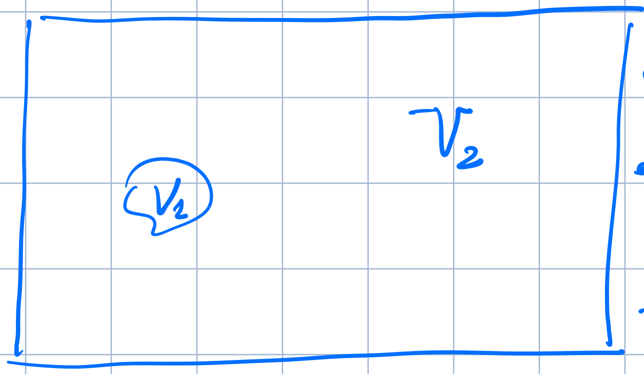
$$\mathcal{H}(\Gamma;N) = \mathcal{H}_1(\Gamma_1;N_1) + \mathcal{H}_1(\Gamma_2;N_2) + \cancel{V}$$



- CANONICO N, V, T
- Regione di osservazione V_1

$V_1 + V_2 = V$

- In un dato istante in V_1 abbiamo N_1 particelle e in V_2 N_2; $N_1 + N_2 = N$
- Prendiamo $V_1 \ll V_2 \Rightarrow N_1 \ll N_2$

  $\Gamma_1 = (q_1; p_1)$; $\Gamma_2 = (q_2; p_2)$
- Vogliamo calcolare la media di $f(\Gamma_1; N_1)$ con la restrizione che le N_1 particelle siano in V_1 e le N_2 in V_2

$$\langle f(\Gamma_1;N_1)\rangle = \frac{1}{Q_N(V,T)} \frac{1}{N!\,h^{3N}} \times$$

$$\times \sum_{N_1=0}^{N} \frac{N!}{N_1!\,N_2!} \int_{V_1} d\Gamma_1\, f(\Gamma_1)\, e^{-\beta \mathcal{H}_1} \int_{V_2} d\Gamma_2\, e^{-\beta \mathcal{H}_2}$$

$$= \sum_{N_1=0}^{N} \frac{1}{N_1!\,h^{3N_1}} \int_{V_1} d\Gamma_1 f(\Gamma_1) e^{-\beta \mathcal{H}_1} \frac{1}{Q_N\, N_2!\, h^{3N_2}} \int_{V_2} d\Gamma_2\, e^{-\beta \mathcal{H}_2}$$

- Limite termodinamico: (1) $N_2, V_2 \to \infty$; (2) $V_1 \to \infty$.

1)
$$\frac{1}{Q_N}\frac{1}{N_2!\,h^{3N_2}}\int_{V_2} d\Gamma_2\, e^{-\beta \mathcal{H}_2} = \frac{Q_{N-N_1}(V-V_1;T)}{Q_N(V,T)}$$

$$= \exp\left[\beta\left\{A(N,V,T) - A(N-N_1, V-V_1, T)\right\}\right]$$

$$\simeq \exp\left[\beta\mu N_1 - \beta P V_1\right]$$

$$\langle f(\Gamma_1;N_1)\rangle = \sum_{N_1=0}^{N}\frac{1}{N_1!\,h^{3N_1}}\int d\Gamma_1\, e^{-\beta \mathcal{H}_1} f(\Gamma_1)\, e^{\beta[\mu N_1 - PV_1]}$$

- Limite termodinamico 2) $V_1 \to \infty$

$$\langle f(\Gamma_1,N_1)\rangle = e^{-\beta P V_1}\sum_{N_1=0}^{\infty} e^{\beta\mu N_1} Q_{N_1}\langle f(\Gamma_1)\rangle_c$$

- Da questo momento trascuriamo il pedice 1 e ci restringiamo alla regione di osservazione V (ex V_1)

