

1.4 Linear irreversible processes

So far discussed macroscopic descriptions
of non-equilibrium systems based on
local equilibrium assumption

discrete systems



State of each sub-system described by
extensive macroscopic variables

$$X_i^{(A,B)} \in \{U^{(A,B)}(t), V^{(A,B)}(t), N_i^{(A,B)}(t)\}$$

continuous systems



described by
densities

$$x_i(t, \vec{r}) \in \{e(t, \vec{r}), n_i(t, \vec{r})\}$$

which characterizes the thermodynamic state

Dynamics of the system described
by fluxes of X_i or x_i

→ balance equations

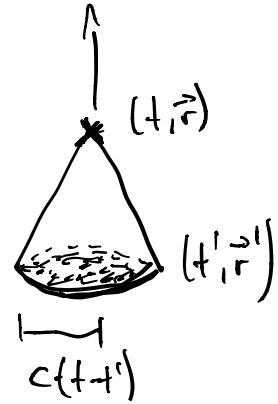
$$\frac{d}{dt} X_i^{(A)} = \sum_B J_i^{B \rightarrow A}$$

$$\frac{\partial}{\partial t} x_i(t, \vec{r}) + \nabla \cdot \vec{J}_i(t, \vec{r}) = \sigma_i(t, \vec{r})$$

Question: What determines the flux $J_i^{B \rightarrow A}$ or \vec{J}_i

General considerations:

Generally the flux $\vec{J}_i(t, \vec{r})$ at a given space-time point can and will depend on everything that happened in its causal past



→ micro causality

However for systems which evolve slowly ($\tau_{\text{Macro}} \gg \tau_{\text{Micro}}$) and remain close to local thermal equilibrium this criterion appears to do to restrict

Instead on macroscopic timescales it is reasonable to ignore retardation effects and instead assume that the system is Markovian

Markovian: Evolution is instantaneously
determined by local thermodynamic
properties

NB: Even though this seems to be
problematic wrt to causality,
causal descriptions of e.g. relativistic
hydrodynamics can be formulated
in this way
see e.g. Exercise Sheet 2

NB: Note that there are well known
circumstances where this assumption
fails

Ex: Hysteresis

Solutions can be cured by introduction
of additional slow variables, e.g.
order parameters of phase trans

Since macroscopic state of system
 is described by $X_i(t, \vec{r})$ or
 alternatively $\psi_i(t, \vec{r})$ this means
 that flux $\vec{J}_i(t, \vec{r})$ in Markovian system
 must be determined by

Constitutive relation:

$$\vec{J}_i(t, \vec{r}) = \vec{J}_i \left(\underbrace{\{\psi_k(t, \vec{r})\}}_{\text{local thermodynamic properties}}, \underbrace{\{\vec{F}_j(t, \vec{r})\}}_{\text{affinities}}, \dots \right)$$

higher order derivatives

$\vec{F}_j = -\vec{\nabla} \psi_j(t, \vec{r})$

We will typically truncate
 this Derivative (Gradient expansion
 at first order, i.e. higher order
 derivatives will be neglected
 for systems which vary slowly
 on macroscopic scales ($\lambda \ll l$)

Clearly the next question is
how to determine constitutive
relations $\vec{J}_i(Y_u, T_u, \dots)$

If system is locally in equilibrium
everything is described by thermodynamics

$$\vec{J}_i(t, \vec{r}) = \vec{J}_i^{eq}(\{Y_u(t, \vec{r})\})$$

Note that $\vec{J}_i(t, \vec{r})$ can be non-zero
for an equilibrium system, e.g.
consider moving equilibrium
system

However equilibrium currents do
not lead to entropy production
and the entropy production rate
is modified in this case as

$$\sigma_S(t, \vec{r}) = \sum_i \vec{F}_i(t, \vec{r}) \cdot (\vec{J}_i(t, \vec{r}) - \vec{J}_i^{eq}(t, \vec{r}))$$

Now if we have non-vanishing affinity
 $\vec{F}_i(t, \vec{r}) \neq 0$, this will drive the
 system out of equilibrium and
 give rise to additional contributions
 to the flux. If deviations from
 equilibrium are small, can expand
 in Taylor series

$$\begin{aligned} \mathcal{J}_i^\alpha(t, \vec{r}) = & \mathcal{J}_{i,eq}^\alpha(t, \vec{r}) + \sum_k \underline{L_{ik}^{\alpha\beta}} F_k^\beta(t, \vec{r}) \\ & + \frac{1}{2} \sum_{kl} \underline{L_{ikl}^{\alpha\beta\gamma}} F_k^\beta(t, \vec{r}) F_l^\gamma(t, \vec{r}) + \dots \end{aligned}$$

with "kinetic/response coefficients"

$$L_{ik}^{\alpha\beta} = L_{ik}^{\alpha\beta}(\{Y_l(t, \vec{r})\})$$

depending on local thermodynamic variables
 \rightarrow microscopic input to macroscopic
 description

