Formularium Statistical Mechanics

KULeuven – 2013/2014

Random walks, Diffusion and Polymers

End-end vector of a random walk:

$$\langle \vec{R} \rangle = 0 \qquad \langle \vec{R}^2 \rangle = a^2 N \tag{1}$$

Diffusion equation:

$$\frac{\partial P(\vec{R},t)}{\partial t} = D\nabla^2 P(\vec{R},t) \tag{2}$$

Solution in d-dimensions (gaussian):

$$G_{\vec{R}_0}(\vec{R},t) = \left(\frac{1}{4\pi D t}\right)^{d/2} e^{-\frac{(\vec{R}-\vec{R}_0)^2}{4Dt}} \tag{3}$$

End-end distance self-avoiding walks

$$\langle \vec{R}^2 \rangle \sim a^2 N^{2\nu} \tag{4}$$

Flory exponent in $d \leq 4$ dimensions

$$\nu = \frac{3}{2+d} \tag{5}$$

General formalism of Classical Statistical Mechanics

Hamiltonian

$$\mathcal{H}(\Gamma) = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} + \Phi(\vec{q}_1, \vec{q}_2 \ldots \vec{q}_N) \tag{6}$$

Equilibrium average of an observable

$$\langle A(\Gamma) \rangle = \int d\Gamma \rho(\Gamma) A(\Gamma) \tag{7}$$

Microcanonical ensemble

$$\rho(\Gamma) = \frac{\delta(E - \mathcal{H}(\Gamma))}{\omega(E,N,V)N!h^{3N}} \tag{8}$$

Microcanonical density of states

$$\omega(E,N,V) = \int \frac{d\Gamma}{N!h^{3N}} \delta\left(E - \mathcal{H}(\Gamma)\right) \tag{9}$$

$$\Omega(E,N,V) = \int \frac{d\Gamma}{N!h^{3N}} \theta\left(E - \mathcal{H}(\Gamma)\right) \tag{10}$$

$$\omega(E,N,V) = \frac{\partial \Omega(E,N,V)}{\partial E} \tag{11}$$

Entropy:

$$S(E,N,V) = k_B \log \omega(E,N,V) \tag{12}$$

Canonical ensemble

$$\rho(\Gamma) = \frac{e^{-\beta \mathcal{H}(\Gamma)}}{N!h^{3N} Z(N,V,T)} \tag{13}$$

with $\beta = 1/(k_B T)$. Partition function:

$$Z(N,V,T) = \int \frac{d\Gamma}{N!h^{3N}}\, e^{-\beta \mathcal{H}(\Gamma)} \tag{14}$$

Integration over momenta

$$Z(N,V,T) = \frac{Q(N,V,T)}{N!\lambda_T^{3N}} \tag{15}$$

thermal wavelength

$$\lambda_T = \frac{h}{\sqrt{2\pi m k_B T}} \tag{16}$$

Relation with canonical ensemble

$$Z(N,V,T) = \int dE\; e^{-\beta E} \omega(E,N,V) \tag{17}$$

Connection with thermodynamics

$$F = E - TS = -k_B T \log Z \tag{18}$$

Grandcanonical ensemble

$$\rho(\Gamma, N) = \frac{e^{-\beta\mathcal{H}(\Gamma)}e^{\beta\mu N}}{N!h^{3N}\Xi(\mu, V, T)} \tag{19}$$

Grand canonical partition function

$$\Xi(\mu, V, T) = \sum_N e^{\beta\mu N} Z(N, V, T) \tag{20}$$

Connection with thermodynamics

$$\frac{pV}{k_B T} = \log \Xi(\mu, V, T) \tag{21}$$

Equipartition Theorem

$$\left\langle x_r \frac{\partial\mathcal{H}}{\partial x_s} \right\rangle = k_B T \delta_{rs} \tag{22}$$

