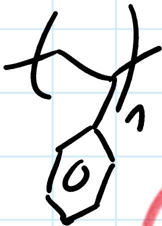
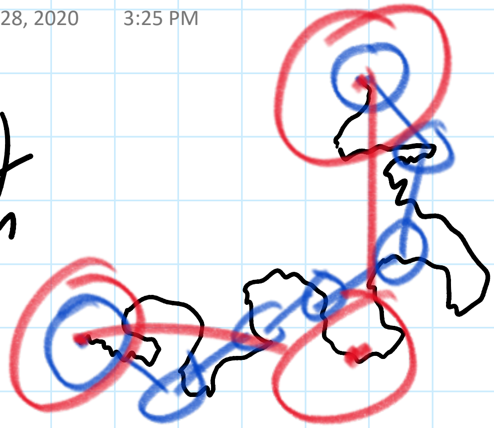
Lecture 4: Polymers in fields

Thursday, May 28, 2020 3:25 PM





Discrete Gaussian model: $(N+1)$ monomers w/ step size b

Bonding potential: $\beta U_0 = \sum_{s=1}^{N} \frac{3}{2b^2} |\underline{r}_s - \underline{r}_{s+1}|^2$

Partition of one $(n=1)$ Gaussian chain:

$$Z = \frac{1}{n! \lambda_T^{3n(N+1)}} \int d\underline{r}^{N+1} e^{-\beta U_0}$$

Consider $N=1$

$$Z = \frac{1}{n! \lambda_T^{3n(2)}} \int d\underline{r}_1 \int d\underline{r}_2 \, e^{-\frac{3}{2b^2} |\underline{r}_1 - \underline{r}_2|^2}$$

$\underline{r}_{21} = \underline{r}_2 - \underline{r}_1$

$d\underline{r}_{21} = d\underline{r}_2$

$$Z = \frac{1}{n! \lambda_T^{3n \cdot 2}} \int d\underline{r}_1 \int d\underline{r}_{21} \, e^{-\frac{3}{2b^2} |\underline{r}_{21}|^2}$$

$$= \frac{1}{n! \lambda_T^{3n \cdot 2}} \left(\frac{2\pi b^2}{3} \right)^{3/2} \cdot V$$

Now for $N=2$:

$$Z = \frac{1}{n!\lambda_T^{3n\cdot 3}} \int d\underline{r}_1 \, d\underline{r}_2 \, d\underline{r}_3 \, e^{-\frac{3}{2b^2}|\underline{r}_3 - \underline{r}_2|^2} \cdot e^{-\frac{3}{2b^2}|\underline{r}_2 - \underline{r}_1|^2}$$

$$r_{32} = r_3 - r_2 \qquad dr_{32} = dr_3$$

$$Z = \frac{1}{n!\lambda_T^{3n\cdot 3}} \int d\underline{r}_1 \int d\underline{r}_2 \, e^{-\frac{3}{2b^2}|\underline{r}_2 - \underline{r}_1|^2} \times \int dr_{32} \, e^{-\frac{3}{2b^2}|r_{32}|^2}$$

$$Z = \frac{1}{n!\lambda_T^{3n\cdot 3}} \cdot V \cdot \left(\frac{2\pi b^2}{3}\right)^{3\cdot 2/2}$$

In general: $Z = \frac{V}{n!\lambda_T^{3n(N+1)}} \left(\frac{2\pi b^2}{3}\right)^{\frac{3N}{2}}$

Single polymer in an external field:

$$\beta U = \beta U_0 + W$$

$$W = \int d\underline{r} \, w(\underline{r}) \, \hat{\rho}(\underline{r})$$

$$\hat{\rho}(\underline{r}) = \sum_{s=1}^{N+1} \delta(\underline{r} - \underline{r}_s)$$

$$W = \sum_{s=1}^{N+1} w(\underline{r}_s)$$

$$Z = \frac{1}{n!\lambda_T^{3n(N+1)}} \int d\underline{r}^{N+1} \, e^{-\beta U_0 + W}$$

$$Q[w] \equiv \frac{1}{V} \cdot g_0^N \int d\underline{r}^{N+1} \, e^{-\beta U_0 - W}$$