Since $F_n^\alpha = \frac{\partial}{\partial x_\alpha} Y_n$ this can
 again be viewed as a gradient
 expansion and we should
 again truncate at the same order
 for consistency

Note that L_{in} include

"direct effects" $L_{in} \propto S_{in}$

e.g. $\vec{J}_e \propto \vec{\nabla} Y_e$
energy flux = $\frac{1}{T}$
temperature gradient

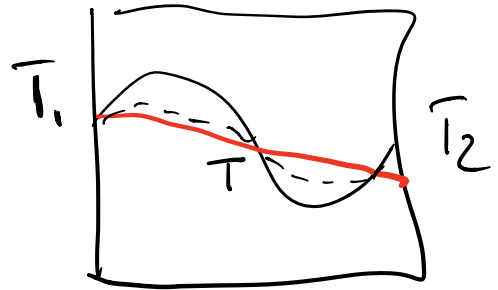
as well as "indirect effects"

e.g. $\vec{J}_n \propto \vec{\nabla} Y_e$
particle flux = $\frac{1}{T}$
temperature gradient

Selected examples of phenomenological transport equations

Heat transport:

We consider a system with temperature gradients



$$\vec{\nabla} \left(\frac{1}{T} \right) = -\frac{1}{T^2} \vec{\nabla} T \neq 0$$

non-zero affinity \vec{F}_e will induce energy flux (and possibly other fluxes)

Based on linear constitutive relations

$$J_e^\alpha = L_{ee}^{\alpha\beta} \left(\vec{\nabla} \frac{1}{T} \right)_\beta$$

where $L_{ee}^{\alpha\beta}$ is a rank two tensor

If the medium is isotropic
Symmetry dictates

$$L_{ee}^{\alpha\beta} = \delta^{\alpha\beta} \mathcal{L}_{ee}$$

so

$$\begin{aligned} \vec{J}_e &= \mathcal{L}_{ee} \vec{\nabla} \frac{1}{T} \\ &= -\frac{\mathcal{L}_{ee}}{T^2} \vec{\nabla} T \end{aligned}$$

phenomenologically heat transfer
is described by

Fourier's law: $\vec{J}_e = -\mathcal{K} \vec{\nabla} T$

So we identify

heat conductivity: $\mathcal{K} = \frac{\mathcal{L}_{ee}}{T^2}$



Now to calculate the evolution
of the system we need
to combine

Conservation equations + constitutive relations

$$\underline{\frac{\partial \varepsilon}{\partial t} + \vec{\nabla} \cdot \vec{J}_e = 0}$$

$$\underline{\vec{J}_e = -\chi \vec{\nabla} T}$$

$$\Rightarrow \boxed{\frac{\partial \varepsilon}{\partial t} = +\vec{\nabla} \cdot (\chi \vec{\nabla} T)}$$

Since ε, T are related by
local EOS we can identify

$$\left. \frac{\partial \varepsilon}{\partial T} \right|_V = C_V \quad \text{specific heat capacity}$$

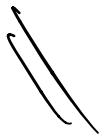
So we get

$$\frac{\partial T}{\partial t} = \frac{1}{c_v} \vec{\nabla} \cdot (\alpha \vec{\nabla} T)$$

if further variations of T are
not too large $\alpha \approx \text{const}$

$$\Rightarrow \frac{\partial T}{\partial t} = \frac{\alpha}{c_v} \Delta T$$

which is the standard form
of the heat equation



Note that in the above discussion we have neglected coupling to other conserved quantities, which is applicable e.g. to insulators where heat transfer is mediated by phonons whose number is not conserved

Conversely in e.g. conductors heat conduction is mostly due to mobile charge carriers, whose number is conserved meaning that particles & heat transport are coupled

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Next example is
particle diffusion

Empirically described by

Fick's law: $\vec{J}_n = -D \vec{\nabla} n$

Based on our formalism of
linear irreversible processes

we get

$$\vec{J}_n^\alpha = \sum_j L_{ij}^{\alpha\beta} (\vec{\nabla} Y_j)_\beta$$

If we neglect temperature
gradients $\vec{\nabla} Y_e = 0$

$$\vec{\nabla} \frac{1}{n} = \vec{\nabla} \left(-\frac{\mu}{T} \right) = -\frac{1}{T} \vec{\nabla} \mu = -\frac{1}{T} \left(\frac{\partial \mu}{\partial n} \right)_T \vec{\nabla} n$$

