Chapter 1

ThermoS26-07

1.1 Equilibrium with a heat Bath

Consider two isolated systems that are initially isolated from each other.

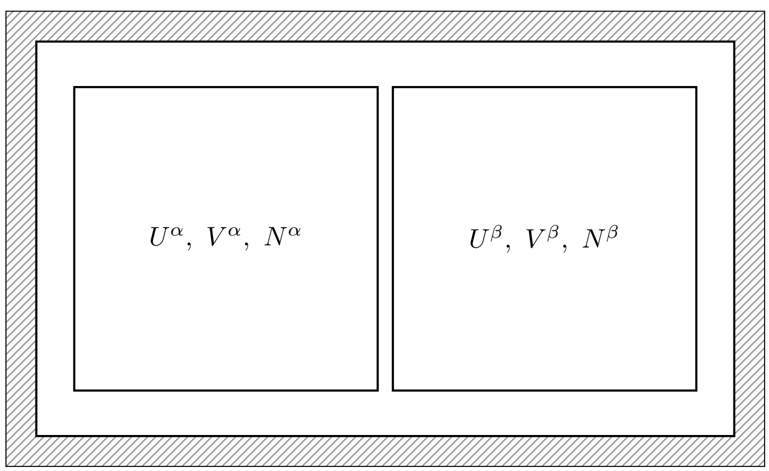

Figure 1.1: Two isolated systems initially separated by insulating walls.

Now, let us remove the isolating walls so that energy, volume, and mass may be exchanged.

The entropy will attain its maximum at equilibrium and

$$T^\alpha = T^\beta$$

$$P^\alpha = P^\beta$$

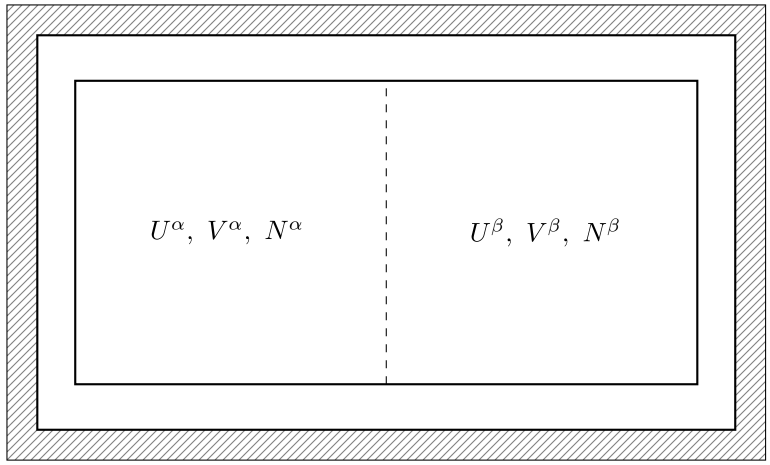

Figure 1.2: Isolating wall removed so energy, volume, and mass can be exchanged.

$$\mu_i^\alpha = \mu_i^\beta, \qquad i = 1, \ldots, r.$$

How can we characterize equilibrium?

Now, suppose that instead of isolating from the universe, our composite system is put into contact with a heat bath.

Definition 1.1.1. (5.9) A heat bath is an otherwise- isolated thermodynamic system that is so large that, when it exchanges a finite amount of energy with an otherwise-isolated, composite system, its temperature, pressure, and chemical potential changes are so small as to be negligible.

Similarly, we have

heat-pressure bath: finite exchanges of energy and volume lead to negligible changes in T, P, and μ in baths.

A heat-pressure-chemical bath is defined analogously.

Let us consider a picture for the case of the heat bath.

Let us recall the "integrated form" of the entropy function.

$$\tilde{S}^B = \tilde{S}^B(U^B, V^B, N^B) = \frac{1}{T^0}U^B + \frac{P^0}{T^0}V^B - \frac{\mu^0}{T^0} \cdot N^B$$

where

$$T^0 = T^0(U^0, V^0, N^0)$$

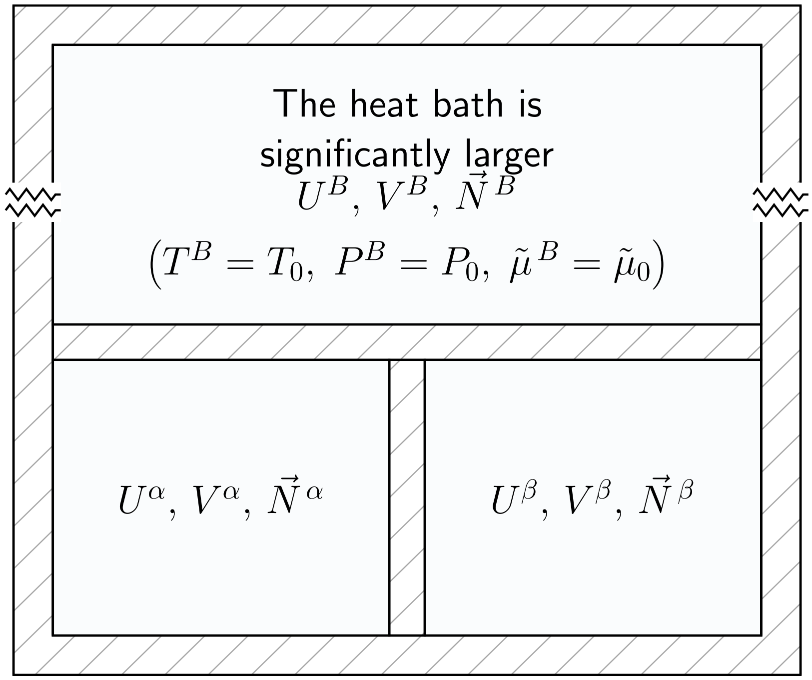

Figure 1.3: Composite system in contact with a heat bath.

