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 \( dE = -\Sigma dW_\alpha = -\Sigma_\alpha F_\alpha dx_\alpha \), 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 \( dQ = C_1dT \), 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 \( T_f \).

\[
\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T} = \int_i^f \frac{C_1dT}{T} = C_1ln\left(\frac{T_f}{T_i}\right)
\]

Example 3: suppose that we heat a system quasi-statically so that the system increases its internal energy by \( dE = C_2dT \) 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.

\[
\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T} = \int_i^f \frac{dE + PdV}{T} = \int_i^f \frac{C_2dT + PdV}{T}
\]

*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 \(dQ = C_ydT\), 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:

\[
dS = \frac{dE}{T} + \frac{1}{T} \Sigma_{\alpha} F_{\alpha} dx_{\alpha}
\]

there are:

\[
\left(\frac{\partial S}{\partial E}\right)_{x_{\alpha}} = \frac{1}{T}
\]

\[
\left(\frac{\partial S}{\partial x_{\alpha}}\right)_{E, x_{\beta}, \beta \neq \alpha} = \frac{F_{\alpha}}{T}
\]

Specifically for work done by pressure:

\[
dS = \frac{dE}{T} + \frac{P}{T} dV
\]

\[
\left(\frac{\partial S}{\partial E}\right)_V = \frac{1}{T}
\]

\[
\left(\frac{\partial S}{\partial V}\right)_E = \frac{P}{T}
\]

*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.