

## 10.D.I. Onsager's Relations

Onsager's relations are relations between transport coefficients in a coupled transport. They are consequences of the restraints placed on the macroscopic fluctuations by the time-reversal invariance of the microscopic Hamiltonian dynamics.

### 10.D.I.I. Microscopic Reversibility

The fluctuations of state variables  $\mathbf{A} = \{A_1, \dots, A_n\}$  at time  $t$  are defined as

$$\begin{aligned}\boldsymbol{\alpha}(t) &\equiv \mathbf{A}(t) - \mathbf{A}^0 \\ &= \{A_1(t) - A_1^0, \dots, A_n(t) - A_n^0\} \\ &= \{\alpha_1(t), \dots, \alpha_n(t)\}\end{aligned}\tag{10.75a}$$

or

$$\alpha_j(t) = A_j(t) - A_j^0$$

where the superscript  $^0$  denotes an equilibrium value.

Consider now the correlation

$$\begin{aligned}\langle \alpha_j(t) \alpha_k(t') \rangle &\equiv \int d\alpha_j \int d\alpha_k' P_2(\alpha_j, t; \alpha_k', t') \alpha_j \alpha_k' \\ &= \int d\alpha_j \int d\alpha_k' f(\alpha_j, t) P(\alpha_j, t | \alpha_k', t') \alpha_j \alpha_k' \end{aligned}\tag{10.75b}$$

$$= \int d\alpha_j \int d\alpha_k' f(\alpha_k', t') P(\alpha_k', t' | \alpha_j, t) \alpha_j \alpha_k' \tag{10.75c}$$

where  $P_2$ ,  $f$  &  $P$  denote the joint probability, probability & conditional probability densities, respectively [see §4.D.4 & §5.B].

Using (5.12) & (5.6), we have

$$\begin{aligned}\int d\alpha_j \int d\alpha_k' f(\alpha_j, t) P(\alpha_j, t | \alpha_k', t') &= \int d\alpha_k' f(\alpha_k', t') = 1 \\ \int d\alpha_j \int d\alpha_k' f(\alpha_k', t') P(\alpha_k', t' | \alpha_j, t) &= \int d\alpha_j f(\alpha_j, t) = 1\end{aligned}$$

so that (10.75b,c) can be written as

$$\langle \alpha_j(t) \alpha_k(t') \rangle = \int d^n \alpha \int d^n \alpha' f(\boldsymbol{\alpha}, t) P(\boldsymbol{\alpha}, t | \boldsymbol{\alpha}', t') \alpha_j \alpha_k' \tag{10.75d}$$

$$= \int d^n \alpha \int d^n \alpha' f(\boldsymbol{\alpha}', t') P(\boldsymbol{\alpha}', t' | \boldsymbol{\alpha}, t) \alpha_j \alpha_k' \tag{10.75e}$$

Since we are dealing with fluctuations from equilibrium, the system itself is in equilibrium. As discussed in §5.B for stationary processes,

$$f(\boldsymbol{\alpha}, t) = f(\boldsymbol{\alpha}) \quad \forall t \quad [\text{See (5.9).}]$$

$$P_2(\boldsymbol{\alpha}, t; \boldsymbol{\alpha}', t') = P_2(\boldsymbol{\alpha}, t + \tau; \boldsymbol{\alpha}', t + \tau) \quad \forall \tau \quad [\text{See (5.8).}]$$

$$\rightarrow P(\boldsymbol{\alpha}, t | \boldsymbol{\alpha}', t') = P(\boldsymbol{\alpha} | \boldsymbol{\alpha}', t' - t) = P(\boldsymbol{\alpha}, t - t' | \boldsymbol{\alpha}')$$

The correlation matrix of fluctuations is therefore defined as

$$\langle \boldsymbol{\alpha}(t) \boldsymbol{\alpha}^T(t') \rangle \equiv \int d^n \alpha \int d^n \alpha' f(\boldsymbol{\alpha}) P(\boldsymbol{\alpha}, t | \boldsymbol{\alpha}', t') \boldsymbol{\alpha} \boldsymbol{\alpha}'^T \quad [(\text{10.75d}) \text{ used.}] \tag{10.76a}$$

$$\begin{aligned}
&= \int d^n \alpha \int d^n \alpha' f(\alpha) P(\alpha | \alpha', t' - t) \alpha \alpha'^T = \langle \alpha \alpha^T(t' - t) \rangle \\
&= \int d^n \alpha \int d^n \alpha' f(\alpha') P(\alpha', t' | \alpha, t) \alpha \alpha'^T \quad [(10.75e) \text{ used.}] \\
&= \int d^n \alpha \int d^n \alpha' f(\alpha') P(\alpha' | \alpha, t - t') \alpha \alpha'^T = \langle \alpha(t - t') \alpha^T \rangle
\end{aligned}$$

