Lecture 10 Polymer Statistics and Critical Phenomena

In critical phenomena (P. G. de Gennes 1972)
Correlation length

$$\xi \simeq a_0 |\tau|^{-\nu}, \text{ where } \tau = \frac{T-T_c}{T_c}$$

For polymers Flory radius

$$R_F \simeq a N^{\nu}$$

We will see, that there is correspondence between N^{-1} and τ.

Polymer statistics (self avoiding walks) is equivalent to the $O(n)$ vector model with $\underline{n=0}$!!!

n-vector model: n component spins $S_{i\alpha}$ with the length S fixed by normalisation

$$S^2 = \sum_{\alpha=1}^{n} S_{i\alpha}^2 = n$$

O(1) - Ising model
O(2) - XY —"—
O(3) - Heisenberg —"—

Hamiltonian:

$$H = -\sum_{i>j} K_{ij} \vec{S}_i \cdot \vec{S}_j$$

nearest neighbour interaction $K_{ij} = K$ for near. neigh.

$$Z = \prod_i \int d\Omega_i \exp\left(-\frac{H}{T}\right)$$

angular integration

Usual expansion in interaction

$$\exp(K_{ij}\,\vec{S}_i\vec{S}_j/T) = 1 + \frac{K_{ij}}{T}\vec{S}_i\vec{S}_j + \frac{1}{2}\left(\frac{K_{ij}}{T}\right)^2\left(\vec{S}_i\cdot\vec{S}_j\right)^2 + \ldots$$

and we should average over the angles of each spin. Let us denote such average as $\langle\ \rangle_0$

Thermal average is $\langle G\rangle = \dfrac{\langle \exp(-\frac{H}{T})\,G\rangle_0}{\langle \exp(-\frac{H}{T})\rangle_0}$

Consider one of the vectors $\vec{S}_i$, then

$\langle S_\alpha\rangle_0 = 0$ (the same for all odd powers)

$\langle S_\alpha S_\beta\rangle_0 = \delta_{\alpha\beta}$. All diagonal terms are equal and their sum $= n$ (normalization).

For $n=0$ all higher order products $= 0$!

Really from $O(n)$ symmetry

$$\langle S_\alpha S_\beta S_\gamma S_\delta\rangle_0 = A(n)\left[\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\gamma\beta}\right]$$

Setting $\alpha=\beta$, $\gamma=\delta$ and summing over α ang γ we obtain $n^2 = A(n)\left[n^2 + 2n\right]$

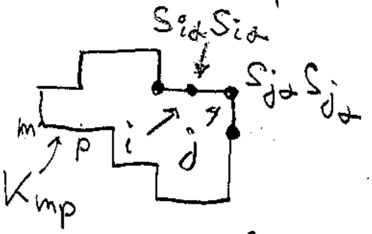
For $n\to 0$ $A(n)\sim \frac{n}{2}\to 0$. Thus

$\langle S^4\rangle_0 = 0$. In this case expansion of $\langle e^{-\frac{H}{T}}\ \rangle_0$ is strongly simplified

$$\frac{Z}{\Omega} = \langle \prod_{i>j} \exp \frac{K_{ij}}{T} \sum S_{i\alpha} S_{j\alpha} \rangle_0 =$$

$$= \langle \prod_{i>j} \left(1 + \frac{K_{ij}}{T} \sum_\alpha S_{i\alpha} S_{j\alpha} + \frac{1}{2} \left(\frac{K_{ij}}{T}\right)^2 \sum_{\alpha\beta} S_{i\alpha} S_{j\alpha} S_{i\beta} S_{j\beta} \right\rangle_0$$

Every term can be represented as a graph on the lattice



To each bond $\frac{K_{ij}}{T}$

To each site $S_{i\alpha} S_{i\alpha}$

Nonzero contribution is only from the closed loops

Loop can never cross itself. Otherwise $\langle S_i^4 \rangle_0 = 0$

Quadratic term – smallest loop i ⊂⊃ j $\left(\frac{K_{ij}}{T}\right)^2$

Each loop has a single index α at all sites

When we sum over α for one loop we obtain

$$\left(\frac{K}{T}\right)^N n = 0 \qquad (N - \text{number of bonds})$$

Thus contribution from all loops vanishes and

$$\frac{Z}{\Omega} = 1 \qquad (n=0)$$

Consider now spin-spin correlation function

$$\langle S_{i\alpha} S_{j\alpha} \rangle = \frac{\langle \exp -\frac{H}{T} S_{i\alpha} S_{j\alpha} \rangle_0}{\langle \exp -\frac{H}{T} \rangle_0} = G(R, X) \quad (3)$$

no summation over α $\qquad \langle \exp -\frac{H}{T} \rangle_0 = 1 \qquad X = \frac{K}{T}$

