

We discussed macroscopic description of continuous systems

Local equilibrium hypothesis:

Based on separation of scales ($l_{\text{micro}} \ll l_{\text{macro}}$)
 System can be treated as eq. in equilibrium at each space-time point

EOS, fundamental relations valid locally each (t, \vec{r})

Description in terms of densities and flux densities (ϵ, n, s)

Conserved quantities:

continuity equation
$$\frac{\partial \rho(t, \vec{r})}{\partial t} + \vec{\nabla} \cdot \vec{J}_\rho(t, \vec{r}) = 0$$

Entropy balance:

$$\frac{\partial S(t, \vec{r})}{\partial t} + \vec{\nabla} \cdot \vec{J}_S(t, \vec{r}) = \sigma_S(t, \vec{r})$$

where entropy flow

$$\vec{J}_S(t, \vec{r}) = \sum_i \gamma_i(t, \vec{r}) \vec{J}_i(t, \vec{r}) \quad (i \neq V)$$

and entropy production

$$\sigma_S(t, \vec{r}) = \sum_i \vec{F}_i(t, \vec{r}) \cdot \vec{J}_i(t, \vec{r}) \quad \text{with} \quad \vec{F}_i(t, \vec{r}) = \vec{\nabla} \gamma_i(t, \vec{r})$$

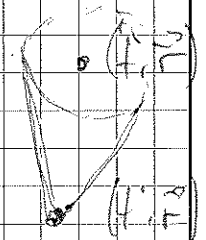
1.4 Linear irreversible processes

We have seen that affinities and fluxes describe entropy-production in systems which satisfy the local equilibrium assumption.

However the local equilibrium assumption is by itself not sufficient to determine the explicit form of the fluxes

$$\vec{J}_i = \frac{d}{dt} X_i \quad \text{or} \quad \vec{J}_i(t, \vec{r})$$

Generally the flux $\vec{J}_i(t, \vec{r})$ at a given space-time point will depend on the evolution history of the system and can be affected by everything that happened in the causal past \rightarrow microcausality



However for systems which evolve slowly (thermodynamic variables change on timescales $t_{\text{macro}} \gg t_{\text{micro}}$) and remain in local thermal equilibrium it is reasonable to neglect the constraint (retardation effect) and instead assume that the system is

Markovian: evolution instantaneously determined by local thermodynamic properties \rightarrow

In practice this means that

$$\vec{J}_i(\mathbf{u}, \mathbf{r}) = \vec{J}_i \left(\left\{ T_j(\mathbf{u}, \mathbf{r}) \right\}, \left\{ Y_k(\mathbf{u}, \mathbf{r}) \right\} \right)$$

"constitutive relation" local affinity local TD properties

Note that instead of $\{Y_k\}$ could also use $\{X_k\}$ here \rightarrow related by EOS

However it is customary to describe this in terms of intensive properties $\{Y_k\}$

Note also that there are certain situations where this assumption fails

e.g. hysteresis phenomena in 1st order PT

\rightarrow can sometimes be cured by introducing additional slow variables e.g. order parameter

Now how can we determine the constitutive relation?

If the system is equilibrium

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

is determined by **Equilibrium thermodynamics**

Note that there can be situations where the system features equilibrium currents

e.g. spin polarized Fermi gas in \vec{B} -field (CME)

However as these do not lead to entropy production (already maximal due to Equilibrium)

Entropy production rate is modified

$$\dot{\sigma}_S = \sum_i \vec{F}_i \cdot (\vec{J}_i - \vec{J}_i^{eq})$$

Now out-of-equilibrium, the affinities ($\vec{F}_i \neq 0$) will be non-zero. If we limit ourselves to small deviations, can expand in Taylor series

$$\vec{J}_i = \vec{J}_i^{eq} + \sum_k L_{ik} \vec{F}_k + \frac{1}{2} \sum_{kl} L_{ikl} \vec{F}_k \vec{F}_l + \dots$$

with "kinetic coefficients" (response coefficients)

$$L_{ik} = L_{ik}(\{Y_k(t, \vec{r})\})$$

Note that since $\vec{F}_k \sim \vec{\nabla} Y_k$ this can be viewed as gradient expansion

Note that L_{ik} include "direct effects" e.g. heat flow due to temperature gradients as well as "indirect effects" related to off-diagonal components e.g. heat flow due to differences in chemical potentials

Most frequently the eigenvalues are bounded
of lower order.

