

Non-equilibrium physics

Content / Materials

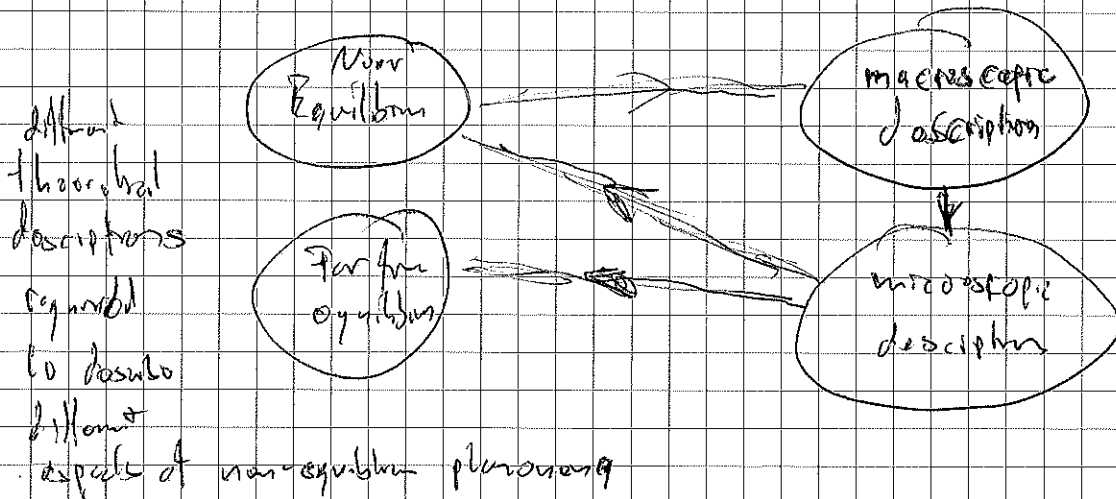
Non-equilibrium physics is a wide field
active research. I faculty Bogner, Bodens, Schlotter

will cover only aspects of it compatible
with undergraduate physics knowledge

programmed: stat. mech, quant. mech,

but will be briefly reviewed when necessary

Conceptually seen linkages



We will follow the book

1) N. Pottier "Nonequilibrium Statistical Physics"
Oxford Press 2010

2) physik.uni-bielefeld.de/~rbogner/Teaching/Nonequilibrium/Nonequilibrium.pdf

Can provide additional references if desired

No ppt lecture notes but can provide handwritten notes if desired

Topics:

- Thermodynamics of irreversible processes
- Statistical description of non-equilibrium systems (classical & quantum)
- Kinetic theory
- Stochastic evolution models
- Linear response theory

Questions / Wishes / Comments

Your feedback is important!

1) Thermodynamics of r -processes

Processes

Basic idea will be to generalize
concepts of equilibrium thermodynamics
to out-of-equilibrium systems

Power of thermodynamics lies in macroscopic
nature

→ complex many body systems
can be characterized by few
macroscopic quantities

Will investigate under what circumstances
the same holds for non-eg systems

- Outline
- Equilibrium thermodynamics (review)
 - Entropy production in irreversible (out-of-eg) processes
 - Linear transport phenomena

2.1 Equilibrium thermodynamics (review)

We'll follow the formulation of thermodynamics due to H.B. Callen (1960), based on description of extensive macroscopic variables and entropy.

Simple systems: (homogeneous, isotropic, chemically inert)

macroscopic variables

U
internal energy

V
Volume

N_i
particle numbers

Q: what means extensive?

A: additive under composition

Note that except V the other quantities are related to conserved quantities for simple systems

→ makes them well suited for nonequilibrium description

Collectively described as

$$X_i \in \{U, V, N_i, \dots\}$$

Postulates:

i) Existence of equilibrium states which are completely characterized by $\{X_i\}$

(stat-mech \rightarrow micro-canonical ensemble)

ii) Existence of an entropy function $S(X_i)$ for each equilibrium state, with the property that $S(X_i)$ is extensive and

if the system is divided into subsystems (total (A)) thus characterized by $\{X_i^{(k)}\}$, the entropy is maximal wrt to variables of $\{X_i^{(k)}\}$

iii) $S(X_i)$ is continuously differentiable wrt $\{X_i\}$ and monotonically increasing as a function of U

iv) $S(X_i) = 0$ for all states with $\left(\frac{\partial U}{\partial S}\right)_{V, N_i} = 0$

Based on the postulates, often formulated
 as thermodynamic properties considered
 as function

$$S = S(\{X_i\}) \quad \text{e.g.} \quad S = S(U, V, N)$$

~~thermodynamic fundamental relation~~

"thermodynamic fundamental equation"

Differential form characterizes
 change of equilibrium state under
 allowed variables of X_i

"Gibbs fundamental relation"

$$dS = \sum_i \frac{\partial S}{\partial X_i} dX_i$$

Since S, X_i are extensive, the quantities

$$Y_i = \left. \frac{\partial S}{\partial X_i} \right|_{\{X_j\}_{j \neq i}}$$

are intensive. The functional dependences

$$Y_i = \left. \frac{\partial S}{\partial X_i} \right|_{\{X_j\}_{j \neq i}} (\{X_i\})$$

is called EOS (equation of state)

