From Dynamics to Thermodynamics

Stefano Olla – CEREMADE, Paris

PUC, Rio de Janeiro
September 10, 2014

the problem with thermodynamics

> *With Clausius' formulation of the second law of thermodynamics, the conflict between thermodynamics and dynamics became obvious. There is hardly a single question in physics that has come moe often and more actively discussed than the relation between thermodynamics and dynamics. Even now, a 150 years after Clausius, the question arouses* **strong feelings.**

I. Prigogine, I. Stengers, Order out of chaos (1984).

the problem with thermodynamics

> *Perhaps, after all, the wise man's attitude towards thermodynamics should be to have* **nothing to do with it**. *To deal with thermodynamics is to look for trouble. This is not the citation of a famous scientist, but the result of a deep cogitation following mere observations. Why do we need to get involved in a field of knowledge which, within the last hundred years, has exhibited the largest number of schizophrenics and megalomaniacs, imbalanced scientists, paranoiacs, egocentrists, and probably insomniacs and sleepwalkers?*

Gérard A Maugin, The Thermomechanics Of Nonlinear Irreversible Behaviors.

the problem with thermodynamics

> *Every mathematician knows that it is impossible to understand any elementary course in thermodynamics.*

V.I. Arnold, Contact Geometry: the Geometrical Method of Gibbs's Thermodynamics. (1989)

the problem with statistical mechanics

> *The objective of statistical mechanics is to explain the macroscopic properties of matter on the basis of the behavior of the atom and molecules of which it is composed.*

Oscar R. Lanford III, 1973

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If we want to make the above definition specific for the *non-equilibrium* statistical mechanics, we can refrase it as

The objective of non-equilibrium statistical mechanics is to explain the macroscopic evolution (in space and time) of matter on the basis of the behaviour of the atom and molecules of which it is composed.

the connection

Microscopic Dynamics

$\Downarrow$

statistical mechanics
(equilibrium, non-equilibrium, local equilibrium)

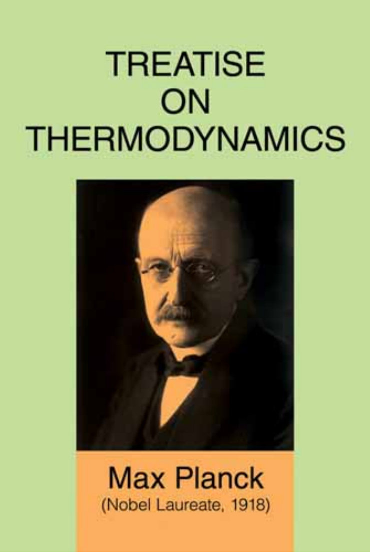
$\Downarrow$

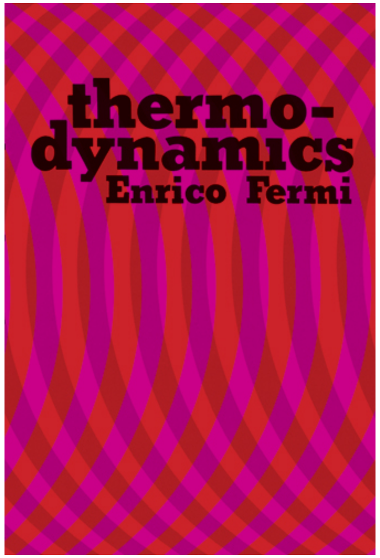
thermodynamics
(Carnot Cycles, entropy, 1st and 2nd principles...)

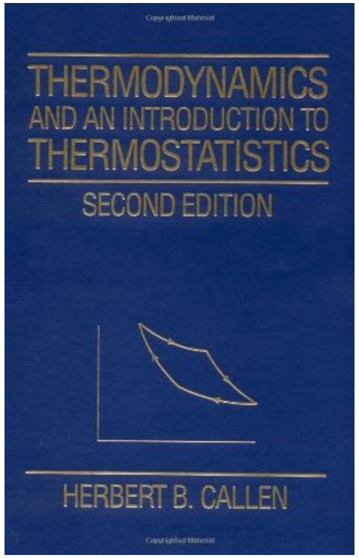
The mathematical connection is through *space-time* scaling limits (*Hydrodynamic Limits*).

What is (equilibrium) *thermodynamics*?

I take seriously as defined in these classical books:



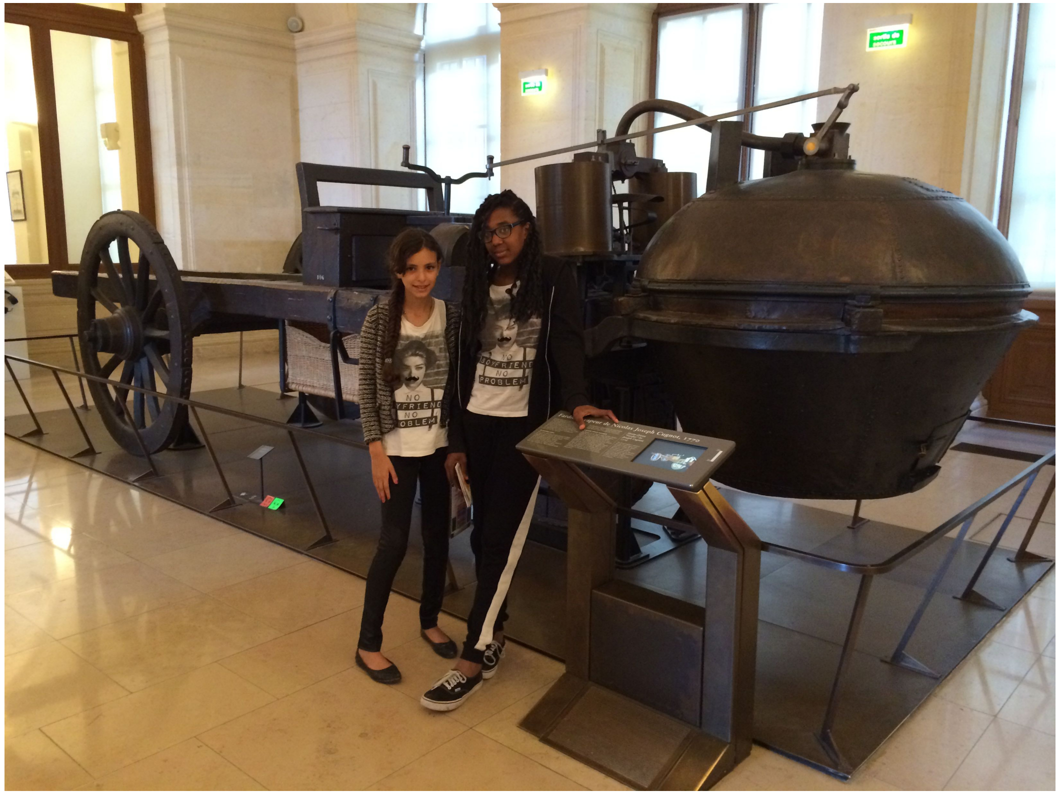




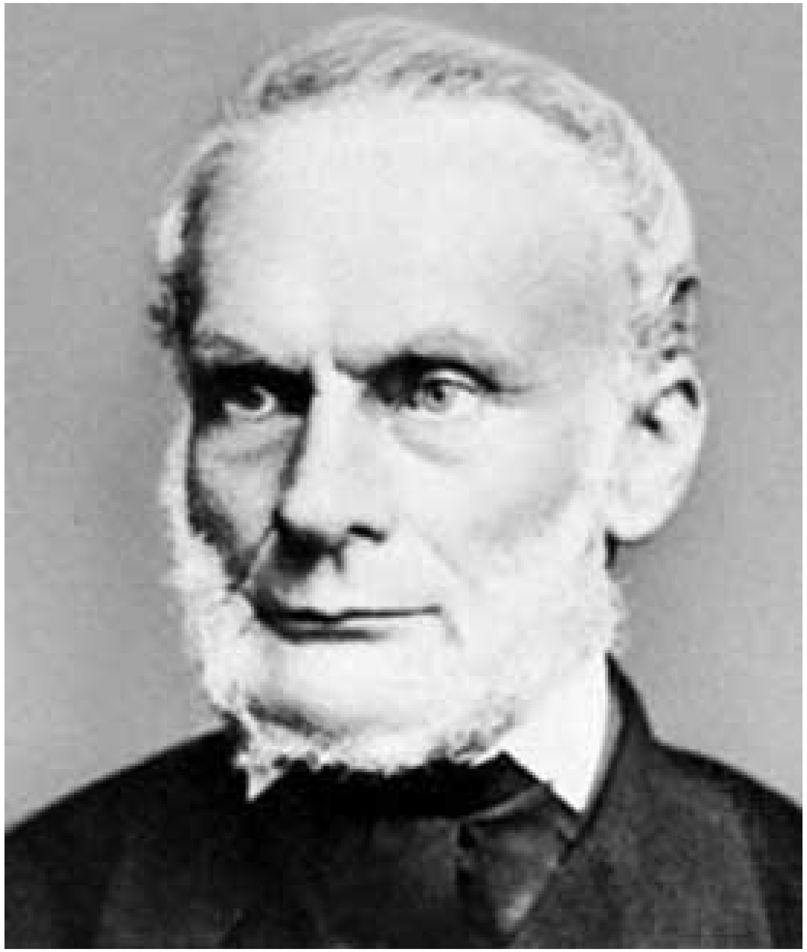
Connections between measurable quantities as:
pressure, *tension*, *volume*, *'temperature'*, *energy*
and *heat*, *work*, *entropy*.

