Mathematical identities

$$N! \approx N^N e^{-N}\,(\cdot\sqrt{2\pi N}),\quad \ln(N!) \approx N\ln N - N,\ \sum_{n=0}^{\infty} x^n = \frac{1}{1-x},\quad \lim_{x\to 0} x\ln x = 0$$

$$\int dx\,\delta(u-ax) = \frac{1}{a}\int dx\,\delta(u/a - x),\ \int f(x)\delta(g(x))\,dx = \sum_j \frac{f(x_j)}{g'(x_j)}$$

$$\langle x\rangle = NP,\ \sigma_x^2 = NP(1-P),\ N\text{ large}:\quad P = \frac{1}{\sqrt{2\pi\sigma_x^2}} e^{-\frac{(x-NP)^2}{2\sigma_x^2}}$$

Standard set of second derivatives

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N},\ \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N},\ c_{P/V} = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_{P/V,N}$$

$$c_P = c_V + \frac{\alpha^2 TV}{N\kappa_T},\quad \kappa_S = \kappa_T - \frac{TV\alpha^2}{Nc_P}$$

Phase Transitions

To illustrate, consider the van der Waals Fluid. From ideal gas, add attraction term, $-aN^2/V$, for neighboring particles, and restrict volume due to hard particle spheres, $V \to V - bN$. This yields

$$F_{IG} = -Nk_BT\left[\ln(V/N) + \frac{3}{2}\ln(k_BT) + X\right]$$

$$F_{VdW} = -Nk_BT\left[\ln\left(\frac{V-bN}{N}\right) + \frac{3}{2}\ln(k_BT) + X\right] - a(N^2/V)$$

This yields the following expression for pressure and energy

$$P = \frac{Nk_BT}{V-bN} - \frac{aN^2}{V^2},\quad U = \frac{3}{2}Nk_BT - a\left(\frac{N^2}{V}\right)$$

PT BOLTZMANN+MAX-BOLT

Classical statistical mechanics

Microcanonical ensemble: Assign equal prob. to each microstate, $P_s = 1/W$, where W is the number of microstates in energy range.

$$\Omega_{E,V,N} = \frac{1}{h^{3N}N!}\int dq\,dp\,\delta(E - H(p,q))$$

$$Z = \int dE\,\Omega\exp(-\beta E) = \int \frac{dq\,dp}{h^{3N}N!}e^{-\beta H},\ \mathcal{Z} = \sum_{N=0}^{\infty}\int_0^{\infty} dE\,\Omega e^{-\beta E + \beta\mu N}$$

Liouville Theorem

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = \frac{\partial\rho}{\partial t} + \sum_{\alpha=1}^{3N}\left(\frac{\partial\rho}{\partial q_\alpha}\dot{q}_\alpha + \frac{\partial\rho}{\partial p_\alpha}\dot{p}_\alpha\right) = 0$$

$$\frac{\partial\rho}{\partial t} = \{H,\rho\},\quad \{A,B\} = \sum_\alpha\left(\frac{\partial A}{\partial q_\alpha}\frac{\partial B}{\partial p_\alpha} - \frac{\partial A}{\partial p_\alpha}\frac{\partial B}{\partial q_\alpha}\right)$$

QM statistical mechanics

$$P_n = \frac{e^{-\beta E_n}}{Z},\ Z = \sum_l \Omega(l)\exp(-\beta E_l),\quad \Omega(l) = \text{Deg. of } E_l$$

$$S = -k_B\sum_n P_n\ln P_n,\quad \beta F = -\ln Z + f(V,N).\ (f = -\ln N!\text{ for dist. part.})$$

$$Z = \sum_{\{n_j\}}\prod_{j=1}^{N}\exp\left(-\beta E_{n_j}\right) = \prod_{j=1}^{N}\left(\sum_{n_j}\exp\left(-\beta E_{n_j}\right)\right)$$

$$\epsilon_{\vec{k}} = \frac{\hbar^2}{2m}k^2 = \frac{\hbar^2\pi^2}{2mL^2}n^2 = \epsilon_{\vec{k}},\ D(\epsilon) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\epsilon^{1/2}\ (\cdot 2,\ s=1/2)$$

$$\lambda_{\text{th}} = \frac{h}{\sqrt{2\pi mk_BT}},\ Z = L/\lambda_{th},\ V/N \le \lambda_{\text{th}}^3$$

