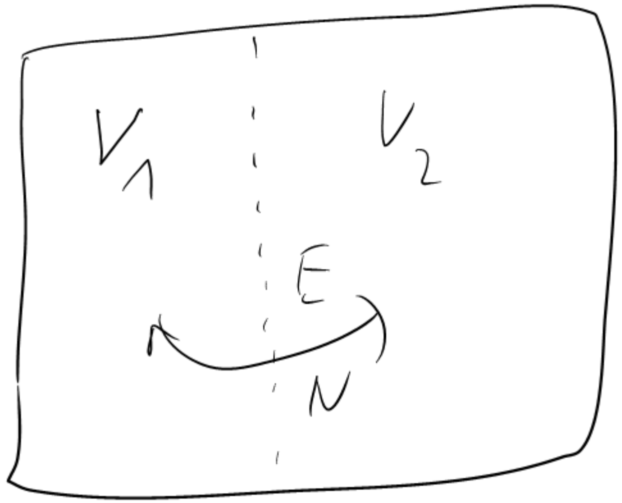
Gibbs Distribution, Grand-Canonical Partition Function, Grand-Canonical Potential



V_1, V_2 fixed

interested in the limit

$V_2 \to \infty$, $\frac{V_2}{N_2}$, $\frac{E_2}{V_2}$ fixed

(V_2 becomes an infinite reservoir of energy & particles)

Wedhad

$$\Omega_{tot}(E,N) = \sum_{N_1=0}^{N} \frac{1}{\Delta E} \int_0^E dE_1 \, \Omega_1(E_1, N_1) \, \Omega_2(E-E_1, N-N_1) =$$

$$\sum_{N_1=0}^{N} \frac{1}{\Delta E} \int_0^E dE_1 \, \frac{1}{N_1!} \frac{\Delta E}{(2\pi\hbar)^{3N_1}} \int d\Gamma_1 \, \delta\left(H_1(\Gamma_1) - E_1\right)$$

$$\frac{1}{(N-N_1)!} \frac{\Delta E}{(2\pi\hbar)^{3(N-N_1)}} \int d\Gamma_2 \, \underbrace{\delta\left(H_2(\Gamma_2) - E + E_1\right)}_{E_1 = E - H_2(\Gamma_2)} =$$

$$=$$

$$= \frac{\Delta E}{(2\pi\hbar)^{3N}} \sum_{N_1=0}^{N} \underbrace{\frac{1}{N_1!}\,\frac{1}{(N-N_1)!}}_{} \int d\Gamma_1 \int d\Gamma_2\, \delta\left(H_1(\Gamma_1) + H_2(\Gamma_2) - E\right)$$

particles "left"/"right" are distinguishable!

$\rho(N_1, \Gamma_1, \Gamma_2)\, d\Gamma_1\, d\Gamma_2 \equiv$ probability to find N_1 particles in the left box near phase space point Γ_1, <u>and</u> the remaining $N-N_1$ particles in the right box near phase space point Γ_2.

$$\Rightarrow \quad p(N_1, \Gamma_1, \Gamma_2) = \frac{1}{\Omega_{tot}(E,N)} \frac{\Delta E}{(2\pi\hbar)^{3N}} \frac{1}{N_1!} \frac{1}{(N-N_1)!} \times$$

$$\times \, \delta\big(H_1(\Gamma_1) + H_2(\Gamma_2) - E \big)$$

$p(N_1, \Gamma_1)\, d\Gamma_1$: probability to find N_1 particles in the left box near phase space point Γ_1

$$p(N_1, \Gamma_1) = \frac{1}{\Omega_{tot}(E,N)} \frac{\Delta E}{(2\pi\hbar)^{3N}} \frac{1}{N_1!} \frac{1}{(N-N_1)!}$$

$$\int d\Gamma_2 \, \delta\big(H_1(\Gamma_1) + H_2(\Gamma_2) - E \big) =$$

$$= \frac{1}{\Omega_{tot}(E,N)} \frac{1}{(2\pi\hbar)^{3N_1}} \frac{1}{N_1!} \frac{\Delta E}{(2\pi\hbar)^{3(N-N_1)}} \frac{1}{(N-N_1)!}$$

$$\int d\Gamma_2 \; \delta\Big(H_2(\Gamma_2) - \big(E - H_1(\Gamma_1)\big)\Big) =$$

$$= \frac{1}{(2\pi\hbar)^{3N_1}} \frac{1}{N_1!} \frac{\Omega_2\left(E - H_1(\Gamma_1), N - N_1\right)}{\Omega_{tot}(E,N)}$$

$$\Omega_{tot}(E,N) = \exp\{S(E,N)\}$$

$$\Omega_2(E - H_1, N - N_1) = \exp\{S(E - H_1, N - N_1)\}$$

$$S(E-H_1, N-N_1) = S(E,N) - \underbrace{\frac{\partial S}{\partial E}}_{=\beta} H_1 - \underbrace{\frac{\partial S}{\partial N}}_{-\beta\mu} N_1 + O\left(\frac{N_1^2}{N}\right)$$

