From Dynamics to Thermodynamics.

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May, 2018

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 more 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)

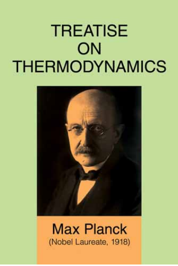
$\Downarrow$

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

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

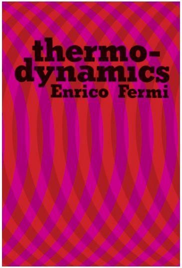
What is (equilibrium) *thermodynamics*?

I take seriously thermodynamics as defined in these classical books:

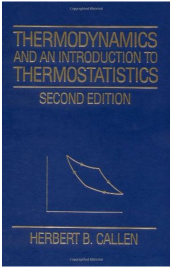


TREATISE
ON
THERMODYNAMICS

Max Planck
(Nobel Laureate, 1918)



thermo-
dynamics
Enrico Fermi



THERMODYNAMICS
AND AN INTRODUCTION TO
THERMOSTATISTICS
SECOND EDITION

HERBERT B. CALLEN

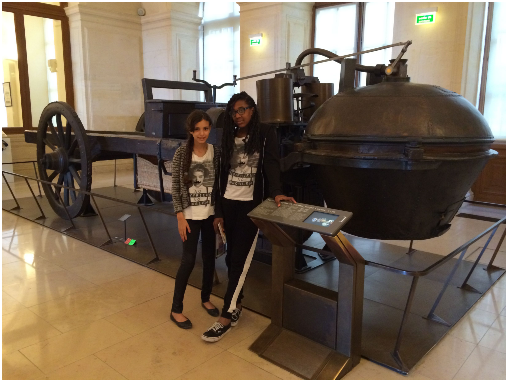
SEVENTH EDITION
HEAT AND
THERMODYNAMICS

MARK W. ZEMANSKY
RICHARD H. DITTMAN

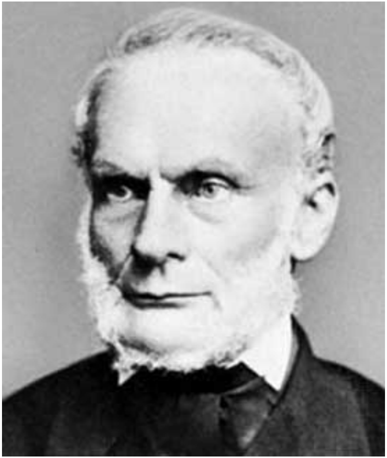
Connections between measurable quantities as:
pressure, *tension*, *volume*, *'temperature'*, *energy*
and *heat*, *work*, *entropy*.

Thermodynamics concern **Macroscopic Objets**

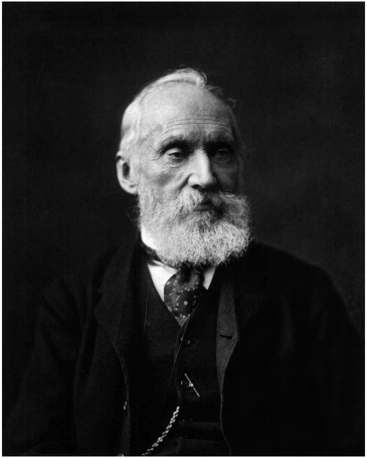
Vapor machine of Joseph Cugnot (1770)



Fathers of Thermodynamics:



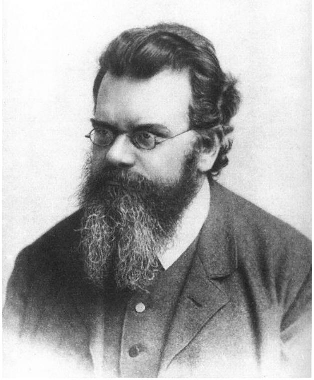
Clausius,



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 **something** in these objects is changing very slowly, compared with the typical frequency of the jiggling of these atoms.

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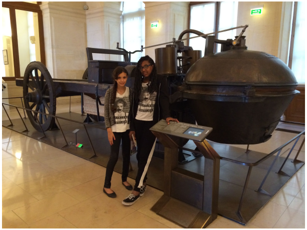

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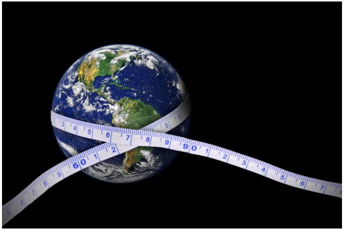

and the Earth?

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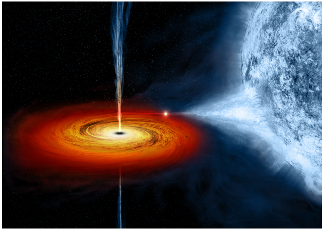

a black hole?

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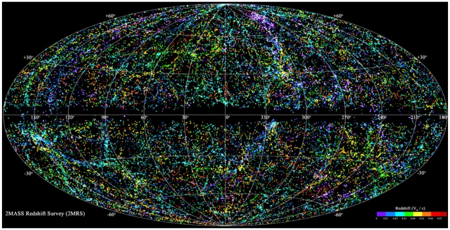

the entire universe?

God Given postulate or laws (principles)

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

- 0th law: *existence of equilibrium states*, (Fowler 1931)
- 1st law: *energy conservation* (and much more!), (Mayer 1842, Helmholtz and Thompson 1848),
- 2nd law: possible and impossible transformations from an equilibrium to another (1824, Carnot).

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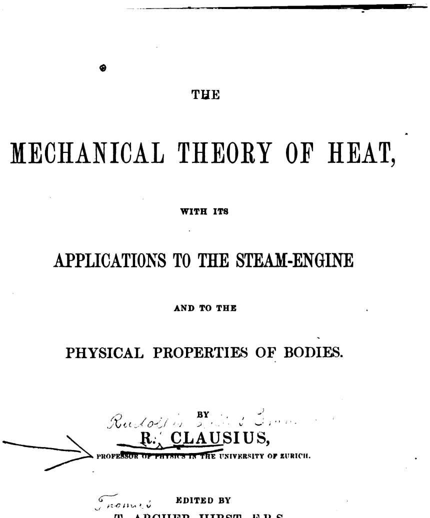
In particular we cannot apply (directly) these ideas to system that have no equilibrium states or we do not know them.
Galaxy? Universe?

