

Second Law

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Introduction

- **Why we interested in the second law ?**
- **the “arrow of time”**
 - **It is vividly recognized by consciousness**
 - **It is equally insisted on by our reasoning faculty (capability to reason)**
 - **Increase in randomness in the study of organization a number of individuals**

Hamilton's Equation

- For a single particle

$$\frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i}$$

$$\frac{dq_i}{dt} = \frac{\partial H}{\partial p_i}$$

$$H = T + V$$

$$= \frac{1}{2m} \mathbf{p}^2 + V(\mathbf{r})$$

$$H = \sum_{i=1}^3 \frac{p_i^2}{2m} + V(q_1, q_2, q_3)$$

Hamilton's Equations

- Energy is a constant of the motion

$$\frac{dH(p_i, q_i)}{dt} = \sum_i \left(\frac{\partial H}{\partial p_i} \frac{dp_i}{dt} + \frac{\partial H}{\partial q_i} \frac{dq_i}{dt} \right)$$

$$\frac{dH}{dt} = \sum_i \left(-\frac{\partial H}{\partial p_i} \frac{\partial H}{\partial q_i} + \frac{\partial H}{\partial q_i} \frac{\partial H}{\partial p_i} \right)$$

$$\frac{dH}{dt} = 0$$

- At microscopic level no sense of “arrow of time”, events can equally unfold forward or backward.

- **It seems increase in randomness can equally possible forward or backward.**
- **This lead us to the big band.**
- **At the beginning of the time, everything is highly ordered, with the expansion, randomness set in.**
- **Before the “final” state of equilibrium, randomness increases with time.**

- With the big bang theory, Friedmann-Lemaitre-Robertson-Walker (FLRW) metric, we may introduce the Hubble parameter,

$$\mathcal{H}(t) = \frac{\frac{da(t)}{dt}}{a(t)}$$

- where a is a time dependent dimensionless scale factor.

- Using pseudo-Newtonian representation

$$\frac{d\underline{p}}{dt} = - \frac{\partial U(\underline{q})}{\partial \underline{q}} + \frac{d^2 a}{dt^2} \cdot \underline{q}$$

- where $U(x)$ is the potential energy

- **The i -th component of the observed velocities is then,**

$$\frac{dq_i}{dt} = \frac{p_i}{m_i} + \frac{da}{a} \cdot q_i = \frac{p_i}{m_i} + \mathcal{H} \cdot q_i$$

- **Obviously the last term breaks the time symmetry, when ($t \rightarrow -t$),**

$$\frac{dq_i}{dt} = \frac{p_i}{m_i} - \mathcal{H} \cdot q_i$$

- **metric expansion of space gives a small correction to the Hamiltonian time evolution of the system.**

- For times much shorter than $1/l$, ($1/l$ is the Lyapunov time, the characteristic timescale on which a dynamical system is chaotic), this small correction to the Hamiltonian time evolution result in the entropy difference is,

$$\Delta S \approx k_B (t - t_0) \int \rho(\underline{x}_0, \underline{p}_0) \Lambda d\underline{x}_0 d\underline{p}_0$$

- Then $\Delta S \approx k_B (t - t_0) N H_0$
- This difference is always positive. This means that the direction of the deviation from the Hamiltonian path due to FLRW expansion is **always towards an entropy increase.**

Second Law of Thermodynamics

- **Postulate:** There is an extensive function of state, $S(E, \underline{X})$, which is a monotonically increasing function of E , and if state B is adiabatically accessible from state A, then

$$S_B \geq S_A$$

- Notice that if this state B was reversibly accessible from state A, this postulate also implies that

$$S_A = S_B$$

- If A and B are adiabatically and reversibly accessible,

$$S_A \geq S_B$$

Second Law of Thermodynamics

- The extensive function of state, $S(E, \underline{X})$ is called the entropy.

$$dS = (\partial S / \partial E)_{\underline{X}} dE + (\partial S / \partial \underline{X})_E \cdot d \underline{X}$$

$$dE = (dQ)_{rev} + \underline{f} \cdot d \underline{X}$$

$$dS = (\partial S / \partial E)_{\underline{X}} (dQ)_{rev} + \left[(\partial S / \partial \underline{X})_E + (\partial S / \partial E)_{\underline{X}} \underline{f} \right] \cdot d \underline{X}$$

