Physics 210B

Lecture 4c: Transport/Onsager Matrix and Onsager Symmetry

Recall: For modest gradients of thermodynamic parameters $\nabla V T \text{ etc. calculate fluxes via 'Chapman - Enskog Exp}

\[ \mathbf{J} = - \kappa \cdot \mathbf{F} \quad \Omega \quad \left( \frac{\partial}{\partial t} \right) \]

"Onsager Matrix"

\[ \mathbf{\epsilon}_{ik} \left( \mathbf{A} \right) = - \left( \frac{\partial}{\partial x_i} \frac{\partial}{\partial x_k} \right) \left( \frac{\partial N}{\partial A} \right) \]

$D, \kappa$ diagonal

$\frac{\partial N}{\partial x_i}, \frac{\partial N}{\partial t}$ off diagonals

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

$\rightarrow$ Off diagonals can be $< 0$ though overall $dS/dt \geq 0$
\[ \frac{dS}{dt} = \mathbf{T} \cdot \mathbf{F}_{\text{th}} \cdot \mathbf{f} \cdot \mathbf{F}_{\text{th}} \]

We will show:

**Symmetry:**

**If** microscopic (dynamical) is time reversible (i.e., required for detailed balance), then the matrix is symmetric.

\[ k_{ij} = k_{ji} \]

why care?

- Reduced computational load of \( k \)
- Insight into off-diagonal processes (e.g., "Bootstrap Current" in MFE)
- Theoretical insight linked to linear response
A concrete example: Dissipation Function, Entropy Production, etc.

\[ du = Tds - \mu d\nu + \rho dV \]

- Internal energy
- Chemical potential
- Fixed volume (Not fixed)

\[ \Rightarrow ds = \frac{du}{T} - \mu \, d\nu \]

\[ U, P \rightarrow \text{thermo variables} \]
\[ \frac{1}{T}, -\frac{\mu}{T} \rightarrow \text{conjugate (entropic)} \]

- Intensive analogous to potential energies
- \( \frac{\partial}{\partial T}, \frac{\partial (\mu/\mathcal{T})}{\partial \mathcal{T}} \) are thermodynamic forces driving fluxes.
For the flow fluxes:

\[ \frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{J}_\rho = 0 \]

mass flux - (Diff)

\[ \frac{\partial \mathbf{u}}{\partial t} + \nabla \cdot \mathbf{J}_\mathbf{u} = 0 \]

internal energy flux (c.e. heat conductivity)

For entropy:

\[ \frac{\partial s}{\partial t} + \nabla \cdot \mathbf{J}_s = \frac{\partial s}{\partial t} \]

entropy flux (increase in entropy due to irreversible process of relaxation (c.e. CUF = local))

For fluxes:

\[ J_v = -K \frac{\partial C}{\partial T} \]

\[ = K T^2 \frac{\partial (1/T)}{\partial T} \]

\[ J_\rho = \mathbf{0} - \nabla P \]
\( n = n(c) \), \( \frac{dn}{dc} \geq 0 \)

so could just as easily write:

\[
\frac{\dot{Y}}{P} = O'P \left( -\frac{\mu}{T} \right)
\]

In general:

\[
\begin{align*}
\frac{\dot{Y}_n}{P} &= L_{2n} \frac{\partial}{\partial \left( \frac{1}{T} \right)} + L_{3n} \frac{\partial}{\partial \left( -\frac{\mu}{T} \right)} \\
\frac{\dot{Y}_P}{P} &= L_{2P} \frac{\partial}{\partial \left( \frac{1}{T} \right)} + L_{3P} \frac{\partial}{\partial \left( -\frac{\mu}{T} \right)}
\end{align*}
\]

\( \Phi \) have Omegaen matrix

\[
\frac{\dot{X}}{X} = \sum_{\alpha} L_{\alpha, \beta} \frac{\partial F_\beta}{\partial \phi} \quad \text{as proposed, expected}
\]

Thermodynamic Forces:

\[
\begin{align*}
\frac{\partial F_n}{\partial \phi} &= \frac{\partial}{\partial \left( \frac{1}{T} \right)} \\
\frac{\partial F_P}{\partial \phi} &= \frac{\partial}{\partial \left( -\frac{\mu}{T} \right)}
\end{align*}
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Thermodynamic Forces:

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\end{align*}
\]
To show:

\[ \frac{dS}{dt} = \frac{1}{T} \left( \frac{u}{T} \frac{d\mu}{dt} - \mu \frac{d\rho}{dt} \right) \]

and:

\[ \bar{J}_S = \frac{1}{T} \bar{J}_u - \mu \bar{J}_\rho \]