From here come most of the abuses of 2nd principle and Entropy: *2nd principle cannot be applied to systems that do not satisfy the 0th principle.*

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]

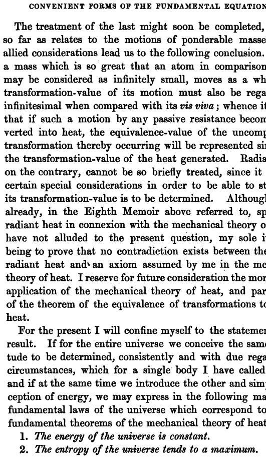
R. CLAUSIUS,

PROFESSOR OF PHYSICS IN THE UNIVERSITY OF ZURICH.

Thomas

EDITED BY

T. ARCHER HIRST, F.R.S.



CONVENIENT FORMS OF THE FUNDAMENTAL EQUATION

The treatment of the last might soon be completed,
so far as relates to the motions of ponderable masse
allied considerations lead us to the following conclusion.
a mass which is so great that an atom in comparison
may be considered as infinitely small, moves as a wh
transformation-value of its motion must also be rega
infinitesimal when compared with its *vis viva*; whence i
that if such a motion by any passive resistance becom
verted into heat, the equivalence-value of the uncomp
transformation thereby occurring will be represented si
the transformation-value of the heat generated. Radia
on the contrary, cannot be so briefly treated, since it
certain special considerations in order to be able to st
its transformation-value is to be determined. Althoug
already, in the Eighth Memoir above referred to, sp
radiant heat in connexion with the mechanical theory o
have not alluded to the present question, my sole i
being to prove that no contradiction exists between the
radiant heat and an axiom assumed by me in the me
theory of heat. I reserve for future consideration the mor
application of the mechanical theory of heat, and par
of the theorem of the equivalence of transformations to
heat.

For the present I will confine myself to the statemen
result. If for the entire universe we conceive the same
tude to be determined, consistently and with due rega
circumstances, which for a single body I have called
and if at the same time we introduce the other and sim
ception of energy, we may express in the following ma
fundamental laws of the universe which correspond to
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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Equilibrium thermodynamics only talks about which are the possible transformation, without specifying any time scale or any inhomogeneity.

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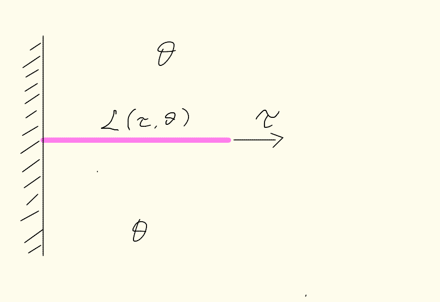
A non equilibrium statistical mechanics should explain, from microscopic dynamics of atoms, why only some transformations can happens, and how: space-time scale etc.

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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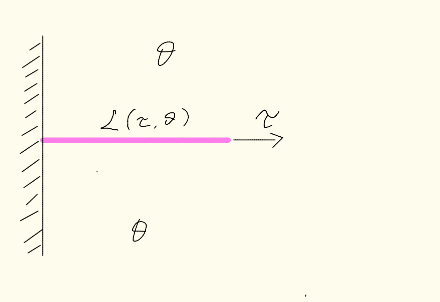

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Thermodynamic Equilibrium

$$\mathcal{L} = \mathcal{L}(\tau, \theta)$$

θ is the **temperature**

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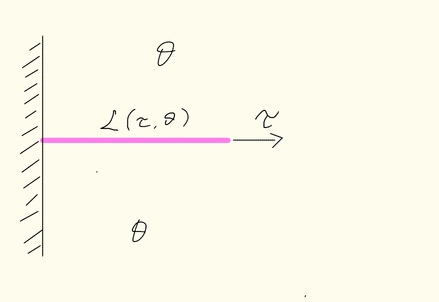

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θ is the **temperature**
Empirical definition of temperature.

0th Law

There exists a family of thermodynamic equilibrium states, parametrized by certain extensive or intensive variables.

For our one-dimensional bar:

– lenght (volume) L and energy U (extensive)

– tension $\bar{\tau}$ applied and temperature $\theta > 0$ (intensive).

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There exists a family of thermodynamic equilibrium states, parametrized by certain extensive or intensive variables.
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– lenght (volume) L and energy U (extensive)
– tension $\bar{\tau}$ applied and temperature $\theta > 0$ (intensive).

- If we do not know if a particular system (let's say the *Universe* for example) has equilibrium states or we do not know how they are parametrized, we cannot apply thermodynamic theory.
- Stronger statement: when it is under a tension $\bar{\tau}$ and in contact with a heat bath at temperature θ, the system is able to reach the corresponding equilibrium state.
- no time-scale at which equilibrium is reached.

Remarks on the 0-law

- In principle it only defines class of equivalence of equilibrium states. In order to put a complete order and characterize them by a real parameter θ we need to compare with a *real* material and that gives $\theta_{ref}(L, \tau)$.

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- **Heat bath or thermostats**: a very large system that is in equilibrium at a given temperature θ, and when in contact with our (smaller) syatem, it is reacheed equilibrium at the same temperature θ. Ideally it is an *infinite* system.

1st Law: Work and Energy

1. System is isolated. Start in equilibrium (L_0, τ_0). This is a temperature $\theta_0 = \theta(L_0, \tau_0)$.

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3. Change back to an applied tension τ_0. You will reach the equilibrium state (L_2, τ_0) that has temperature $\theta_2 = \theta(L_2, \tau_0)$. The work is now
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In general $L_2 \neq L_1$ and we observe empirically that $W_{1\to 2} \neq W_{0\to 1}$.

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   In general $L_2 \neq L_1$ and we observe empirically that $W_{1\to2} \neq W_{0\to1}$.
4. This means that there has been a change in the (*internal*) energy of the system $\Delta U = W_{0\to1} + W_{1\to2}$. It allows to define another (extensive) equilibrium variable $U = U(L, \theta)$.

1st law: isothermal transformations

Now the system is in contact with a thermostat at temperature θ. At beginning it is in state (τ_0, θ).

1. We change tension to τ_1 doing work $W_{0\to 1} = \tau_1(L_1 - L_0)$, where $L_1 = L(\tau_1, \theta)$.

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3. Total work is

$$W = (\tau_1 - \tau_0)(L_1 - L_0) = -Q$$

in the heat, i.e. the energy ended up in the thermostat.