Conveniently for simple fluids

$$S = S(U, V, N)$$

and

$$dS = \underbrace{\frac{\partial S}{\partial U}}_T dU + \underbrace{\frac{\partial S}{\partial V}}_p dV + \sum_i \underbrace{\frac{\partial S}{\partial N_i}}_{-\frac{\mu_i}{T}} dN_i$$

$T = \text{temperature}$

$p = \text{pressure}$

$\mu_i = \text{chemical potential}$

EOS

$$\frac{1}{T} = \left. \frac{\partial S}{\partial U} \right|_{V, N} \Rightarrow T(U, V, N)$$

1.2 Description of irreversible

(out-of-equilibrium) processes

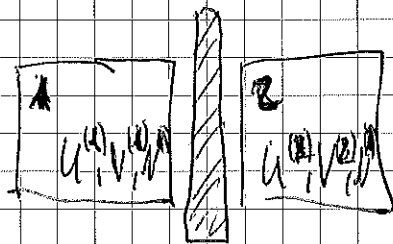
Generally out-of-equilibrium situations will arise in real world systems only due to external influence \rightarrow system needs time to react to new circumstances

evolution, finite lifetime \rightarrow system hasn't had enough time to reach equilibrium

fluctuations \rightarrow system fluctuates around its equilibrium state

Challenge: How to characterize such systems?

Consider first simple systems



can schematize so far suggest description in terms of extensive variables

$X_i^{(s)}$, and we can assume for simplicity that initially isolated systems 1 & 2 are in equilibrium states.

Now if we lift wall, make wall permeable or make wall movable

1 \leftrightarrow 2 can exchange U, V, N
system is out-of-equilibrium

Now what is expected is - if no wait long enough - system will again reach equilibrium state

→ non-equilibrium states are of transient nature

Ultimately everything is described by

$$X_i^{(tot)} = X_i^{(A)} + X_i^{(B)}$$

Q: What happens in between?

Answer: Depends on time scale

Can stability at least two relevant time scales

τ_{macro} - individual constituents (atoms, molecules, ...)

$\tau_{micro}^{X_i}$ - changes of X_i occur

If $\tau_{macro}^{X_i} \gg \tau_{micro}$ the variables

X_i are referred to as slow variables

each subsystem ~~is able to~~ has enough time to stay close to equilibrium throughout the entire evolution

Can parameterize the evolution as
 a sequence of equilibrium states of
 each sub system

$$\{X_i^{(A)}(t)\}$$

with which we can associate
 an ~~instantaneous~~ entropy

$$S^{(A)}(\{X_i^{(A)}(t)\})$$

for each sub-system.

Atmosphere & Fluxes

Consider isolated system such that X_i are
 globally conserved

$$\begin{aligned} X_i^{\text{tot}} &= X_i^{(1)}(t) + X_i^{(2)}(t) = \text{const} \\ \Rightarrow dX_i^{(1)} &= -dX_i^{(2)} \end{aligned}$$

Since entropy is additive

$$S^{\text{tot}} = S^{(1)}(X_i^{(1)}) + S^{(2)}(X_i^{(2)})$$

can get EQ state by requiring

$$\frac{\partial S^{\text{tot}}}{\partial X_i^{(1)}} = - \frac{\partial S^{\text{tot}}}{\partial X_i^{(2)}} = \frac{\partial S^{(1)}}{\partial X_i^{(1)}} - \frac{\partial S^{(2)}}{\partial X_i^{(2)}} = \mu_i^{(1)} - \mu_i^{(2)}$$

is zero (in accordance with S-uniform)

Equilibrium state is characterized by same value of intensive variables

$$\boxed{\bar{F}_i \equiv Y_i^{(1)} - Y_i^{(2)} = \left. \frac{\partial S^{(tot)}}{\partial X_i^{(1)}} \right| \{X_i^{(tot)}\}}$$

is called affinity or generalized force.

In equilibrium

$$\bar{F}_i^{(eq)} = 0$$

When system is out-of-equilibrium ($\bar{F}_i \neq 0$) the system will naturally change its state $\{X_i^{(1)}\}$. This is characterized

$$J_i = \frac{d}{dt} X_i^{(1)}$$

called flux of e.g. energy, particle number, ... corresponding to amount of X_i transferred from B to A per unit time.

~~Fluxes characterize~~

Fluxes J_i characterize the (macroscopic) changes of non-equilibrium systems

Entropy production:

$$\frac{dS^{(tot)}}{dt} = \sum_i \frac{\partial S^{(tot)}}{\partial X_i^{(i)}} \frac{dX_i^{(i)}}{dt} = \sum_i F_i J_i$$

remember

$$dX_i^{(ii)} = -dX_i^{(i)}$$

Entropy production has a balance form
in affinities and fluxes