Thermodynamics concern **Macroscopic Objets**

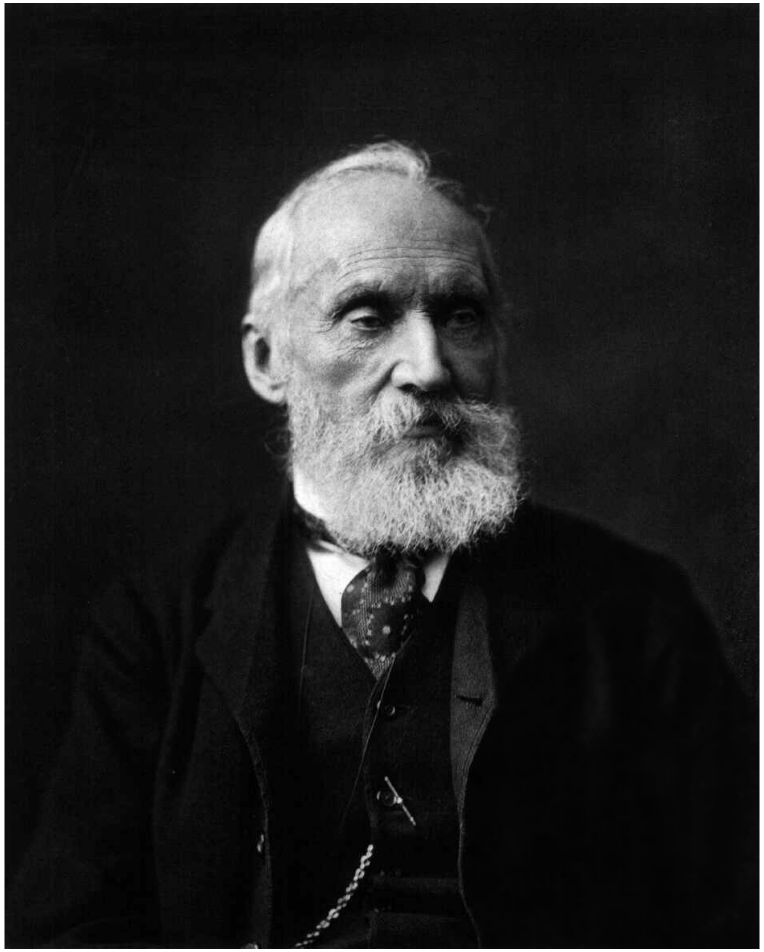
Vapor machine of Joseph Cugnot (1770)



Fathers of Thermodynamics:



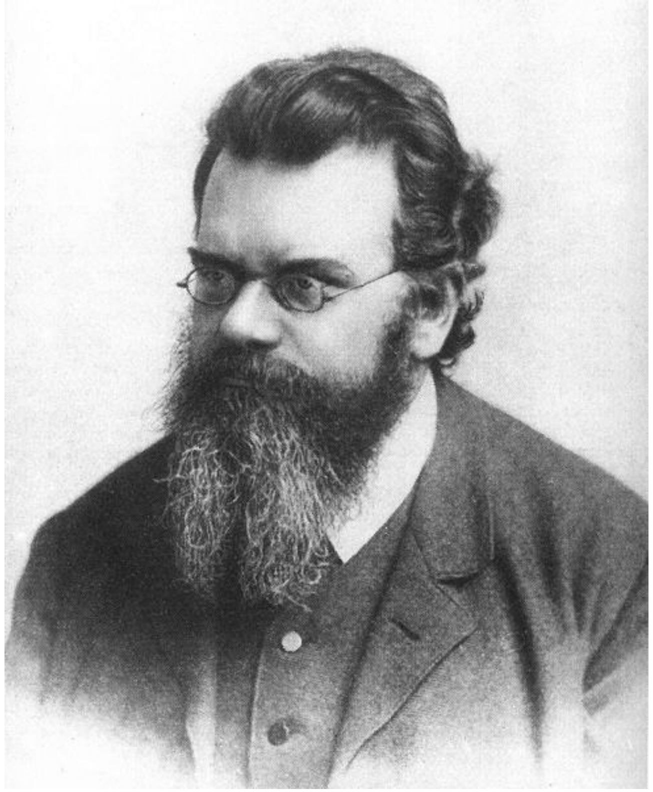
Clausius,



Thompson (Lord Kelvin)

Fathers of Statistical Mechanics

Maxwell



Boltzmann

atoms in a machine $\sim 10^{23} \sim \infty$, and they *move fast!*

relation between thermodynamics and microscopic dynamics: different space-time scale

thermodynamics describe objects that are big (**macroscopic**), constituted by an enourmous number of atoms, but these objects are moving very slowly, compared with the typical frequency of the jiggling of these atoms.

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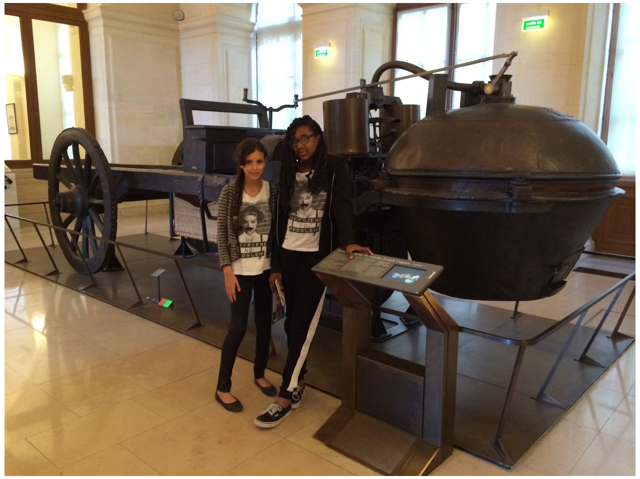

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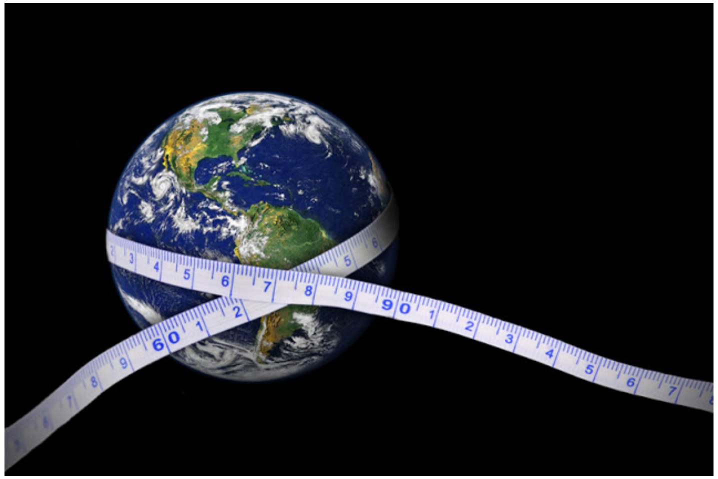

and the Earth?

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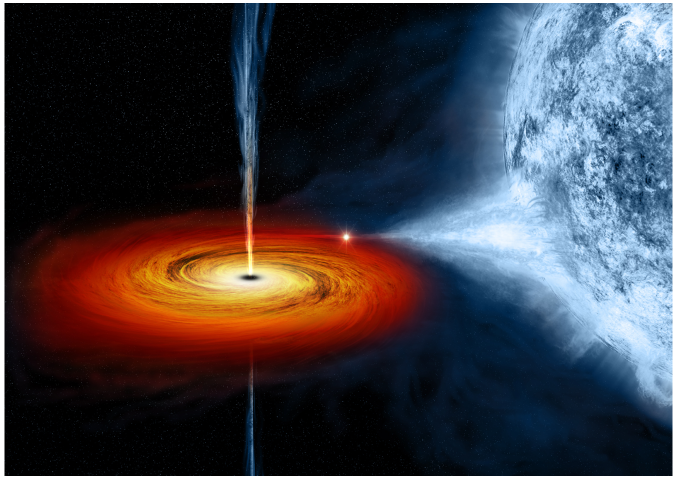

a black hole?

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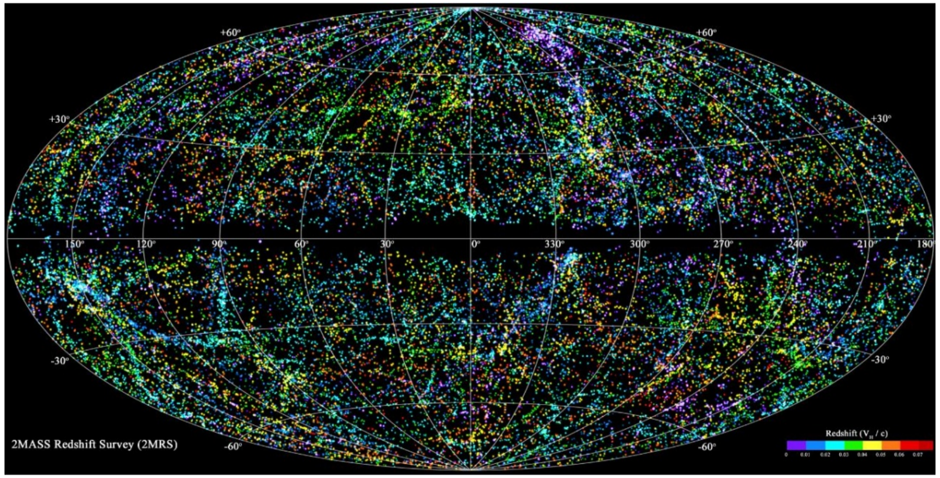

the entire universe?

God Given postulate or principles

As any physical and mathematical theory, **thermodynamics** studies the consequences of his postulates, here called *principles of thermodynamics*:

- 0th principle: *existence of equilibrium states*,
- 1st principle: *energy conservation* (and much more!),
- 2nd principle: possible and impossible transformations from an equilibrium to another,

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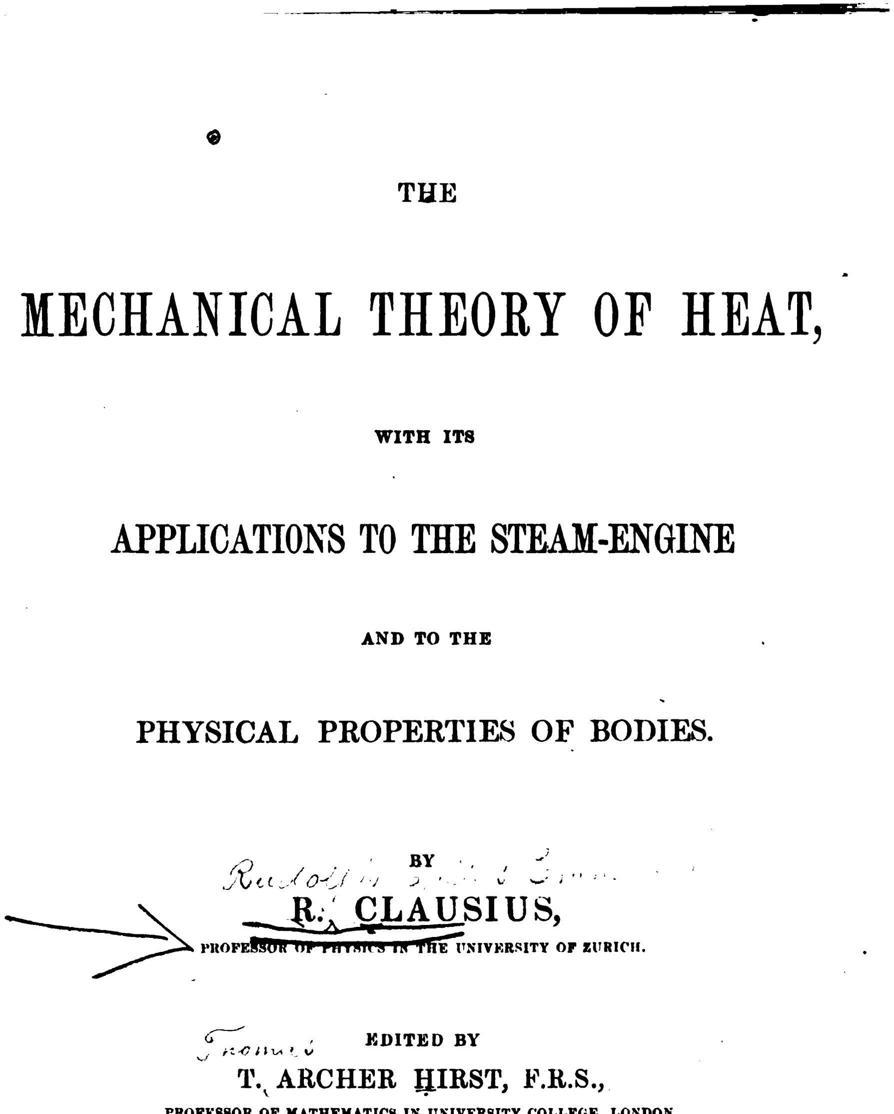
In particular we cannot apply (directly) these ideas to system that have no equilibrium states or we do not know them.
Galaxy? Universe?