Notice that if $L(\tau, \theta)$ is increasing with L, we have $W > 0$.

1st Law

In a thermodynamics transformation,

$$\Delta U = W + Q$$

W : mechanical work done by the force $\bar{\tau}$,
Q : energy exchanged with the heat bath (*Heat*).

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More than just energy conservation:

- separation of scales between the ordered (deterministic) macroscopic *slow* work done by the tension $\bar{\tau}$ and the disordered (random) microscopic *fast* collisions with the heat bath.
- Q is the total exchange of energy with the heat bath during the complete thermodynamic trasformation, resulting out of a fast fluctuating istantaneous flux.

Quasi-Static Transformations

Existence of thermodynamic processes where the system is always at some equilibrium. These processes are described by continuous curves on the space of parameters. This way we can define *isothermal* lines and *adiabatic* lines etc.

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We can consider this as a
hidden principle of thermodynamics,
or Law 1.5.
What is the physical meaning of these differential changes of *equilibrium* states?
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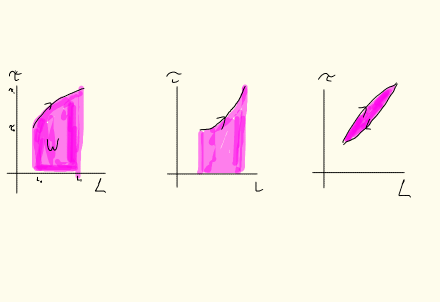
What is the physical meaning of these differential changes of *equilibrium* states?
In principle, as we actually change the tension of the cable, the system will go into a sequence of non-equilibrium states before to relax to the new equilibrium. But, quoting Zemanski,

> *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.*

Thermodynamic transformations and Cycles

- reversible or quasi-static tranformations:
  Often is used the $\tau - L$ diagrams.



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

$$W = \oint \tau dL = -Q \tag{1}$$

Irreversible thermodynamic transformations

In principle any transformation that is not quasi-static, but brings the system from an initial equilibrium state $A = (\mathcal{L}_0, \tau_0)$ to a final state $B = (\mathcal{L}_1, \tau_1)$.

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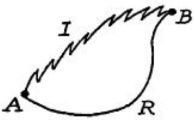

Fig. 11.

from the Fermi's *Thermodynamics*

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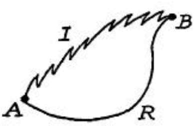

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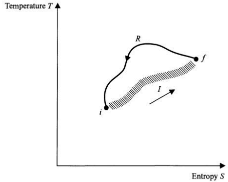


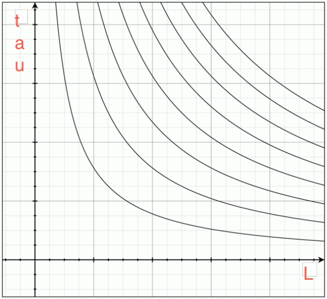
FIGURE 8-8
An irreversible process followed by a reversible process to complete an irreversible cycle.

from the Zemanski *Heat and*

Special quasi-static transformations

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

$$đW = \tau d\mathcal{L} = \tau \left(\frac{\partial \mathcal{L}}{\partial \tau} \right)_\theta d\tau = -đQ + dU$$



Special quasi–static Transformations

- **Adiabatic:** $\text{đ}Q = 0$.

$$\text{đ}W = \tau \, d\mathcal{L} = dU$$

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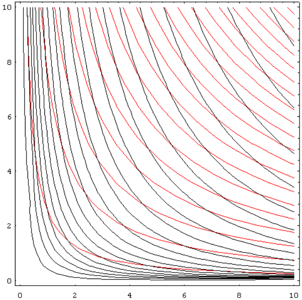
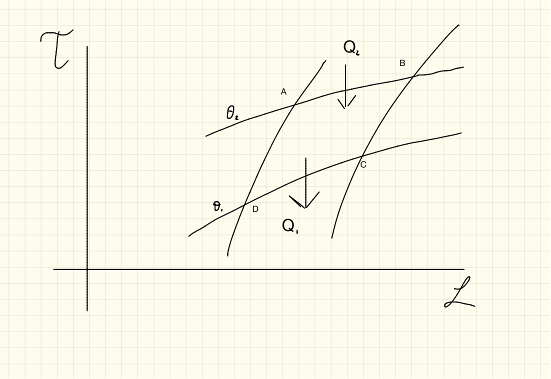
- **Adiabatic:** $đQ = 0$.

$$đW = \tau d\mathcal{L} = dU$$

$$\frac{d\tau}{d\mathcal{L}} = -\frac{\partial_{\mathcal{L}} U}{\partial_{\tau} U}$$

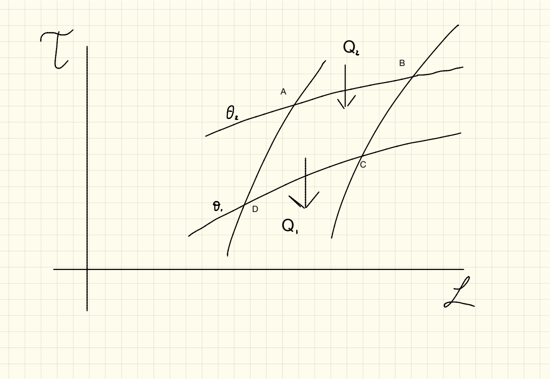


Carnot Cycles



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

Carnot Cycles

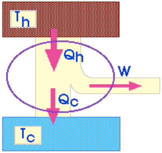


$A \to B$, $C \to D$ isothermal transformations
$B \to C$, $D \to A$ adiabatic transformations

$$W = \oint \tau d\mathcal{L} = Q_h - Q_c = -\oint \text{đ}Q$$

Carnot Cycles

$W > 0$ is a heat machine:



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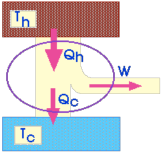
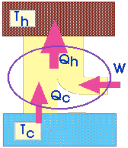


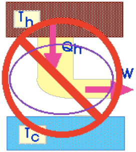
in a reverse mode is a *Carnot refrigerator*: $W < 0$



Second Principle of Thermodynamics

Lord Kelvin statement:
if $W < 0$ then

- $Q_2 > 0$ and $Q_1 > 0$
- or $Q_2 < 0$ and $Q_1 < 0$



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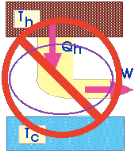

If $Q_2 > 0$ and $Q_1 > 0$, then we say that $\theta_2 > \theta_1$ (*definition!*).