Grand Canonical Ensemble

In equilibrium with a reservoir. Can exchange energy and particles.

$$\mathcal{Z} = \sum_{\{n_\epsilon\}}\prod_\epsilon e^{-\beta(\epsilon-\mu)n_\epsilon} = \prod_\epsilon\sum_{n_\epsilon}e^{-\beta(\epsilon-\mu)n_\epsilon} = \prod_\epsilon\mathcal{Z}_\epsilon$$

$$\langle n_\epsilon\rangle = \frac{1}{\mathcal{Z}_\epsilon}\sum_{n_\epsilon}n_\epsilon e^{-\beta(\epsilon-\mu)n_\epsilon},\quad \langle N\rangle = \frac{1}{\beta}\frac{\partial\ln\mathcal{Z}}{\partial\mu} = \sum_\epsilon\langle n_\epsilon\rangle,\quad U = \sum_\epsilon\epsilon\langle n_\epsilon\rangle$$

Bosons and Fermions

Using + for fermions and − for bosons:

$$\langle n_\epsilon\rangle = \frac{1}{e^{\beta(\epsilon-\mu)}\pm 1},\quad \mathcal{Z} = \begin{cases}\prod_\epsilon(1+\exp(-\beta(\epsilon-\mu))), & \textbf{f}\\ \prod_\epsilon 1-\exp[-\beta(\epsilon-\mu)]^{-1}, & \textbf{b}\end{cases}$$

$$\ln\mathcal{Z} = \pm\sum_\epsilon\ln\left(1\pm e^{-\beta(\epsilon-\mu)}\right) \approx \pm\int_0^\infty d\epsilon\,D(\epsilon)\ln\left(1\pm e^{-\beta(\epsilon-\mu)}\right)\ [=\beta PV]$$

$$N = \int_0^\infty d\epsilon\,D(\epsilon)(\exp[\beta(\epsilon-\mu)]\pm 1)^{-1}.\ U = \int_0^\infty d\epsilon\,\epsilon D(\epsilon)(\exp[\beta(\epsilon-\mu)]\pm 1)^{-1}$$

Bose-Einstein statistics

Since $\langle n_\epsilon\rangle > 0$, must have $\epsilon > \mu$ for bosons. Set lowest energy state as $\epsilon = 0 \implies \mu < 0$. At low-T, using $x = \beta\epsilon$, $D(\epsilon) = \chi\epsilon^{1/2}$ and $e^{\beta\mu} = \lambda$

$$N = \chi(k_BT)^{3/2}\int_0^\infty dx\,\frac{x^{1/2}}{\lambda^{-1}e^x - 1} \xrightarrow{\lambda^{-1}=1} \chi(k_BT_E)^{3/2}2.315$$

$$k_BT_E = \left(\frac{2\pi\hbar^2}{m}\right)\left(\frac{N}{2.612V}\right)^{2/3},\ N(T<T_E) = N_0 + N(T/T_E)^{3/2}$$

$$N_0 = f(0) = N[1-(T/T_E)]^{3/2} \approx -1/\beta\mu \implies \mu \approx -\frac{k_BT}{N}\left[1 - \left(\frac{T}{T_E}\right)^{3/2}\right]^{-1}$$

Fermi-Dirac statistics

The occupation number $f(\epsilon; T\to 0) = \Theta(\epsilon_F - \epsilon)$, $\epsilon_F \equiv \mu(T\to 0, M)$. Then $N = 2X/3\epsilon_F^{3/2}$, $U = 2X/5\epsilon_F^{5/2}$, $\epsilon_F \propto (N/V)^{2/3}$. From Euler eq.: $PV = 2/5\,\epsilon_F N$. With $\epsilon_F = y(N/V)^{2/3}$, $\kappa_T^{-1} = 2/3\,\epsilon_F(N/V)$