From here come most of the abuse of 2nd principle and Entropy.

the first one to start this abuse was Clausius himself:



THE

MECHANICAL THEORY OF HEAT,

WITH ITS

APPLICATIONS TO THE STEAM-ENGINE

AND TO THE

PHYSICAL PROPERTIES OF BODIES.

BY

Rudolph [illegible]

R. CLAUSIUS,

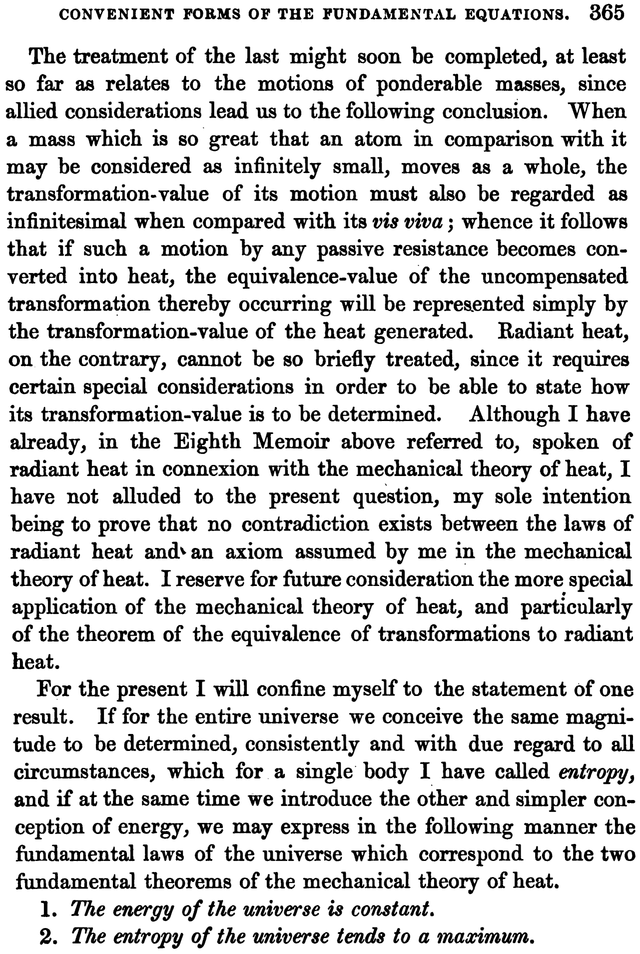
PROFESSOR OF PHYSICS IN THE UNIVERSITY OF ZURICH.

Thomas

EDITED BY

T. ARCHER HIRST, F.R.S.,

PROFESSOR OF MATHEMATICS IN UNIVERSITY COLLEGE, LONDON



CONVENIENT FORMS OF THE FUNDAMENTAL EQUATIONS. 365

The treatment of the last might soon be completed, at least so far as relates to the motions of ponderable masses, since allied considerations lead us to the following conclusion. When a mass which is so great that an atom in comparison with it may be considered as infinitely small, moves as a whole, the transformation-value of its motion must also be regarded as infinitesimal when compared with its *vis viva*; whence it follows that if such a motion by any passive resistance becomes converted into heat, the equivalence-value of the uncompensated transformation thereby occurring will be represented simply by the transformation-value of the heat generated. Radiant heat, on the contrary, cannot be so briefly treated, since it requires certain special considerations in order to be able to state how its transformation-value is to be determined. Although I have already, in the Eighth Memoir above referred to, spoken of radiant heat in connexion with the mechanical theory of heat, I have not alluded to the present question, my sole intention being to prove that no contradiction exists between the laws of radiant heat and an axiom assumed by me in the mechanical theory of heat. I reserve for future consideration the more special application of the mechanical theory of heat, and particularly of the theorem of the equivalence of transformations to radiant heat.

For the present I will confine myself to the statement of one result. If for the entire universe we conceive the same magnitude to be determined, consistently and with due regard to all circumstances, which for a single body I have called *entropy*, and if at the same time we introduce the other and simpler conception of energy, we may express in the following manner the fundamental laws of the universe which correspond to the two fundamental theorems of the mechanical theory of heat.

1. *The energy of the universe is constant.*
2. *The entropy of the universe tends to a maximum.*

Non-equilibrium

EQUILIBRIUM A $\Longrightarrow$ EQUILIBRIUM B

we have to go through some *non-equilibrium states*.

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A non equilibrium statistical mechanics should explain, from microscopic dynamics of atoms, why only some transformations can happens, and how: space-time scale etc.

Classical Irreversible Thermodynamics

These non-equilibrium developpements have been much more controversial, and many proposals had been done from teh beginning of teh 20th century. One of these is called

Classical Irreversible Thermodynamics,

and it is based on the postulate of **local equilibrium**:
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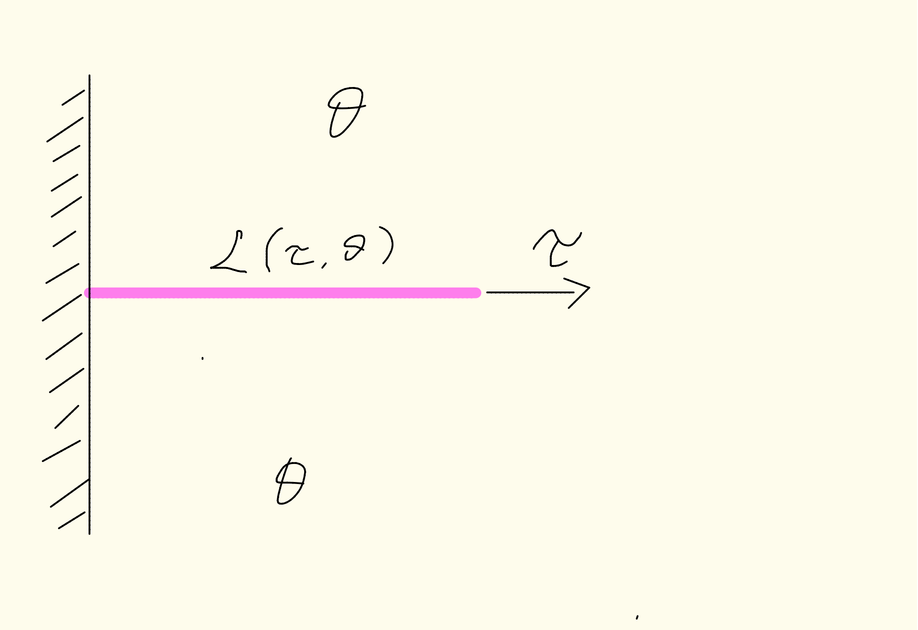
Such theory is well justified for system where there is a clear separation of space-time scale between macroscopic evolution of the thermodynamic parameters and microscopic dynamics.

What is nice of this approach is that it is possible to give a precise mathematical statement about obtaining thermodynamics from microscopic dynamics, through a limiting process:
Hydrodynamic limits

A crash course in thermodynamics

A one dimensional system (rubber under tension):



Mechanical Equilibrium:

$$\mathcal{L} = \mathcal{L}(\tau), \qquad \tau = \text{tension}$$

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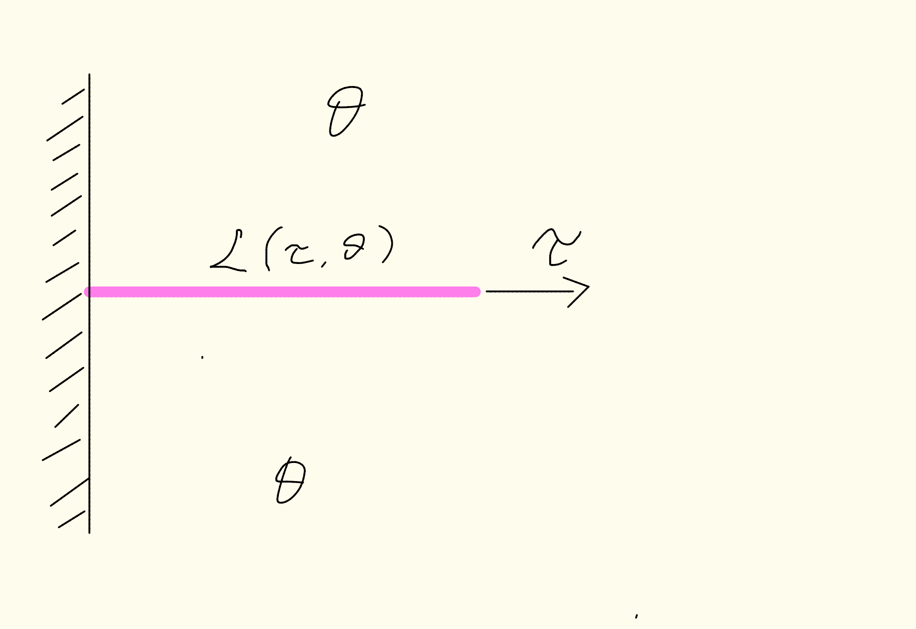

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θ is the **temperature**

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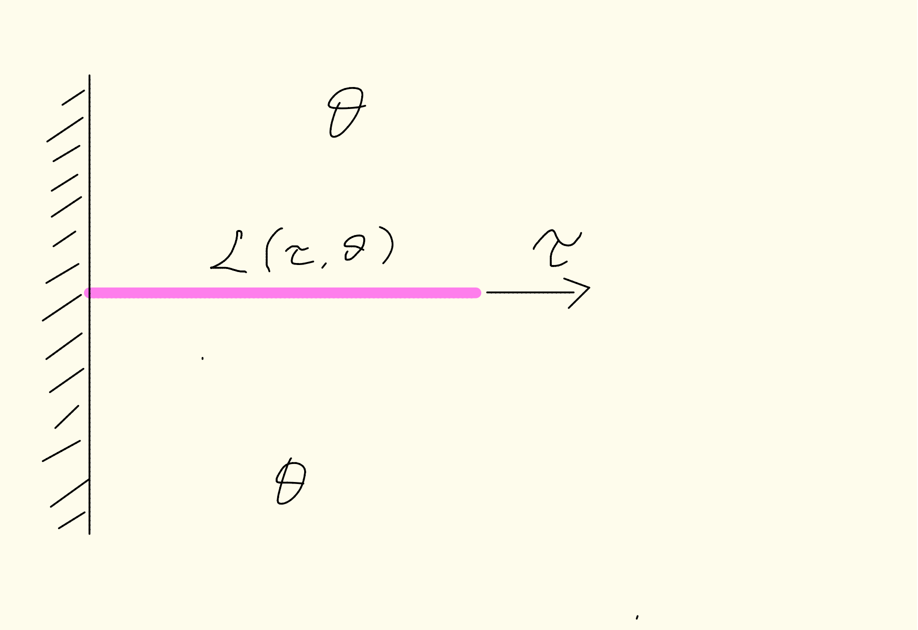

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Empirical definition of temperature.

