Termodinàmica Estadística

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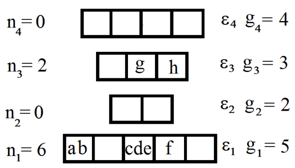
Partícules discernibles



g_i = *degeneració (nombre de caselles)*

n_i = *nombre de partícules en el nivell d'energia* ε_i

$$\Omega_1 = \frac{8!}{6!\,2!}5^6 \quad \Omega_2 = 1$$

$$\Omega_3 = \frac{2!}{2!\,0!}3^2 \quad \Omega_4 = 1$$

$$\Omega = \frac{8!}{6!\,2!}5^6\frac{2!}{2!\,0!}3^2 = 8!\,\frac{5^6 3^2}{6!\,2!}$$

$$N_i = N - \sum_{j=1}^{i-1} n_j \qquad t_i = {g_i}^{n_i} \qquad \Omega_i = \frac{N_i!}{n_i!\,(N_i - n_i)!}t_i$$

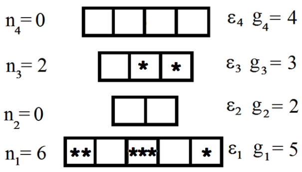
Maxwell-Boltzman

$$\Omega_{MB} = N! \prod \frac{{g_i}^{n_i}}{n_i!}$$

Maxwell-Boltzman corregida

$$\Omega_{MB}^{corr} = \prod \frac{{g_i}^{n_i}}{n_i!}$$

Partícules indiscernibles bosòniques



$$\Omega_1 = \frac{(6+(5-1))!}{6!\,(5-1)!} \qquad \Omega_2 = 1$$

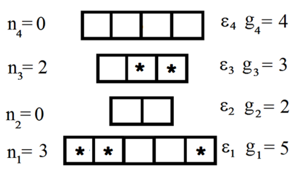
$$\Omega_3 = \frac{(2+(3-1))!}{2!\,(3-1)!} \qquad \Omega_4 = 1$$

$$\Omega_i = \frac{(n_i+g_i-1)!}{n_i!\,(g_i-1)!}$$ Bose-Einstein $$\Omega_{BE} = \prod \frac{(n_i+g_i-1)!}{n_i!\,(g_i-1)!}$$

$$\Omega_i = \frac{(g_i+n_i-1)\cdot\ldots g_i\cdot(g_i-1)!}{n_i!\cdot(g_i-1)!} = \frac{g_i(1+\frac{n_i-1}{g_i})\cdot g_i(1+\frac{n_i-2}{g_i})\cdot\ldots g_i\cdot(1+0)}{n_i!}$$

$$= \frac{(g_i)^{n_i}}{n_i!}(1+\frac{n_i-1}{g_i})(1+\frac{n_i-2}{g_i})\cdot\ldots\cdot 1 \approx \frac{(g_i)^{n_i}}{n_i!}$$ Maxwell-Boltzman corr

Partícules indiscernibles fermiòniques



$$\Omega_1 = \frac{5!}{3!\,(5-3)!} \qquad \Omega_2 = 1$$

$$\Omega_3 = \frac{3!}{2!\,(3-2)!} \qquad \Omega_4 = 1$$

$$\Omega_i = \frac{g_i!}{n_i!\,(g_i-n_i)!}$$ Fermi-Dirac $$\Omega_{FD} = \prod \frac{g_i!}{n_i!\,(g_i-n_i)!}$$

$$\Omega_i = \frac{g_i!}{n_i!\cdot(g_i-n_i)!} = \frac{g_i\cdot(g_i-1)\cdot\ldots\cdot(g_i-n_i+1)(g_i-n_i)!}{n_i!\cdot(g_i-n_i)!}$$

$$= \frac{g_i\cdot(1-0)\cdot g_i\cdot(1-\frac{1}{g_i})\ldots g_i\cdot(1-\frac{n_i-1}{g_i})}{n_i!} = \frac{(g_i)^{n_i}}{n_i!}1\cdot(1-\frac{1}{g_i})\ldots(1-\frac{n_i-1}{g_i}) \approx \frac{(g_i)^{n_i}}{n_i!}$$

Maxwell-Boltzman corr

Distribució més probable (MB-corr)