- For an adiabatic process that is reversible, both dS and $(dQ)_{rev}$ are zero

Second Law of Thermodynamics

- **Since, all displacements connecting the manifold of equilibrium states**

$$(\partial S / \partial \underline{X})_E = -(\partial S / \partial E)_{\underline{X}} \underline{f}$$

- **Notice all quantities involved in this equation are functions of state, therefore, it holds for nonadiabatic as well as adiabatic processes.**

Second Law of Thermodynamics

- In the postulate, it states that S is a monotonically increasing function of E ;

$$(\partial S / \partial E)_{\underline{X}} > 0, \text{ or } (\partial E / \partial S)_{\underline{X}} \geq 0$$

$$\text{Let } T \equiv (\partial E / \partial S)_{\underline{X}} \geq 0$$

- Note that both E and S are extensive, the **temperature** is intensive, that is, independent of the size of the system.

The definition of temperature

Second Law of Thermodynamics

- **Substitute back,**

$$(\partial S / \partial \underline{X})_E = -\underline{f} / T$$

- **Therefore,**

$$dS = (1/T)dE - (\underline{f} / T) \cdot d\underline{X}$$

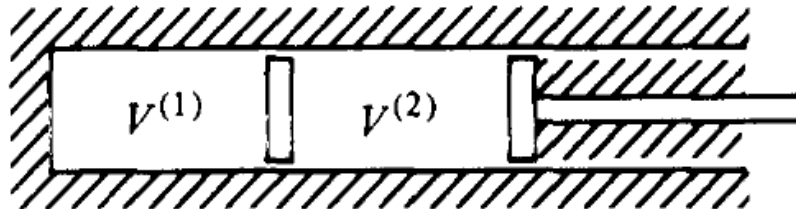
$$dE = TdS + \underline{f} \cdot d\underline{X}$$

$$(\Delta S)_{adiabatic} \geq 0$$

- **These equations constitute the mathematical statement of the second law**

Variational Statement of Second Law

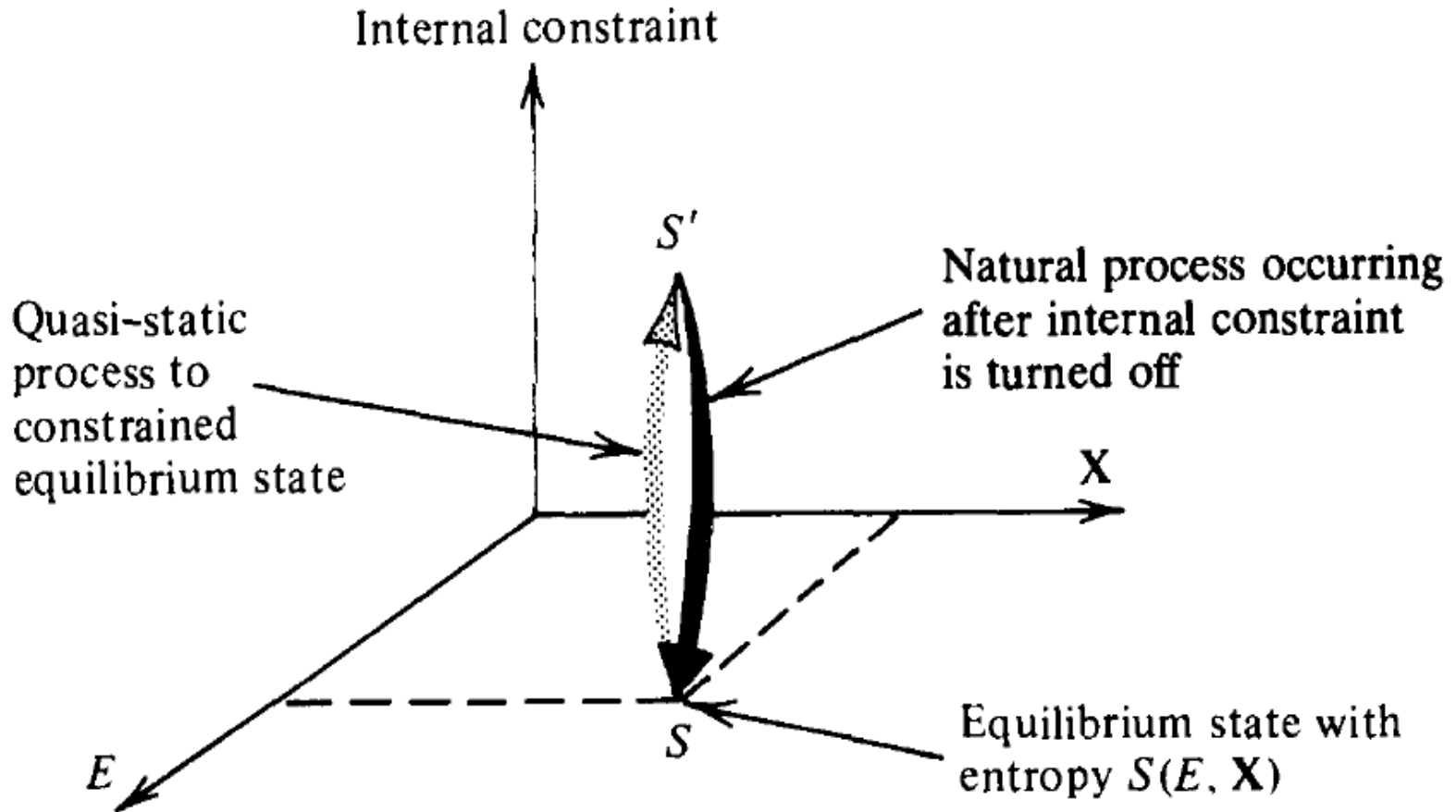
- Internal constraints: are constraints that couple to extensive variables but not alter the total value of those extensive variables (e.g. partition)