Internal Energy and Heat
1st Principle

Changing tension $\tau_0 \to \tau_1$ we arrive after *some time* to a new equilibrium characterized by $(\mathcal{L}_1, \tau_1)$, and there exists a energy U function of the equilibrium state satisfy

$$U(\mathcal{L}_1, \tau_1) - U(\mathcal{L}_0, \tau_0) = W + Q$$

W = work done by the external tension (force) $= \tau_1(\mathcal{L}_1 - \mathcal{L}_0)$
Q = **heat** exchanged with the environment

1st principle of thermodynamics

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- the external work W done by a *known*, *slow*, *controllable*, *macroscopic* force τ,
- from the work Q done by *unknown*, *fast*, *microscopic* forces, we call *heat* this work,

I think this is the main conceptual point of thermodynamics, in particular in its connection to the microscopic mechanics.The first principle contains the **separation of scales** *(time and space) between microscopic and macroscopic.*

Quasi-Static or Reversible transformations

Performing (slowly) a *small* (differential) change of tension $d\tau$ or a change of temperature $d\theta$, the equilibrium length will change

$$d\mathcal{L} = \left(\frac{\partial \mathcal{L}}{\partial \theta}\right)_{\tau} d\theta + \left(\frac{\partial \mathcal{L}}{\partial \tau}\right)_{\theta} d\tau \tag{1}$$

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What is the physical meaning of these differential changes of *equilibrium* states?
In principle, as we actually change the tension of the cable, the system will go into a sequence of non-equilibrium states before to relax to the new equilibrium. But, quoting Zemanski,

> *Every infinitesimal in thermodynamics must satisfy the requirement that it represents a change in a quantity which is small with respect to the quantity itself and large in comparison with the effect produced by the behavior of few molecules.*

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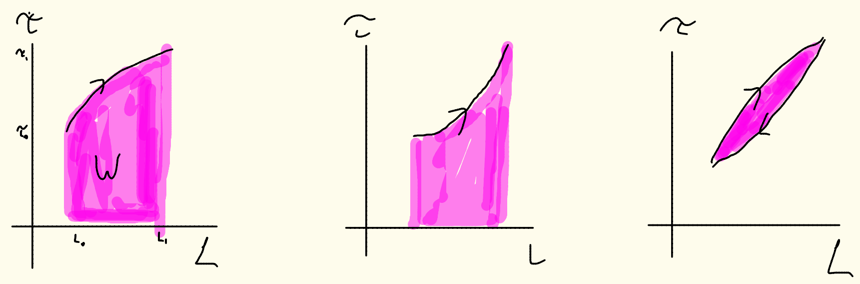
In principle, as we actually change the tension of the cable, the system will go into a sequence of non-equilibrium states before to relax to the new equilibrium.

We should consider the existence of these quasi-static transformations as kind of an hidden principle. Then eventually obtain them from a mathematical scaling limit process.

Thermodynamic transformations and Cycles

- reversible or quasi-static tranformations:
  Often is used the $\mathcal{T} - L$ diagrams.



In the third transformation the work is given by the integral along the cycle

$$W = \oint \tau dL = -Q \tag{2}$$

Irreversible themodynamic transformations

In principle any transformation that is not quasi-static, but brings the system from an initial equilibrium state $A = (\mathcal{L}_0, \mathcal{T}_0)$ to a final state $B = (\mathcal{L}_1, \mathcal{T}_1)$.

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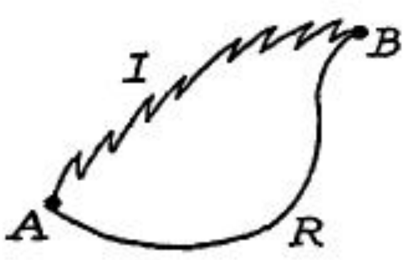

Fig. 11. from the Fermi's *Thermodynamics*

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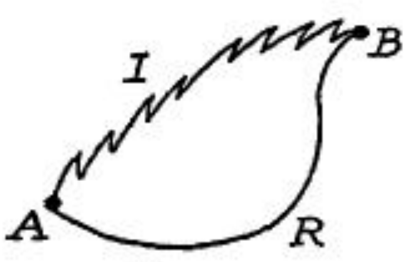

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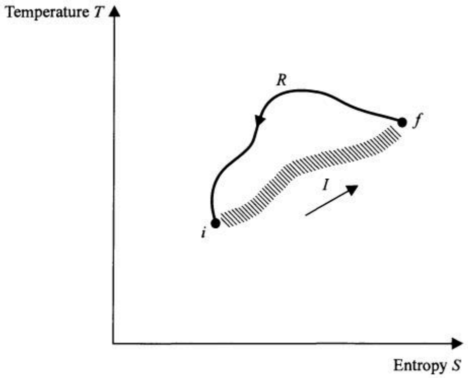
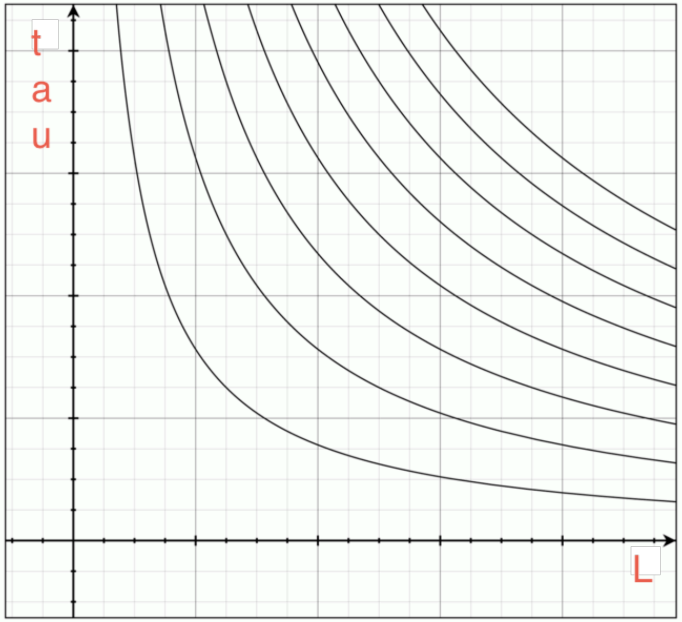


FIGURE 8-8
An irreversible process followed by a reversible process to complete an irreversible cycle. from the Zemanski *Heat and Thermodynamics*

Special quasi-static transformations

- **Isothermal:**
  System in contact with a *thermostat* while the external force τ is doing work:

$$\require{cancel}\cancel{d}W = \tau d\mathcal{L} = \tau \left(\frac{\partial \mathcal{L}}{\partial \tau}\right)_\theta d\tau = -\cancel{d}Q + dU$$



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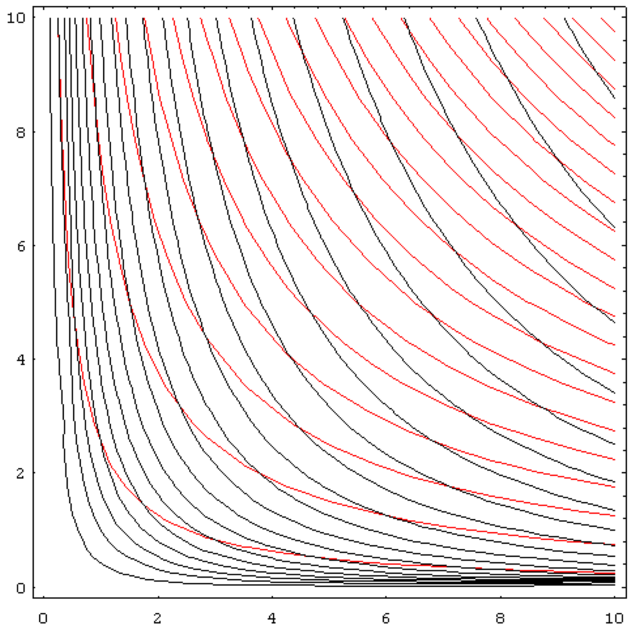
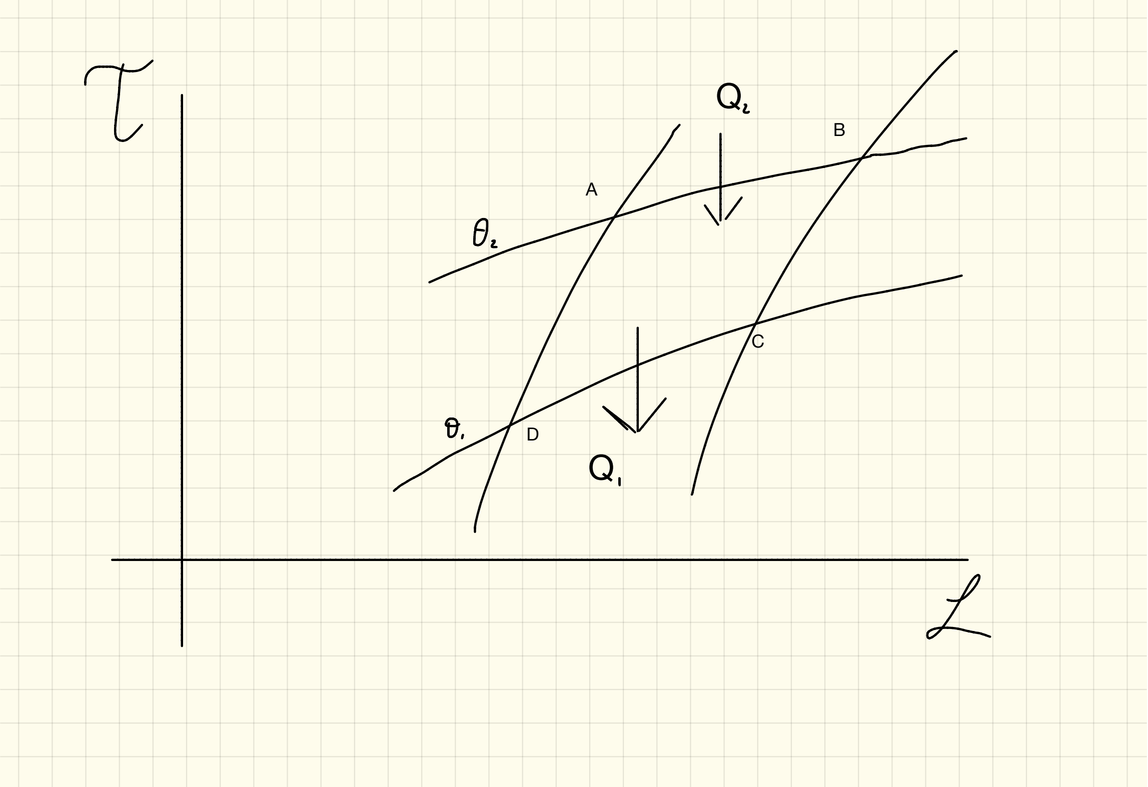


