Statistical Mechanics of Polymers

(A) Polymers with repulsive contact interactions

Random walk in a square lattice of length N

$$\vec{e} = (\bar{r}_0, \bar{r}_1, \dots \bar{r}_N) \quad \text{with } |\bar{r}_i - \bar{r}_{i-1}| = a \quad \forall i = 1, \dots, N$$

Energy: $\mathcal{H} = J_0 \sum_{\substack{i=0 \\ i \neq j}}^{N} \sum_{j=i}^{N} \delta_{\bar{r}_i \bar{r}_j}$

limiting cases $\begin{cases} \beta J_0 \to 0 \text{ - no interaction} \\ \qquad \text{Gaussian chain} \\ \beta J_0 \to \infty \text{ - excluded volume} \\ \qquad \text{interaction} \end{cases}$

polymer with self-avoidance

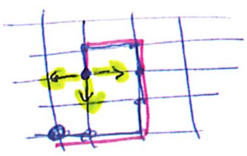
End-to end distance

$$\langle R^2 \rangle = \frac{\sum_{\bar{e}} (r_N - r_0)^2 \exp[-\beta \mathcal{H}\{\bar{e}\}]}{\sum_{\bar{e}} \exp[-\beta \mathcal{H}\{\bar{e}\}]}$$

⇝ the summation considers all random walks

- In case $\beta_0 J_0 \to \infty$ the Boltzmann factor suppreses all configurations with overlapps.
  → such configurations don't need to be considered for followed, but it is important that they all appear with the same probability

(B) Biased sampling - Rosenbluth method



To calculate the averages, the biased configuration should be considered with a lower probability

K - unbiased step probability factor
ℓ - biased " "

in the previous example $\begin{cases} K_i = 3 \\ \ell_i = 2 \end{cases}$

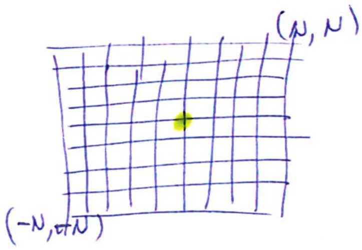
$$\rightsquigarrow Q = \prod_{i=1}^{N} \frac{l_i}{K}$$

The final average length over all configurations then

$$\langle R_e^2 \rangle = \frac{\langle \sum_{m=1}^{M} Q^m R_e^{2\,m} \rangle}{\sum_{m=1}^{M} Q^m}$$; with $M \equiv$ # polymer configurations

(C) Effective self-avoidance check

- In principle each new vector $\bar{r}_i$ has to be verified with all the previous ones $\bar{r}_0, \dots, \bar{r}_{i-1}$
- Improvement: define an occupancy grid field in 2d matrix $OG(i_1, i_2)$ with $i_1, i_2 \in [-N, N]$

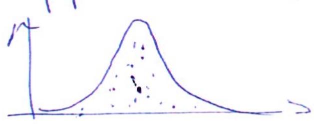


- Starting configuration $OG(i_1, i_2) = 0 \ \forall i_1, i_2$
- then $OG(0,0) = 1$
- For each new position vector accepted $\underline{r}_k = i_x \underline{e}_x + i_y \underline{e}_y \Rightarrow OG(i_x, i_y) = 1$

- self-avoidance means that only places with $OG(i_1, i_2) = 0$ can be newly accepted

(D) Central limit theorem (CLT)

The sum of a large number of independent and identically distributed random variables will be approximately normally distributed



$\rightsquigarrow$ Gaussian or bell-shaped distribution

(E) Flory theory of self-avoiding polymers

- The distribution of the end-to-end lengths of ideal chains (no self-avoidance) has the Gaussian form.

$$P_N(R_e) = \left(\frac{3}{2\pi N a^2}\right)^{3/2} \exp\left(-\frac{3R_e^2}{2Na^2}\right) \qquad \text{from CLT}$$

polymer $\longleftrightarrow$ random walk $\longleftrightarrow$ diffusion

- Estimation of the free energy: two contributions

i) Entropic elasticity

$$F_{elast} \sim -k_BT \ln P_N(R) \sim \frac{3k_BT}{2Na^2} R^2 \sim \frac{R^2}{\beta N}$$

ii) Interaction energy

$$F_{int} \sim \omega \int_{V_{Pol}} d^d r \, \underbrace{\rho^2}_{\text{2 particle interaction}} \sim \omega \frac{N^2}{R^d}$$

with $\begin{cases} \rho \sim N/V_{pol} \\ V_{pol} \sim R^d \end{cases}$

Total free energy can be approximated as: $F = F_{int} + F_{elas}$

To determine the average polymer radius R, the free energy can be minimized with respect to R.

$$\frac{\partial F}{\partial R} \stackrel{!}{=} 0 \simeq -\frac{\omega N^2}{R^{d+1}} + \frac{R}{\beta N} \rightsquigarrow N^3 \sim R^{d+2}$$

$$\Rightarrow \boxed{R \sim N^{\nu_F} \quad \text{with} \quad \begin{array}{l} \nu_F \equiv \text{Flory exponent} \\ \nu_F = \dfrac{3}{d+2} \end{array}}$$

