Notes 1: Section VI

1. Onsager Matrix and Onsager Symmetry.

Recall can calculate by Chapman-Enskog method (linear response) the vector of fluxes:

\[ \Pi = \begin{pmatrix} \Pi_1 \\ \Pi_2 \\ \vdots \\ \Pi_N \end{pmatrix} = \begin{pmatrix} \Pi \\ \nabla \end{pmatrix} \]

2. \( D \Phi_{eq} \) ultimately drives fluxes

\[ \Phi_{eq} = \Phi_{eq} \left( n(x), T(x), V(x) \right) \]

\( \Phi_{eq} \) determined by thermodynamic quantities

\[ D \Phi_{eq} \] determined by gradients of thermodynamic quantities, i.e.

\[ \delta n, \delta T, \delta V \]

\( \Rightarrow \) thermodynamic forces

i.e. drive relaxation
\[ \begin{align*}
\n\Gamma &= -k \cdot \dot{F} \\
\frac{\dot{F}}{\dot{F} \cdot \dot{E}} &= \text{vector of thermodynamic forces} \\
\text{matrix of transport coefficients} &\rightarrow \text{Onsager Matrix} \\
\text{N.B. - Of course, diagonal processes} \\
\text{i.e.} &\quad \frac{\partial}{\partial T} \text{ driver } \dot{F} \\

\left( \begin{array}{c}
\Gamma \\
\Theta
\end{array} \right) &= -
\left( \begin{array}{cc}
0 & \frac{\partial}{\partial \phi} \\
\frac{\partial}{\partial \phi} & \frac{\partial}{\partial \phi}
\end{array} \right)
\left( \begin{array}{c}
\Theta \\
\Theta
\end{array} \right) \\
\text{\( D \phi \rightarrow \text{diagonals}\)} \\
- \text{But } \frac{\partial}{\partial T} \text{ can drive } \Gamma \\
\text{\( \frac{\partial}{\partial \phi} \rightarrow \text{off-diagonals}\)} \\
\rightarrow \text{Entropy production: (H - Thm.)} \\
\frac{dS}{dt} &= + \frac{\dot{F}}{\dot{F} \cdot \dot{E}} \cdot k \cdot \dot{F} \\
\frac{d}{dt} &= \frac{\dot{F}}{\dot{F} \cdot \dot{E}} \cdot k \cdot \dot{F}
\end{align*} \]
If microscopic process is time reversible (i.e. detailed balance).

\[ K_{ij} = K_{ji} \quad \rightarrow \quad \text{Onsager Symmetry.} \]

\[ \nabla \cdot \mathbf{J} > 0 \rightarrow \text{transport down gradient} \]

\[ \text{Off-diagonal can be } < 0 \text{ though } H \text{-thm. demands } \frac{d}{dt} \geq 0. \]

\[ = 0 \text{ here } \Rightarrow \text{uniform} \quad \Rightarrow \quad \nabla \rho = 0. \]

An example: Fluid.

\[ du = Tds - pdV + \mu d\lambda \text{ (Therm.)} \]

\[ \frac{\partial}{\partial t} \text{ int. energy} \quad \frac{\partial}{\partial \mu} \text{ fixed chemical potential} \]

\[ du = Tds - pdV + \mu d\rho \]

Do
entropy change from first law

\[ \frac{ds}{T} = \frac{dy}{T} - \frac{y}{T} \text{ d}P \]

\[ \frac{1}{T} \quad \text{d}y \quad \rightarrow \text{ entropic conjugate variables} \]

\[ \frac{1}{T} \quad \rightarrow \text{ intensive } \rightarrow \text{ analogous to potential energy} \]

\[ - \frac{\partial (\frac{1}{T})}{\partial (u/T)} \rightarrow \]

thermodynamically

variables

"drive flows"

Flows - Continuity Eqns.

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

\[ \frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x} \left( \rho \mathbf{u} \right) = 0 \]

mass flux (i.e. divergence)

\[ \frac{\partial u}{\partial t} + \nabla \cdot (u \mathbf{u}) = 0 \]

internal energy flux (i.e. heat conduction)

hence assume macro velocity

negligible
For entropy, have form:

\[ \frac{dS}{dt} + \nabla \cdot \mathbf{J}_S = \frac{dS}{dt} \]

*Entropy* \( \rightarrow \) increase in entropy

*Flux* \( \rightarrow \) due irreversible process of relaxation

(i.e. CER) \( \rightarrow \) L0cy.

