Thermodynamic Processes: The Limits of Possible

Thermodynamics put severe restrictions on what processes involving a change of the thermodynamic state of a system (U,V,N,…) are possible.

In a *quasi-static process* system moves from one equilibrium state to another via a series of other equilibrium states.

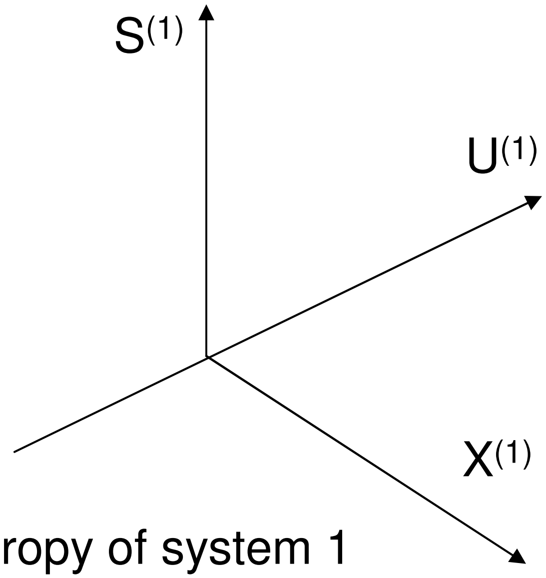
All quasi-static processes fall into two main classes: **reversible** and **irreversible** processes.

Processes with decreasing total entropy of a thermodynamic system and its environment are prohibited by Postulate II

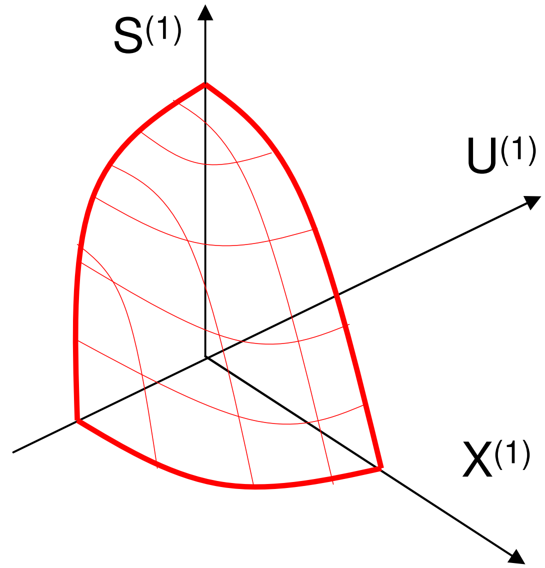
Notes

Graphic representation of a single thermodynamic system

Phase space of extensive coordinates of a thermodynamic system



The fundamental relation $S^{(1)}=S(U^{(1)}, X^{(1)})$ defines a hypersurface in the coordinate space



$S^{(1)}$ – entropy of system 1

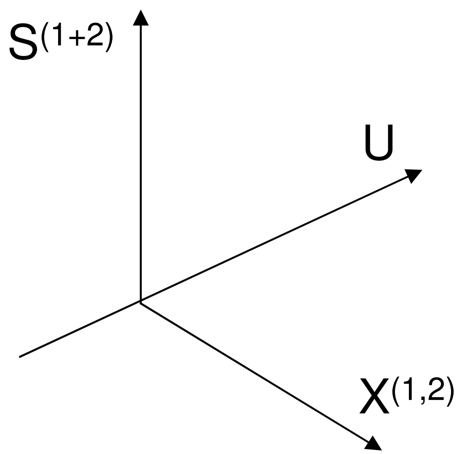
$U^{(1)}$ – energy of system 1

$X^{(1)} = V^{(1)}, N_1^{(1)}, \ldots N_m^{(1)}$ – coordinates of system 1

Notes

Graphic representation of a composite thermodynamic system

Phase space of extensive coordinates of a *composite* thermodynamic system (system 1 and system 2).

