Notes 1 : Section VI

→ Onsager Matrix and Onsager Symmetry.

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

$$\underline{\Gamma} = \begin{pmatrix} \Gamma_1 \\ \Gamma_2 \\ \vdots \\ \Gamma_N \end{pmatrix} = \begin{pmatrix} \Gamma \\ Q \\ \vdots \\ \vdots \end{pmatrix}$$

- $\nabla f_{eq}^{(0)}$ ultimately drives fluxes

$$f_{eq}^{(0)} = f_{eq}^{(0)}(n(x), T(x), \underline{V}(x) \ldots)$$

→ determined by thermodynamic quantities

so

$\nabla f_{eq}^{(0)}$ → determined by gradients of thermodynamic quantities, i.e.
∇n, ∇T, $\underline{\nabla V}$, ...

⇒ thermodynamic forces
i.e. drive relaxation

$\Gamma \to$ vector of thermodynamic forces

so $\underline{\Gamma} = -\underline{\underline{K}} \cdot \underline{f}_{Th}$

$\Downarrow$

matrix of transport coefficients $\to$ "Onsager Matrix"

N.B. – Of course, diagonal processes

i.e. ∇T drives Q

$$\begin{pmatrix} \Gamma \\ Q \end{pmatrix} = - \begin{pmatrix} D & d_{n,T} \\ d_{T,n} & \chi \end{pmatrix} \begin{pmatrix} \nabla n \\ \nabla T \end{pmatrix}$$

$D, \chi \to$ diagonals.

– But ∇T can drive Γ

$d_{n,T}, d_{T,n} \to$ "off-diagonals".

$\to$ Entropy production: (H-Thm.).

$$\frac{ds}{dt} = + \underline{f}_{Th}^{T} \cdot \underline{\underline{K}} \cdot \underline{f}_{Th}$$

→ If microscopic process is time reversible (i.e. detailed balance).

$K_{i,j} = K_{j,i}$ ⇒ Onsager Symmetry.

→ Diagonals > 0 ⇒ transport down gradient

Off-diagonals can be < 0, though H-thm. demands $\frac{dS}{dt} \geq 0$.

$= 0$ here ⇒ uniform
⇒ $\nabla f_{eq} = 0$.

An example : Fluid

$dU = TdS - pdV + \mu dN$ (Thermo).

U ↑ int. energy; μ ↑ chemical potential

$$du = Tds - \cancel{pdV} + \mu d\rho$$

fixed

$\nabla \Theta$

entropy change, from first law

$$ds = \frac{du}{T} - \frac{\mu}{T}\,d\rho$$

$1/T$, $-\frac{\mu}{T}$ → entropic conjugate of variables u, ρ.

→ intensive → analogous to potential energies

$-\nabla(1/T)$, $\nabla(\mu/T)$ → thermodynamic variables – drive flows.

Flows – Continuity Eqns.:

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

mass flux (i.e. diffn)

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

internal energy flux (i.e. heat conduction)

(here assume macro velocity negligible)

For entropy, have form:

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

entropy flux

↳ increase in entropy due irreversible process of relaxation (i.e. $C(f)$) – local.

For the fluxes:

$$\underline{J}_H = -\kappa \nabla T \quad , \quad \text{if } \nabla T$$

(heat flux driven by ∇T)

can just as easily write:

$$\underline{J}_H = \kappa T^2 \nabla (1/T)$$

and

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

but $\mu = \mu(\rho)$, $\delta\mu/\delta\rho > 0$

can just as easily write

$$\underline{J}_\rho = D' \,\underline{\nabla}(-\mu/T)$$

In general:

(both driven)

$$\boxed{\begin{aligned} \underline{J}_u &= L_{u,u}\,\underline{\nabla}(1/T) + L_{u,\rho}\,\underline{\nabla}\left(\frac{-\mu}{T}\right) \\ \underline{J}_\rho &= L_{\rho,u}\,\underline{\nabla}(1/T) + L_{\rho,\rho}\,\underline{\nabla}\left(\frac{-\mu}{T}\right) \end{aligned}}$$

so

$$\boxed{\underline{J}_\alpha = \sum_\beta L_{\alpha,\beta}\,\nabla f_\beta}$$ as proposed.