So for isohoric medium

$$\vec{J}_n = -\frac{1}{T} \rho_{nm} \left(\frac{\partial \mu}{\partial n} \right)_T \vec{\nabla} n$$

such that by comparison

diffusion
constant

$$D = \frac{1}{T} \rho_{nm} \left(\frac{\partial \mu}{\partial n} \right)_T$$

It is analogous to heat equation, M_0 density dependence of D can be neglected

balance equation + constitutive relation

$$\Rightarrow \frac{\partial n}{\partial t} (t, \vec{r}) = D \Delta n (t, \vec{r})$$

which is of the same form
as the heat equation



Solution for initial value problem
is most conveniently obtained
in Fourier space

$$\tilde{n}(t, \vec{u}) = \int d^3\vec{r} n(t, \vec{r}) e^{-i\vec{u}\vec{r}}$$

$$\stackrel{FT}{\Rightarrow} \frac{\partial \tilde{n}}{\partial t}(t, \vec{u}) = -D\vec{u}^2 \tilde{n}(t, \vec{u})$$

Solution in Fourier space

$$\tilde{n}(t, \vec{u}) = \tilde{n}(t=0, \vec{u}) e^{-D\vec{u}^2 t}$$

Solution in coordinate space

$$\mathcal{F}T^{-1}$$

$$\begin{aligned} n(t, \vec{r}) &= \int \frac{d^3\vec{h}}{(2\pi)^3} \tilde{n}(t, \vec{h}) e^{+i\vec{h}\vec{r}} \\ &= \int \frac{d^3\vec{h}}{(2\pi)^3} \tilde{n}(t=0, \vec{h}) e^{-i\vec{h}\vec{r}} e^{+i\vec{h}\vec{r}} \end{aligned}$$

If we consider eq

$$n(t=0, \vec{r}) = n_0 \delta^{(3)}(\vec{r})$$

then $\tilde{n}(0, \vec{h}) = n_0$ and

we can compute $\mathcal{F}T^{-1}$

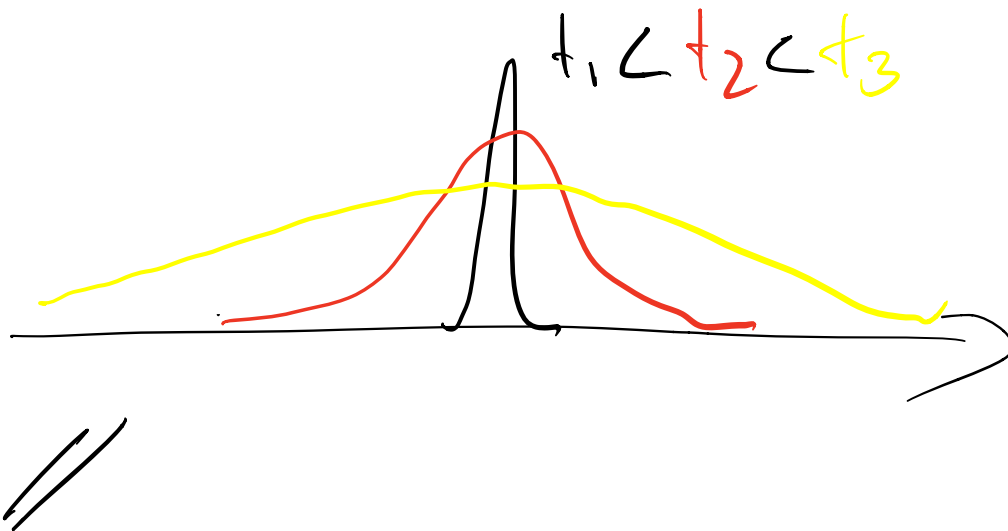
by Gaussian integral

$$\int_{-\infty}^{+\infty} dx \frac{e^{-\frac{(x-x_0)^2}{2\sigma^2}}}{\sqrt{2\pi\sigma^2}} = 1$$