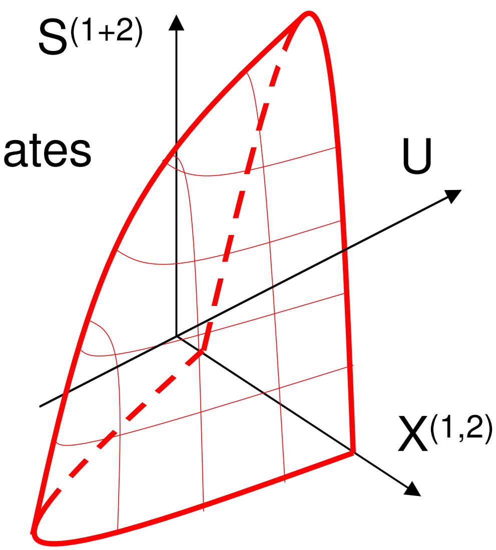


S – entropy of a composite system

U – energy of a composite system

The fundamental relation $S = S^{(1)}(U^{(1)}, X^{(1)}) + S^{(2)}(U-U^{(1)},X^{(2)})$ defines a hyper-surface in the coordinate space of the composite system

$X^{(1,2)} = V, N_1, \ldots N_m$ – coordinates of subsystems (1 and 2)

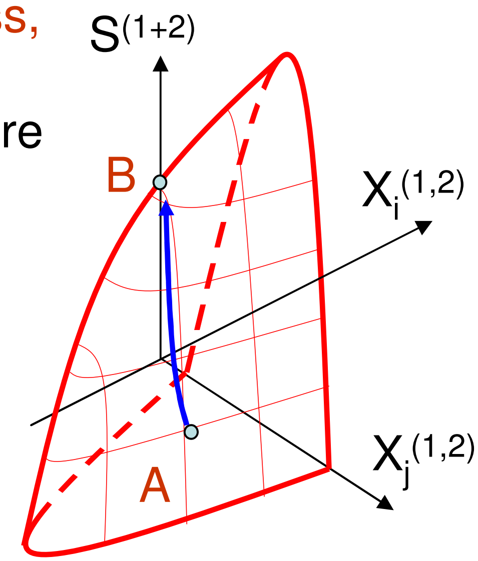


Notes

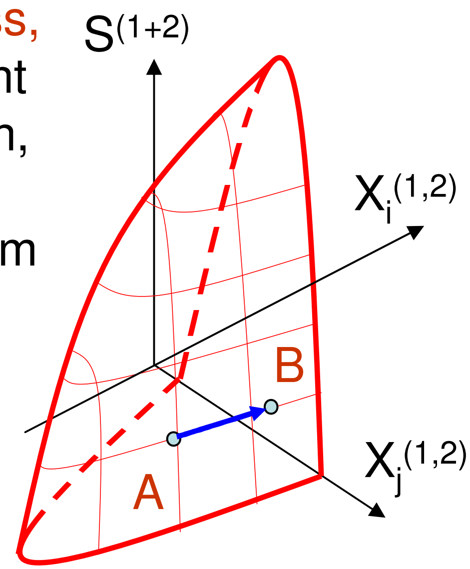
Irreversible and reversible processes

If we change constraints on some of the composite system coordinates, (e.g. X_i and X_j) the composite system relaxes to a new equilibrium state with the maximum possible entropy consistent with the new constraints

Irreversible process, entropy increases (most processes are like that)



Reversible process, Entropy is constant (idealized situation, there is no real drive for the system as Postulate II Is not at work)



Notes

Heat and Entropy

If we have flow of heat between two subsystems, then: $\delta Q_1 = -\delta Q_2$

$$\delta Q_1 = T_1 dS_1 \qquad \delta Q_2 = T_2 dS_2$$

If temperatures of the two subsystems are equal to each other: $T_1 = T_2$

$$dS_1 = -dS_2 \quad \Longrightarrow \quad dS = dS_1 + dS_2 = 0$$

then the process is reversible.

Heat flow between systems with different temperatures is always irreversible.

Notes

Heat capacity and heat flow

Let us consider a situation of $T_1 > T_2$ before we remove adiabatic wall between the two systems.