Clausius statement

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

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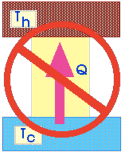
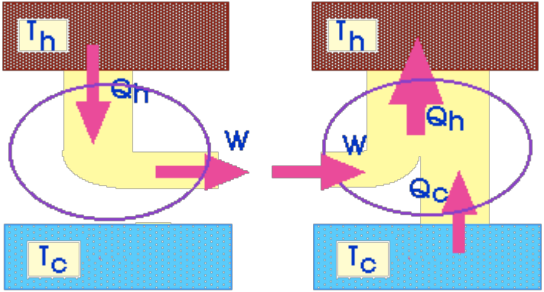
Equivalence of Kelvin and Clausius statement:





Kelvin's theorem

Assume Kelvin Statement is satisfied, then for **any** Carnot cycle operating between temperatures θ_2 and θ_1, the ratio $\frac{Q_2}{Q_1}$ depends only from (θ_2, θ_1), i.e. there exist a universal function $f(\theta_1, \theta_2)$ such that

$$\frac{Q_2}{Q_1} = f(\theta_1, \theta_2).$$

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Corollary: There exist a function $g(\theta)$ (independent of the cycle) such that

$$\frac{Q_2}{Q_1} = \frac{g(\theta_2)}{g(\theta_1)}$$

$T = g(\theta)$ absolute temperature

Proof of corollary

Take three thermostats $\theta_0, \theta_1, \theta_2$.

$$\frac{Q_1}{Q_0} = f(\theta_0, \theta_1)$$

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and we deduce that

$$\frac{Q_2}{Q_0} = f(\theta_0, \theta_1) f(\theta_1, \theta_2) = \frac{f(\theta_1, \theta_2)}{f(\theta_1, \theta_0)}$$

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Thermodynamic Entropy

From Kelvin's theorem:

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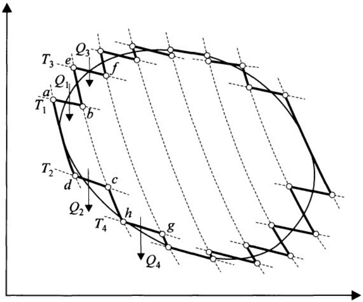
Extension to any cycle C: $\oint_c \frac{\text{đ}Q}{T} = 0$



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There exists a function S of the thermodynamic state such that

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- In quasi-static isothermal transformations: $dS = \text{đ}Q/T$.
- Adiabatic quasi-static transformations are isoentropic.
- Temperature as a *thermal* force:

$$dU = \text{đ}Q + \text{đ}W = TdS + \tau dL.$$

Irreversible (non-quasistatic) transformations

Now that we have defined $S(U,L)$ using quasi-static isothermal and adiabatic transformation, we can state his behaviour in irreversible non-quasistatic tranformations:

- in an adiabatic transformation, $(\tau_0, L_0) \to (\tau_1, L_1)$, the work done is $W = \tau_1(L_1 - L_0)$. The change in energy is $U_1 = U_0 + W$ and the entropy change is $S(U_1, L_1) - S(U_0, L_0)$. The irreversible statement of the second law is that

$$S(U_1, L_1) \geq S(U_0, L_0),$$

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Example: Free collapse, $\tau_0 > 0, L_0 > 0$ and $\tau_1 = 0$, then $W = 0$ and $U_1 = U_0$. Let $L(\tau = 0, \beta) = 0 = L_1 \ \forall \beta > 0$, then

$$S(U_1, L_1) = S(U_0, 0) > S(U_0, L_0)$$

since $\partial_L S(u, L) = -\beta\tau < 0$ if $\tau > 0$.

Irreversible (non-quasistatic) isothermal transformations

- in an isothermal transformation, $(\tau_0, \beta) \to (\tau_1, \beta)$, the work done is $W = \tau_1(L_1 - L_0)$. The change in energy is $U_1 = U_0 + W$. It is useful to define the Free Energy

$$F(L, T) = U - TS, \qquad \partial_L F(L, \beta) = \tau(L, \beta),$$

and the statement is $T\Delta S \geq 0$, i.e.

$$F(L_1, T) - F(L_0, T) = W - T\Delta S \leq W.$$

Axiomatic approach

Extensive quantities: $M, U, L =$ (mass, energy, length)

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

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

such that

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

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This function S contains all the informations about the thermodynamics of the system. One can proceed in inverse way as before and construct Carnot cycles and deduce Kelvin or the equivalent Clausius statement of the second law.

Axiomatic Approach

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$$\beta = \frac{1}{T} = \frac{\partial S}{\partial U} \qquad \text{inverse temperature}$$

$$\tau = -\beta^{-1}\frac{\partial S}{\partial L} \qquad \text{tension}$$

T, τ are homogeneous of degree 0 (*intensive*).

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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.

Thermodynamic Potentials

$\beta = T^{-1}$
Gibbs potential:

$$\mathcal{G}(\tau, \beta) = \sup_{U,L} \{-\beta U + \beta \tau L + S(U, L)\}$$

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free energy:

$$F(L,\beta) = \inf_{U>0}\left\{U - \beta^{-1}S(U,L)\right\} = \sup_{\tau}\left\{\tau L - \beta^{-1}\mathcal{G}(\tau,\beta)\right\}$$

$$\partial_L F = \tau \ .$$

Heat and work differential form:

$$đQ = TdS = \beta^{-1} dS, \qquad đW = \tau dL$$

Since $dS = -\beta\tau dL + \beta dU$, it implies that

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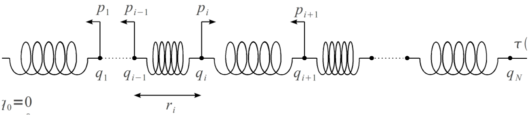
Thermodynamic transformations that are quasi-static and reversible, are integrals of these differential forms on the corresponding lines defining the transformations.
exercice: Prove that, in a Carnot cycle, the Kelvin statement of 2nd law follows.

