathbf{R}_{ee}) \sim e^{-MI(\mathbf{R}_{ee})}$$

where the function $r(g)$ is called the Langevin function and is of great interest in single molecule force-extension experiments. In fact, Pade' interpolation has already been used extensively as a way of accurately representing the more complicated Langevin function with simple ratios of polynomials.

Furthermore, we recover an old mathematical result from Kuhn and Grun,

$$P(\mathbf{R}_{ee}) \sim \left(\frac{\sinh \beta(r)}{\beta(r) \exp\left(r\beta(r)\right)}\right)^M$$

where $\beta(r)$ is the inverse function of the Langevin function. Basically this is a manifestation of the fact that the Gaertner-Ellis theorem is derived through a saddle point approximation method.

3.3 Low g limit

The cumulant generating function for the low field g simplifies to,

$$\lambda(g) = \ln \frac{\sinh g}{g} \approx \frac{g^2}{6} + \mathcal{O}(g^4), \quad g \to 0$$

and the equation of state reads,

$$r(g) = \coth g - \frac{1}{g} \approx \frac{g}{3} + \mathcal{O}(g^3), \quad g \to 0$$

which yields the following central limit theory equation of state,

$$g^{clt}(r) \approx 3r + \mathcal{O}(r^3), \quad r \to 0$$

3.4 Large g limit

$$r(g) = \coth g - \frac{1}{g} \approx 1 - \frac{1}{g} + \mathcal{O}(e^{-2g}), \quad g \to \infty$$

which implies,

$$g(r) = \frac{1}{1-r} + \eta^{uncorr}, \quad r \to 1$$

In the case of 2D liquid crystals we had $\eta^{uncorr} = \frac{1}{4}$. In our case I think it is $\eta^{uncorr} = 0$ because the remainder terms from the power series in the large limit all include exponentials. I am not sure though so I will keep it as η^{uncorr}.

3.5 Simulation

It is a trivial sampling of 3D unit vectors. A 20-line Python code.

4 Interacting case

4.1 Central limit theory answer and contact with simple models in the polymer physics literature

For the interacting case we can solve the low field limit exactly using the standard methods of statistics,

$$\lambda(g) \approx \frac{\chi}{6} g^2 + \mathcal{O}(g^4), \quad g \to 0$$

with

$$\chi = \left\langle \frac{1}{M} \sum_{l,l'=1}^{M} \hat{\Omega}_l \cdot \hat{\Omega}'_l \right\rangle = \frac{\left\langle R_{ee}^2 \right\rangle}{Md^2} = M \left\langle r^2 \right\rangle$$

$$\text{In general} \quad \langle x_\mu x_\nu \rangle = \frac{1}{D} \langle \mathbf{x} \cdot \mathbf{x} \rangle$$

We can make connections with the polymer-physics literature. In the context of the so called "Freely jointed chain model",

$$\left\langle R_{ee}^2 \right\rangle = \chi_M M d^2$$

χ_M is called Flory's characteristic ratio and when the chain obtains its maximum end-to-end distance we have,

$$Mb = R_{max}$$

where b is called the Kuhn monomer length. For large polymers we can approximate the characteristic ratio with its saturated value at $M \to \infty$ (Thermodynamic limit for us) and say,

$$\left\langle R_{ee}^2 \right\rangle \approx \chi_\infty M d^2$$

e.g. for 1,4-Polyisoprene (PI) with ,

$$-(CH_2CH = CHCH(CH_3))-, \quad \chi_\infty = 4.6 \quad \text{and} \quad b = 8.2\mathring{A}$$

(Values taken from M. Rubinstein, Ralph H. Colby - Polymer Physics).

Back to large deviations. It can be proven rigorously that the odd-body terms in the scaled cumulant generating function vanish because of symmetry reasons. The corresponding equation of state now is,

$$g^{clt}(r) = \frac{3}{\chi} r + \mathcal{O}(r^3), \quad r \to 0$$

This linear relation between the field and the extension of the rubber band is known as Hooke's law. In D dimensions we have,

$$g^{clt}(r) = \frac{D}{\chi} r$$

4.2 Large g limit

The large field limit of the equation of state will be modified by a mean field correlation constant just as in the case of liquid crystals,

$$g(r) = \frac{1}{1-r} + \eta^{corr}, \quad \eta^{corr} = -\eta^{uncorr} - c$$

Again, η^{uncorr} will be derived from inverting the field limit power series. In our case it is going to be zero. Again, in D dimensions we get,

$$g(r) = \frac{D-1}{2} \frac{1}{1-r}$$

4.3 Pade' interpolation

We know only the limiting behaviors,

$$g(r) = \begin{cases} \frac{3}{\chi} r + O(r^3), & r \to 0 \\ \\ \frac{1}{(1-r)} + \eta^{corr}, & r \to 1 \end{cases} \quad \text{or} \quad g(r) = \begin{cases} \frac{D}{\chi} r + O(r^3), & r \to 0 \\ \\ \frac{D-1}{2}\frac{1}{(1-r)} + \eta^{corr}, & r \to 1 \end{cases}$$