Sommerfeld expansion

At low non-zero T, valid for $k_BT/\epsilon_F \ll 1$. integrate $\phi(\epsilon)f(\epsilon)$, sep. integral at μ, write $f(\epsilon)$ for lower and upper integrand as $1 - \frac{1}{e^{-\beta x}+1} = \frac{1}{e^{\beta x}+1}$. Use $z = -\beta(\epsilon-\mu)$ for low-int, approx low-lim $z = \beta\mu \to \infty$, and $z = \beta(\epsilon-\mu)$ for up-int.

$$I = \int_0^\mu d\epsilon\,\phi(\epsilon) + \int_0^\infty \frac{d\epsilon}{\beta}\,\frac{\phi(\mu+z/\beta) - \phi(\mu-z/\beta)}{e^z+1}$$

$$\phi(\mu+z/\beta) - \phi(\mu-z/\beta) = \frac{2z}{\beta}\phi'(\mu) + \frac{2}{3!}\left(\frac{z}{\beta}\right)^3\phi'''(\mu) + \ldots$$

$$I = \int_0^\mu d\epsilon\,\phi(\epsilon) + (k_BT)^2\phi'(\mu)2\int_0^\infty dz\,\frac{z}{e^z+1} + \ldots$$

$$= \int_0^\mu d\epsilon\,\phi(\epsilon) + (k_BT)^2\phi'(\mu)\frac{\pi^2}{6} + (k_BT)^4\phi'''(\mu)7\frac{\pi^4}{360} + \mathcal{O}(T^6)$$

$$U: \phi(\epsilon) = X\epsilon^{3/2} \implies U = X[2/5\mu^{5/2} + \pi^2/4(k_BT)^2\mu^{1/2}] + \mathcal{O}(T^4)$$

$$\mu \approx \epsilon_F\left(1 - \frac{\pi^2}{12}\left(\frac{k_BT}{\epsilon_F}\right)^2 + \ldots\right),\quad \text{iterate, expand use N(T=0)}$$

Plugging in for U and expanding $\mu^{5/2}$ and $\mu^{1/2}$ up to T^2 gives

$$U = \frac{2}{5}X\epsilon_F^{5/2} + \frac{\pi^2}{6}(k_BT)^2X\epsilon_F^{1/2} \implies C_V = \frac{\pi^2}{2}Nk_B\left(\frac{k_BT}{\epsilon_F}\right) + \mathcal{O}(T^3)$$

where $X\epsilon_F^{3/2} = 3/2\cdot N$. The linear dependence is observed for metals at low T.

The Harmonic solid

1D crystal lattice with spacing a. Pos.: $r_j = R_j + x_j$, $R_j = a\cdot j$ is equil. pos., x_j is the deviation and $j = 0, 1, \ldots, N-1$. Model as springs, with P.BC,

$$H = \frac{m}{2}\sum_k\left|\dot{X}_k\right|^2 + \frac{K}{2}\sum_k 4\sin^2(ka/2)|X_k|^2$$

$$K_k = 4K\sin^2(ka/2),\quad \omega_k^2 = K_k/m = \tilde{\omega}^2 4\sin^2(ka/2)$$

$$Z = \prod_k\sum_{n=0}^{\infty}e^{-\beta\hbar\omega_k(n+1/2)},\ F = \sum_k\left(\frac{\hbar\omega_k}{2} + k_BT\ln\left(1 - e^{-\beta\hbar\omega_k}\right)\right)$$

