Lecture 6

Physics 404

The multiplicity function has one more contribution to statistical mechanics – it can be turned into a probability distribution function (PDF). In other words $P(N,s) = g(N,s)/2^N = \sqrt{\frac{2}{\pi N}}e^{-2s^2/N}$ represents the probability that a spin system made up of N spins will have a spin excess of 2s, *assuming each and every microscopic state is equally likely*. We can now calculate average values, and therefore macroscopic quantities, as $\langle f(s)\rangle = \int_{-\infty}^{\infty} f(s)P(N,s)ds$, where $f(s)$ is some function that depends on the microscopic state of the system. We did the example of the mean spin excess $\langle(2s)\rangle = 0$ and the variance of the spin excess $\langle(2s)^2\rangle = N$ as examples in class (check Appendix A of Kittel and Kroemer for the details of how to perform the integrals). These results say that the spin system is most likely to be found in a state of zero spin excess, with root-mean-square deviation $\sqrt{\langle(2s)^2\rangle} = \sqrt{N}$ from zero. For a macroscopic spin system (N ~ 10^{24}) the fractional width of this distribution is incredibly narrow: $F = \frac{\sqrt{\langle(2s)^2\rangle}}{N} = \frac{1}{\sqrt{N}} \sim 10^{-12}$.

The Fundamental Assumption of Statistical Physics is that a closed system is equally likely to be in any of the quantum states accessible to it. By closed we mean a system with fixed total number of particles N and energy U, and subject to constant electric, magnetic, gravitational fields, etc. By accessible states we mean those quantum states that are consistent with the constraints of fixed N and U and constant fields. This situation is often called the *microcanonical* ensemble.

Now consider two spin systems brought into "thermal contact." Assume that each system experiences the same uniform magnetic field $\vec{B}$, and the moments of the spins are the same, m_e. Thus the energy difference between successive states $\Delta U = 2m_eB$ is the same in both systems. We shall assume that the two systems cannot exchange particles, but they can exchange energy. In other words, N = N_1 + N_2 is fixed, along with N_1 and N_2. However, s= s_1 + s_2 is also fixed (along with the total energy $U = -(2s)m_eB$), but s_1 and s_2 can vary. To see how s_1 and s_2 can vary, consider a spin "down" particle in system 1 and a spin "up" particle in system 2. Here "up" and "down" refer to their quantum spin orientation relative to the external magnetic field $\vec{B}$. The "down" spin in system 1 is in a higher energy state ($+m_eB$), while the "up" spin in system 2 is in a lower energy state ($-m_eB$). Now, they can undergo a coordinated pair of flips in which the spin in system 1 flips to "up" and at the same time the spin in system 2 flips to "down". This involves an exchange of energy $\Delta U = 2m_eB$ from system 1 to system 2, but does not violate the constraints of fixed N, N_1, N_2, and s. Such coordinated spin flips constitute the "thermal contact" and greatly enhance the number of accessible states for the coupled system.

We showed in class that the multiplicity of the coupled system that can exchange energy but not particles is given by $g(N,s) = \sum_{s_1=-N_1/2}^{s_1=+N_1/2} g_1(N_1,s_1)g_2(N_2,s-s_1)$. The product of multiplicities comes about because the combined system has quantum states described by a combination of any possible state in spin system 1 with any possible state in spin system 2. The sum comes about because the two systems can exchange any amount of energy between the two extremes of all spins "up" in spin system 1 ($s_1 = +N_1/2$) to all spins "down" in spin system 1 ($s_1 = -N_1/2$). Note that we assumed system 1 is smaller than system 2, $N_1 < N_2$. This sum is dominated by one term with a maximum value for the product $g_1(N_1,s_1)g_2(N_2,s-s_1)$, as was the case for the multiplicity function of a single isolated system. We take the derivative with respect to s_1 and set it equal to zero to find the value of s_1 that maximizes the multiplicity. To find the condition for maximum multiplicity we first took the logarithm of the function (to cut it down to size) and used the Gaussian approximation for the multiplicities, valid in the limit of large N and small |s|. Note that the value of s_1 that gives a zero of $\frac{d}{ds_1}g_1(N_1,s_1)g_2(N_2,s-s_1)$ is the same value of s_1 that gives a zero of $\frac{d}{ds_1}log[g_1(N_1,s_1)g_2(N_2,s-s_1)]$, hence no error is introduced by taking the logarithm. The result of the maximization process was a condition for "equilibrium" of the two systems in thermal contact: $\frac{s_1}{N_1}=\frac{s_2}{N_2}=\frac{s}{N}$, i.e. that the fractional spin excesses of the two systems be equal. (The sign of $\frac{s}{N}$ is dictated by the constant total energy U.) In other words, after thermal equilibrium is achieved, the two parts of the system adopt a common value for the fractional spin excess, which is also equal to the global value of the fractional spin excess of the entire system. This situation is reminiscent of what happens when a "hot" object is brought into thermal contact with a "cold" object and they eventually come to thermal equilibrium at a shared value for the temperature – the 0th Law of Thermodynamics. In fact we show exactly this in the next lecture.

To illustrate how sharply peaked the $g(N,s)$ function is, use the Gaussian approximation for the multiplicities and set $s_1 = \widehat{s_1}+\delta$, and $s_2 = \widehat{s_2}-\delta$, where $\widehat{s_1}$ and $\widehat{s_2}$ are the values of s_1 and s_2 that maximize $g(N,s)$, and δ is the deviation from equilibrium. The multiplicity now becomes $g_1(N_1,\widehat{s_1}+\delta,)g_2(N_2,\widehat{s_2}-\delta)=(g_1g_2)_{max}e^{-2\delta^2/N_1}e^{-2\delta^2/N_2}$. Take $N_1 = N_2 = 10^{24}$ and a deviation of $\delta = 10^{13}$, so that $\delta/N = 10^{-11}$, giving $g_1(N_1,\widehat{s_1}+\delta,)g_2(N_2,\widehat{s_2}-\delta)=(g_1g_2)_{max}e^{-400}=(g_1g_2)_{max}10^{-174}$, which is an amazingly smaller number than the maximum value of the function, $(g_1g_2)_{max}$. This calculation shows that even small deviations from the equilibrium spin configuration (1 part in 10^{11}) are unbelievably unlikely. **The multiplicity function is so strongly peaked that only that state which maximizes the multiplicity, and a narrow range of states nearby, completely dominate the equilibrium properties of the system**. This is an extremely important concept that is fundamental to the study of statistical mechanics. We will generalize this result to more complicated and interesting systems. But first we need to define entropy and temperature…