File Edit View Insert Actions Tools Help

Gibbs canonical Ensemble : (N, J, T)

J → generalized force

Eg. Ideal gas at (N, P, T) : $J = P$ $\Delta V \neq 0$ $V \equiv$ Volume

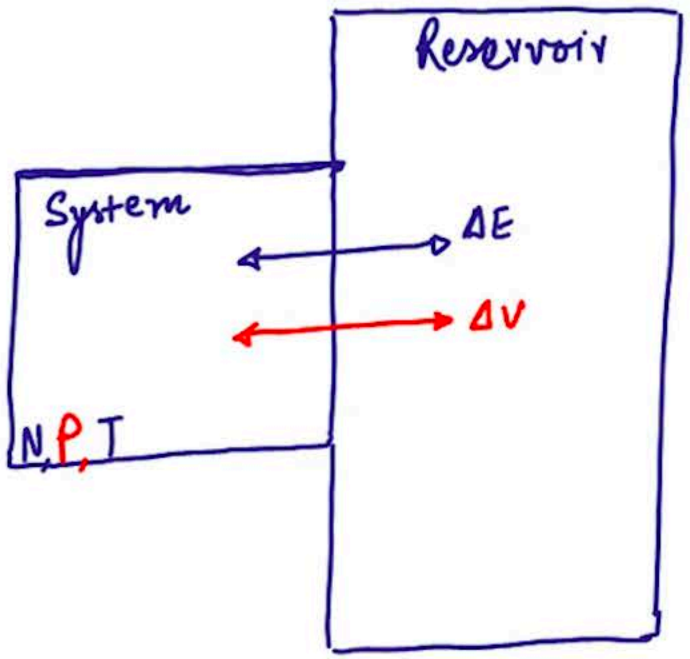
Magnetic spins in uniform (N, B, T) : $J = B$ $\Delta M \neq 0$ $M \equiv$ Magnetization

1/1

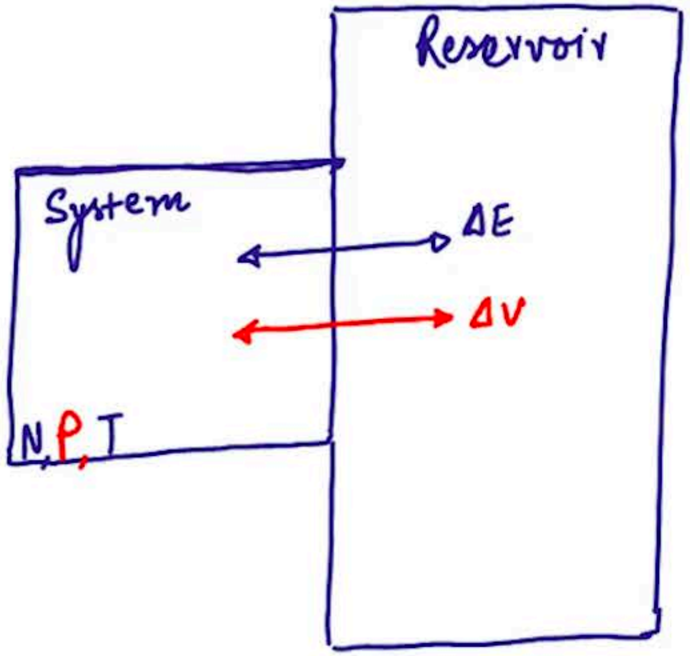
File Edit View Insert Actions Tools Help

Eg. Ideal gas at (N, P, T) : $J = P$ $\quad \Delta V \neq 0$ $\quad V \equiv$ Volume

Magnetic spins in uniform (N, B, T) : $J = B$ $\quad \Delta M \neq 0$ $\quad M \equiv$ Magnetization



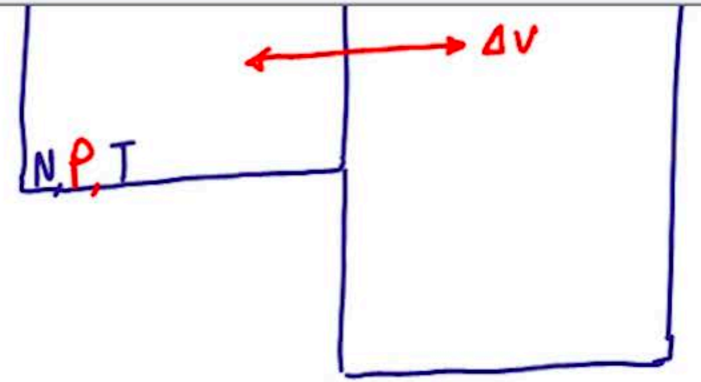
Magnetic



Reservoir: Thermostat + Barostat.