$$Q[\omega] = V g_0 \int d\mathbf{r} \;\; e$$

$$g_0 = \left(\frac{3}{2\pi b^2}\right)$$

$$Z = \frac{V}{n!\,\lambda_T^{3n(N+1)}} \frac{1}{g_0^N} Q[w]$$

$$Q[w] = \frac{g_0^N}{V} \int d\mathbf{r}_1\, d\mathbf{r}_2 \dots d\mathbf{r}_{N+1} \cdot e^{-w(\mathbf{r}_{N+1})} \cdot e^{-\frac{3}{2b^2}|\mathbf{r}_{N+1}-\mathbf{r}_N|^2} \cdot e^{-w(\mathbf{r}_N)}$$
$$\dots\; e^{-w(\mathbf{r}_2)}\, e^{-\frac{3}{2b^2}|\mathbf{r}_2-\mathbf{r}_1|^2} \cdot e^{-w(\mathbf{r}_1)}$$

Bond transition probability:

$$\phi(\mathbf{r}) = \left(\frac{3}{2\pi b^2}\right) e^{-\frac{3}{2b^2}|\mathbf{r}|^2}$$

Each $\phi(r)$ is a normalized Gaussian distribution
$\int dr\, \phi(r) = 1$

$$Q = \frac{1}{V} \int d\mathbf{r}_1\, d\mathbf{r}_2 \dots d\mathbf{r}_{N+1}\, e^{-\omega(r_{N+1})}\, \phi(r_{N+1}-r_N)\, e^{-\omega(r_N)}$$
$$\dots\; e^{-\omega(r_2)}\, \phi(r_2-r_1)\, e^{-\omega(r_1)}$$

$$e^{-\omega_{N+1}} \equiv e^{-\omega(r_{N+1})}$$

$$Q = \frac{1}{V} \int d\mathbf{r}_2\, dr_3 \dots dr_{N+1}\, e^{-\omega_{N+1}} \dots e^{-\omega_2}$$
$$\times \underline{\int dr_1\, \phi(r_2-r_1)\, e^{-\omega_1}}$$

Convolution operation result is "$q(\underline{r}_2)$"

$$Q = \frac{1}{V}\int dr_3 \dots dr_{N+1}\, e^{-\omega_{N+1}} \dots e^{-\omega_3} \times \int d\underline{r}_2\, \underline{\Phi(r_3 - r_2)} \cdot \underline{e^{-\omega(r_2)}\, q}(r_2)$$

Convolution, result "$q(\underline{r}_3)$"

Same operations repeated

Define in general our propagator

$$q(\underline{r}, s+1; [\omega]) = e^{-\omega(r)} \int dr'\, \Phi(r - r')\, q(r', s; [\omega])$$

with the initial condition

$$q(\underline{r}, s=1; [\omega]) = e^{-\omega(\underline{r})}$$

The molecular partition function:

$$Q[\omega] = \frac{1}{V}\int d\underline{r}\; q(\underline{r}, N+1; [\omega])$$

Many chains in fields

"Edwards model" Proc Phys Soc, 1965

Microscopic density $\hat{\rho}(\underline{r}) = \sum_{j=1}^{n} \sum_{s=1}^{N+1} \delta(\underline{r} - \underline{r}_{j,s})$

Non-bonded potential: $u(r) = kT\, u_0 \cdot \delta(r)$

$$u_0 > 0$$

Total non-bonded energy:

$$\beta U_1 = \frac{u_0}{2} \int dr \left[\hat{\rho}(r)\right]^2 - n\frac{(N+1)u_0}{2}$$

Bonded energy

$$\beta U_0 = \sum_{j=1}^{n} \sum_{s=1}^{N+1} \frac{3}{2b^2} \left| \underline{r}_{j,s} - \underline{r}_{j,s+1} \right|^2$$

Partition function:

$$Z = \frac{1}{n!\, \lambda_T^{3n(N+1)}} \int d\underline{r}^{n(N+1)}\, e^{-\beta U_0 - \beta U_1}$$

$$Z = \frac{1}{n!\, \lambda_T^{3n(N+1)}} \frac{1}{\Omega_0} \int \mathcal{D}\omega \int d\underline{r}^{n(N+1)} \cdot e^{-\frac{1}{2u_0} \int dr \left[\omega(r)\right]^2} \cdot e^{-i \int dr\, \omega(r) \hat{\rho}(r) - \beta U_0}$$

