Many-particle Systems, 4

Absolute temperature

When a system is in statistical equilibrium it can usefully be characterized by a few macroscopic variables. **Temperature** is one of the most important of these. The *absolute temperature scale* (measured in kelvins, K) has the following properties. (1) $T = 0$ K is the temperature of a macroscopic system found *permanently* in its *ground state*. Such a system has **no excitations**; it has its lowest possible energy and is completely isolated from the rest of the universe.

<u>Example</u>: A fermion deck of 52 same-backed cards has one of each different face and suit: one A♦, one 2♦, …, one K♠. This is the fermion deck ground state, the state the deck would be in at $T = 0$ K. A boson deck at $T = 0$ K, on the other hand, would have 52 A♦s.

Of course, such a condition is impossible to achieve in practice, so ***absolute zero* is an idealized state not a real one**. (2) $T = \infty$ K is the temperature of a macroscopic system found ***equally likely* in any of its allowed states**. In other words, if one could measure the $4N$ quantum numbers of the system again-and-again, each possible combination would be observed with equal frequency. Again, this is really an idealization, **not an achievable reality**. (3) For a system at constant temperature and constant chemical potential, the **probability** of finding the system in a $4N$ quantum number microstate, S, is

$$P(N, E_S) = \frac{\exp[(\mu N - E_S)/k_B T]}{Z_S}, \qquad (1)$$

where E_S is the energy of the state, k_B is a fundamental constant known as *Boltzmann's constant*, the value of which is 8.617x10^{-5} eV/K, and Z_S is a temperature dependent coefficient that ensures that the sum of all of the Ps for all system particle numbers and energies adds up to 1 (i.e., the system when measured has to be found in one of its allowed microstates). Note that the chemical potential (an energy) is a function of temperature, as we discuss below.

<u>Note</u>: In the Kelvin scale, pure water freezes at about 273 K and boils at about 373 K (at a pressure of 1 atm). Human body temperature is about 310 K and "room temperature" is taken to be 300 K (though that might be uncomfortably warm). At room temperature, $k_B T$ = 0.0249 eV = 1/40 eV (among friends).

Average occupation numbers

As stated in Mn3, the important quantity for calculating macroscopic thermodynamic quantities for an ideal gas is the average number of particles in single-particle quantum states. For an ideal gas system, $N = \sum_\sigma N_\sigma$ and $E_S = \sum_\sigma N_\sigma \varepsilon_\sigma$. If these are inserted in (1) above, then

$$\exp[(\mu N - E_S)/k_B T] = \exp[(\mu \sum_\sigma N_\sigma - \sum_\sigma N_\sigma \varepsilon_\sigma)\Big/ k_B T] = \prod_\sigma \exp[N_\sigma(\mu - \varepsilon_\sigma)/k_B T].$$

The symbol $\prod_\sigma$ means, "multiply all of the terms that depend on σ" ("big sigma" stands for "sum" and "big pi" stands for "product"). Defining $Z_S = \prod_\sigma Z_\sigma$ allows the system probability in (1) above to be written

$$P(N,E_S)=\prod_\sigma P(N_\sigma,\varepsilon_\sigma)$$

where

$$P(N_\sigma,\varepsilon_\sigma)=\frac{\exp[N_\sigma(\mu-\varepsilon_\sigma)/k_BT]}{Z_\sigma}. \quad (2)$$

This is the probability that a single-particle state σ is occupied by N_σ particles (the state's "occupation number") calculated as if the single-particle state were an independent statistical mechanical system. In other words, **for an ideal gas system, every single particle state in the system is independently in thermal equilibrium with the system's surroundings!** The quantity of interest for all of the systems we analyze below is the average number of particles occupying state σ

$$\bar{N}_\sigma=\sum_{N_\sigma}N_\sigma P(N_\sigma,\varepsilon_\sigma)\ . \quad (3)$$

To make progress using (2) requires evaluating Z_σ. Because the state has to be "occupied" by some number of particles (where "some" includes zero), the sum of all probabilities from (2) is

$$\sum_{N_\sigma}P(N_\sigma,\varepsilon_\sigma)=1.$$

This allows us to write

$$Z_\sigma=\sum_{N_\sigma}\exp[N_\sigma(\mu-\varepsilon_\sigma)/k_BT].$$

To compress the notation, let $x_\sigma=\exp[(\mu-\varepsilon_\sigma)/k_BT]$. Then

$$P(N_\sigma,\varepsilon_\sigma)=x_\sigma^{N_\sigma}/Z_\sigma \text{ and } Z_\sigma=\sum_{N_\sigma}x_\sigma^{N_\sigma}.$$

