Veliki kanonski ansambl

Makroskopski uslovi: fiksirana zapremina, sistem razmenjuje energiju i čestice sa rezervoarom temperature T i hemijskog potencijala μ

Fazna gustina verovatnoće

$$f_N(\vec{p},\vec{q}) = \frac{e^{-\beta(\mathcal{H}_N(\vec{p},\vec{q})-\mu N)}}{\Xi}$$

Velika statistička suma

$$\Xi(T,V,\mu) = \sum_{N=0}^{\infty} e^{\beta\mu N} \int_{\Gamma_N} e^{-\beta\mathcal{H}_N(\vec{p},\vec{q})} d\Gamma_N$$

Veza sa TERMODINAMIKOM

$$\Xi = \sum_{N=0}^{\infty} \lambda^N Z_N$$

λ - fugacitet

$$\Omega(T,V,\mu) = -kT\ln\Xi$$

$\downarrow$

Veliki TD potencijal

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

$\longrightarrow$

1. Idealni gas se sastoji od N jednoatomskih molekula. Koristeći formalizam velikog kanonskog ansambla izračunati hemijski potencijal μ, pritisak p i entropiju S.

$$\Xi = \sum_{N=0}^{\infty} \lambda^N Z_N$$

$$Z_N = \int_{\Gamma_N} e^{-\beta \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}} \prod_{i=1}^{N} \frac{d\vec{p}_i \, d\vec{q}_i}{N! \, h^{3N}}$$

$$Z_N = \frac{V^N}{h^{3N} N!} \int \dots \int e^{-\beta (\vec{p}_1^{\,2} + \dots \vec{p}_N^{\,2})} d\vec{p}_1 \dots d\vec{p}_N$$

$$Z_N = \frac{V^N}{h^{3N} N!} \left[\int e^{-\frac{\beta \vec{p}^{\,2}}{2m}} d\vec{p} \right]^N$$

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

$$Z_N = \frac{V^N}{h^{3N} N!} \left[\frac{\pi}{\frac{\beta}{2m}} \right]^{\frac{3N}{2}}$$

$$Z_N = \frac{V^N}{h^{3N} N!} \left[2\pi m k T \right]^{\frac{3N}{2}}$$

- $$\lambda_T = \sqrt{\frac{h^2}{2\pi m k T}}$$

$$Z_N = \frac{V^N}{N!}\left[\frac{2\pi m kT}{h^2}\right]^{\frac{3N}{2}}$$

$$Z_N = \frac{V^N}{N!}\left[\frac{1}{\lambda_T^3}\right]^N$$

$$Z_N = \frac{1}{N!}\left[\frac{V}{\lambda_T^3}\right]^N$$

$$\Xi = \sum_{N=0}^{\infty} \lambda^N Z_N = \sum_{N=0}^{\infty} \lambda^N \frac{1}{N!}\left[\frac{V}{\lambda_T^3}\right]^N$$

$$= \sum_{N=0}^{\infty} \frac{1}{N!}\left[\frac{\lambda V}{\lambda_T^3}\right]^N$$

$$\Xi = e^{\frac{\lambda V}{\lambda_T^3}} = e^{\frac{e^{\beta\mu} V}{\lambda_T^3}}$$

$$\Omega = -kT \ln \Xi$$

$$\Omega = -kT \ln e^{\frac{e^{\beta\mu} V}{\lambda_T^3}} = -kT \frac{e^{\beta\mu} V}{\lambda_T^3}$$

$$\langle N \rangle = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V}$$

$$\langle N \rangle = \frac{kTV}{\lambda_T^3} \beta e^{\beta\mu} = \frac{V}{\lambda_T^3} e^{\beta\mu}$$

$$\frac{\lambda_T^3 \langle N \rangle}{V} = e^{\beta\mu} \Longrightarrow \mu = \frac{1}{\beta} \ln \frac{\lambda_T^3 \langle N \rangle}{V}$$

$$\boxed{\mu = kT \ln \frac{\lambda_T^3}{V} \langle N \rangle}$$

Domadi

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu} \quad , \quad p = -\left(\frac{\partial \Omega}{\partial V}\right)_{T,\mu}$$

