

Lecture 8 Summary

Phys 404

The multiplicity of a system will depend on the number of particles N and energy U , as we saw with the spin-1/2 system. For more general systems, the multiplicity will also depend on the volume. For example in the ideal gas we will find that multiplicity $g \sim V/V_Q$, where V_Q is a quantum volume. Thus in general, the entropy ($\sigma = \log(g)$) will also depend on particle number N , energy U , and volume V : $\sigma = \sigma(N, U, V)$. Consider a system with a fixed number of particles N (canonical ensemble), then a general change in entropy is given by $d\sigma(U, V) = \left. \frac{\partial \sigma}{\partial U} \right|_V dU + \left. \frac{\partial \sigma}{\partial V} \right|_U dV$. A coordinated change in U and V that maintains a fixed entropy is said to be an isentropic process, and yields $0 = \left. \frac{\partial \sigma}{\partial U} \right|_V (\delta U)_\sigma + \left. \frac{\partial \sigma}{\partial V} \right|_U (\delta V)_\sigma$, where the special changes in U and V that keep σ constant are noted with subscript σ . Dividing by $(\delta V)_\sigma$, and recognizing the temperature as $\frac{1}{\tau} = \left. \frac{\partial \sigma}{\partial U} \right|_V$, and $p = -\left. \frac{\partial U}{\partial V} \right|_\sigma$, this yields a new expression for the pressure: $p = \tau \left. \frac{\partial \sigma}{\partial V} \right|_U$.

Returning to the full differential of entropy (at fixed N), it can now be written as $d\sigma(U, V) = \frac{1}{\tau} dU + \frac{p}{\tau} dV$, or after multiplying through by τ , $\tau d\sigma = dU + p dV$ (fixed N), which is called the Thermodynamic Identity. It is a statement of the first law of thermodynamics, or conservation of energy, for a system in equilibrium with a reservoir at temperature τ . It will be generalized later to include variable particle number and different types of work beyond the mechanical variety ($p dV$).

Re-writing the Thermodynamic Identity, $dU = \tau d\sigma - p dV$, one can look at this as an expression for how energy changes with variations in entropy and volume. However, one may have different parameters at one's control, such as temperature and volume. A Legendre transformation can be used to change the independent variables. In this case consider the differential $d(\tau\sigma) = \tau d\sigma + \sigma d\tau$. Substituting for $\tau d\sigma$ yields $dU = d(\tau\sigma) - \sigma d\tau - p dV$, or bringing the full differentials together on the LHS yields $d(U - \tau\sigma) = -\sigma d\tau - p dV$. We call the quantity $F = U - \tau\sigma$ the Helmholtz free energy.

The Helmholtz free energy is a minimum for a system at fixed volume and temperature in equilibrium with the reservoir. On pages 68 and 69 of K+K it is shown that the differential $dF = 0$, showing that it is an extremum. Further arguments show that F is also a minimum with respect to variations away from equilibrium.

The differential form of the Helmholtz free energy suggests that two other thermodynamic quantities can be calculated from F by taking partial derivatives: $-\sigma = \left. \frac{\partial F}{\partial \tau} \right|_V$, and $-p = \left. \frac{\partial F}{\partial V} \right|_\tau$. Equating the cross derivatives of F with respect to volume and temperature yields the first of four Maxwell relations: $\left. \frac{\partial p}{\partial \tau} \right|_V = \left. \frac{\partial \sigma}{\partial V} \right|_\tau$.

We can now relate the Helmholtz free energy $F = U - \tau\sigma$ to the partition function (and therefore the original quantum mechanical solution). We just found that the entropy can be found from

F as $\sigma = -\frac{\partial F}{\partial \tau} \Big|_V$, which means we have a differential equation for F: $F = U + \tau \frac{\partial F}{\partial \tau} \Big|_V$. This can be rewritten as $U = -\tau^2 \frac{\partial(F/\tau)}{\partial \tau}$, which bears resemblance to a result from the last lecture: $U = \tau^2 \frac{\partial \text{Log}(Z)}{\partial \tau}$. Comparing, we find that $-\frac{F}{\tau} = \text{Log}(Z) + c$, and it is shown in K+K that the constant c is equal to zero to reproduce the correct entropy at zero temperature.

The probability of occupation of any state "s" can now be written as: $P(\epsilon_s) = \frac{e^{-\epsilon_s/\tau}}{Z} = e^{(F-\epsilon_s)/\tau}$.

Because the partition function is a sum of non-negative terms (even for negative temperature) of the form $e^{-\epsilon_s/\tau}$, it can never have a value smaller than the largest Boltzmann factor, hence the probability of occupation of any state will be bounded above by 1. Using the Helmholtz free energy in the expression for $P(\epsilon_s)$ rather than the partition function does not change this basic fact.

We finished by considering again the example of a two-level system with states at energy 0 and energy ϵ . The partition function is $Z = 1 + e^{-\epsilon/\tau}$. The free energy is just $F = -\tau \text{Log}(Z) = -\tau \text{Log}(1 + e^{-\epsilon/\tau})$. The entropy is calculated as $\sigma = -\frac{\partial F}{\partial \tau} \Big|_V = \text{Log}\left(1 + e^{-\frac{\epsilon}{\tau}}\right) + \frac{(\epsilon/\tau)e^{-\epsilon/\tau}}{1 + e^{-\frac{\epsilon}{\tau}}}$, where we interpret the fixed volume constraint to mean that the energy levels are fixed. The energy U can be calculated directly from the free energy and entropy as $U = F + \tau\sigma = \frac{\epsilon}{e^{\tau/\epsilon} + 1}$. These functions are plotted versus $\frac{\tau}{\epsilon}$ in the accompanying file posted on the class website. From these plots we see that the free energy is always negative, or zero. It shows a slope of $-\text{Log}(2)$ in the limit of large $\frac{\tau}{\epsilon}$, which is the limiting value of the entropy at high temperature. The probability of occupation of each state approached $\frac{1}{2}$ in the high temperature limit, giving the system a multiplicity of 2, hence entropy $\text{Log}(2)$. At low temperature ($\epsilon/\tau \rightarrow \infty$) there is effectively only one state that can be occupied (the ground state) and the entropy is $\text{Log}(1) = 0$. It may seem odd that a discrete two-level system generates the continuous functions of free energy, entropy and energy versus $\frac{\tau}{\epsilon}$. We are implicitly assuming that an ensemble of identical two-level systems has been created and we are forming an average of macroscopic observable properties over this ensemble. Although the outcome of an observation of any particular system is discrete, the ensemble average is a continuous function of $\frac{\tau}{\epsilon}$.