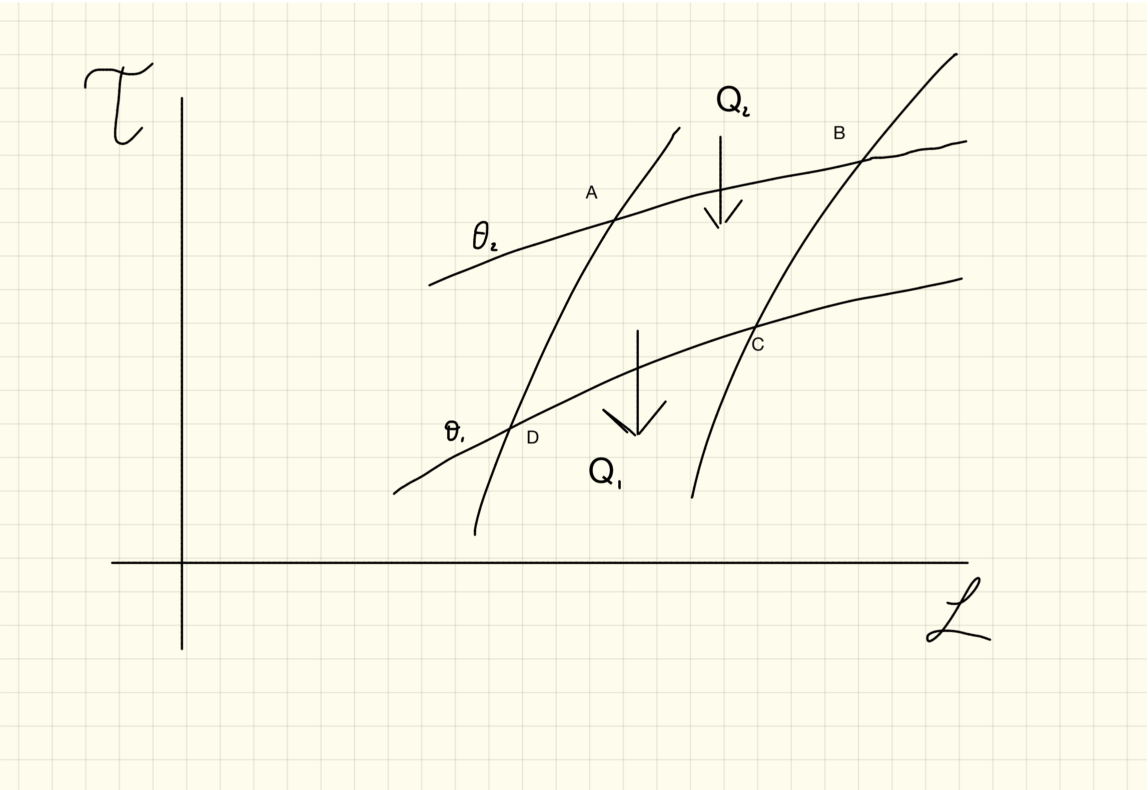
Carnot Cycles



$A \rightarrow B$, $C \rightarrow D$ isothermal

$B \rightarrow C$, $D \rightarrow A$ adiabatic

Carnot Cycles

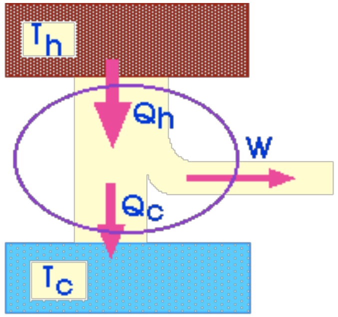


$A \to B$, $C \to D$ isothermal
$B \to C$, $D \to A$ adiabatic

$$W = \oint \tau \, d\mathcal{L} = Q_h - Q_c = -\oint \not{d}Q$$

Carnot Cycles

$W > 0$ is a heat machine:



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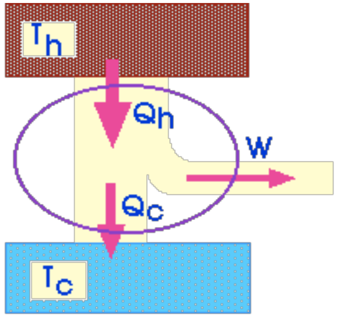
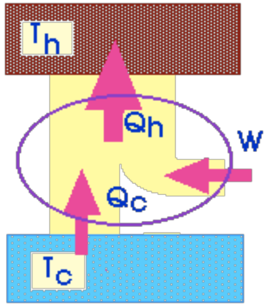
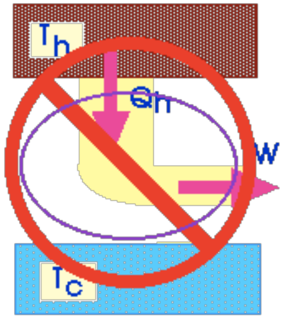


in a reverse mode is a *Carnot refrigerator*: $W < 0$



Second Principle of Thermodynamics

Lord Kelvin statement: if $W > 0$ then $Q_2 > 0$ and $Q_1 > 0$:



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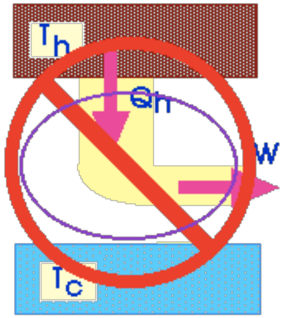
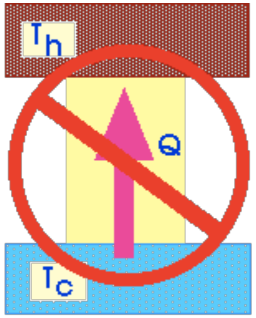
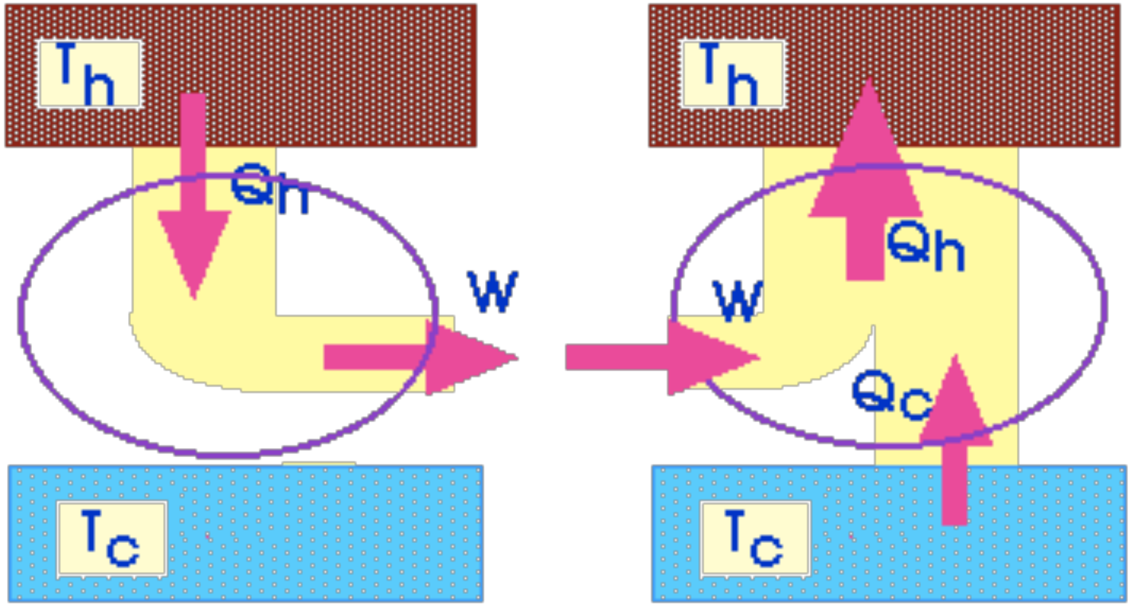


Clausius Statement: if $W = 0$, then $Q_2 = Q_1 > 0$:



Equivalence of Kelvin and Clausius statement



Kelvin's theorem

For **any** Carnot cycle operating between temperatures θ_h and θ_c, the ratio $\frac{Q_h}{Q_c}$ depends only from (θ_h, θ_c) and there exist a universal function $g(\theta)$ such that

$$\frac{Q_h}{Q_c} = \frac{g(\theta_h)}{g(\theta_c)}$$

Kelvin's theorem

For **any** Carnot cycle operating between temperatures θ_h and θ_c, the ratio $\frac{Q_h}{Q_c}$ depends only from (θ_h, θ_c) and there exist a universal function $g(\theta)$ such that

$$\frac{Q_h}{Q_c} = \frac{g(\theta_h)}{g(\theta_c)}$$

$T = g(\theta)$ absolute temperature

Thermodynamic Entropy

From Kelvin's theorem:

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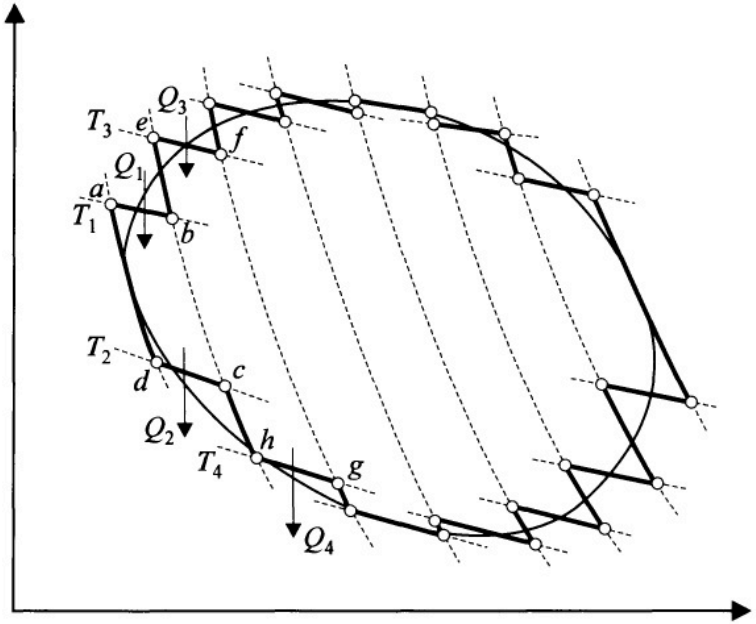
Extension to any cycle C: $\oint_C \frac{\not{d}Q}{T} = 0$



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$$dS(U, \mathcal{L}) = -\frac{\tau}{T} d\mathcal{L} + \frac{1}{T} dU$$

- In isothermal transformation $\Delta S = \Delta Q / T$.
- Adiabatic quasistatic transformations are isoentropic.