In graphic representation we obtain

If $n_N(R)$ is the number of selfavoiding walks between two points a distance R apart, then

$$\sum n_N(R)\, x^N = \lim_{n\to 0} G(R,x)$$

Consider the total number $n_N \equiv \sum n_N(R)$

Susceptibility is related to the correlation function. Really, if h is small magnetic field then

$$\langle S\rangle_h = \int \mathcal{D}s\; e^{-\int \frac{H(s) - s\cdot h}{T} dV} \cdot S(r_1), \text{ expanding in } h$$

$$\approx \int \mathcal{D}s \int h \cdot \frac{S(r_1)\, S(r_2)}{T} dV_1\, e^{-\int \frac{H(s)}{T} dV} =$$

$$= \frac{h}{T} \int \langle S(0), S(r)\rangle\, dV \Rightarrow$$

$$\chi_T = \frac{1}{T} \sum_R G(R,T)$$

Thus we obtain that

$$\chi_T \propto \sum n_N\, x^N$$

Here n_N is the total number of random walks of N steps, $n_N = \sum_R n_N(R)$

At the transition susceptibility diverges as $(x_c - x)^{-\gamma}$. Expanding in Taylor series

$$\frac{1}{(x_c-x)^\gamma} = \frac{1}{x_c^\gamma}\sum_N \frac{(\gamma+N-1)!}{(\gamma-1)!\,N!}\,\frac{x^N}{x_c^N} \propto \sum \frac{(\gamma+N-1)^{(\gamma+N-1)}}{N^N}\,\frac{x^N}{x_c^N}$$

$$\propto \sum \frac{N^{\gamma-1}}{x_c^N}\,x^N \quad \text{for large } N$$

Thus we see that $n_N \sim \text{const}\, N^{\gamma-1}\tilde{z}^N$,

where γ is susceptibility of $O(n)$ model with $n \to 0$ and $\tilde{z} = x_c^{-1}$.

This is general feature, singularities of thermodynamic quantities at x_c correspond to behaviour of coefficients $n_N(R)$ at large N

Similarly $\langle R^2 \rangle_N = \sum_R \frac{R^2 n_N(R)}{n_N}$

Taking $\sum_R R^2 G(R,x) = \sum_{R,N} n_N(R) R^2 x^N$

and using $\sum_R R^2 G(R,x) \sim \xi^{4-\eta} \sim (x_c - x)^{-\gamma - 2\nu}$

we obtain that $G(R,x) = \xi^{-(d-2+\eta)} \phi(\frac{R}{\xi})$, $\gamma = \nu(2-\eta)$, $\xi = (x_c - x)^{-\nu}$

$$(x_c - x)^{-\gamma-2\nu} = \sum_N \langle R^2 \rangle_N \, x^N \cdot n_N \simeq \sum_N \langle R^2 \rangle_N N^{\gamma-1} \frac{x^N}{x_c^N}$$

Expanding as before near x_c we obtain

$\langle R^2 \rangle_N \, N^{\gamma-1} \sim N^{\gamma+2\nu-1} \Rightarrow$

$$\langle R^2 \rangle \sim N^{2\nu}$$

and we see that Flory exponent ν is the correlation length exponent

From RG

$$\nu = \frac{1}{2} + \frac{n+2}{4(n+8)}\varepsilon + \frac{(n+2)(n^2+23n+60)}{8(n+8)^3}\varepsilon^2 + \dots ,$$

that gives $\nu(d=3) = 0.588$

(Note the Flory result $\nu_3 = 0.6$!)

When we expand the numerator then we again obtain self-avoiding paths, but now they are not closed loops, but just paths connecting i and j

If the walk involves N step then its contribution to corr. function is $\left(\frac{K}{T}\right)^N$. We do not sum over α $\Rightarrow$

$$\langle S_{i\alpha} S_{j\alpha} \rangle_{n=0} = \sum_N \mathcal{N}_N(ij) \left(\frac{K}{T}\right)^N \qquad (4)$$

where $\mathcal{N}_N(ij)$ is the number of self avoiding walks of N steps between i and j.

