Statistical Mechanics

Distribution Functions

For f(*something*) that describes the distribution of a particle quantity over something (like the number of particles distributed over energy or location over a span of space), then

f(*something*) d*something* = Probability of finding a particle between *something* and *something* + d*something*

f(x) dx = Probability of finding a particle with a location between x and x + dx

f(E) dE = Probability of finding a particle with energy between E and E + dE

The expectation value of *something* described by this distribution is

$$\langle \textit{something} \rangle = \int_{-\infty}^{\infty} \textit{something}\ f(\textit{something})\ d\textit{something}$$

Energy Distributions of Particles

To describe how the energy is distributed among particles in large collections (gases, liquids and solids), physicists developed different energy distributions based on the types of particles

$$n(E)dE = g(E)F_{\text{smart guys}}$$

→ smart guy factor expressing behavior of particle type: classical, Fermion, or Boson

→ density of states (number of E < available energy states < E + dE

→ number of particles with E < energy < E + dE [n(E) = number/energy …number energy density]

Maxwell-Boltzmann Statistics: Classical Particles

Classical particles are distinguishable, only interact with each other through elastic collisions and are at a low enough density that the wave functions don't overlap.

The Maxwell-Boltzmann factor is

$$F_{MB} = Ae^{-\beta E} \qquad \text{TRex (9.27)}$$

Maxwell-Boltzmann Speed Distribution

The speed distribution of classical particles in a gas is

$$F(v)dv = 4\pi\left(\frac{\beta m}{2\pi}\right)^{3/2} v^2 e^{-\frac{1}{2}\beta m v^2} dv$$

which can be used to determine the root-mean-square speed

$$v_{rms}^2 = \langle v^2 \rangle = 4\pi\left(\frac{\beta m}{2\pi}\right)^{3/2} \int_0^{\infty} v^4 e^{-\frac{1}{2}\beta m v^2} dv = \frac{3kT}{m}$$

that is the average preferred by physicists because it gives the familiar mean kinetic energy

$$\left\langle \frac{1}{2} m v^2 \right\rangle = \frac{3}{2} kT$$

Over a small interval, an expectation value can be approximated by a product instead of an integral,

$$\langle v\rangle = \int_0^\infty vF(v)dv \approx F(v)\Big|_{v_{min}} \Delta v = 4\pi\left(\frac{\beta m}{2\pi}\right)^{3/2} v^3 e^{-\frac{1}{2}\beta m v^2}\Big|_{v_{min}} \Delta v$$

Maxwell-Boltzmann Energy Density

For an ideal gas, the density of states is the same as the number of particles, N, since a particle can have any energy, thus the number of particles with an energy between E and E + dE is

$$n_{MB}(E)dE = \frac{8\pi N}{\sqrt{2}}\left(\frac{\beta}{2\pi}\right)^{3/2} E^{1/2}e^{-\beta E}dE \qquad \text{After TRex (9.26)}$$

so the fraction of particles with energies bewteen E and E + dE is this divided by N. The expectation value of the energy is thus

$$\langle E\rangle = \frac{8\pi}{\sqrt{2}}\left(\frac{\beta}{2\pi}\right)^{3/2}\int_0^\infty E^{3/2}e^{-\beta E}dE = \frac{3}{2}kT$$

Classical vs. Quantum Statistics

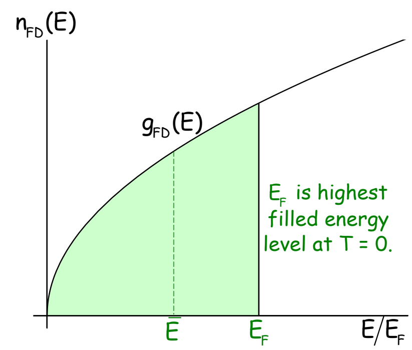
Quantum statistics must be used if the particles are dense enough that their wave functions overlap. For N particles in a volume, V at temperature T, with a de Broglie wavelength, $\lambda = h/p$, gives the criterion for using classical statistics:

$$\left(\frac{N}{V}\right)\frac{h^3}{(3mkT)^{3/2}} \ll 1 \qquad \text{TRex p.336}$$

