'Separable/Free/Non-interacting' Hamiltonians and their partition f^n

A Hamiltonian of the form

$$\hat{H} = \sum_i \hat{h}_i$$ is called non-interacting/free/separable system

where different $\hat{h}_i$ commute i.e. $[\hat{h}_i, \hat{h}_j] = 0$.

The most interesting feature of such H is that the partition f^n factorizes.

Classically,

$$Z = \sum_{c_1 \ldots c_N} e^{-\beta H}$$ where c_i denote phase-space of i'th particle

$$= \sum_{c_1 \ldots c_N} e^{-\beta \sum_i h_i}$$

$$= \sum_{c_1} e^{-\beta h_1} \sum_{c_2} e^{-\beta h_2} \cdots \sum_{c_n} e^{-\beta h_n}$$

$$= Z_1 Z_2 \cdots Z_n = \prod_i Z_i$$ where

$$Z_i = \sum_i e^{-\beta h_i}$$

Quantumly,

$$Z = \mathrm{Tr}_{1,2,\ldots N}\, e^{-\beta\hat{H}}$$

$$= \mathrm{Tr}_1\, e^{-\beta\hat{h}_1}\, \mathrm{Tr}_2\, e^{-\beta\hat{h}_2} \cdots \mathrm{Tr}_N\, e^{-\beta\hat{h}_N}$$

(recall $[h_i, h_j] = 0$ by assumption).

$$= \prod_i Z_i \qquad \underbrace{[\hat{h}_i, \hat{h}_j]}_{=0}$$

Examples of separable systems:

- $$\hat{H} = \sum_i \underbrace{\left[\frac{\hat{p}_i^2}{2m} + V_i(\hat{x}_i)\right]}_{h_i}$$

- $H = h\sum_i \hat{\sigma}_i^z$, ($\hat{\sigma}_i^z$ = Pauli matrix along $\hat{z}$)

Examples of non-separable systems:

- $$\hat{H} = \sum_i \frac{\hat{p}_i^2}{2m} + \hat{V}_i(\hat{x}_i) + \sum_{i\neq j} \hat{U}(\hat{x}_i - \hat{x}_j)$$

interaction between particles

- $$\hat{H} = J \sum_{\langle ij\rangle} \hat{\sigma}_i^z \sigma_j^z$$ - ij belong to vertices of some graph/lattice.

Sometimes, a seemingly non-separable system can be made separable after change of variables.

e.g. $H = \sum_i \frac{\hat{p}_i^2}{2m} + \sum_i (\hat{x}_i - \hat{x}_{i+1})^2 = \sum_k \frac{p_k^2}{2m} + \omega_k^2 \hat{x}_k^2$ ← normal modes.

A couple examples :

① Free non-relativistic gas (again) :

$$H = \sum_i \frac{p_i^2}{2m} + V(x_i)$$ where $V(x_i) = 0$ inside the box and ∞ outside.

This is a separable system.

$$Z = \frac{\prod_{i=1}^{N} Z_i}{N!}$$ ← due to identical particles

where $$Z_i = \frac{\int d^3p\, d^3x \; e^{-\frac{\beta \vec{p}^2}{2m}}}{h^3}$$

$$= \left[\sqrt{\frac{2\pi m}{\beta}}\right]^3 \frac{V}{h^3} = \frac{V}{\lambda^3}$$

where $\lambda = \frac{h}{\sqrt{2\pi m T}}$ = thermal de-Broglie length.

$$\Rightarrow \quad Z = \frac{1}{N!}\left[\frac{V}{\lambda^3}\right]^N$$

$$F = -T \log Z$$

$$= -T\left[N\log\frac{V}{\lambda^3} - N\log N + N\right]$$

$$= -T\,N\log\left[\frac{Ve}{N\lambda^3}\right] = \text{extensive since } \frac{V}{N} = \frac{1}{\rho} \text{ is intensive.}$$

Now let's use $dF = -SdT - PdV + \mu dN$ to calculate physical properties.