For the Fluxes:

\[ \mathbf{J}_h = -k \nabla T, \quad \text{i.e. } DT \]

(Cheat flux driven by DT)

Can just as easily write:

\[ \mathbf{J}_h = kT^2 \nabla \left( \frac{1}{T} \right) \]

and

\[ \mathbf{J}_p = -\nabla \mathbf{P} \]
but \( m = m(\phi) \), \( \partial m / \partial \phi > 0 \)

can just as easily write

\[ \bar{J}_B = D' \frac{\partial}{\partial (-u/T)} \]

In general:

\[
\bar{J}_B = \ln u \frac{\partial}{\partial \left( \frac{1}{T} \right)} + \ln \phi \frac{\partial}{\partial \left( \frac{-u}{T} \right)}
\]

\[
\bar{J}_D = \ln x \frac{\partial}{\partial \left( \frac{1}{T} \right)} + \ln \phi \frac{\partial}{\partial \left( \frac{-u}{T} \right)}
\]

\[
\bar{J}_x = \sum \ln \phi \frac{\partial}{\partial \phi}
\]

as proposed.

thermodynamic forces

\[
\frac{\partial \phi}{\partial \phi} = \frac{\partial}{\partial \left( \frac{1}{T} \right)}
\]

\[
\frac{\partial \phi}{\partial \phi} = \frac{\partial}{\partial \left( \frac{-u}{T} \right)}
\]

\[ L \phi \phi \equiv (\text{Larsen}) \text{ Onsager Matrix} \]
Entropy Production Rate

\[ \frac{dS}{dt} = \mathcal{J}_S (I + A) \]

To show:

\[ \frac{dS}{dt} = \frac{d}{dt} \left( \frac{dy}{I} \right) \frac{dy}{dt} = \frac{1}{I} \frac{dy}{dt} - \frac{y}{I} \frac{dI}{dt} \]

and:

\[ \mathcal{J}_S = \frac{a}{I} \mathcal{J}_y - b I \mathcal{J}_p \]

but: local entropy production

\[ \frac{dS}{dt} = \frac{dS}{dt} + D \cdot \mathcal{J}_S \]

\[ = \frac{1}{I} \left( \frac{dy}{dt} \right) - \frac{y}{I} \frac{dI}{dt} \]

\[ = \frac{D}{I} \left( \frac{\partial y}{\partial t} \right) - D \left( \frac{\partial y}{\partial \mathcal{J}_S} \right) \]
\[ \frac{dS_0}{d\tau} = \frac{4}{7} \frac{dV}{d\tau} - \frac{4}{7} \frac{dF}{d\tau} \]
\[ - \frac{1}{7} \frac{dI}{d\tau} + \frac{1}{7} \frac{dF}{d\tau} \]
\[ + \frac{1}{7} \frac{dJ_1 \cdot D}{d\tau} \left( \frac{1}{7} \right) - \frac{1}{7} \frac{dF}{d\tau} \left( \frac{1}{7} \right) \]
\[ \frac{dS_0}{d\tau} = \sum \sum \frac{dF}{d\tau} \]

but

\[ J_1 = \sum \sum \frac{dF}{d\tau} \]

\[ \frac{dS_0}{d\tau} = \sum \sum \frac{dF}{d\tau} \]

Now, entropy production must be positive.
for 2x2

\[
\frac{\partial x}{\partial t^2} = 0, \quad (\frac{\partial x}{\partial x})^2 + D_2 (\frac{\partial x}{\partial x})^2
\]

\[+ \epsilon_{ij} \frac{\partial}{\partial x} (\frac{\partial x_i \partial x_j}{\partial x}) + \delta_{ij} (\frac{\partial x_i \partial x_j}{\partial x}) \]

\[= 0, \quad \text{need } D_1, D_2 > 0. \]

- more generally, Laplace positive semi-definite matrix.

Now, \textbf{Symmetry}.

- will show \( L_{ij} \) = \( L_{ji} \) generally.

For time-reversible micro-dynamics.

- \( x_1, x_2, x_3 \ldots x_n \)

\( \sigma (x_1, x_2 \ldots x_n) \rightarrow \) entropy

then probability

\[ W = c \exp \left[ \sigma \right] \]
For small fluctuations about equilibrium:

\[ \delta = \delta_0 + \frac{\partial S}{\partial x} x + \frac{\partial^2 S}{\partial x_i \partial x_j} x_i x_j \]

\[ \delta t = -\left( \frac{\partial^2 S}{2 \partial x_i \partial x_j} \right) x_i x_j \]

\[ \delta x = C \exp \left[ -\frac{B_{ij} x_i x_j}{2} \right] \]

where \( B_{ij} \) is positive definite.