Setting  $\tau = t' - t$ , we have

$$\langle \alpha \alpha^T(\tau) \rangle \equiv \int d^n \alpha \int d^n \alpha' f(\alpha) P(\alpha | \alpha', \tau) \alpha \alpha'^T \quad (10.76)$$

$$= \langle \alpha(-\tau) \alpha^T \rangle \quad (10.76b)$$

or

$$\langle \alpha_j \alpha_k(\tau) \rangle = \langle \alpha_j(-\tau) \alpha_k \rangle \quad (10.76c)$$

The probability density of a closed system in equilibrium was derived in §7.C.1 as [see (7.24)]

$$f(\alpha) = \sqrt{\frac{\det \mathbf{g}}{(2\pi k_B)^n}} \exp\left(-\frac{1}{2k_B} \alpha^T \mathbf{g} \alpha\right) \quad (10.77)$$

where  $\mathbf{g}$  is the positive symmetric matrix with elements

$$g_{jk} = -\left(\frac{\partial^2 S}{\partial A_j \partial A_k}\right)_{A=A^0} = g_{kj} \quad (10.77a)$$

so that

$$\Delta S = -\frac{1}{2} \alpha^T \mathbf{g} \alpha \quad (10.78)$$

is the decrease of the entropy  $S$  from its maximal value at equilibrium, as induced by  $\alpha$ . Since  $g_{jk}$  is the 2nd derivative of  $S$ , it is related to the response functions (or general susceptibilities).

In an isolated system,  $dU = 0$  and the 1st law becomes [see § 2.D.2]

$$\bar{d}Q = \bar{d}W$$

$$\rightarrow T dS = -\mathbf{F} \cdot d\mathbf{A} \quad (\text{reversible processes})$$

where  $\mathbf{F}$  is the **generalized force** coupled to extensive variable  $\mathbf{A}$ .

In terms of

$$\mathbf{F} = -T \frac{\partial S}{\partial \mathbf{A}} = -T \frac{\partial \Delta S}{\partial \alpha} = \frac{1}{2} T [\mathbf{g} \alpha + (\alpha^T \mathbf{g})^T] = T \mathbf{g} \alpha \quad (10.79)$$

and the **generalized current**

$$\mathcal{J} = \frac{d\mathbf{A}}{dt} = \frac{d\alpha}{dt} \quad (10.80)$$

we can write the time-derivative of (10.78) as

$$T \frac{d\Delta S}{dt} = -\frac{1}{2} T [\mathcal{J}^T \mathbf{g} \alpha + (\alpha^T \mathbf{g} \mathcal{J})^T] = -\frac{1}{2} [\mathcal{J}^T \mathbf{F} + (\mathbf{F}^T \mathcal{J})^T] = -\mathcal{J} \cdot \mathbf{F} \quad (10.81)$$

From the microscopic point of view, the correlation matrix of an equilibrium system is defined as an ensemble average

$$\langle \alpha_j(t) \alpha_k(t') \rangle \equiv \iint d\mathbf{q}^N d\mathbf{p}^N \rho(\mathbf{q}^N, \mathbf{p}^N) \alpha_j[\mathbf{q}^N(t), \mathbf{p}^N(t)] \alpha_k[\mathbf{q}^N(t'), \mathbf{p}^N(t')] \quad (10.82a)$$

where  $\rho(\mathbf{q}^N, \mathbf{p}^N)$  is the equilibrium probability density of the ensemble and  $\{\mathbf{q}^N(t), \mathbf{p}^N(t)\}$  is the solution

to the Hamilton's equations

$$\dot{\mathbf{q}}^N = \frac{\partial H}{\partial \mathbf{p}^N} \quad \dot{\mathbf{p}}^N = -\frac{\partial H}{\partial \mathbf{q}^N} \quad (10.82b)$$

with initial conditions

$$\mathbf{q}^N(0) = \mathbf{q}^N \quad \mathbf{p}^N(0) = \mathbf{p}^N$$

In the micro-canonical ensemble, (10.82a) becomes

$$\langle \alpha_j(t) \alpha_k(t') \rangle = \frac{1}{\Omega_{\Delta E}(E)} \int \int_{(E, E+\Delta E)} d\mathbf{q}^N d\mathbf{p}^N \alpha_j[\mathbf{q}^N(t), \mathbf{p}^N(t)] \alpha_k[\mathbf{q}^N(t'), \mathbf{p}^N(t')] \quad (10.82c)$$

where  $E$  is the (constant) total energy of the system.

