Statistical Physics: Workshop Problems 6

(1) (a) Maxwell-Boltzmann is for localised, distinguishable particles occupying single particle states, and there is no limit on the number of particles in a state. With α constraining particle number and $\beta = 1/k_B T$ the average number of particles per state with energy ϵ_j and degeneracy g_j is

$$\frac{n_j}{g_j} = \frac{1}{e^{\alpha} e^{\beta\epsilon_j}}.$$

Fermi-Dirac is for a system made of Fermions which are indistinguishable and, following the Pauli exclusion principle, can only have one particle per state. The average number of particles per energy state is

$$\frac{n_j}{g_j} = \frac{1}{e^{\alpha} e^{\beta\epsilon_j} + 1}.$$

Bose-Einstein statistics is for a system made of Bosons which are indistinguishable and are not limited in the number of particles that can be in a state. The average number of particles per energy state is

$$\frac{n_j}{g_j} = \frac{1}{e^{\alpha} e^{\beta\epsilon_j} - 1}.$$

(b) From the average number of particles per state it can be seen that when $e^{\alpha} \gg 1$ the difference between the statistics becomes unimportant. In lectures we saw that this can be determined by the thermal de Broglie wavelength

$$\begin{aligned} \lambda_D &= \sqrt{\frac{\beta h^2}{2\pi M}} \\ &= \sqrt{\frac{h^2}{2\pi M k_B T}}. \end{aligned}$$

A small λ_D (relative to volume) indicates we are in the classical regime, so note that as T increases then λ_D decreases, i.e. the three statistics become the same at high T.

We an understand this from a physical point of view; when $e^{\alpha} \gg 1$ the fraction of states filled is very small. This means that the number of microstates available must be very large, much larger than the total number of particles. Therefore the probability of two particles trying to be in the same state is very small so quantum effects such as Pauli exclusion is satisfied "without trying".

(c) If there are 10^{18} neutrons per cubic centimeter this means they are separated by, on average, 10^{-6}cm$= 10^{-8}$m. Set λ_D to this gives a temperature $T \approx 0.03$K. So temperatures around/below this will require Fermi-Dirac statistics, and for temperatures significantly above this the Fermions can be considered classical.

(2) (a) The partition function for the atom is

$$Z = e^{-\beta\epsilon} + e^{\beta\epsilon},$$

so the mean energy per atom is

$$\begin{aligned} U &= -\frac{\delta \ln Z}{\delta \beta} \\ &= \epsilon \frac{e^{-\beta\epsilon} - e^{\beta\epsilon}}{e^{-\beta\epsilon} + e^{\beta\epsilon}} \\ &= \epsilon \tanh\left(\frac{\epsilon}{k_B T}\right). \end{aligned}$$

The contribution of one atom to the specific heat is

$$C_V^1 = \left.\frac{\delta U}{\delta T}\right|_V = 4k_B \left(\frac{\epsilon}{k_B T}\right)^2 \frac{1}{\left(e^{\epsilon/k_B T} + e^{-\epsilon/k_B T}\right)^2}$$

and so the total specific heat is

$$C_V = 4Nk_B \left(\frac{\epsilon}{k_B T}\right)^2 \frac{1}{\left(e^{\epsilon/k_B T} + e^{-\epsilon/k_B T}\right)^2}.$$

(b) Using the result above we can immediately step to the contribution of the specific heat from the i^{th} atom,

$$C_V^i = 4k_B \left(\frac{\epsilon_i}{k_B T}\right)^2 \frac{1}{\left(e^{\epsilon_i/k_B T} + e^{-\epsilon_i/k_B T}\right)^2}.$$

When $k_B T \ll \epsilon_i$ then

$$C_V^i \approx 4k_B \left(\frac{\epsilon_i}{k_B T}\right)^2 e^{-2\epsilon_i/k_B T},$$

therefore summing this for all atoms gives

$$C_V \approx 4k_B \sum_i \left(\frac{\epsilon_i}{k_B T}\right)^2 e^{-2\epsilon_i/k_B T}.$$

Without an explicit statement about the values of ϵ_i this is as far as we can go. However one final step could be to approximate this as an integral

$$C_V \approx 4k_B \int \left(\frac{\epsilon}{k_B T}\right)^2 e^{-2\epsilon/k_B T} g(\epsilon) d\epsilon$$

where $g(\epsilon)$ is the density of states, which is often of the form $g(\epsilon) \approx \sqrt{\epsilon}$.