Variational Statement of Second Law

- The system is initially at equilibrium $S = S(E, \underline{X})$
- Then, by applying an internal constraint, the system is reversibly brought to a constrained equilibrium with the same E and \underline{X} , but with entropy $S' = S(E, \underline{X}; \text{internal constraint})$

Variational Statement of Second Law



Variational Statement of Second Law

- The states on the E - X plane are the manifold of equilibrium states in the absence of the internal constraint
- The application of the internal constraint lifts the system off this manifold. It will require work to do this
- and the requirement that there is no change in energy for the process means that there must also have been a flow of heat

Variational Statement of Second Law

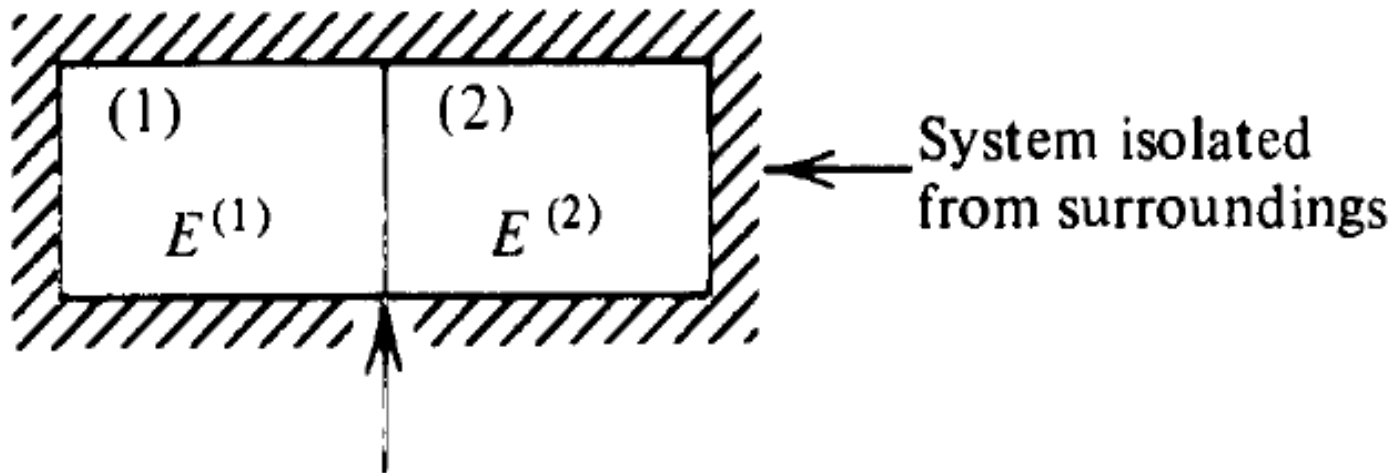
- After attaining and while maintaining this constrained state, the system will be adiabatically insulated.
- Then, the internal constraint is suddenly shut off
- The system will relax naturally at constant E and \underline{X} back to the initial state with entropy S