Similarly,  $\alpha_j(\mathbf{q}^N, \mathbf{p}^N)$  divides the phase space into a foliage of  $(6N - 1)$ -D surfaces of constant values of  $\alpha_j$ . Hence,

$$\begin{aligned} \alpha_j[\mathbf{q}^N(t), \mathbf{p}^N(t)] &= \int \int d\mathbf{q}'^N d\mathbf{p}'^N \alpha_j(\mathbf{q}'^N, \mathbf{p}'^N) \delta[\mathbf{q}'^N - \mathbf{q}^N(t)] \delta[\mathbf{p}'^N - \mathbf{p}^N(t)] \\ &= \int_{-\infty}^{\infty} d\alpha_j \alpha_j \int \int_{(\alpha_j, \alpha_j+\Delta\alpha_j)} d\mathbf{q}'^N d\mathbf{p}'^N \delta[\mathbf{q}'^N - \mathbf{q}^N(t)] \delta[\mathbf{p}'^N - \mathbf{p}^N(t)] \\ \alpha_k[\mathbf{q}^N(t'), \mathbf{p}^N(t')] &= \int \int d\mathbf{q}''^N d\mathbf{p}''^N \alpha_k(\mathbf{q}''^N, \mathbf{p}''^N) \delta[\mathbf{q}''^N - \mathbf{q}^N(t')] \delta[\mathbf{p}''^N - \mathbf{p}^N(t')] \\ &= \int_{-\infty}^{\infty} d\alpha_k' \alpha_k' \int \int_{(\alpha_k', \alpha_k'+\Delta\alpha_k')} d\mathbf{q}''^N d\mathbf{p}''^N \delta[\mathbf{q}''^N - \mathbf{q}^N(t')] \delta[\mathbf{p}''^N - \mathbf{p}^N(t')] \end{aligned}$$

(10.82c) then becomes

$$\begin{aligned} \langle \alpha_j(t) \alpha_k(t') \rangle &= \frac{1}{\Omega_{\Delta E}(E)} \int \int_{(E, E+\Delta E)} d\mathbf{q}^N d\mathbf{p}^N \\ &\quad \times \int_{-\infty}^{\infty} d\alpha_j \alpha_j \int \int_{(\alpha_j, \alpha_j+\Delta\alpha_j)} d\mathbf{q}'^N d\mathbf{p}'^N \delta[\mathbf{q}'^N - \mathbf{q}^N(t)] \delta[\mathbf{p}'^N - \mathbf{p}^N(t)] \\ &\quad \times \int_{-\infty}^{\infty} d\alpha_k' \alpha_k' \int \int_{(\alpha_k', \alpha_k'+\Delta\alpha_k')} d\mathbf{q}''^N d\mathbf{p}''^N \delta[\mathbf{q}''^N - \mathbf{q}^N(t')] \delta[\mathbf{p}''^N - \mathbf{p}^N(t')] \end{aligned}$$

Comparing with (10.75b), we have

$$\begin{aligned} f(\alpha_j) P(\alpha_j, t | \alpha_k', t') &= \frac{1}{\Omega_{\Delta E}(E)} \int \int_{(E, E+\Delta E)} d\mathbf{q}^N d\mathbf{p}^N \\ &\quad \times \int \int_{(\alpha_j, \alpha_j+\Delta\alpha_j)} d\mathbf{q}'^N d\mathbf{p}'^N \delta[\mathbf{q}'^N - \mathbf{q}^N(t)] \delta[\mathbf{p}'^N - \mathbf{p}^N(t)] \\ &\quad \times \int \int_{(\alpha_k', \alpha_k'+\Delta\alpha_k')} d\mathbf{q}''^N d\mathbf{p}''^N \delta[\mathbf{q}''^N - \mathbf{q}^N(t')] \delta[\mathbf{p}''^N - \mathbf{p}^N(t')] \end{aligned}$$

