The main ensembles: Canonical

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Let's first assume we have a fixed number of particles N $\rightarrow$ absolute knowledge about this part of the problem

$$D_B = \frac{1}{Z} \exp -\beta \hat{H}$$

Let's now use the basis that diagonalizes $\hat{H}$

$$\hat{H}|r\rangle = E_r |r\rangle$$

$$\Rightarrow \langle r|D_B|r'\rangle = \frac{1}{Z}\langle r| \underbrace{\exp -\beta H}_{f(H)} |r'\rangle = \frac{1}{Z} \exp -\beta E_r \, \delta_{rr'}$$

$$D_B = \frac{1}{Z} \sum_r e^{-\beta E_r} |r\rangle\langle r|$$

if $H = H^{(a)} + H^{(\alpha)}$ with $[H^{(a)}, H^{(\alpha)}] = 0$

$$\Rightarrow D_B = D_B^{(a)} \otimes D_B^{(b)}$$

Let $|\ell\rangle = |a\rangle \otimes |\alpha\rangle$ ← eigenstate of $H^{(\alpha)}$

eigenstate of $H^{(a)}$

$|m\rangle = |b\rangle \otimes |\beta\rangle$

$$\langle \ell|\hat{H}|m\rangle = \left(H^{(a)}_{ab} + H^{(\alpha)}_{\alpha\beta}\right)\delta_{ab}\delta_{\alpha\beta}$$

The same way

$$\langle \ell| e^{-\beta H}|m\rangle = \underbrace{\left(e^{-\beta H^{(a)}_{ab}} e^{-\beta H^{(\alpha)}_{\alpha\beta}}\right)}\delta_{ab}\delta_{\alpha\beta}$$

True only if they commute

Campbell-Baker-Hausdorff formula

Satisfied if the Hamiltonian is separable

$$Z = \mathrm{Tr}\, e^{-\beta \hat{H}} = \sum_{\ell} \langle \ell| e^{-\beta H}|\ell\rangle = \sum_{a\alpha} \langle a|\otimes\langle\alpha| e^{-\beta H}|a\rangle\otimes|\alpha\rangle$$

$$= \sum_{a\alpha} e^{-\beta H^{(a)}_{aa}} e^{-\beta H^{(\alpha)}_{\alpha\alpha}} = \sum_{a} e^{-\beta H^{(a)}_{aa}} \sum_{\alpha} e^{-\beta H^{(\alpha)}_{\alpha\alpha}}$$

$$\Rightarrow \quad Z = Z^{(a)} Z^{(\alpha)}$$

Canonical ensemble

$$Z = \mathrm{Tr}\, e^{-\beta H} = \sum_{r} e^{-\beta E_r}$$

In the continuum limit $\sum_r \to \int dE\, \rho(E)$

$$Z = \int dE\, \rho(E)\, e^{-\beta E}$$

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$$E(\beta, x) = -\frac{\partial \ln Z}{\partial x_i}\Bigg|_{\beta, x_{j\neq x_i}}$$

Let's also call

$$X_i = \left\langle \frac{\partial H}{\partial x_i} \right\rangle = \mathrm{Tr}\left[\frac{\partial H}{\partial x_i} D\right] = \mathrm{Tr}\left[\frac{1}{Z}\frac{\partial H}{\partial x_i} e^{-\beta H}\right]$$

$$= \mathrm{Tr}\left[-\frac{1}{Z}\frac{1}{\beta}\frac{\partial e^{-\beta H}}{\partial x_i}\right] = -\frac{1}{\beta}\frac{1}{Z}\mathrm{Tr}\left[\frac{\partial}{\partial x_i} e^{-\beta H}\right]$$

$$= -\frac{1}{\beta}\frac{1}{Z}\frac{\partial}{\partial x_i}\underbrace{\left[\mathrm{Tr}\, e^{-\beta H}\right]}_{Z} = -\frac{1}{\beta}\frac{1}{Z}\frac{\partial Z}{\partial x_i}$$

$$\Rightarrow X_i = \left\langle \frac{\partial H}{\partial x_i} \right\rangle = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial x_i}\Bigg|_{\beta, x_j \neq x_i}$$

Note: The $\hat{A}_i$ associated with Lagrange multiplier λ_i have the form $\langle A_i \rangle \propto \frac{\partial \ln Z}{\partial \lambda_i}$