Now, assuming:

- small fluctuations
- small deviations from equilibrium

\[ \dot{x}_i = -B_{ij} x_j \]

\[ \delta \]

relaxation
And can define thermodynamically conjugate (i.e. flux - gradient) variables:

$$\mathbf{X}_i = -\frac{\partial S}{\partial X_i} = \mathbf{B}_{in} \mathbf{X}_n$$

$$\mathbf{X}_i = \mathbf{B}_{in} \mathbf{X}_n$$

thus

$$\mathbf{X}_c = -\mathbf{A}_{jn} \mathbf{X}_n$$

$$\mathbf{X}_c = -\mathbf{A}_{jn} \mathbf{X}_n$$

Symmetry: $\mathbf{A}_{ij} = \mathbf{A}_{ji}$

To show:

$$\mathbf{E}_c = \mathbf{E}_c (t) = \mathbf{X}_c$$

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$$\mathbf{E}_c = \mathbf{E}_c (t) = \mathbf{X}_c$$
\[ x_\nu(t) = -\sum_{\mu} x_{\mu} \]  
so that 
\[ \Sigma_c(t) = -\sum_{\mu} x_{\mu} \]  

Now, major assumption:
- Time reversible dynamics
- Detailed balance  

\[ \langle x_{\nu}(t) x_{\mu}(0) \rangle = \langle x_{\mu}(t) x_{\nu}(0) \rangle = \langle x_{\nu}(0) x_{\mu}(t) \rangle \]  

Aside: Correlation fctns.
\[ \langle a(0) a(t) \rangle \] measures memory or time coherence of \( \nu \).

\[ g_f \] vs. \[ g_c \]  
decay rate – correlation time
N.B. Correlation functions can be power laws (self-similar): 
\[ \langle \Delta \xi(t) \Delta \xi(t') \rangle \sim \Phi^2 (t / t_\xi)^{-\tau} \]

\( t > t_\xi \)

not necessarily exponential:
\[ \langle \Delta \xi(t) \Delta \xi(t') \rangle \sim \Phi^2 e^{-|t-t'|/t_\xi} \]

What do the brackets mean?

\( \xi \) ensemble avg.

\[ \langle \Delta \xi(t) \Delta \xi(t') \rangle = \frac{\int d\tau \ P(\tau) \ \langle \Delta \xi(t) \Delta \xi(t') \rangle}{\int d\tau \ P(\tau)} \]

\( P(\tau) \) specfunc pdf of \( \tau \).

\( \to \) time avg.

\[ \int_{-\infty}^{\infty} \frac{dt}{T} \ \langle \Delta \xi(t) \Delta \xi(t+\tau) \rangle = \langle \Delta \xi(t) \Delta \xi(t+\tau) \rangle \]

obviously \( T \gg T_c \) needed.
and symmetry of fluctuations under time reversal:

$$\langle x_i(t) x_j(t) \rangle = \langle x_i(t^-) x_j(t^0) \rangle = \langle x_i(-t^-) x_j(t^0) \rangle$$

Similarly, if:

$$\langle x_i(t^+) x_j(t^-) \rangle = \langle x_i(t^-) x_j(t^+) \rangle$$

then we have:

$$\langle \bar{x}_i(t^-) x_j(t^+) \rangle = \langle \bar{x}_j(t^-) x_i(t^+) \rangle$$

$$\langle \bar{x}_i(t^-) x_j(t^-) \rangle = \langle \bar{x}_i(t^-) \bar{x}_j(t^-) \rangle$$

$$\langle \bar{x}_i(t^+) x_j(t^-) \rangle = \langle \bar{x}_i(t^+) \bar{x}_j(t^-) \rangle$$

So:

$$\langle \bar{x}_i(t^+) x_j(t^-) \rangle = \langle \bar{x}_i(t^-) \bar{x}_j(t^+) \rangle$$

so evaluating at $t = 0$
\[ \delta_{ij} \langle x_i x_j \rangle = \gamma_{\mathbf{k}} \langle x_i x_j \rangle \]

\[ \delta_{ij} \langle x_i x_j \rangle = \gamma_{\mathbf{k}} \langle x_i x_j \rangle = \gamma_{\mathbf{k}} \langle x_i x_j \rangle \]

but \[ \langle x_i x_j \rangle = \delta_{ij} \quad (\text{Gaussian dist.}) \]

\[ \gamma_{\mathbf{k}} = \gamma_{\mathbf{k}} \delta_{ij} \]

\[ \Rightarrow \gamma_{\mathbf{k}} = \gamma_{\mathbf{k}} \]

\[ \Rightarrow \delta_{ij} \]

Matrix of kinetic coefficients symmetric

\[ \Rightarrow \text{Onsager Symmetry} \checkmark \]

see L. Onsager paper,

"Reciprocal Relations in Irreversible Processes"