

# Physics 112 : Lecture 8

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## 1 The Thermodynamic Identity

Let's start thinking about pressure. Usually, pressure is defined along the lines:

$$\Delta U = P\Delta V$$

where  $\Delta U$  is the change in energy of a system,  $P$  is the pressure you apply to the system, and  $\Delta V$  is the change in the volume of the system, which is *positive* when we are pushing the system inwards. So, we can just define pressure in the following way:

$$P = \left( - \frac{\partial U}{\partial V} \right)_{\sigma}$$

where the minus sign is introduced since our  $\Delta V$  for the system is *negative* when we are applying positive pressure. Now, thinking about the entropy as a function of energy and volume, (and holding all other free variables constant), we have:

$$d\sigma = \left( \frac{\partial \sigma}{\partial U} \right)_V (dU)_{\sigma} + \left( \frac{\partial \sigma}{\partial V} \right)_U (dV)_{\sigma}$$

Now, we can consider an *isoentropic* process (which is reversible) where the change in the entropy  $d\sigma = 0$ . In this case, we can substitute  $(\partial \sigma / \partial U) = 1/\tau$ ,  $(\partial U / \partial V)_{\sigma} = -P$  to derive the equation:

$$P = \tau \left( \frac{\partial \sigma}{\partial V} \right)_U$$

Now, we can wave our hands a little and substitute this formula for  $P$  that we found into our original equation for  $d\sigma$  (even though we derived our formula for  $P$  by considering an isoentropic process), and find that:

$$\tau d\sigma = dU + PdV$$

We can think of the  $\tau d\sigma$  term as the 'heat flow', and  $PdV$  as the 'mechanical work' on the system. This equation is known as the thermodynamic identity.

## 2 Helmholtz Free Energy

A quantity of special interest is the Helmholtz free energy, defined by:

$$F = U - \tau\sigma$$

When considering the Helmholtz free energy, we usually consider it for a system in contact with a thermal reservoir; so the temperature is a constant. We can look at the entropy of the universe (system and thermal reservoir):

$$\begin{aligned}\sigma &= \sigma_S(U_S) + \sigma_R(U - U_S) = \sigma_S(U_S) + \sigma_R(U) - \left(\frac{\partial\sigma_R}{\partial U}\right)_V U_S = \sigma_S(U_S) + \sigma_R(U) - \frac{U_S}{\tau} \\ &= \sigma_R(U) - \frac{1}{\tau} \left( U_S - \tau\sigma_S(U_S) \right) = \sigma_R(U) - \frac{F_S}{\tau}\end{aligned}$$

Since  $\tau$  is assumed to be a constant (as the system is in contact with a thermal reservoir), it's clear that to maximize the global entropy we must minimize  $F_S$ , the Helmholtz free energy for the system of consideration.

Now, we can keep squeezing the Helmholtz free energy for what its worth. Note that:

$$dF = dU - \tau d\sigma - \sigma d\tau = -\sigma d\tau - PdV = \left(\frac{\partial F}{\partial \tau}\right)_V d\tau + \left(\frac{\partial F}{\partial V}\right)_\tau dV$$

where at the second equality we substitute in  $dU$  given by the thermodynamic identity, and at the third equality we use the definition of  $dF$  in terms of its partials. Note that this implies:

$$\left(\frac{\partial F}{\partial \tau}\right)_V = -\sigma; \quad \left(\frac{\partial F}{\partial V}\right)_\tau = -P$$

so:

$$P = -\left(\frac{\partial F}{\partial V}\right)_\tau = -\left(\frac{\partial(U - \tau\sigma)}{\partial V}\right)_\tau = -\left(\frac{\partial U}{\partial V}\right)_\tau + \tau\left(\frac{\partial \sigma}{\partial V}\right)_\tau$$

We can think of the first term as the 'normal pressure', and the second term as the 'entropy pressure'.

But wait, there's more! We have:

$$F = U - \tau\sigma = U + \tau\left(\frac{\partial F}{\partial \tau}\right)_V$$

where we use our formula for  $\sigma$  in terms of a partial of  $F$  found before. Now, we have:

$$U = F - \tau\left(\frac{\partial F}{\partial \tau}\right)_V = -\tau^2\left(\frac{\partial(F/\tau)}{\partial \tau}\right)_V$$

But recalling our formula for  $U$  in terms of the partition function, we had that:

$$U = \tau^2\left(\frac{\partial \ln Z}{\partial \tau}\right)$$

Hence, equating these two last equations, we find that:

$$F = -\tau \ln Z$$

and from this, we can find the two relations:

$$Z = e^{-F/\tau}; \quad P(\epsilon_s) = e^{(F-\epsilon_s)/\tau}$$

### 3 Two state paramagnet

Returning to our example of the two state paramagnet, we had that:

$$g(s) = \frac{N!}{(N/2 - s)!(N/2 + s)!}; \quad \sigma(s) = -(N/2 + s) \ln(1/2 + s/N) - (N/2 - s) \ln(1/2 - s/N)$$

Now, our Helmholtz free energy is given by:

$$F = U - \tau \sigma = -2smB - \tau \sigma$$

so, to maximise the entropy we minimise  $F$  (when in contact with a thermal reservoir at temperature  $\tau$ ), so we have:

$$\left( \frac{\partial F}{\partial s} \right)_{\tau, B} = 0 = -2mB + \tau \ln \left( \frac{N + 2s}{N - 2s} \right)$$

and from this we find:

$$\langle 2s \rangle = N \tanh \left( \frac{mB}{\tau} \right)$$

as we had found previously. Suppose we wanted to calculate something a bit trickier, the energy of the system. Well, we have the partition function:

$$Z = e^{mB/\tau} + e^{-mB/\tau} = 2 \cosh \left( \frac{mB}{\tau} \right)$$

and Helmholtz Free Energy:

$$F = -\tau \ln Z = -\tau \ln \left( 2 \cosh \left( \frac{mB}{\tau} \right) \right)$$

so we have entropy:

$$\sigma = - \left( \frac{\partial F}{\partial \tau} \right) = \ln \left( 2 \cosh \left( \frac{mB}{\tau} \right) \right) - \left( \frac{mB}{\tau} \right) \tanh \left( \frac{mB}{\tau} \right)$$

so we have energy:

$$U = F + \tau \sigma = -mB \tanh \left( \frac{mB}{\tau} \right)$$