Lecture 18

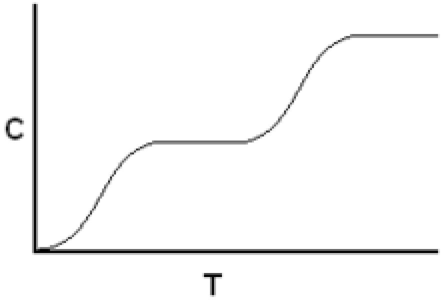
Physics 404

We consider the classical limit of the ideal gas, where $\frac{\varepsilon-\mu}{\tau} \gg 1$, and the gas is in the dilute limit $f(\varepsilon_s) \ll 1$, or $\frac{n}{n_Q} \ll 1$. As discussed in lecture 15, μ/τ is large and negative in a dilute ideal gas. In this case both the Fermi-Dirac and Bose-Einstein distributions have the same limiting form for the thermal average occupation number of an orbital: $f(\varepsilon) \cong e^{-(\varepsilon-\mu)/\tau} = \lambda e^{-\varepsilon/\tau} \ll 1$.

The expression for $f(\varepsilon)$ was derived for a single orbital chosen arbitrarily, in thermal and diffusive equilibrium with all the other orbitals (the reservoir). Because the orbital was chosen arbitrarily, the expression applies to any single orbital. Now we shall assume that the N-particle system consists of N particles independently choosing orbitals to occupy at temperature τ and chemical potential μ. We then add the constraint that the sum of $f(\varepsilon_S)$ over all states "s" of the system must add up to the total number of particles in the material, which we call N. In other words: $N = \sum_s \lambda e^{-\varepsilon_s/\tau} = \lambda \sum_s e^{-\varepsilon_s/\tau}$. The activity comes out of the sum over states because it depends only on the properties imposed by the reservoir, namely the chemical potential μ and the temperature τ. The sum is proportional to the partition function for the single-particle-in-a-box problem that was solved in lecture 10 as $Z_1 = \sum_s e^{-\varepsilon_s/\tau} = n_Q V$, where $n_Q = (M\tau/2\pi\hbar^2)^{3/2}$ is the quantum concentration and V is the volume of the box. We can now solve for the chemical potential: $N = \lambda n_Q V$, which leads to $\mu = \tau \log(n/n_Q)$. This same result was obtained previously in lecture 15 by a more 'brute force' method.

The Helmholtz free energy can be obtained by integrating the chemical potential, using the fact that $\mu = \frac{\partial F}{\partial N}|_{\tau,V}$. This yields $F(N,\tau,V) = N\tau[\log(n/n_Q) - 1]$. With the free energy, we can now calculate all the other thermodynamic quantities. The pressure is $p = -\frac{\partial F}{\partial V}|_{\tau,N} = N\tau/V$, which gives the ideal gas law $pV = N\tau$. The entropy is $\sigma = -\frac{\partial F}{\partial \tau}|_{V,N} = N\left[\log(n_Q/n) + \frac{5}{2}\right]$, which is the Sackur-Tetrode equation. The energy of the gas can be obtained from the free energy and entropy, and is $U = F + \tau\sigma = \frac{3}{2}N\tau$. This can also be seen as a result of 'equipartition of energy' between the three translational degrees of freedom. Each degree of freedom acquires $\tau/2$ of energy on average, so a particle translating in a three dimensional box acquires $3\tau/2$ of energy, and there are N particles, hence the result for U.

Heat capacity basically counts the number of degrees of freedom of the particles making up the ideal gas. The figure below sketches the dependence of the heat capacity of a gas on temperature. As the temperature increases there are steps in the heat capacity as different internal degrees of freedom (such as rotation and vibration) become excited. The energies of these internal states are quantized, and the thermal energy has to reach that quantization energy scale before the modes are excited to an appreciable extent.



If the particles have internal degrees of freedom, such as rotation and vibration of poly-atomic molecules, then the system can acquire energy in those internal modes as well. If the temperature is much higher than the typical energy level spacing of those internal states, then equipartition applies to those degrees of freedom as well. In general, if a molecule has internal states with energies ε_{int}, then one can define an internal partition function $Z_{int} = \sum_{int\ states} e^{-\varepsilon_{int}/\tau}$. The statistical mechanics of such a system is identical to that of a monatomic ideal gas except that the activity is modified as $\lambda \to \lambda Z_{int}$.