

## 2.F.1. Internal Energy

As discussed in §2.F.0, the **internal energy**  $U = U(X_1, \dots, X_N)$  is the prototype of the thermodynamic potentials. Its explicit form is given by the fundamental equation (2.61) as

$$U = ST + \mathbf{Y} \cdot \mathbf{X} + \sum_j \mu_j' N_j = \sum_{k=1}^N X_k \mathcal{Y}_k = \mathcal{Y} \cdot \mathbf{X} \quad (2.66)$$

For any process that takes the system from a point (or equilibrium state)  $\mathbf{X}$  to point  $\mathbf{X} + d\mathbf{X}$  on  $\mathcal{M}_U$ , we always have

$$dU = \mathcal{Y} \cdot d\mathbf{X} = TdS + \mathbf{Y} \cdot d\mathbf{X} + \sum_j \mu_j' dN_j \quad (2.67a)$$

If the process is irreversible, then the 2nd law gives

$$dU > \bar{d}Q + \mathbf{Y} \cdot d\mathbf{X} + \sum_j \mu_j' dN_j \quad (2.67b)$$

Combing the 1st & 2nd law [ see (2.21) & (2.28) ] gives

$$\begin{aligned} dU &= \bar{d}Q - \bar{d}W \\ &\leq TdS - \bar{d}W \end{aligned} \quad (2.67c)$$

**Caution:** For irreducible processes,  $\bar{d}W$  cannot be written in the form  $-\mathbf{Y} \cdot d\mathbf{X}$ . (2.67c) is therefore not equivalent to Reichl's (2.67).

From (2.67a), we have

$$\mathcal{Y} = \frac{\partial U}{\partial \mathbf{X}} \quad \text{or} \quad \mathcal{Y}_k = \frac{\partial U}{\partial X_k} \quad (2.68a)$$

More specifically,

$$T = \left( \frac{\partial U}{\partial S} \right)_{\mathbf{X}, \{N_j\}} \quad (2.68)$$

$$Y_k = \left( \frac{\partial U}{\partial X_k} \right)_{S, \{X_{l \neq k}\}, \{N_j\}} \quad (2.69)$$

$$\mu_j' = \left( \frac{\partial U}{\partial N_j} \right)_{S, \mathbf{X}, \{N_{k \neq j}\}} \quad (2.70)$$

From the necessary condition (2.4) of an exact differential, we have

$$\begin{aligned} \frac{\partial}{\partial X_j} \left( \frac{\partial U}{\partial X_k} \right) &= \frac{\partial}{\partial X_k} \left( \frac{\partial U}{\partial X_j} \right) \\ \rightarrow \frac{\partial \mathcal{Y}_k}{\partial X_j} &= \frac{\partial \mathcal{Y}_j}{\partial X_k} \quad [ (2.68a) \text{ used. } ] \end{aligned} \quad (2.71a)$$

which are called **Maxwell relations**.

As an example,

$$\frac{\partial}{\partial X_j} \left( \frac{\partial U}{\partial S} \right) = \frac{\partial}{\partial S} \left( \frac{\partial U}{\partial X_j} \right) \quad (2.71)$$

$$\rightarrow \frac{\partial T}{\partial X_j} = \frac{\partial Y_j}{\partial S} \quad [ (2.68-9) \text{ used. } ] \quad (2.71a)$$

or, in its full notations,

$$\left(\frac{\partial T}{\partial X_j}\right)_{S, \{X_{k \neq j}\}, \{N_j\}} = \left(\frac{\partial Y_j}{\partial S}\right)_{X, \{N_j\}} \quad (2.72)$$

where the variables that are held constant can be read directly from the list of independent variables

$$\mathcal{X} = \{S, X, \{N_j\}\}$$

The full notational form of (2.72) is necessary since the list of independent variables is not obvious if we are given only (2.71a).

Similarly,

$$\begin{aligned} \frac{\partial}{\partial N_j} \left(\frac{\partial U}{\partial S}\right) &= \frac{\partial}{\partial S} \left(\frac{\partial U}{\partial N_j}\right) \\ \rightarrow \left(\frac{\partial T}{\partial N_j}\right)_{S, X, \{N_{k \neq j}\}} &= \left(\frac{\partial \mu_j'}{\partial S}\right)_{X, \{N_j\}} \end{aligned} \quad (2.73)$$

$$\begin{aligned} \frac{\partial}{\partial N_j} \left(\frac{\partial U}{\partial X_k}\right) &= \frac{\partial}{\partial X_k} \left(\frac{\partial U}{\partial N_j}\right) \\ \rightarrow \left(\frac{\partial Y_k}{\partial N_j}\right)_{S, X, \{N_{i \neq j}\}} &= \left(\frac{\partial \mu_j'}{\partial X_k}\right)_{S, \{X_{i \neq k}\}, \{N_j\}} \end{aligned} \quad (2.74)$$

and

$$\begin{aligned} \frac{\partial}{\partial N_j} \left(\frac{\partial U}{\partial N_k}\right) &= \frac{\partial}{\partial N_k} \left(\frac{\partial U}{\partial N_j}\right) \\ \rightarrow \left(\frac{\partial \mu_k'}{\partial N_j}\right)_{S, X, \{N_{i \neq j}\}} &= \left(\frac{\partial \mu_j'}{\partial N_k}\right)_{S, X, \{N_{i \neq k}\}} \end{aligned} \quad (2.75)$$

As already discussed in §2.E, we can also replace  $\mathcal{X}$  with its density  $x = \mathcal{X}/\mathcal{D}$  where  $\mathcal{D}$  is a quantity related to the size of the system. The foregoing equations can then be put into a form that is size independent [see (2.63a,b), (2.64a), & (2.63-5a)].

