Lecture 34 Highlights

We are in the process of understanding the unique macroscopic thermodynamic properties of liquid ^{4}He at low temperatures. The liquid is held in a cube of sides $a \times a \times a = V$. We must now find the energies and degeneracies of the states of the system. Assume that the Helium atoms act like free particles in a box (3-dimensional infinite square well). Assume that 'weak interactions' occur between the atoms to enable the system to be ergodic (i.e. to explore all microscopic configurations consistent with the fixed energy and number constraints).

The single particle states are given by solutions to the Hamiltonian $\mathrm{H} = -\frac{\hbar^2}{2m}\nabla^2 + V$, where $V = \begin{cases} 0 & \text{for points inside the box} \\ \infty & \text{for points on the wall of the box} \end{cases}$. This problem was done in HW #1, problem 4.2. It is solved by standard separation of variables techniques, and using the fact that the wavefunction goes to zero at the walls. The resulting single-particle wavefunctions are of the form $\psi(x,y,z) = A\sin\left(\frac{\ell\pi x}{a}\right)\sin\left(\frac{m\pi y}{a}\right)\sin\left(\frac{n\pi z}{a}\right)$, where ℓ, m, n are positive integers. The energy of the state is given by a triplet of integers as $E = \frac{\hbar^2 k^2}{2m}$, with $k^2 = k_x^2 + k_y^2 + k_z^2$, and $k_x = \frac{\ell\pi}{a}$, $k_y = \frac{m\pi}{a}$, $k_z = \frac{n\pi}{a}$, with $\ell = 1,2,3,\ldots$, $m = 1,2,3,\ldots$, $n = 1,2,3,\ldots$. The states are labeled by points on a regular cubic lattice of spacing π/a in k-space.

We can calculate how many states are within an octant in k-space of radius *k* as follows. The number of states up to *k* is:

$$G(k) = \frac{\text{Volume of octant in k-space}}{\text{Volume occupied per state in k-space}} = \frac{\frac{1}{8}\frac{4}{3}\pi k^3}{(\pi/a)^3}.$$ Written in terms of energy, this becomes $G(E) = \frac{V}{6\pi^2}\left(\frac{2mE}{\hbar^2}\right)^{3/2}$. The degeneracy is the rate at which new states are added as the sphere expands. This density of states (another name for degeneracy) is given by

$$g(E) = \frac{dG}{dE} = 2\pi V\left(\frac{2m}{h^2}\right)^{3/2} E^{1/2}.$$

We can now find the chemical potential μ by enforcing the number constraint for the particles in the box: $N = \sum_{s=1}^{\infty} n_s = \sum_{s=1}^{\infty} \frac{g_s}{e^{(E-\mu)/kT} - 1}$. Rather than carry out this tedious sum, we will make a continuum approximation and convert the (discrete) sum on *k* to an integral on (continuous) energy. Thus we get:

$$N = \int_0^{\infty} \frac{g(E)dE}{e^{(E-\mu)/kT} - 1}. \qquad (1)$$

Note that we are taking the ground state of the system ($\ell = m = n = 1$) to be at zero energy. Plugging in the density of states yields:

$$N = 2\pi V\left(\frac{2m}{h^2}\right)^{3/2}(k_BT)^{3/2}\int_0^\infty \frac{x^{1/2}dx}{e^x e^{-\mu/kT}-1}$$

The integral can be solved by pulling out the two exponentials in the denominator:

$I = \int_0^\infty \frac{x^{1/2}dx}{e^x e^{-\mu/kT}(1-e^{-x}e^{\mu/kT})}$. Note that since μ must be negative (last lecture) and x is greater than or equal to zero, the factor $e^{-x}e^{\mu/kT}$ is less than 1 in magnitude. Therefore the following expansion will converge:

$\frac{1}{1-z} = 1+z+z^2+z^3+...$ where in this case $z = e^{-x}e^{\mu/kT}$. This leads to an infinite number of integrals, each of which is closely related to the Gamma function, and yields the following result for the number constraint:

$$N = 2\pi V\left(\frac{2m}{h^2}\right)^{3/2}(k_BT)^{3/2}\Gamma\left(\frac{3}{2}\right)f(\mu/k_BT), \qquad (2)$$

where $f(\mu/k_BT) \equiv \sum_{p=1}^{\infty}\frac{e^{p\mu/k_BT}}{p^{3/2}}$, and $\Gamma\left(\frac{3}{2}\right) = \frac{\sqrt{\pi}}{2}$. The function f has a maximum value when it has zero argument, and that value is about 2.61 (see the plot on the web site). Equation (2) for the total number of particles gives rise to a crisis in the limit of temperature going to zero. The right hand side of the equation goes to zero because the function f is bounded above and nothing else is temperature dependent. This shows that there has been a major flaw in the theory up to this point.

The problem was in making the continuum approximation in Equation (1). The continuum version leaves out one very important state – the ground state at E=0. This state takes up the burden of holding all of the particles in the limit as $T \to 0$! The correct expression for the particle number becomes:

$$N = n_1(T) + 2\pi V\left(\frac{2m}{h^2}\right)^{3/2}(k_BT)^{3/2}\Gamma\left(\frac{3}{2}\right)f(\mu/k_BT)$$

$$= \frac{1}{e^{-\mu/k_BT}-1} + 2\pi V\left(\frac{2m}{h^2}\right)^{3/2}(k_BT)^{3/2}\Gamma\left(\frac{3}{2}\right)f(\mu/k_BT) \qquad (3)$$

Note from Eq. (3) that the occupation number of the ground state (n_1) can be made arbitrarily large by taking the chemical potential very close to 0 (but still negative!). We can estimate the "crisis temperature" as the point at which the function $f(\mu/k_BT)$ is forced to take on its maximum value of 2.612. This gives for the "critical temperature" T_c:

$$T_c = \left(\frac{N/V}{2\pi\left(\frac{2mk_B}{h^2}\right)^{3/2}\Gamma\left(\frac{3}{2}\right)2.612}\right)^{2/3}$$

For ^{4}He, with N/V = 2 x 10^{28} /m^3, this gives $T_c = 3.1K$, which is remarkably close to the experimental value for the λ-transition, $T_\lambda = 2.2K$. Similar calculations can be done for a gas of cold Na atoms, as found in atom traps. There the mass of the atom is about 23 amu and the density that can be achieved experimentally is much lower, on the order of $N/V = 10^{20}$ /m^3, giving a predicted crisis temperature of $T_c = 1.5\ \mu K$. The observed condensation temperature is about $2\ \mu K$.

The phenomenon of macroscopic occupation of the ground state in the limit of zero temperature in a collection of many identical Bosons with overlapping wavefunctions is called Bose-Einstein Condensation (BEC).