Variational Statement of Second Law

- According to the second law, the entropy change is positive $S - S' > 0$,
- Or $S(E, \underline{X}) > S(E, \underline{X}; \text{internal constraint})$ —the equilibrium state is the state at which $S(E, \underline{X}; \text{internal constraint})$ has its global maximum

Variational Statement of Second Law

The Energy minimum principle:



Heat conducting wall
divides subsystems (1) and (2)

- **Repartitioning the system**

Variational Statement of Second Law

- When $\Delta E \neq 0$, and allow

$$S(E^{(1)} - \Delta E, \underline{X}^{(1)}) + S(E^{(2)} + \Delta E, \underline{X}^{(2)}) = S(E, \underline{X}^{(1)} + \underline{X}^{(2)})$$

- **To raise left hand from less to equal, energy must be added**
- That is, apply internal constraints at constant S and \underline{X} , will necessarily raise the total energy of the system
- Therefore, the equilibrium state $E(S, \underline{X})$ is the state at which $E(S, \underline{X}; \text{internal constraint})$ has its global minimum

Variational Statement of Second Law

- Scenario I: at equilibrium

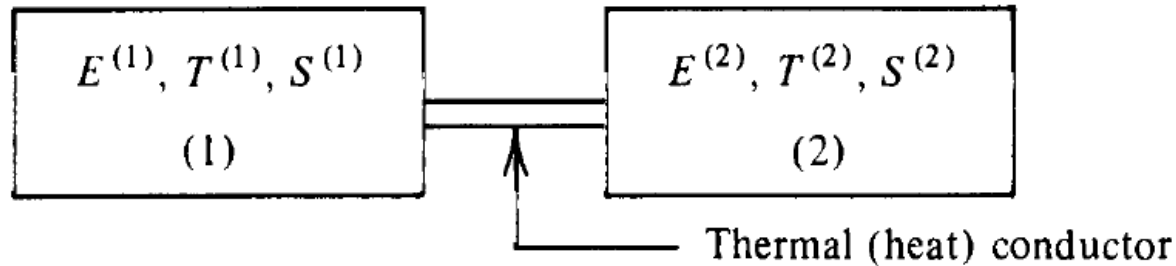


Fig. 1.6. Heat conducting system.

- How are $T^{(1)}$ and $T^{(2)}$ related?

Variational Statement of Second Law

- Consider a small displacement about equilibrium due to an internal constraint,

$$(\delta S)_{E, \underline{X}} \leq 0 \quad (\text{entropy maximum})$$

- Since $E = E^{(1)} + E^{(2)}$ is constant during the displacement (see diagram),

$$\delta E^{(1)} = -\delta E^{(2)}$$

- Since S is extensive, $S = S^{(1)} + S^{(2)}$

Variational Statement of Second Law

- **Thus**
$$\begin{aligned}\delta S &= \delta S^{(1)} + \delta S^{(2)} \\ &= \left(\frac{\partial S^{(1)}}{\partial E^{(1)}} \right)_{\underline{x}} \delta E^{(1)} + \left(\frac{\partial S^{(2)}}{\partial E^{(2)}} \right)_{\underline{x}} \delta E^{(2)} \\ &= \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} \right) \delta E^{(1)} \leq 0\end{aligned}$$

For all δE , therefore, $T^{(1)} = T^{(2)}$

Variational Statement of Second Law

- **Scenario II: initially not at equilibrium, then eventually reach equilibrium**
- **From the second law,**

$$\Delta S^{(1)} + \Delta S^{(2)} = \Delta S > 0$$

- **Assuming differences are small**

$$\left(\frac{\partial S^{(1)}}{\partial E^{(1)}} \right)_{\underline{X}} \Delta E^{(1)} + \left(\frac{\partial S^{(2)}}{\partial E^{(2)}} \right)_{\underline{X}} \Delta E^{(2)} > 0$$

Variational Statement of Second Law

- Then

$$\Delta S = \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} \right) \Delta E^{(1)} > 0$$

- Therefore,

- $T^{(1)} > T^{(2)} \rightarrow \Delta E^{(1)} < 0$

- $T^{(1)} < T^{(2)} \rightarrow \Delta E^{(1)} > 0$

- That is energy flow is from the hot body to cold body