Now recall:

\[ \frac{dS}{dt} = \frac{\partial S}{\partial t} + \mathbf{u} \cdot \nabla S \]

\[ = \frac{1}{T} \left( \frac{d\mu}{dt} - \mu \frac{d\rho}{dt} \right) + \mathbf{u} \cdot \left( \frac{1}{T} \bar{J}_u \right) - \mathbf{u} \cdot \left( \frac{1}{T} \bar{J}_\rho \right) \]
\[
\frac{\partial \sigma_i}{\partial t} = \frac{4}{T} \frac{\partial \mu_i}{\partial t} - \frac{4}{T} \mu_i \frac{\partial \mu_i}{\partial \mu_i} + \frac{2}{T} \mu_i \frac{\partial \mu_i}{\partial \mu_i} - \frac{2}{T} \mu_i \frac{\partial \mu_i}{\partial \mu_i} + \sum \mu_i \frac{\partial}{\partial \mu_i} \left( \frac{1}{\mu_i} \right) - \sum \mu_i \frac{\partial}{\partial \mu_i} \left( \frac{1}{\mu_i} \right)
\]

\[
\frac{\partial \sigma_i}{\partial t} = \sum \mu_i \frac{\partial}{\partial \mu_i} \left( \frac{1}{\mu_i} \right)
\]

but \[ \sum \mu_i = \mu_1 \mu_2 \mu_3 \mu_4 \]

so finally:
\[
\frac{\partial \sigma_i}{\partial t} = \sum \sum \left( \mu_1 \mu_2 \mu_3 \mu_4 \right) \frac{\partial}{\partial \mu_i} \left( \frac{1}{\mu_i} \right)
\]

Local gradient \Rightarrow \text{local entropy production rate}!
\[ \frac{\partial^2 \phi}{\partial t^2} = D_1 \left( \frac{\partial \phi}{\partial x} \right)^2 + D_2 \left( \frac{\partial \phi}{\partial x} \right) + \phi_{\text{non-linear}} \left( \frac{\partial \phi}{\partial x} \cdot \frac{\partial \phi}{\partial x} \right) + \phi_{\text{linear}} \left( \frac{\partial \phi}{\partial x} \cdot \frac{\partial \phi}{\partial x} \right) \]

- If \( D_1, D_2 > 0 \)
- Gradients aligned:

\[ \frac{\partial^2 \phi}{\partial x^2} \geq \frac{(\phi_{\text{linear}} + \phi_{\text{non-linear}})^2}{4 + D_1} \]

- Positive semi-definite condition
- Can have \( \phi_{\text{linear}} \), etc. \( < 0 \)
- "Pitch" \( \rightarrow \) i.e. DT
driver up-gradient particle flux.

This brings us to Onsager symmetry. 1
Symmetry of $L_j, \beta$

- Consider $X_1, X_2, \ldots, X_n$

\[ \tilde{T} = T - T_{eq} \]
\[ \tilde{n} = n - n_{eq} \] etc

Then $S' = S(X_1, X_2, \ldots, X_n)$

To entropy

For small fluctuations (linear response)

\[ S = S_0 + \frac{\partial S}{\partial \tilde{T}} \cdot \tilde{T} + \frac{\partial^2 S}{\partial \tilde{X}_i \partial \tilde{X}_j} \tilde{X}_i \tilde{X}_j \]

\[ \kappa = -\left( \frac{\partial^2 S}{\partial \tilde{X}_i \partial \tilde{X}_j} \right) \frac{1}{2} \tilde{X}_i \tilde{X}_j = -\frac{\beta c_{ij} \tilde{X}_i \tilde{X}_j}{2} \]
\[ B_{ik} = -\frac{\partial^2 S}{\partial x_i \partial x_k} \]

⇒ probability,

\[ S = \exp[w] \]

\[ = c \exp\left[-\frac{B_{ik} x_i x_k}{2}\right] \]

System seeks maximize entropy ⇒ Fluctuations decay

\[ x_i = -\lambda x_i \]

⇒ Fluctuations relax

Now, consistent with \( \{ \text{linear response, flux-gradient relation, quadratic form, entropy} \} \)

define thermo-dynamically conjugate (in flux-gradient sense) variables:

\[ \mathcal{X}_i = -\frac{\partial S}{\partial x_i} = B_{ik} x_k \]
\[ X_i = B_i \chi_i \chi_i \]

thus

\[ x_i = -\gamma_{ik} x_k \Rightarrow \text{relate to } \overline{X} \]

\[ = -\gamma_{ik} \overline{X}_k \Rightarrow \text{has transport form.} \]

\[ \gamma_{ik} = \lambda_{ik} + B_{ik} \]

\[ \Rightarrow \text{kinetic constant} \]

\[ \Rightarrow \text{transport coefficient} \]

\[ \Rightarrow \text{relate relaxation of fluctuations in thermo variables to conjugate thermo forces} \]

\[ \text{e.g. } \ln S = -\frac{B_{ik} x_i x_k}{2} \]

\[ \Rightarrow \overline{S} = \frac{1}{2} \gamma_{ik} \overline{X}_i \overline{X}_k \]

\[ \frac{dS}{dt} = + \sum T \cdot K \cdot \Delta \]

Now show if micro-dynamics reversible, then \( \gamma_{ik} = \gamma_{ki} \Rightarrow \gamma \text{ matrix symmetric.} \]
To show:

Define $\bar{x} = \frac{1}{T_0} \int_0^T x$ \quad $\rightarrow$ time avg.