Debye approximation

$\omega_k \approx \tilde{\omega}ka$ for small k. *Debye approximation:* $\hbar\omega_k = \hbar v|\vec{k}|$ as lin. rel., v is speed of sound (interpolate between known low and high T sol). Sphere of radius $k_D = (6\pi^2/a^3)$. Debye energy and temperature: $\hbar\omega_D \equiv \hbar vk_D$ and $\theta_D \equiv \hbar\omega_D/k_B$. $x = \beta\hbar vk$, we get

$$U = \text{const} + 3N\left(\frac{a}{2\pi}\right)^3\int_{\text{1st B.Z}} d^3k\,\frac{\hbar v|\vec{k}|}{e^{\beta\hbar v|\vec{k}|} - 1}\ \text{(gen. HS in 3D)}$$

$$= \text{const} + 9N\frac{k_BT}{(\theta_D/T)^3}\int_0^{\theta_D/T} dx\,\frac{x^3}{e^x - 1}$$

$$U(T \gg \theta_D) = \text{const} + 3Nk_BT,\quad U(T \ll \theta_D) = \text{const} + \frac{3N\pi^4}{5}\frac{(k_BT)^4}{(\hbar\omega_D)^3}$$

Ising model

$$Z = \sum_{\tau_1}\prod_{i=2}^{N}\left(\sum_{\tau_i}e^{\beta J\tau_i}\right) = 2(2\cosh(\beta J))^{N-1}\quad (\text{1D},\ h = 0)$$

$$U = -(N-1)J\tanh(\beta J),\quad c = k_B\beta^2J^2\left(1 - \frac{1}{N}\right)\frac{1}{\cosh^2(\beta J)}$$

Ising chain with transfer matrices

$J \ne 0$, $h \ne 0$, use P.BC. ($\sigma_{N+1} = \sigma_1$). Write H symmetrically

$$H = -J\sum_{i=1}^{N}\sigma_i\sigma_{i+1} - \frac{h}{2}\sum_{i=1}^{N}(\sigma_i + \sigma_{i+1}),\ Z = \sum_{\{\sigma\}}\prod_{i=1}^{N}T_{i,i+1} = \lambda_1^N + \lambda_2^N$$

$$\lambda_1 = e^{\beta J}\cosh(\beta h) + \sqrt{e^{2\beta J}\cosh^2(\beta h) - 2\sinh(2\beta J)}$$

$$(\lambda_1 > \lambda_2) \to \frac{F}{N} = -k_BT\ln\lambda_1 \xrightarrow{h=0} -k_BT\ln(2\cosh(\beta J))$$

$$m = \frac{1}{N}\langle\sigma_j\rangle = \frac{1}{\beta N}\frac{\partial\ln Z}{\partial h} = -\frac{1}{N}\frac{\partial F}{\partial h},\quad \chi = \frac{\partial m}{\partial h} = \frac{1}{\beta N}\frac{\partial^2\ln Z}{\partial h^2}$$

Mean Field Approximation

$\tilde{\sigma} = \sigma - m \implies \sigma_j\sigma_k \approx -m^2 + m(\sigma_j + \sigma_k)$ In the Hamiltonian, include factor 1/2 for the double counting of spin. Sum over $\sigma_j\sigma_{j+\delta}$. Introduce $z = 2d = \sum_\delta 1$. PBC: Shift $j \to j' = j + \delta$

$$H = -J/2\sum_{j,\delta}(-m^2 + m(\sigma_j + \sigma_{j+\delta})) \to Jm^2\frac{Nz}{2} - h_{\text{eff}}\sum_j \sigma_j$$
$$Z = e^{-\beta Jm^2Nz/2}\left(2\cosh(\beta h_{\text{eff}})\right)^N = e^{-\beta Jm^2Nz/2}Z_1^N$$
$$m = \frac{1}{Z_1}\sum_{\sigma_1=-1}^{+1}\sigma_1 e^{(\beta h_{\text{eff}}\sigma_1)} = \tanh(\beta h + \beta Jzm) \quad (m = m_1)$$

where $h_{\text{eff}} = Jmz + h$, and we summed over σ_1 N times.