Fermi-Dirac Statistics: Fermion Quantum Particles

Fermions have ½-integer spins and obey the Pauli Exclusion Principal stating that only one can occupy any quantum state. The density of states for a Fermion gas is

$$g_{FD}(E) = \frac{3N}{2}E_F^{-3/2}E^{1/2} \qquad \text{TRex (9.43)}$$



where the Fermi Energy, E_F is the highest occupied state at T = 0 and is given by

$$E_F = \frac{h^2}{8m}\left(\frac{3}{\pi}\frac{N}{L^3}\right)^{2/3} \qquad \text{TRex (9.42)}$$

The Fermi temperature and velocity are then

$$T_F = \frac{E_F}{k} \qquad v_F = \sqrt{\frac{2E_F}{m}} = \frac{h}{2m}\left(\frac{3}{\pi}\frac{N}{L^3}\right)^{1/3}$$

Fermi-Dirac Factor

The probability that a given state will be occupied is given by F_{FD}:

$$F_{FD} = \frac{1}{e^{(E-E_F/kT)}+1} \qquad \text{TRex (9.34)}$$

Which is equal to 1 for $E < E_F$ and zero for $E > E_F$. Since $F_{FD}(T = 393K)$ is only slightly different from $F_{FD}(T = 0) = 1$, we can work as though room temperature is equal to zero.

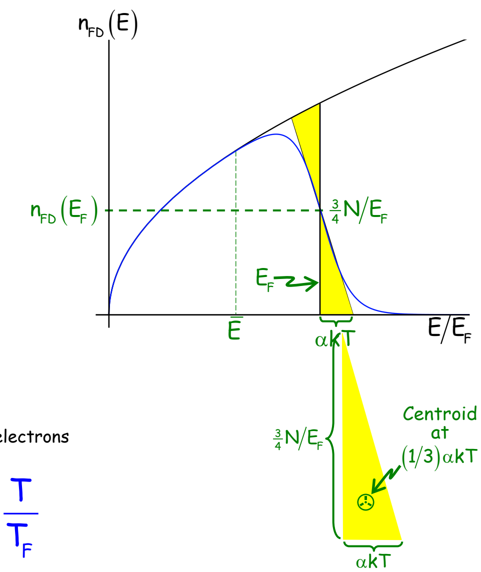
Fermi-Dirac Energy Density

For metals such as Silver, with 5.86 x 10^{28} conduction electrons per meter, the Fermi Energy is quite large, 5.503 eV (8.82 x 10^{-19} J) which gives a Fermi Temperature of, $kT_F = E_F \Rightarrow T_{F,\,Silver} = 63{,}750K$. Since room temperature is so much smaller than this, we can consider that we work at T = 0. Thus,

$$n_{FD}(E)dE = \frac{3N}{2}E_F^{-3/2}E^{1/2}dE \text{ at } T = 0 \qquad \text{TRex (9.44)}$$

Fermi-Dirac Electron Energies

In a metal, the Fermion gas is made up of the valence electrons with an average energy of $\bar{E}$ given by



$$\bar{E} = \frac{1}{N}\int_0^\infty En(E)dE = \frac{1}{N}\int_0^\infty Eg(E)F_{FD}dE$$

Since $n_{FD}(E > E_F) = 0$ and $n_{FD}(E < E_F)$ is given by TRex (9.44), this becomes

$$\bar{E}_{T=0} = \frac{1}{N}\left(\frac{3N}{2}\right)\int_0^{E_F} E_F^{-3/2}E^{3/2}dE = \frac{3}{5}E_F$$

From thermal energy, $n_{excited}$ electrons will absorb $\Delta E_{excoted}$

$$n_{excited} = \frac{3}{8}N\frac{\alpha kT}{E_F} \qquad \Delta E = \frac{2}{3}\alpha kT$$

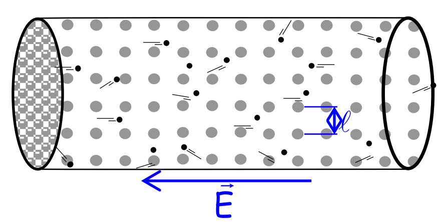
Increasing the internal energy of the conductor to $U_{excited}$ giving $C_{V,\,electrons}$

$$U_{excited} = n_{excited}\Delta E_{excited} = \frac{1}{4}\frac{N(\alpha kT)^2}{E_F}, \text{ and } C_{V,mole} = \frac{\pi^2}{2}R\frac{T}{T_F}$$

Electrical Conductivity

Ohm's Law, expressed in terms of the current density (C/m^2) and electric field is

$$\vec{J} = \sigma\vec{E}$$



where σ is the electrical conductivity. In a conductor, this is modeled as a gas of electrons at high random velocities and a smaller "drift" velocity due to accelerating in response to the electric field.

