Review

Macroscopic system: (from pure mechanics point of view)
  Extensive/Intensive dichotomy
  Irreversibility
    time-reversal asymmetry of the world is broken due to ‘openness.’
    time’s arrow problem is a pseudo problem.

∃ **Fundamental difference** between Mechanics & Thermodynamics
Phenomenology

Thermodynamics = (energetic phenomenology of macroequilibrium states

Macrosopic phenomenology of equilibrium systems.

∗ Choose right states
∗ Choose right variables

Equilibrium states
States where Thermodynamics holds
Lecture 8 Critical Review of Thermodynamics

Let us answer all the elementary questions.

Thermodynamic coordinates 12.4.

spanning **Thermodynamic Space**

No thermodynamics needed

**Unique description** of equilibrium states

lucky or logic circular? chopping head parable

State functions/quantities 12.7

functions with domains in the thermodynamic space
memoryless/historyless,

making thermodynamics very useful

∃ other reasons, as well.
Fourth Law 11.6: extensive/intensive dichotomy
    Partitioning/rejoining invariance 12.11

Quasistatic process 12.6
    Why does slowing down often work?
    Do not forget hot coffee in a thermos.

The so-called zeroth law 12.13 is probably meaningless.

Axiomatic formulation??
    Note: Löwenheim-Skolem theorem
The First law = energy conservation. Really?

\[ \Delta E = W + Q \]

Never write \( \Delta W \) or \( \Delta Q \)

\[ d'W = -PdV + xdX \]

ONLY under quasistatic conditions.

Mayer, Joule, Helmholtz

‘conservation of mechanical energy.’ [explained as]
The second law: prehistory

<table>
<thead>
<tr>
<th>Year</th>
<th>Inventor</th>
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<tbody>
<tr>
<td>1712</td>
<td>Newcomen</td>
</tr>
<tr>
<td>1760-70</td>
<td>Watt</td>
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<tr>
<td>1804</td>
<td>Puffing Devil</td>
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<td>1807</td>
<td>Fulton</td>
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<td>1829</td>
<td>Stevenson</td>
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<tr>
<td>Carnot’s theorem 1824</td>
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<td>Mayer’s work equivalence 1842</td>
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<td>Helmholtz: First law 1847</td>
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<tr>
<td>Clausius Second law 1850</td>
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Joule: denied Carnot
Thomson: accepted I and Carnot + X needed
Clausius: I and Carnot enough
The Second Law

Planck’s principle:

adiabatic cycle cannot decrease energy.

What is adiabaticity?

\( \neq \) QM adiabaticity

\exists \text{ Entropy (can be made differentiable)}

foliating the thermodynamic space, extensive, \( dS \propto d'Q \).

\[ d'Q = dS/T \]

This \( T \) is \( T \) on \( PV = Nk_B T \).

Entropy principle: to reduce \( S \) you must cool...

**Gibbs’ relation**

\[ dE = TdS - PdV + BdM + xdX \]

Only for quasistatic processes
Principle of increasing entropy (for spontaneous...)

Entropy maximization principle

Adiabatic spontaneous change 14.2 \( \delta S \geq 0. \)

\[ \text{eq} \Rightarrow \text{no spontaneous change} \]
\[ \Rightarrow \delta S \geq 0 \text{ never happens} \]

\[ S_{\text{max}} \Rightarrow \text{eq} \]

Entropy is concave.14.3

\[ S((1-\alpha)E_1+\alpha E_2, \cdots) \geq (1-\alpha)S(E_1, \cdots)+\alpha S(E_2, \cdots) \]

Internal energy is convex 14.5

Fluctuations substantiate variational principles.
Clausius’ inequality 14.7

\[ \Delta S + \Delta S_{\text{bath}} \geq 0 \Rightarrow \Delta S \geq \frac{\Delta Q}{T}. \]

Entropy exercise 15.x