Axiomatic approach

Extensive quantities: $M, U, \mathcal{L} =$ (mass, energy, length)

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There exist an open cone set $\Gamma \subset \mathbb{R}_+ \times \mathbb{R}_+ \times \mathbb{R}$, and $(M, U, \mathcal{L}) \in \Gamma$.
There exists a C^1–function

$$S(M, U, \mathcal{L}) : \Gamma \to \mathbb{R}$$

such that

- S is concave,
- $\frac{\partial S}{\partial U} > 0$,
- S is positively homogeneous of degree 1:

$$S(\lambda M, \lambda U, \lambda \mathcal{L}) = \lambda S(M, U, \mathcal{L}), \qquad \lambda > 0$$

this scaling property means it refers to **macroscopic** objects.

Axiomatic Approach

Choose S and $\mathcal{L}$ as thermodynamic coordinates,
there exists a function $U(M, S, \mathcal{L})$ such that $\frac{\partial U}{\partial S} > 0$.

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$U(M, S, \mathcal{L})$ is homogeneous of degree 1 (*extensive*), and T, τ are homogeneous of degree 0 (*intensive*).

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$U(M, S, \mathcal{L})$ is homogeneous of degree 1 (*extensive*), and T, τ are homogeneous of degree 0 (*intensive*).
Since M is constant in most transformations we can set $M = 1$ or just omit it if not necessary.

Irreversible Transformations

For *irreversible* thermodynamic transformations (not quasi-static), we find in thermodynamics books the expression

$$\oint \frac{\delta Q}{T} < 0 \qquad \text{Clausius Inequality}$$

or

$$\int_A^B \frac{\delta Q}{T} \leq S(B) - S(A)$$

Not very clear the meaning of this.

Isothermal Irreversible Transformations

$A = (\mathcal{L}_0, T), \; B = (\mathcal{L}_1, T)$

$$Q \leq T\left[S(B) - S(A)\right]$$

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$$F(\mathcal{L}, T) = \inf_U \{U - TS(U, \mathcal{L})\} \qquad \text{free energy} \tag{3}$$

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$F = U - TS$ convex function of $\mathcal{L}$.

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$$\boxed{\text{đ}Q = TdS}$$

has a meaning only in quasistatic processes.

Local equilibrium thermodynamics

Two systems: $(M_1, U_1, \mathcal{L}_1)$, $(M_2, U_2, \mathcal{L}_2)$.
If attached they are **not in equilibrium**.
We can define the total entropy as

$$S(M_1, U_1, \mathcal{L}_1) + S(M_2, U_2, \mathcal{L}_2)$$

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By concavity and 1-homogeneity:

$$
\begin{aligned}
S(M_1, U_1, \mathcal{L}_1) + S(M_2, U_2, \mathcal{L}_2) &\leq 2S\left(\frac{M_1 + M_2}{2}, \frac{U_1 + U_2}{2}, \frac{\mathcal{L}_1 + \mathcal{L}_2}{2}\right) \\
&= S(M_1 + M_2, U_1 + U_2, \mathcal{L}_1 + \mathcal{L}_2)
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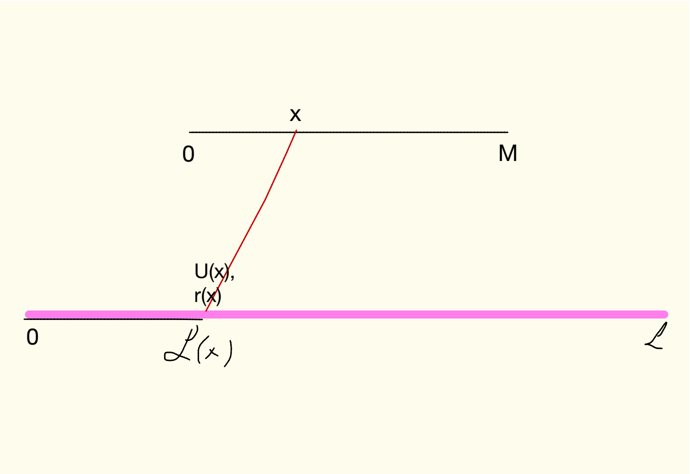
Irreversible transformations from non-equilibrium

Second principle of thermodynamics intended as a strict increase of the entropy if the system undergoes a non-reversible transformation

$$\Uparrow$$

Property of this transformation to bring the system towards global equilibrium

Local equilibrium thermodynamic states



$$x \in [0, M], \qquad U(x), r(x).$$

$$\mathcal{L}(x) = \int_0^x r(x')dx' \qquad \text{displacement of } x$$

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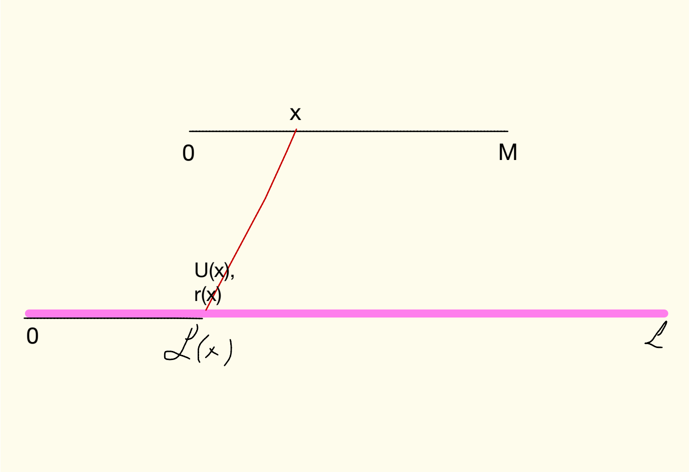

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$$\mathcal{L}_{tot} = \int_0^M r(x)dx, \quad U_{tot} = \int_0^M U(x)dx, \quad S_{tot} = \int_0^M S(1, U(x), r(x))dx.$$

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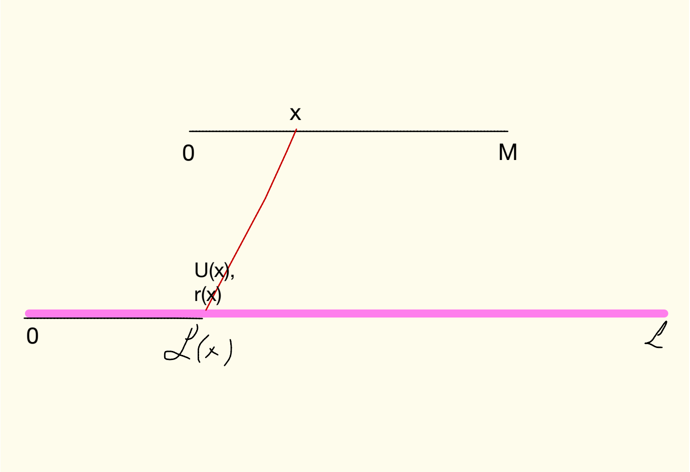

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$$S_{tot} \le MS(1, M^{-1}U_{tot}, M^{-1}\mathcal{L}_{tot}) = S(M, U_{tot}, \mathcal{L}_{tot})$$

Example: isothermal transformations by diffusion equations

The rubber is immersed in a very viscous liquid at temperature T. Velocity are dumped down by the viscosity. $\bar{\tau}(x,t) = \tau(r(x,t),T)$

$$\partial_t r(x,t) = \partial_x^2 \bar{\tau}(x,t)$$
$$\partial_x r(0,t) = 0, \quad \bar{\tau}(1,t) = \tau_1$$

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free energy of the nonequilibrium profile $\{r(x,t), x \in [0,1]\}$:

$$\mathcal{F}(t) = \int_0^1 F(r(x,t),T)\, dx, \qquad (F = U - TS) \tag{5}$$

$$\frac{d}{dt}\mathcal{F}(t) = -\int_0^1 \left(\partial_x \bar{\tau}(x,t)\right)^2\, dx + \tau_1 \partial_x \tau(1,t)$$

Isothermal by diffusion

$$\frac{d}{dt}\mathcal{L}(t) = \int_0^1 \partial_{xx}\bar{\tau}(x,t)\,dx = \partial_x\tau(1,t)$$

i.e.

$$\begin{aligned}\mathcal{F}(t) - \mathcal{F}(0) &= \tau_1\left(\mathcal{L}(t) - \mathcal{L}(0)\right) - \int_0^t ds \int_0^1 \left(\partial_x\bar{\tau}(x,s)\right)^2\,dx \\ &= W - \int_0^t ds \int_0^1 \left(\partial_x\bar{\tau}(x,s)\right)^2\,dx\end{aligned}$$

---

initial global equilibrium $r(x,0) = r_0, \qquad \tau_0 = \tau(r_0, T)$.
$t \to \infty$ we have $r(x,t) \to r_1, \qquad \tau_1 = \tau(r_1, T)$.

$$F(r_1, T) - F(r_0, T) = \tau_1(r_1 - r_0) - \int_0^\infty ds \int_0^1 \left(\partial_x\bar{\tau}(x,t)\right)^2\,dx$$

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Inverse transformation: initial global equilibrium

$r(x,0) = r_1, \qquad \tau_1 = \tau(r_1, T)$,
and we apply the tension $\tau_0 = \tau(r_0, T)$.
$t \to \infty$ we have $\tilde{r}(x,t) \to r_0, \qquad \tau_0 = \tau(r_0, T)$.

$$F(r_0, T) - F(r_1, T) = \tau_0(r_0 - r_1) - \int_0^\infty ds \int_0^1 (\partial_x \tau(\tilde{r}(x,t), T))^2 \; dx$$

Irreversible Isothermal Cycle

Summing up we have a cycle and

$$\begin{aligned} W &= (\tau_1 - \tau_0)(r_1 - r_0) \\ &= \int_0^\infty ds \int_0^1 \left[(\partial_x \tau(r(x,t),T))^2 + (\partial_x \tau(\tilde{r}(x,t),T))^2 \right] dx \end{aligned}$$

this work is gone to the thermostat as *heat*.