2. Polazeći od izraza za entropiju u formalizmu VKA, potvrditi važenje relacije

$$pV = kT \ln \Xi .$$

Gibbs-ova definicija entropije

$$S = -k \langle \ln f(\vec{p}, \vec{r}, t) \rangle$$

Budući da smo u formalizmu VKA ansambla

$$S = -k \sum_{N=0}^{\infty} \langle \ln f_N(\vec{p}, \vec{r}, t) \rangle$$

tj.

$$S = -k \sum_{N=0}^{\infty} \int_{\Gamma_N} f_N(\vec{p}, \vec{r}, t) \ln f_N(\vec{p}, \vec{r}, t) \, d\Gamma_N$$

Proučavamo ravnotežne ansamble pa je:

$$f_N(\vec{p}, \vec{r}, t) = f_N(\vec{p}, \vec{r}).$$

$$S = -k \sum_{N=0}^{\infty} \int_{\Gamma_N} f_N(\vec{p}, \vec{r}) \ln f_N(\vec{p}, \vec{r}) \, d\Gamma_N$$

$$S = -k \sum_{N=0}^{\infty} \int_{\Gamma_N} f_N \ln\left(\frac{e^{-\beta(\mathcal{H}_N - \mu N)}}{\Xi}\right) d\Gamma_N$$

$$S = k\beta \sum_{N=0}^{\infty} \int_{\Gamma_N} \mathcal{H}_N f_N \, d\Gamma_N - k\beta\mu \sum_{N=0}^{\infty} \int_{\Gamma_N} N f_N \, d\Gamma_N$$

$$+ k \ln \Xi \sum_{N=0}^{\infty} \int_{\Gamma_N} f_N \, d\Gamma_N$$

$$S = \frac{1}{T} \langle \mathcal{H}_N \rangle - \frac{\mu}{T} \langle N \rangle + k \ln \Xi$$

$$S = \frac{U}{T} - \mu \frac{\langle N \rangle}{T} + k \ln \Xi$$

$$TS = U - \mu \langle N \rangle + kT \ln \Xi$$

$$\left.\begin{aligned} -kT \ln \Xi &= U - TS - \mu \langle N \rangle \\ G &= \mu \langle N \rangle \\ G &= U - TS + pV \end{aligned}\right\} \rightarrow pV = kT \ln \Xi$$

$$\Omega = -kT \ln \Xi \;\wedge\; pV = kT \ln \Xi \;\rightarrow$$

$$\Omega = -pV \;\rightarrow\; \text{Kramersova relacija}$$

Pokazati da statistička suma VKA za klasični idealni gas, koji se sastoji od N jednoatomskih molekula ima oblik:

$$\Xi = e^{\lambda Z}$$

Raspraviti značenje veličina Z i λ. Ako se gas nalazi u zapremini V, koristeći VK raspodelu pokazati da je broj molekula, koji se nalaze u maloj zapremini v $(v \ll V)$ dat Poisson-ovom raspodelom, tj. verovatnoća da taj broj bude n iznosi:

$$P_n = e^{-\langle n \rangle} \frac{\langle n \rangle^n}{n!},$$

gde je $\langle n \rangle$ srednji broj molekula u zapremini v

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$$\Xi = \sum_{N=0}^{\infty} \lambda^N Z_N, \quad Z_N = \frac{Z^N}{N!} \qquad (*)$$

$$Z = \frac{V}{h^3} (2\pi m k T)^{\frac{3}{2}}$$

$$\Xi = e^{\lambda Z} \Leftarrow (*)$$

Sa druge strane

$$\langle A_N \rangle = \sum_{N=0}^{\infty} \int_{\Gamma_N} A_N f_N(\vec{p}, \vec{q}) \, d\Gamma_N$$

