L65-Temperature and Chemical Potential

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* The meaning of the Lagrange Multipliers:

Recall that the distribution of energy is obtained by maximizing

$$S = k\left[G = \underbrace{\ln(Q)}_{\#\text{ microstates}} + \alpha(\overbrace{\underbrace{N}_{\#\text{particles}} - \Sigma N_n}^{=0}) + \beta(\overbrace{\underbrace{E}_{\text{total Energy}} - \Sigma N_n E_n}^{=0})\right]$$

For Maxwell-Boltzmann statistics,

$$S = kG = \sum_n N_n(\ln d_n - \ln N_n + 1 - \alpha - \beta E_n) + \alpha N + \beta E$$

$$\frac{\partial G}{\partial N_n} = \ln d_n - \ln N_n - \alpha - \beta E_n = 0 \Rightarrow N_n(\alpha,\beta) = d_n e^{-\alpha-\beta E_n}$$

$$G(\alpha,\beta) = \sum_n N_n(\alpha,\beta)\left(\cancel{\ln d_n} - \cancel{\ln}\, \underbrace{d_n e^{\cancel{-\alpha}\cancel{-\beta E_n}}}_{N_n(\alpha,\beta)} + 1 \cancel{-\alpha} \cancel{-\beta E_n}\right) + \alpha N + \beta E$$

$= N(\alpha,\beta) + \alpha N + \beta E$. Maximize this by setting $\frac{\partial G}{\partial \alpha} = \frac{\partial G}{\partial \beta} = 0$

so that $N(\alpha,\beta) = \sum_n N_n = \sum_n d_n e^{-\alpha-\beta E_n} = N$ and $E(\alpha,\beta) = \sum_n N_n E_n = E$

then $dN(\alpha,\beta) = \sum_n d\left[d_n e^{-(\alpha+\beta E_n)}\right] = \Sigma - d_n e^{-(\alpha+\beta E_n)}\, d(\alpha + \beta E_n) = -(N d\alpha + E d\beta)$

and $dG = dN(\alpha,\beta) + d\alpha\, N + d\beta\, E = (N-N)\,d\alpha + (E-E)\,d\beta = 0$

then $N(\alpha,\beta) = N \Rightarrow S = k[(\alpha+1)N + \beta E] = Nk\left[\ln e^{\alpha} + \beta \frac{E}{N} + 1\right]$

* Conservation of energy: "1st Law Therodynamics"

Now vary $S = kG(\alpha,\beta)$ with respect to N and E:

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

Solving for dE gives us the 1st law: $dE = đQ - đW$

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

Including external forces and multiple species N_i,

$$\boxed{dE = \underbrace{T\,dS}_{đQ} + \sum_i \mu_i dN_i \underbrace{- (p\,dV + B\,dM + \dots)}_{đW}}$$

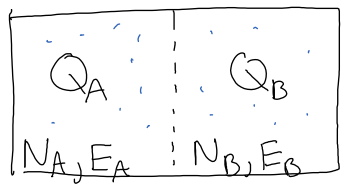
E, S, N, V, M: extensive
T, μ, P, B: intensive

(T,S) & (μ,N) & (p,V) etc. are conjugate variables w/r E
The first is constant over the material, the second scales.

* To see physical significance of taking the log of Q, divide the system (single-particle states) into 2 parts: A, B

$$\begin{array}{ccccc} Q & = & Q_A & \cdot & Q_B \\ \downarrow \ln(Q) & & \downarrow & & \downarrow \\ S & = & S_A & + & S_B \end{array}$$

μ-states multiply
entropy adds!
like $E, N, V, \dots$



- in thermal equilibrium $dS = dS_A + dS_B = 0$ "max. ent."
  also energy balance $dE = \frac{1}{\beta_A k} dS_A + \frac{1}{\beta_B k} dS_B = 0$
  Since $dS_A = -dS_B$, $\frac{1}{\beta_A} = \frac{1}{\beta_B} \equiv kT$ "temperature"
  There is no "energy" gradient transfering heat between A & B
  "k" = conversion factor from units of T to E (Boltzman const)
  and also units of $S = k \ln Q$, since $dE = T\,dS$

- likewise, in chemical equilibrium, $dE = \frac{\alpha_A}{\beta_A} dN_A + \frac{\alpha_B}{\beta_B} dN_B = 0$
  Since $dN_A = -dN_B$ $\frac{\alpha_A}{\beta_A} = \frac{\alpha_B}{\beta_B} \equiv \mu$ "chemical potential"
  There is no "energy" gradient pushing on particles.

- Other quantities: $z = e^{\alpha} = e^{-\mu/kT}$ "absolute activity" (normalization)

  And $Z(\beta) = \sum_n d_n e^{-E_n/kT} = \frac{N}{z}$ "partition function"

* Example: Free Gas (recall Fermi Gas!)

In this case, $n \to k = |\vec{k}|$, a continuous degree of freedom

$$E_n \to E_k = \frac{\hbar^2 k^2}{2m} \qquad \vec{k} = \left(\frac{\pi n_x}{l_x}, \frac{\pi n_y}{l_y}, \frac{\pi n_z}{l_z}\right),$$ one state per V/π^3

$$d_n \to d^3 n(k) = \frac{V}{\pi^3} d^3k = \frac{V}{\pi^3}\left(\frac{1}{8} 4\pi k^2 dk\right) = \frac{V}{2\pi^2} k^2 dk$$ (one octant)

$$N = \sum_n N_n \to \int d^3n \, e^{-\alpha - \beta E} = \frac{V}{2\pi^3} e^{-\alpha} \int_0^\infty e^{-\beta \frac{\hbar^2 k^2}{2m}} k^2 dk$$

$$= \frac{V}{2\pi^3} e^{-\alpha} \cdot \frac{1}{4}\left(\frac{\pi}{\left(\frac{\beta \hbar^2}{2m}\right)^3}\right)^{1/2} = V \underbrace{e^{-\alpha}}_{\text{solve for this.}} \left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2}$$

$$-\frac{d}{da}\left[\int_0^\infty e^{-ax^2} dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}\right]$$
$$= \int_0^\infty e^{-ax^2} x^2 dx = \frac{1}{4}\sqrt{\frac{\pi}{a^3}}$$

$$z = e^{\alpha} = \frac{V}{N\Lambda^3} = \frac{n_c}{n} \qquad n_c = \Lambda^{-3}$$ "quantum concentration"

where $$\Lambda = \frac{h}{p_{th}} = \frac{h}{\sqrt{2\pi m k T}}$$ "thermal deBroglie wavelength"

$$E = \sum_n N_n E_n \to \underbrace{\int d^3n \, e^{-\alpha - \beta E}}_{N(\beta)} E = -\frac{d}{d\beta} N(\beta) = \frac{3N}{2\beta} = \frac{3}{2} NkT$$

"Equipartition theorem": ave. energy / degree of freedom $= \frac{1}{2}kT$

$$S = k\left[(\alpha+1)N + \beta E\right] \qquad S/Nk = \ln(e^{\alpha}) + \frac{E}{NkT} + 1 = \ln\frac{n}{n_c} + \frac{5}{2}$$

"Sakur-Tetrode equation"