Discussed linear Markovian transport

→ Developed theory for near-equilibrium systems

$$J_i^{\alpha} = J_i^{eq\,\alpha} + \sum_j L_{ij}^{\alpha\beta} F_j^{\beta}$$

Studied applications to simple transport phenomena

Diffusion, Heat conduction, Electric conduction

General strategy: combine constitutive relations, conservation laws, EQ

Symmetry principles

Curie principle, Onsager relation

Symmetries of effect same as symmetries of cause.

$L_{ab} = L_{ba}$ (for a, b same under T)

1.4.2 Coupled transport phenomena

We can now also look at coupled transport phenomena, e.g. heat transport in conductor mediated by electrons

Consider single species with charge q and uniform density ($\vec{\nabla} n = 0$) subject to $\vec{E}$ described by ϕ

Based on linear transport formula constitutive relations takes the form

$$\vec{J}_N = L_{NN} \vec{\nabla}\left(-\frac{\mu_\phi}{T}\right) + L_{NE} \vec{\nabla}\left(\frac{1}{T}\right)$$
$$\vec{J}_E = L_{EN} \vec{\nabla}\left(-\frac{\mu_\phi}{T}\right) + L_{EE} \vec{\nabla}\left(\frac{1}{T}\right)$$

Onsager: $L_{EN} = L_{NE}$

Curie: L_{NN} is scalar (as opposed to tensor) if material is isotropic

Heat conduction in open circuit:

~~[illegible]~~ No electric current can flow

$\Rightarrow \vec{J}_N = 0$

$$-L_{11}\frac{1}{T}\vec{\nabla}\mu_\phi + L_{12}\vec{\nabla}\frac{1}{T} = 0$$

$$\Rightarrow \boxed{\vec{\nabla}\mu_\phi = -\frac{L_{12}}{L_{11}}\frac{1}{T}\vec{\nabla}T}$$

So we obtain

$$\vec{J}_Q = -\frac{L_{11}L_{22} - L_{21}L_{12}}{T^2 L_{11}}\vec{\nabla}T$$

Compare with result for insulator

$$\left(\vec{J}_E = -\kappa\vec{\nabla}T \quad , \quad \kappa = \frac{L_{EE}}{T^2}\right)$$

$\Rightarrow$ Different because charge carriers (e^-) contribute to heat transfer

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$$\sigma_S = \vec{J}_N \vec{\nabla}\left(-\frac{\mu_\phi}{T}\right) + \vec{J}_E \vec{\nabla}\left(\frac{1}{T}\right)$$

$$= -\frac{1}{T}\vec{J}_N \vec{\nabla}\mu_\phi + \underbrace{\left(\vec{J}_E - \mu_\phi \vec{J}_N\right)}_{= \vec{J}_Q \,=\, T\vec{J}_S} \vec{\nabla}\left(\frac{1}{T}\right)$$

„heat flux"

Heat flux includes heat transport due to convection in addition to usual heat conduction

Equivalently can write

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

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

where by comparison

$$L_{11} = L_{NN}$$

$$L_{21} = L_{12} = L_{NE} - \mu_\phi L_{NN}$$

$$L_{22} = L_{EE} - \mu_\phi\left(L_{NE} + L_{EN}\right) + \mu_\phi^2 L_{NN}$$

Note that $\vec{\nabla} T \Rightarrow \vec{\nabla} \mu_\phi$

in the open circuit $(\vec{J}_N = 0)$

$\Rightarrow$ temperature difference leads to difference in electrochemical potential

this is called Seebeck effect

usually written as

$$\frac{1}{q} \vec{\nabla} \mu_\phi = - \underbrace{\varepsilon_S}_{\text{Seebeck coefficient}} \vec{\nabla} T$$