$$= \frac{1}{\Xi} \sum_{N=0} A_N \lambda^N Z_N$$

Srednji broj čestica

$$\langle N \rangle = \frac{\sum_{N=0}^{\infty} N \lambda^N Z_N}{\sum_{N=0}^{\infty} \lambda^N Z_N} = \lambda \frac{\sum_{N=0}^{\infty} N \lambda^{N-1} Z_N}{\sum_{N=0}^{\infty} \lambda^N Z_N}$$

$$= \frac{\lambda}{\Xi} \frac{\partial \Xi}{\partial \lambda} = \lambda \frac{\partial \ln \Xi}{\partial \lambda}$$

$$\left.\begin{array}{l} \boxed{\langle N \rangle = \lambda \frac{\partial \ln \Xi}{\partial \lambda}} \\ \Xi = e^{\lambda Z} \Rightarrow \ln \Xi = \lambda Z \end{array}\right\} \Rightarrow$$

$$\Rightarrow \quad \langle N \rangle = \lambda Z = \lambda \frac{V}{h^3} (2\pi m kT)^{\frac{3}{2}}$$

Kako je $\lambda_T = \frac{h}{\sqrt{2\pi m kT}}$ $\Rightarrow$ termalna talasna dužina

$$\langle N \rangle = \lambda \frac{V}{\lambda_T^3}$$

odnosno

$$\lambda = \frac{\langle N \rangle}{V} \lambda_T^3$$

(srednji broj čestica u zapremini λ_T^3)

Posmatrajmo sada podsistem zapremine v sa n čestica kao podsistem na koji primenjujemo formalizam VKA

$$f_n(\vec{p},\vec{q}) = \frac{e^{-\beta(\mathcal{H}_n(\vec{p},\vec{q}) - \mu n)}}{\Xi}$$

$$dw_n(\vec{p},\vec{q}) = \frac{e^{-\beta(\mathcal{H}_n(\vec{p},\vec{q}) - \mu n)}}{\Xi} \quad \frac{d\Gamma_n}{h^{3n} n!}$$

$$\Xi = e^{\lambda Z}$$

$$\langle n \rangle = \lambda Z$$

$$\Xi = e^{\langle n \rangle} \qquad \lambda = \frac{\langle n \rangle}{Z}$$

$$dw_n = \frac{\lambda^n \, e^{-\beta \mathcal{H}_n(\vec{p},\vec{q})}}{\Xi} \quad \frac{d\Gamma_n}{h^{3n} n!}$$

$$dw_n = \frac{\langle n \rangle^n}{Z^n} \, \frac{1}{e^{\langle n \rangle}} \quad e^{-\beta \mathcal{H}_n} \frac{d\Gamma_n}{n! \, h^{3n}}$$

$$w_n = \frac{\langle n \rangle^n}{\cancel{Z^n}} \, \frac{1}{e^{\langle n \rangle}} \, \frac{\cancel{Z^n}}{n!}$$

$$w_n = e^{-\langle n \rangle} \frac{\langle n \rangle^n}{n!}$$

Za ispit

Koliko iznosi $D(N)$ za sistem koji se pokorava VK raspodeli? $D(N) = \kappa T \frac{\partial \langle N \rangle}{\partial \mu}$

Da li je zadovoljeno $D(N) = \langle N \rangle$? $\longrightarrow$

4. Pokazati da i u formalizmu velikog kanonskog ansambla vaŝi

$$p_N = -\left\langle \frac{\partial \mathcal{H}_N}{\partial V} \right\rangle$$

kao i u formalizmu MKA. Hamiltonijan je dat kao $\mathcal{H}_N = \mathcal{H}_N(\vec{q}, \vec{p}; V)$

$$\Omega = -kT \ln \Xi$$

$$\frac{\partial \Omega}{\partial V} = -kT \frac{\partial}{\partial V} \ln \Xi$$

$$= -\frac{kT}{\Xi} \frac{\partial \Xi}{\partial V}$$

$$\Xi = \sum_{N=0}^{\infty} \lambda^N Z_N$$

$$\frac{\partial \Omega}{\partial V} = -\frac{kT}{\Xi} \frac{\partial}{\partial V} \left(\sum_{N=0}^{\infty} \lambda^N Z_N \right)$$

