L64-Temperature and Chemical Potential

Friday, February 26, 2016 08:04

* Review and elaboration of Lagrange Multipliers:

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

$$dE = \frac{1}{\beta k} dS - \frac{\alpha}{\beta} dN - đW \quad \text{(work)} \qquad E, S, N, V, M: \text{ extensive}$$

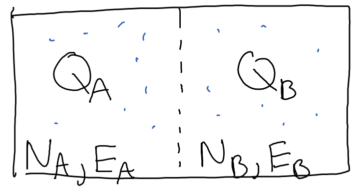
$$= T\,dS + \mu\,dN - (P\,dV + B\,dM + \ldots) \qquad T, \mu, P, B: \text{ intensive}$$

- to see physical significance of $\ln Q$, divide the system (single-particle states) into 2 parts: A, B

$Q = Q_A \cdot Q_B$ μ-states multiply

$\ln(Q) = \ln(Q_A) + \ln(Q_B)$ entropy adds!

$S = S_A + S_B$ like $E, N, V, \ldots$



- 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.
  "k" = conversion factor from units of T to E (Boltzman const)
  and also units of $S = k \ln Q$, since $dE = T\,dS$

- like wise, 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.

* Example: Free Gas (recall Fermi Gas!)

- now $n \to k = |\vec{k}|$, a continuous degree of freedom

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

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

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

$= \frac{V}{2\pi^3} e^{-\alpha} \cdot \frac{1}{4}\left(\frac{\pi}{\left(\frac{\beta\hbar^2}{2m}\right)^3}\right)^{1/2} = V e^{-\alpha}\left(\frac{m}{2\pi\beta\hbar}\right)^{3/2}$

solve for α.

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

$E = \sum N_n E_n \to \int d_k e^{-\alpha - \beta E} E_k = \frac{-d}{d\beta} N = \frac{3}{2}\frac{N}{\beta} = \frac{3}{2} NkT$

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

* Summary:

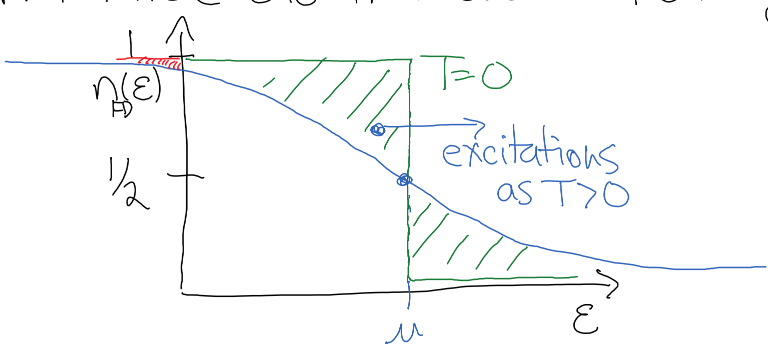
$n(\varepsilon) = \left[e^{(\mu-\varepsilon)/kT} + \begin{matrix} 1 & \text{Fermi-Dirac} \\ 0 & \text{Maxwell-Boltzmann} \\ -1 & \text{Bose-Einstein} \end{matrix}\right]^{-1}$

T : stretches distribution out in energy. $E = \sum_\varepsilon d_\varepsilon n_\varepsilon \cdot \varepsilon$

μ : shifts distribution left / right $N = \sum_\varepsilon d_\varepsilon n_\varepsilon$

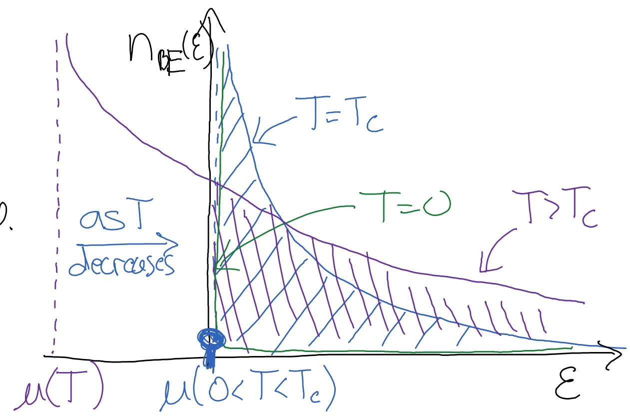
Note: for M-B distribution $e^{(\mu-\varepsilon)/kT} = e^{\mu/kT} e^{-\varepsilon/kT}$
acts like a normalization. if d_ε const.

- Fermi-Dirac distribution $\to$ Fermi gas as $T \to 0$



note shift in $\mu(\varepsilon)$ to accomodate lost states at $\varepsilon < 0$

- Bose-Einstein dist.



$\mu(T)<0$ at high temp. As $T\to 0$, exponential contracts, and μ increases to accomodate new particles. But $\mu<0$ so when $\mu(T_c)=0$, the maximum # of particles can fit in the distribution. The rest condense into the ground state. (A finite fraction of all particles) This is called the "Bose-Einstein Condensate".

examples: superfluid helium
ultra cold bosonic atoms

* Example: Blackbody Radiation

assumptions: a) $E=\hbar\omega$ b) $c=\frac{\omega}{k}$ c) $d_s=2$ left/right circ. pol

d) N is not conserved, but $\mu=0$ constant instead

then $d_k=\frac{2V}{2\pi^2}k^2dk=\frac{V}{\pi^2c^3}d\omega$ $dN_k=d_ke^{-\beta E}$

$\rho(\omega)=\frac{dN_kE_k}{Vd\omega}=\frac{\hbar\omega}{\pi^2c^3(e^{\hbar\omega/kT}-1)}$ as discussed last semester