- consideriamo $f=1$

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

$$\langle f(\Gamma)\rangle_{G.C.} = \frac{1}{Z}\sum_{N=0}^{\infty} e^{\beta\mu N} Q_N(V,T)\langle f(\Gamma)\rangle_c$$

- (·) $e^{\beta\mu} = z$, fugacità

(2) $\langle f(\vec{r}) \rangle_{G.C} = \dfrac{1}{Z(\mu, V, T)} \sum_{N=0}^{\infty} e^{\beta \mu N} Q_N \langle f(\vec{r}) \rangle_C$

$= \dfrac{1}{Z(z, V, T)} \sum_{N=0}^{\infty} z^N Q_N \langle f(\vec{r}) \rangle_C$

TERMODINAMICA

(a) $Z(\mu, V, T) = e^{-\beta \Omega}$

- per un sistema omogeneo

(b) $\Omega = -P V$

(c) $d\Omega = -S\,dT - P\,dV - N\,d\mu$

- per un sistema inomogeneo (potenziale esterno $v(\vec{r})$) la (a) vale ancora, la (b) non vale più e la (c) diventa

(c') $\delta \Omega = -S\,\delta T - \int d\vec{r}\, \rho(\vec{r})\, \delta v(\vec{r}) - N\,\delta\mu$

NUMERO MEDIO

L'equazioni (1) e (2) danno

$$\langle N \rangle_{G.C.} = \frac{1}{Z(\mu, V, T)} \sum_{N=0}^{\infty} N e^{\beta \mu N} Q_N(V,T)$$

$$= \frac{1}{\beta} \frac{\partial \ln Z}{\partial \mu}\bigg|_{V,T} = \frac{1}{\beta} \frac{\partial \beta P V}{\partial \mu}\bigg|_{V,T} = V \frac{\partial P}{\partial \mu}$$

e

$$\frac{1}{\beta} \frac{\partial \langle N \rangle}{\partial \mu} = \langle N^2 \rangle - \langle N \rangle^2 =$$

$$= k_B T V \frac{\partial \langle N \rangle / V}{\partial \mu} = k_B T V \frac{\partial \rho}{\partial \mu}\bigg|_{T}$$

- $\dfrac{\partial \mu}{\partial \rho}$

$$A(N,V,T) = V a(\rho, T)$$

$$\mu = \frac{\partial A}{\partial N} = V \frac{\partial a}{\partial \rho} \frac{\partial \rho}{\partial N} = V a'(\rho) \frac{\partial}{\partial N}\left(\frac{N}{V}\right) = a'(\rho)$$

$$\mu = a'(\rho) = \frac{\partial a(\rho, T)}{\partial \rho}$$

$$\frac{\partial \mu}{\partial \rho} = \frac{\partial^2 a(\rho, T)}{\partial \rho^2} = a''(\rho)$$

$$P = -\frac{\partial A}{\partial V} = -\frac{\partial}{\partial V}\left[V a(\rho, T)\right] = -a - a'(\rho) V \frac{\partial \rho}{\partial V}$$

$$\underline{P} = -a + \rho a'(\rho)$$

$$\frac{1}{K_T} = -V \frac{\partial P}{\partial V} = \rho \frac{\partial P}{\partial \rho} = \rho\left[-a' + a' + \rho a''\right]$$

$$= \rho^2 a''(\rho)$$

$$\Rightarrow \quad \frac{\partial \mu}{\partial \rho} = a''(\rho) = \frac{1}{\rho^2 K_T}$$

$$\langle N^2 \rangle - \langle N \rangle = k_B T V \frac{\partial \rho}{\partial \mu} = k_B T V \rho^2 K_T$$

$$= k_B T \rho K_T \langle N \rangle$$

$$\text{r.m.s.} = \sqrt{\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle^2}} = \sqrt{\frac{k_B T \rho K_T}{\langle N \rangle}}$$

$$= \sqrt{\frac{k_B T \; K_T}{V}} \sim \frac{1}{\sqrt{V}} \xrightarrow[L.T.]{} 0$$