$N_2 \gg N_1$

<u>per definition</u>

$$\Omega_2(E-H_1, N-N_1) = e^{S(E,N)} \exp(+\beta\mu N_1) \exp(-\beta H_1)$$

$$\Rightarrow \rho(N_1, \Gamma_1) \simeq \frac{1}{(2\pi\hbar)^{3N_1}} \frac{1}{N_1!} \exp(\beta\mu N_1) \exp(-\beta H_1)$$

taking into account normalization $\Rightarrow$

$$\underbrace{\rho(N_1, \Gamma_1) = \frac{1}{Z_{GC}} \frac{1}{(2\pi\hbar)^{3N_1}} \frac{1}{N_1!} \exp(+\beta\mu N_1) \exp(-\beta H_1(\Gamma_1))}_{}$$

Gibbs distribution

$$\underbrace{Z_{GC} = \sum_{N=0}^{\infty} \frac{1}{(2\pi\hbar)^{3N}} \frac{1}{N!} \exp(\beta\mu N) \int d\Gamma \exp(-\beta H(\Gamma))}_{}$$

grand - canonical partition function

$$Z_{GC}(\mu, \beta) = \sum_{N=0}^{\infty} \exp(\beta\mu N) \; Z_{can}(\beta, N)$$

$$= \sum_{N=0}^{\infty} \exp(\beta\mu N) \exp(-\beta F_N(\beta))$$

Back to the potentials:

$$dE = T\,dS - P\,dV + \mu\,dN \qquad \Big| \cdot \beta$$

$$\Phi = E - TS - \mu N \qquad \Big| \cdot (-\beta)$$

$$d\Phi = -S\,dT - P\,dV - N\,d\mu$$

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

$$-\beta\Phi = S - \beta E + \beta\mu N \qquad \to \beta\,d\mu + \mu\,d\beta$$

$$d(-\beta\Phi) = -E\,d\beta + \beta P\,dV + N\,d(\beta\mu)$$

$$= -(E - \mu N)\,d\beta + \beta P\,dV + \beta N\,d\mu$$

CLAIM: $\boxed{-\beta \Phi = \ln Z_{GC}}$ Proof:

(i) $\frac{\partial}{\partial \beta} \ln Z_{GC} = -E + \mu N$

(ii) $\frac{\partial}{\partial V} \ln Z_{GC} = \beta P$

(iii) $\frac{\partial}{\partial \mu} \ln Z_{GC} = \beta N$

(iv) there is no integration constant

$\frac{\partial}{\partial \beta} \ln Z_{GC} =$

$= \frac{1}{Z_{GC}} \underbrace{\frac{\partial}{\partial \beta} Z_{GC}}$

(i) $\frac{\partial}{\partial\beta} Z_{GC} = \sum_N \frac{1}{(2\pi\hbar)^{3N} N!} \exp(\beta\mu N) \int d\Gamma \exp(-\beta H)$

$$(\mu N - H) = Z_{GC} \langle \mu N - H \rangle$$

$$= -(E - \mu N) Z_{GC} \quad \checkmark$$

(ii) $\frac{\partial}{\partial V} \ln Z_{GC} = \frac{1}{Z_{GC}} \frac{\partial}{\partial V} \sum_N e^{\beta\mu N} e^{-\beta F_N} =$

$$= \frac{1}{Z_{GC}} \sum_N e^{\beta\mu N} e^{-\beta F_N} (-\beta) \underbrace{\frac{\partial F}{\partial V}}_{-P} = \langle \beta P \rangle_{GC} = \beta P \quad \checkmark$$

(iii) $$\frac{\partial}{\partial\mu} \ln Z_{GC} = \frac{1}{Z_{GC}} \frac{\partial}{\partial\mu} \sum_N e^{\beta\mu N} e^{-\beta F_N}$$

$$= \frac{1}{Z_{GC}} \sum_N e^{\beta\mu N} e^{-\beta F_N} (\beta N) =$$

$$= \langle \beta N \rangle_{GC} = \beta N \quad \checkmark$$

(iv) $$\ln Z_{GC} = \ln \sum_N \exp[-\beta(\underbrace{F_N - \mu N}_{\text{EXTENSIVE}})]$$

$$\underset{N\to\infty}{\simeq} \ln \max_N \exp[-\beta(F_N - \mu N)]$$

$$= \ln \exp\left[-\beta \min_N (F_N - \mu N)\right] =$$

$$= -\beta \min_N (F_N - \mu N) \Rightarrow \ln Z_{GC} \text{ is EXTENSIVE}$$

$-\beta\bar{\Phi}$ is extensive

$$-\beta\bar{\Phi} = (-\beta\bar{\Phi})(\beta, \mu, V)$$

$$\ln Z_{GC} = (\ln Z_{GC})(\beta, \mu, V)$$

$$\ln Z_{GC} = -\beta\bar{\Phi} + \text{const.}$$

scaling transformation:

$$V \rightarrow \lambda V$$

$$-\beta \bar{\Phi} \rightarrow \lambda(-\beta \bar{\Phi})$$

$$\ln Z_{GC} \rightarrow \lambda \ln Z_{GC}$$

$$\text{const.} \rightarrow \text{const.}$$

this is only consistent if const. $= 0$!

