

## Part II: Thermodynamics

### II.3 General Interaction

Class schedule: Feb 10, 12

Reading assignments: S8, R3.8-3.12, R4.3-4.5

Examples marked with \* are important and should be studied carefully.

#### II.3.1 Generalized force and work

From the first law:  $dE = dQ - dW$ , all sorts of work may lead to the change of internal energy in a way  $dE = -\sum dW_\alpha = -\sum_\alpha F_\alpha dx_\alpha$ , where  $x_\alpha$  is the infinitesimal change in a certain external parameter of the system, and  $F_\alpha$  is the corresponding force, or generalized force, which can be derived as  $F_\alpha = -\partial E / \partial x_\alpha$ .

Example 1: examples of generalized work and force.

#### II.3.2 Change of entropy with external parameters

The change of external parameters, such as the volume of a gas, will change the number of accessible micro-states or entropy of the system as

$$\frac{\partial S}{\partial x_\alpha} = \frac{F_\alpha}{T}$$

Specifically,

$$\frac{\partial S}{\partial V} = \frac{P}{T}$$

Remark: 1.  $dS = dQ/T$ , the second law holds for a system with both thermal and general interactions with other systems; 2.  $S$  is a state parameter, only depending on the macroscopic properties, and  $dS$  is an exact differential indicating the infinitesimal difference between two macro-states, even though  $dQ$  is an inexact differential dependent on the evolution path. However, for macroscopic measurement of  $\Delta S$  of a system, we can heat (or cool) the system quasi-statically to very gradually raise (or lower) the temperature, and the integral of  $dQ/T$  along all quasi-static steps will yield  $\Delta S$ .

Example 2: suppose that a system absorbs heat quasi-statically by  $dQ = C_1 dT$ , where  $C_1$  indicates the amount of heat needed by the system to raise the temperature of the system by 1 K degree. Find the entropy change when the system evolves quasi-statically from an initial state with  $T_i$  to the final state with  $T_f$ .

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T} = \int_i^f \frac{C_1 dT}{T} = C_1 \ln\left(\frac{T_f}{T_i}\right)$$

Example 3: suppose that we heat a system quasi-statically so that the system increases its internal energy by  $dE = C_2 dT$  as well as expands quasi-statically at the mean pressure  $P$ . Find the entropy

change when the system evolves from the initial  $(T_i, V_i)$  state to the final  $(T_f, V_f)$  state.

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T} = \int_i^f \frac{dE + PdV}{T} = \int_i^f \frac{C_2 dT + PdV}{T}$$

*heat capacity:*  $C_1$  and  $C_2$  in the above examples are, by definition, *heat capacities*, indicating the amount of heat a system needs to increase its temperature by 1 K degree. Depending on the constraints the system is subject to, the heat capacity may vary.

In general, if  $dQ = C_y dT$ , thus  $C_y = \partial Q / \partial T$ , while keeping  $y$  as a constant, then  $C_y$  is the heat capacity with  $y$  as a constant.

### II.3.3 Equilibrium between interacting systems

The full expression of the second law:

$$dS = \frac{dE}{T} + \frac{1}{T} \sum_{\alpha} F_{\alpha} dx_{\alpha}$$

there are:

$$\begin{aligned} \left. \frac{\partial S}{\partial E} \right)_{x_{\alpha}} &= \frac{1}{T} \\ \left. \frac{\partial S}{\partial x_{\alpha}} \right)_{E, x_{\beta}, \beta \neq \alpha} &= \frac{F_{\alpha}}{T} \end{aligned}$$

Specifically for work done by pressure:

$$\begin{aligned} dS &= \frac{dE}{T} + \frac{P}{T} dV \\ \left. \frac{\partial S}{\partial E} \right)_{V} &= \frac{1}{T} \\ \left. \frac{\partial S}{\partial V} \right)_{E} &= \frac{P}{T} \end{aligned}$$

\*Example 4: find the condition of equilibrium for combined systems of  $A_1$  and  $A_2$  that have thermal and mechanical interactions with the constraints  $E_1 + E_2 = E_0$  and  $V_1 + V_2 = V_0$ .

With the maximum entropy argument as in II.2, but now with two independent variables  $E_1$  and  $V_1$ , we reach the conditions for the final equilibrium:  $T_1 = T_2$ , i.e., thermal equilibrium, and  $P_1 = P_2$ , i.e., mechanical equilibrium.