2.8 The classical and quantum mechanical phase volume

We investigate as an example the Hamiltonian of a free particle in s-dimensional space: (s is the number of degrees of freedom)

$$H = \sum_{j=1}^{s} \frac{p_j^2}{2m} \tag{2.50}$$

The classical phase volume, i.e. the classical partition function, is

$$\Phi_{cl}(\epsilon) = \int_{V_s} d^s q \int_{H \leq \epsilon} d^s p = V_s K_s(\sqrt{2m\epsilon}) = V_s \frac{\pi^{\frac{s}{2}}}{\left(\frac{s}{2}\right)!}(2m\epsilon)^{\frac{s}{2}} \quad . \tag{2.51}$$

In quantum mechanics we get for periodic boundary conditions the solution of the Schrödinger equation

$$\psi_k(q) = a \exp\left(i \sum_{j=1}^{s} k_j q_j\right) \quad , \tag{2.52}$$

with $k_j = \frac{2\pi n_j}{l}$, respectively $p_j = \hbar k_j = \frac{h n_j}{l}$, $n_j = 0, \pm 1, \pm 2, ...$
In an s-dimensional momentum space the Eigenvalues have a lattice distance of h/l.
The number of momentum Eigenvalues with $0 \leq \epsilon_k \leq \epsilon$ equals the number of Eigenvalues within the sphere $K_s(\sqrt{2m\epsilon})$. This number we can determine just by counting. As an approximation we substitute the counting by calculating the number of volume elements $\left(\frac{h}{l}\right)^s$ within the sphere $K_s(\sqrt{2m\epsilon})$:

$$\Phi_{qm}(\epsilon) = \frac{V_s}{h^s} K_s(\sqrt{2m\epsilon}) = \frac{V_s}{h^s} \frac{\pi^{\frac{s}{2}}}{\left(\frac{s}{2}\right)!}(2m\epsilon)^{\frac{s}{2}} \quad . \tag{2.53}$$

By comparison of Eq. (2.51) and Eq. (2.53) we find

$$\Phi_{qm}(\epsilon) = \frac{\Phi_{cl}(\epsilon)}{h^s} \quad . \tag{2.54}$$

For a many particle system we have to add some factors, since the quantum mechanical particles are not distinguishable

$$\Phi_{qm}(\epsilon, V_s, N) = \frac{\Phi_{cl}(\epsilon, V_s, N)}{N! h^{Ns}} \quad . \tag{2.55}$$

These approximations do not hold e.g. for free electrons in general! (Only e.g. for the conduction band electrons of a non degenerated semiconductor).
As an example we calculate the case $s = 3$.
First we define

$$v := \frac{V}{N} \; , \qquad \epsilon := \frac{E}{N} \; , \text{ and } \quad \lambda := \frac{h}{p} = \frac{h}{\sqrt{2m\epsilon}} \quad . \tag{2.56}$$

λ is the de Broglie wave length, λ^3 is the uncertainty of a particle in volume.
For $v \gg \lambda^3$ we are allowed to neglect the exact quantum mechanical character of the particles and use the above approximations.
Including real numbers for e.g. Helium gas ($N = 10^{20}$, $T = 300^o$K, $m = 4$, $m_p = 4 * 1.67 * 10^{-24} g$), we find

$$E = \frac{3}{2} NkT \approx \frac{1}{27} 10^{20} \text{eV} \; , \quad v = \frac{24 * 10^3}{6 * 10^{23}} \text{cm}^3 \; , \text{ and } \quad \lambda = \frac{h}{\sqrt{2m\frac{1}{27}}} = 2.3 * 10^{-9} \text{cm} \; , \text{ i.e. } \quad \frac{v}{\lambda^3} \approx \frac{1}{3} 10^7 \quad . \tag{2.57}$$

So for a classical gas under normal conditions the premise is fulfilled easily.