$\leadsto$ there is NO integration constant

$$\boxed{-\beta \bar{\Phi} = \ln Z_{GC}} \qquad \boxed{\bar{\Phi} = -T \ln Z_{GC}}$$

Fluctuation Relations

So far: potentials $S/E, F, H, G, \Phi$

+ FIRST derivatives, e.g. $\beta = \frac{\partial S}{\partial E}\Big|_{N,V}$

$$P = -\frac{\partial F}{\partial V}\Big|_{N,T} \qquad \mu = +\frac{\partial F}{\partial N}\Big|_{V,T}$$

You would always like to match potentials & natural variables!

now: 2ND derivatives

Specific Heat (or heat capacity)

$N = \text{const.}, \quad V = \text{const.}$

extensive

$T \to T + dT$

$$\boxed{\left.\frac{dE}{dT}\right|_{N,V} = C_V}$$

$E \to E + dE$

heat capacity

Specific heat

C_V: Heat capacity AT CONSTANT VOLUME

$$dE = T\,dS - P\underbrace{dV}_{=0} + \mu \underbrace{dN}_{=0}$$

$$\boxed{C_V = T \left.\frac{\partial S}{\partial T}\right|_{N,V}}$$

(N, V, T) as natural variables $\Rightarrow F$ should be the potential

$$F = E - TS$$

$$dF = -S\,dT - P\,dV + \mu\,dN$$

$$S = -\left.\frac{\partial F}{\partial T}\right|_{V,N} \Rightarrow \boxed{C_V = -T \left.\frac{\partial^2 F}{\partial T^2}\right|_{N,V}}$$

$$T \to \beta : \quad \frac{\partial}{\partial T} = \frac{d\beta}{dT}\frac{\partial}{\partial \beta} = -\frac{1}{T^2}\frac{\partial}{\partial \beta} = -\beta^2\frac{\partial}{\partial \beta}$$

$$-T\frac{\partial^2}{\partial T^2} = -\frac{1}{\beta}\beta^2\frac{\partial}{\partial \beta}\beta^2\frac{\partial}{\partial \beta} = -\beta\frac{\partial}{\partial \beta}\beta^2\frac{\partial}{\partial \beta}$$

$$F = -\frac{1}{\beta}\ln Z \Rightarrow -T\frac{\partial^2}{\partial T^2}F = \beta\frac{\partial}{\partial \beta}\beta^2\frac{\partial}{\partial \beta}\left(\frac{1}{\beta}\ln Z\right)$$

$$= \beta\frac{\partial}{\partial \beta}\beta^2\left[-\frac{1}{\beta^2}\ln Z + \frac{1}{\beta}\frac{\partial}{\partial \beta}\ln Z\right] =$$

$$= \beta\frac{\partial}{\partial \beta}\left[-\ln Z + \beta\frac{\partial}{\partial \beta}\ln Z\right] =$$

$$= -\beta \frac{\partial}{\partial\beta}\ln Z + \beta^2 \frac{\partial^2}{\partial\beta^2}\ln Z + \beta\frac{\partial}{\partial\beta}\ln Z =$$

$$= \beta^2 \frac{\partial^2}{\partial\beta^2}\ln Z = C_V \Rightarrow \boxed{T^2 C_V = \frac{\partial^2}{\partial\beta^2}\ln Z}$$

$$\frac{\partial}{\partial\beta}\ln Z = \frac{1}{Z}\frac{\partial Z}{\partial\beta} \Rightarrow \frac{\partial^2}{\partial\beta^2}\ln Z = -\frac{1}{Z^2}\left(\frac{\partial Z}{\partial\beta}\right)^2 + \frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2}$$

$$T^2 C_V = \frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2} - \left(\frac{1}{Z}\frac{\partial Z}{\partial\beta}\right)^2$$

$$Z = \frac{1}{(2\pi\hbar)^{3N}} \frac{1}{N!} \int d\Gamma \, e^{-\beta H}$$

$$\frac{\partial Z}{\partial \beta} = \frac{1}{(2\pi\hbar)^{3N}} \frac{1}{N!} \int d\Gamma \, (-H) \, e^{-\beta H} =$$

$$= \langle -H \rangle \cdot Z \quad \Rightarrow \quad \boxed{\frac{1}{Z} \frac{\partial Z}{\partial \beta} = - \langle H \rangle}$$

$$\frac{\partial^2 Z}{\partial \beta^2} = \frac{1}{(2\pi\hbar)^{3N}} \frac{1}{N!} \int d\Gamma \, H^2 e^{-\beta H} = \langle H^2 \rangle \, Z$$

$$\boxed{\frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} = \langle H^2 \rangle}$$

$$T^2 C_V = \langle H^2 \rangle - \langle H \rangle^2$$

$$\boxed{C_V = \frac{1}{T^2}\left\{\langle H^2 \rangle - \langle H \rangle^2\right\}}$$

2nd derivative of the potential

$\longleftrightarrow$ 2nd moment of " distribution!!

$$\Rightarrow \boxed{C_V \geq 0}$$