Lecture 7

Physics 404

We address two related questions: How is thermal equilibrium achieved? What condition is satisfied when it is achieved? First, generalize from the spin system with spin excess (2s) to a system with energy U = -(2s)mB. Two initially isolated systems with multiplicities $g_1(N_1,U_1)$ and $g_2(N_2,U_2)$ are brought into thermal contact, where they can exchange energy U, but not particle number, N. The combined system can explore many more microscopic states by exchanging energy, hence their joint multiplicity is increased greatly. When this was done with two spin systems, we found a condition for equilibrium of: $\frac{s_1}{N_1}=\frac{s_2}{N_2}$. This result seems to be sending us a message. There is a "hidden" quantity that equalizes between the two systems when they are brought into thermal contact and allowed to equilibrate. We would like to identify this "hidden" information.

We showed in class that the maximum product of multiplicities g_1g_2 gives rise to the following condition: $\frac{1}{g_1}\frac{\partial g_1}{\partial U_1}|_{N_1}=\frac{1}{g_2}\frac{\partial g_2}{\partial U_2}|_{N_2}$. We recognize the derivative as a logarithmic derivative: $\frac{1}{g}\frac{\partial g}{\partial U}=\frac{\partial \log(g)}{\partial U}$, suggesting that the logarithm of the multiplicity is an important quantity. In fact we define the fundamental entropy as: $\sigma=\log(g)$. By starting with quantum mechanical solutions with discrete spectra, we are able to count the microscopic states available to the system and come up with this very clear and sensible definition of entropy . The conventional entropy is given by $S=k_B\sigma$, where $k_B=1.381\times10^{-23}J/K$ is Boltzmann's constant.

More interesting is the statement that the derivative of the fundamental entropy with respect to energy has a common value in the two systems when equilibrium is achieved. This is in fact a statement that the temperatures of the two systems are equal. We thus define the fundamental temperature τ as $\frac{1}{\tau}=\frac{\partial \sigma}{\partial U}|_N$, and the absolute temperature T through $\tau=k_BT$. We showed in class that the result of bringing two spin systems into thermal contact: $\frac{s_1}{N_1}=\frac{s_2}{N_2}$ is equivalent to the statement $\frac{1}{\tau_1}=\frac{1}{\tau_2}$.

It is possible to have negative absolute temperature. Systems that have a bounded excitation energy spectrum (like the spin model with energy states of only $+mB$ and $-mB$) will have an entropy that decreases as a function of increasing internal energy U, at some point. Nuclear spin systems show this property, as explored by Norman Ramsey in the accompanying paper. Most systems have unbounded energy spectra for their constituents (such as the kinetic energy of a particle in an ideal gas), thus their entropy is a monotonically increasing function of energy, and the temperature is always positive.

We also considered a situation in which one system is initially "hot" and the other is "cold", or in other words $\tau_1 > \tau_2$. When the two systems are brought into thermal contact, the multiplicity of the joint system will increase if the energy is shared between the systems in such a way that energy moves from the "hot" object to the "cold" object. Such a transfer increases the multiplicity and hence the entropy. This leads to a statement of **the second law of thermodynamics**: The entropy of a closed system will either stay the same or increase whenever a constraint internal to the system is released. This is a law in the sense that its violation is extremely unlikely for macroscopic systems in which the temperature (i.e. $\partial\sigma / \partial U \,|_N$) is a well-defined quantity. The example of energy transfer between a hot and cold system on pages 44 and 45 of the text shows that the changes in multiplicity when the energy flows "the right way" are enormous, suggesting that the 2nd law is not likely to be violated in macroscopic systems.