Disordered: $m = 0$. Ordered: $k_BT/Jz < 1$, 3 solutions: $\beta Jzm = x = \pm 1, 0$, but $x = 0$ unstable. $k_BT_c = zJ$. For $t \equiv (T - T_c)/T_c \sim 0$ with $h = 0$, m is small, and we can expand to solve for m

$$m \approx \beta Jmz - \frac{1}{3}(\beta mJz)^3 \implies m^2 = 3\left(\frac{T}{T_c}\right)^2\left(1 - \frac{T}{T_c}\right), \to m \propto (-t)^{1/2} \quad (T \sim T_c)$$

Existence of PT

$$k_BT_c = \frac{E_{ex} - E_g}{\ln N_{ex} - \ln N_g} \approx \frac{\Delta E}{\ln N_{\text{ex}}}, \quad (F_g = F_{ex})$$
$$k_BT_c = 2J/(\ln(N-1) - \ln 2) \to 0, \quad \text{for } N \to \infty \quad \text{(1D Ising)}$$
$$k_BT_c = \frac{2J \cdot l}{\ln\left(2N(z-1)^l\right) - \ln 2} = \frac{2J \cdot l}{\ln N + l \cdot \ln 3} \quad \text{(2D Ising)}$$

Landau argument for PT existence

A symmetry can't be continuously deformed into another symmetry. Thus: Two phases with different symmetries are always separated by one or more PT's (There can still be PT between phases of same symmetries).

Critical exponents

Power law behaviour of t close to T_c for cont. PT.

$$\alpha: c_V \sim \frac{1}{|t|^\alpha}, \quad \beta: m \sim (-t)^\beta \text{ (order param. } t < 0)$$
$$\gamma: \chi = \partial_H m(H = 0) \sim \frac{1}{|t|^\gamma}, \quad \delta: m \sim |H|^{1/\delta}\ (t = 0)$$
$$\nu: \xi \sim \frac{1}{|t|^\nu}, \quad \eta: C(r) \sim \frac{1}{|r|^{d-2+\eta}}, \ (r \ll \xi)$$
$$\nu(2 - \eta) = \gamma,\ \alpha + 2\beta + \gamma = 2,\ \beta(\delta - 1) = \gamma,\ 2 - \alpha = \nu d$$

Renomrmalization group

Universality: Same behavior at PT for several different microscopic systems.

RG-trans: Trans. betw. different microscopic models behaving the same at macroscopic scales.

Example: 1D Ising with a const., C.

$$Z = \sum_{\{\sigma\}} T_{s_a s_{2a}} \dots T_{s_{Na} s_a}. \quad T_{i=j} = e^{\beta J + \beta C},\ T_{i \neq j} = e^{-\beta J + \beta C}$$

Now, perform sum over every second site. Sum over s_{2a} yields $T^2 = 2e^{2\beta C}\begin{pmatrix}\cosh(2\beta J) & 1 \\ 1 & \cosh(2\beta J)\end{pmatrix} = e^{\beta C'}\exp\left(\beta J'\begin{pmatrix}1 & -1 \\ -1 & 1\end{pmatrix}\right) = T'$. The new transfer matrix is for the Ising chain with spin on every second site. Now, $H' = -\sum_r (J's_rs_{r+a'} + C')$, $a' = 2a$, with

$$2e^{2\beta C}\cosh(2\beta J) = e^{\beta C'}e^{\beta J'}, \quad 2e^{2\beta C} = e^{\beta C'}e^{-\beta J'}$$
$$K_1 \equiv e^{-2\beta J}, \quad K_1' \equiv e^{-2\beta J'}, \quad K_2 \equiv e^{-2\beta C}, \quad K_2' \equiv e^{-2\beta C'}$$

Now, $K_1 = 1 \implies \beta J \to 0$ (disordered) and $K_1 \implies \beta J \to \infty$ (ordered). Solving for K_1', we get $K_1' = \frac{2K_1}{1+K_1^2}$. Since $K_1 \in (0, 1)$ then $1 + K_1^2 > 1$. Iterating (subsequent RG trans.) for $K_1 > 0$ we will converge to $K_1 = 1$. Then, for $K_1 \gtrsim 0$, $K_1' \approx 2K_1$. We have $K_1 = K_1(a)$, $K_1' = K_1(2a)$.