Susceptibility $\chi_M = \frac{1}{T} \sum_{ij} \langle S_{i\alpha} S_{j\alpha} \rangle =$

$$= \frac{1}{T} \sum \mathcal{N}_N(\text{total}) \left(\frac{K}{T}\right)^N$$

total number of S.a. walks of N steps

we assume $\mathcal{N}_N(\text{total}) \cong \tilde{z}^N N^{\gamma-1}$ $\Rightarrow$

$$\chi_M \cong \frac{1}{T} \sum_N \left(\frac{K\tilde{z}}{T}\right)^N N^{\gamma-1}$$

This sum converges for large T and diverges at $T_c = K\tilde{z}$. For $T = T_c(1+\tau) \cong T_c \exp\tau$ $\Rightarrow$

$$\chi_M \cong \frac{1}{T_c} \sum_N e^{-N\tau} N^{\gamma-1} \cong \frac{1}{T_c} \int dN\, e^{-N\tau} N^{\gamma-1} \simeq \frac{1}{T_c} \tau^{-\gamma}$$

Thus our γ is equal to γ of susceptibility in critical phenomena

Close to the transition point

$$\langle S_{i\alpha} S_{j\alpha} \rangle = \sum_N \tilde{z}^{-N} \exp(-N\tau)\, \mathcal{N}_N(ij)$$

Introducing $P_N(ij) = \dfrac{\mathcal{N}_N(ij)}{\mathcal{N}_N(tot)}$ we obtain

$$\langle S_{i\alpha} S_{j\alpha} \rangle \cong \sum_N N^{\gamma-1} \exp(-N\tau)\, P_N(ij)$$

(Thus $\langle SS \rangle$ and $\langle p \rangle$ are related via Laplace transform and N & τ are "conjugated" variables

$N \nearrow \infty \to \tau \to 0$

correlation length $\xi \sim \tau^{-\nu}$ corresponds to Flory radius $R_F \sim N^{\nu}$

For $r \gg \xi$ $\quad \langle S(r)S(0) \rangle \sim \exp\left(-\frac{r}{\xi}\right) \sim \exp(-r\tau^{\nu})$

(Assuming $P_N(r) \sim \exp\left(-\frac{r^\alpha}{N^\beta}\right)$ with Laplace trasform

$\int \exp\left(-N\tau - \frac{r^\alpha}{N^\beta}\right) dN$ is determined by

$$N\tau \sim \frac{r^\alpha}{N^\beta} \Rightarrow N \sim \frac{r^{\frac{\alpha}{\beta+1}}}{\tau^{1/(\beta+1)}} \text{ and } \langle S(r)S(0) \rangle \sim e^{-r^{\frac{\alpha}{\beta+1}} \tau^{\frac{\beta}{\beta+1}}}$$

But $\langle S(r)S(0) \rangle \sim e^{-r\tau^{\nu}} \Rightarrow \frac{\alpha}{\beta+1} = 1$, $\frac{\beta}{\beta+1} = \nu \Rightarrow \beta = \frac{\nu}{1-\nu}$

$\alpha = \frac{1}{1-\nu} \Rightarrow$

$$P(r) \sim e^{-\left(\frac{r}{N^\nu}\right)^{\frac{1}{1-\nu}}} \sim e^{-\left(\frac{R}{R_F}\right)^{\frac{1}{1-\nu}}}$$

with $R_F \sim N^{\nu}$ | From RG

$$\nu = \frac{1}{2} + \frac{(n+2)}{4(n+8)}\varepsilon + \frac{(n+2)(n^2+23n+60)}{8(n+8)^3}\varepsilon^2 \sim 0.588$$

More formal derivation of the mapping to $(\varphi^2)^2$ theory

We start with the Edwards model

$$\langle A \rangle = \int \mathcal{D}r(t) \exp\Big[-\int_0^N \frac{\dot{r}^2(t)}{2}\, dt + g \int_0^N dt_1 dt_2\, \delta^d(r(t_1)-r(t_2))\Big]$$

