Statistical Physics: Workshop Problems 4

(1) (a) A particle in a 3D box: density of states in 3D, Schrödinger's equation is

$$\left[-\frac{1}{2}\frac{d^2}{dx^2}-\frac{1}{2}\frac{d^2}{dy^2}-\frac{1}{2}\frac{d^2}{dz^2}+v(x)+v(y)+v(z)\right]\Phi(x,y,z)=E\,\Phi(x,y,z).$$

This is a separable problem, so $\Phi_{\mathbf{k}}(x,y,z)=\psi_{k_x}(x)\,\psi_{k_y}(y)\,\psi_{k_z}(z)$ with

$$k_x=\frac{\pi}{a}n,\quad k_y=\frac{\pi}{a}m,\quad k_z=\frac{\pi}{a}l,\qquad n,m,l=1,2,\ldots$$

The discretisation in 3D k space is $(\pi/a)^3$, so the number $n(k)$ of independent solutions, $\Phi_{\mathbf{q}}$ with $0\le q\le k$ is:

$$n(k)=\frac{\text{Volume in first octant in 3D }\mathbf{q}\text{ space}}{(\pi/a)^3}=\frac{1}{8}\,\frac{4\pi k^3}{3}\,\frac{a^3}{\pi^3}=\frac{k^3V}{6\pi^2}$$

The number of independent solutions between $k\le q\le k+\delta k$ is

$$g(k)\,\delta k=\frac{\delta n(k)}{dk}\,\delta k=\frac{Vk^2}{2\pi^2}\,\delta k,$$

where, $V=a^3$. The result is valid for $V\,k^2\,\delta k\gg 1$.
To find the number of states in energy space we have

$$\epsilon=\frac{\hbar^2\,k^2}{2M}\;\Rightarrow\;d\epsilon=\frac{\hbar^2\,k\,dk}{M}\;\Rightarrow\;kd\epsilon=\frac{\hbar^2\,k^2\,dk}{M}\;\Rightarrow\;\frac{\sqrt{2M^3\epsilon}}{\hbar^3}\,d\epsilon=k^2\,dk$$

So,

$$g(\epsilon)d\epsilon=g(k)dk=2\pi V\frac{(2M)^{3/2}}{h^3}\sqrt{\epsilon}\,d\epsilon$$

The DOS increases with the square root of ϵ.

(b) A particle in a 2D box follows exactly the same process. A similar analysis as before $\Phi_{\mathbf{k}}(x,y)=\psi_{k_x}(x)\,\psi_{k_y}(y)$ with

$$k_x=\frac{\pi}{a}n,\quad k_y=\frac{\pi}{a}m,\qquad n,m=1,2,\ldots$$

The discretisation in 2D q space is $(\pi/a)^2$ and so he number $n(k)$ of independent solutions, $\Phi_{\mathbf{q}}$ with $0\le q\le k$ is:

$$n(k)=\frac{\text{Area in first quadrant in 2D }\mathbf{q}\text{ space}}{(\pi/a)^2}=\frac{1}{4}\pi k^2\,\frac{a^2}{\pi^2}=\frac{1}{4}\pi k^2\,\frac{A}{\pi^2}=\frac{Ak^2}{4\pi}$$

where $A=a^2$. So the number of states in k space with $k\le q\le k+\delta k$ is

$$g(k)\,\delta k=\frac{A\,k}{2\pi}\,\delta k,$$

and the result is valid for $A\,k\,\delta k\gg 1$.

The number of states in energy space is obtained as follows

$$\epsilon = \frac{\hbar^2\, k^2}{2M} \;\Rightarrow\; d\epsilon = \frac{\hbar^2\, k\, dk}{M} \;\Rightarrow\; k\, dk = \frac{M}{\hbar^2}\, d\epsilon$$

s,

$$g(\epsilon)d\epsilon = g(k)dk = 2\pi A\,\frac{M}{h^2}\, d\epsilon.$$

The DOS in energy is constant and does not increase with ϵ.

