Formulari Física Estadística

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1. Microcanonical ensemble (N, V, E)

1.1. Introduction

$S = K_b \log \Omega$.

Basic relations:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V} \qquad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N}$$

$$\mu = -T\left(\frac{\partial S}{\partial N}\right)_{E,V} \qquad C(T) = \frac{\partial E}{\partial T}$$

$$\text{Potentials: } \begin{cases} F = E - TS, \\ G = F + PV, \\ H = E + PV \end{cases}$$

1.2. Ideal gas

$$H(\vec{q}, \vec{p}) = \sum_{i=1}^{N} H_i(\vec{q_i}, \vec{p_i}) = \sum_{i=1}^{N} \frac{p_i^2}{2m}$$

$PV = \frac{2}{3}E$ (valid for ideal classic and quantum gasses)

For a reversible adiabatic process the entropy is constant, and thus: $PV^{\frac{5}{3}} = \text{const.}$

$$C_V = \frac{3}{2}NK_B,\ C_P = \frac{5}{2}NK_B$$

$$\mu = K_B T \log\left(\frac{N\lambda^3}{V}\right)$$

$$\lambda = \sqrt{\frac{h^2}{2\pi m K_B T}}$$

$$S(E,N,V) = \frac{3}{2}NK_B\left(-\log(\lambda) + \frac{2}{3}\log\left(\frac{V}{N}\right) + \frac{5}{3}\right)$$

2. Canonical ensemble (N, V, T)

Partition function:

$$Z = \sum_{E_i} \Omega(E_i) e^{-\beta E_i}$$

$$P(E_i) = \frac{1}{Z}\Omega(E_i)e^{-\beta E_i}$$

$$\langle E \rangle = -\left(\frac{\partial \log Z}{\partial \beta}\right)_{N,V}$$

$$\sigma_E = \sqrt{K_B T^2 C_v}$$

$$F = -K_B T \log Z$$

Thermodynamic relations:

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

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

Identical part.: $Z(N) = \frac{[Z(1)]^N}{N!}$

Localized part.: $Z(N) = [Z(1)]^N$

Single-particle partition function:

$$Z(1) = \frac{1}{h^3}\int e^{-\beta H(\vec{q_i}, \vec{p_i})} d\vec{q_i} d\vec{p_i}$$

Equipartition theorem: $\langle x_i \cdot \frac{\partial H}{\partial x_j}\rangle = K_B T \delta_{ij}$

$$H = \sum_{i=1}^{n} a_i x_i^{\eta_i} \Rightarrow E = K_B T \sum_{i=1}^{6n} \frac{1}{\eta_i}$$

3. Grand canonical ensemble (μ, V, T)

$$Q = \sum_{N=0}^{\infty} \sum_{E} \Omega(N,E) e^{-\beta(E - \mu N)}$$

$$P(E,N) = \frac{1}{Q}\Omega(N,E)e^{-\beta(E-\mu N)}$$

Fugacity: $z := e^{\beta\mu}$

$$Q = \sum_{N=0}^{\infty} z^N \sum_E \Omega(N,E) e^{-\beta E} = \sum_{N=0}^{\infty} z^N Z(N)$$

$$\begin{cases} Z(N) = \frac{1}{N!}[Z(1)]^N \implies Q = e^{zZ(1)} \\ Z(N) = [Z(1)]^N \implies Q = \frac{1}{1 - zZ(1)} \end{cases}$$

$$\alpha = -\beta\mu$$

$$\langle E \rangle = -\left(\frac{\partial \log Q}{\partial \beta}\right)_{\alpha,V}$$

$$\sigma_E^2 = \left(\frac{\partial^2 \log Q}{\partial \beta^2}\right)_{\alpha,V} = -\left(\frac{\partial \langle E \rangle}{\partial \beta}\right)_{\alpha,V}$$

$$\langle N \rangle = -\left(\frac{\partial \log Q}{\partial \alpha}\right)_{\beta,V} = z\left(\frac{\partial \log Q}{\partial z}\right)_{T,V}$$

$$\sigma_N^2 = \left(\frac{\partial^2 \log Q}{\partial \alpha^2}\right)_{\beta,V} = -\left(\frac{\partial \langle N \rangle}{\partial \alpha}\right)_{\beta,V}$$

$$\Xi = U - TS - \mu N = -K_B T \log Q$$

Thermodynamic relations:

$$PV = -\Xi \qquad N = -\left(\frac{\partial \Xi}{\partial \mu}\right)_{T,V}$$

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

(isolating μ from the first 2 eqs. we get the eq. of state)

4. Quantum statistical mechanics

$$E_k = \sum_i n_i \varepsilon_i,\ Z = \sum_k e^{-\beta E_k}$$

$$Z = \sum_{\{n_i\}} f(\{n_i\}) e^{-\beta E_k}$$

Distinguishable: $g(\{n_i\}) = \frac{N!}{n_1! n_2! \cdots n_N!}$

Indistinguishable: $g(\{n_i\}) = 1$

$$Q = \prod_i \sum_{n_i=0}^{n_{i,max}} (ze^{-\beta\varepsilon_i})^{n_i}$$

5. Miscelanea

Vol(d-sphere): $V_d(R) = \frac{\pi^{\frac{d}{2}} R^d}{\Gamma\left(1 + \frac{d}{2}\right)}$