After new equilibrium is reached, the final temperature of the two systems is T_f.

Let us also make a simplifying assumption that heat capacity ($C_V = dU/dT$) at constant volume for these systems does not depend on temperature:

$$\Delta U_1 = C_1 \left(T_f - T_1 \right) \qquad \Delta U_2 = C_2 \left(T_f - T_2 \right)$$

Notes

Equilibrium temperature

$$\Delta U_1 = C_1 \left(T_f - T_1\right) \qquad \Delta U_2 = C_2 \left(T_f - T_2\right)$$

Total energy of the composite system must be conserved:

$$\Delta U = \Delta U_1 + \Delta U_2 = \left(C_1 + C_2\right) T_f - \left(C_1 T_1 + C_2 T_2\right) = 0$$

$$T_f = \frac{\left(C_1 T_1 + C_2 T_2\right)}{\left(C_1 + C_1\right)}$$

Notes

Entropy Change

$$dS_1 = \frac{\delta Q_1}{T_1} = \frac{C_1 dT_1}{T_1} \Longrightarrow \Delta S_1 = C_1\left(\ln(T_f) - \ln(T_1)\right) = C_1 \ln\left(\frac{T_f}{T_1}\right)$$

For the composite system:

$$\Delta S = \Delta S_1 + \Delta S_2 = C_1 \ln\left(\frac{T_f}{T_1}\right) + C_2 \ln\left(\frac{T_f}{T_2}\right)$$

$$\Delta S = C_1 \ln\left(\frac{C_1 T_1 + C_2 T_2}{T_1(C_1 + C_2)}\right) + C_2 \ln\left(\frac{C_1 T_1 + C_2 T_2}{T_2(C_1 + C_2)}\right) > 0$$

Notes

Heat flow is irreversible

$$\Delta S = C_1 \ln\left(\frac{C_1T_1 + C_2T_2}{T_1(C_1 + C_2)}\right) + C_2 \ln\left(\frac{C_1T_1 + C_2T_2}{T_2(C_1 + C_2)}\right) > 0$$

Taking for simplicity, $C_1 = C_2$:

$$\Delta S = C \ln\left(\frac{T_1 + T_2}{2T_1}\right) + C \ln\left(\frac{T_1 + T_2}{2T_2}\right) = C \ln\left(\frac{(T_1 + T_2)^2}{4T_2T_1}\right) > 0$$

Irreversible process $\quad T_1 > T_2$

Notes

Utilizing Entropy to do Work

Let us start thinking about how to extract work from a thermodynamic system.

We have a system that goes form one equilibrium state to another: $A \rightarrow B$.

As it undergoes this transformation, it does work $-\delta W$ and releases heat $-\delta Q$.

We would like to know, what is the maximum work that this system can do in the process $A \rightarrow B$.

In particular, we would like to compare reversible and irreversible processes.