thermodynamic forces $\underline{\nabla} f_u = \underline{\nabla}(1/T)$

$\underline{\nabla} f_\rho = \underline{\nabla}\left(\frac{-\mu}{T}\right)$

$L_{\alpha,\beta} \equiv (L_{\alpha\beta})$ Onsager Matrix

→ Entropy Production Rate

expect: $$\frac{dS_u}{dt} = \underline{J} \cdot (\underline{\nabla} f)$$

To show:

$$\frac{\partial s}{\partial t} = \frac{\partial}{\partial t}\left(\frac{dy}{T} - \frac{\mu}{T} d\rho\right)$$

$$= \frac{1}{T}\frac{\partial y}{\partial t} - \frac{\mu}{T}\frac{\partial \rho}{\partial t}$$

and:

$$\underline{J_s} = \frac{1}{T}\underline{J_y} - \frac{\mu}{T}\underline{J_\rho}$$

but: → local entropy production

$$\frac{\partial S_0}{\partial t} = \frac{\partial s}{\partial t} + \underline{\nabla} \cdot \underline{J_s}$$

$$= \frac{1}{T}\frac{\partial y}{\partial t} - \frac{\mu}{T}\frac{\partial \rho}{\partial t}$$

$$\underline{\nabla} \cdot \left(\frac{\underline{J_y}}{T}\right) - \underline{\nabla} \cdot \left(\frac{\mu}{T}\underline{J_\rho}\right)$$

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$$\frac{\partial S_0}{\partial t} = \frac{1}{T}\frac{\partial u}{\partial t} - \frac{\mu}{T}\frac{\partial \phi}{\partial t}$$

$$+ \frac{1}{T}\nabla\cdot\underline{J}_u - \frac{\mu}{T}\nabla\cdot\underline{J}_\phi$$

$$+ \underline{J}_u\cdot\nabla\left(\frac{1}{T}\right) - \underline{J}_\phi\cdot\nabla\left(\frac{\mu}{T}\right)$$

$$\boxed{\frac{\partial S_0}{\partial t} = \sum_\alpha \underline{J}_\alpha \cdot \underline{\nabla} f_\alpha}$$

but

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

$$\boxed{\frac{\partial S_0}{\partial t} = \sum_\alpha\sum_\beta \underline{\nabla} f_\alpha \cdot \underline{\underline{L}}_{\alpha,\beta} \cdot \underline{\nabla} f_\beta}$$

Now, entropy production must be positive:

for 2x2

$$\frac{\partial S_i}{\partial t} = D_1 \left(\frac{\partial f_1}{\partial x}\right)^2 + D_2 \left(\frac{\partial f_2}{\partial x}\right)^2$$

$$+ d_{1,2}\left(\frac{\partial f_1}{\partial x} \cdot \frac{\partial f_2}{\partial x}\right) + d_{2,1}\left(\frac{\partial f_1}{\partial x} \cdot \frac{\partial f_2}{\partial x}\right)$$

$\geq 0.$

– need $D_1, D_2 > 0.$

→ more generally, $L_{\alpha,\beta}$ positive semi-definite matrix.

Now; Symmetry;

→ will show $L_{\alpha,\beta} = L_{\beta,\alpha}$ generally, for time-reversible micro-dynamics.

– $x_1, x_2, x_3 \text{ ---- } x_n$

↳ fluctuations from eq'brm in thermodynamic quantities

$S(x_1, x_2, \ldots x_n) \rightarrow$ entropy

then probability

$$W = c \exp[S].$$

For small fluctuations about equilibrium:

$$S = \cancel{S_0}_{\text{ref}} + \cancel{\nabla S \cdot \underline{x}}^{\,0} + \frac{\partial^2 S}{\partial \underline{x}_i \partial x_k} x_i x_k$$

$$\cong - \left(- \frac{\partial^2 S}{2 \partial x_i \partial x_k} \right) x_i x_k$$

$$= - \frac{\beta_{i,k}}{2} x_i x_k$$

so

$$w = C \exp\left[- \frac{\beta_{i,k}}{2} x_i x_k \right]$$

$\beta_{i,k}$ positive definite

Now, assuming:

- <u>small</u> fluctuations
- small deviations from equilibrium

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

to

relaxation

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

$$X_i = -\frac{\partial S}{\partial x_i} = \beta_{ik} x_k$$

so

$$\overline{X}_i = \beta_{ik} x_k$$

thus,

$$\dot{x}_i = -\lambda_{ik} x_k$$
$$= -\gamma_{ik} X_k$$
$$\boxed{\lambda_{il}\,\beta^{-1}_{lk} = \gamma_{ik}}$$

kinetic coeff

symmetry: $\boxed{\gamma_{ik} = \gamma_{ki}}$

To show:

$$\xi_i = \xi_i(t) = \overline{x_i}$$
$$\Xi_i = \Xi_i(t) = \overline{X_i}$$

time avgs $\frac{1}{T}\int_0^T$

then

$$x_i'(t) = -\gamma_{ijk} \overline{X}_{ik}$$

so avg.

$$\boxed{\overline{x}_i'(t) = -\gamma_{ijk} \overline{\overline{X}}_k}$$

Now: major assumption:

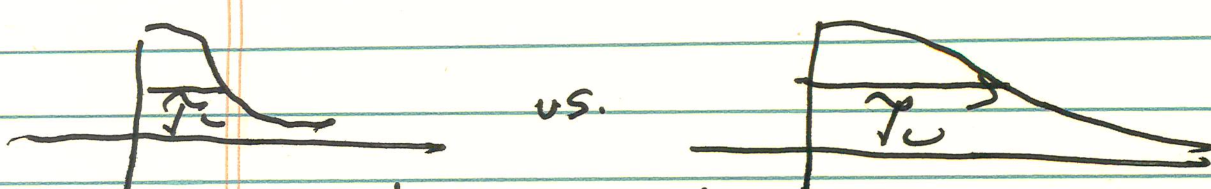
time reversible dynamics
Detailed balance

⇒ no time correlation fctns.

$$\Rightarrow \boxed{\begin{aligned} \langle x_i(t)\, x_k(0) \rangle &= \langle x_i(-t)\, x_k(0) \rangle \\ &= \langle x_i(0)\, x_k(t) \rangle \end{aligned}}$$

Aside: Correlation fctns.

$\langle a(0)\, a(t) \rangle$ measures memory or time coherence of a.



decay rate - correlation time

N.B. Correlation functions can be power laws (self-similar)

i.e. $\langle a(0)\, a(t) \rangle \sim a_0^2 \left(t/\tau_0\right)^{-\alpha}$

$\alpha > 0$

not necessarily exponential

$$\langle a(0)\, a(t) \rangle \sim a_0^2\, e^{-|t|/\tau_0}$$

What do the brackets mean?

→ ensemble avg.

$$\langle a(0)\, a(t)[\Gamma] \rangle = \frac{\int d\Gamma\, P(\Gamma)\, \left(a(0)\, a(t)[\Gamma]\right)}{\int d\Gamma\, P(\Gamma)}$$

$P(\Gamma)$ specifies pdf of Γ.

or

→ time avg.

$$\int_0^T \frac{dt}{T} \left[a(t)\, a(t+\tau) \right] = \langle a(0)\, a(\tau) \rangle$$

obviously $T \gg \tau_c$ needed.

and symmetry of fluctuations under time reversal ⇒

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

Similarly, if:

$$\langle x_i(t)\, x_k \rangle = \langle x_i\, x_k(t) \rangle$$

then avg:

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

⇒

$$\langle \varepsilon_i(t)\, x_k \rangle = \langle x_i\, \varepsilon_k(t) \rangle$$

so

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

$$-\langle \gamma_{i\ell}\, \Xi_\ell(t)\, x_k \rangle = -\langle x_i\, \gamma_{k\ell}\, \Xi_\ell(t) \rangle$$

so evaluating at $t=0$

$$\gamma_{i\ell} \langle \Xi_\ell^{(0)} x_k \rangle = \gamma_{k\ell} \langle x_i \Xi_\ell \rangle$$

$$\gamma_{i\ell} \langle X_\ell x_k \rangle = \gamma_{k\ell} \langle x_i X_\ell \rangle$$

$$= \gamma_{k\ell} \langle X_\ell x_i \rangle$$

but $\langle X_i x_k \rangle = \delta_{i,k}$ (Gaussian dist).

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

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

→ Matrix of kinetic coefficients symmetric

→ Onsager Symmetry ✓

see L. Onsager paper.

"Reciprocal Relations in Irreversible Processes"