Stirling: $\log n! \approx n \log n - n$

$$\sum_{n=0}^{N} x^n = \frac{x^{N+1} - 1}{x - 1}$$

ESTADÍSTICA QUÀNTICA

Mecànica Estadísitca Quàntica

Els efectes quàntics seran menyspreables quan

$$\Lambda_T \ll l = \left(\frac{V}{N}\right)^{1/3}$$

Estadísitques de FD i BE

$$\mathcal{Z}_{FD/BE}(\beta, V, \mu) = \prod_i \left(1 \pm ze^{-\beta\varepsilon_i}\right)^{\pm 1}$$

$$\sum_i n_i = N \quad \text{BE: } n_i = 0, 1, ..., N \quad \text{FD: } n_i = 0, 1$$

$$Ln\mathcal{Z}_{GC} = \frac{PV}{k_B T} = \frac{1}{a}\int_0^\infty \ln\left(1 + aze^{-\beta\varepsilon}\right) g(\varepsilon)d\varepsilon$$

Connexió amb la Termodinàmica

$$\langle N \rangle = \sum_{\text{estats monop.}} \langle n_i \rangle \quad \text{continu: } \sum_\epsilon \to \int g(\epsilon)d\epsilon$$

$$\langle n_i \rangle = \frac{1}{z^{-1}e^{\beta\varepsilon_i} + a} \quad a = 0 \quad (MB), \quad 1 \quad (FD), \quad -1 \quad (BE)$$

$$\text{FD} \to \quad \frac{\sigma_n^2}{\langle n_i \rangle^2} = \frac{1}{\langle n_i \rangle} - 1 \quad \text{BE} \to \quad \frac{\sigma_n^2}{\langle n_i \rangle^2} = \frac{1}{\langle n_i \rangle} + 1$$

$$\text{MB} \to \quad \frac{\sigma_n^2}{\langle n_i \rangle^2} = \frac{1}{\langle n_i \rangle} \quad 0 < \langle n_i \rangle_{FD} < 1 \quad \langle n_i \rangle_{BE} \geq 0$$

Límit clàssic

1. Per $x = \beta(\epsilon_i - \mu) \to \infty$ les dues estadístiques tendeixen a MB
2. En aquest límit, $\langle n_i \rangle \to 0$ i $n_i = 0, 1o2$.
3. És quivalent a $\phi(\varepsilon) \gg N \Rightarrow \Lambda_T \ll \left(\frac{V}{N}\right)^{1/3}$ $\Rightarrow \Lambda_T^3 n \ll 1 \Rightarrow \mu < 0 \Rightarrow z = e^{\beta\mu} < 1$

Aplicacions

Densitats d'estats per una partícula lliure en una caixa

$$\text{1D: } g(\varepsilon)d\varepsilon = \frac{L}{h}(2m)^{1/2}\varepsilon^{-1/2}d\varepsilon \quad \text{2D: } g(\varepsilon)d\varepsilon = \frac{\pi S}{h^2}(2m)d\varepsilon$$

$$\text{3D: } g(\varepsilon)d\varepsilon = \frac{\pi}{4}\left(\frac{8m}{h^2}\right)^{3/2} V\varepsilon^{1/2}d\varepsilon$$

Gas ideal quàntic

$$\langle \text{N} \rangle = \frac{2\text{V}}{\sqrt{\pi}\Lambda^3}\int_0^\infty \frac{x^{1/2}}{z^{-1}e^x + a}$$

$$\langle E \rangle = \frac{k_B T 2\text{V}}{\sqrt{\pi}\Lambda^3}\int_0^\infty \frac{x^{3/2}}{z^{-1}e^x + a}$$

Gas feblement degenerat de fermions

$$g(\varepsilon)d\varepsilon = \frac{\pi}{4}\left(\frac{8m}{h^2}\right)^{3/2} g_s V\varepsilon^{1/2}d\varepsilon \qquad g_s = 2s + 1$$

$$U = \langle E \rangle = \frac{3}{2}Nk_B T\sum_{l=1}^\infty (-1)^{l-1}a_l\left(\frac{n\Lambda^3}{g_s}\right)^{l-1}$$

$$C_v = \frac{3}{2}Nk_B\sum_{l=1}^\infty (-1)^{l-1}a_l\left(\frac{5-3l}{2}\right)\left(\frac{n\Lambda^3}{g_s}\right)^{l-1}$$

