Going from single particle to many-particle distribution functions

Assume non-interacting particles

Distinguishable particles $Q(N,V,T) = q^N$

Indistinguishable particles $Q(N,V,T) = \frac{q^N}{N!}$

Boltzmann statistics, holds approximately

Consider two distinguishable particles

$$Q = \sum_{i,j} e^{-\left(\varepsilon_i^a + \varepsilon_j^b\right)/kT} = \Sigma e^{-\varepsilon_i^a/kT} \Sigma e^{-\varepsilon_j^b/kT} = q^2$$

Now suppose the particles are indistinguishable

$$Q = \sum_{i,j} e^{-\left(\varepsilon_i + \varepsilon_j\right)/kT} \neq \Sigma e^{-\varepsilon_i/kT} \Sigma e^{-\varepsilon_j/kT} = q^2$$

The sum no longer factors

If fermions – two particles cannot be in the same level

If bosons, $\varepsilon_i + \varepsilon_j$, $\varepsilon_j + \varepsilon_i$ should not be counted separately

One can approximately fix this problem by ÷ by *N!*

$$Q = \frac{q^N}{N!} \longleftarrow$$

many-body problem reduced to a one-body problem

Boltzmann statistics

- assumes # states >> # particles
- ignores symmetry of wave function

valid at high *T* (classical limit)

$$E = N\bar{\varepsilon} = kT^2 \left(\frac{\partial \ell n Q}{\partial T}\right)_{N,V}$$

$$= kT^2 \left[N \frac{\partial q / \partial T}{q} \right] = \frac{kT^2 N}{q} \frac{\sum \varepsilon_i e^{-\varepsilon_i / kT}}{kT^2}$$

$$= N \frac{\Sigma \varepsilon_i e^{-\varepsilon_i / kT}}{q}$$

$$Q = q^N / N!$$

$$\ell n Q = N \ell n q - \ell n N!$$

$$= N \ell n q - N \ell n N + N$$

Fermi-Dirac and Bose-Einstein Statistics

fermions – no two can be in the same state
bosons – two or more can be in the same state

$n_k(E_j)$= # molecules in k[th] molecular level with total energy E_j

$$E_j = \sum \varepsilon_K n_K, \quad N = \sum n_K$$

$$Q(N,V,T) = \sum e^{-\beta E_j} = \sum_{\{n_K\}}{}^{*} e^{-\beta \sum_i \varepsilon_i n_i}$$

$$* \Rightarrow \sum n_K = N$$

Different spin combinations are treated as different states

It is very difficult to simplify this.
The problem is simpler in the grand canonical ensemble

$$\Xi(V,T,\mu) = \sum_{n=0}^{\infty} e^{\beta\mu N} Q(N,V,T)$$

$$\lambda = e^{\beta\mu}$$

$$= \sum_{N=0}^{\infty} \lambda^N \sum_{\{n_K\}}{}^{*} e^{-\beta\Sigma_i \varepsilon_i n_i}$$

$$= \sum_{N=0}^{\infty} \sum_{\{n_K\}}{}^{*} \lambda^{\sum n_i} e^{-\beta\Sigma_j \varepsilon_j n_j}$$

$$= \sum_{N=0}^{\infty} \sum_{\{n_K\}}{}^{*} \prod_k \left(\lambda e^{-\beta\varepsilon_k}\right)^{n_k}$$

The last step is possible because we are summing over all N

$$= \sum_{n_1=0}^{n_1^{\max}} \sum_{n_2=0}^{n_2^{\max}} \cdots \prod_k \left(\lambda e^{-b\varepsilon_k} \right)^{n_k}$$

$$= \sum_{n_1=0}^{n_1^{\max}} \left(\lambda e^{-b\varepsilon_1} \right)^{n_1} \sum_{n_2=0}^{n_2^{\max}} \left(\lambda e^{-b\varepsilon_2} \right)^{n_2} \cdots$$

$$= \prod_k \sum_{n_k=0}^{n_k^{\max}} \left(\lambda e^{-b\varepsilon_k} \right)^{n_k}$$

fermi-dirac

$$n_k = 0 \text{ or } 1$$

$$\Xi_{FD} = \prod_k \left(1 + \lambda e^{-b\varepsilon_k} \right)$$

Bose-Einstein

$$n_k = 0, 1, 2, \ldots \infty$$

$$\Xi_{BE} = \prod_k \sum_{n_k=0}^{\infty} \left(\lambda e^{-\beta\varepsilon_k}\right)^{n_k} = \prod_k \left(1 - \lambda e^{-\beta\varepsilon_k}\right)^{-1}, \quad \lambda e^{-\beta\varepsilon_k} < 1$$

Fermi-dirac

$$\bar{N} = N = \sum \overline{n_k} = kT\left(\frac{\partial \ell n \Xi}{\partial \mu}\right)_{V,T} = \lambda\left(\frac{\partial \ell n \Xi}{\partial \lambda}\right)_{V,T}$$

$$= \sum_k \frac{\lambda e^{-\beta\varepsilon_k}}{1 \pm \lambda e^{-\beta\varepsilon_k}}$$

