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**

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

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

$$H = T + V$$

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

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

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 seams 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 ban theory, the Friedmann-Lemaitre-Robertson-Walker (FLRW) metric, we may introduce the Hubble parameter,**

$$\mathscr{H}(t) = \frac{\frac{d\,a(t)}{dt}}{a(t)}$$

where *a* is a time dependent dimensionless scale factor.

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

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

$$H = T + V$$

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

- **Using pseudo-Newtonian representation, the new equation of motion is given as**

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

force like

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

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

velocity like

$$\frac{dq_i}{dt} = \frac{p_i}{m_i} + \frac{\frac{d\,a}{dt}}{a} \cdot q_i = \frac{p_i}{m_i} + \mathscr{H} \cdot q_i$$

- **Obviously the last term breaks the time symmetry, when (t→-t),**

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

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

- **For times much shorter than $1/\lambda$, ($1/\lambda$ 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.**

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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.**

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

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

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

- **For an adiabatic process that is reversible, both *dS* and $(\delta Q)_{rev}$ 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,**

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

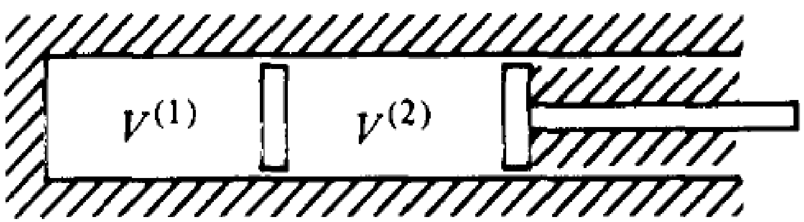
$$dE = TdS + \underline{f}\cdot d\underline{X}$$

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

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

Variational Statement of Second Law

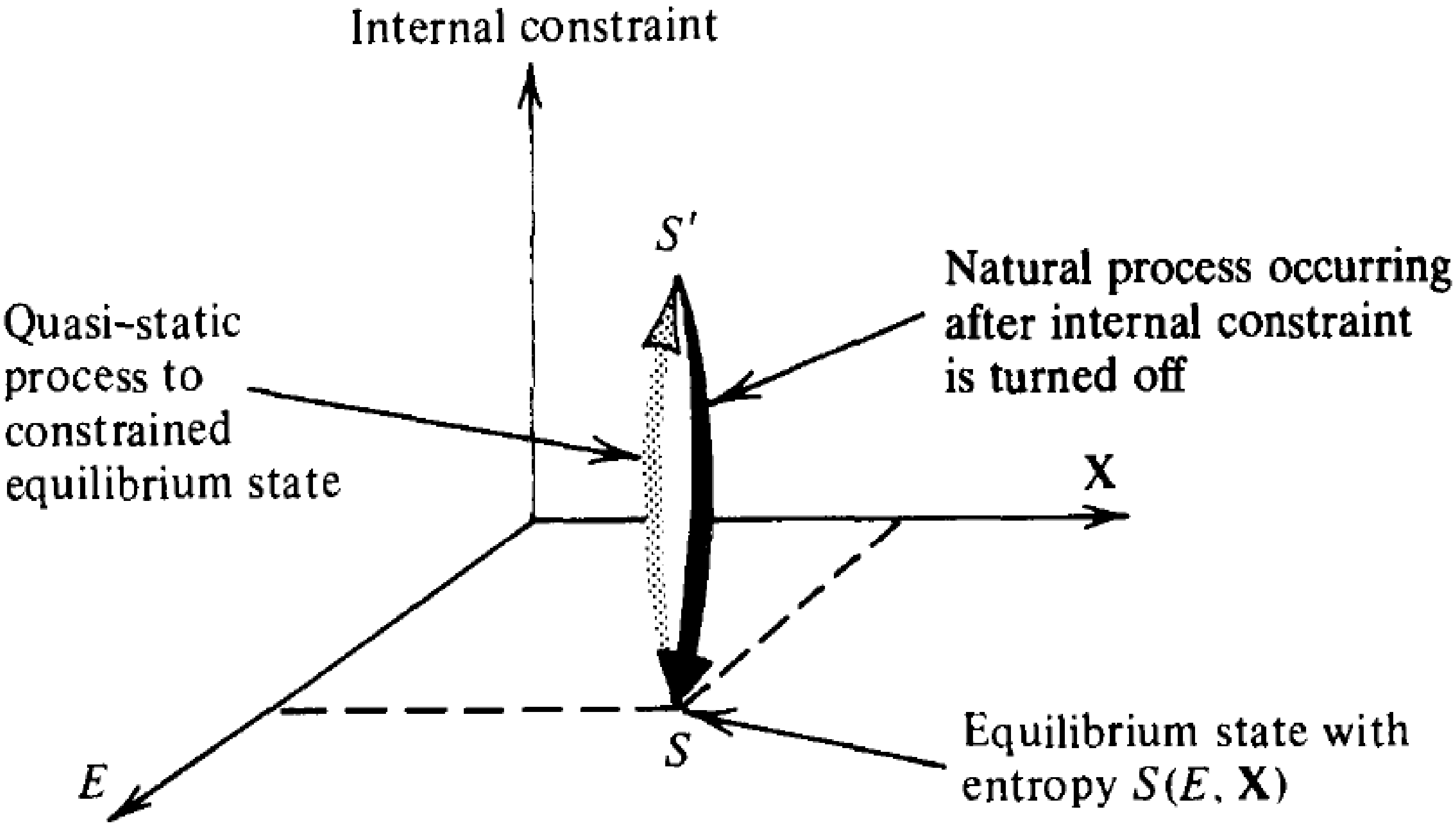
- <u>Internal constraints</u>: are constraints that couple to extensive variables but not alter the total value of those extensive variables (e.g. partition)



