Lecture 9 Summary

Phys 404

We considered a single particle of mass *M* in a cubic box of side *L* and solved the Schrödinger equation, giving energy levels $E = \frac{\pi^2\hbar^2}{2ML^2}(n_x^2 + n_y^2 + n_z^2)$, where the three quantum numbers can independently take on the value of any positive integer. We then considered this particle to be in thermal equilibrium with a reservoir at temperature τ. The single particle partition function is $Z_1 = \sum_s e^{-\varepsilon_s/\tau} = \sum_{n_x=1}^{\infty} \quad \sum_{n_y=1}^{\infty} \quad \sum_{n_z=1}^{\infty} e^{-\frac{\pi^2\hbar^2}{2ML^2}(n_x^2+n_y^2+n_z^2)/\tau}$. The sum can be converted into an integral and evaluated to give $Z_1 = n_Q V$, where $V = L^3$ is the volume of the box and $n_Q = (\frac{M\tau}{2\pi\hbar^2})^{3/2}$is called the quantum concentration. We argued in class that the quantum concentration is the number of deBroglie cubes per unit volume, where the deBroglie cube is a volume whose sides are equal to the deBroglie wavelength ($\lambda_{dB} = \frac{\hbar}{M<v>}$) of a particle with kinetic energy equal to τ. Helium gas at room temperature has a concentration $n = 0.025/nm^3$, compared to the quantum concentration of $n_Q = 8000/nm^3$. The concentration of He gas is far below the quantum concentration, meaning that we are in the dilute limit, which is appropriate for the ideal gas calculation that we are about to do. On the other hand, liquid Helium at 4.2 K is a different story. There $n = 51/nm^3$ and $n_Q = 16/nm^3$, showing that liquid Helium is a "quantum liquid" and must be treated from a very different point of view (more on that later in the course).

We next considered the situation of N non-interacting particles in the same box in the dilute limit. If the particles are distinguishable, one can show that the partition function of the composite system is $Z_N = Z_1^N$. If the N particles are <u>in</u>distinguishable then Z_1^N over-counts the number of unique states by $N!$ since there are $N!$ ways to distribute N identical particles into N states, all of which must be considered the same state of the composite system in the partition function summation over states. Thus the N identical particle partition function is $Z_N = \frac{1}{N!}Z_1^N$.

An ideal gas of N identical non-interacting particles has the partition function $Z_N = \frac{1}{N!}(n_Q V)^N$. The energy is given by $U = \tau^2 \frac{\partial Log\,(Z)}{\partial\tau} = \frac{3}{2}N\tau = \frac{3}{2}Nk_BT$, which is the well known result for an ideal gas. The Helmholtz free energy is $F = -\tau\log(Z) = N\tau\left[logN - \log\left(n_Q V\right) - 1\right]$. The pressure is given by $p = -\frac{\partial F}{\partial V}|_\tau = \frac{N\tau}{V}$, or in other words $pV = Nk_BT$, which is the famous ideal gas law. Finally the entropy follows from $\sigma = -\frac{\partial F}{\partial\tau}|_V = N\left[\log\left(\frac{n_Q}{n}\right) + \frac{5}{2}\right]$, which is known as the Sackur-Tetrode equation, and was derived in 1911 as an early application of quantum mechanics to statistical physics (note that there is an $\hbar$ in n_Q).