

## 4.3: Thermal Equilibrium

### Two Systems in Thermal Contact

Consider two systems in thermal contact, as depicted in Figure 4.3.1. The two subsystems #1 and #2 are free to exchange energy, but their respective volumes and particle numbers remain fixed. We assume the contact is made over a surface, and that the energy associated with that surface is negligible when compared with the bulk energies  $E_1$  and  $E_2$ . Let the total energy be  $E = E_1 + E_2$ . Then the density of states  $D(E)$  for the combined system is

$$D(E) = \int dE_1 D_1(E_1) D_2(E - E_1). \quad (4.3.1)$$

The probability density for system #1 to have energy  $E_1$  is then

$$P_1(E_1) = \frac{D_1(E_1) D_2(E - E_1)}{D(E)}. \quad (4.3.2)$$

Note that  $P_1(E_1)$  is normalized:  $\int dE_1 P_1(E_1) = 1$ . We now ask: what is the most probable value of  $E_1$ ? We find out by differentiating  $P_1(E_1)$  with respect to  $E_1$  and setting the result to zero. This requires

$$\begin{aligned} 0 &= \frac{1}{P_1(E_1)} \frac{dP_1(E_1)}{dE_1} = \frac{\partial}{\partial E_1} \ln P_1(E_1) \\ &= \frac{\partial}{\partial E_1} \ln D_1(E_1) + \frac{\partial}{\partial E_1} \ln D_2(E - E_1). \end{aligned}$$

We conclude that the maximally likely partition of energy between systems #1 and #2 is realized when

$$\frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2}. \quad (4.3.3)$$

This guarantees that

$$S(E, E_1) = S_1(E_1) + S_2(E - E_1) \quad (4.3.4)$$

is a maximum with respect to the energy  $E_1$ , at fixed total energy  $E$ .

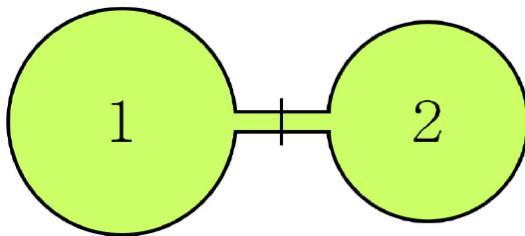


Figure 4.3.1: Two systems in thermal contact.

The *temperature*  $T$  is defined as

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{V,N}, \quad (4.3.5)$$

a result familiar from thermodynamics. The difference is now we have a more rigorous definition of the entropy. When the total entropy  $S$  is maximized, we have that  $T_1 = T_2$ . Once again, two systems in thermal contact and can exchange energy will in equilibrium have equal temperatures.

According to [Equations \ref{phinrel} and \ref{phiurel}](#), the entropies of nonrelativistic and ultrarelativistic ideal gases in  $d$  space dimensions are given by

$$S_{NR} = \frac{1}{2} N d k_B \ln \left( \frac{E}{N} \right) + N k_B \ln \left( \frac{V}{N} \right) + \text{const.} \quad (4.3.6)$$

$$S_{UR} = N d k_B \ln \left( \frac{E}{N} \right) + N k_B \ln \left( \frac{V}{N} \right) + \text{const.} \quad (4.3.7)$$

Invoking Equation 4.3.5, we then have

$$E_{NR} = \frac{1}{2} N d k_B T, \quad E_{UR} = N d k_B T. \quad (4.3.8)$$

We saw that the probability distribution  $P_1(E_1)$  is maximized when  $T_1 = T_2$ , but how sharp is the peak in the distribution? Let us write  $E_1 = E_1^* + \Delta E_1$ , where  $E_1^*$  is the solution to Equation ????. We then have

$$\ln P_1(E_1^* + \Delta E_1) = \ln P_1(E_1^*) + \frac{1}{2k_B} \frac{\partial^2 S_1}{\partial E_1^2} \Big|_{E_1^*} (\Delta E_1)^2 + \frac{1}{2k_B} \frac{\partial^2 S_2}{\partial E_2^2} \Big|_{E_2^*} (\Delta E_1)^2 + \dots, \quad (4.3.9)$$