$$\varepsilon_S = \frac{1}{qT} \frac{L_{12}}{L_{11}}$$

Solely due to indirect transport

Now

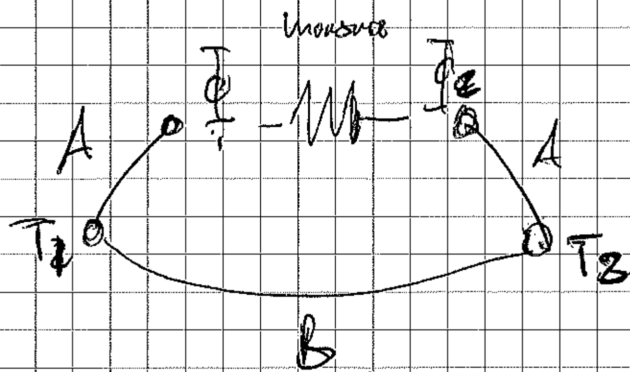
$$\vec{\nabla} \mu_\phi = \vec{\nabla} (\mu + q\phi)$$

$$= \underbrace{\left(\frac{\partial \mu}{\partial n}\right)_T \vec{\nabla} n}_{=0 \text{ uniform density}} + q \vec{\nabla} \phi$$

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

$$\vec{E} = \varepsilon_S (\vec{\nabla} T)$$

Can be measured as follows



$$\phi_2 - \phi_1 = \int_1^2 (\vec{\nabla}\phi)\cdot(d\vec{l})$$

$$= \frac{1}{q}\int_1^2 (\vec{\nabla}\mu_\phi)(d\vec{l})$$

$$= -\int_1^2 \mathcal{E}_S (\vec{\nabla}T)\, d\vec{l}$$

$$= \int_{T_1}^{T_2} \left(\mathcal{E}^{(A)} - \mathcal{E}^{(B)} \right)$$

Can measure $\mathcal{E}^{(B)}$ if $\mathcal{E}^{(A)}$ is known

If both $\mathcal{E}^{(A)}$ and $\mathcal{E}^{(B)}$ are known can use to measure ΔT

Seebeck effect: $\vec{\nabla} T \Rightarrow \vec{\nabla} \mu_{el}$

Similarly coupling between e, N transport also means that

$$\underbrace{\vec{J}_{el} = q \vec{J}_N \neq 0}_{\text{electric current}} \Rightarrow \underbrace{\vec{J}_Q \neq 0}_{\text{heat transfer}}$$

⇒ Peltier effect: $\vec{J}_Q = \underbrace{\Pi}_{\text{Peltier coefficient}} \vec{J}_{el}$

Specifically at material is kept at const temperature $\vec{\nabla} T = 0$

$$\vec{J}_N = - L_{11} \frac{1}{T} \vec{\nabla} \mu_\phi$$

$$\vec{J}_Q = - L_{21} \frac{1}{T} \vec{\nabla} \mu_\phi$$

$$\Pi = \frac{1}{q} \frac{L_{21}}{L_{11}}$$ ⇒ again purely due to coupled transport

Comparison with $\varepsilon_S = \frac{1}{qT} \frac{L_{12}}{L_{11}}$

$\xRightarrow{\text{Onsager}}$ $\Pi = \varepsilon_S T$ Second Thompson relation

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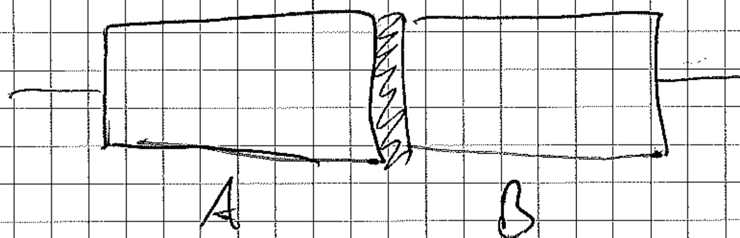
Can be measured by creating a junction between two materials