Complexions distribució D: $\Omega_D = \prod \frac{(g_j)^{n_j}}{n_j!}$

Lligadures: constància energia i nombre de partícules

$$\sum n_j \varepsilon_j = E \qquad \sum n_j = N$$

La més probable: màxim Ω_D restringit per lligadures:

$$\frac{\partial}{\partial n_i}(\ln \Omega_D - \alpha(\sum_j n_j - N) - \beta(\sum_j n_j \varepsilon_j - E) = 0 \quad \Rightarrow \quad \frac{\partial \ln \Omega_D}{\partial n_i} - \alpha - \beta \varepsilon_i = 0$$

$$\ln \Omega_D = \ln \prod \frac{(g_j)^{n_j}}{n_j!} = \sum (n_j \ln g_j - \ln n_j!) = \sum (n_j \ln g_j - n_j \ln n_j + n_j)$$

$$\Rightarrow \boxed{n_i^{MB} = \frac{g_i}{e^{\alpha} e^{\beta \varepsilon_i}} = g_i \, e^{-\alpha} e^{-\beta \varepsilon_i}}$$

$$\boxed{n_i^{FD} = \frac{g_i}{e^{\alpha} e^{\beta \varepsilon_i} + 1}} \; ; \; \boxed{n_i^{BE} = \frac{g_i}{e^{\alpha} e^{\beta \varepsilon_i} - 1}}$$

Significat dels paràmetres α i β:

Lligadures en el cas de dos subsistemes amb complexions Ω_1, Ω_2, en contacte tèrmic:

$$\sum N_i^{(1)} = N_1 \leftarrow \alpha_1$$

$$\sum N_i^{(2)} = N_2 \leftarrow \alpha_2$$

$$\sum_i N_i^{(1)} \varepsilon_i^{(1)} + \sum_j N_j^{(2)} \varepsilon_j^{(2)} = E \leftarrow \beta$$

Si permetem el flux de matèria:

$$\sum_i N_i^{(1)} + \sum_j N_j^{(2)} = N \leftarrow \alpha$$

Per tant, β té sentit de temperatura empírica (es pot demostrar que $\beta = 1/kT$)

i α té sentit de potencial químic μ (es pot demostrar que $\alpha = -\mu/RT$)

$$f_{BE}(E) = \frac{1}{e^{(E-\mu)/k_B T} - 1},$$

$$f_{FD}(E) = \frac{1}{e^{(E-\mu)/k_B T} + 1}.$$

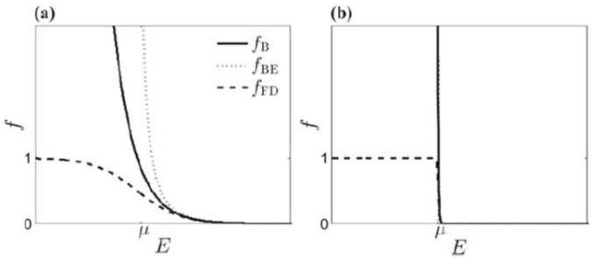


Fig. 2.6 The Boltzmann, Bose–Einstein and Fermi-Dirac distribution functions for **a** $T \gg 0$ and **b** $T \approx 0$

- For $(E-\mu)/k_B T \gg 1$, the Bose–Einstein and Fermi-Dirac distributions approach the Boltzmann distribution. Here, the average state occupancy is much less than unity, such that the effects of particle indistinguishability become negligible. Note that the classical limit condition $(E-\mu)/k_B T \gg 1$ should not be interpreted too directly, as it seems to predict, counter-intuitively, that low temperatures favour classical behaviour; this is because μ itself has a non-trivial temperature dependence.
- As $E \to \mu$ from above, the Bose–Einstein distribution diverges, i.e. particles accumulate in the lowest energy states.
- For $E \ll \mu$, the Fermi-Dirac distribution saturates to one particle per state, as required by the Pauli exclusion principle.
- For decreasing temperature, the distributions develop a sharper transition about $E = \mu$, approaching step-like forms for $T \to 0$.

La funció de partició y magnituds termodinàmiques

$$n_i = g_i\, e^{-\alpha} e^{-\beta\varepsilon_i} \quad \Rightarrow \quad \sum n_i = N = e^{-\alpha} \sum g_i\, e^{-\beta\varepsilon_i} = e^{-\alpha} \cdot f$$