Microscopic dynamics: statistical mechanics

FPU type chain of N-oscillators:



$$U_N = \sum_{i=1}^{N} \left(\frac{p_i^2}{2} + V(r_i) \right) := \sum_{i=1}^{N} \mathcal{E}_i \qquad \text{internal energy}$$

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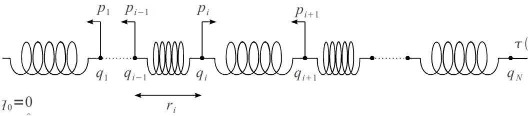

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Isobaric Hamiltonian:

$$\mathcal{H}^\tau := \sum_{x=1}^{N} \left(\frac{p_x^2}{2} + V(r_x) \right) - \tau q_N = \sum_{x=1}^{N} \left(\frac{p_x^2}{2} + V(r_x) - \tau r_x \right)$$

Isobaric Dynamics

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

For any $\beta > 0$, define the canonical Gibbs measure

$$d\mu^N_{\tau,\beta} = \prod_{j=1}^N e^{-\beta(\mathcal{E}_j - \tau r_j) - \mathcal{G}(\tau,\beta)} dr_j dp_j, \qquad \mathcal{E}_j = \frac{p_j^2}{2} + V(r_j).$$

where $\mathcal{G}$ is the Gibbs potential:

$$\mathcal{G}(\tau, \beta) = \log\left[\sqrt{2\pi\beta^{-1}} \int e^{-\beta(V(r) - \tau r)} dr\right].$$

For all $\beta > 0$, $\mu^N_{\tau,\beta}$ is a stationary probability for this dynamics.

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Equilibrium lenght $L(\tau, \beta)$ and internal energy $u(\tau, \beta)$ are given by:

$$\begin{aligned} \partial_\tau \mathcal{G}(\tau,\beta) &= \beta L(\tau,\beta) = \int r_j d\mu^N_{\tau,\beta} \\ \partial_\beta \mathcal{G}(\tau,\beta) &= -u(\tau,\beta) + \tau L(\tau,\beta) = \int \left(-\mathcal{E}_j + \tau r_j\right) d\mu^N_{\tau,\beta}, \end{aligned}$$

MIcrocanomical ensemble and entropy

Microcanonical Dynamics: $p_0 = p_N = 0$ and

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Microcanonical surface:

$$\Sigma_N(U, L) = \left\{ (r_1, p_1, \dots, r_N, p_N) : \frac{U_N}{N} = U, \frac{L_N}{N} = L \right\}.$$

The projection of the Lebesque measure of $\mathbb{R}^{2N}$ over $\Sigma_N(U, L)$, properly normalized, is called *microcanonical probability measure*.

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$W_N(U, L)$: volume of $\Sigma_N(U, L)$ (i.e. the normalization constant). The *Boltzmann* formula for the entropy is

$$S(U, L) = \lim_{N \to \infty} \frac{1}{N} \log W_N(U, L).$$

Boltzmann entropy

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$$k = \frac{R}{N_A} = 1.38 \cdot 10^{-23} J/K$$

Gibbs thermodynamic analogy

From

$$S(U,L) = \lim_{N\to\infty} \frac{1}{N} \log W_N(U,L).$$

we obtain:

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In order to indentify S with the thermodynamic entropy obtained with the Carnot cycles, we have to derive the (quasistatic) isothermal and adiabatic transformations from the microscopic dynamics, through a proper space time scaling limit.

Example: harmonic chain

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

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

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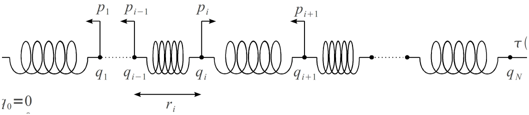
$$W_N(U, L) = \frac{(2\pi)^{N-1}[N(U - L^2/2)]^{N-3/2}}{2 \cdot 4 \ldots (2N-4)} = 2\frac{\pi^{N-1}[N(U - \mathcal{L}^2/2)]^{N-3/2}}{\Gamma(N-1)}$$

$$S(U, L) = \left(1 + \log\pi + \log\left[U - \mathcal{L}^2/2\right]\right) = S(U, \mathcal{L})$$

$$\beta = T^{-1} = \frac{\partial S}{\partial U} = \left[U - L^2/2\right]^{-1}, \qquad \tau = -\beta^{-1}\frac{\partial S}{\partial L} = L$$

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

Isothermal Transformations



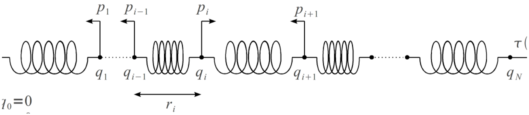
Slowly changing tension:

$$\mathcal{H}_N(t) = \sum_{i=1}^{N} \left(\frac{p_i^2}{2} + V(r_i) \right) + \bar{\tau}(t/N^{\alpha}) q_N$$

plus random collisions with particles of the *heat bath*: at independent random times

$$p_i(t) \longrightarrow \tilde{p}_j \sim \mathcal{N}(0, T)$$

Isothermal Transformations



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More effective is to use Langevin thermostats:

$$dp_j(t) = -\partial_{q_j} \mathcal{H}_N(t) dt - \gamma p_j(t) dt + \sqrt{2\gamma T} dw_j(t)$$

Isothermal: time rescaled dynamics

$$\begin{cases} dr_x(t) = N^\alpha (p_x(t) - p_{x-1}(t))dt, \qquad x = 1, \dots N \\ dp_x(t) = N^\alpha \left(V'(r_{x+1}(t)) - V'(r_x(t)) \right) dt - N^\alpha \gamma p_x(t) dt + N^{\alpha/2} \sqrt{\frac{2\gamma}{\beta}} dw_x(t), \\ dp_N(t) = N^\alpha \left(\bar{\tau}(t) - V'(r_N(t)) \right) dt - N^\alpha \gamma p_N(t)\, dt + N^{\alpha/2} \sqrt{\frac{2\gamma}{\beta}} dw_N(t). \end{cases}$$

$\mu^N_{\bar{\tau},\beta}$ is the *unique* stationary measure if $\bar{\tau}$ constant in time.

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$\alpha > 2$ gives a *quasi-static* time scale:
At time t we expect the distribution of p_x, r_x to be *close* to $\mu^N_{\bar\tau(t),\beta}$.