Law of mass action

For a reaction

$$B_1 + B_2 \rightleftharpoons 2B_3 \tag{23}$$

the law of mass action takes the form:

$$\frac{[B_3]^2}{[B_1][B_2]} = K_{eq}(T) = \left(\frac{\lambda_1\lambda_2}{\lambda_3^2}\right)^3 e^{-\beta\Delta F} \tag{24}$$

with ΔF internal free energoes difference

Interacting Systems

Virial theorem

$$p = \frac{N k_B T}{V} - \frac{1}{3}\sum_{i,j=1}^{N}\left\langle \vec{q}_i \cdot \vec{F}_{ij} \right\rangle = n k_B T - \frac{n^2}{6}\int r\,\frac{d\phi(r)}{dr} g(r) d\vec{r} \tag{25}$$

with $\vec{F}_{ij}$ force exerted by particle j on particle i, $\phi(r)$ interparticle potential[1] and where the pair correlation function $g(\rho)$

$$n^{(2)}\left(\vec{r}, \vec{r} + \vec{\rho}\right) = \left\langle \sum_{i=1}^{N} \delta\left(\vec{r} - \vec{q}_i\right) \sum_{j\neq i}^{N} \delta\left(\vec{r} + \vec{\rho} - \vec{q}_j\right) \right\rangle = n^2 g(\rho) \tag{26}$$

Virial expansion

$$p = n k_B T \left(1 + b_2 n + b_3 n^2 + \ldots\right) \tag{27}$$

[1]for spherically symmetric interactions.

Second virial coefficient

$$b_2 \equiv -\frac{1}{2}\int d\vec{r}\,\left(e^{-\beta\phi(r)}-1\right) \tag{28}$$

Bogoliubov inequality - Given $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1$:

$$F \leq F_0 + \langle \mathcal{H} \rangle_0 \tag{29}$$

van der Waals model

$$p = \frac{Nk_BT}{V-Nb} - \frac{aN^2}{V^2} \tag{30}$$

Critical exponents

$$\begin{array}{lcl} \delta p & \sim & (\delta v)^{\delta} \\ \delta v & \sim & (\delta t)^{\beta} \\ \kappa_T & \sim & |\delta t|^{-\gamma} \\ c_V & \sim & |\delta t|^{-\alpha} \end{array} \tag{31}$$

Critical exponents

	α	β	δ	γ
van der Waals	0	1/2	3	1
gas/liquid	0.13	0.33	4.8	1.24

Ising model

$$\mathcal{H} = -J\sum_{\langle i,j\rangle} s_i s_j - H\sum_i s_i \tag{32}$$

magnetization

$$M = \sum_k \langle s_k \rangle = \frac{1}{Z}\sum_{\{s_i\}} s_k e^{-\beta\mathcal{H}(\{s_i\})} \tag{33}$$

Spontaneous magnetization in 2d (exact)

$$m_0(T) = \left[1 - \sinh^{-4}\left(\frac{2J}{k_BT}\right)\right]^{1/8} \tag{34}$$

Critical temperatures

	$d=1$ $(z=2)$	$d=2$ $(z=4)$	$d=3$ $(z=6)$
Mean Field	$k_BT_c = 2J$	$k_BT_c = 4J$	$k_BT_c = 6J$
Exact	$T_c = 0$	$k_BT_c = 2.269J$	$k_BT_c = 4.5J$

Spontaneous magnetization ($H = 0$)

$$m_0(T) \sim (T_c - T)^\beta \tag{35}$$

Specific heat:

$$c \sim |T - T_c|^{-\alpha} \tag{36}$$

Magnetic susceptibility:

$$\chi = \frac{\partial M}{\partial H} \sim |T - T_c|^{-\gamma} \tag{37}$$

Magnetic field ($T = T_c$)

$$H \sim |M|^\delta \tag{38}$$

Correlation function

$$G^{(2)}(\vec{x}, \vec{y}) = \langle (s_{\vec{x}} - \langle s \rangle)(s_{\vec{y}} - \langle s \rangle) \rangle \sim e^{-\dfrac{|\vec{x} - \vec{y}|}{\xi}} \tag{39}$$

correlation length

$$\xi \sim |T_c - T|^{-\nu} \tag{40}$$

Correlation function at $T = T_c$

$$G^{(2)} \sim \frac{1}{r^{d-2+\eta}} \tag{41}$$

Critical exponents

	α	β	γ	δ	ν	$\alpha + 2\beta + \gamma$	$\beta(\delta - 1)$
Mean Field	0	1/2	1	3	1/2	2	1
2d	0	1/8	7/4	15	1	2	7/4
3d	0.11	0.32	1.24	4.8	0.68	1.99	1.22

Relations between exponents

$$\alpha + 2\beta + \gamma = 2 \tag{42}$$

$$\gamma = \beta(\delta - 1) \tag{43}$$