et cetera. We will write

$$\begin{aligned} S^{tot} &= \tilde{S}^B + \tilde{S}^\alpha + \tilde{S}^\beta \\ &= \tilde{S}^B + \tilde{S}^{\alpha+\beta} \end{aligned}$$

Now, our system will not exchange volume or mass with the bath, only energy, because we will replace the horizontal isolations wall with a diathermal wall.

We know that, at equilibrium

$$T^\alpha = T^\beta = T^B = T_0.$$

Recall the deviations of T^B from T_0 at equilibrium is assumed negligible.

System α and β can exchange energy. System α and β can exchange volume and mass with each other but not with the bath.

Thus,

$$S^{tot,eq} = \max_{C}\{\tilde{S}^B + \tilde{S}^{\alpha+\beta}\}$$

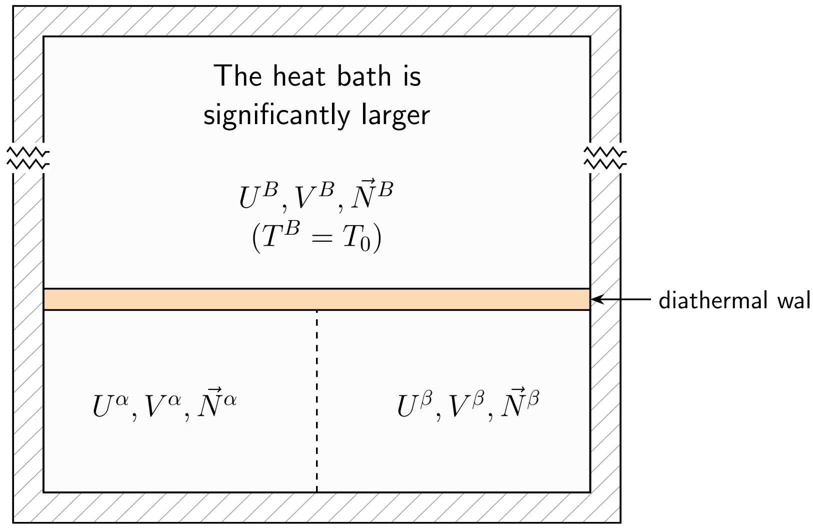

Figure 1.4: Diathermal wall configuration: only energy exchange with the bath.

Now

$$\tilde{S}^B = \frac{1}{T_0}U^B + \frac{P_0}{T_0}V^B - \frac{\mu_0}{T_0} \cdot N^B$$

The changes in T^B, P^B, μ^B from T_0, P_0, μ_0 is negligible because the bath is so large.

Writing

$$U^B = U_0 - U^\alpha - U^\beta$$

$$\tilde{S}^B = -\frac{U^\alpha}{T_0} - \frac{U^\beta}{T_0} + \frac{U_0}{T_0} + C_1$$

$$= -\frac{U^\alpha}{T_0} - \frac{U^\beta}{T_0} + C_2$$

Thus,

$$\begin{aligned} S^{tot,eq} &= \max_C \left\{ -\frac{U^\alpha}{T_0} - \frac{U^\beta}{T_0} + C_2 + \tilde{S}^{\alpha+\beta} \right\} \\ &= C_2 + \max_C \left\{ -\frac{U^\alpha + U^\beta}{T_0} + \tilde{S}^\alpha + \tilde{S}^\beta \right\} \\ &= C_2 + \max_C \left\{ -\frac{F^\alpha + F^\beta}{T_0} \right\} \\ &= C_2 - \frac{1}{T_0} \min_C \left\{ F^\alpha(T_0, V^\alpha, N^\alpha) + F^\beta(T_0, V^\beta, N^\beta) \right\} \end{aligned}$$

Postulate VI: Consider a compound, otherwise- isolated thermodynamic system in contact with an otherwise-isolated heat bath at temperature T_0. Equilibrium of the compound system is the state satisfying the isothermal condition

$$T^\alpha = T^\beta = T_0$$

which minimizes

$$F^\alpha(T_0, V^\alpha, N^\alpha) + F^\beta(T_0, V^\beta, N^\beta)$$

subject to the constraints

$$V^\alpha + V^\beta = V_0, \qquad \text{(volume conservation)}$$

$$N_i^\alpha + N_i^\beta = N_{i,0}, \qquad \text{(mass conservation)}$$

Remark: Since the system $\alpha + \beta$ exchanges energy with the heat bath, energy is not conserved in $\alpha + \beta$.

Energy is conserved in the system $B + \alpha + \beta$.