$\vec{J}_{el}^{(A)}$ $\vec{J}_{el}^{(B)}$



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

$$\vec{J}_{Q}^{(A/B)} = \Pi^{(A/B)} \vec{J}_{el}$$

$$\Rightarrow \quad \vec{\nabla} \vec{J}_Q \neq 0 \quad \text{at the junction}$$

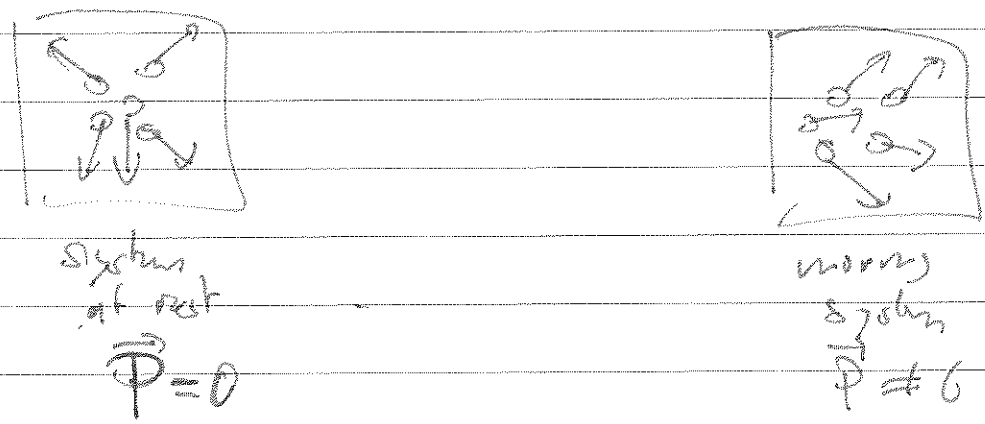
~~heat accumulates at junction~~

$$\frac{dQ}{dt} = \left(\Pi^{(A)} - \Pi^{(B)}\right) \left|\vec{J}_{el}\right|$$

heat is deposited / absorbed at the junction

1.4.3 Linear Markovian dynamics of simple fluids

So far dealt with systems at rest
→ need to generalize to moving systems



Can be related by Galilei transformation
→ always possible to define
comoving frame „local rest frame"
where $\vec{P}=0$

Call $R_{\vec{v}}$ local rest frame
and R_0 laboratory frame

In LRF energy $E = U$ describing statistical motion of particles

In general frame $E = U + \frac{1}{2}\frac{\vec{P}^2}{2M}$
COM motion also contributes

~~Since entropy is frame independent need to modify entropy function~~

Need to modify entropy functional

Since entropy is frame independent

$$S(E, N, \vec{P}) = S\left(E - \frac{\vec{P}^2}{2M}, N\right)$$

Similarly need

$S(\varepsilon, n, \vec{p})$ momentum density

Usually in NR Hydro use velocity $\vec{v}$
instead of momentum $\vec{p}$

$\vec{p} = \rho\vec{v}$ $\varepsilon_{com} = \frac{1}{2}\rho\vec{v}^2$

where

$\rho(t, \vec{r}) = m\, n(t, \vec{r})$ for single component

Need

$$S(\varepsilon, n, \vec{v}) = S\left(\varepsilon - \tfrac{1}{2}\rho\vec{v}^2, n\right)$$

So

$$dS = \frac{\partial S}{\partial \varepsilon}\left(d\varepsilon - \frac{1}{2} d(\rho\vec{v})^2\right) + \frac{\partial S}{\partial n} dn$$

$$= \frac{1}{T} d\varepsilon - \frac{\frac{1}{2} m\vec{v}^2}{T} dn - \left(\frac{\rho\vec{v}}{T}\right) d\vec{v} + \frac{\mu}{T} dn$$

$$d\vec{p} = \rho d\vec{v}$$

$$\Big|_{\varepsilon, n} = \underbrace{\frac{1}{T}}_{Y_\varepsilon} d\varepsilon - \underbrace{\frac{\vec{v}}{T}}_{Y_{\vec{p}}} d\vec{p} - \underbrace{\frac{\mu + \frac{1}{2} m\vec{v}^2}{T}}_{Y_n = -\frac{\mu_{\vec{v}}}{T}} dn$$

$$\boxed{dS = \frac{1}{T} d\varepsilon - \frac{\vec{v}}{T} d\vec{p} - \frac{\mu + \frac{1}{2} m\vec{v}^2}{T} dn}$$

What about the pressure?