(3) (a) The partition function is

$$\begin{aligned} Z &= \sum_{j=0}^{\infty} g_j e^{-\epsilon_j/k_B T} \\ &= \sum_{j=0}^{\infty} (2j+1) e^{-j(j+1)h^2/(8\pi^2 m a^2 k_B T)}. \end{aligned}$$

Let $x = h^2/(8\pi^2 ma^2 k_B T)$ and for high temperatures $x \ll 1$, and we integrate over j, i.e. at high temperatures high-j values dominate and at that point j can be thought of as a continuous variable, hence

$$\begin{aligned} Z &\approx \int_0^\infty (2j+1)e^{-j(j+1)x} dj \\ &= -\frac{1}{x}e^{-j(j+1)x}\Big|_0^\infty \\ &= \frac{1}{x} \\ &= 8\pi^2 ma^2 k_B T/h^2. \end{aligned}$$

(b) It follows immediately that the internal energy is

$$U = k_B T^2 \frac{\delta}{\delta T} \ln Z = k_B T$$

and the heat capacity is

$$C_V = \frac{\delta U}{\delta T} = k_B.$$

(c) For low temperature we approximate Z by just taking the lowest terms in the expression for Z. Taking the lowest term alone gives $Z = 1$ giving $C_V = 0$ and this is the $T = 0$ behaviour. We are asked for low temperature approximations, so let's take the first two levels which will describe the behaviour just above $T = 0$. Gather some terms to simplify, let $\theta = h^2/(8\pi^2 ma^2 k_B)$ so that

$$\begin{aligned} Z &\approx 1 + 3e^{-2\theta/T}, \\ \Rightarrow U &= \frac{6k_B\theta}{Z}e^{-2\theta/T}, \\ \text{and } C_V &= \frac{12k_B\theta^2}{Z^2T^2}e^{-2\theta/T}. \end{aligned}$$

(4) (a) The partition function is

$$Z = \sum_{n=1}^{\infty} 2n^2 e^{E_0/(n^2 k_B T)}.$$

When $T = 0$ this expression is not physically meaningful. However when $T \neq 0$ it also diverges.

(b) The divergence has nothing to do with the choice of zero of energy. If we had chosen $E_n = -E_0/n^2 + E'$ then

$$Z' = e^{-E'/k_B T}\left(\sum_{n=1}^{\infty} 2n^2 e^{E_0/(n^2 k_B T)}\right)$$

which still contains our divergent sum.

(c) The average energy is

$$
\begin{aligned}
\langle E \rangle &= \frac{\sum\limits_{n=1}^{\infty} \left(-\frac{E_0}{n^2}\right) 2n^2 e^{E_0/(n^2 k_B T)}}{\sum\limits_{n=1}^{\infty} 2n^2 e^{E_0/(n^2 k_B T)}} \\
&= 0.
\end{aligned}
$$

Note on the above, one has to be careful in dealing with divergent series. In the above, for a given finite length of sum on both the denominator and numerator (set the sums to N rather then ∞), then sum the in the denominator is much larger than the numerator so the fraction tends to zero as sums head off to infinity.

(d) The divergence has the origin in the very large degeneracy of the excited states of hydrogen and that the wavefunctions for hydrogen are extended. If we can limit this degeneracy and infinite extent of the wavefunction (for example with external interactions, putting the atom in a large box) these highly excited, highly degenerate states no longer exist and there is no divergence. This illustrates problems that may arise unexpectedly by "model" systems.