In this case the entropy production
becomes

$$\mathcal{D}_S = \sum_i \mathbb{F}_i \mathbb{J}_i = \sum_{j,k} L_{jk} \mathbb{F}_j \mathbb{F}_k$$

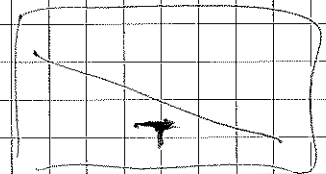
Since $\mathcal{D}_S \geq 0$ the matrix (L_{jk}) has
to be positive semi-definite

$$L_{ii} \geq 0 \quad L_{ii} L_{kk} \geq \frac{1}{4} (L_{ik} + L_{ki})^2$$

So to make things a little more concrete, we will now deconstruct some phenomenological transport equations and discuss some simple transport processes

Heat equation / Heat transport

Consider system with temperature gradient



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

Based on linear constitutive relations

$$\vec{J}_E^i = L_{EE}^{ij} \left(\vec{\nabla} \frac{1}{T} \right)_j \quad \text{where } L_{EE}^{ij} \text{ is rank two tensor}$$

Phenomenologically, heat transport is described by Fourier's law

$$\vec{J}_E = -\kappa \vec{\nabla} T$$

where κ is "heat conductivity"

If medium is isotropic, symmetry dictates

$$L_{EE}^{ij} = \delta^{ij} \kappa$$

So we obtain

$$\mathcal{H} = \frac{1}{T^2} \int EE$$

Now what does this mean for evolution of system

Combine continuity equation + constitutive relations

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

$$\frac{\partial \varepsilon}{\partial t} = + \vec{\nabla} \cdot (\mathcal{H} \vec{\nabla} T)$$

Since ε, T are related by EOS, we can express the change of $d\varepsilon$ in terms of dT

Since we are working at constant volume

$$\left. \frac{\partial \varepsilon}{\partial T} \right|_V = C_V$$

$$\Rightarrow \frac{\partial T}{\partial t} = \frac{1}{C_V} \vec{\nabla} \cdot (\mathcal{H} \vec{\nabla} T)$$

if further variables \mathcal{H} is approx independent of thermodynamic variables

$$\Rightarrow \frac{\partial T}{\partial t} = \frac{\mathcal{H}}{C_V} \Delta T$$

Most considerations apply e.g. to insulating solids, where heat transfer is achieved microscopically via phonons (lattice vibrations) whose number is not conserved

Conversely e.g. in conductors heat conduction is mainly due to charge carriers and therefore heat & particle transfer couple

Particle Diffusion

Similarly we can look at particle diffusion

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

In the absence of temperature gradients we have (for isotropic media)

$$\vec{J}_N = L_{NN} \vec{\nabla} \left(-\frac{\mu}{T} \right)$$

with

$$d\mu = \left(\frac{\partial \mu}{\partial n} \right)_T dn$$

so we find

$$D = \frac{1}{i} L_{NN} \left(\frac{\partial \mu}{\partial n} \right)$$

If the diffusion coefficient is density independent we have (in analogy to heat equation)

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

which we can solve for n in Fourier space

$$\tilde{n}(t, \vec{k}) = \int d^3k' n(\vec{r}, t) e^{-i\vec{k}' \cdot \vec{r}}$$

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

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

Solve in coordinate space by inverse FT

$$n(t, \vec{r}) = \int \frac{d^3k}{(2\pi)^3} e^{-D k^2 t} e^{i\vec{k} \cdot \vec{r}} \tilde{n}(0, \vec{k})$$

If we consider $n(t > 0, \vec{r}) = n_0 \delta^{(3)}(\vec{r})$
 then $\tilde{n}(0, \vec{k}) = n_0$ and we can directly calculate FT of Gaussian

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

Electrical conduction:

$$\vec{E} = -\vec{\nabla}\phi \quad \text{is applied}$$

ϕ electrostatic potential

If there are mobile charge carriers with charge q in the material

$$\vec{J}_{\text{tot}} = q \vec{J}_N$$

Now to account for the presence of \vec{E} we need to account for the fact that internal energy is modified