Reversible quasi static isothermal transformation

Pull slowly: $\bar{\tau}(t)$ smooth and $\bar{\tau}(0) = \tau_0$, $\bar{\tau}(1) = \tau_1$

$$\partial_t r^\epsilon(x,t) = \partial_x^2 \tau(r^\epsilon(x,t))$$
$$\partial_x r^\epsilon(0,t) = 0, \quad \tau(r^\epsilon(1,t)) = \bar{\tau}(\epsilon t)$$

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\end{aligned}
$$

introduce the time scale $t' = \epsilon t$, $r_\epsilon(x,t') = r_\epsilon(x,t)$:

$$
\begin{aligned}
&\partial_{t'} r_\epsilon = \epsilon \partial_x^2 \tau(r^\epsilon(x,t'))\\
&\partial_x r^\epsilon(0,t) = 0, \quad \tau(r^\epsilon(1,t')) = \bar{\tau}(t')
\end{aligned}
$$

after the limit as $t' \to \infty$:

$$
\begin{aligned}
F(r_1,T) - F(r_0,T) &= \int_0^\infty \tau(r_\epsilon(1,t')\partial L^\epsilon(t') dt'\\
&+\epsilon \int_0^\infty dt' \int_0^1 \left(\partial_x \tau(r_\epsilon(x,t'),T)\right)^2 \, dx\\
&= W_\epsilon + \epsilon \int_0^\infty dt' \int_0^1 \left(\partial_x \tau(r(x,t'),T)\right)^2 \, dx
\end{aligned}
$$

and take $\epsilon \to 0$: $\Delta F = W$!!!

Example: adiabatic evolution by Euler Equations

$x \in [0,1]$. The velocity of the material point x is

$$\pi(x,t) = \partial_t \mathcal{L}(x,t)$$

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$$\begin{aligned} \partial_t r &= \partial_x \pi \\ \partial_t \pi &= \partial_x \tau \\ \partial_t \mathcal{E} &= \partial_x (\tau \pi) \end{aligned}$$

$$\pi(0,t) = 0, \quad \tau(1,t) = \bar{\tau}(t)$$

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$$\begin{aligned}\partial_t r &= \partial_x \pi\\ \partial_t \pi &= \partial_x \tau\\ \partial_t U &= \tau \partial_x \pi\end{aligned}$$

$$\frac{d}{dt} S(U(x,t), r(x,t)) = \frac{1}{T}\partial_t U - \frac{\tau}{T}\partial_t r = 0$$

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$$\frac{d}{dt} S(U(x,t), r(x,t)) = \frac{1}{T}\partial_t U - \frac{\tau}{T}\partial_t r = 0$$

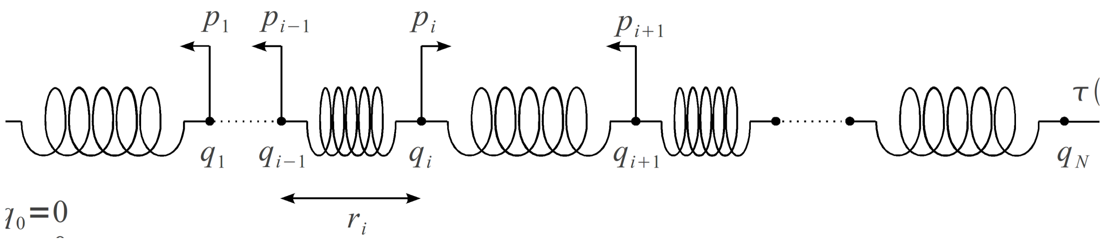
After shock appears, Entropy should increase:

$$\frac{d}{dt} S(U(x,t), r(x,t)) \geq 0$$

Uniqueness of the weak *entropy solution* is an open problem.

Statistical Mechanics: deduction of the above theory from the microscopic dynamics.

Microscopic Dynamics: Chain of Oscillators



Isobar Dynamics:

$$\begin{aligned}
\dot{r}_j(t) &= p_j(t) - p_{j-1}(t), \qquad j = 1, \dots, m, \\
\dot{p}_j(t) &= V'(r_{j+1}(t)) - V'(r_j(t)), \qquad j = 1, \dots, m-1, \\
\dot{p}_m(t) &= \tau - V'(r_m(t)),
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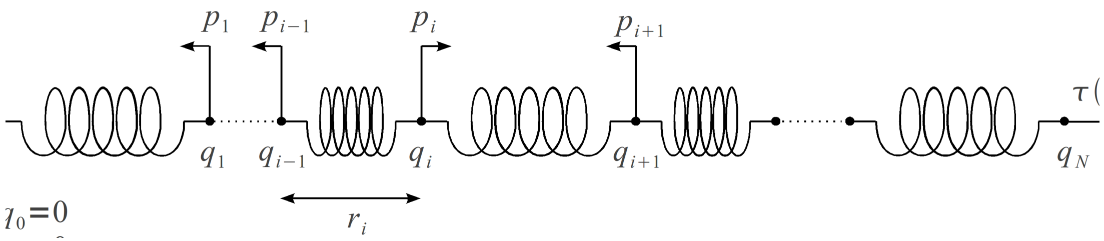

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\end{aligned}$$

Equilibrium measures:

$$d\alpha^{m,gc}_{\tau,\beta} = \prod_{j=1}^{m} \frac{e^{-\beta(\mathcal{E}_j - \tau r_j)}}{\sqrt{2\pi\beta^{-1}}Z(\beta\tau,\beta)} dr_j dp_j \qquad \forall \beta > 0.$$

$$\mathcal{E}_j = \frac{p_j^2}{2} + V(r_j), \quad Z(\beta\tau,\beta) = \int_{\mathbb{R}} e^{-\beta(V(r)-\tau r)} dr$$

Microcanonical surface: $M > 0, U > 0, \mathcal{L} \in \mathbb{R}$,

$$\tilde{\Sigma}_m(M, MU, M\mathcal{L}) := \left\{ (r_1, p_1, \dots, r_m, p_m) : \frac{1}{n} \sum_{j=1}^{m} \mathcal{E}_j = MU, \frac{1}{n} \sum_{j=1}^{m} r_j = M\mathcal{L} \right\}$$

$$= \Sigma_m(U, \mathcal{L}) = \left\{ (r_1, p_1, \dots, r_m, p_m) : \mathcal{E}^{(m)} = U, r^{(m)} = \mathcal{L} \right\}.$$

Entropy!

$$\Sigma_m(U,\mathcal{L}) = \left\{(r_1, p_1, \dots, r_m, p_m) : \mathcal{E}^{(m)} = U, r^{(m)} = \mathcal{L}\right\}.$$

$$\begin{aligned} W_m(U,\mathcal{L}) &= \int_{\Sigma_m(U,\mathcal{L})} \gamma_m(dr_1, dp_1, \dots, dp_m; U, \mathcal{L}) \\ &= \text{microcanonical volume}(\Sigma_m(U,\mathcal{L})) \end{aligned}$$

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Boltzmann formula (made precise):

$$S(M,MU,M\mathcal{L}) := \lim_{n\to\infty} \frac{1}{n} \log W_{nM}(U,\mathcal{L}) = M\; S(1,U,\mathcal{L})$$

the limit exists and is concave and homogeneous function of degree 1,

$$S(U,\mathcal{L}) := S(1,U,\mathcal{L}) = \inf_{\lambda,\beta>0}\left\{-\lambda\mathcal{L} + \beta U - \log\left(Z(\lambda,\beta)\sqrt{2\pi\beta^{-1}}\right)\right\}.$$

Thermodynamic relations

$U, \mathcal{L}$ are here the coordinates:

$$\tau\beta = \lambda = -\frac{\partial S}{\partial \mathcal{L}}, \qquad \beta = \frac{1}{T} = \frac{\partial S}{\partial U}$$

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They can be inverted:

$$\begin{aligned}
\mathcal{L}(\lambda,\beta) &= \frac{\partial \log Z(\lambda,\beta)}{\partial \lambda} = \int r\, \frac{e^{\lambda r - \beta V(r)}}{Z(\lambda,\beta)}\, dr = \int r_j \, d\mu^{gc}_{\tau,\beta} \\
U(\lambda,\beta) &= -\frac{\partial \log\left(Z(\lambda,\beta)\sqrt{2\pi/\beta}\right)}{\partial \beta} = \int V(r) \frac{e^{\lambda r - \beta V(r)}}{Z(\lambda,\beta)}\, dr + \frac{1}{2\beta} \\
&= \int \mathcal{E}_j \, d\mu^{gc}_{\tau,\beta}
\end{aligned}$$

In particular $\beta^{-1} = \int p_j^2 \, d\mu^{gc}_{\tau,\beta}$.

Gibbs Thermodynamics: orthodic ensembles

i.e. defining a heat differential form:

$$\text{đ}Q = -\tau d\mathcal{L} + dU$$

we have

$$dS = \beta \text{đ}Q = \beta dU - \beta\tau d\mathcal{L}$$

but this is only a mathematical definition!!
Clausius was not talking about Gibbs measures.

Example: harmonic chain

$V(r) = r^2$, so that, for $\mathcal{L}^2 \leq 2U$, $\tilde{\Sigma}_m(M, MU, M\mathcal{L})$ is the $2m-2$-dimensional sphere (even dimension) of radius $\sqrt{m(U-\mathcal{L}^2/2)}$, and γ_m the uniform measure and

$$W_m(U,\mathcal{L}) = \frac{(2\pi)^{m-1}[m(U-\mathcal{L}^2/2)]^{m-3/2}}{2\cdot 4 \ldots (2m-4)} = 2\frac{\pi^{m-1}[m(U-\mathcal{L}^2/2)]^{m-3/2}}{\Gamma(m-1)}$$

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$$S = 1 + \log(\pi T), \qquad F(\mathcal{L}, T) = U - T^{-1}S, \qquad \partial_{\mathcal{L}} F = \partial_{\mathcal{L}} U = \mathcal{L}$$

Isocore dynamics: microcanonical measure.

$$\begin{aligned}
\dot{r}_j(t) &= p_j(t) - p_{j-1}(t), \qquad j = 1, \dots, m-1, \\
\dot{p}_j(t) &= V'(r_{j+1}(t)) - V'(r_j(t)), \qquad j = 1, \dots, m-1, \\
r_m(t) &= m\mathcal{L} - \sum_{j=1}^{m-1} r_j(t) \; .
\end{aligned}$$

$\mathcal{H} = \sum_j \mathcal{E}_j = mU$ and $\sum_{j=1}^m r_j = m\mathcal{L}$ are conserved.

