3-D system : density of states in k-space is

$$g(k)\,\delta k = \frac{\overset{V}{a^3}}{(2\pi)^3}\, 4\pi k^2\, \delta k \qquad (\times 2 \text{ for spin})$$

Often we want $g(\varepsilon)\delta\varepsilon$ rather than $g(k)\delta k$, we can calculate this using the dispersion relation

$$\boxed{\varepsilon = \frac{\hbar^2 k^2}{2m}.}$$

Do a substitution: $k = \left(\dfrac{2m\varepsilon}{\hbar^2}\right)^{1/2} \Rightarrow \dfrac{dk}{d\varepsilon} = \tfrac{1}{2}\left(\dfrac{2m\varepsilon}{\hbar^2}\right)^{-1/2} \cdot \dfrac{2m}{\hbar^2}$

$$\Rightarrow dk = \frac{m}{\hbar^2 k}\, d\varepsilon.$$

giving $g(\varepsilon)\,d\varepsilon = \overset{V}{a^3}\,\dfrac{2\pi}{\hbar^3}\,(2m)^{3/2}\,\varepsilon^{1/2}\,d\varepsilon.$

Thermal Averages - The Maxwell Boltzmann Limit.

Let's have a single particle quantity, Q, that takes the value Q_i when a particle is in energy state ε_i. We know a system containing a large number of particles is described by the most probable distribution (thermal equilibrium). e.g. N particles with n_1 in ε_1, n_2 in ε_2, etc.

Then the average of Q is (per particle):

$$\langle Q \rangle = \frac{1}{N} \sum_{i=1}^{\text{states}} n_i Q_i \qquad (i \text{ indexes states})$$

Let ε_i have degeneracy g_i so that $n_i = f_i g_i$ then:

e.g. lets say we have energy states :

Energy → degeneracy

$\varepsilon_1 \to g_1$

$\varepsilon_2 \to g_2$

$\varepsilon_3 \to g_3$

$\vdots$

Sum is $\sum_{i}^{\text{energy states}} Q_i \overbrace{f_i g_i}^{n_i}$

$$\underbrace{\overbrace{\varepsilon_1 \quad \varepsilon_1 \quad \varepsilon_1}^{n_1}}_{g_1 = 3} \quad \underbrace{\overbrace{\varepsilon_2 \quad \varepsilon_2}^{n_2}}_{g_2 = 2} \quad \underbrace{\overbrace{\varepsilon_3}^{n_3}}_{g_3 = 1} \quad \underbrace{\overbrace{\varepsilon_4 \quad \varepsilon_4 \quad \varepsilon_4}^{n_4}}_{g_4 = 3} \quad \cdots$$

$$\begin{array}{llll} 1\; n_1 \varepsilon_1 & +\, 4\; n_2 \varepsilon_2 & +\, 6\; n_3 \varepsilon_3 & +\, 7\; n_4 \varepsilon_4 \quad + \cdots \\ +\, 2\; n_1 \varepsilon_1 & +\, 5\; n_2 \varepsilon_2 & & +\, 8\; n_4 \varepsilon_4 \\ +\, 3\; n_1 \varepsilon_1 & & & +\, 9\; n_4 \varepsilon_4 \end{array}$$

$$\Rightarrow \sum_{i} n_i \varepsilon_i$$

sum over single particle states.

Average for Q is $\langle Q \rangle = \frac{1}{N}\sum_i n_i Q_i$ (i labels states).

we also have $f_i = \frac{N}{Z} e^{-\beta \varepsilon_i}$ and partition function $Z = \sum_i g_i e^{-\beta \varepsilon_i}$

energy levels

Hence $\langle Q \rangle = \sum_i \frac{f_i g_i Q_i}{N} = \sum_i \frac{g_i e^{-\beta \varepsilon_i} Q_i}{Z}$

{energy levels}

$$= \frac{\sum_i g_i e^{-\beta \varepsilon_i} Q_i}{\sum_i g_i e^{-\beta \varepsilon_i}}$$

Energy levels of bulk systems become continuous so sums become integrals.

i.e. $\varepsilon_i \to \varepsilon$

$g_i \to g(\varepsilon)\,\delta\varepsilon$ and $\dfrac{n_i}{g_i} \to f(\varepsilon) = \dfrac{\delta n}{g(\varepsilon)\,\delta\varepsilon}$.

so
$$\langle Q \rangle = \frac{\int_0^\infty g(\varepsilon)\, e^{-\beta\varepsilon}\, Q(\varepsilon)\, d\varepsilon}{\int_0^\infty g(\varepsilon)\, e^{-\beta\varepsilon}\, d\varepsilon}.$$

Similarly in k-space we have

dispersion relation

$$\langle Q \rangle = \frac{\int_0^\infty g(k)\, e^{-\beta\varepsilon(k)}\, Q(k)\, dk}{\int_0^\infty g(k)\, e^{-\beta\varepsilon(k)}\, dk}.$$