$$Z_N = Z_N(T, V, N) \equiv Z_N(V)$$

$$\frac{\partial \Omega}{\partial V} = -\frac{kT}{\Xi} \sum_{N=0}^{\infty} \lambda^N \frac{\partial Z_N(V)}{\partial V}$$

$$Z_N = \int_{\Gamma_N} e^{-\beta \mathcal{H}_N(\vec{p},\vec{q};V)} d\Gamma_N$$

$$\frac{\partial Z_N}{\partial V} = -\beta \int_{\Gamma_N} \frac{\partial \mathcal{H}_N}{\partial V} e^{-\beta \mathcal{H}_N} d\Gamma_N$$

$$= -\beta Z_N \left\langle \frac{\partial \mathcal{H}_N}{\partial V} \right\rangle$$

$$\frac{\partial \Omega}{\partial V} = -\frac{kT}{\Xi} \sum_{N=0}^{\infty} \lambda^N \left(-\beta Z_N \left\langle \frac{\partial \mathcal{H}_N}{\partial V} \right\rangle\right)$$

$$\frac{\partial \Omega}{\partial V} = \frac{kT}{\Xi} \beta \sum_{N=0}^{\infty} \lambda^N Z_N \left\langle \frac{\partial \mathcal{H}_N}{\partial V} \right\rangle$$

$$P = -\frac{\partial \Omega}{\partial V}$$

$$P = \frac{1}{\Xi} \sum_{N=0}^{\infty} \langle P_N \rangle \lambda^N Z_N$$

$$\left(P = \sum_{N=0}^{\infty} P_N W_N \qquad W_N = \frac{e^{-\beta(E_N - \mu N)}}{\Xi} \right)$$

Uporeďujući, sledi da važi

$$P_N = -\left\langle \frac{\partial \mathcal{H}_N}{\partial V} \right\rangle$$

6. Koristeći formalizam velikog kanonskog ansambla, izračunati hemijski potencijal $\mu(T,P)$ za ultrarelativistički idealni gas koji se nalazi u zapremini V.

Za neinteragujući sisteme (nelokalizovane)

$$\Xi = \sum_{N\geq 0}^{\infty} \frac{1}{N!} \lambda^N Z_1^N$$

$Z_1 \rightarrow$ statistička suma jedne čestice

$$\Xi = e^{\lambda Z_1}$$

$Z_1 = ?$; $\varepsilon = cp$, $p = |\vec{p}|$

$$Z_1 = \frac{1}{h^3} \int d^3\vec{q}\, d^3\vec{p}\, e^{-\beta c |\vec{p}|}$$

$$= \frac{4\pi V}{h^3} \int_0^{\infty} dp\, p^2 e^{-\beta c p}$$

Γ funkcija

$$= \frac{8\pi V}{(\beta c h)^3}$$

$\Gamma(n) = (n-1)!$, $n \in \mathbb{Z}$

$$\Xi = \sum_{N=0}^{\infty} \frac{1}{N!} \left[\frac{8\pi V \lambda}{(\beta c h)^3}\right]^N$$

$$\Xi = e^{\frac{8\pi V \lambda}{(\beta c h)^3}}$$

$$pV = kT \frac{8\pi V \lambda}{(\beta c h)^3} \qquad (pV = kT \ln \Xi)$$

$$p\cancel{V} = \frac{(kT)^4}{(ch)^3} 8\pi \cancel{V} \lambda$$

$$\frac{p\, c^3 h^3}{8\pi (kT)^4} = e^{\beta\mu}$$

$$\Downarrow$$

$$\mu = kT \ln \left[\frac{p c^3 h^3}{8\pi (kT)^4} \right]$$

Za pismeni deo ispita: Umesto $\mu(p,T)$ tražiti $\mu(T,\langle N\rangle)$ koristeći izraz $\langle N\rangle = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V}$

Domaći!

Koristeći $\langle N\rangle = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V}$ i poslednju relaciju, odrediti kako glasi TERMIČNA j-na za fizički sistem iz postavke zadatke

pozadi