$A_i = A_i(t) = \frac{x_i}{\bar{x}}$

$B_i = B_i(t) = \frac{x_i}{\bar{x}}$

$\bar{x}_c(t) = -\gamma_{c\nu_0} \bar{x}_k$

$A_i(t) = -\gamma_{c\nu_0} B_i$

Assume: Consistent with detailed balance,

$\rightarrow$ time reversible microdynamics

Correlations invariant to order

$\therefore \langle x_c(t) x_k(0) \rangle = \langle x_c(0) x_k(t) \rangle$
Aside: What is a correlation function? 

\[ \langle a(0) a(t) \rangle \rightarrow \text{measure memory, or time coherence of } a. \] 
(Can also state for space range of order)

\[ \langle a(0) a(t) \rangle = F(t) \]

\[ F \]

\[ F \]

decay time 
\[ \tau_c \]

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 \( a_0 \) \( \tau_c \).
What do the brackets mean?

- It depends

- No ensemble avg.

\[ \langle a(x) a(x) [T] \rangle = \int dt \, P(T) \left\langle a(x) a(x) [T] \right\rangle \]

\[ \int dt \, P(T) \]

\[ = \langle a(x) a(x) \rangle \]

- Time average

\[ \frac{1}{T} \int_0^T \left[ a(x(t)) a(x(t+\tau)) \right] = \langle a(x) a(x) \rangle \]

Obviously, \( T > T_c \) needed.

- Heuristic non-stationary series/evolution

- Time and ensemble averaging are [sometimes] equivalent \( \Rightarrow \) Ergodic Theorem.
but not always......

time reversible dynamics

\[ (X_i(t), X_k(0)) = (X_i(0), X_k(t)) \]

and

\[ (X_i(0), X_k(t)) = (X_i(-t), X_k(0)) \]

Now average:

\[ \langle \overline{X_i(t)} X_k \rangle = \langle X_i \overline{X_k(t)} \rangle \]

\[ \langle \cdot A_i(t) X_k \rangle = \langle X_i A_k(t) \rangle \]

\[ \Rightarrow \quad \langle \dot{A}_i(t) X_k \rangle = \langle \overline{X_i} \cdot \dot{A}_k(t) \rangle \]

and recall \( \dot{A}_i = - \gamma_{ij} B_k \)

\[ = \langle \delta_{0i} B_k(t) X_k \rangle = - \langle X_i \cdot X_k B_k(t) \rangle \]
so evaluating at $t = 0$,

$$
\delta_{ij} \langle B_i (0) \chi_k \rangle = \delta_{ik} \langle \chi_i B_e \rangle
$$

Now at $t = 0$,

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

$$
\delta_{ij} \langle \bar{X}_i \chi_k \rangle = \delta_{ik} \langle \chi_i \bar{X}_e \rangle
$$

$$
= \delta_{ik} \langle \chi_i \chi_i \rangle
$$

but

$$
\langle \bar{X}_i \chi_k \rangle = \delta_{ik} \begin{bmatrix} \text{Equation} \\
\text{Diff.} \\
\text{Op} \end{bmatrix}
$$

$$
\Rightarrow \delta_{ij} \delta_{ek} = \delta_{ik} \delta_{ej}
$$

$$
\delta_{ij} \delta_{ek} = \delta_{ik} \delta_{ej}
$$

$$
\Rightarrow \begin{bmatrix} \text{Matrix of} \\
\text{Kinet.} \\
\text{(Transport) Coefs.} \\
\text{Symmtrd} \end{bmatrix}
$$
Onsager Principle / Onsager Symmetry

For time-reversible microdynamics (Detailed Balance),

Matrix of kinetic coefficients is symmetric:

\[ \kappa_{ij} = \kappa_{ji} \]

Note:

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

- \[ B \text{ field, } \Omega \text{ can introduce } \text{sign} \]
  \[ \tilde{\kappa}_{ij} = -\kappa_{ij} \]

- N.B.:
  \[ \Psi = \frac{1}{2} \kappa_{ij} \dot{X}_i \dot{X}_j \]
  Dissipation \( \propto \frac{d\Psi}{dt} \)