

1.4 Linear irreversible processes

Based on local equilibrium assumption and
hypothesis of Markovian dynamics, derived

constitutive equations:

$$J_i^k(t, \vec{r}) = J_{ieq}^k + \sum_j L_{ij}^{kB} F_j^B(t, \vec{r}) + \text{higher orders in derivative expansion}$$

with linear coefficients L_{ij}^{dB} determined from
microphysics

Now combining

balance equations + constitutive relations + EOS
 \Rightarrow closed set of evolution equations

Will investigate, what general statements
can be made about L_{ij}^{dB} without
calculating them directly from underlying
microscopic theory

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1.4.1 Symmetry principles

General relations between kinetic coefficients
can be derived from symmetry principles
→ naturally emerges in microscopic calculation
of kinetic coefficients

However for phenomenology, it is useful to
know which effects can/can not occur

Cause principle:

Physical effects have the same symmetries
as their causes*

$$\text{Effect: } \vec{J}_i \neq 0$$

$$\text{Cause: } \vec{F}_i = -\vec{\nabla} \psi_i \neq 0 \\ \text{+ material properties}$$

* (all causes need to be considered)

Consequences of Curie principle:

Generally we would have constitutive equations

$$\text{e.g. } \mathcal{J}_n^A = L_{n\eta}^{AB} \bar{F}_n^B$$

If we restrict ourselves to

isotropic (symmetric under rotation)
& parity even (symmetric under space reflection)

media

Isotropy \Rightarrow Curie principle \mathcal{J}_n^A has to transform in the same way under rotations as \bar{F}_n^B

$$\Rightarrow L_{n\eta}^{AB} \text{ is trivial under rotations}$$

$$\Rightarrow L_{n\eta}^{AB} = \delta^{AB} \varphi_{n\eta}$$

Generally one can say that one can not couple fluxes & affinities whose tensorial rank differs by an odd number. e.g. coupling a scalar to vector is not possible unless there is a preferred direction

$$S = \underbrace{\vec{v}}_{\vec{v}} \cdot \vec{v} \quad \times \quad S = \eta \quad S' \quad \checkmark$$

Note that even in anisotropic media, the principle may still hold substantially, e.g. when there is one preferred axis and symmetry in the other directions

$$\underline{SO(3)} \rightarrow \underline{SO(2)}$$

3D rotations 2D rotations

still have rotational symmetry in 2D components

SO(3) symmetry

$$L_{nm}^{dA} = \int d^3x \mathcal{L}_{nm}$$

$$\begin{pmatrix} \mathcal{L}_{nm} & & \\ & \mathcal{L}_{nm} & \\ & & \mathcal{L}_{nm} \end{pmatrix}$$

SO(2) symmetry

$$L_{nm}^{dB} = \int d^3x \mathcal{L}_{nm} + n^\alpha n^\beta \mathcal{L}'_{nm}$$

anisotropy direction

$$\begin{pmatrix} \mathcal{L}_{nm} & \mathcal{L}'_{nm} & & \\ & \mathcal{L}_{nm} & & \\ & & \mathcal{L}_{nm} & \\ & & & \mathcal{L}_{nm} \end{pmatrix}$$

Parity \Rightarrow If material is parity symmetric
 can only couple quantities that behave the same way under parity

Causality
Principle

Example:

a) $\vec{J}_{ee} = \sigma_{ee}^E \vec{E} \quad \checkmark \quad (\vec{J}, \vec{E} \text{ P-odd})$

b) $\vec{J}_{ee} = \sigma_{ee}^B \vec{B} \quad \times \quad (\vec{J} \text{ P-odd}, \vec{B} \text{ P-even})$

Note that couplings of type b) are possible
 in system that breaks P, where σ_{oe} is
 P-odd, e.g. Chiral magnetic effect
 in Z_2 TEs

Beyond the Curie principle, further
 information can be deduced from
 the possibility of entropy production

isohm
 unbroken

$$\sigma_S = \sum_i \bar{T}_i^\alpha (z_i^\alpha - z_i^{\alpha'})$$

$$= \underbrace{\sum_{ik} L_{ik} \bar{T}_i^\alpha \bar{T}_k^\alpha}_{\text{quadratic form}} \stackrel{?}{\geq} 0$$

Since $\sigma_S \geq 0$ for entropy production
 to be positive, the matrix

$\frac{1}{2}(L+L^T)$ has to be positive
 semi-definite

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

Onsager relations: (Nobel prize in chemistry 1968)

Symmetry relation between indirect/cross-terms for coefficients (Like with $i \neq k$) which can be derived in linear response theory from microscopic physics.

