

2.F.0. Overview

Thermodynamics begins by dividing the states of a system into two separate categories, equilibrium and non-equilibrium, and proceeds to deal exclusively with the former. The role of the non-equilibrium states is merely to impose constraints via the 2nd law.

Every equilibrium state is represented by a (system) point in a phase space Γ . For a system described by \mathcal{N} conjugate pairs of state variables, Γ is $2\mathcal{N}$ -D. This corresponds to the Hamiltonian formalism in classical mechanics.

In the analog of the Lagrangian formalism in classical mechanics, we choose the set of \mathcal{N} extensive variables

$$\mathcal{X} = \{\mathcal{X}_k; k = 1, \dots, \mathcal{N}\} = \{S, \mathbf{X}, \{N_j\}\} \quad (2.66a)$$

to form the configuration space. The internal energy $U(\mathcal{X})$ is then defined as an analytic function on the configuration space. This means dU is an exact differential so that

$$dU = \frac{\partial U}{\partial \mathcal{X}} \cdot d\mathcal{X} = \frac{\partial U}{\partial S} dS + \frac{\partial U}{\partial \mathbf{X}} \cdot d\mathbf{X} + \sum_j \frac{\partial U}{\partial N_j} dN_j \quad (2.66b)$$

which is just the 1st law for reversible processes

$$dU = T dS + \mathbf{Y} \cdot d\mathbf{X} + \sum_j \mu_j' dN_j$$

if we define the intensive variables as

$$\mathcal{Y}_j = \frac{\partial U}{\partial \mathcal{X}_j} \quad \text{or} \quad \mathcal{Y} = \frac{\partial U}{\partial \mathcal{X}} = \{T, \mathbf{Y}, \{\mu_j'\}\} \quad (2.66c)$$

i.e., the conjugates of the extensive variables with respect to U .

Note that $\mathcal{Y} \cdot d\mathcal{X}$ is the work done on the system by the external force \mathcal{Y} . In contrast, in the electrostatic relation

$$\mathbf{E} = -\frac{\partial \phi}{\partial \mathbf{r}} \quad (a)$$

where ϕ is the electric potential, \mathbf{E} is the “force” exerted by the system (the electric field) on any external charges present. Hence the opposite signs used in (2.66b) & (a).

Now, for a fixed value of U , the system point (or equilibrium state) is restricted to a \mathcal{N} -D manifold \mathcal{M}_U in the phase space Γ with coordinates

$$(\mathcal{X}_1, \dots, \mathcal{X}_N, \mathcal{Y}_1, \dots, \mathcal{Y}_N) = \left(\mathcal{X}_1, \dots, \mathcal{X}_N, \frac{\partial U}{\partial \mathcal{X}_1}, \dots, \frac{\partial U}{\partial \mathcal{X}_N} \right) \quad (2.66d)$$

Owing to the equation of state, trajectories of the system are further restricted to a $(\mathcal{N} - 1)$ -D sub-manifold \mathcal{M}_{sys} of \mathcal{M}_U .

By (2.66c), \mathcal{Y} is a **conservative force**, meaning that

$$\oint \mathcal{Y} \cdot d\mathcal{X} = \oint dU = 0 \quad (2.66e)$$

for any closed path in \mathcal{M}_U , i.e., dU is exact.

For convenience, the system is said to be described by the set of quantities

$$\mathcal{I}_U = \{U, \mathcal{X}_1, \dots, \mathcal{X}_N\}$$

From a mathematical point of view, all variables in Γ are equivalent. The choice of \mathcal{X} as the generalized displacements (or independent variables) is therefore arbitrary. Thus, we can pick any \mathcal{N} phase space variables as the generalized displacements, leaving the other \mathcal{N} as generalized forces.

The role switching between the conjugate pair $(\mathcal{X}_i, \mathcal{Y}_i)$ can be accomplished by the **Legendre transform**,

$$L \equiv U - \frac{\partial U}{\partial \mathcal{X}_i} \mathcal{X}_i = U - \mathcal{Y}_i \mathcal{X}_i \quad (2.66f)$$

$d(2.66f)$ gives

$$\begin{aligned} dL &= dU - \mathcal{Y}_i d\mathcal{X}_i - \mathcal{X}_i d\mathcal{Y}_i \\ &= -\mathcal{X}_i d\mathcal{Y}_i + \sum_{k \neq i} \mathcal{Y}_k d\mathcal{X}_k \quad [(2.66c) \text{ used. }] \quad (2.66g) \end{aligned}$$

so that

$$L = L(\mathcal{X}_1, \dots, \mathcal{X}_{i-1}, \mathcal{Y}_i, \mathcal{X}_{i+1}, \dots, \mathcal{X}_N)$$

with

$$\mathcal{X}_i = -\frac{\partial L}{\partial \mathcal{Y}_i} \quad \mathcal{Y}_k = \frac{\partial L}{\partial \mathcal{X}_k} \quad \forall k \neq i \quad (2.66h)$$

Thus, the Legendre transform (2.66f) replaces any \mathcal{X}_i in \mathcal{I}_U with its conjugate \mathcal{Y}_i , and hence \mathcal{I}_U by

$$\mathcal{I}_L = \{L, \mathcal{X}_1, \dots, \mathcal{X}_{i-1}, \mathcal{Y}_i, \mathcal{X}_{i+1}, \dots, \mathcal{X}_N\}$$

The system point is again restricted to a \mathcal{N} -D manifold \mathcal{M}_L in Γ , with coordinates

$$\left(\mathcal{X}_1, \dots, \mathcal{X}_{i-1}, -\frac{\partial L}{\partial \mathcal{Y}_i}, \mathcal{X}_{i+1}, \dots, \mathcal{X}_N, \frac{\partial L}{\partial \mathcal{X}_1}, \dots, \frac{\partial L}{\partial \mathcal{X}_{i-1}}, \mathcal{Y}_i, \frac{\partial L}{\partial \mathcal{X}_{i+1}}, \frac{\partial L}{\partial \mathcal{X}_N} \right) \quad (2.66i)$$

Since \mathcal{I}_U & \mathcal{I}_L are two equivalent descriptions of the system, we expect \mathcal{M}_U and \mathcal{M}_L to be the same manifold in Γ , albeit expressed in different coordinates. Proof of this falls into the purview of differential geometry and shall not be pursued here.

Obviously, we can continue to replace other \mathcal{X}_k 's with their conjugates \mathcal{Y}_k and obtain other state functions of the corresponding set of independent state variables. Like U , these state functions are also called **thermodynamic potentials**. They are potential energies on \mathcal{M}_U expressed in different sets of independent coordinates.