Gibbs-Duhem relation:

$$P = Ts - \varepsilon + \mu n$$

$$= Ts - \left(\varepsilon + \tfrac{1}{2}\rho\vec{v}^2\right) + \left(\mu + \tfrac{1}{2} m\vec{v}^2\right) n$$

$\Rightarrow$ pressure is the same in every frame

Now we have the intensive quantities $Y_i(t,\vec{r})$ for $\varepsilon, n, \vec{p}$ from which we can construct the corresponding affinities

$$F_i^{\alpha} = \frac{\partial}{\partial x_\alpha} Y_i(t,\vec{r}) \qquad i = \varepsilon, n$$

$$F_i^{\alpha\beta} = \frac{\partial}{\partial x_\alpha} Y_i^{\beta}(t,\vec{r}) \qquad i = \vec{p}$$

However to construct constitutive relations

$$J_i = J_i^{eq} + \text{-- } \overset{\text{non-eq}}{\text{affinity}} \text{ dependent terms}$$

we also need equilibrium fluxes

Now what are equilibrium fluxes?

→ Consider system in LRF where symmetries are easier to understand

rotational invariance in LRF

$\vec{J}_E, \vec{J}_N$ transform non-trivially under rotations

$\Rightarrow \vec{J}_E = 0, \vec{J}_N = 0$ (as discussed before)

$J_{\vec{p}}^{\alpha\beta}$ is rank two tensor

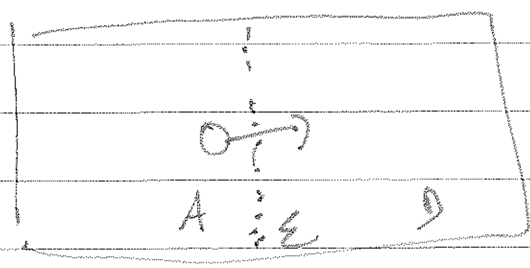
⇒ has to be proportional to rotationally invariant rank two tensor

$$J_{\vec{p}}^{\alpha\beta} = C_{\vec{p}} \mathbb{1}^{\alpha\beta} = C_{\vec{p}} \delta^{\alpha\beta}$$

where $C_{\vec{p}}$ describes the isotropic flow of momentum

and $J^{\alpha\beta}$ denotes flux of p^α in x^β direction

Consider a fluid in the local rest frame sub-divided into two cells



Momentum flux $J_{\vec{p}}^{\alpha\beta}$ corresponds to particle crossing border

Change momentum on the left of wall

$$\int d\Sigma^{\alpha} \, \underline{J_{\vec{p}}} = \cancel{+} \frac{d\vec{P}_A}{dt} = \vec{F}_{B \to A}$$

In fluid in mechanical equilibrium the force exerted per unit area on a wall (or another fluid cell) is isotropic and given by the pressure

$$\Rightarrow \quad J_{\vec{p}}^{\alpha\beta} = P \, \delta^{\alpha\beta}$$

So we have a LRF

<u>LRF:</u> $\vec{J}_E = 0 \quad \vec{J}_n = 0 \quad J_{\vec{p}}^{\alpha\beta} = P\,\delta^{\alpha\beta}$

However, to describe motion of fluid and expressions in general frame (laboratory frame)

Consider first an infinitesimal transformation

~~laboratory~~ $R_{\vec{v}'}$ where fluid cell has velocity $\vec{v}-\vec{v}'$

$R_{\vec{v}'+d\vec{v}'}$ where fluid cell has velocity $\vec{v}-\vec{v}'-d\vec{v}'$

Start by looking at densities

$(\tilde{\mathcal{E}}, n, \vec{p})$ measured in $R_{\vec{v}'}$

$$\mathcal{E} + \tfrac{1}{2}\rho(\vec{v}-\vec{v}')^2,\ n,\ \rho(\vec{v}-\vec{v}')$$