+ $\Rightarrow$ FD
- $\Rightarrow$ BE

$$E = N\bar{\varepsilon} = \sum_k \frac{\lambda \varepsilon_k e^{-\beta\varepsilon_k}}{1 \pm \lambda e^{-\beta\varepsilon_k}}$$

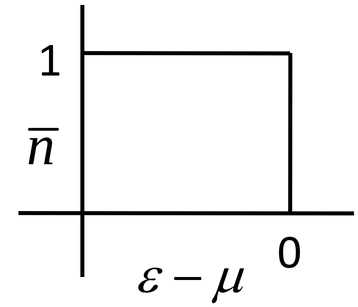
$$\bar{n}_k = \frac{\lambda e^{-\beta\varepsilon_k}}{1 \pm \lambda e^{-\beta\varepsilon_k}}$$

$$pV = \pm kT \sum_k \ell n\left[1 \pm \lambda e^{-\beta\varepsilon_k}\right]$$

With FD or BE statistics *q* is no longer the key quantity.

Fermi-dirac

$$\overline{n}_k = \frac{\lambda e^{-\beta\varepsilon_k}}{1+\lambda e^{-\beta\varepsilon_k}} = \frac{e^{-\beta(\varepsilon_k-\mu)}}{1+e^{-\beta(\varepsilon_k-\mu)}} \text{ as } T \to 0 \quad \begin{cases} \to 0 \text{ if } \varepsilon_k > \mu \\ \to 1 \text{ if } \varepsilon_k < \mu \end{cases}$$



at finite *T* the populations are smeared out

Expect classical limit as $\lambda \to 0$

$$\overline{n_k} \to 0 \quad \Rightarrow \quad \lambda \to 0$$

small λ: $\overline{n_k} = \lambda e^{-\beta\varepsilon_k}$

As $N/V \to 0$ or $T \to \infty$

In these limits # quantum states >> # of particles

$$\lambda = \frac{\sum \overline{n}_k}{\sum e^{-\beta\varepsilon_k}} = \frac{N}{q}$$

Sum both sides over *k* and solve for λ

$$\frac{\overline{n_k}}{N} = \frac{e^{-\beta\varepsilon_k}}{q}, \qquad \mathrm{q} = \sum_j e^{-\beta\varepsilon_j}$$

for small λ we also have

$$pV = kT\lambda\sum_k e^{-\beta\varepsilon_k} = kT\lambda q$$

$$\beta pV = \lambda\sum e^{-\beta\varepsilon_k} = \lambda q$$

$$\beta pV = \ell n\Xi$$

Shown previously for the GCE

$$\Xi = e^{\lambda q} = \sum\frac{(\lambda q)^N}{N!} = \sum Q\lambda^N$$

$$\Rightarrow Q = \frac{q^N}{N!}$$

Boltzmann statistics

McQuarrie – Chapter 5: Ideal Gas of Atoms

electronic partition function – open shall systems
have to be treated carefully

$$O\left(1s^2 2s^2 2p^4\right) \quad {}^3P_2\left(2J+1=5\right) \quad 0$$
$$ {}^3P_1\left(2J+1=3\right) \quad 158\,cm^{-1}$$
$$ {}^3P_0\left(2J+1=1\right) \quad 226\,cm^{-1}$$

keep in mind *kT* (room temp) ~200 cm^{-1}

Also there is the possibility of excited nuclear levels (such states are separated by millions of eV – so can ignore.

There is a nuclear degeneracy term. Doesn't change in chemical reactions – so does not impact *ΔE* or *ΔS.*

$$Q = \frac{(q_{e1})^N q_{tr}^N}{N!}$$

Partition function for ideal gas of atoms

$$q_{tr} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V = \frac{V}{\Lambda^3},$$

$$q_{el} = \omega_1 + \omega_2 e^{-\beta\Delta\varepsilon_{12}} + \ldots$$

$$A = -kT\,\ell nQ = -NkT\,\ell n\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \frac{Ve}{N}\right] \boxed{-NkT\,\ell n\left[\omega_{e1} + \omega_{e2} e^{-\beta\Delta\varepsilon_{12}} + \ldots\right]}$$

Small-----

$$E = kT^2\left(\frac{\partial \ell nQ}{\partial T}\right)_{N,V} = \underbrace{\frac{3}{2}NkT}_{\text{transl}} + \boxed{\frac{N\omega_{e2}\Delta\varepsilon_{12}e^{-\beta\varepsilon_{12}}}{q_{el}} + \ldots}$$

small

$$\mu(T,P) = -kT\left(\frac{\partial \ell nQ}{\partial N}\right)_{T,V} = -kT\ln\frac{q}{N}$$

$$= -kT\,\ell n\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2} kT\right] - kT\,\ell n q_e q_n + kT\ln P$$

$$= \mu_o(T) + kT\ln P$$