We are interested in correlation function

$$G(k,N) = \langle e^{ik\cdot(r(N)-r(0))} \rangle \simeq 1 - \frac{k^2}{2}\langle (r(N)-r(0))^2 \rangle + \dots$$

and its Laplace transform

$$Z(k,\tau) = \int_0^\infty e^{-N\tau}\, G(k,N)\, dN$$

To calculate G we rewrite the interaction term in the following way through auxiliary field $\mathfrak{z}(r)$ (imaginary)

$$\int \mathcal{D}\mathfrak{z}(r) \exp\Big[\frac{1}{4g}\int d^d r\, \mathfrak{z}^2(r) - \int dt\, \mathfrak{z}(r(t))\Big] =$$

$$= \exp\Big[-g \int dt_1 dt_2\, \delta^d(r(t_1)-r(t_2))\Big] \qquad (1)$$

Really,

$$\int \mathcal{D}z \exp\left[\frac{1}{4g}\int d^d r\, z^2(r) - \int dt\, z(r(t))\right] =$$

$$= \int \mathcal{D}z \exp\left[\frac{1}{4g}\int d^d r\, z^2(r) - \int d^d r \int dt\, z(r)\, \delta^d(r - r(t))\right] =$$

$$= \int \mathcal{D}z \exp\Big[\frac{1}{4g}\int d^d r \left\{ z(r) - 2g\int dt\, \delta^d(r - r(t))\right\}^2$$

$$- g\int d^d r \int dt_1 dt_2\, \delta^d(r - r(t_1))\, \delta^d(r - r(t_2))\Big] =$$

$$= \exp\left[g \int dt_1 dt_2\, \delta^d(r(t_1) - r(t_2))\right]$$

Using Eq. (1) we can consider then

$$\langle A \rangle = \int \mathcal{D}z\, \mathcal{D}r(t)\, A \exp\Big(\frac{1}{4g}\int d^d r\, z^2(r) -$$

$$- \underbrace{\int_0^N \left[\frac{\dot{r}^2(t)}{2} + z(r(t))\right] dt}\Big)$$

This corresponds to path integral representation of the evolution operator in imaginary time t of a d-dimensional quantum system with potential $z(r)$.

Then

$$Z(\kappa,\tau) = \int \mathcal{D}z(r) \exp\left[\frac{1}{4g}\int d^d r\, z^2(r)\right] \int_0^\infty e^{-N\tau} dN \cdot$$

$$\int d^d r\, d^d r' \, e^{i\kappa(r-r')} \langle r' | e^{-NH} | r \rangle$$

with quantum Hamiltonian $H = -\nabla^2 + z(r)$

Laplace transform ($\int dN \dots$) is then simple and

$$Z(\kappa,\tau) = \int \mathcal{D}z(r) \exp\left[\frac{1}{4g}\int d^d z^2(r)\right] \int d^d r\, d^d r' e^{i\kappa(r-r')} \cdot$$

$$\cdot \underbrace{\langle r' | (-\nabla^2 + \tau + z)^{-1} | r \rangle}$$

This can be calculated using

$$\lim_{n\to 0} \int \mathcal{D}\varphi(r)\, \varphi_1(r)\varphi_1(r') \exp\left[-\frac{1}{2}\int d^d r\left[(\partial_\mu\varphi)^2 + \tau\varphi^2 + z(r)\varphi^2\right]\right] =$$

$$= \langle r' | (-\nabla^2 + \tau + z)^{-1} | r \rangle$$

where n is the number of components of the field $\varphi(r)$. Indeed the gaussian integral over the field φ yields $\varphi\varphi$ propagator divided by $[\det(-\Delta + \tau + z)]^{n/2} = 1$ for $n = 0$!

(Replica trick)

Then

$$Z(k,\tau) = \int \mathcal{D}\varphi(r)\ \varphi_1(k)\,\varphi_1(-k)\ \cdot$$

$$\cdot \int \mathcal{D}\sigma(r)\ \exp\left[\int d^d r\left(\frac{1}{4}\sigma^2 - \frac{\sigma\varphi^2}{2} - \frac{1}{2}(\partial_\mu\varphi)^2 - \frac{\tau}{2}\varphi^2\right]$$

We can then integrate over σ

$$Z = \int \mathcal{D}\varphi\ \varphi_1(k)\,\varphi_1(-k)\,\exp\left[-\int d^d r\left[\frac{\tau\varphi^2}{2} + \frac{(\partial_\mu\varphi)^2}{2} + \frac{(\varphi^2)^2}{4}\right]\right]$$

And we obtain the desired mapping.

Using

$$Z(k,\tau) = \int_0^\infty e^{-N\tau}\,G(k,N)\,dN$$

and behaviour of $\langle \varphi(k)\varphi(-k)\rangle \sim f(k\xi)$

with $\xi \propto \tau^{-\nu}$

Then $G(k,N) \sim g(kN^\nu) \Rightarrow$

$$\langle (r(N) - r(0))^2 \rangle \sim N^{2\nu}$$