Physical significance of the various statistical quantities in the canonical ensemble

$$P_r \equiv \frac{\langle n_r \rangle}{\mathcal{N}} = \frac{n_r^*}{\mathcal{N}} = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} = -\frac{1}{\beta}\frac{\partial}{\partial E_r}\ln\left\{\sum_r e^{-\beta E_r}\right\}$$

$$U = \frac{\sum_r e^{-\beta E_r} E_r}{\sum_r e^{-\beta E_r}} = -\frac{\partial}{\partial \beta}\ln\left\{\sum_r e^{-\beta E_r}\right\}$$

$$A = -\frac{1}{\beta}\ln\left\{\sum_r e^{-\beta E_r}\right\} \rightarrow \quad \beta A = -\ln\left\{\sum_r e^{-\beta E_r}\right\}$$

$$d(\beta A) = \frac{\partial(\beta A)}{\partial \beta} d\beta + \frac{\partial(\beta A)}{\partial E_r} dE_r = U d\beta + \beta \frac{\langle n_r \rangle}{\mathcal{N}} dE_r$$

$$= U d\beta + \beta dU - \beta dU + \beta \frac{\langle n_r \rangle}{\mathcal{N}} dE_r$$

$$= d(\beta U) - \beta dU + \beta \frac{\langle n_r \rangle}{\mathcal{N}} dE_r$$

$$d(\beta A) = d(\beta U) - \beta dU + \beta \frac{\langle n_r \rangle}{\mathcal{N}} dE_r$$

$$d[\beta(A-U)] = -\beta dU + \beta \frac{\langle n_r \rangle}{\mathcal{N}} dE_r$$

$$d[\beta(U-A)] = \beta dU - \beta \frac{\langle n_r \rangle}{\mathcal{N}} dE_r$$

$$dU = dQ - dW = TdS - dW$$

$$\beta dU = \beta T dS - \beta dW$$

$$\beta T dS = \beta dU + \beta dW$$

$$\beta(U-A) = \beta T S = \frac{S}{k} \qquad \sum_r \frac{\langle n_r \rangle}{\mathcal{N}} dE_r = dW$$

$$(U-A) = ST$$

$A = U - ST \longrightarrow A = -\frac{1}{\beta}\ln\left\{\sum_r e^{-\beta E_r}\right\}$ is really the Helmholtz free energy

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Partition function $\rightarrow Q_N(V,T) = \sum_r e^{-\beta E_r} = \sum_r e^{(-E_r/kT)}$

$$A(N,V,T) = -kT \ln Q_N(V,T)$$

A = E - TS

dA = $\cancel{d}$E - T$\cancel{d}$S - SdT

$\cancel{d}$E = T$\cancel{d}$S – PdV + μdN $\oplus$

dA = -SdT - PdV + μdN

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dA = -SdT - PdV + μdN

$$S = -\left(\frac{\partial A}{\partial T}\right)_{N,V}, \quad P = -\left(\frac{\partial A}{\partial V}\right)_{N,T}, \quad \mu = \left(\frac{\partial A}{\partial N}\right)_{V,T}$$

$$\begin{cases} S = k\dfrac{\partial}{\partial T}[T \ln Q_N(V,T)]_{N,V} \\ P = kT\dfrac{\partial}{\partial V}[\ln Q_N(V,T)]_{N,T} \\ \mu = -kT\dfrac{\partial}{\partial N}[\ln Q_N(V,T)]_{T,V} \end{cases}$$

$$U = A + TS = -kT \ln Q_N(V,T) + Tk\frac{\partial}{\partial T}[T \ln Q_N(V,T)]_{N,V}$$

$$= \cancel{-kT \ln Q_N(V,T)} + \cancel{kT \ln Q_N(V,T)} + kT^2 \frac{\partial}{\partial T}\ln Q_N(V,T)$$

$$= kT^2 \frac{\partial}{\partial T}\ln Q_N(V,T)$$

$$U = kT^2 \frac{\partial}{\partial \beta}\ln Q_N(V,T)\left(\frac{\partial \beta}{\partial T}\right) = -\frac{\partial}{\partial \beta}\ln Q_N(V,T)$$

$$U = \frac{\sum_r e^{-\beta E_r} E_r}{\sum_r e^{-\beta E_r}} = -\frac{\partial}{\partial \beta}\ln Q_N(V,T)$$