For $s > 1$, $K(sa) = s^{y_k}K(a)$. $y_k = \{> 0, 0, < 0\} = \{$repuslive,stat.,attract.$\}$ fp (relevant,marginal (go beyond lin.),irrel.). In general, for any dim-full Q, with spatial dim D, measured in units off latt. spacing, $\boxed{\tilde{Q}(\{K\}) = s^D\tilde{Q}(\{Ks^{y_k}\})}$.

Usually two relevant coupling, t and h. Drop hats $\xi(h, t) = s\xi(hs^{y_h}, ts^{y_t})$, $y_h, y_t > 0$. arbitrary $s > 1$, choose it s.t. $ts^{y_t} = 1 \implies s = t^{-1/y_t}$.

$$\xi(h, t) = t^{-1/y_t}\xi(ht^{-y_h/y_t}, 1),\ h = 0 \implies \xi(0, t) = \frac{1}{t^{1/y_t}}\xi(0, 1)$$

where $x(0, 1)$ is a number. Compare to crit. exp. we see that $\xi \sim 1/|t^\nu| \implies \nu = 1/y_t$. For $m = -Tdf(h = 0)/dh$, choose $s = (-t)^{-1/y_t}$.

Finite size scaling

Numerics: Finite system size, L. Intr. dimless len $L^{-1} = (L/a)^{-1}$, for $a' = as$ dimless len incr. as $L'^{-1} = sL^{-1}$. Then, corr.len (drop h) scales as (choose $s = L$)

$$\xi(t, L^{-1}) = L\xi(tL^{y_t}, 1) = Lg(tL^{y_t}), \quad \xi(tL^{y_t} \to \infty) \sim 1/t^\nu \implies g(x) \to 1/x^{1/y_t}$$
$$\text{(Fin.L near t=0): } g(x) = g(0) + xg'(0) \implies \xi(t, L^{-1})/L = g(0) + tL^{y_t}g'(0)$$

At $t = 0$, RHS ind. of L. Compute ξ/L for different L, T_c found where curves cross. Exponent, ν, gotten by computing $\partial_T(\xi/L)_{(T=T_c)} = L^{y_t}g'(0)/T_c$. Plot log of LHS vs. log of L, get straight line with slope y_t.

Cumulant expansion

Use mom. gen. func.

$$P_k = \int dx\, P(x)e^{-ikx} = \sum_{m=0}^{\infty}\frac{(-ik)^m}{m!}\langle x^m\rangle$$
$$\ln P_k \equiv \sum_{l=1}^{\infty}\frac{(-ik)^\ell}{\ell!}\left\langle x^\ell\right\rangle_c$$

Equate P_k with the exponentiated $\ln P_k$, compare powers of $(-ik)$. Yields $\langle x\rangle_c = \langle x\rangle$, $\left\langle x^2\right\rangle_c = \left\langle x^2\right\rangle - \langle x\rangle^2$, ... $\langle x^p\rangle$: Draw p dots, connect in all possible ways. Cluster of m dots is $\langle x^m\rangle_c$, (disjoint: $m = 0$).

Part. func. for interacting gas, $H = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + \tilde{u}(\mathbb{Q})$.

$$Z = Z_0\int\frac{d\mathbb{Q}}{V^N}e^{-\beta\tilde{u}} = Z_0\sum_{m=0}^{\infty}\frac{(-\beta)^m}{m!}\int\frac{d^3q_1}{V}\cdots\frac{d^3q_N}{V}[\tilde{u}(q_1, \dots, q_n)]^m$$

so $Z = Z_0\sum_m(-\beta)^m/m!\,\langle\tilde{u}^m\rangle$. For free energy, $\ln Z \sim F$, we get

$$\ln Z = \ln Z_0 + \sum_{\ell=1}^{\infty}\frac{(-\beta)^\ell}{\ell!}\left\langle\tilde{u}^\ell\right\rangle_c$$