By looking at the odd symmetry in r of the low field limit we can write down an odd Pade' approximant for $g(r)$,

$$g(r) = \frac{3}{\chi}\frac{r + Ar^3 + Br^5}{1 - r^2} \quad \text{or} \quad g(r) = \frac{D}{\chi}\frac{r + Ar^3 + Br^5}{1 - r^2}$$

where

$$A + B + 1 = \frac{2\chi}{3}$$

$$\frac{3B}{4\chi} = \frac{1}{4}(\delta^{pol} + c + \eta^{uncorr} - \frac{1}{2}), \quad \delta^{pol} = \frac{3}{\chi} - 2$$

$$\text{in D-dim:} \quad \frac{D}{\chi}B = -\frac{1}{4}(D-1) - \eta^{corr} + \delta^D$$

$$\delta^D = \frac{D}{\chi} - (D-1)$$

By integration we get the rate function,

$$I(\mathbf{R}_{ee}) = \frac{1}{2}\delta^{pol} r^2 - \frac{3B}{4\chi} r^4 - \ln(1 - r^2)$$

$$I(\mathbf{R}_{ee}) = \frac{1}{2}\delta^{D} r^2 - \frac{DB}{4\chi} r^4 - \frac{1}{2}(D-1)\ln(1 - r^2)$$

Finally the probability density is,

$$P(r) \sim r^2(1 - r^2)^M \exp\left(-\frac{M}{2}\delta^{pol} r^2\right) \exp\left(M\frac{3B}{4\chi} r^4\right)$$

$$P(r) \sim r^2(1 - r^2)^{M(D-1)/2} \exp\left(-\frac{M}{2}\delta^{D} r^2\right) \exp\left(M\frac{DB}{4\chi} r^4\right)$$

5 Radius of gyration

The radius of gyration is defined as,

$$R_g^2 = \sum_k \sum_l c_{k,l} \vec{r}_k \cdot \vec{r}_l$$

which is the square of the modulus of the vector that has components,

$$(\vec{R}_g)_l = \sum_k \sqrt{c_{k,l}} r_k$$

The low field limit of the probability distribution of the modulus of the vector has been worked out by Fixman. The answer reads,

$$P(R_g) \approx 18 \left(\frac{6}{\pi \left\langle R_g^2 \right\rangle}\right)^{1/2} t^{-5/2} \exp\left(-\frac{9}{4t}\right)$$

$$t = \frac{R_g^2}{\left\langle R_g^2 \right\rangle} = \frac{6R_g^2}{Mb}$$

6 Appendix

6.1 Symmetry of the non-interacting cumulant generating function

6.2 Symmetry of the interacting cumulant generating function

By definition,

$$e^{N\lambda(\vec{g})} = \left\langle \exp\left(\vec{g} \cdot \sum_{j=1}^{N} \hat{e}_j\right) \right\rangle$$

The logarithm of the MGF will give a power series where each term is an n-body correlation,

$$N\lambda(\vec{g}) = \frac{1}{2!}\left\langle \sum_{j,k}^{N}\sum_{p,q}^{3} e_j^p e_k^q g^p g^q \right\rangle + \frac{1}{3!}\left\langle \sum_{j,k,l}^{N}\sum_{p,q,r}^{3} e_j^p e_k^q e_l^r g^p g^q g^r \right\rangle + \mathcal{O}(g^4)$$

$$\hat{e}_j = \{e_j^p\}_{\{p=1,2,3\}} = \begin{pmatrix} \cos\phi_j \sin\theta_j \\ \sin\phi_j \sin\theta_j \\ \cos\theta_j \end{pmatrix}$$

$$\hat{e}_k = \{e_k^q\}_{\{q=1,2,3\}} = \begin{pmatrix} \cos\phi_k \sin\theta_k \\ \sin\phi_k \sin\theta_k \\ \cos\theta_k \end{pmatrix}$$

$$\hat{e}_l = \{e_l^r\}_{\{r=1,2,3\}} = \begin{pmatrix} \cos\phi_l \sin\theta_l \\ \sin\phi_l \sin\theta_l \\ \cos\theta_l \end{pmatrix}$$

The first cumulant will be identically zero as we are in the isotropic phase. Insight from the non-interacting case dictates that the odd terms will be zero as well. The second cumulant is a matrix and only the diagonal elements ($p = q = r$) are non-zero. In fact they are the same,

$$\left\langle \sum_{j,k}^{N}\sum_{p}^{3} e_j^p e_k^p \right\rangle = \frac{1}{3}\left\langle \sum_{j,k=1}^{N} P_1(\hat{e}_j \cdot \hat{e}_k) \right\rangle$$

And the third (odd) term is,

$$\left\langle \sum_{j,k,l}^{N}\sum_{p}^{3} e_j^p e_k^p e_l^p \right\rangle = \sum_{j,k,l}^{N} \langle P_1(\hat{e}_j \cdot \hat{x}) P_1(\hat{e}_k \cdot \hat{x}) P_1(\hat{e}_l \cdot \hat{x}) \rangle = 0$$

It does not matter which axis we measure the orientations from,

$$P_1(\hat{e}_j \cdot \hat{x}) P_1(\hat{e}_k \cdot \hat{x}) P_1(\hat{e}_l \cdot \hat{x}) = \int d\hat{x} P_1(\hat{e}_j \cdot \hat{x}) P_1(\hat{e}_k \cdot \hat{x}) P_1(\hat{e}_l \cdot \hat{x})$$

because we integrate odd functions over a whole cycle the result is zero. In general,

$$\int d\hat{x} \prod_{t=1}^{T} P_1(\hat{e}_t \cdot \hat{x}) = \begin{cases} = 0, & T = 2n+1 \\ \neq 0, & T = 2n \end{cases}$$

In the 3D liquid crystal case, the odd terms consist of even functions and so they do not go to zero,

$$\int d\hat{x} \prod_{s=1}^{S} P_2(\hat{e}_s \cdot \hat{x}) = \begin{cases} \neq 0, & S = 2n+1 \\ \neq 0, & S = 2n \end{cases}$$