Practice Problem: Repeat the analysis on this page in d-dimensions

$$P = -\left.\frac{dF}{dV}\right|_{T,N} = \frac{TN}{V}$$

$$\Rightarrow \boxed{PV = NT} \text{ as expected.}$$

$$\text{Average energy}_{E} = \frac{\sum_c E(c)\, e^{-\beta E(c)}}{\sum_c e^{-\beta E(c)}}$$

$$= -\frac{\partial}{\partial\beta}(\log Z_1)$$

Since $\log Z_1 \sim -N\log\lambda^3 \sim N\log T^{3/2} \sim -\frac{3N}{2}\log(\beta)$

$$\Rightarrow \boxed{E = \frac{3}{2}NT} \Rightarrow \boxed{C_V = \frac{3}{2}N}$$

$$S = -\left.\frac{dF}{dT}\right|_{V,N} = N\log\left[\frac{Ve}{N\lambda^3}\right] + \frac{3}{2}N$$

$$= (E - F)/T \text{ as expected.}$$

(2) $H = -h \sum_i S_i \qquad S_i = \pm 1$

Again separable.

$$Z = \left[\sum_{S_i = \pm 1} e^{\beta h S_i} \right]^N = \left[2\cosh(\beta h) \right]^N$$

Note that here we do not divide by $N!$ because different spins live on different lattice sites and hence are distinguishable.

(3) $H = \sum_{i=1}^{N} \left[\frac{\vec{p}_i^{\,2}}{2m} + \frac{1}{2} m \omega^2 \vec{q}_i^{\,2} \right]$ in d-dimensions

Again separable.

$$Z = \left[\frac{\int d^d p \; e^{-\frac{\beta p^2}{2m}} \int d^d q \; e^{-\frac{\beta m \omega^2 q^2}{2}}}{h^d} \right]^N$$

$$= \left[\frac{\sqrt{\frac{2\pi m}{\beta}} \sqrt{\frac{2\pi}{m \beta \omega^2}}}{h} \right]^{dN}$$

$$= \left[\frac{T}{\hbar \omega} \right]^{dN}$$

$$\Rightarrow \quad F = -NTd \log\left[\frac{T}{\hbar\omega}\right]$$

$$E = -\frac{\partial \log Z}{\partial \beta} = +\frac{\partial}{\partial \beta} dN \log(\beta\hbar\omega)$$

$$= TdN$$

['equipartition' of energy : each gaussian mode contributes $\frac{NT}{2}$ energy]

specific heat $\boxed{c_N = \frac{1}{N}\frac{dE}{dT}\Big|_N = d}$

(4) Homework : $H = \sum_{i=1}^{N}\left[c\,|\vec{p}_i|^{\alpha} + d\,|q_i|^{\beta}\right]$

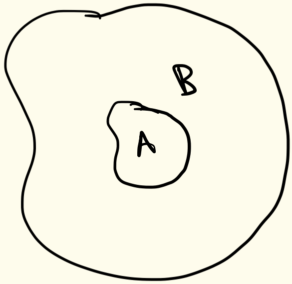
Use the integral $\displaystyle\int_0^{\infty} e^{-ax^{\mu}} x^{\nu-1}\,dx$

$$= \frac{1}{\mu}\Gamma\left(\frac{\nu}{\mu}\right)\frac{1}{a^{\nu/\mu}}$$

To get an intuition for this integral, work it out for $a \gg 1$ using saddle point.

Grand Canonical Ensemble

Sometimes it's easier to let not just the energy, but also particle number fluctuate. This is called grand canonical ensemble.



Probability of finding a specific config. in A with partle # N_A and energy E_A

$$P(C_A(E_A, N_A))$$

$$\propto \Omega_B(E - E_A, N - N_A)$$

$$= e^{S_B(E - E_A,\, N - N_A)}$$

$$\propto e^{-\left.\frac{\partial S_B(E')}{\partial E'}\right|_{E'=E,N,V} E_A - \left.\frac{\partial S_B(N')}{\partial N'}\right|_{N'=N,E,V} N_A}$$

$$dE = T\,dS - P\,dV + \mu\,dN$$

$$\Rightarrow \left.\frac{\partial S}{\partial E}\right|_{V,N,E} = \beta \quad , \quad \left.\frac{\partial S}{\partial N}\right|_{E,V} = -\beta\mu$$

$$\Rightarrow P(C_A(E_A, N_A)) \propto e^{-\beta[E_A - \mu N_A]}$$

Again, restricting focus to subsystem A, and dropping the subscript A, the expectation value of any observable within GCE is:

$$\langle \hat{O} \rangle = \frac{\mathrm{Tr}\ \hat{O}\ e^{-\beta(\hat{H}-\mu\hat{N})}}{\mathrm{Tr}\ e^{-\beta(\hat{H}-\mu\hat{N})}}$$

The trace is over all configurations with all possible values of $\langle \hat{N} \rangle$.