$(\tilde{\mathcal{E}}, n, \vec{p})$ measured in $R_{\vec{v}}$

$$\mathcal{E} + \tfrac{1}{2}\rho(\vec{v}-\vec{v}'-d\vec{v}')^2,\ n,\ \rho(\vec{v}-\vec{v}'-d\vec{v}')$$

$$\|$$

$$\mathcal{E} + \tfrac{1}{2}\rho(\vec{v}-\vec{v}')^2 - \cancel{\rho}\,d\vec{v}',\ n,\ \rho(\vec{v}-\vec{v}') - \rho\,d\vec{v}'$$

So for the static density
we infer that change from $\rho\vec{v}'$ to $\rho\vec{v}'+d\vec{v}'$
yields, setting $\vec{w} = v - \vec{v}'$, $d\vec{w} = -d\vec{v}$

$$d\left(\varepsilon + \frac{1}{2}\rho\vec{w}^2\right) = +\rho\,\vec{w}\,d\vec{w} = \vec{p}\,d\vec{w}$$

$$dn = 0$$

$$d(\rho\vec{w}) = \rho\,d\vec{w} = \cancel{m}\,\cancel{m}\,d\vec{w}$$

Now we can look at the fluxes/currents when we have to account for two effects

1) Currents that are already present in $R_{\vec{V}'}$ will change in $R_{\vec{V}'+d\vec{V}'}$ in the same way that the densities change

2) Densities at rest in $R_{\vec{V}'}$ will move with $-d\vec{V}'$ in $R_{\vec{V}'+d\vec{V}'}$ and contribute additionally to the currents

$$d J_N^{eq\,\alpha} = n\, dW^\alpha \iff \left(d\vec{J}_N^{eq} = n\, d\vec{W} \right)$$

$$d J_E^{eq\,\alpha} = J_{\vec{p}}^{\alpha\beta}\, dW_\beta + \left(\varepsilon + \tfrac{1}{2}\vec{W}^2 \right) dW^\alpha$$

$$d J_{\vec{p}}^{\alpha\beta} = m J_N^{\beta}\, dW^\alpha + \rho W^\alpha dW^\beta$$

Differential equations describing changes of fluxes w.r.t to changing frame

$\Rightarrow$ Need to integrate from LRF to lab frame to obtain general expressions

$$\boxed{\vec{J}_N^{eq} = \vec{J}_N^{eq}\Big|_{LRF} + \int_0^{\vec{V}} n\, d\vec{w} = n\vec{V}}$$

$$J^{\alpha\beta}_{eq,\vec{P}} = J^{eq}_{P}\Big|^{\alpha\beta}_{LRF} + \int_0^{\vec{V}} m\underbrace{(n\vec{w})^{\beta}}_{\vec{J}_N} dw^{\alpha} + \rho w^{\alpha} dw^{\beta}$$

$$= P\delta^{\alpha\beta} + \rho \int_0^{\vec{V}} w^{\beta} dw^{\alpha} + w^{\alpha} dw^{\beta}$$

$$\boxed{J^{\alpha\beta}_{\vec{P},eq} = P\delta^{\alpha\beta} + \rho V^{\alpha} V^{\beta}}$$

$$J^{eq\,\alpha}_{E} = \underbrace{J^{eq}_{E}\Big|_{LRF}}_{=0} + \int_0^{\vec{V}} \left(P\delta^{\alpha\beta} + \rho \vec{w}^{\alpha}\vec{w}^{\beta}\right) d\vec{w}^{\beta}$$

$$+ \int_0^{\vec{V}} \left(e + \tfrac{1}{2}\rho \vec{w}^2\right) d\vec{w}^{\alpha}$$

$$= (e+P)\vec{V}^{\alpha} + \rho \underbrace{\int_0^{\vec{V}} \left(\vec{w}^{\alpha}\vec{w}^{\beta} + \tfrac{1}{2}\delta^{\alpha\beta}\vec{w}^2\right) d\vec{w}^{\beta}}_{\left[\frac{1}{2}\rho \vec{w}^2 w^{\alpha}\right]_{\vec{w}=0}^{\vec{w}=\vec{V}}}$$

$$\boxed{J^{\alpha}_{E,eq} = \left(e + \tfrac{1}{2}\rho\vec{V}^2 + P\right)\vec{V}^{\alpha}}$$