L64-Thermal Equilibrium

Tuesday, February 23, 2016 08:18

* Summary: (redraw diagram of states)

- the probability of a configuration is proportional to $Q(N_1, N_2, N_3 \ldots)$,
  $Q(\ldots)$ = degeneracy of multiparticle states $\psi_{E_1E_2E_3}(\vec{r}_1, \vec{r}_2 \ldots \vec{r}_{\Sigma N_i})$
- it depends on how we build them from single-particle states $\psi_E(\vec{r})$ with degeneracy d_E
- in particular, depends on the exchange symmetry $P_{ij}\psi_{1234\ldots}(\vec{r}_1, \vec{r}_2 \ldots)$ or the "quantum statistics", which depends on the spin

* Goal: develop the probability of finding a single particle in the state $\psi_i(\vec{r})$ with energy E_i: the distribution $n(E) = e^{-E/kT}/Z$ (classical)

- this involves maximizing $Q(N_1, N_2, N_3 \ldots)$ w/r N_i, since this probability is sharply peaked for high N.

* Assumptions:

- large-N statistics: $\frac{\delta Q}{Q} \sim \frac{1}{\sqrt{N}} \xrightarrow{N \to N_A} 0$
  Sterling's approx: $\ln N! \approx N \ln N - N$ $\quad d \ln N! = \frac{dN!}{N!} = \ln N \, dN$
- principle of indifference - each microstate $\psi(\vec{r}_1, \vec{r}_2 \ldots)$ equally likely
  ergodicity (chaos): each particle cycles through all states
- conservation of particle number $N = \sum_n N_n$ (no creation/annihilation)
  this isn't true for photons, positrons, ...
- conservation of energy $E = \sum_n N_n E_n$ (pretty safe!)

* Maximization of Q with constraints on N, E: Lagrange Multipliers

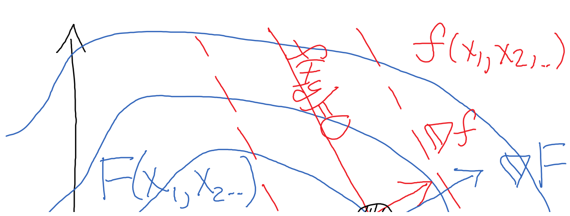
- goal: maximize $F(x_1, x_2, \ldots)$, keeping $f_1(x_1, x_2, \ldots) = f_2(x_1, x_2, \ldots) = 0$

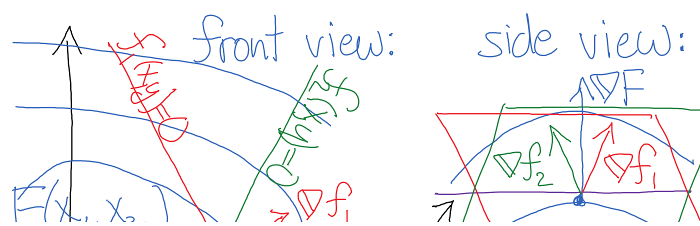
- with only one constraint, the normals are parallel at the common tangent.

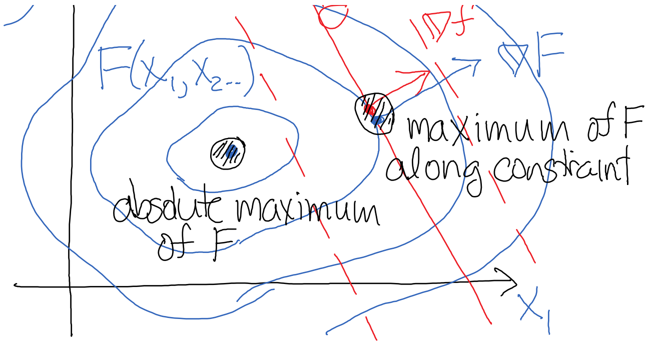
  ie. $\nabla F = \lambda \nabla f$

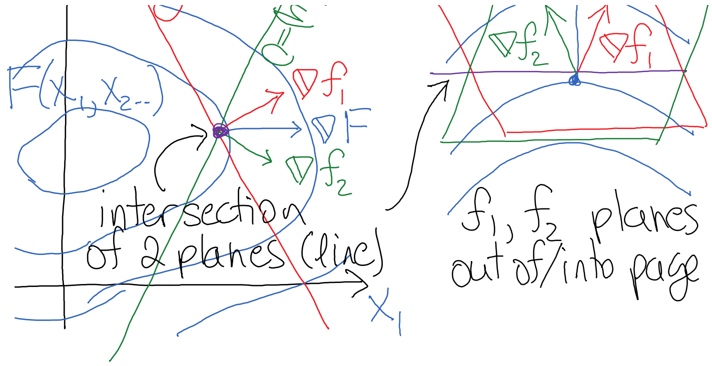
- with two constraints, the normal of F lies in the common plane of f_1, f_2 normals