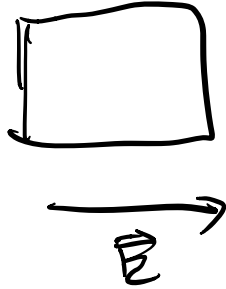
so identifying $\frac{1}{2\sigma^2} \hat{=} Dt$

and completing the square

$$n(\underline{t}, \vec{r}) = \frac{n_0}{(4\pi Dt)^{3/2}} e^{-\frac{r^2}{4Dt}}$$



Electrical conduction



Electric field

$$\vec{E} = -\vec{\nabla}\phi$$

electrostatic
potential

is applied to a
conducting material

Microscopically electric charge transport
is achieved by transport of mobile
charge carriers (electrons, holes, defects, ...)
in the material

$$\vec{J}_{el} = q \vec{J}_n$$

electric
current

charge

particle current
of mobile
charge carrier

Now to account for the presence of electric field, we need to consider how the electrostatic potential ϕ modifies the internal energy e

$$e \rightarrow e + nq\phi$$

so the entropy functional gets modified

$$S_{\phi}(e, n, \phi) = S(e - nq\phi, n)$$

usual entropy functional is a source of ϕ

which will change EOS and other thermodynamic relations

$$\begin{aligned}
\frac{dS_\phi}{dn} &= \left. \frac{dS}{de} \right|_T (-q\phi) + \left. \frac{dS}{dn} \right|_e \\
&= \frac{1}{T} (-q\phi) + -\frac{\mu}{T} \\
&= -\left(\frac{\mu + q\phi}{T} \right) \\
&\equiv \mu_\phi \text{ electrochemical potential}
\end{aligned}$$

Due to this modification
the linear constitutive relation
for \vec{J}_n takes the form

$$\vec{J}_n = \sigma_{nn} \vec{\nabla} \left(-\frac{\mu + q\phi}{T} \right)$$

which for $T = \text{const}$ gives
two contributions

$$\vec{J}_n = \underbrace{\frac{q D_{nn}}{T} \left(\frac{\partial n}{\partial x} \right)_T}_{\text{particle diffusion}} \vec{\nabla} n$$

$$- \underbrace{\frac{q}{T} D_{nn} \vec{\nabla} \phi}_{\text{response to electric field } \vec{E} = -\vec{\nabla} \phi}$$

response to electric field $\vec{E} = -\vec{\nabla} \phi$

so in the absence of density gradients ($\vec{\nabla} n = 0$) we find

$$\vec{J}_{ol} = q \vec{J}_n = \frac{q^2}{T} D_{nn} \vec{E}$$

such that by comparison with Ohm's law

$$\vec{J}_{el} = \sigma_{el} \vec{E}$$

no identity

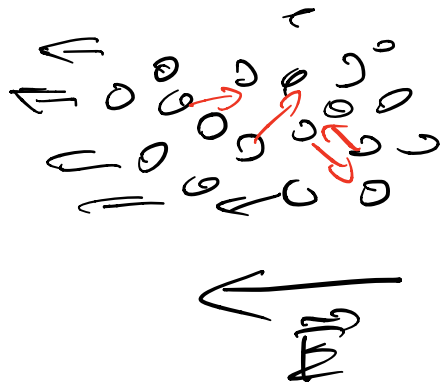
// electronic conductivity: $\sigma_{el} = \frac{q^2}{T} L_{11}$

In particular D (diffusion constant)
and σ_{el} (electronic conductivity)
both follow from the kinetic
coefficient L_{11}

Einstein relation: $D = \frac{\sigma_{el}}{q^2} \left(\frac{\partial \mu}{\partial n} \right)_T$

// $\sigma_{el} = \frac{q^2 D}{\left(\frac{\partial \mu}{\partial n} \right)_T}$

Now let's consider what this means in a simple microscopic model (Drude model) of conductors



Electric field accelerates charge carriers

Microscopic interactions induce friction to decelerate charge carriers

Due to this competition eventually charge carriers reach terminal Drift velocity, which is of the order of 10^6 m/s

$$\vec{v}_{\text{Drift}} = \mu_{\text{el}} \vec{E}$$

electrical mobility

Electric current of moving charges is given by

$$\vec{J}_{\text{el}} = nq \vec{v}_{\text{Drift}} = nq \mu_{\text{el}} \vec{E}$$

$$\Rightarrow \sigma_{\text{el}} = nq \mu_{\text{el}}$$

Now diffusion on the other
hand smooths out density
gradients



microscopically this occurs
due to the fact that on average
more particles move from
high density to low density
region than the other way

Now the fact that the two are related by Einstein relation

$$D = \frac{\mu_{\text{od}}}{q} n \left(\frac{\partial \mu}{\partial n} \right)_T$$

can be viewed as a consistency relation for the system to be in thermal equilibrium, where fluctuations that determine diffusion and dissipation that determines electrical conduction are related