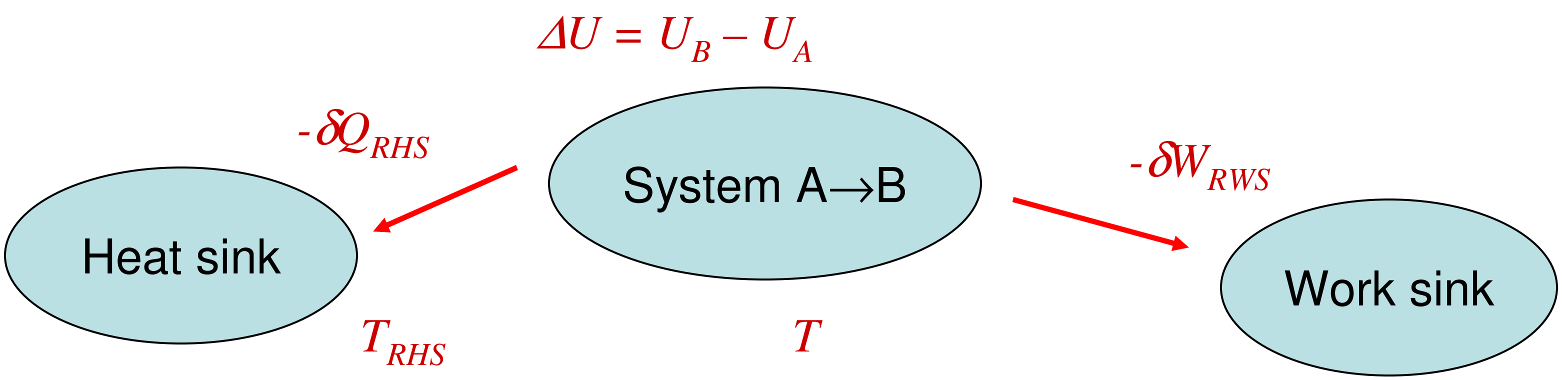
Notes

Heat Engine Model

We model the environment of the system as two objects:

- reversible work source (sink) RWS
- reversible heat source (sink) RHS

Heat engine model



Rigid walls, so no work can be done on the heat sink !

Adiabatic walls, so no heat can be transferred to the work sink! ($dS_{RWS}=0$)

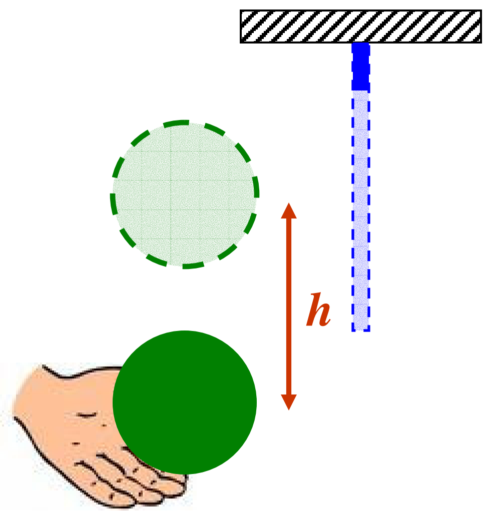
Notes

Energy-efficient use of Entropy

Problem: to minimize energy E spent to lift a weight using a stretched rubber band.

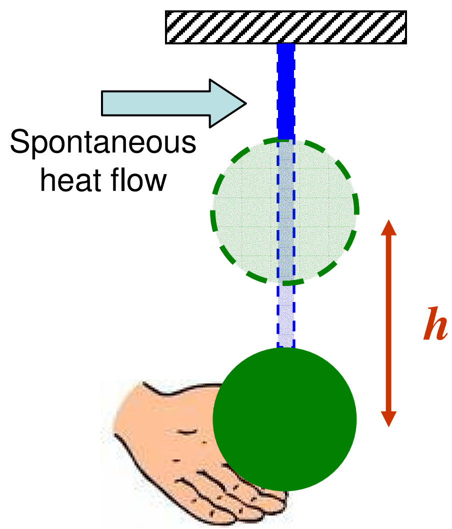
Lift by hand, no help from the rubber band

$$E_0 = W = Mgh$$



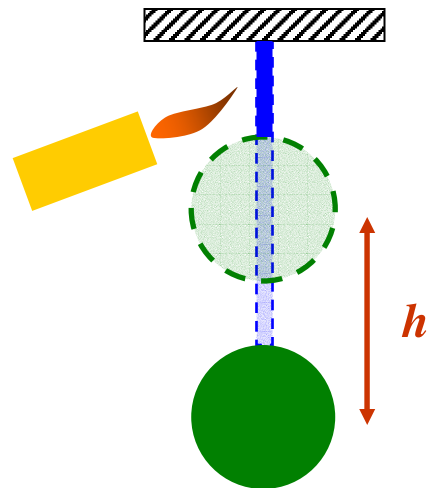
Lift by hand at constant T, rubber band helps

$$E_{T=const} = W' = ?$$



Lift by warming the rubber band

$$E_{\Gamma=const} = Q = ?$$



$$\min\left(E_{\Gamma=const}, E_{T=const}\right) = ?$$

Notes