L65-Distributions

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* Ensembles

- Microcanonical (Boltzman) : # of microstates / macrostate.
- Canonical : # of microstates in thermally linked heat reservoir
- Grand Canonical : thermal & diffusive links with reservoir.

* Microcanonical Ensemble:

M.B.: $$\ln Q = \underbrace{\cancel{\ln N!}}_{} + \sum_i [N_i \ln d_i - \ln N_i!] + \overbrace{\alpha(N - \sum_i N_i) + \beta(E - \sum_i N_i E_i)}^{=0\,!}$$

non-extensive part, due to indistinguishability of particles.
omit in "correct Boltzmann counting"
See wikipedia: "Maxwell-Boltzmann statistics."

F.D.: $$\ln Q = \sum_i \ln(d_i)! - \ln(N_i)! - \ln(d_i - N_i)! + \alpha(N - \sum_i N_i) + \beta(E - \sum_i N_i E_i)$$

B.E.: $$\ln Q = \sum_i \ln(N_i + d_i - 1)! - \ln(N_i)! - \ln(d_i - 1)! + \alpha(N - \sum_i N_i) + \beta(E - \sum_i N_i E_i)$$

note: no term out of $\sum_i$: thus F.-D. & B.-E. distributions are extensive

- entropy of M-B. distribution:

$$S = k \ln Q = \sum_i N_i \left[\ln d_i - \ln N_i + 1 = \ln d_i - \ln \frac{d_i}{e^{\alpha + \beta E_i}} + 1 = \alpha + \beta E_i + 1 \right]$$

$$= k[(\alpha+1)N + \beta E] \qquad S/Nk = \ln(e^{\alpha}) + \frac{E}{NkT} + 1$$

for a free gas, $\frac{\partial S}{\partial \alpha} = 0$: $e^{\alpha} = \frac{V}{N\Lambda^3} = \frac{n_c}{n}$ $\quad \frac{\partial S}{\partial \beta} = 0$: $\beta E = \frac{E}{kT} = 3/2\, N$

$$N = Ve^{-\alpha}\left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2} \Rightarrow \Lambda = \frac{h}{\sqrt{\underset{?}{\boxed{2\pi}}\, \underbrace{m\,kT}_{E}}} = \frac{h}{p_{th.}}$$ "thermal deBroglie wavelength"

$n_c = \Lambda^{-3}$ "quantum concentration"

$$S/Nk = \ln \frac{n_c}{n} + 5/2$$ "Sakur-Tetrode equation"

for F.-D. (+) or B.-E. (−) distributions, α, β more difficult do integrate:

$$N = \int d_k\, n(k) = \frac{V}{2\pi^2} \int_0^{\infty} \frac{k^2 dk}{e^{(\hbar^2 k^2/2m - \mu)/kT} \pm 1}$$ ⇒ normalization $e^{-\mu/kT}$

$$\frac{V}{}\,\frac{\hbar^2}{}\int^{\infty} \frac{k^4 dk}{}$$ heat

$$E = \int d_k\, n(k)\, \varepsilon(k) = \frac{V}{2\pi^2}\frac{\hbar^2}{2m}\int_0^\infty \frac{k^4\,dk}{e^{(\hbar^2k^2/2m-\mu)/kT} \pm 1} \Rightarrow C_V = \frac{dE}{dT}$$ heat capacity.

- conservation of energy: "1st Law. Therm." recall $\partial_\alpha G = \partial_\beta G = 0$:

$$dS = k[d\alpha N + d\beta E + (\alpha+1)\,dN + \beta\, dE] = \alpha\, dN + \beta\, dE$$ [const V]

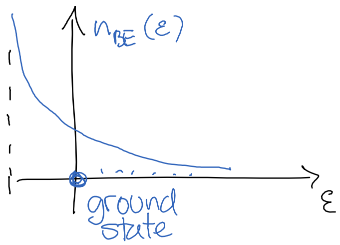
since $dN = \sum_i d[d_i e^{-(\alpha+\beta E_i)}] = \sum_i -d_i e^{-(\alpha+\beta E_i)}\, d(\alpha+\beta E_i) = -d\alpha N - d\beta E$

note: dN, dE performed after maximization of S w/r const. N, E

thus $dE = \frac{1}{k\beta} dS - \frac{\alpha}{k\beta} dN = T\,dS + \mu\, dN$ $\quad \beta = \frac{1}{kT} \quad \alpha = \frac{-\mu}{kT}$

* review Fermi-Dirac distributions (α, β), B.B. radiation here.

* Example: Bose-Einstein condensate. #5.29



$$n(\varepsilon) = [e^{(\varepsilon-\mu)/kT} - 1]^{-1} > 0 \Rightarrow \frac{\varepsilon-\mu}{kT} > 0$$

$$N = \frac{V}{2\pi^2}\int_0^\infty \frac{k^2\,dk}{e^{(\hbar^2k^2/2m-\mu)/kT} - 1} = \text{constant}$$

As T increases μ must also increase to compensate.

let $x = \frac{E}{kT} = \frac{\hbar^2k^2}{2mkT}$ $\quad k = \frac{\sqrt{2mkTx}}{\hbar}$ $\quad dk = \frac{\sqrt{2mkT}}{2\hbar\sqrt{x}}dx$

$$\text{at } \mu = 0,\ \frac{N}{V} = \frac{1}{2\pi^2}\left(\frac{2mkT}{\hbar^2}\right)^{3/2}\cdot\frac{1}{2}\underbrace{\int_0^\infty \frac{x^{1/2}}{e^x-1}dx}_{\substack{\Gamma(3/2)\ \zeta(3/2)\\ =\sqrt{\pi}/2\ \ =2.61}} = 2.61\underbrace{\left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2}}_{n_c}$$

$$n/n_c = \zeta(3/2) \qquad T_c = \frac{2\pi\hbar^2}{mk}\left(\frac{n}{\zeta(2/3)}\right)^{2/3}$$