The particles in the systems we will study are either identical fermions or identical bosons. If they are fermions the sum is simple: N_σ is only either 0 or 1. In that case, we have

$$Z_{\sigma F}=x_\sigma^0+x_\sigma^1=1+x_\sigma.$$

For bosons, the sum is more complicated: N_σ can be any positive integer (including 0) up to the total number of particles in the system, a number so large it is essentially infinite. The essentially infinite sum for bosons diverges if $x\ge 1$. Thus, for bosons, μ must be just right to make $0\le x<1$. When that's the case the infinite sum is the sum of a geometric series:

$$Z_{\sigma B}=x_\sigma^0+x_\sigma^1+x_\sigma^2+...=\frac{1}{1-x_\sigma}.$$

The average occupation number, $\bar{N}_\sigma$, in (3) is the same as

$$\bar{N}_\sigma=(\sum_{N_\sigma}N_\sigma x_\sigma^{N_\sigma})/Z_\sigma.$$

Again, for fermions the sum in the numerator, $\sum_{N_\sigma}N_\sigma x_\sigma^{N_\sigma}$, is easy: it's just $0x_\sigma^0+1x_\sigma^1=x_\sigma$. That is, $\bar{N}_\sigma=x_\sigma/(1+x_\sigma)$. Dividing numerator and denominator by x_σ yields

$$\bar{N}_{\sigma F}=\frac{1}{\exp[(\varepsilon_\sigma-\mu)/k_BT]+1}; \quad (4)$$

note that after dividing, the $\mu - \varepsilon_\sigma$ becomes $\varepsilon_\sigma - \mu$. For bosons, we use the trick of differentiating: $dZ_\sigma / dx_\sigma = \sum_{N_\sigma} N_\sigma x_\sigma^{N_\sigma - 1}$, which shows that the required sum is $x_\sigma \, dZ_\sigma / dx_\sigma$. In other words,

$$\bar{N}_{\sigma B} = \frac{x_\sigma (dZ_\sigma / dx_\sigma)}{Z_\sigma} = (1 - x_\sigma) x_\sigma \frac{1}{(1 - x_\sigma)^2} = \frac{x_\sigma}{1 - x_\sigma}.$$

Finally, dividing by x_σ again we get

$$\bar{N}_{\sigma B} = \frac{1}{\exp[(\varepsilon_\sigma - \mu)/k_B T] - 1}. \tag{5}$$

Consequences of the average occupation numbers at low temperature

The average occupation numbers of single-particle states for an ideal gas of fermions (4) and an ideal gas of bosons (5) look almost identical, differing only in the sign of the 1 in the denominator. *That*, however, has huge consequences at low temperatures. As defined above $x_\sigma = \exp[(\mu - \varepsilon_\sigma)/k_B T]$ which is always greater than or equal to zero. For fermions, x_σ can have any positive value. Thus, **for fermions the chemical potential can have any value**. On the other hand, in order to perform the Z sum for bosons, x_σ has to be < 1. Therefore, the chemical potential for bosons has to be less than the lowest single-particle energy—i.e., the single particle ground state energy. If the latter is taken to be zero (remember only energy *differences* matter) then **the chemical potential for bosons must be strictly negative** for all temperatures.

Suppose in (4), the expression for average state occupation for fermions, that $\varepsilon_\sigma - \mu < 0$. In the limit as $T \to 0$, the exponential in (4) for these energies also $\to$ 0. In other words, for all states with $\varepsilon_\sigma - \mu < 0$, the occupation number is 1: *all* states with energies less than μ are filled at $T = 0$. Conversely, for $\varepsilon_\sigma - \mu > 0$, the exponential $\to \infty$ as $T \to 0$. *No* states with energies greater than μ are filled at $T = 0$. The **value of the fermion chemical potential at $T = 0$ that separates filled states from unfilled states is called the *Fermi energy* and is denoted** ε_F.

The low temperature limit of (5), the expression for average state occupation for bosons, is different. The chemical potential has to be < 0, the single particle ground state energy, for bosons. As $T \to 0$, the exponential in (5) $\to \infty$ for all states, with the exponentials for higher energy states "blowing up" first. That produces the logically uncomfortable result that the average occupation number vanishes for all states. What actually happens is that the occupation numbers for all states with energies above the ground state go to zero before the ground state. This begins to happen abruptly when the temperature reaches a critical value called the **Bose-Einstein condensation** temperature, T_{BEC}. **Below T_{BEC} a large fraction of the system's particles are in the ground state**. **All of the bosons in the ground state move coherently together with one giant wavefunction, producing the astonishing "super" properties observed in superfluids ("zero" viscosity, "infinite" heat conductivity) and superconductors ("zero" resistance, "complete" expulsion of magnetic fields)**.

(*Historical comment*: Bosons are named in honor of Satyendra Nath Bose ("boh-zee") who first discovered how to derive the Planck blackbody spectrum from the statistical mechanics of a photon gas (see below). Bose had studied Einstein's relativity papers and, after asking Einstein's permission, translated one of them from German to English to be published in a collection of papers on the subject. After making his photon discovery, Bose sent Einstein a copy of a manuscript about it asking that it be translated into German and published in what was then the leading journal on physics. At the same time he sent Einstein a copy of the translation of *Einstein's* paper Bose had made. Einstein was impressed (and had his ego puffed a bit) and did the translation for Bose, but along the way he realized that it was possible to get condensation of massive bosons at low temperatures. Einstein's 1921 Nobel Prize was for his explanation of the "photoelectric effect" (awarded a year later in 1922!—some unpleasant folks on the Nobel committee didn't like Einstein), but he could have received Prizes for at least four other major contributions as well, including the prediction of BEC. Bose was nominated after the BEC work, but the committee didn't like him either, so he never got one—although over the years he obtained a prominent university position and lots of public praise from the Indian government. Experimental verification of BEC in the 1990s led to the Physics Nobel Prize in 2001, long after both Bose and Einstein had died. [You don't get the Nobel Prize if you are dead.])