L63-Thermal Equilibrium

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* Summary: (redraw diagram of states)

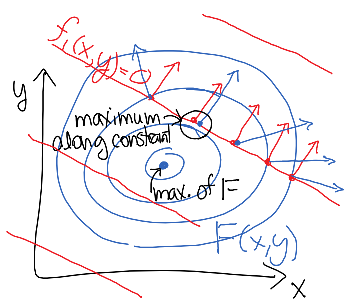
- the probability of a configuration $P(N_1, N_2, N_3 \ldots) \propto Q(N_1, N_2, N_3 \ldots)$,
  $Q(\ldots) =$ degeneracy of multiparticle states $\psi_{E_1 E_2 E_3 \ldots}(\vec{r}_1, \vec{r}_2, \ldots \vec{r}_{\Sigma N_i})$
- depends on how we build them from single-particle states $\psi_E(\vec{r})$ 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 $Q(N_1, N_2, N_3 \ldots)$, since this probability is sharply peaked for high N.

* Assumptions:

- large-N statistics: $\frac{\delta Q}{Q} \sim \frac{1}{\sqrt{N}} \xrightarrow{N \to N_A} 0$ $\qquad N! = e^{\int_0^N dN \ln N}$
  Sterling's approx: $\ln N! \approx N \ln N - N \qquad d \ln N! = \frac{dN!}{N!} = \ln N \, dN$
- 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 $N = \Sigma N_i$ (no creation/annihilation)
  this isn't true for photons, positrons, ...
- conservation of energy $E = \Sigma N_i E_i$ (pretty safe!)



* Maximization: use Lagrange multipliers

- to maximize $F(x_1, x_2 \ldots) \ni f_1(x_1, x_2) = f_2(x_1, x_2) \ldots = 0$
  set $\frac{\partial G}{\partial x_i} = 0 \quad \frac{\partial G}{\partial \lambda_i} = 0$ where $G = F - \lambda_1 f_1 - \lambda_2 f_2 \ldots$
- let $G = \underbrace{\ln Q}_{\text{monotonic, easier to treat}} + \alpha(N - \Sigma N_i) + \beta(E - \Sigma N_i E_i)$

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

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

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

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

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

$$N_n = d_n e^{-\alpha-\beta E_n} \quad (\text{M.-B.}) \rightarrow \boxed{n_{MB}(\overset{E_n}{\varepsilon}) = \left[e^{\overset{\alpha}{(\varepsilon-\mu)}/\underset{\beta}{kT}}\right]^{-1}}$$

(single state, no d_ε)

2) Fermi-Dirac distribution

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

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

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

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

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

3) Bose-Einstein distribution

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

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

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

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

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

* 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 $\bar{\varepsilon} N = E = \sum_i N_i E_i$

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