Now, the origin of time in Hamiltonian dynamics has no physical significance except for specifying the initial conditions. Since the integral  $\int \int_{(E, E+\Delta E)} d\mathbf{q}^N d\mathbf{p}^N$  includes all possible initial conditions, we can

shift the origin of time arbitrarily without affecting the results. Setting  $t = 0$  then

$$\begin{aligned}
 & \int\int_{(E, E+\Delta E)} d\mathbf{q}^N d\mathbf{p}^N \int\int_{(\alpha_j, \alpha_j+\Delta\alpha_j)} d\mathbf{q}'^N d\mathbf{p}'^N \delta[\mathbf{q}'^N - \mathbf{q}^N(t)] \delta[\mathbf{p}'^N - \mathbf{p}^N(t)] \\
 = & \int\int_{(E, E+\Delta E)} d\mathbf{q}^N d\mathbf{p}^N \int\int_{(\alpha_j, \alpha_j+\Delta\alpha_j)} d\mathbf{q}'^N d\mathbf{p}'^N \delta(\mathbf{q}'^N - \mathbf{q}^N) \delta(\mathbf{p}'^N - \mathbf{p}^N) \\
 = & \int\int_{(\alpha_j, \alpha_j+\Delta\alpha_j)} d\mathbf{q}'^N d\mathbf{p}'^N \\
 & (E, E+\Delta E)
 \end{aligned}$$

Writing

$$\mathbf{q}^N(t') = \mathbf{q}'^N + \Delta\mathbf{q}^N(t')$$

$$\mathbf{p}^N(t') = \mathbf{p}'^N + \Delta\mathbf{p}^N(t')$$

where  $\Delta\mathbf{q}^N(t')$  is the change of  $\mathbf{q}^N$  from  $\mathbf{q}^N(0) = \mathbf{q}'^N$  after time  $t'$ , and similarly for  $\Delta\mathbf{p}^N(t')$ , we have

$$\begin{aligned}
 f(\alpha_j) P(\alpha_j | \alpha_k', t') = & \int\int_{(\alpha_j, \alpha_j+\Delta\alpha_j)} d\mathbf{q}'^N d\mathbf{p}'^N \int\int_{(\alpha_k', \alpha_k'+\Delta\alpha_k')} d\mathbf{q}''^N d\mathbf{p}''^N \\
 & (E, E+\Delta E) \quad (E, E+\Delta E) \\
 & \times \frac{1}{\Omega_{\Delta E}(E)} \delta[\mathbf{q}''^N - \mathbf{q}'^N - \Delta\mathbf{q}^N(t')] \delta[\mathbf{p}''^N - \mathbf{p}'^N - \Delta\mathbf{p}^N(t')]
 \end{aligned} \tag{10.82d}$$

where we've used the fact that a trajectory  $\{\mathbf{q}^N(t), \mathbf{p}^N(t)\}$  starting on the surface  $E$  must remain on it forever.

In matrix form,

$$\begin{aligned}
 f(\alpha) P(\alpha | \alpha', t') = & \int\int_{(\alpha, \alpha+\Delta\alpha)} d\mathbf{p}'^N d\mathbf{q}'^N \int\int_{(\alpha', \alpha'+\Delta\alpha')} d\mathbf{p}''^N d\mathbf{q}''^N \\
 & (E, E+\Delta E) \quad (E, E+\Delta E) \\
 & \times \frac{1}{\Omega_{\Delta E}(E)} P(\mathbf{q}'^N, \mathbf{p}'^N | \mathbf{q}''^N, \mathbf{p}''^N, t')
 \end{aligned} \tag{10.82}$$

where

$$\begin{aligned}
 & P(\mathbf{q}'^N, \mathbf{p}'^N | \mathbf{q}''^N, \mathbf{p}''^N, t') \\
 = & \delta[\mathbf{q}''^N - \mathbf{q}'^N - \Delta\mathbf{q}^N(t')] \delta[\mathbf{p}''^N - \mathbf{p}'^N - \Delta\mathbf{p}^N(t')]
 \end{aligned} \tag{10.83}$$

Let

$$\begin{aligned}
 \Gamma(\alpha) = & \int\int_{(\alpha, \alpha+\Delta\alpha)} d\mathbf{p}'^N d\mathbf{q}'^N & \Gamma(\alpha') = & \int\int_{(\alpha', \alpha'+\Delta\alpha')} d\mathbf{p}''^N d\mathbf{q}''^N
 \end{aligned} \tag{10.83a}$$

be the surfaces in phase space that satisfy the conditions indicated. Then (10.82) gives

$$f(\alpha) P(\alpha | \alpha', t') = \frac{1}{\Omega_{\Delta E}(E)} \Gamma(\alpha) \cap \Gamma(\alpha', t') \tag{10.83b}$$

where  $\Gamma(\alpha', t')$  is the evolution of  $\Gamma(\alpha')$  for time  $t'$ .