Particles in the 3D square well had

$$g(\varepsilon) \propto \varepsilon^{1/2}$$
$$g(k) \propto k^2$$

$$\langle Q \rangle = \frac{\int_0^\infty \varepsilon^{1/2} e^{-\beta\varepsilon} Q(\varepsilon)\, d\varepsilon}{\int_0^\infty \varepsilon^{1/2} e^{-\beta\varepsilon}\, d\varepsilon} = \frac{\int_0^\infty k^2 e^{-\beta \varepsilon(k)} Q(k)\, dk.}{\int_0^\infty k^2 e^{-\beta\varepsilon(k)}\, dk.}$$

Examine the monoatomic gas where $f_i \ll 1$. We also have

$$g(k)\,\delta k = \frac{V}{(2\pi)^3} 4\pi k^2 \,\delta k$$

and we also know $f_i = n_i / g_i = e^{-\alpha} e^{-\beta\varepsilon_i}$

If $f_i \ll 1$ we have that

$$e^{-\alpha} e^{-\beta \varepsilon_i} \ll 1 \text{ for all } \varepsilon_i.$$

As this must ~~xxxx~~ be true for all ε_i, e.g. $\varepsilon_0 = 0$ so it must be that $e^{-\alpha} \ll 1$. The partition function is

$$Z = \underbrace{\sum_i}_{\text{single particle states}} e^{-\beta \varepsilon_i} = \underbrace{\sum_i}_{\text{sum over energy states.}} g_i e^{-\beta \varepsilon_i}$$

There are $g(k)\delta k$ single particle states between k and $k + \delta k$

" " $g(\varepsilon)\delta\varepsilon$ " " " " ε and $\varepsilon + \delta\varepsilon$

$$\Rightarrow \quad Z = \int_0^\infty g(\varepsilon) e^{-\beta\varepsilon} \, d\varepsilon$$

or equivalently

$$Z = \int_0^\infty g(k)\, e^{-\beta \varepsilon(k)}\, dk = \frac{V}{(2\pi)^3} 4\pi \int_0^\infty k^2 e^{-\beta\left(\frac{\hbar^2 k^2}{2m}\right)} dk$$

note that $\int_0^\infty x^2 e^{-\lambda x^2} dx = \frac{1}{4}\sqrt{\pi/\lambda^3}$. Use this to evaluate integral:

$$Z = V\left(\frac{2\pi M}{\beta h^2}\right)^{3/2} = V/\lambda_D^3 \text{ , defining } \lambda_D = h\sqrt{\beta/2\pi M}$$

or in terms of temperature $\boxed{\lambda_D(T) = \frac{h}{\sqrt{2\pi M k_B T}}}$.

Z does not have units hence λ_D has units of distance. It is called the "thermal de Broglie wavelength".

λ_D is a measure that allows us to determine whether or not a system can be considered classical or quantum. If λ_D is comparible to inter-particle spacing then a quantum description is required, but if $\boxed{\lambda_D}$ is much smaller then inter-particle spacing then they can be considered to be in the dilute limit.

e.g. ^4He, 5K, we get $\lambda_D \sim 0.1$ (Classical).

Note that dilute gas limit $V/N \gg \lambda_D^3$ since $V/\lambda_D^3 = Z$:

Example: Maxwell - Boltzmann speed distribution.

What is the density of particles with speeds lying between v and $v+dv$?

Note: $\hbar k = mv$ (non-relativistic)

$$\frac{\hbar^2 k^2}{2m} = \tfrac{1}{2} m v^2$$

Lets evaluate the average of some quantity Q:

$$\langle Q \rangle = \frac{\int_0^\infty v^2 e^{-\beta(\frac{1}{2}mv^2)} Q(v)\, dv}{\int_0^\infty v^2 e^{-\beta(\frac{1}{2}mv^2)}\, dv}$$

noting that $v^2 e^{-\beta(\frac{1}{2}mv^2)}$ is the Maxwell - Boltzmann distribution for speeds.

It gives the number of particles $v \to v + dv$.

i.e. $n(v)\,dv = g(v)\,dv\, e^{-\alpha} e^{-\beta \varepsilon(v)} = C v^2 e^{-\beta(\frac{1}{2} m v^2)} dv$

and then integrating gives $C = 4\pi N \left(\frac{\beta M}{2\pi}\right)^{3/2}$.

Most probable speed - the one for which $n(v)$ is a maximum.

$$\frac{dn}{dv} = C\, 2v\, e^{-\beta(\frac{1}{2} m v^2)} \left(1 - \frac{\beta m v^2}{2}\right) = 0$$

Rearrang for V_{max}: $\quad V_{max} = \sqrt{\frac{2}{\beta M}} \simeq 1.41 \cdot \frac{1}{\sqrt{\beta M}}$.