Comparison with more precise evaluations of ν

d	ν_F	ν
1	1	exact
2	3/4	exact
3	3/5	0.588

2.2 - Importance sampling

This is a weighted scanning of the phase space

2.2.1 Markov process and master equation

The Boltzmann factor leads to a probability concentrated on an ~~any~~ extremely small subset of the phase space

Goal: selection of configurations already according to the Boltzmann weight $\{s_j\}$

The average is then trivial $\langle A \rangle = \frac{1}{M} \sum_{j=1}^{M} A\{s_j\}$

Markov process: These are stochastic processes in which the probability $p(x,t)$ of an outcome 'x' at time 't' is determined exclusively by the distribution $p(x,t')$ at an earlier time t'

- A Markov process is completely determined by the conditional probability $p(\underline{x}, t | \underline{x}', t')$

$$p(x,t) = \sum_{x'} p(\underline{x}, t | \underline{x}', t') \, p(x', t')$$

- A Markov process is called time homogeneous if

$$p(x, t | x', t') = p(x, t-t' | x', 0) = p(x, x'; t)$$

which we assume in the following

- The dynamics of a Markov process is determined by

$$\boxed{\frac{\partial}{\partial t} p(x, x''; t) = \sum_{x'} \omega(x|x') p(x', x''; t) - \omega(x'|x) p(x, x''; t)}$$

a Master equation

with $\omega(x|x') \equiv$ transition probability for $x' \to x$ in each time unit

1^{st} term : win process $\bar{x}' \to \bar{x}$
2^{nd} term : loose process $\bar{x} \to \bar{x}'$

$\rightsquigarrow$ the transition probabilities should be defined with a Physical basis

Normalization :

$$\frac{d}{dt} \sum_x p(x, x''; t) = \sum_x \frac{\partial}{\partial t} p(x, x''; t)$$

$$= \sum_x \sum_{x'} \left[\omega(x|x') p(x', x''; t) - \omega(x'|x) p(x, x''; t) \right] = 0$$

normalization translates into $\sum_x p(x, x'' t) = 1$

2.2.2 Detailed balance

- In case of thermal equilibrium i.e. for $t \to \infty$ the probability has to be given by the Boltzmann distrib.

$$p(x, x'; t) \xrightarrow[t \to \infty]{} \tilde{A} \exp[-\beta \mathcal{H}(x)]$$

- with $\tilde{A}$ normalization factor $\tilde{A} = 1/Z$
- independent from the starting configuration

- Sufficient condition for a stationary distribution

$$\omega(x|x') p(x') = \omega(x'|x) p(x)$$

for the Boltzmann distribution it follows

$$\boxed{\frac{\omega(x|x')}{\omega(x'|x)} = \frac{p(x)}{p(x')} = \exp\{-\beta [\mathcal{H}(x) - \mathcal{H}(x')]\}}$$

Important

- Normalization factor $\tilde{A}$ does <u>not</u> appear
$\rightsquigarrow$ this means that the knowledge of the partition function is <u>not</u> necessary to determine the transition rates $\rightsquigarrow$ otherwise the procedure would be worthless)

- the transition rates are not fixed by the detailed balance conditions since there are always infinitely many possibilities.

Mostly two versions are used.

(i) Metropolis version

$$\omega(x|x') = \min\left[1, \exp(-\beta\,\Delta E)\right]$$

$$\Delta E = \mathcal{H}(x) - \mathcal{H}(x')$$

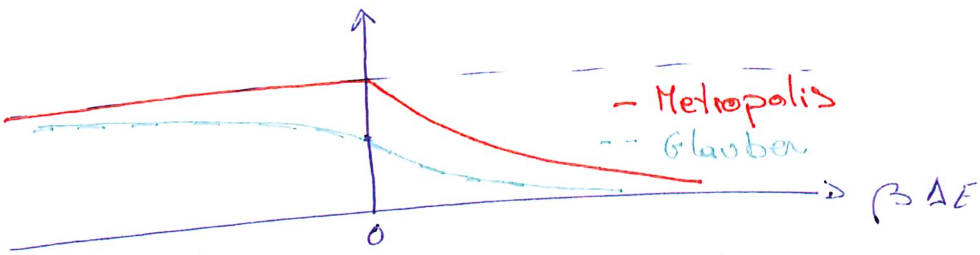
when the new state $\underline{x}$ has lower energy than the previous one x', then the transition occurs with probability 1; otherwise the probability is

$$p = \exp(-\beta\,\Delta E) < 1$$

(ii) Glauber - version

smoother version of the Metropolis algorithm

$$\omega(x, x') = \frac{1}{2}\left[1 - \tanh\left(\frac{\beta}{2}\,\Delta E\right)\right]$$



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