With assumptions of potential, can now find contr. to F from cumulants. Assuming $\tilde{u}(q\ldots) = \sum_{i<j}u(\vec{q}_i - \vec{q}_j)$ and $u(-q) = u(q)$, the first cum. is

$$\left\langle\tilde{u}^1\right\rangle_c = \langle\tilde{u}\rangle = \frac{N(N-1)}{2}\int d^3q/Vu(\vec{q})$$

Diag. for pair-wise int. P pairs for $\langle\tilde{u}^p\rangle$, connect each by dotted line. Label points, numbers on different pairs can be equal. Merge opints if numbers on different pairs are equal. Find the number of ways, G, to assign labels to diagram to get a spec. topology. For a given diagram there is a factor $u(q_i - q_j)$ for each dotted line. An integral $\int d^3q/V$ for each point. A factor G. The sum of G for each order p should equal $(N(N-1)/2)^p$. **Disconnected and one-particle reducable diagrams don't contribute**.

Cluster expansion

For hard-core (u big for $q \to 0$), the p-th term is $\sim\int u^p(q)$. But $p + 1$ term is bigger, so the series can't be truncated. Use

$$p_1(-\beta) + p_2(-\beta)^2/2! + \cdots + p_p(-\beta)^p/p! = \frac{N(N-1)}{2V}\int d^3q(e^{-\beta u} - 1)$$

where the integrand is $f(q)$. The GC-PF becomes

$$Z(\mu, T, V) = \sum_{N=0}^{\infty}\frac{1}{N!}\left(\frac{e^{\beta\mu N}}{\lambda^3}\right)^N S_N$$
$$S_N = \int d^3q_1\dots d^3q_Ne^{-\beta\tilde{u}} = \int\prod_{i<j}\left(e^{-\beta u(q_i - q_j)} - 1 + 1\right) = \int\prod(f_{ij} + 1)$$
$$= \sum_{\{n_\ell\}}{}'\prod b_\ell^{n_\ell}W(\{n_\ell\}), \quad \sum{}': \sum_{\ell=1}^{N}n_\ell\ell = N$$
$$b_1 = \int d^3q = V,\ b_2 = V\int f(q),\ b_3 = \int dq_{123}(f_{12}f_{23} + f_{13}f_{32} + f_{12}f_{13} + f_{12}f_{23}f_{31})$$

b_ℓ all ways to connect points, S_N: how to connect N points. Connected$=f_{ij} \to V\int d^3qf(q)$, disc.: 1, contributes a factor V. W =number of ways of labeling groups of n_ℓ ℓ clusters. $W = N!/(n_1!(2!)^{n_2}n_2!\dots) = N!/\prod_\ell(\ell!)^{n_\ell}n_\ell!$. Final expression for PF

$$\ln\mathcal{Z} = \sum_{\ell=1}^{\infty}(e^{\beta\mu}/\lambda^3)^\ell\frac{b_\ell}{\ell!}$$

Only linked-cluster-diags contr. to $\ln Z$.

Virial expansion

Deviation from IGL as exp. in N/V. GC.PF: $\Omega = -\ln\mathcal{Z}/\beta$, $N = \frac{\partial\ln\mathcal{Z}}{\partial(\beta\mu)}$, $x = e^{\beta\mu}/\lambda^3$

$$\beta P = N/V\left(1 + B_2(T)\frac{N}{V} + B_3(T)\left(\frac{N}{V}\right)^2 + \dots\right)$$
$$N/V = \sum_{\ell=1}^{\infty}\frac{x^\ell}{(l-1)!}\tilde{b}_\ell \to x + x^2\tilde{b}_2 \to x = N/V - (N/V)^2\tilde{b}_2 + \mathcal{O}(x^3)$$

where $\tilde{b}_\ell = b_\ell/V$. For x, N/V small, inverted iteratively for x.