(2) (a) For classical particles the N-particle partition function is

$$Z_N = Z_1^N.$$

(b) The internal energy is

$$U = -\frac{\partial}{\partial \beta} \ln Z_N = \frac{3}{2}\, N k_B T.$$

The free energy is:

$$F = -k_B T \ln Z_N = -N k_B T \left[\ln V + \frac{3}{2} \ln \left(\frac{2\pi M}{\beta h^2} \right) \right].$$

The entropy is

$$S = \frac{(U-F)}{T} = \frac{3}{2}\, N k_B + N k_B \left[\ln V + \frac{3}{2} \ln \left(\frac{2\pi M}{\beta h^2} \right) \right].$$

(c) U is linear in N, so it is extensive. The free energy is not extensive since

$$F(2N, 2V) = -2 N k_B T \left[\ln(2V) + \frac{3}{2} \ln \left(\frac{2\pi M}{\beta h^2} \right) \right] \neq 2\, F(N, V).$$

The entropy is not extensive either, since $S = (U - F)/T$.

(d) The number of ways of arranging N objects is $N!$. So, one must divide the partition function by $N!$:

$$Z_N = \frac{Z_1^N}{N!}$$

Using the Striling approximation ($\ln N! \approx N \ln N - N$), the free energy becomes

$$F = -k_B T \ln[(Z_1)^N / N!] = -N k_B T \left[\ln \frac{V}{N} + 1 + \frac{3}{2} \ln \left(\frac{2\pi M}{\beta h^2} \right) \right],$$

and the entropy becomes

$$S = \frac{5}{2}\, N k_B + N k_B \left[\ln \frac{V}{N} + \frac{3}{2} \ln \left(\frac{2\pi M}{\beta h^2} \right) \right]$$

(e) (i) Because the expression for the entropy is extensive, there will be no change in entropy when we calculate the total entropy with and without the partition. This is what we expect, since there is no exchange of heat or work in this reversible process.

(ii) In the second case, before (subscript b) the removal of the partition, the total entropy is the sum of entropies

$$S_b = S_1 + S_2, \quad \text{with } S_{1,2} = \frac{5}{2}(N/2)k_B + (N/2)k_B \left[\ln \frac{V}{N} + \frac{3}{2} \ln \left(\frac{2\pi M_{1,2}}{\beta h^2} \right) \right].$$

The sum is

$$S_b = \frac{5}{2} N k_B + N k_B \left[\ln \frac{V}{N} + \frac{3}{2} \ln \left(\frac{2\pi}{\beta h^2} \right) \right] + \frac{3 N k_B}{4} \ln (M_1 \, M_2).$$

After (subscript a) the removal of the partition, the two gases do not interact; each gas has $N/2$ particles and occupies volume V instead of $V/2$. The entropy is the sum of entropies, which is

$$S_a = S_1 + S_2, \quad \text{with } S_{1,2} = \frac{5}{2}(N/2)k_B + (N/2)k_B \left[\ln \frac{2V}{N} + \frac{3}{2} \ln \left(\frac{2\pi M_{1,2}}{\beta h^2} \right) \right].$$

The sum is

$$S_a = \frac{5}{2} N k_B + N k_B \left[\ln \frac{2V}{N} + \frac{3}{2} \ln \left(\frac{2\pi}{\beta h^2} \right) \right] + \frac{3 N k_B}{4} \ln (M_1 \, M_2).$$

The difference is the entropy of mixing

$$\Delta S = S_a - S_b = N k_B \ln 2.$$

The two gases cannot be separated without doing work in the system equal at least to $T \Delta S$.

(3) (a) The same as in problem (1) but multiplied by 2 for spin.

(b) The Fermi energy is calculated from the constraint that the number of particles is N. In 3D (with factor of 2) we have

$$n(k) = 2 \times \frac{V k^3}{6\pi^2} \;\Rightarrow N = n(k_F) = \frac{V k_F^3}{3\pi^2} \Rightarrow k_F = \left(3\pi^2 \frac{N}{V} \right)^{1/3}$$

$$\epsilon_F = \mu_0 = \frac{\hbar^2 k_F^2}{2M} = \frac{\hbar^2}{2M} \left(3\pi^2 \frac{N}{V} \right)^{2/3}$$

Similarly in 2D,

$$n(k) = 2 \times \frac{A k^2}{4\pi} \;\Rightarrow N = n(k_F) = \frac{A k_F^2}{2\pi} \Rightarrow k_F^2 = 2\pi \frac{N}{A}$$

$$\epsilon_F = \mu_0 = \frac{\hbar^2 k_F^2}{2M} = \frac{\hbar^2 \pi}{M} \frac{N}{A} = \frac{h^2}{4\pi M} \frac{N}{A}.$$