$$U = A + TS = A - T\left(\frac{\partial A}{\partial T}\right)_{N,V}$$

$$= -T^2\left[\frac{\partial}{\partial T}\left(\frac{A}{T}\right)\right]_{N,V}$$

$$= -T^2\left[\frac{\partial}{\partial \beta}\left(\frac{A}{T}\right)\right]_{N,V}\left(\frac{\partial \beta}{\partial T}\right)$$

$$= -T^2\left[\frac{\partial}{\partial \beta}\left(\frac{A}{T}\right)\right]\left(\frac{-1}{kT^2}\right)$$

$$= \frac{\partial}{\partial \beta}\left(\frac{A}{kT}\right)$$

&

$$U = \frac{\sum_r e^{-\beta E_r} E_r}{\sum_r e^{-\beta E_r}} = -\frac{\partial}{\partial \beta}\ln Q_N(V,T)$$

$$A = -\frac{1}{\beta}\ln\left\{\sum_r e^{-\beta E_r}\right\}$$

$$C_v = \left(\frac{\partial U}{\partial T}\right)_{N,V} = T\left(\frac{\partial S}{\partial T}\right)_{N,V}$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_{N,V}$$

$$C_V = -T\left(\frac{\partial^2 A}{\partial T^2}\right)_{N,V} = k\beta^2\left[\frac{\partial^2}{\partial \beta^2}\ln Q_N(V,T)\right]$$

$$G = A + PV$$

G = E – TS +PV

dG = ~~dE~~ - ~~TdS~~ – SdT + ~~PdV~~ +VdP

~~dE~~ = ~~TdS~~ – ~~PdV~~ + μdN ⊕

dG = -SdT + VdP + μdN

$$G = A + PV = A - V\left(\frac{\partial A}{\partial V}\right)_{N,T}$$

A = E - TS → **G = A + PV**

G = E - TS + PV

E - TS + PV = μ N

E = TS – PV + μ N

G = μ N

$$\boxed{\mathbf{G = E - TS + PV = A + PV = \mu\, N}}$$

$$G = A + PV = A - V\left(\frac{\partial A}{\partial V}\right)_{N,T} = N\mu$$

$$G = A + PV = A - V\left(\frac{\partial A}{\partial V}\right)_{N,T} = N\mu$$

dA = -SdT - PdV + μdN

$$G = A + PV = A - V\left(\frac{\partial A}{\partial V}\right)_{N,T} = N\mu = N\left(\frac{\partial A}{\partial N}\right)_{V,T}$$

$$A = -kT\ln\left\{\sum_r e^{-\beta E_r}\right\}$$

$$dA = -SdT - PdV + \mu dN$$

$$P = -\left(\frac{\partial A}{\partial V}\right)_{T,N} = kT\frac{\partial}{\partial V}\left[\ln\left\{\sum_r e^{-\beta E_r}\right\}\right] = kT\frac{\sum_r \frac{\partial}{\partial V}e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

$$= kT\frac{\sum_r \frac{\partial}{\partial E_r}e^{-\beta E_r}\frac{\partial E_r}{\partial V}}{\sum_r e^{-\beta E_r}} = kT\frac{\sum_r (-\beta)e^{-\beta E_r}\frac{\partial E_r}{\partial V}}{\sum_r e^{-\beta E_r}} = -\frac{\sum_r \frac{\partial E_r}{\partial V}e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

$$PdV = -\frac{\sum_r e^{-\beta E_r} dE_r}{\sum_r e^{-\beta E_r}} = -\sum_r P_r dE_r$$

$$\frac{S}{k} = \frac{U - A}{kT} = \frac{U + kT \ln Q_N(V,T)}{kT} = \frac{U}{kT} + \ln Q_N(V,T)$$

$$= \frac{1}{kT}\left[-\frac{\partial}{\partial \beta} \ln Q_N(V,T) \right] + \ln Q_N(V,T)$$

$$\frac{\partial}{\partial \beta} \ln Q_N(V,T) = -\frac{\sum_r E_r\, e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} = -\sum_r P_r E_r$$

$$\frac{S}{k} = \frac{1}{kT} \sum_r P_r E_r + \ln Q_N(V,T) \qquad \sum_r P_r = 1 \,\&\, \ln Q_N(V,T) \neq f(r)$$

$$= \beta \sum_r P_r E_r + \sum_r P_r \ln Q_N(V,T)$$

$$P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \Rightarrow \ln P_r = -\beta E_r - \ln \sum_r e^{-\beta E_r} = -[\beta E_r + \ln Q_N(V,T)]$$