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

So the entropy function

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

where the RHS denotes usual entropy function a absence of ϕ

$\mu \pm q\phi$ electrochemical potential

$$\frac{\delta S}{\delta n} = \frac{1}{T} (-q\phi) - \frac{\mu}{T} = - \left(\frac{\mu + q\phi}{T} \right)$$

Consequently in linear response approximation

$$\vec{J}_N = L_{NN} \vec{\nabla} \left(- \frac{\mu + q\phi}{T} \right)$$

where for $T = \text{const}$

$$\begin{aligned} \vec{J}_N &= - \frac{1}{T} \left(\frac{\delta \mu}{\delta n} \right)_T L_{NN} \vec{\nabla} n \\ &= - \frac{q}{T} L_{NN} \vec{\nabla} \phi \end{aligned}$$

first term same as in diffusion,

\rightarrow vanishes in absence of density gradients

second term corresponds to Ohm's law

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

with

$$\sigma_{\text{el}} = \frac{q^2}{T} L_{NN}$$

Introspectively $\textcircled{1}$ (diffusion coefficient) and electrical conductivity σ are both related to the same kinetic coefficient L_{NN} and therefore also to each other

$$\textcircled{1} = \frac{\sigma_{el}}{q^2} \left(\frac{\delta \mu}{\delta n} \right)_T$$

In a microscopic picture of conduction, the conduction is due to drift of charge carriers:

to lower order for weak field

$\vec{v}_{drift} = \mu_{el} \vec{E}$

$\vec{v}_{drift} \leftarrow \vec{E}$

- \vec{E} field accelerates charge carrier
- friction forces slow down charge carriers

where μ_{el} is called electrical mobility

Microscopically $\vec{J}_{el} = n q \vec{v}_{drift}$

$$\Rightarrow \sigma_{el} = n q \mu_{el}$$

hence $\textcircled{1} = \frac{\mu_{el}}{q} n \left(\frac{\delta \mu}{\delta n} \right)_T$ which is an

example of Einstein relation

In ideal gas $\left(\frac{\delta \mu}{\delta n} \right)_T = \frac{n}{k_B T}$

$\textcircled{1} = \frac{\mu_{el}}{q} k_B T \rightarrow$ www.uni-bielefeld.de

1.4.1 Symmetry principles

General relations between kinetic coefficients can be derived from symmetry principles

When the coefficients are calculated microscopically this naturally emerges

However it is useful, in particular for phenomenology, to know which effects can occur

Curci principles:

Physical effects have the same symmetries as their causes

$$\text{Effect: } \vec{J}_i \text{ cause } \vec{\nabla} \chi_i$$

Consequences: ~~Effect~~ causing themselves to isotropic media (Symmetric under rotation) and parity even (reflection symmetric):

most generally: $\vec{J}_N^i = L_{NN}^{ij} \vec{\nabla}_N^j$

\vec{J}_i has to transform in the same way under rotations

as $\vec{\nabla}_i \Rightarrow L_{NN}^{ij}$ trivial under rotation $\Rightarrow L_{NN}^{ij} \propto \delta_{ij}$ L_{NN}

also can not couple tensors of different rank

rank(J) = rank(L) \Rightarrow forbidden by parity

Similarly consider a parity over internal

a) $\vec{J} = \epsilon_{ij} \vec{E} \vec{P}^j$ allowed $(\vec{J}, \vec{E}, P\text{-odd})$

b) $\vec{J} = \epsilon_{ij} \vec{B} \vec{P}^j$ not allowed $(\vec{B}, P\text{-even})$

More examples of type b) can be possible in P-odd materials
 e.g. helicity polarized Fermi gases
 \rightarrow Chiral magnetic effect

Even if medium is not isotropic, residual symmetries still translate into constraints

e.g. uniaxial ferromagnet $SO(3) \rightarrow SO(2) \times \mathbb{Z}_2$

Observer relations (Mandel 1968
chemistry)

Symmetric relation between
indirect transport coefficients (Las, 1975)

Will derive later in linear response
theory based on microscopic laws.

If a, b behave identically under T
(time reversal) then

$$L_{ab} = L_{ba}$$

More generally if

$$TX_a = \epsilon_a X_a$$

$$TX_b = \epsilon_b X_b$$

and $L_{ab} = L_{ba}(\epsilon_a, \epsilon_b, \vec{B}, \vec{H}, \dots)$

$$L_{ab}(\dots) = \epsilon_a \epsilon_b L_{ba}(T \dots)$$