

Physics 210B

Lecture 4c: Transport/Onsager Matrix and Onsager Symmetry

Recall: - For modest gradients in thermodynamic parameters $n, \bar{V}, T$ etc. calculate fluxes via Chapman-Enskog Exp

①

example

$$\underline{\Pi} = - \underline{L} \cdot \underline{F}_{Th} \quad \text{for } \underline{F}_{Th} \propto (l/L_m)$$

"Onsager Matrix"

$$\underline{e.g.} \quad \begin{pmatrix} \underline{\Pi} \\ \underline{Q} \end{pmatrix} = - \begin{pmatrix} D & d_{n,T} \\ d_{T,n} & \chi \end{pmatrix} \begin{pmatrix} \underline{\nabla} n \\ \underline{\nabla} T \end{pmatrix}$$

D, χ "diagonals"
 $d_{n,T}, d_{T,n} \rightarrow$ "off diagonals"

$\rightarrow$ Diagonals > 0 (for entropy production)

$\rightarrow$ off-diagonals can be < 0 ,
 though overall $dS/dt \geq 0$

$$\rightarrow \frac{dS}{dt} = + F_{Th}^T \cdot \underline{H} \cdot F_{Th}$$

We'll show $\rightarrow$

Symmetry:

⑤ If microscopic (dynamics) process is time reversible (i.e. required for detailed balance), then H matrix is ~~reversible~~ symmetric.

$$K_{ij} = K_{ji}$$

Why care?
- reduces computational 'load' of H

- insight into off-diagonal processes (c.f. "Bootstrap Current" in MFE)

- Theoretical insight $\rightarrow$ linked to linear response

①

→ A concrete example: Dissipation Function, Entropy Production, etc.

$$dU = TdS - pdV + \mu dM$$

$\downarrow$ internal energy $\downarrow$ chemical potential

Fixed p $\nearrow$ dV $\nearrow$ fixed volume

$$= TdS + \mu dp$$

$\therefore$

$$dS = \frac{dU}{T} - \mu dp$$

$U, p \rightarrow$ thermo variables

$1/T, -\frac{\mu}{T} \rightarrow$ conjugate (entropic)

- intensive analogous to potential energies

- $\nabla(1/T), \nabla(-\mu/T)$ are thermodynamic forces driving fluxes.

For the flows / fluxes:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \underline{J}_\rho = 0$$

↓
mass flux - (diffn)

$$\frac{\partial u}{\partial t} + \nabla \cdot \underline{J}_u = 0$$

↓
internal energy flux
(i.e. heat conductivity)

(ignore mass flows for convenience)

For entropy:

$$\frac{\partial s}{\partial t} + \nabla \cdot \underline{J}_s = \frac{\partial s_c}{\partial t}$$

↓
entropy flux

→ increase in entropy due (local) irreversible process of relaxation.
(i.e. CGF = local)

For Fluxes:

$$\underline{J}_u = -K \nabla(T)$$

$$= K T^2 \nabla(1/T)$$

$$\underline{J}_\rho = -D \nabla \rho$$

$$\mu = \mu(p), \quad d\mu/dp > 0$$

so, could just as easily write:

$$\underline{J}_p = D' \underline{D} (-\mu/T)$$

In general:

$$\begin{cases} \underline{J}_u = L_{u,u} \underline{D}(1/T) + L_{u,p} \underline{D}(-\mu/T) \\ \underline{J}_p = L_{p,u} \underline{D}(1/T) + L_{p,p} \underline{D}(-\mu/T) \end{cases}$$

⇒ have $\uparrow$ Onsager matrix

$$\underline{J}_\alpha = \sum_{\beta} L_{\alpha,\beta} \underline{D} F_{\beta}, \quad \text{as proposed, expected}$$

Thermodynamic Forces: $\underline{D} f_u = \underline{D}(1/T)$

$$\underline{D} f_p = \underline{D}(-\mu/T)$$

Thermodynamic forces,

$$\underline{D} f_u = \underline{D}(1/T), \quad \underline{D} f_p = \underline{D}(-\mu/T)$$

→ then, Entropy Production Rate

expect $\frac{dS}{dt} = \underline{J} \cdot \underline{\nabla} F$

To show:

$$\frac{\partial S}{\partial t} = \frac{\partial}{\partial t} \left(\frac{u}{T} - \frac{u}{T} p \right)$$

$$= \frac{1}{T} \frac{\partial u}{\partial t} - \frac{u}{T} \frac{\partial p}{\partial t}$$

and:

$$\underline{J}_S = \frac{1}{T} \underline{J}_u - \frac{u}{T} \underline{J}_p$$

Now, recall:

$$\frac{\partial S_0}{\partial t} = \frac{\partial S}{\partial t} + \underline{\nabla} \cdot \underline{J}_S$$

$$= \frac{1}{T} \frac{\partial u}{\partial t} - \frac{u}{T} \frac{\partial p}{\partial t} + \underline{\nabla} \cdot \left(\frac{\underline{J}_u}{T} \right) - \underline{\nabla} \cdot \left(\frac{u}{T} \underline{J}_p \right)$$