  $\nabla F = \lambda_1 \nabla f_1 + \lambda_2 \nabla f_2$









let $G(x_1, x_2, \dots, \lambda_1, \lambda_2) = F - \lambda_1 f_1 - \lambda_2 f_2$ then $\frac{\partial G}{\partial x_i} = 0$, $\frac{\partial G}{\partial \lambda_i} = 0$ (constraints)

- application: max. entropy, (N, E) conserved.

$$S = k\Big[G = \underbrace{\overbrace{\ln(Q)}^{F(N_1,N_2,\dots)}}_{\#\text{ microstates}} + \overbrace{\alpha}^{\lambda_1}\big(\underbrace{\overbrace{N - \Sigma N_n}^{f_1=0}}_{\#\text{particles}}\big) + \overbrace{\beta}^{\lambda_2}\big(\underbrace{\overbrace{E - \Sigma N_n E_n}^{f_2=0}}_{\text{total Energy}}\big)\Big]$$

* Derivation of statistical distributions:

1) Classical Maxwell-Boltzman distribution $n_{MB}(E)$

$$Q(N_1, N_2 ..) = \binom{N}{N_1\, N_2 \dots} \prod_n d_n^{N_n} = N! \prod_n \frac{d_n^{N_n}}{N_n!}$$

[sort N into bins of N_n counts with degeneracy d_n]

$$G = \Big[\ln(N!) + \sum_n N_n \ln d_n - \ln N_n!\Big] - \sum_n(\alpha N_n + \beta N_n E_n) + \alpha N + \beta E$$

$$\partial_{N_n} G = \ln d_n - \ln N_n - \alpha - \beta E_n = 0$$

$$N_n = d_n e^{-\alpha - \beta E_n} \quad \text{(M.-B.)} \rightarrow \boxed{n_{MB}(\overbrace{\varepsilon}^{E_n}) = \big[e^{\overbrace{(\varepsilon - \mu)}^{\alpha}/\underbrace{kT}_{\beta}}\big]^{-1}}$$

(number per sublevel)

2) Fermi-Dirac distribution

$$Q(N_1, N_2 \dots) = \prod_n \binom{d_n}{N_n} = \prod_n \frac{d_n!}{N_n!\,(d_n - N_n)!}$$

[in each bin n, sort d_n into N_n occupied levels, $d_n - N_n$ empty.]

$$G = \Big[\sum_n \ln(d!) - \ln(N_n!) - \ln((d_n - N_n)!)\Big] - \sum_n(\alpha N_n + \beta N_n E_n) + \alpha N + \beta E$$

$$\partial_{N_n} G = -\ln N_n + \ln(d_n - N_n) - \alpha - \beta E_n = 0$$

$$N_n = d_n\left(e^{\alpha + \beta E} + 1\right)^{-1} \qquad \boxed{n_{FD}(\varepsilon) = \left[e^{(\varepsilon - \mu)/kT} + 1\right]^{-1}}$$

3) Bose-Einstein distribution

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$$Q(N_1, N_2 \ldots) = \prod_n \binom{N_n + d_n - 1}{d_n - 1} = \prod_n \frac{(N_n + d_n - 1)!}{N_n! \, (d_n - 1)!}$$

in each bin n, sort $N_n + d_n - 1$ symbols into $d_n - 1$ partitions dividing up N_n particles.

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

$$\partial_{N_n} G = \ln(N_n + d_n - 1) - \ln N_n - \alpha - \beta E_n = 0$$

$$N_n = \underbrace{d_n}_{\sim d_n - 1} \left(e^{\alpha + \beta E} - 1\right)^{-1}$$

$$\boxed{n_{BE}(\varepsilon) = \left[e^{(\varepsilon - \mu)/kT} - 1\right]^{-1}}$$

* meaning of Lagrange multipliers α, β
  - used to satisfy the constraints:

$\beta = \frac{1}{kT}$: Temperature "T" spreads out excitations into spectrum to obtain average energy $\varepsilon N = E = \sum_i N_i E_i$

$\alpha = \frac{\mu}{kT}$: Chemical Potential "μ" normalizes distribution to obtain correct # of particles $N = \sum N_i$ $\int d\varepsilon \; d(\varepsilon) n(\varepsilon) = 1$