Gas fortament degenerat de fermions

Energia de Fermi

$$N = \int_0^{\epsilon_F} g_s g(\varepsilon)d\varepsilon = \int_0^{n_F} g_s g(n)dn \qquad p = \frac{2U}{3V}$$

$$E = \int_0^{n_F} g_s g(n)\epsilon(n)dn \qquad T_F = \epsilon_F/K_B \quad p(T=0K) = \frac{2n\varepsilon_F}{5}$$

$$\varepsilon_F = \frac{h^2}{2m}\left(\frac{3}{4\pi g_s}\right)^{2/3}\left(\frac{N}{V}\right)^{2/3}$$

$$p_F = (2m\varepsilon_F)^{1/2} = \left(\frac{3Nh^3}{4\pi g_s V}\right)^{1/3}$$

Electrons de conducció d'un metall

$$\vec{p} = \hbar\vec{k}$$

$$\langle E \rangle = U = \int_0^\infty \epsilon g(\epsilon)f(\epsilon)d\epsilon = \int_0^\infty \frac{\epsilon g(\epsilon)}{e^{\beta(\epsilon-\mu)} + 1}d\epsilon$$

$$N = \int_0^\infty g(\epsilon)f(\epsilon)d\epsilon = \int_0^\infty \frac{g(\epsilon)}{e^{\beta(\epsilon-\mu)} + 1}d\epsilon$$

Per baixes temperatures $K_B T << \epsilon_F$

$$C_v^e = g\left(\varepsilon_F\right)k_B^2 T\frac{\pi^2}{3}$$

Radiació de cos negre

Gas de fotons

$$\mu = 0 \quad g(p)dp = \frac{4\pi V}{h^3}p^2dp \quad \varepsilon = cp = h\nu \quad g(\varepsilon)d\varepsilon = \frac{4\pi V}{h^3}\frac{\varepsilon^2}{c^3}d\varepsilon$$

$$g(\nu)d\nu = \frac{8\pi V}{c^3}\nu^2 d\nu \quad U = \int_0^\infty \langle n_\nu \rangle h\nu g(\nu)d\nu = u_0 V T^4$$

$$P = \frac{u_0}{3}T^4 \quad u_0 = \frac{\pi^2}{15}\frac{k_B^4}{c^3\hbar^3}$$

Gas de fonons

El nombre mig de fonons amb energia $h\nu_j$ és

$$\langle n_j \rangle = \frac{1}{e^{\beta h\nu_j - 1}}$$

i l'energia del gas:

$$\langle E \rangle = \int_0^\infty \frac{\hbar\omega}{c^{\beta\hbar\omega} - 1}g(\omega)d\omega \quad \text{amb } g(\omega)d\omega = \frac{3V}{2\pi^2}\frac{\omega^2}{v_0^3}\text{d}\omega$$

En termes de ω_D

$$g(\omega) = 9N\frac{\omega^2}{\omega_D^3} \quad \omega \leq \omega_D$$

$$g(\omega) = 0 \qquad \omega > \omega_D$$

$$\langle E \rangle = \frac{9N}{\omega_D^3}\frac{(k_B T)^4}{\hbar^3}\int_0^{x_D}\frac{x^3dx}{e^x - 1} \quad \text{amb } x = \beta\hbar\omega$$

Partícula lliure ultrarelativista

$$\text{3D: } g(\varepsilon)d\varepsilon = \frac{4\pi L^3}{c^3 h^3}\varepsilon^2 d\varepsilon$$

$$\text{2D: } g(\varepsilon)d\varepsilon = \frac{2\pi L^2}{c^2 h^2}\varepsilon d\varepsilon$$

$$\text{1D: } g(\varepsilon)d\varepsilon = \frac{2L}{ch}d\varepsilon$$

Condensació de Bose-Einstein

Les equacions que descriuen el comportament del cas de bosons són

$$ln\mathcal{Z}_{GC} = \frac{PV}{k_B T} = \frac{2}{3}\frac{2V}{\sqrt{\pi}\Lambda^3}\int_0^\infty \frac{x^{3/2}dx}{z^{-1}e^x - 1}$$

$$\langle N \rangle = \frac{2V}{\sqrt{\pi}\Lambda^3}\int_0^\infty \frac{x^{1/2}dx}{z^{-1}e^x - 1}$$

$$\langle E \rangle = \frac{k_B T 2V}{\sqrt{\pi}\Lambda^3}\int_0^\infty \frac{x^{3/2}dx}{z^{-1}e^x - 1}$$

Es poden expressar en termes de la funció

$$G_n(z) = \frac{1}{\Gamma(n)}\int_0^\infty \frac{x^{n-1}dx}{z^{-1}e^x - 1}$$

obtenint

$$\frac{p}{k_B T} = \frac{1}{\Lambda^3}G_{5/2}(z)$$

$$\langle N \rangle = \frac{V}{\Lambda^3}G_{3/2}(z)$$

$$\langle E \rangle = \frac{3V}{2}\frac{k_B T}{\Lambda^3}G_{5/2}(z)$$

Diem que hi ha condensació quan $\mu = min\{\epsilon_k\}$. El nombre de bosons que es troben excitats a una temperatura $T < T_C$ per sota de la temperatura de condensació és

$$\langle N \rangle_{ex} = \int_0^\infty \frac{g(\epsilon)}{e^{\beta\epsilon} - 1}d\epsilon$$

on hem considerat que per $T < T_C$ la fugacitat és $z = 1$, o, equivalentment, que $\mu = 0$.

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