so

$$\frac{\partial S_c}{\partial t} = \frac{1}{T} \frac{\partial U}{\partial t} - \frac{\mu}{T} \frac{\partial \rho}{\partial t} + \frac{1}{T} \nabla \cdot \underline{J}_u - \frac{\mu}{T} \nabla \cdot \underline{J}_\rho + \underline{J}_u \cdot \nabla \left(\frac{1}{T} \right) - \underline{J}_\rho \cdot \nabla \left(\frac{\mu}{T} \right)$$

so

$$\frac{\partial S_c}{\partial t} = \sum_{\alpha} \underline{J}_{\alpha} \cdot \nabla f_{\alpha}$$

but $\underline{J}_{\alpha} = L_{\alpha\beta} \cdot \nabla f_{\beta}$

so Finally;

$$\frac{\partial S_c}{\partial t} = \sum_{\alpha} \sum_{\beta} (\nabla f)_{\alpha} \cdot \underline{L}_{\alpha\beta} \cdot (\nabla f)_{\beta}$$

Local gradient $\Rightarrow$ local entropy production rate!!

$$P_{MFP} L \rightarrow 0$$

{ see posting on
Non-Equ. Thermo.

$$\frac{\partial \mathcal{F}}{\partial t} = D_1 \left(\frac{\partial f_1}{\partial x_1} \right)^2 + D_2 \left(\frac{\partial f_2}{\partial x_1} \right)^2 \\ + d_{1,2} \left(\frac{\partial f_1}{\partial x_1} \cdot \frac{\partial f_2}{\partial x_1} \right) + d_{2,1} \left(\frac{\partial f_1}{\partial x_1} \cdot \frac{\partial f_2}{\partial x_1} \right)$$

- $D_1, D_2 > 0$

= gradients aligned:

$$\frac{D_2}{D_1} \geq \frac{(d_{1,2} + d_{2,1})^2}{4 D_1^2}$$

↔ positive semi-definite condition

- Can have $d_{1,2}$ etc. < 0

⇒ "Pinch" → i.e. DT

drives up-gradient
particle flux.

This brings us to Onsager Symmetry!

⑥ Symmetry of L, B

→ See Onsager paper
See Max-Eq. Thermo
Section

— consider $x_1, x_2, \dots, x_n$

↳ Fluctuations from
equilibrium for
Thermodynamic quantities

$$\begin{aligned}\tilde{T} &= T - T_{eq} \\ \tilde{n} &= n - n_{eq}\end{aligned} \quad \left. \vphantom{\begin{aligned}\tilde{T} &= T - T_{eq} \\ \tilde{n} &= n - n_{eq}\end{aligned}} \right\} \text{etc}$$

then $\phi = S(x_1, x_2, \dots, x_n)$

↳ entropy

For small Fluctuations (linear response!)

$$S = \underset{\text{ref}}{\cancel{S_0}} + \underset{\text{ref}}{\cancel{\nabla S \cdot \underline{x}}} + \frac{\partial^2 S}{\partial x_i \partial x_k} \frac{x_i x_k}{2}$$

$$\approx - \left(- \frac{\partial^2 S}{\partial x_i \partial x_k} \right) \frac{x_i x_k}{2} = - \frac{\beta_{ik}}{2} x_i x_k$$

$$\beta_{ij,k} = - \frac{\partial^2 \mathcal{S}}{\partial x_i \partial x_k} \quad !$$

$\Rightarrow$ probability,

$$\mathcal{S} = \exp[W]$$

$$= c \exp \left[- \frac{\beta_{ij,k} x_i x_k}{2} \right]$$

rpt index
summed.

System seeks maximize
entropy $\Rightarrow$ fluctuations
decay

$\beta_{ij,k}$
positive
definite

$$\dot{x}_i = - \lambda_{ij,k} x_k$$

$\Rightarrow$ fluctuations
relax

Now, consistent with $\left\{ \begin{array}{l} - \text{linear response} \\ - \text{flux-gradient relation} \\ - \text{quadratic form} \\ \text{entropy} \end{array} \right.$

define thermodynamically conjugate
(in flux-gradient sense) variables:

$$X_i = - \frac{\partial \mathcal{S}}{\partial x_i} = \beta_{ij,k} x_k$$

$$\underline{X}_i = \beta_{ij} x_j$$

thus

$$\dot{x}_i = -\lambda_{ij} x_j \rightarrow \text{relate to } \underline{X}$$

$$= -\gamma_{ij} \underline{X}_j$$

→ (has transport form.)

$$\boxed{\gamma_{jk} = \lambda_{ij} \beta_{ik}^{-1}}$$

→ "kinetic, or transport" coeff.

→ relate relaxn of fluctuations in thermo variables to conjugates
↔ thermo forces

$$\text{e.g. } \ln \Omega = - \underbrace{\beta_{ij} x_i x_j}_2$$

$$\psi = \frac{1}{2} \gamma_{ij} \underline{X}_i \underline{X}_j$$

$$\frac{d\underline{S}}{dt} = \pm \underline{\Gamma}^T \cdot \underline{K} \cdot \underline{\Gamma}$$

Now, show if micro-dynamics reversible, then $\gamma_{jk} = \gamma_{kj}$

⇒ γ matrix symmetric.