$$\frac{S}{k} = \sum_r [\beta P_r E_r + P_r \ln Q_N(V,T)] = -\sum_r P_r \ln P_r \qquad \Rightarrow S = -k \sum_r P_r \ln P_r$$

$$S = -k \sum_r P_r \ln P_r$$

$$= -k \sum_{r=1}^{\Omega} \left\{ \frac{1}{\Omega} \ln\left(\frac{1}{\Omega}\right) \right\} = \frac{-k}{\Omega} \ln\left(\frac{1}{\Omega}\right) \sum_{r=1}^{\Omega} 1$$

$$\sum_{r=1}^{\Omega} 1 = \Omega$$

$$S = -k \ln\left(\frac{1}{\Omega}\right) = k \ln \Omega$$

Alternative expressions for the partition function

$$Q_N(V,T) = \sum_i g_i \exp(-\beta E_i) \qquad Q_N(V,T) = \int_0^{\infty} e^{-\beta E} g(E)\, dE$$

$$P_i = \frac{g_i \exp(-\beta E_i)}{\sum_i g_i \exp(-\beta E_i)} \qquad P(E)\, dE = \frac{\exp(-\beta E) g(E)\, dE}{\int_0^{\infty} \exp(-\beta E) g(E)\, dE}$$

$$\langle f \rangle \equiv \sum_i f_i P_i = \frac{\sum_i f(E_i) g_i e^{-\beta E_i}}{\sum_i g_i e^{-\beta E_i}} \qquad \frac{\int_0^{\infty} f(E) e^{-\beta E} g(E)\, dE}{\int_0^{\infty} e^{-\beta E} g(E)\, dE}$$

$$Q_N(V,T) = \int_0^{\infty} e^{-\beta E} g(E)\, dE$$

$$\mathcal{L}\, \mathrm{g(E)} = \mathrm{Q_N(V,T)}$$

$$\mathcal{L}^{-1}\, \mathrm{Q_N(V,T)} = \mathrm{g(E)}$$

$$g(E) = \frac{1}{2\pi i} \int_{\beta' - i\infty}^{\beta' + i\infty} e^{\beta E} Q(\beta)\, d\beta \quad (\beta' > 0)$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{(\beta' + i\beta'')E} Q(\beta' + i\beta'')\, d\beta''$$

$$\langle f \rangle = \frac{\int f(q,p) \rho(q,p)\, d^{3N}q\, d^{3N}p}{\int \rho(q,p)\, d^{3N}q\, d^{3N}p}$$

$$\rho(q,p) \propto \exp\{-\beta H(q,p)\}$$

$$\langle f \rangle = \frac{\int f(q,p) \exp(-\beta H)\, d\omega}{\int \exp(-\beta H)\, d\omega}$$

$$d\omega\, (\equiv d^{3N}q\, d^{3N}p) \qquad \frac{d\omega}{N!h^{3N}}$$

$$Q_N(V,T) = \frac{1}{N!h^{3N}} \int e^{-\beta H(q,p)}\, d\omega$$

$$H(q,p) = \sum_{i=1}^{N} (p_i^2/2m)$$

$$Q_N(V,T) = \frac{1}{N!h^{3N}} \int e^{-(\beta/2m)\sum_i p_i^2} \prod_{i=1}^{N} (d^3q_i\, d^3p_i)$$

$$\mathrm{Q_N(V,T)} = \frac{\mathrm{V^N}}{\mathrm{N!h^{3N}}} \left[\int \mathrm{e}^{-\beta\, \mathrm{p}^2/2\mathrm{m}} (4\pi\, \mathrm{p}^2 \mathrm{dp}) \right]^{\mathrm{N}}$$

$$\int_0^\infty e^{-\alpha x^2}dx = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}$$

$$\int_0^\infty x^2 e^{-\alpha x^2}dx = -\frac{\partial}{\partial\alpha}\left[\int_0^\infty e^{-\alpha x^2}dx\right] = -\frac{1}{\partial\alpha}\left(\frac{1}{2}\sqrt{\frac{\pi}{\alpha}}\right) = \frac{\sqrt{\pi}}{2}\frac{1}{\sqrt{\alpha^3}}$$

$$Q_N(V,T) = \frac{V^N}{N!h^{3N}}\left[\int e^{-\beta\, p^2/2m}(4\pi\, p^2 dp)\right]^N$$