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$\mathcal{H} = \sum_j \mathcal{E}_j = mU$ and $\sum_{j=1}^{m} r_j = m\mathcal{L}$ are conserved.
Corresponding conditioned measure (microcanonical) are stationary.
Usually not the only one! Other conservation laws can be present.

Local Equilibrium probability measures

Definition

Given two *profiles* $\beta(y) > 0, \tau(y), y \in [0,1]$, we say that the sequence of probability measures μ_n on $\mathbb{R}^{2n}$ has the **local equilibrium property** (with respect to the profiles $\beta(\cdot), \tau(\cdot)$) if for any $k > 0$ and $y \in (0,1)$,

$$\lim_{n\to\infty} \mu_n\Big|_{([ny],[ny]+k)} = \mu^{k,gc}_{\tau(y),\beta(y)}$$

Example: Local Gibbs

$$\prod_{j=1}^{n} \frac{e^{-\beta(j/n)(\mathcal{E}_j - \tau(j/n) r_j)}}{\sqrt{2\pi\beta(j/n)^{-1}} Z(\beta(j/n)\tau(j/n), \beta(j/n))} dr_j dp_j = g^n_{\tau(\cdot),\beta(\cdot)} \prod_{j=1}^{n} dr_j dp_j$$

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or 1st order perturbations:

$$e^{\frac{1}{n}\sum_j F_j(r_{j-h}, p_{j-h}, \dots, r_{j+h}, p_{j+h})} g^n_{\tau(\cdot),\beta(\cdot)} \prod_{j=1}^{n} dr_j dp_j \tag{6}$$

with F_j local functions.

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As in extended thermodynamics, define entropy of the local equilibrium

$$S(r(\cdot), u(\cdot)) = \int_0^1 S(r(y), u(y))\, dy$$

where $r(y), u(y)$ are computed from $\tau(y), \beta(y)$

Isothermal dynamics

Modelling the interaction with the viscous fluid at temperature T:
Langevin heat bath in each site:

$$\begin{aligned}
\dot{r}_j(t) &= p_j(t) - p_{j-1}(t), \qquad j = 1, \dots, n, \\
dp_j(t) &= \left(V'(r_{j+1}(t)) - V'(r_j(t))\right) dt - p_j(t)dt + \sqrt{\beta} dw_j(t), \\
&\qquad\qquad\qquad\qquad\qquad\qquad j = 1, \dots, n-1, \\
dp_n(t) &= \left(\tau_1 - V'(r_n(t))\right) dt - p_n(t)dt + \sqrt{\beta} dw_n(t)
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$w_j(t)$ i.i.d. standard Wiener processes.

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$w_j(t)$ i.i.d. standard Wiener processes.
$d\alpha^n_{\beta,\tau_1}$ is the only stationary probability.

Non-equilibrium isothermal dynamics

We start instead with $d\alpha^{n}_{\beta,\tau_0}$, for $\tau_0 \neq \tau_1$.

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Empirical Distribution: diffusive scaling

$$\mu_n(t)(G) = \frac{1}{n}\sum_{i=1}^{n} G\left(\frac{i}{n}\right) r_i(n^2 t)$$

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$\mu_n(0) \to r_0 dy$, with $\tau(r_0, \beta^{-1}) = \tau_0$.

Isothermal diffusion limit

Theorem

$$\frac{1}{n}\sum_{i=1}^{n} G\left(\frac{i}{n}\right) r_i(n^2 t) \xrightarrow[n\to\infty]{} \int_0^1 G(y) r(y,t) dy$$

in probability, with $r(y,t)$ solution of

$$\partial_t r(y,t) = \partial_y^2 \tau(r(y,t),T)$$

$$\partial_y r(0,t) = 0, \qquad \tau(r(1,t),T) = \tau_1$$

with $T = \beta^{-1}$.

Isothermal Dynamics: heat exchanged

Average internal energy at time $n^2 t$:

$$\mathcal{U}_n(n^2 t) = \frac{1}{n}\sum_{i=1}^{n} \mathcal{E}_i(n^2 t) = \frac{1}{n}\sum_{i=1}^{n}\left(\frac{p_i^2(n^2 t)}{2} + V(r_i(n^2 t))\right)$$

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$$\begin{aligned}\mathcal{U}_n(n^2t) - \mathcal{U}_n(0) &= \int_0^t ds\ n\sum_{i=1}^{n}(p_i^2(n^2s) - T) + \tau_1\frac{q_n(n^2t) - q_n(0)}{n} \\ &= Q_n(t)\ +\ W_n(t)\end{aligned}$$

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$$= Q_n(t) \; + \; W_n(t)$$

after $n \to \infty$

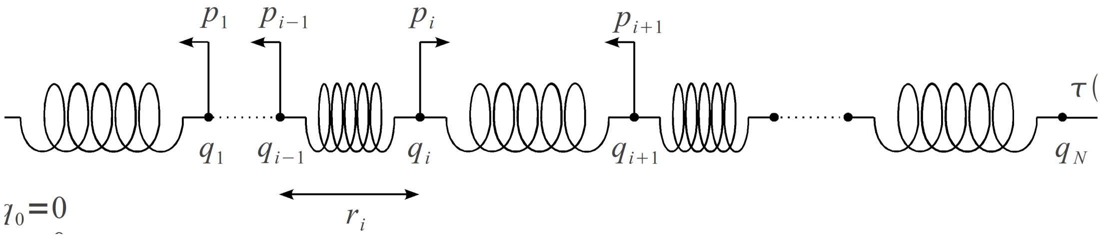
$$\int_0^1 [U(r(x,t), T) - U(\mathcal{L}_0, T)] \, dx = \lim_{n \to \infty} Q_n(t) + \tau_1 \left(\mathcal{L}(1,t) - \mathcal{L}_0 \right)$$

and $t \to \infty$ to reach the new equilibrium:

$$[U(\mathcal{L}, T) - U(\mathcal{L}_0, T)] = Q + \tau_1 \left(\mathcal{L}_1 - \mathcal{L}_0 \right)$$

i.e. the first principle!.

Adiabatic dynamics



Balistic dynamics:

$$\dot r_j(t) = p_j(t) - p_{j-1}(t), \qquad j = 1, \dots, n,$$

$$dp_j(t) = \left(V'(r_{j+1}(t)) - V'(r_j(t))\right) dt, \qquad j = 1, \dots, n-1,$$

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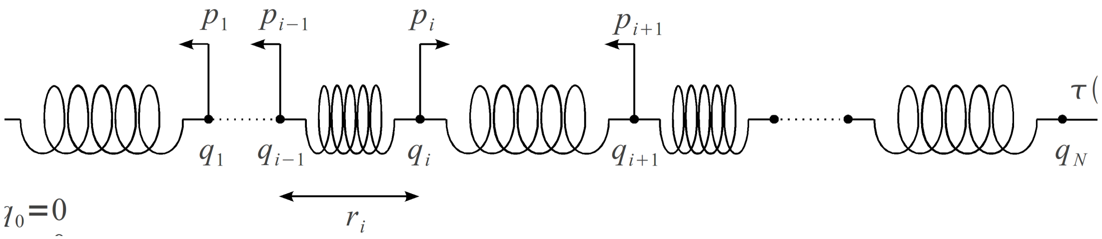

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Deterministic dynamics: difficult!

Locally momentum and energy are also conserved: $\Longrightarrow$ hyperbolic scaling and (non-linear) wave equations.

Hyperbolic Adiabatic Dynamics

3 conserved quantities:

stretch $\mathcal{R}_n(t)[G] = \frac{1}{n}\sum_i G(i/n) r_i(nt)$

momentum $\pi_n(t)[G] = \frac{1}{n}\sum_i G(i/n) p_i(nt)$

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$$(\mathcal{R}_n(t), \pi_n(t), \mathfrak{e}_n(t)) \longrightarrow (r(x,t)dx, \pi(x,t)dx, \mathfrak{e}(x,t)dx)$$

$$\begin{aligned}
\partial_t r &= \partial_x \pi \\
\partial_t \pi &= \partial_x \tau \\
\partial_t \mathfrak{e} &= \partial_x(\tau\pi) \\
\partial r(0,t) = 0, &\qquad \tau(r(1,t), U(1,t)) = \tau_1
\end{aligned}$$

Ergodicity of the infinite dynamics

Consider the dynamics of the infinite system:

$$\begin{aligned} \dot{r}_j(t) &= p_j(t) - p_{j-1}(t), \qquad && j \in \mathbb{Z} \\ dp_j(t) &= \left(V'(r_{j+1}(t)) - V'(r_j(t))\right) dt \qquad && j \in \mathbb{Z}, \end{aligned}$$

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We say that it is *ergodic* if all stationary translational invariant probability measures locally absolutely continuous are convex combinations of the Gibbs measures:

$$d\alpha_{\beta,\pi,\tau} = \prod_{j\in\mathbb{Z}} e^{-\beta\mathcal{E}_j + \pi p_j + \tau r_j - \mathcal{Z}(\beta,\pi,\tau)} dr_j dp_j$$

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Not true for harmonic chain or any other completely integrable system.

Velocity echeangeability

Theorem (**Fritz, Funaki, Lebowitz, 1993**)

if $d\nu$ *is a (regular) translation invariant probability on* $(\mathbb{R}^2)^{\mathbb{Z}}$ *stationary for the infinite dynamics and such that*

$$d\nu(\mathbf{p}|\mathbf{r})$$

is excheangeable, then it is a convex combination of Gibbs measures.

Stochastic dynamic perturbations

We search for stochastic perturbations that conserve *energy*, *momentum*, *length*, and that will give the ergodic property requested:

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momentum exchange For each couple of nearest neighbor particle, we randomly exchange momentum, $(p_i, p_{i+1}) \to (p_{i+1}, p_i)$, with intensity 1. The resulting infinite dynamics has the ergodic property.

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- diffusive exchange of momentum Done with three body exchange.

With this stochastic perturbation, we can prove the convergence to the Euler system of PDE, at least in the smooth regime.

Conclusion

- Thermodynamics is a **macroscopic** theory
- It can be deduced from the microscopic dynamics in a large space-time scale limit. This is a **mathematical** difficult but precise problem.
- The mathematical deduction needs to prove the ergodicity and eventually the chaoticity of the **infinite** system.
- The ergodicity (or the non-ergodicity) of the *finite* system is irrelevant for this problem.