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Quasi-Static Isothermal Hydrodynamic Limit:
(De Masi-Olla JSP 2015) For any $\alpha > 2$:

$$\frac{1}{N}\sum_{x=1}^N G(x/N) r_x(t) \underset{n\to\infty}{\longrightarrow} \bar r(t) \int_0^1 G(y)\, dy$$

$$\bar L(t) = \beta^{-1}(\partial_\tau \mathcal{G})(\beta, \bar\tau(t))$$

Proof of isothermal QS limit

$$g^N_{\bar\tau(t),\beta}(r_1,p_1,\dots,r_N,p_N) = \prod_{j=1}^N e^{-\beta(\mathcal{E}_j - \bar\tau(t) r_j) - \mathcal{G}(\bar\tau(t),\beta)}$$

$f_t^N(r_1,p_1,\dots,r_N,p_N)$ the density of the distribution at time t with respect to $\mu^N_{\bar\tau(t),\beta} = g^N_{\bar\tau(t),\beta} d\mathbf{r} d\mathbf{p}$:

$$\partial_t \left(f_t^N g^N_{\bar\tau(t),\beta} \right) = \left(\mathcal{L}_N^{\bar\tau(t)*} f_t^N \right) g^N_{\bar\tau(t),\beta}$$

$$\mathcal{L}_N^{\bar\tau(t)} = N^\alpha \mathcal{A}_N^{\bar\tau(t)} + N^\alpha B_N, \qquad \mathcal{L}_N^{\bar\tau(t)*} = -N^\alpha \mathcal{A}_N^{\bar\tau(t)} + N^\alpha B_N$$

$$\mathcal{A}_N^{\bar\tau(t)} = \sum_{x=1}^N (p_x - p_{x-1}) \partial_{r_N} + \sum_{x=1}^{N-1} (V'(r_{x+1}) - V'(r_x)) \partial_{p_x} + (\bar\tau(t) - V'(r_N)) \partial_{p_N}$$

$$B_N = \sum_{x=1}^N \left(\beta^{-1} \partial^2_{p_x} - p_x \partial_{p_x} \right)$$

proof of isothermal QS limit

$$\partial_t \left(f_t^N g_{\bar{\tau}(t),\beta}^N \right) = \left(\mathcal{L}_N^{\bar{\tau}(t)*} f_t^N \right) g_{\bar{\tau}(t),\beta}^N$$

The (Shannon) relative entropy with respect to $\mu_{\bar{\tau}(t),\beta}^N$ is

$$H_N(t) = \int f_t^N \log f_t^N \; d\mu_{\bar{\tau}(t),\beta}^N, \quad H_N(0) = 0$$

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$$H_N(t) = \int f_t^N \log f_t^N \; d\mu^N_{\bar\tau(t),\beta}, \qquad H_N(0) = 0$$

$$\begin{aligned} \frac{d}{dt} H_N(t) &= -N^\alpha \gamma \beta^{-1} \int \sum_{i=1}^N \frac{(\partial_{p_i} f_t^N)^2}{f_t^N} \; d\mu^N_{\bar\tau(t),\beta} \\ &\quad -\beta \bar\tau'(t) \int \sum_{i=1}^N \left(r_i - \bar L(t) \right) f_t^N \; d\mu^N_{\bar\tau(t),\beta} \\ &\le -\beta \bar\tau'(t) \int \sum_{i=1}^N \left(r_i - \bar L(t) \right) f_t^N \; d\mu^N_{\bar\tau(t),\beta}. \end{aligned}$$

proof of isothermal QS limit

By entropy inequality, for any $\lambda > 0$ small enough

$$\begin{aligned}
\frac{d}{dt} H_N(t) &\le \beta \bar{\tau}'(t) \int \sum_{i=1}^{N} \left(r_i - \bar{L}(t) \right) f_t^N \, d\mu^N_{\bar{\tau}(t),\beta} \\
&\le \lambda^{-1} \log \int e^{\lambda \beta \bar{\tau}'(t) \sum_{i=1}^{N} \left(r_i - \bar{L}(t) \right)} \, d\mu^N_{\bar{\tau}(t),\beta} + \lambda^{-1} H_N(t) \\
&\qquad \le \lambda C N + \lambda^{-1} H_N(t),
\end{aligned}$$

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By entropy inequality, for any $\lambda > 0$ small enough

$$\begin{aligned} \frac{d}{dt} H_N(t) &\le \beta \bar{\tau}'(t) \int \sum_{i=1}^{N} \left(r_i - \bar{L}(t) \right) f_t^N \, d\mu^N_{\bar{\tau}(t),\beta} \\ &\le \lambda^{-1} \log \int e^{\lambda \beta \bar{\tau}'(t) \sum_{i=1}^{N} (r_i - \bar{L}(t))} \, d\mu^N_{\bar{\tau}(t),\beta} + \lambda^{-1} H_N(t) \\ &\qquad \le \lambda C N + \lambda^{-1} H_N(t), \end{aligned}$$

and since $H_N(0) = 0$, it follows that $H_N(t) \le e^{t/\lambda} \lambda C t \, N$. This is not yet what we want to prove but it implies that

$$\int_0^T \int \sum_{i=1}^{N} \frac{(\partial_{p_i} f_t^N)^2}{f_t^N} \, d\mu^N_{\bar{\tau}(t),\beta} \, dt \le \frac{C}{N^{\alpha-1}}.$$

proof of isothermal QS limit

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This gives only information on the distribution of the velocities. Uning *entropic hypocoercive bounds* we have the same for

$$\int_0^T \int \sum_{i=1}^N \frac{(\partial_{q_i} f_t^N)^2}{f_t^N} \, d\mu^N_{\bar{\tau}(t),\beta} \, dt \le \frac{C}{N^{\alpha-1}}.$$

where $\partial_{q_i} = \partial_{r_i} - \partial_{r_{i+1}}$. and, since $\alpha > 2$, this is enough to prove that

$$\left(\frac{d}{dt} H_N(t) \le\right) \qquad \beta \int \frac{1}{N} \sum_{i=1}^N \left(r_i - \bar{L}(t)\right) f_t^N \, d\mu^N_{\bar{\tau}(t),\beta} \longrightarrow 0,$$

i.e.