In the classical Drude model, the electrons have a Maxwell-Boltzmann speed distribution and collide with every ion, giving a mean-free-path equal to the interatomic spacing, ℓ. This gives an electrical conductivetity that is 10 times too small and depended on the inverse square root of the temperature instead of the inverse temperature.

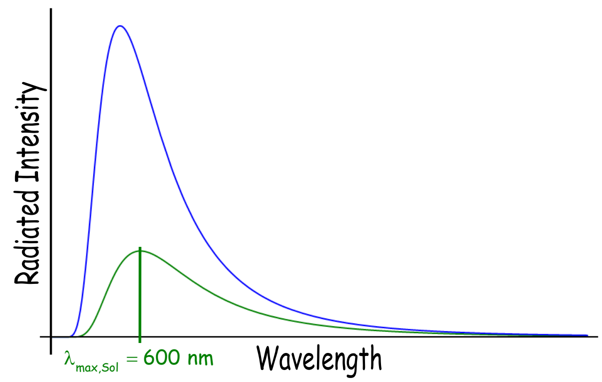
$$v_{rms,MB} = \sqrt{\frac{3kT}{m_e}} \qquad v_{drift} = a_E\tau = \left(\frac{eE}{m_e}\right)\left(\frac{\ell}{v_{MB}}\right)$$

$$j_{Drude} = nev_{drift} = ne(a_E\tau) = \left(\frac{ne^2\ell}{\sqrt{3m_ek}}T^{-1/2}\right)E$$

Einstein asserted that the electrons should move with the Fermi speed (above), that is about 10 times greater than the Maxwell-Boltzmann speed and not collide with every ion, but have a mean-free-path of 100 ℓ. He included the dependence of the ion's cross sectional area dependence on the temperatue to give the dependence on the inverse of the temperature. This gave a value of $\sigma_{Einstein}$ 10 times greater than σ_{Drude} and about equal to measured values.

Bose-Einstein Statistics: Boson Quantum Particles

Bosons have zero or integer spins and do not obey the Pauli Exclusion Principal, thus any number can occupy a given quantum state. It was developed by Bose to put Planck's blackbody radiation equation on statistical footing. Other descriptions of the law were described by Wien, Stefan and Boltzmann.



Wien Displacement Law

Describes how the wavelength of the maximum emission depends on temperature,

$$\lambda_{max}T = 2.898\times10^{-3}\text{mK} \qquad \text{TRex (3.14)}$$

Stefan-Boltzmann Law

Describes how the radiated flux through the surface of a blackbody depends on the temperature,

$$R(T) = \epsilon\sigma T^4 \qquad \text{TRex (3.16)}$$

where ε is the emissivity, the fraction of energy going into radiation, and the Stefan-Boltzmann constant is $\sigma = 5.67 \times 10^{-8}$ W/(m^{2}K^4).

Bose-Einstein Energy Density

The Bose-Einstein factor does not have a normalization constant since some Bosons (e.g. photons and phonons) can come in and out of existence spontaneously, thus it is

$$F_{BE} = \frac{1}{e^{E/kT}-1}$$

The density of states found by determining the number of energy states in a cube of side L where waves must have nodes at the boundaries is

$$g_{BE}(E) = \frac{8\pi L^3}{(hc)^3}E^2 \qquad \text{TRex (9.53)}$$

Thus, the energy density is

$$n_{BE}(E)dE = \frac{8\pi L^3}{(hc)^3}\frac{E^2}{e^{E/kT}-1} \qquad \text{TRex (9.53)}$$

But, to explain the Planck curve, we need the energy density distribution, the energy density per volume

$$u_{BE}(E)dE = \frac{8\pi}{(hc)^3}\frac{E^2}{e^{E/kT}-1}$$

Converting this to an expression in wavelength using E = hc/λ gives

$$u_{BE}(\lambda)d\lambda = \frac{8\pi hc}{\lambda^5}\frac{1}{e^{E/kT}-1}$$

The radiative energy is thus found to be Planck's Radiation Law

$$\vartheta(\lambda,T) = \frac{8\pi hc}{\lambda^5}\frac{1}{e^{E/kT}-1} \qquad \text{TRex (9.57)}$$