Macrostate: N, P, T

Microstate: $\mu \equiv \{\vec{q}_i, \vec{p}_i\}$, V_μ



Macrostate: N, P, T

Microstate: $\mu \equiv \{\vec{q}_i, \vec{p}_i\}, \; \underline{\underline{V_\mu}}$

Relevant Energy scale: $\left(\mathcal{H}(\mu) = \sum_{i=1}^{N} p_i^2/2m\right) + P V_\mu$

Relevant Energy scale: $\left(\mathcal{H}(\mu) = \sum_{i=1} p_i^2/2m \right)$

$$p(\mu, V_\mu) = \frac{e^{-\beta\left[H(\mu) + PV_\mu\right]}}{\sum_{\mu, V_\mu} e^{-\beta\left[H(\mu) + PV_\mu\right]}} = \frac{e^{-\beta\left[H(\mu) + PV_\mu\right]}}{Z(N,P,T)}$$

$$Z(N,PT) = \sum_{\mu, V_\mu} e^{-\beta\left[H(\mu) + PV_\mu\right]}$$

"Gibbs Canonical partition function"

Fluctuating Quantities in N, P, T :

$\mathcal{H}(\mu)$

V_μ

(i) $$V = \langle V_\mu \rangle = \sum_{\mu, V_\mu} V_\mu \, p(\mu, V_\mu) = \frac{\sum_{\mu, V_\mu} V_\mu \, e^{-\beta [H(\mu) + P V_\mu]}}{Z(N, P, T)}$$

V_μ

(i) $$V = \langle V_\mu \rangle = \sum_{\mu, V_\mu} V_\mu \, p(\mu, V_\mu) = \frac{\sum\limits_{\mu, V_\mu} V_\mu \, e^{-\beta[H(\mu) + P V_\mu]}}{Z(N, P, T)}$$

$$= \frac{1}{Z} \cdot \frac{\partial}{\partial(-\beta P)} \sum_{\mu, V_\mu} e^{-\beta[H(\mu) + P V_\mu]}$$

$$= \frac{1}{Z} \cdot \frac{\partial Z}{\partial(-\beta P)}$$

File Edit View Insert Actions Tools Help

$$= -\frac{1}{\beta}\cdot\frac{1}{Z}\frac{\partial Z}{\partial P}$$

Average volume $\quad V = -\frac{1}{\beta}\cdot\frac{\partial}{\partial P}(\ln Z) \quad \text{——} \quad (1)$

From thermodynamics: Gibbs free energy $\quad G = H - TS$

$$= E + PV - TS$$

2/2

File Edit View Insert Actions Tools Help

$$dG = \mu\, dN + V\, dp - S\, dT$$

.... 1^{st} law : $T dS = dE + P dV - \mu dN$

$$V = \left.\frac{\partial G}{\partial p}\right|_{N,T} \quad \text{——} \; (2)$$

$$G = -\frac{1}{\beta} \ln Z \quad \text{——} \; (3)$$

"Bridge connects Stat Mech to Thermo-dynamics"

Average Enthalpy :

$$\langle \mathcal{H}(\mu) + P V_\mu \rangle = H$$

$$\therefore \quad H = \sum_{\mu, V_\mu} \left(\mathcal{H}(\mu) + P V_\mu \right) p(\mu, V_\mu)$$

$$= \frac{\sum_{\mu, V_\mu} \left(\mathcal{H}(\mu) + P V_\mu \right) e^{-\beta \left[\mathcal{H}(\mu) + P V_\mu \right]}}{\mathcal{Z}(N, P, T)}$$

$$= \frac{1}{\mathcal{Z}} \cdot \frac{\partial \mathcal{Z}}{\partial(-\beta)}$$

File Edit View Insert Actions Tools Help

Enthalpy Fluctuations: $\langle H^2 \rangle_c = \langle H^2 \rangle - \langle H \rangle^2$,

$$= \sum_{\mu, V_\mu} \left(H(\mu) + P V_\mu \right)^2 p(\mu, V_\mu) - \left(\sum_{\mu, V_\mu} \left(H(\mu) + P V_\mu \right) p(\mu, V_\mu) \right)^2$$

$$= \frac{\sum_{\mu, V_\mu} \left(H(\mu) + P V_\mu \right)^2 e^{-\beta[H(\mu) + P V_\mu]}}{Z(N, P, T)} - \left(\frac{\sum_{\mu, V_\mu} \left(H(\mu) + P V_\mu \right) e^{-\beta[H(\mu) + P V_\mu]}}{Z(N, P, T)} \right)^2$$

$$= \frac{\partial}{\partial \beta}\left(\frac{1}{Z}\cdot\frac{\partial Z}{\partial \beta}\right)$$

$$= \frac{\partial}{\partial \beta}\underbrace{\frac{\partial}{\partial \beta}\ln Z(N,P,T)}_{\displaystyle \parallel}$$

$$H = \langle \mathcal{H}(\mu) + P V_\mu \rangle \qquad \ldots \text{refer}$$

$$= \frac{\partial}{\partial \beta} H$$

File Edit View Insert Actions Tools Help

$$= -\frac{\partial}{\partial \beta} H$$

$$= -\frac{\partial}{\partial (1/k_B T)} H \quad = k_B T^2 \frac{\partial H}{\partial T} \quad = k_B T^2 C_p$$

$C_p \equiv$ Heat capacity at const. Pressure

$$\langle H^2 \rangle_c = k_B T^2 C_p \sim N$$ "Extensive"

3/3

File Edit View Insert Actions Tools Help

$$= -\frac{\partial}{\partial(1/k_B T)} H \qquad = k_B T^2 \frac{\partial H}{\partial T} = k_B T^2 C_p$$

$C_p \equiv$ Heat capacity at const. Pressure

$$\langle H^2 \rangle_c = k_B T^2 C_p \sim N \quad \text{"Extensive"}$$

Recall N, V, T:

$$\langle \mathcal{H}^2 \rangle_c = k_B T^2 C_v$$

3/3