Random Walks

$x_N = (2R - N)\ell$ gives $\langle x_N\rangle = Nl(2P - 1)$ and $\langle x_N^2\rangle = 4l^2NP(1 - P) + \langle x_N\rangle^2$, $\sigma_x^2 = 4l^2NP(1 - P)$. For R, N large, with $P = 1/2$, Guass. approx. Introduce prob. dens $P_N(x) \equiv P(x)/2l$, since x in $P(x)$ is discr. Use $t = N\Delta t$ and $D \equiv \frac{l^2}{2\Delta t}$. For M RW's with $x_0 = 0$, dens of RW pr un.-len. at t, $\rho(x, t)$ fulfills diffusion eq.

$$P_N(x) \to P(x, t) = \frac{e^{-\frac{x^2}{2\cdot 2Dt}}}{\sqrt{2\pi 2Dt}}, \quad \rho = MP_N \implies \frac{\partial\rho}{\partial t} = D\frac{\partial^2\rho}{\partial x^2}$$

Holds for any RW with symm step distr., $\chi(l)$, with RV l, $l = 1/2 \to \chi(l) = \frac{1}{2}(\delta(l - a) + \delta(l + a))$. $\langle\chi\rangle = 0$, $\langle\chi^2\rangle = a^2$. Want $p(x, t + \Delta t) = \int dl\, p(x - l, t)\chi(l)$. Expanding $p(x - l, t)$ around x and use properties the χ distr.

$$p(x, t + \Delta t) = p(x, t) + \frac{a^2}{2}\frac{\partial^2p(x, t)}{\partial x^2} \xrightarrow{\Delta t \to 0} \frac{\partial p}{\partial t} = D\frac{\partial^2p}{\partial x^2}, \quad D = a^2(2\Delta t)$$

Diffusion, currents, ext. forces

Current J, $n(x,t) = \rho(x,t)\Delta x$. $\Delta n = -\Delta J \Delta t \implies \frac{\partial \rho}{\partial t} = -\frac{\partial J}{\partial x}$, $J = -D\frac{\partial \rho}{\partial x}$ for $\Delta \to d$ (CE if DE is obeyed, Fick's law).

Often have steady motion, e.g. gravity. Add mean to RW step, $x(t+\Delta t) = x(t) + l + \bar{\Delta x}$. Let $\bar{\Delta x} = \gamma F \Delta t$ (mobility times net drift). Assuming const. acc. during collisions for particles in dilute gas (approx. mean vel. as zero), we get $\bar{\Delta x} = F\Delta t(\Delta t/2m) \implies \gamma = \Delta t/2m = D/m\bar{v}^2$, $\bar{v} = a/\Delta t$ is RW vel, for $Var(\chi) = a^2$. Repeat derivation of DE with $p(x - \bar{\Delta x} + l)$ in integrand. Get DE with drift term.

$$\frac{\partial \rho}{\partial t} = -\gamma F \frac{\partial \rho}{\partial x} + D\frac{\partial^2 \rho}{\partial x^2} \implies J = \gamma F \rho - D\frac{\partial \rho}{\partial x}$$

Compare steady-state solution with thm.equil. to get $\boxed{D = \gamma k_B T}$. Einstein's relation (Fluct./dissip. rel.).

Markov Chains

$$\begin{aligned}
\begin{pmatrix} P_1(n+1) \\ P_2(n+1) \end{pmatrix} &= \begin{pmatrix} W_{11} & W_{12} \\ W_{21} & W_{22} \end{pmatrix} \begin{pmatrix} P_1(n) \\ P_2(n) \end{pmatrix} \\
\frac{\mathrm{d}P_i}{\mathrm{d}t} &= \sum_j \left(\omega_{ij}P_j - \omega_{ji}P_i\right), \quad \omega_{ii} = 0, \quad \text{Master equation}
\end{aligned}$$