But also other observables will also be of the form $\langle \hat{O} \rangle \propto \frac{\partial \ln Z}{\partial x}$

where x is some parameter

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In general

$\rightarrow \langle H \rangle = E$

$$S = k\ln Z - k\sum_i \lambda_i A_i$$

$$S = k\ln Z + \beta k E$$

Reorganizing

$$k\ln Z = S - \beta k E = S - \left(\frac{1}{T}\right)E$$

We note that

$S(E,V)$

and $\frac{\partial S}{\partial E} = \frac{1}{T}$

Legendre transform

$f(x) \qquad \frac{\partial f}{\partial x} = u$

$$\Rightarrow g(u) = f(x) - ux$$

$\Rightarrow$

$f(x) \rightarrow S(E,V)$

$u = \frac{\partial f(x)}{\partial x} \rightarrow \frac{1}{T}$

$x \rightarrow E$

$g(u) \rightarrow \Phi_1\left(\frac{1}{T}, x\right)$

$$\ln Z(\beta, V) = \frac{1}{k}\Phi_1\left(\frac{1}{T}, V\right)$$

Rearranging again

$$-kT\ln Z = \underbrace{E - TS}_{\text{Legendre transform}} = F(T,V)$$

$$\Rightarrow F(T, X_i) = -\frac{1}{\beta}\ln Z$$

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In differential form

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$$\frac{1}{k} dS = d(\ln Z) + d(\beta E)$$

$$Z \equiv Z[\beta, x_i]$$

$$\Rightarrow \quad d \ln Z = \underbrace{\frac{\partial \ln Z}{\partial \beta}}_{-E} d\beta + \sum_{x_i} \underbrace{\frac{\partial \ln Z}{\partial x_i}}_{-\beta X_i} dx_i$$

$$= -E d\beta - \beta \sum_i X_i dx_i$$

$$d(\beta E) = E d\beta + \beta dE$$

$$\Rightarrow \quad \frac{1}{k} dS = -\cancel{E d\beta} - \beta \sum_i X_i dx_i + \cancel{E d\beta} + \beta dE$$

$$\frac{1}{k} dS = \beta dE - \beta \sum_i X_i dx_i$$

$$① \quad T dS = dE - \sum_i X_i dx_i$$

Also

$$dF = -k_B \underbrace{\ln Z}_{\frac{S}{k} - \beta E} dT - k_B T \underbrace{d \ln Z}_{-E d\beta - \beta \sum_i X_i dx_i}$$

$$= -S dT + \cancel{\frac{E}{T} dT} + \cancel{\frac{E}{\beta} d\beta} + \sum_i X_i dx_i \qquad ⑥$$

$$\beta = \frac{1}{kT} \qquad d\beta = \frac{-1}{kT^2} dT$$

$d\beta = \frac{\beta}{T}$

(2) $$\boxed{dF = -S\,dT + \sum_i X_i\,dx_i}$$

From our thermodynamic relation

$dE = T\,dS - P\,dV$ (1) $dE = T\,dS - X_i\,dV$

$\Rightarrow x_i = -V \qquad X_i = P$

$$X_i = \left\langle \frac{\partial H}{\partial x_i} \right\rangle \rightarrow -\left\langle \frac{\partial H}{\partial V} \right\rangle \equiv \text{units of pressure}$$

consistent

From thermodynamics

(2) $$\frac{\partial F}{\partial V} = -P \qquad -\left.\frac{\partial F}{\partial V}\right|_{T,N} = P$$

consistent

$$\Rightarrow \boxed{P = \frac{1}{\beta} \left.\frac{\partial \ln Z}{\partial V}\right|_{\beta,N}} \qquad \left.\frac{\partial F}{\partial N}\right|_{T,V} = \mu$$

$$\boxed{\mu = \frac{-1}{\beta} \left.\frac{\partial \ln Z}{\partial N}\right|_{\beta,V}}$$

Fluctuations

$$-\frac{\partial E}{\ } = \int^1 dx\, \mathrm{Tr}\left[(\hat{H}-E) D^{x} (\hat{H}-E) D^{(1-x)} \right] = \mathrm{Tr}\left[(\hat{H}-E) D \right]$$

$\partial\beta$

$$D = \frac{1}{Z} e^{-\beta H}$$ $\Rightarrow$ commutes with H

$$= \langle (\hat{H} - E)^2 \rangle = \langle \hat{H}^2 \rangle - E^2$$

$$E = -\frac{\partial \ln Z}{\partial \beta}$$

$$\langle (H - E)^2 \rangle = \frac{\partial^2 \ln Z}{\partial \beta^2}$$

The heat capacity

$$C_x = T \frac{\partial S}{\partial T}\Big|_x \equiv \text{heat capacity at constant } x$$

but $$\frac{\partial S}{\partial T}\Big|_x = \underbrace{\frac{\partial S}{\partial E}\Big|_x}_{\frac{1}{T}} \frac{\partial E}{\partial T}\Big|_x \Rightarrow C_x = \frac{\partial E}{\partial T}\Big|_x$$

$$\frac{\partial E}{\partial T}\Big|_x = \frac{\partial E}{\partial \beta}\Big|_x \frac{\partial \beta}{\partial T}\Big|_x = -\frac{1}{kT^2} \frac{\partial E}{\partial \beta}$$

but
$$\frac{\partial E}{\partial \beta} = -\langle (\hat{H} - E)^2 \rangle$$

$\ln Z$ is convex

$$C_x = \frac{\langle (\hat{H} - E)^2 \rangle}{kT^2} \geqslant 0$$

Consistent