$$= \frac{1}{N!}\left[\frac{V}{h^3}(2\pi mkT)^{3/2}\right]^N$$

$$A(N,V,T) \equiv -kT\ln Q_N(V,T)$$

$$= -kT\left[-\ln(N!) + N\ln\left\{\frac{V}{h^3}(2\pi\ mkT)^{3/2}\right\}\right]$$

$$= kT\left[N\ln N - N - N\ln\left\{V\left(\frac{2\pi\ mkT}{h^2}\right)^{3/2}\right\}\right]$$

$$= NkT\left[\ln\left\{\frac{N}{V}\left(\frac{h^2}{2\pi\ mkT}\right)^{3/2}\right\} - 1\right]$$

$$dA = -SdT - PdV + \mu dN$$

$$S \equiv -\left(\frac{\partial A}{\partial T}\right)_{N,V} = Nk\left[\ln\left\{\frac{V}{N}\left(\frac{2\pi\ mkT}{h^2}\right)^{3/2}\right\} + \frac{5}{2}\right]$$

$$P \equiv -\left(\frac{\partial A}{\partial V}\right)_{N,T} = \frac{NkT}{V}$$

$$\mu \equiv \left(\frac{\partial A}{\partial N}\right)_{T,V} = kT\ln\left\{\frac{N}{V}\left(\frac{h^2}{2\pi\ mkT}\right)^{3/2}\right\}$$

$$U \equiv -\left[\frac{\partial}{\partial\beta}(\ln Q_N(V,T))\right]_{E_r} \equiv -T^2\left[\frac{\partial}{\partial T}\left(\frac{A}{T}\right)\right]_{N,V}$$

$$\equiv A + TS = \frac{3}{2}NkT$$

$$Q_N(V,T) = \frac{1}{N!}[Q_1(V,T)]^N$$

$$\Sigma(N,V,T) \approx \left(\frac{V}{h^3}\right)^N \frac{(2\pi Em)^{3N/2}}{(3N/2)!}$$

$$g(E) = \frac{\partial\Sigma}{\partial E} \approx \frac{1}{N!}\left(\frac{V}{h^3}\right)^N \frac{(2\pi\ m)^{3N/2}}{\{(3N/2)-1\}!}E^{(3N/2)-1}$$

$$Q_N(V,T) = \int g(E)e^{-\beta E}dE = \frac{1}{N!}\left(\frac{V}{h^3}\right)^N\left(\frac{2\pi m}{\beta}\right)^{3N/2}$$

$$\Sigma(P) \approx \frac{1}{N!h^3}\iint(d^3q\ d^3p) \quad , \frac{1}{N!} = 1$$

$$\Sigma(P) = V\int 4\pi p^2 dp = V\left(\frac{4}{3}\pi p^3\right) \quad , E = \frac{p^2}{2m}$$

$$\Sigma(E) \approx \frac{V}{h^3}\frac{4\pi}{3}(2mE)^{3/2}$$

$$(\varepsilon)d\varepsilon = \frac{d\Sigma(\varepsilon)}{d\varepsilon}d\varepsilon$$

$$a(\varepsilon) \approx \frac{2\pi V}{h^3}(2m)^{3/2}\varepsilon^{1/2}$$

$$Q_1(\beta) = \int_0^\infty e^{-\beta\varepsilon}a(\varepsilon)d\varepsilon = \frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}$$

$$\frac{1}{2\pi i}\int_{s'-i\infty}^{s'+i\infty}\frac{e^{sx}}{s^{n+1}}\,d\beta = \begin{cases}\dfrac{x^n}{n!} & for \quad x \ge 0\\ 0 & for \quad x \le 0\end{cases}$$

$$Q_N(\beta) = \frac{1}{N!}\left(\frac{V}{h^3}\right)^N\left(\frac{2\pi m}{\beta}\right)^{3N/2}$$

$$g(E) = L^{-1}Q_N(\beta) = \frac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty}e^{\beta E}Q_N(\beta)d\beta$$

$$= \frac{V^N}{N!}\left(\frac{2\pi m}{h^2}\right)^{3N/2}\frac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty}\frac{e^{\beta E}}{\beta^{3N/2}}\,d\beta \quad (\beta' > 0)$$

$$g(E) = \begin{cases}\dfrac{V^N}{N!}\left(\dfrac{2\pi m}{h^2}\right)^{3N/2}\dfrac{E^{(3N/2)-1}}{\{(3N/2)-1\}!} & for \quad E \ge 0\\ 0 & for \quad E \le 0\end{cases}$$