Funció de partició f:

$$\boxed{f = \sum g_i\, e^{-\beta\varepsilon_i}}$$

Energia interna:

$$E = \sum_i N_i \varepsilon_i = \sum_i g_i e^{-\alpha} e^{-\beta\varepsilon_i} \varepsilon_i = \frac{N}{f} \sum_i g_i e^{-\beta\varepsilon_i} \varepsilon_i = -\frac{N}{f} \frac{\partial}{\partial\beta} \sum_i g_i e^{-\beta\varepsilon_i}$$

$$\Rightarrow \quad \boxed{E = -N\left(\frac{\partial \ln f}{\partial\beta}\right)_V = NkT^2\left(\frac{\partial \ln f}{\partial T}\right)_V}$$

Capacitat calorífica:

$$\boxed{C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{\partial}{\partial T}\left[NkT^2\left(\frac{\partial \ln f}{\partial T}\right)_V\right] = 2NkT\left(\frac{\partial \ln f}{\partial T}\right)_V + NkT^2\left(\frac{\partial^2 \ln f}{\partial T^2}\right)_V}$$

Un exemple de càlcul de funció de partició

Les energies d'un oscil·lador harmònic, respecte del seu nivell bassal, venen determinades per: $E_n - E_0 = nh\nu$. A més, no hi ha degeneració. Aleshores,

$$f = \sum_{n=1}^{\infty} \left(e^{-h\nu/kT}\right)^n$$

Si anomenem $x = e^{-h\nu/kT}$, tenim que $f = 1 + x + x^2 + ... = \frac{1}{1-x}$. Am la qual cosa tenim la funció de partició vibracional en la forma:

$$\boxed{f = \frac{1}{1 - e^{-h\nu/kT}}}.$$

Entropia i nombre de complexions

$$\Omega = \prod_i \frac{(g_i)^{n_i}}{n_i!} \qquad n_i = g_i\, e^{-\alpha} e^{-\beta\varepsilon_i}$$

distribució més probable: $\ln \Omega_0 = \sum_i (n_i \ln g_i - n_i \ln(g_i\, e^{-\alpha}\, e^{-\beta\varepsilon_i}) + n_i)$

$$= \alpha \sum_i n_i + \beta \sum_i n_i \varepsilon_i + \sum_i n_i = \alpha N + \beta E + N$$

$e^{-\alpha} = f/N \quad \Rightarrow \quad \ln \Omega_0 = N \ln f - N \ln N + \beta E + N$

$$\boxed{d \ln \Omega_0 = \ln \Omega_0' - \ln \Omega_0 = N d \ln f + \beta dE + E d\beta}$$

amb: $N\, d \ln f = N \left(\frac{\partial \ln f}{\partial \beta}\right)_V d\beta + N \left(\frac{\partial \ln f}{\partial V}\right)_\beta dV$

Entropia i nombre de complexions

El primer terme: $N\,(\frac{\partial \ln f}{\partial \beta})_V = \frac{N}{f}(\frac{\partial f}{\partial \beta})_V = e^{-\alpha}\sum_i g_i\, e^{-\beta\varepsilon_i}(-\varepsilon_i) = -\sum_i n_i\varepsilon_i = -E$

El segon: $N\,(\frac{\partial \ln f}{\partial V})_\beta = \frac{N}{f}(\frac{\partial f}{\partial V})_\beta = e^{-\alpha}\sum_i g_i\, e^{-\beta\varepsilon_i}(-\beta\frac{d\varepsilon_i}{dV}) = -\beta\sum_i n_i \frac{d\varepsilon_i}{dV}$

$$d'Q = \sum_i \varepsilon_i\, dn_i \qquad d'W = -\sum_i n_i\, d\varepsilon_i$$

$$\Rightarrow \quad d\ln\Omega_0 = -E\,d\beta + \beta\, d'W + \beta\, dE + E\, d\beta = \beta\, d'Q = \beta\, T\, dS = k\, dS$$

$\Omega \approx \Omega_0$: $\boxed{S = k\ln\Omega}$

Magnituds Termodinàmiques en termes de la funció de partició

$$U = N\,k\,T^2\left(\frac{\partial \ln f}{\partial T}\right)_V \qquad \mu = -k\,T\,N_A\,\alpha$$

$$S = k\,N\ln\left(\frac{f\,e}{N}\right) + \frac{U}{T} \qquad P = NkT\left(\frac{\partial \ln f}{\partial V}\right)_T$$

$$F = -k\,T\,N\,\ln\left(\frac{f\,e}{N}\right)$$

$$K_N = \prod_i f_i^{\nu_i} \cdot\, e^{-\Delta\varepsilon^0/kT} \qquad \vec{k} = \frac{kT}{\hbar}\frac{f_\sharp}{f_A f_B}e^{-E_0/kT}$$