To show:

Define $\bar{x} = \frac{1}{T} \int_0^T x$ $\rightarrow$ time avg.

$$A_i = A_i(t) = \bar{x}_i$$

time scales
long rel. to t

$$B_i = B_i(t) = \bar{x}_i$$

$$\dot{x}_i(t) = -\gamma_{ik} \bar{x}_k$$

$$\dot{A}_i(t) = -\gamma_{ik} B_k$$

Assume: Consistent with detailed balance,

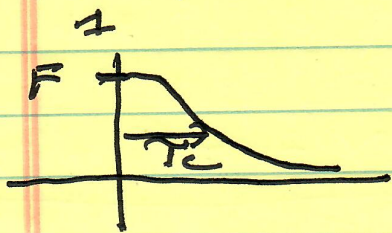
$\rightarrow$ time reversible microdynamics,
correlations invariant to order

$$\text{c.e. } \langle x_i(t) x_k(0) \rangle = \langle x_i(0) x_k(t) \rangle$$

Aside: What is a correlation function? [Brackets?]

$\langle a(0) a(t) \rangle \rightarrow$ measure memory, or time coherence of q .
(Can also state for space $\rightarrow$ range of order)

$$\langle a(0) a(t) \rangle = F(t)$$



decay time
 $\leftrightarrow$ correlation time

i.e. often implied

$$\langle a(0) a(t) \rangle = a_0^2 e^{-|t|/\tau_c}$$

but note correlation functions can be power laws (i.e. for self-similar systems (tail))

$$\langle a(0) a(t) \rangle \sim a_0^2 (t/\tau_c)^{-\alpha}, \quad \alpha > 0$$

invariant to rescaling a_0 , τ_c .

What do the brackets mean?

- It depends

→ ensemble avg,

$\tau \rightarrow$ variable distributed according to pdf $P(\tau)$

$$\langle a(\omega) a(\omega) [\tau] \rangle = \frac{\int d\tau P(\tau) \langle a(\omega) a(\omega) [\tau] \rangle}{\int d\tau P(\tau)}$$

Q^n , (as here)

→ time average

$$\int_0^T \frac{dt}{T} [a(t) a(t+\tau)] = \langle a(\omega) a(\omega) \rangle$$

obviously, $T > \tau_c$ needed.

- however non-stationary series/evolution

- time and ensemble averaging are [sometimes] equivalent $\Rightarrow$ Ergodic Theorem.

but not always

$x \rightarrow \text{flctn.}$

time reversible dynamics

So $\langle x_i(t) x_k(0) \rangle = \langle x_i(0) x_k(t) \rangle$ (a)

and

$\langle x_i(0) x_k(t) \rangle = \langle x_i(-t) x_k(0) \rangle$ (b)

Now, average (a)

$$\langle \overline{x_i(t)} x_k \rangle = \langle x_i \overline{x_k(t)} \rangle$$

$$\langle \dot{A}_i(t) x_k \rangle = \langle x_i \dot{A}_k(t) \rangle$$

$$\Rightarrow \langle \dot{A}_i(t) x_k \rangle = \langle x_i \dot{A}_k(t) \rangle$$

and recall $\dot{A}_i = -\gamma_{ij} B_j$

So

$$- \langle \gamma_{ij} B_j(t) x_k \rangle = - \langle x_i \gamma_{kj} B_j(t) \rangle$$

so evaluating at $t=0$,

$$\gamma_{i,e} \langle B_e(0) x_k \rangle = \gamma_{k,e} \langle x_i B_e \rangle$$

Now, at $t=0$,

$$B_i = \bar{x}_i$$

$$\begin{aligned} \gamma_{i,e} \langle \bar{x}_e x_k \rangle &= \gamma_{k,e} \langle x_i \bar{x}_e \rangle \\ &= \gamma_{k,e} \langle \bar{x}_e x_i \rangle \end{aligned}$$

but,

$$\langle \bar{x}_i x_k \rangle = \delta_{i,k}$$

[Gaussian
Dist
chp]

$\Rightarrow$

$$\gamma_{i,e} \delta_{e,k} = \gamma_{k,e} \delta_{e,i}$$

$$\boxed{\gamma_{i,k} = \gamma_{k,i}}$$

$\rightarrow$ Matrix of
Kinetic
(Transport)
Coeffs.
Symmetric

→ Onsager Principle / Onsager Symmetry

For time-reversible microdynamics
[Detailed Balance],

Matrix of kinetic coefficients is
symmetric

$$\gamma_{ik} = \gamma_{ki}$$

Note:

- based on linear response, quadratic form
for entropy, and time-reversibility.

- B field, Ω can introduce sign

$$\gamma_{ik}^{\Omega} = -\gamma_{ki}^{\Omega}$$

- N.B.: $\mathcal{P} = \frac{1}{2} \gamma_{ik} X_i X_k$

$\downarrow$
dissipation $\Leftrightarrow ds/dt$