Collect the terms that depend on $\underline{r}^{n(N+1)}$:

$$\int d\underline{r}^{n(N+1)}\, e^{-i \int dr\, \omega(r) \sum_{j=1}^{n} \sum_{s} \delta(r - r_{j,s}) - \beta U_0}$$

$$= \int d\underline{r}^{n(N+1)} \prod_{j=1}^{n} e^{-i \sum_s \omega(r_{j,s}) - \sum_s \frac{3}{2b^2} \left| r_{j,s} - r_{j,s+1} \right|^2}$$

$$j=1$$

$$= \left[\int d\underline{r}^{N+1} \exp\left(-i\sum_s \omega(r_s) - \sum_s \frac{3}{2b^2}|r_s - r_{s+1}|^2\right)\right]^n$$

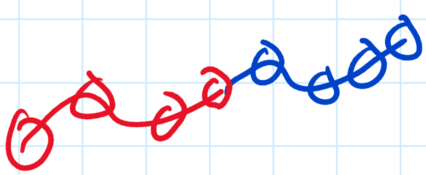
$$= \left(\frac{V}{g_0} Q[i\omega]\right)^n$$

Total partition function:

$$Z = \frac{z_2 V^n}{n!\,\Omega_0}\int D\omega\, e^{-H[\omega]}$$

$$H[\omega] = \frac{1}{2u_0}\int dr\,[\omega(r)]^2 - n\log Q[i\omega]$$

Diblock Copolymer



N_A sites of A
N_B sites of B

$$N_A + N_B = N+1$$

$$f_A = \frac{N_A}{N+1}$$

All the A monomers experience one field $\omega_A(r)$
B monomers $\omega_B(r)$

$$Q[\omega_A, \omega_B] = \frac{1}{V}\int d\underline{r}^{N_A+N_B}\, e^{-\omega_A(r_1)}\phi(r_1-r_2)\, e^{-\omega_A(r_2)}\phi(r_2-r_3)$$
$$\dots\, e^{-\omega_A(r_{N_A})}\phi(r_{N_A}-r_{N_A+1})\, e^{-\omega_B(r_{N_A+1})}$$

$$\ldots\; e^{-\omega_A(r_{N_A})}\,\phi(r_{N_A}-r_{N_A+1})\,e^{-\omega_B(r_{N_A+1})}$$

$$\ldots\; \phi(r_N - r_{N+1})\,e^{-\omega_B(r_{N+1})}$$

$$q(\underline{r}, s+1) = \begin{cases} e^{-\omega_A(r)} \int dr'\, \phi(r-r')\, q(r', s) & s = 2 \ldots N_A \\ e^{-\omega_B(r)} \int dr'\, \phi(r-r')\, q(r', s) & s = N_A+1 \ldots N+1 \end{cases}$$

$$Q = \frac{1}{V}\int dr\, q(r, N+1)$$

Standard field theory model:

- Incompressibility: $\delta[\rho_0 - \hat{\rho}_A(r) - \hat{\rho}_B(\underline{r})]$
- Flory "chi" interaction:

$$\beta U_1 = \chi \int dr\, \hat{\rho}_A(r)\, \hat{\rho}_B(r)$$

Trace through the transformation

$$Z = z_1 \int D\omega_+ \int D\omega_-\, e^{-\mathcal{H}[\omega_+, \omega_-]}$$

$$\mathcal{H} = \frac{1}{\chi}\int dr\,[\omega_-(r)]^2 - i\rho_0 \int dr\, \omega_+(r) - n_D \log Q_D[\omega_A, \omega_B]$$

$$\omega_A(r) = i\omega_+(r) - \omega_-(r)$$

$$\omega_B(r) = i\omega_+(r) + \omega_-(r)$$

Mean-field equations:

$$\frac{\delta \mathcal{H}}{\delta \omega_+} = -i\rho_0 + i\left[\tilde{\rho}_A(r) + \tilde{\rho}_B(r)\right] = 0$$

$$\frac{\delta \mathcal{H}}{\delta \omega_-} = \frac{2}{\chi}\omega_-(r) + \tilde{\rho}_B(r) - \tilde{\rho}_A(r) = 0$$

Numerical solution:

$$\frac{\partial \omega_-(r)}{\partial t} = -\left(\frac{\delta \mathcal{H}}{\delta \omega_-}\right)$$

$$\frac{\omega_-^{t+\delta t} - \omega_-^{t}}{\delta t} = -\underline{\left(\frac{\delta \mathcal{H}}{\delta \omega_-}\right)}_t$$