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 $S' = S(E, \underline{X};$ internal constraint$)$**

Variational Statement of Second Law



Variational Statement of Second Law

- **The states on the *E*-$\underline{X}$ 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

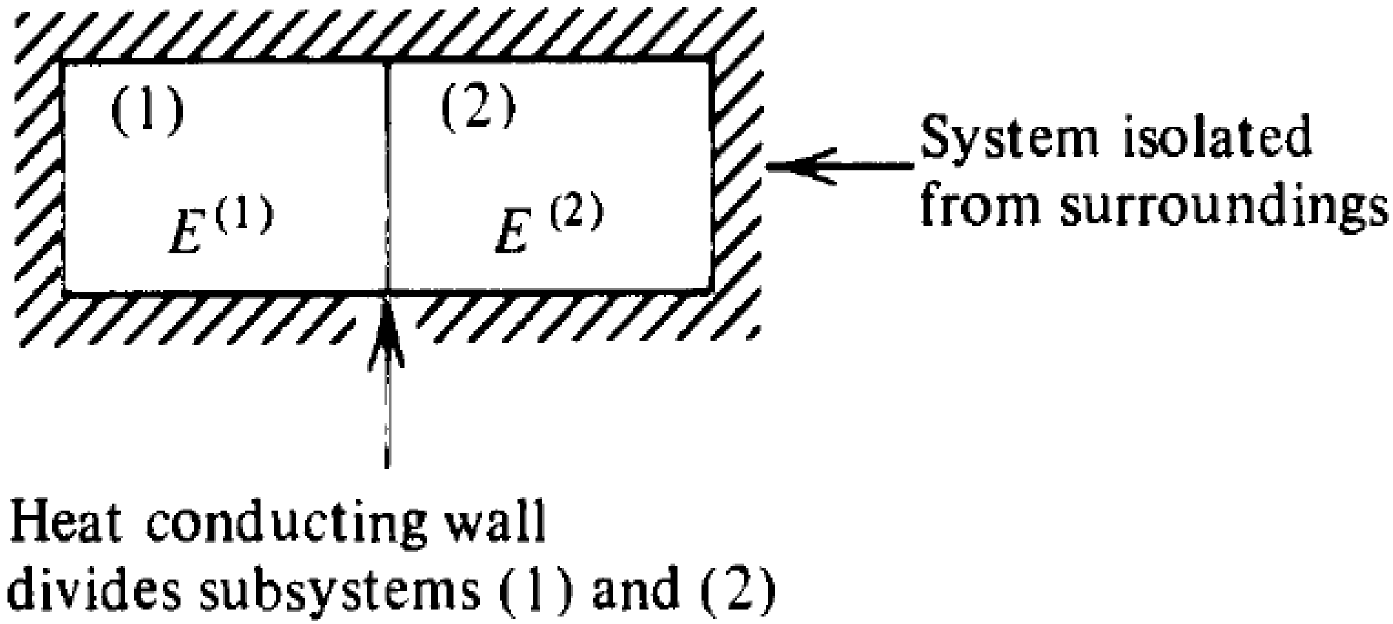
- **After attaining and while maintaining this constrained state, the system will be adiabatically insulated.**
- **Then, the internal constraint is suddenly shut off**
- **The system will relax naturally at constant E and $\underline{X}$ back to the initial state with entropy S**

Variational Statement of Second Law

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

Variational Statement of Second Law

The Energy minimum principle:



- **Repartitioning the system**

Variational Statement of Second Law

The entropy Maximum requires that

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

after repartition before

- **Entropy is extensive, ΔE is an amount of energy removed from subsystem 1 and placed into subsystem 2.**
- **Since *S* is a monotonically increasing function of *E*, (increases in E will led to increase in S, and vice versa, monotonic)**
- **Therefore**

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*, $\underline{X}$; internal constraint) has its global minimum**

Variational Statement of Second Law

- **Scenario I: at equilibrium**

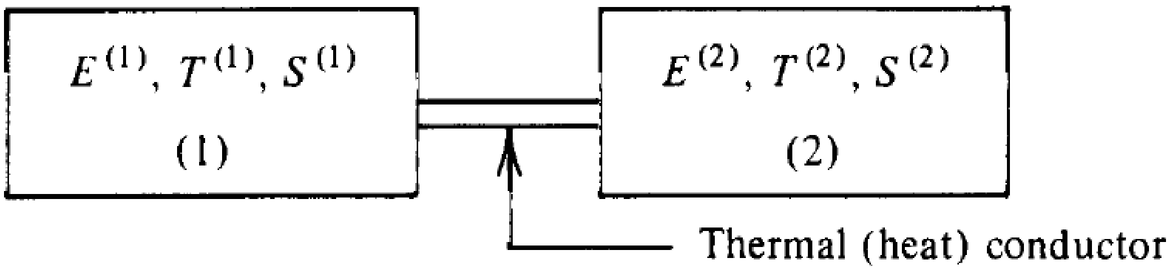


Fig. 1.6. Heat conducting system.

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

Variational Statement of Second Law

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

$$(\delta S)_{E,\underline{X}} \leq 0$$ **(**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** $$\delta S = \delta S^{(1)} + \delta S^{(2)}$$

$$= \left(\frac{\partial S^{(1)}}{\partial E^{(1)}} \right)_{\underline{x}} \delta E^{(1)} + \left(\frac{\partial S^{(2)}}{\partial E^{(2)}} \right)_{\underline{x}} \delta E^{(2)}$$

$$= \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} \right) \delta E^{(1)} \leq 0$$

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**