$$\frac{H_N(t)}{N} \longrightarrow 0. \qquad \square$$

Isothermal limit: Work, Heat and Free Energy

Internal Energy:

$$U_N := \frac{1}{N}\sum_{i=1}^{N}\left(\frac{p_i^2}{2} + V(r_i)\right)$$

$$U_N(t) - U_N(0) = \mathcal{W}_N(t) + Q_N(t)$$

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Work:

$$\mathcal{W}_N(t) = N^{\alpha-1} \int_0^t \bar{\tau}(s) p_N(s) ds = \int_0^t \bar{\tau}(s) \frac{dq_N(s)}{N}$$

$$= \int_0^t \bar{\tau}(s) d \left(\frac{1}{N} \sum_x r_x(t) \right) \longrightarrow \int_0^t \bar{\tau}(s) d\bar{L}(s) := \mathcal{W}(t)$$

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Heat:

$$Q_N(t) = N^{\alpha-1}\sum_{x=1}^{N}\gamma\ \int_0^t \left(p_x^2(s) - \beta^{-1}\right)ds$$

$$+ N^{(\alpha-2)/2}\sum_{x=1}^{N}\sqrt{2\gamma\beta^{-1}}\int_0^t p_x(s)dw_x(s).$$

it may look horribly divergent but...

Isothermal limit: Work, Heat and Free Energy

$$\lim_{n\to\infty} \left(U_n(t) - U_n(0)\right) = u(\bar{\tau}(t), \beta) - u(\bar{\tau}(0), \beta) = \bar{u}(t) - \bar{u}(0)$$

where $u(\tau, \beta) = -\partial_\beta \mathcal{G}(\tau, \beta)$ is the average energy for $\mu_{\beta,\tau}$.

$$Q_N(t) \underset{N\to\infty}{\longrightarrow} Q(t) = \bar{u}(t) - \bar{u}(0) - \mathcal{W}(t).$$

which is the first law of thermodynamics for quasistatic isothermal transformations.

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Notice that $Q(t)$ is a finite *deterministic* quantity!

Isothermal limit: Work, Heat and Free Energy

$$\lim_{n\to\infty}(U_n(t)-U_n(0)) = u(\bar\tau(t),\beta)-u(\bar\tau(0),\beta) = \bar u(t)-\bar u(0)$$

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Notice that $Q(t)$ is a finite *deterministic* quantity!

For the Free Energy:

$$\begin{aligned}\mathcal{F}(\bar L(t),\beta)-\mathcal{F}(\bar L(0),\beta) &= \int_0^t \partial_L\mathcal{F}(\bar L(s),\beta)d\bar L(s)\\ &= \int_0^t \bar\tau(s)d\bar L(s)=\mathcal{W}(t)\end{aligned}$$

i.e. Clausius equality.

Equivalently, by $\mathcal{F}=u-\beta^{-1}S$,

$$\beta^{-1}\left(S(\bar L(t),u(t))-S(\bar L(0),u(0))\right)=Q(t)$$

Thermodynamic (Boltzmann) entropy and Gibbs-Shannon entropy

Let $\tilde{f}_N(t) d\mathbf{r} d\mathbf{p} = f_N(t) g^N_{\bar{\tau}(t),\beta} d\mathbf{r} d\mathbf{p}$. The Gibbs-Shannon entropy is

$$S_G(\tilde{f}_N(t)) = -\int \tilde{f}_N(t) \log \tilde{f}_N(t) d\mathbf{r} d\mathbf{p}$$

and the relation with the relative entropy studied above is:

$$\begin{aligned} H_N(t) &= -S_G(\tilde{f}_N(t)) - \int \log g_{N,\tau,\beta(t)} f_N(t) d\mu^N_{\bar{\tau}(t),\beta} \\ &= -S_G(\tilde{f}_N(t)) + \int \sum_x \left(\beta \mathcal{E}_x - \beta \bar{\tau}(t) r_x - \mathcal{G}(\bar{\tau}(t), \beta)\right) f_N(t) d\mu^N_{\bar{\tau}(t),\beta} \end{aligned}$$

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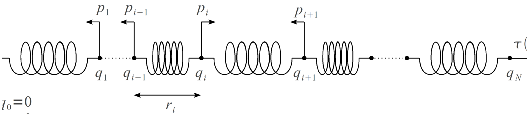
Since $H_N(t)/N \to 0$ we have

$$\begin{aligned} \lim_{N\to\infty} \frac{1}{N} S_G(\tilde{f}_N(t)) &= \beta \bar{u}(t) - \beta \bar{\tau}(t) \bar{L}(t) - \mathcal{G}(\bar{\tau}(t),\beta) \\ &= S(\bar{u}(t), \bar{L}(t)). \end{aligned}$$

Adiabatic Quasi-Static Limit



$$
\begin{aligned}
dr_x(t) &= N^\alpha (p_x(t) - p_{x-1}(t))\, dt \\
dp_x(t) &= N^\alpha (V'(r_{x+1}(t)) - V'(r_x(t)))\, dt, \qquad x = 1, \dots, N-1, \\
dp_N(t) &= N^\alpha (\bar\tau(t) - V'(r_N(t)))\, dt
\end{aligned}
$$

Adiabatic thermodynamic transformation

We start at $t = 0$ with the equilibrium $\mu^N_{\bar\tau(0),\bar\beta(0)}$. Correspondingly there is an average energy $\bar u(0)$ and length $\bar L(0)$ given by

$$\bar u(0) = u(\bar\beta(0), \bar\tau(0)) = -\partial_\beta \mathcal{G}(\bar\beta(0), \bar\tau(0))$$
$$\bar L(0) = L(\bar\beta(0), \bar\tau(0)) = \beta^{-1}(\partial_\tau \mathcal{G})(\bar\beta(0), \bar\tau(0)).$$

The adiabatic quasistatic transformation is isoentropic, i.e.

$$S(\bar u(t), \bar L(t)) - S(\bar u(0), \bar L(0)) = \int_0^t \left(\bar\beta(s)\bar u'(s) - \bar\beta(s)\bar\tau(s)\bar L'(s)\right) ds = 0.$$

so that $\bar u(t)$ and $\bar L(t)$ are determined by

$$\bar u'(s) = \bar\tau(s)\bar L'(s)$$

and

$$\bar\beta(t) = \partial_u S(\bar u(t), \bar L(t)).$$

We expect that for $\alpha > 2$ and all $t > 0$

$$\frac{1}{N}\sum_{x=1}^{N} G(x/N) r_x(t) \underset{n\to\infty}{\longrightarrow} \bar{L}(t) \int_0^1 G(y)\, dy$$

$$\frac{1}{N}\sum_{x=1}^{N} G(x/N) \mathcal{E}_x(t) \underset{n\to\infty}{\longrightarrow} \bar{u}(t) \int_0^1 G(y)\, dy$$

No results yet for deterministic dynamics.
Some preliminary results with some stochastic perturbations that conserve energy and volume.