where  $E_2^* = E - E_1^*$ . We must now evaluate

$$\frac{\partial^2 S}{\partial E^2} = \frac{\partial}{\partial E} \left( \frac{1}{T} \right) = -\frac{1}{T^2} \left( \frac{\partial T}{\partial E} \right)_{V,N} = -\frac{1}{T^2 C_V}, \quad (4.3.10)$$

where  $C_V = (\partial E / \partial T)_{V,N}$  is the heat capacity. Thus,

$$P_1 = P_1^* e^{-(\Delta E_1)^2 / 2k_B T^2 \bar{C}_V}, \quad (4.3.11)$$

where

$$\bar{C}_V = \frac{C_{V,1} C_{V,2}}{C_{V,1} + C_{V,2}}. \quad (4.3.12)$$

The distribution is therefore a Gaussian, and the fluctuations in  $\Delta E_1$  can now be computed:

$$\langle (\Delta E_1)^2 \rangle = k_B T^2 \bar{C}_V \implies (\Delta E_1)_{RMS} = k_B T \sqrt{\bar{C}_V / k_B}. \quad (4.3.13)$$

The individual heat capacities  $C_{V,1}$  and  $C_{V,2}$  scale with the volumes  $V_1$  and  $V_2$ , respectively. If  $V_2 \gg V_1$ , then  $C_{V,2} \gg C_{V,1}$ , in which case  $\bar{C}_V \approx C_{V,1}$ . Therefore the RMS fluctuations in  $\Delta E_1$  are proportional to the *square root* of the system size, whereas  $E_1$  itself is extensive. Thus, the ratio  $(\Delta E_1)_{RMS} / E_1 \propto V^{-1/2}$  scales as the inverse square root of the volume. The distribution  $P_1(E_1)$  is thus *extremely sharp*.

## Thermal, mechanical and chemical equilibrium

We have  $dS|_{V,N} = \frac{1}{T} dE$ , but in general  $S = S(E, V, N)$ . Equivalently, we may write  $E = E(S, V, N)$ . The full differential of  $E(S, V, N)$  is then  $dE = T dS - p dV + \mu dN$ , with  $T = \left( \frac{\partial E}{\partial S} \right)_{V,N}$  and  $p = -\left( \frac{\partial E}{\partial V} \right)_{S,N}$  and  $\mu = \left( \frac{\partial E}{\partial N} \right)_{S,V}$ . As we shall discuss in more detail,  $p$  is the *pressure* and  $\mu$  is the *chemical potential*. We may thus write the total differential  $dS$  as

$$dS = \frac{1}{T} dE + \frac{p}{T} dV - \frac{\mu}{T} dN. \quad (4.3.14)$$

Employing the same reasoning as in the previous section, we conclude that entropy maximization for two systems in contact requires the following:

- If two systems can exchange energy, then  $T_1 = T_2$ . This is *thermal equilibrium*.
- If two systems can exchange volume, then  $p_1 / T_1 = p_2 / T_2$ . This is *mechanical equilibrium*.
- If two systems can exchange particle number, then  $\mu_1 / T_1 = \mu_2 / T_2$ . This is *chemical equilibrium*.

## Gibbs-Duhem Relation

The energy  $E(S, V, N)$  is an extensive function of extensive variables, it is homogeneous of degree one in its arguments. Therefore  $E(\lambda S, \lambda V, \lambda N) = \lambda E$ , and taking the derivative with respect to  $\lambda$  yields

$$\begin{aligned} E &= S \left( \frac{\partial E}{\partial S} \right)_{V,N} + V \left( \frac{\partial E}{\partial V} \right)_{S,N} + N \left( \frac{\partial E}{\partial N} \right)_{S,V} \\ &= TS - pV + \mu N \quad . \end{aligned}$$

Taking the differential of each side, using the Leibniz rule on the RHS, and plugging in  $dE = T dS - p dV + \mu dN$  , we arrive at the *Gibbs-Duhem relation*<sup>5</sup>,

$$S dT - V dp + N d\mu = 0 \quad . \quad (4.3.15)$$

This, in turn, says that any one of the intensive quantities  $(T, p, \mu)$  can be written as a function of the other two, in the case of a single component system.

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