Formularium Statistical Mechanics

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Thermodynamics

All relevant thermodynamic relations can be derived from the first law:

$$\mathrm{d}E = T\mathrm{d}S - P\mathrm{d}V \tag{1}$$

For instance using S and V as independent variables we get

$$T = \left.\frac{\partial E}{\partial S}\right|_V, P = -\left.\frac{\partial E}{\partial V}\right|_S \tag{2}$$

Helmoltz free energy

$$F = E - TS \tag{3}$$

Gibbs free energy

$$G = E - TS + PV \tag{4}$$

Euler relation

$$E = TS - pV + \mu N \tag{5}$$

Random walks, Diffusion and Polymers

End-end vector of a random walk:

$$\langle \vec{R} \rangle = 0 \qquad \langle \vec{R}^2 \rangle = a^2 N \tag{6}$$

Diffusion equation:

$$\frac{\partial P(\vec{R}, t)}{\partial t} = D \nabla^2 P(\vec{R}, t) \tag{7}$$

Solution in d-dimensions (gaussian):

$$G_{\vec{R}_0}(\vec{R}, t) = \left(\frac{1}{4\pi D t}\right)^{d/2} e^{-\frac{(\vec{R} - \vec{R}_0)^2}{4Dt}} \tag{8}$$

The drift-diffusion equation

$$\frac{\partial c(x,t)}{\partial t} = -\frac{\partial j_{tot}}{\partial x} = D\frac{\partial^2 c(x,t)}{\partial x^2} + \frac{1}{\gamma}\,\frac{\partial}{\partial x}\left[c(x,t)\frac{dV}{dx}\right] \tag{9}$$

Using the Einstein relation ($D = k_B T/\gamma$) we can write the drift-diffusion equation in a more compact form

$$\frac{\partial c(x,t)}{\partial t} = D\frac{\partial}{\partial x}\left[e^{-\beta V(x)}\frac{\partial}{\partial x}\left(e^{\beta V(x)}c(x,t)\right)\right] \tag{10}$$

End-end distance self-avoiding walks

$$\langle \vec{R}^2 \rangle \sim a^2 N^{2\nu} \tag{11}$$

Flory exponent in $d \leq 4$ dimensions

$$\nu = \frac{3}{2+d} \tag{12}$$

General formalism of Classical Statistical Mechanics

Hamiltonian

$$\mathcal{H}(\Gamma) = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} + \Phi(\vec{q}_1, \vec{q}_2 \ldots \vec{q}_N) \tag{13}$$

Equilibrium average of an observable

$$\langle A(\Gamma) \rangle = \int d\Gamma \rho(\Gamma) A(\Gamma) \tag{14}$$

Microcanonical ensemble

$$\rho(\Gamma) = \frac{\delta(E - \mathcal{H}(\Gamma))}{\omega(E,N,V) N! h^{3N}} \tag{15}$$

Microcanonical density of states [1]

$$\omega(E,N,V) = \int \frac{d\Gamma}{N! h^{3N}} \delta\left(E - \mathcal{H}(\Gamma)\right) \tag{16}$$

$$\Omega(E,N,V) = \int \frac{d\Gamma}{N! h^{3N}} \theta\left(E - \mathcal{H}(\Gamma)\right) \tag{17}$$

$$\omega(E,N,V) = \frac{\partial \Omega(E,N,V)}{\partial E} \tag{18}$$

Entropy:

$$S(E,N,V) = k_B \log \omega(E,N,V) \tag{19}$$

[1] Note that in this formula and also in the Canonical partition function (21) there is a $N!$; this factor accounts for the degeneracy in the counting and it has a quantum mechanical origin. It should be used only in systems where particles are indistinguishable.