The denominator is sometimes called "grand partition fn".

Recall that in the canonical ensemble,

$Z = \mathrm{Tr}\ e^{-\beta\hat{H}}$ was equal to $e^{-\beta(E-TS)}$

What is $\mathrm{Tr}\ e^{-(\beta\hat{H}-\mu\hat{N})}$ equal to?

$$Q \overset{\mathrm{def}}{=} \mathrm{Tr}\ e^{-\beta(\hat{H}-\mu\hat{N})}$$

$$= \sum_{N'=0}^{\infty} \int dE'\ e^{S(E',N')}\ e^{-\beta E'}\ e^{+\beta\mu N'}$$

In the thermodynamic limit the sum will be dominated by N^* that satisfies

$$\left.\frac{\partial S}{\partial N'}\right|_{N^*} = -\beta\mu$$

denoting $N^* = \langle \hat{N} \rangle$ by just N,

$$\mathcal{Q} = e^{\beta \mu N} \int dE' \, e^{S(E', N) - \beta E'}$$

$$= e^{\beta \mu N - \beta F(N, V, T)}$$

$$\Rightarrow \quad \mathcal{G} \overset{\text{def}}{=} -T \log \mathcal{Q}$$

$$= F - \mu N = E - TS - \mu N$$

where $E = \langle \hat{H} \rangle$.

$$\Rightarrow \quad \boxed{d\mathcal{G} = -S\,dT - P\,dV - N\,d\mu}$$

Further, since $E = TS - PV + \mu N$

$$\Rightarrow \quad \boxed{\mathcal{G} = -PV}$$

Number fluctuations in GCE

Analogous to the discussion of energy fluctuations in canonical ensemble,

$$\langle (\delta N)^2 \rangle_{GCE} = \langle \hat{N}^2 \rangle - \langle \hat{N} \rangle^2$$

$$= \frac{1}{Q} \frac{\partial^2 Q}{\partial(\beta\mu)^2} - \left[\frac{1}{Q} \frac{\partial Q}{\partial(\beta\mu)} \right]^2$$

$$= \frac{\partial [\log Q]}{\partial(\beta\mu)^2} = \frac{\partial \langle N \rangle}{\partial(\beta\mu)} \sim N$$

(extensive)

$$\Rightarrow \frac{\sqrt{\langle (\delta N)^2 \rangle_{GCE}}}{N} \sim \frac{1}{\sqrt{N}}$$

$\Rightarrow$ particle number <u>density</u> is well-defined despite fluctuations in particle number.

Example of GCE:

① Non-interacting gas:

$$\mathcal{Q}(T,\mu,V) = \sum_{N=0}^{\infty} e^{\beta\mu N} \frac{1}{N!} \int \prod d^3q \prod d^3p \, e^{-\beta \sum_i \frac{p_i^2}{2m}}$$

$$= \sum_{N=0}^{\infty} e^{\beta\mu N} Z(N,T,V)$$

$$= \sum_{N=0}^{\infty} \frac{e^{\beta\mu N}}{N!} \left(\frac{V}{\lambda^3}\right)^N$$

$$= e^{\left[e^{\beta\mu}\frac{V}{\lambda^3}\right]}$$

$$\Rightarrow \mathcal{G} = -T\log\mathcal{Q} = -Te^{\beta\mu}\frac{V}{\lambda^3}$$

$$= -PV$$

$$\Rightarrow P = e^{\beta\mu}\frac{T}{\lambda^3} \Rightarrow \mu = T\log\left(\frac{P\lambda^3}{T}\right)$$

$$N = -\frac{\partial\mathcal{G}}{\partial\mu} = \frac{T}{T}e^{\beta\mu}\frac{V}{\lambda^3} = e^{\beta\mu}\frac{V}{\lambda^3}$$

$$= PV/T \Rightarrow \boxed{PV = NT}$$