If we include reversible work  $W_{\text{free}}$  done by the system while keeping  $\mathcal{X}$  constant, the (reversible) work  $W_{\text{rev}}$  done by the system can be written as

$$W_{\text{rev}} = W_X + W_{\text{free}}$$

where

$$W_X = - \int \mathbf{Y} \cdot d\mathbf{X} - \sum_j \int \mu_j' dN_j = \text{reversible work involving changes in } X \text{ \& \{N}_j\}.$$

The 1st law for reversible processes then gives

$$\begin{aligned} \Delta U &= Q - W_{\text{rev}} = \int T dS - (W_X + W_{\text{free}}) \\ &= -W_{\text{free}} \quad \text{for } \mathcal{X} = \text{const} \end{aligned} \quad (2.76)$$

Thus,  $W_{\text{free}}$  is converted entirely into  $U$  for reversible processes that keep  $\mathcal{X}$  constant. According to the definition in classical mechanics,  $U$  is then the potential energy of the system for reversible processes that keep  $\mathcal{X}$  constant.

To see how one can do work on a system without changing  $\mathcal{X}$ , consider a monatomic gas in a closed, insulated box of cross section  $A$ , length  $L$ , and volume  $V = AL$ . The gas is then divided into two chambers, 1 & 2, by a movable and heat conducting partition controlled by an external force  $f$ . We shall

assume that for  $f > 0$ ,  $V_2$  is  $\begin{matrix} \text{reduced} \\ \text{increased} \end{matrix}$  [ see Fig.2.7 ].

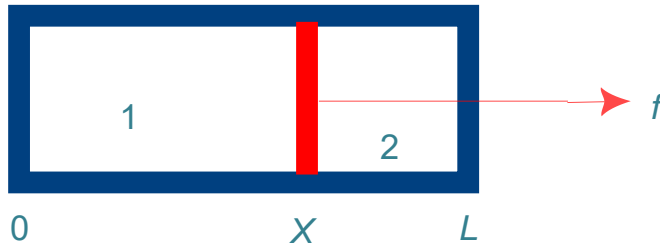


Fig.2.7.

The phase space  $\Gamma'$  of the system is 8-D with coordinates  $(S_1, T_1, V_1, P_1, S_2, T_2, V_2, P_2)$ .

Owing to the equilibrium criteria

$$T_1 = T_2 \equiv T \quad \& \quad P_1 = P_2 - \frac{f}{A} \equiv P$$

the system point is restricted to a 6-D manifold in  $\Gamma'$ . Any state point outside  $\Gamma'$  is expected to move spontaneously back into  $\Gamma'$  through some irreversible process.

The 1st law for reversible processes gives

$$\begin{aligned} dU_1 &= T_1 dS_1 + P_1 dV_1 = T dS_1 + P dV_1 \\ dU_2 &= T_2 dS_2 + P_2 dV_2 = T dS_2 + P dV_2 - \left| \frac{f}{A} dV_2 \right| \end{aligned}$$

where we have used the fact that  $f$  and  $dV_2$  are always opposite in sign.

Combining the 2 expressions gives

$$d(U_1 + U_2) = T d(S_1 + S_2) + P d(V_1 + V_2) - \left| \frac{f}{A} dV_2 \right|$$

$$\rightarrow dU = T dS + P dV - \bar{d}W_{\text{free}} \quad (2.76a)$$

where

$$U = U_1 + U_2 \quad S = S_1 + S_2 \quad V = V_1 + V_2$$

and

$$\bar{d}W_{\text{free}} = - \left| \frac{f}{A} dV_2 \right| \quad (2.76b)$$

Thus, the system can be considered as a gas with phase space  $\Gamma = (S, T, V, P)$  in which every point is an equilibrium state. (2.76b) is what we sought: work without changing  $\mathcal{X}$ .

Let the length of the box be along the  $x$ -axis so that the end faces of the box are at  $x=0$  &  $L$ . Then

$$V_1 = xA \quad V_2 = (L-x)A$$

so

$$\bar{d}W_{\text{free}} = - | f dx |$$

describes the coupling of an external force  $f$  with the internal parameter  $x$ .

Note that the internal degrees of freedom  $(S_j, T_j, V_j, P_j)$  are completely specified for a given state  $(S, T, V, P)$  if  $(f, x)$  is given. Furthermore, the argument can easily extended to systems with arbitrary number of partitions.

Consider the state where the partition is at  $x$ . Its internal energy is therefore

$$U = U_0 + |f(x - x_0)| \\ \geq U_0$$

Thus,  $-W_{\text{free}}$  is stored in the system in the form of internal energy, which can be exacted to do work by reversible processes at a later time.

Furthermore, the state  $(S, T, V, P = P_1 \neq P_2)$  is not on the manifold given by the equation of state. Hence, it is not an equilibrium state. We shall call it a **constrained state**. In general, if the constraint is removed, a constrained state will evolve spontaneously towards a state on the equilibrium manifold. In the present case, if we set  $f = 0$ , the partition will snap back to the equilibrium position  $x_0$ , which corresponds to the state of lowest internal energy  $U_0$  that lies on the equilibrium manifold. During the spontaneously process, no work is done so that the 1st law gives

$$\Delta U = U_0 - U = Q < 0 \quad (2.82)$$

i.e., the work done by  $f$  on the system is given off entirely as heat. According to the 2nd law

$$Q < \int T ds$$

where the integral is along any path in  $\Gamma$  linking the initial & final states.

It is a worthwhile exercise to work out the above conclusions using the ideal gas law.