Canonical ensemble

$$\rho(\Gamma) = \frac{e^{-\beta\mathcal{H}(\Gamma)}}{N!h^{3N}Z(N,V,T)} \tag{20}$$

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

$$Z(N,V,T) = \int \frac{d\Gamma}{N!h^{3N}}\, e^{-\beta\mathcal{H}(\Gamma)} \tag{21}$$

Integration over momenta

$$Z(N,V,T) = \frac{Q(N,V,T)}{N!\lambda_T^{3N}} \tag{22}$$

thermal wavelength

$$\lambda_T = \frac{h}{\sqrt{2\pi m k_B T}} \tag{23}$$

Relation with canonical ensemble

$$Z(N,V,T) = \int dE\; e^{-\beta E}\omega(E,N,V) \tag{24}$$

Connection with thermodynamics

$$F = E - TS = -k_B T \log Z \tag{25}$$

Grandcanonical ensemble

$$\rho(\Gamma,N) = \frac{e^{-\beta\mathcal{H}(\Gamma)}e^{\beta\mu N}}{N!h^{3N}\Xi(\mu,V,T)} \tag{26}$$

Grand canonical partition function

$$\Xi(\mu,V,T) = \sum_N e^{\beta\mu N} Z(N,V,T) \tag{27}$$

Connection with thermodynamics

$$\frac{pV}{k_B T} = \log \Xi(\mu,V,T) \tag{28}$$

Equipartition Theorem

$$\left\langle x_r \frac{\partial \mathcal{H}}{\partial x_s} \right\rangle = k_B T \delta_{rs} \tag{29}$$

Law of mass action

For a reaction

$$B_1 + B_2 \rightleftharpoons 2B_3 \tag{30}$$

the law of mass action takes the form:

$$\frac{[B_3]^2}{[B_1][B_2]} = K_{eq}(T) = \left(\frac{\lambda_1\lambda_2}{\lambda_3^2}\right)^3 e^{-\beta\Delta F} \tag{31}$$

with ΔF internal free energies difference

Interacting Systems

Virial theorem

$$p = \frac{Nk_BT}{V} - \frac{1}{3}\sum_{i,j=1}^{N}\left\langle \vec{q}_i \cdot \vec{F}_{ij}\right\rangle = nk_BT - \frac{n^2}{6}\int r\,\frac{d\phi(r)}{dr}g(r)d\vec{r} \tag{32}$$

with $\vec{F}_{ij}$ force exerted by particle j on particle i, $\phi(r)$ interparticle potential[2] and where the pair correlation function $g(\rho)$

$$n^{(2)}\left(\vec{r}, \vec{r}+\vec{\rho}\right) = \left\langle \sum_{i=1}^{N}\delta\left(\vec{r}-\vec{q}_i\right)\sum_{j\neq i}^{N}\delta\left(\vec{r}+\vec{\rho}-\vec{q}_j\right)\right\rangle = n^2 g(\rho) \tag{33}$$

Virial expansion

$$p = nk_BT\left(1 + b_2 n + b_3 n^2 + \ldots\right) \tag{34}$$

Second virial coefficient

$$b_2 \equiv -\frac{1}{2}\int d\vec{r}\left(e^{-\beta\phi(r)} - 1\right) \tag{35}$$

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

$$F \leq F_0 + \langle\mathcal{H}\rangle_0 \tag{36}$$

van der Waals model

$$p = \frac{Nk_BT}{V - Nb} - \frac{aN^2}{V^2} \tag{37}$$

Critical exponents

$$\begin{aligned} \delta p &\sim (\delta v)^{\delta} \\ \delta v &\sim (\delta t)^{\beta} \\ \kappa_T &\sim |\delta t|^{-\gamma} \\ c_V &\sim |\delta t|^{-\alpha} \end{aligned} \tag{38}$$

Critical exponents

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

[2] for spherically symmetric interactions.

