PY 541 Lecture Notes: Fundamental

Pankaj Mehta

October 3, 2022

These notes explain fundamental thermodynamic identity.

In these notes, we will derive the fundamental thermodynamic identity and then apply it in some settings. This is a subtle topic and much of what I will talk about follows the exposition in Anatoli Polkovnikov's paper "Microscopic diagonal entropy and its connection to basic thermodynamic relations" Annals of Physics 2011.

The basic idea behind the identity is to realize that there are two basic ways that one can change the average internal energy of a system: through the exchange of "heat" and through "work". In what follows, we will make no distinction between "heating" and the non-adiabatic part of work. We will these two kinds of energy gain correspond to very different microscopic processes:

- **Heat:** Heat is the label we give to changes in energy that come from changes in the probability of occupying a micro-states.

- **Work:** Work is what we call changes in energy that come from changing some external control parameter θ_α in the Hamiltonian $H(\{\theta_\alpha\})$ *without* changing the probability of occupying a microstate. Instead, the change in energy comes because changing the parameters θ_α changes the energy associated with a microstate.

Heat

Let us see how this works in practice. Consider changing the energy of a system by exchanging heat with a bath. A system with initial energy E before contact with a heat bath ends up in a state with energy $E + \Delta E$. The microstates accessible to the system before energy exchange are just $\Omega_\theta(E)$. The subscript θ denotes that the the Hamiltonian parameters are fixed to be θ through out this exchange and do not change. After absorbing ΔE of heat, we have that the accessible microstates are those corresponding to $\Omega_\theta(E + \Delta E)$. If $\Delta E \ll E$, then we have that

$$\Omega_\theta(E + \Delta E) \approx \Omega_\theta(E) + \frac{\partial \Omega_\theta(E)}{\partial E}\Delta E \qquad (1)$$

Correspondingly, we have defining entropy as $S = k_B^{-1} \log \Omega(E)$ that to leading order in ΔE:

$$S_\theta(E + \Delta E) = S_\theta(E) + \left(\frac{\partial S}{\partial E}\right)_\theta \Delta E \qquad (2)$$

This implies that

$$\Delta S_\theta = S_\theta(E + \Delta E) - S_\theta(E) = \frac{\Delta E}{T} \quad (3)$$

Hence, we find that the change in internal energy ΔE is

$$\Delta E = T\Delta S_\theta = T(S_\theta(E + \Delta E) - S_\theta(E)). \quad (4)$$

Since by definition, the change in energy is due to heat, we can identify heat with $T\Delta S_\theta$. Again, we emphasize that this is due to what microstates are occupied/accessible to the system after it exchanges energy.

Work

To think about work, we will imagine changing the parameters of the system infinitesimally so that the probability of occupying a microstate does not change (adiabatically). In particular imagine we change the parameters $\theta_\alpha \to \theta_\alpha + \delta\theta_\alpha$. In this way every state of the system with energy $E(\theta)$ now has energy

$$E(\theta_\alpha + \delta\theta_\alpha) \quad = E(\theta_\alpha) + \delta E \quad (5)$$

$$\delta E = \sum_\alpha \left(\frac{\partial E}{\partial \theta_\alpha}\right) \delta\theta_\alpha \quad (6)$$

If we look at a fixed energy window E, then we know that the number of microstates $\Omega_{\theta+\delta\theta}(E + \delta E)$ much identical to $\Omega_\theta(E)$. In particular, this will also be true for entropies. So we have that

$$S_{\theta+\delta\theta}(E) = S_\theta(E - \delta E) \quad (7)$$

Taylor expanding, we have that

$$S_{\theta+\delta\theta}(E) \quad = S_\theta(E) - \frac{\partial S_\theta(E)}{\partial E}\delta E \quad (8)$$

$$= S_\theta(E) - \frac{\delta E}{T}. \quad (9)$$

This implies that

$$-\delta E = T(S_{\theta+\delta\theta}(E) - S_\theta(E)) \quad (10)$$

or substituting Eq. 6 that

$$T(S_{\theta+\delta\theta}(E) - S_\theta(E)) = -\sum_\alpha \left(\frac{\partial E}{\partial \theta_\alpha}\right) \delta\theta_\alpha = \sum_\alpha F_\alpha \delta\theta_\alpha, \quad (11)$$

where in the last line we have defined the generalized forces

$$F_\alpha = -\left(\frac{\partial E}{\partial \theta_\alpha}\right) \quad (12)$$

Thus, we can identify this change with the work.

Performing work and exchanging heat

Now finally, we imagine we allow a reservoir to perform work and exchange heat. Consider a system with micro-states i each with energy E_i. Then we know that the the average energy U of the system can be written as

$$U = \sum_i p_i E_i. \tag{13}$$

Thus, to first order, we can write any change in the average energy as either a change in the E_i due to a change in parameters or a change in the probability of occupying state i:

$$\Delta U = \sum_i \delta p_i E_i + \sum_i p_i \delta E_i \tag{14}$$

We identify the first term with heat and the second with the work and hence

$$\begin{aligned} \Delta U &= \Delta E + \delta E \\ &= T\Delta S_\theta - \sum_\alpha F_\alpha \delta\theta_\alpha. \end{aligned} \tag{15}$$

We can now identify different terms with the total energy and forces.

Ideal Gas at Constant Pressure

We now want to consider an ideal gas at constant pressure and constant volume. We know that we can think about the specific heats. These are associated with change in energy with respect to temperature, either holding volume fixed or holding pressure fixed.

Through out the experiment, we can change the volume of the gas. We also hold pressure fixed. We have that at fixed volume the second term disappears so that

$$T\frac{\Delta S}{\Delta T}\Delta T = C_v \Delta T = \frac{\Delta U}{\Delta T}\Delta T \tag{16}$$

So $T\Delta S$ is the heat needed to change internal energy by ΔU.

So now, at constant pressure, we still want to change internal energy by ΔU. This means that the energy in the heat we absorb goes to two processes: raising the internal energy of the gas and performing work. This is mathematically expressed in the thermodynamic identity:

$$\begin{aligned} T\Delta S &= \Delta U + P\Delta V \\ &= \Delta U + nR\Delta T, \end{aligned} \tag{17}$$

where in the second line we have used differential of ideal gas law at constant pressure $P\Delta V = nR\Delta T$. We now have

$$T\frac{\Delta S}{\Delta T}\Delta T = C_p \Delta T = \frac{\Delta U}{\Delta T}\Delta T + nR\Delta T. \tag{18}$$

Since infinitesimally, we need the same amount of energy to change internal energy of gas whether we do work or not, we have that we have

$$C_p = C_v + nR \tag{19}$$