Where is the difficulty?

$$\frac{d}{dt} H_N(t) = - \int f_t^N \partial_t g^N_{\bar\beta(t),\bar\tau(t)} \prod_{x=1}^N dr_x dp_x$$
$$= \int \sum_{x=1}^N \left[-\bar\beta'(t) \left(\mathcal{E}_x - \bar u(t)\right) + \left(\bar\beta(t)\bar\tau(t)\right)' \left(r_x - \bar L(t) \right) \right] f_t^N d\mu_{\bar\beta(t),\bar\tau(t)}.$$

Then all one has to prove is

$$\begin{aligned} \lim_{N\to\infty} \int_0^T dt \left[\int \frac{1}{N} \sum_{x=1}^N \mathcal{E}_x f_t^N d\mu^N_{\bar\tau(t),\bar\beta(t)} - \bar u(t) \right] = 0 \\ \lim_{N\to\infty} \int_0^T dt \left[\frac{1}{N} \int q_N f_t^N d\mu^N_{\bar\tau(t),\bar\beta(t)} - \bar L(t) \right] = 0 \end{aligned} \qquad (2)$$

Where is the difficulty?

$$\frac{d}{dt}H_N(t) = -\int f_t^N \partial_t g^N_{\bar\beta(t),\bar\tau(t)} \prod_{x=1}^N dr_x dp_x$$

$$= \int \sum_{x=1}^N \left[-\bar\beta'(t)\left(\mathcal{E}_x - \bar u(t)\right) + \left(\bar\beta(t)\bar\tau(t)\right)'\left(r_x - \bar L(t)\right)\right] f_t^N d\mu_{\bar\beta(t),\bar\tau(t)}.$$

Then all one has to prove is

$$\begin{aligned} \lim_{N\to\infty}\int_0^T dt\left[\int \frac{1}{N}\sum_{x=1}^N \mathcal{E}_x f_t^N d\mu^N_{\bar\tau(t),\bar\beta(t)} - \bar u(t)\right] = 0 \\ \lim_{N\to\infty}\int_0^T dt\left[\frac{1}{N}\int q_N f_t^N d\mu^N_{\bar\tau(t),\bar\beta(t)} - \bar L(t)\right] = 0 \end{aligned} \tag{2}$$

that would imply

$$\lim_{N\to\infty}\frac{1}{N}\left(H_N(t) - H_N(0)\right) = 0$$

But (2) would also imply directly that

$$\begin{aligned}\lim_{N\to\infty}\frac{H_N(t)}{N} &= -\lim_{N\to\infty}\frac{S_G(t)}{N} + S(\bar{u}(t),\bar{L}(t))\\ &= -\lim_{N\to\infty}\frac{S_G(0)}{N} + S(\bar{u}(0),\bar{L}(0)) = 0\end{aligned}$$

Adiabatic Transformation: Stochastic model

$$\begin{aligned} dr_x(t) &= N^\alpha (p_x(t) - p_{x-1}(t))\, dt \\ dp_x(t) &= N^\alpha (V'(r_{x+1}(t)) - V'(r_x(t)))\, dt, \qquad x = 1, \dots, N-1, \\ dp_N(t) &= N^\alpha (\bar\tau(t) - V'(r_N(t)))\, dt \end{aligned}$$

plus a random exchance between nearest neighbor configurations, generated by

$$\tilde{\mathcal{S}}_N f(\mathbf{r}, \mathbf{p}) = N^\alpha \sum_{x=1}^{N-1} \big(f(\mathbf{r}^{x,x+1}, \mathbf{p}^{x,x+1}) - f(\mathbf{r}, \mathbf{p}) \big)$$

where $(\mathbf{r}^{x,x+1}, \mathbf{p}^{x,x+1})$ is the configuration $(\mathbf{r}, \mathbf{p})$ with sites x and $x+1$ exchanged.

Adiabatic Transformation: Stochastic model

$$
\begin{aligned}
\frac{d}{dt}H_N(t) &= -\int f_t^N \partial_t g^N_{\bar\beta(t),\bar\tau(t)} \prod_{x=1}^{N} dr_x dp_x \\
&= \int \sum_{x=1}^{N} \left[-\bar\beta'(t)\left(\mathcal{E}_x - \bar u(t)\right) + \left(\bar\beta(t)\bar\tau(t)\right)'\left(r_x - \bar L(t)\right)\right] f_t^N d\mu_{\bar\beta(t),\bar\tau(t)} \\
&\quad + N^\alpha \int f_N(t)\left(\mathcal{S}_N \log f_N(t)\right)\mu_{\bar\beta(t),\bar\tau(t)} \\
&\le \int \sum_{x=1}^{N} \left[-\bar\beta'(t)\left(\mathcal{E}_x - \bar u(t)\right) + \left(\bar\beta(t)\bar\tau(t)\right)'\left(r_x - \bar L(t)\right)\right] f_t^N d\mu_{\bar\beta(t),\bar\tau(t)} \\
&\quad - N^\alpha \int \sum_{x=1}^{N-1} \left(\sqrt{f_N(t,\mathbf{r}^{x,x+1},\mathbf{p}^{x,x+1})} - \sqrt{f_N(t,\mathbf{r},\mathbf{p})}\right)^2 \, d\mu_{\bar\tau(t),\bar\beta(t)}
\end{aligned}
$$

Adiabatic Transformation: Stochastic model

As done before we get the bound

$$\int \sum_{x=1}^{N-1} \left(\sqrt{f_N(t, \mathbf{r}^{x,x+1}, \mathbf{p}^{x,x+1})} - \sqrt{f_N(t, \mathbf{r}, \mathbf{p})} \right)^2 \, d\mu_{\bar{\tau}(t),\bar{\beta}(t)} \leq \frac{C}{N^{\alpha-1}}$$

and if we are able to prove a *one-block bound* at the boundary, this estimate allows to the a *two blocks bound* at macroscopic distance by a telescoping sum + Schwarz inequality, if $\alpha > 2$.