Ising model

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} s_i s_j - H \sum_i s_i \tag{39}$$

magnetization

$$M = \sum_k \langle s_k \rangle = \frac{1}{Z} \sum_{\{s_i\}} s_k e^{-\beta \mathcal{H}(\{s_i\})} \tag{40}$$

Spontaneous magnetization in 2d (exact)

$$m_0(T) = \left[1 - \sinh^{-4}\left(\frac{2J}{k_B T} \right) \right]^{1/8} \tag{41}$$

Critical temperatures

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

Spontaneous magnetization ($H = 0$)

$$m_0(T) \sim (T_c - T)^\beta \tag{42}$$

Specific heat:

$$c \sim |T - T_c|^{-\alpha} \tag{43}$$

Magnetic susceptibility:

$$\chi = \frac{\partial M}{\partial H} \sim |T - T_c|^{-\gamma} \tag{44}$$

Magnetic field ($T = T_c$)

$$H \sim |M|^\delta \tag{45}$$

Correlation function

$$G^{(2)}(\vec{x}, \vec{y}) = \langle (s_{\vec{x}} - \langle s \rangle)(s_{\vec{y}} - \langle s \rangle) \rangle \sim e^{-\frac{|\vec{x} - \vec{y}|}{\xi}} \tag{46}$$

correlation length

$$\xi \sim |T_c - T|^{-\nu} \tag{47}$$

Correlation function at $T = T_c$

$$G^{(2)} \sim \frac{1}{r^{d-2+\eta}} \tag{48}$$

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

$$\alpha + 2\beta + \gamma = 2 \tag{49}$$

$$\gamma = \beta(\delta - 1) \tag{50}$$

Quantum Statistical Mechanics

Quantum partition function (canonical):

$$Z = \sum_{\alpha} e^{-\beta E_\alpha} \tag{51}$$

Identical particles (upper sign Bosons and lower Fermions)

$$\frac{pV}{k_B T} = \log \Xi = \mp \sum_{\gamma} \log\left(1 \mp e^{\beta(\mu - \varepsilon_\gamma)}\right) \tag{52}$$

$$E = -\left.\frac{\partial \log \Xi}{\partial \beta}\right|_{\beta\mu} = \sum_{\gamma} \frac{\varepsilon_\gamma}{e^{\beta(\varepsilon_\gamma - \mu)} \mp 1} = \sum_{\gamma} \langle n_\gamma \rangle \varepsilon_\gamma \tag{53}$$

Free particles ($3d$)

$$\frac{pV}{k_b T} = \pm \frac{V}{\lambda_T^3} \sum_{l=1}^{+\infty} (\pm 1)^l \frac{z^l}{l^{5/2}} \tag{54}$$

$$n\lambda_T^3 = \pm \sum_{l=1}^{+\infty} (\pm 1)^l \frac{z^l}{l^{3/2}}. \tag{55}$$

Low density expansion:

$$p = nk_B T \left(1 \mp \frac{n\lambda_T^3}{4\sqrt{2}} + \dots\right) \tag{56}$$

Bose Einstein condensation ($3d$)

$$n\lambda_T^3 = \frac{\lambda_T^3}{V} \frac{z}{1-z} + \sum_{l=1}^{+\infty} \frac{z^l}{l^{3/2}} \tag{57}$$

Blackbody energy:

$$E = \int_0^\infty d\omega \, \frac{g(\omega)\hbar\omega}{e^{\beta\hbar\omega} - 1} = \frac{V k_B^4 T^4}{\pi^2 c^3 \hbar^3} \int_0^\infty \frac{x^3 \, dx}{e^x - 1} = \frac{V\hbar}{15 c^3} \left(\frac{k_B T}{\hbar}\right)^4 \tag{58}$$

(the integral in x can be calculated exactly and gives $\pi^2/15$).

Ground state fermions:

$$E_0 = \int_0^{\varepsilon_F} \varepsilon g(\varepsilon) \, d\varepsilon \tag{59}$$

$$\lim_{T \to 0} p = \frac{1}{V} \int_0^{\varepsilon_F} d\varepsilon g(\varepsilon)(\varepsilon_F - \varepsilon) = p_0 > 0 \tag{60}$$

Low temperature behavior

$$E = E_0 + \frac{\pi^2}{6} g(\varepsilon_F)(k_B T)^2 + \dots \tag{61}$$