If (i) and (k) behave identically under time reversal T , then

$$L_{ik} = L_{ki}$$

So under the typical circumstances the Matrix L coupling affinity and fluxes is symmetric & positive semi-definite



1.4.2 Coupled transport phenomena

Based on these new insights, we will now consider a few examples of coupled transport phenomena, e.g. heat transport in a conductor modulated by a constant number of mobile charge carriers

Single species of charge carriers with charge q and uniform density n subject to $\vec{E} = -\vec{\nabla}\phi$

Based on linear constitutive relations we find

$$\vec{J}_n = \underline{\underline{L}}_{nm} \vec{\nabla} \left(-\frac{\mu_f}{T} \right) + \underline{\underline{L}}_{ne} \vec{\nabla} \left(\frac{1}{T} \right)$$

$$\vec{J}_e = \underline{\underline{L}}_{en} \vec{\nabla} \left(-\frac{\mu_f}{T} \right) + \underline{\underline{L}}_{ee} \vec{\nabla} \left(\frac{1}{T} \right)$$

Curio: $\underline{\underline{L_{nn}}}$, $\underline{\underline{L_{ne}}}$, $\underline{\underline{L_{ee}}}$ are
scalars if material is
isotropic

Onset: Since ϵ_n are T-ans
 $L_{en} = L_{ne}$

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Heat conduction in an open circuit



No electric current can flow as
circuit is isolated

$$\Rightarrow \vec{J}_{ee} = q \vec{J}_n = 0$$

$$\vec{J}_n = L_{nn} \vec{\nabla} \left(-\frac{\mu\phi}{T} \right) + L_{ne} \vec{\nabla} \left(\frac{1}{T} \right)$$

$$\Rightarrow \vec{\nabla} \left(-\frac{\mu\phi}{T} \right) = -\frac{L_{ne}}{L_{nn}} \vec{\nabla} \left(\frac{1}{T} \right)$$

Now if we consider the energy flux

$$\vec{J}_e = L_{en} \vec{\nabla} \left(-\frac{\mu_e}{T} \right) + L_{ee} \vec{\nabla} \left(\frac{1}{T} \right)$$

$$= \left(-\frac{L_{ee}}{T^2} + \frac{L_{en} L_{ne}}{L_{nn} T^2} \right) \vec{\nabla} T$$

$$\vec{J}_e = -\mathcal{K} \vec{\nabla} T$$

with heat conductivity

$$\mathcal{K} = \frac{1}{T^2} \frac{L_{ee} L_{nn} - L_{en} L_{ne}}{L_{nn}}$$

⇒ Even though there are no currents flowing inside the material ($\vec{J}_n = 0$), the coupling to the conserved density modifies heat transfer

compare to resistor

$$\vec{J}_e = -\chi \vec{\nabla} T, \quad \chi = \frac{L_{00}}{T^2}$$

Now if we take a look at entropy production, we have

$$\begin{aligned}\sigma_S &= \sum_i (\nabla Y_i) \vec{J}_i \\ &= \vec{J}_n \nabla \left(-\frac{\mu_\phi}{T}\right) + \vec{J}_e \nabla \left(\frac{1}{T}\right) \\ &= \frac{1}{T} \vec{J}_n \nabla \mu_\phi + \underbrace{(\vec{J}_e - \mu_\phi \vec{J}_n)}_{\vec{J}_Q} \nabla \left(\frac{1}{T}\right)\end{aligned}$$

"heat flux" $\vec{J}_Q = T \vec{J}_S$

often times thermoelectric effects are discussed in terms of

$$\vec{J}_n \text{ and } \vec{J}_Q \text{ rather than } \vec{J}_n \text{ and } \vec{J}_e$$

By change of basis the corresponding fluxes are given

by

$$\vec{J}_n = -\frac{L_{11}}{T} \vec{\nabla} \mu_f + L_{12} \vec{\nabla} \left(\frac{1}{T} \right)$$

$$\vec{J}_a = -\frac{L_{21}}{T} \vec{\nabla} \mu_f + L_{22} \vec{\nabla} \left(\frac{1}{T} \right)$$

where

$$L_{11} = L_{nn} \quad L_{12} = L_{21} = L_{en} - \mu_f L_{na}$$

$$L_{22} = L_{aa} - \mu_f (L_{an} + L_{ne}) + \mu_f^2 L_{nn}$$

So if we look again at the example of electric conduction at uniform temperature, we have

$$\vec{J}_{\text{oe}} = q \vec{J}_n = -q \frac{L_{11}}{T} \nabla \mu_f$$

so for uniform volume we have

$$\nabla \mu = \left(\frac{\partial \mu}{\partial n} \right)_T \nabla n = 0 \quad \text{and} \quad \nabla \mu_f = -q \vec{E}$$

$$\vec{J}_{\text{oe}} = + \underbrace{\frac{q^2 L_{11}}{T}}_{\sigma} \vec{E}$$

σ electric conductivity

Now we can also look
at entropy production

$$\sigma_S = -\frac{1}{T} \vec{J}_n \nabla \mu_f + \underbrace{J_q \nabla \left(\frac{1}{T} \right)}_{=0}$$

"Joule
effect"

$$\sigma_S = \frac{\sigma E^2}{T} = \frac{J_{\text{oe}}^2}{\sigma T}$$

\Rightarrow Entropy production in conductor
corresponds to heating of the material

Seebeck effect:

We had seen that for an open circuit the fact that $\vec{J}_n = 0$

$$\Rightarrow \vec{\nabla} \left(-\frac{\mu_f}{T} \right) = -\frac{L_{ne}}{L_{nn}} \vec{\nabla} \left(\frac{1}{T} \right)$$

means that

$$\vec{\nabla} \mu_f \propto \vec{\nabla} T$$

which is summarized
by the Seebeck coefficient

$$\vec{\nabla} \mu_f = -q \varepsilon_S \vec{\nabla} T$$

$$\text{with } \varepsilon_S = \frac{1}{qT} \left(\frac{L_{ne}}{L_{nn}} - \mu_f \right)$$

Now evaluating

$$\begin{aligned}\vec{\nabla} \mu_q &= \vec{\nabla} (\mu + q\phi) \\ &= \left(\frac{\partial \mu}{\partial n} \right)_T \vec{\nabla} n + q \vec{\nabla} \phi\end{aligned}$$

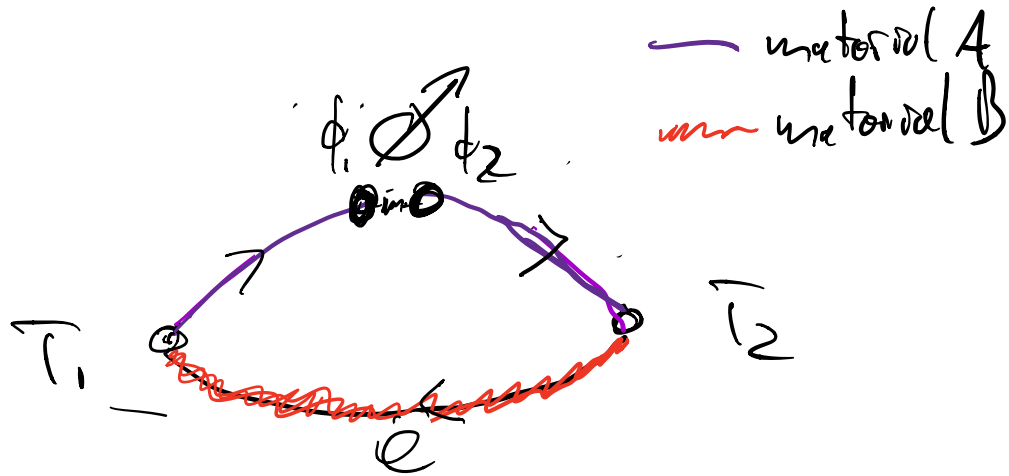
so if we neglect density variations

$$= -q \vec{E}$$

Seebeck $\Rightarrow \vec{E} = \epsilon_S (\vec{\nabla} T)$

\Rightarrow temperature gradients in a conductor can create an electric field

Notably this effect can be used to build temperature sensors



$$\phi_1 - \phi_2 = \int_C \vec{\nabla} \phi \cdot d\vec{l} \stackrel{n \approx \text{const}}{\approx} \frac{1}{\epsilon} \int_C \vec{\nabla} \mu \cdot d\vec{l}$$

$$= - \int_C \epsilon_S \vec{\nabla} T \cdot d\vec{l}$$

$$= - \int_{T_1}^{T_2} (\epsilon_A - \epsilon_B) dT$$

So if $\phi_1 - \phi_2$ is measured and $\epsilon_{A/B}$ known
 can measure $T_1 - T_2$

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Since $L_{en} = L_{ne}$, there must exist
 an analogous inverse effect
 whereby charge transport affects
 energy transport

Peltier effect: $\vec{J}_Q = \underbrace{\pi}_{\text{Peltier coefficient}} \vec{J}_{ce}$

Specifically if $T = \text{const}$

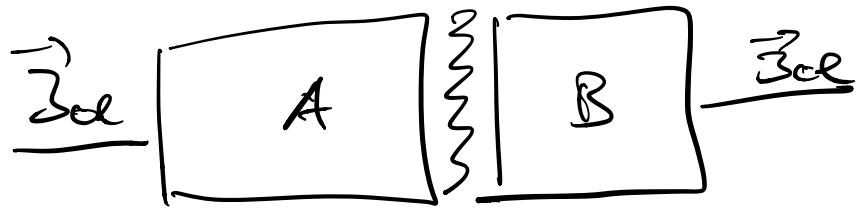
$$q \vec{J}_n = -\frac{qL_{nn}}{T} \vec{\nabla} \mu \phi$$

$$\vec{J}_Q = -\frac{L_{en} - \mu L_{nn}}{T} \vec{\nabla} \mu \phi$$

$$\Rightarrow \pi = \frac{1}{q} \left(\frac{L_{en}}{L_{nn}} - \mu \phi \right) \stackrel{L_{en} = L_{ne}}{\stackrel{\downarrow}{=} \varepsilon_0 T}$$

"Second Thomson/Kelvin voltage"

Can be measured by creating
a junction between two
materials



$$\vec{J}_{eA}^{(A)} = \vec{J}_{eB}^{(B)} = \vec{J}_{eA}$$

but

$$\vec{J}_{eA}^{(A)} \neq \vec{J}_{eB}^{(B)} \Rightarrow \vec{\nabla} \cdot \vec{J}_{eA} \neq 0$$

at the junction

\Rightarrow Heating of the junction