Now, all Lagrangian & Hamiltonian dynamics are invariant under the **time reversal** transformation [see "TimeReversalSymmetry.pdf"]

$$\mathcal{T} t = \tilde{t} = -t \quad \mathcal{T}^{-1} = \mathcal{T}$$

which means if  $\{\mathbf{q}^N(t), \mathbf{p}^N(t)\}$  is a solution with initial conditions

$\{\mathbf{q}^N(t_0), \mathbf{p}^N(t_0)\} = \{\mathbf{q}_0^N, \mathbf{p}_0^N\}$   
 so is  $\{\tilde{\mathbf{q}}^N(t), \tilde{\mathbf{p}}^N(t)\} = \{\mathbf{q}^N(-t), -\mathbf{p}^N(-t)\}$  with initial conditions  
 $\{\tilde{\mathbf{q}}^N(-t_0), \tilde{\mathbf{p}}^N(-t_0)\} = \{\mathbf{q}_0^N, -\mathbf{p}_0^N\}$

In other words, for every system trajectory going from  $(\mathbf{q}^N, \mathbf{p}^N)$  to  $(\mathbf{q}'^N, \mathbf{p}'^N)$  using time  $t$ , there is a time-reversed trajectory that goes from  $(\mathbf{q}'^N, -\mathbf{p}'^N)$  to  $(\mathbf{q}^N, -\mathbf{p}^N)$  using the same amount of time  $t$ . If we film the motion  $\mathbf{q}^N(t)$ , then the time-reversed trajectory corresponds to playing the film backwards.

As stated before, in the Hamiltonian dynamics, the origin of time has no physical significance except for specifying the initial conditions. In an ensemble average, all possible initial conditions are present. Therefore, all averaged quantities can depend only on time intervals, or relative times.

Therefore, for a system described by a Hamiltonian (and hence time-reversal invariant),

$$\begin{aligned}
 P(\mathbf{q}'^N, \mathbf{p}'^N, t \mid \mathbf{q}''^N, \mathbf{p}''^N, t') &= P(\mathbf{q}'^N, \mathbf{p}'^N \mid \mathbf{q}''^N, \mathbf{p}''^N, t' - t) \\
 &= P(\mathbf{q}''^N, -\mathbf{p}''^N, t \mid \mathbf{q}'^N, -\mathbf{p}'^N, t') \\
 &= P(\mathbf{q}''^N, -\mathbf{p}''^N \mid \mathbf{q}'^N, -\mathbf{p}'^N, t' - t) \quad (10.84)
 \end{aligned}$$

(10.82) then gives

$$\begin{aligned}
 f(\alpha) P(\alpha, t \mid \alpha', t') &= \iint_{\substack{(E, E+\Delta E) \\ (\alpha, \alpha+\Delta\alpha)}} d\mathbf{p}'^N d\mathbf{q}'^N \iint_{\substack{(E, E+\Delta E) \\ (\alpha', \alpha'+\Delta\alpha')}} d\mathbf{p}''^N d\mathbf{q}''^N \quad (10.84a) \\
 &\quad \times \frac{1}{\Omega_{\Delta E}(E)} P(\mathbf{q}''^N, -\mathbf{p}''^N, t \mid \mathbf{q}'^N, -\mathbf{p}'^N, t')
 \end{aligned}$$

By the same token, the probability density for a Hamiltonian system must be an even function of  $\mathbf{p}^N$ ,

$$\begin{aligned}
 \rho(\mathbf{q}^N, \mathbf{p}^N) &= \rho(\mathbf{q}^N, -\mathbf{p}^N) \quad (10.84b) \\
 &= \frac{1}{\Omega_{\Delta E}(E)} \quad \text{for microcanonical ensembles}
 \end{aligned}$$

Consider then

$$F(t) = \int \int d\mathbf{p}^N d\mathbf{q}^N \rho(\mathbf{q}^N, \mathbf{p}^N) F(\mathbf{q}^N, \mathbf{p}^N, t)$$

which defines the macroscopic quantity  $F(t)$  in terms of the microscopic  $F(\mathbf{q}^N, \mathbf{p}^N, t)$ . (10.84b) means that the part of  $F(\mathbf{q}^N, \mathbf{p}^N, t)$  that is odd in  $\mathbf{p}^N$  cancels out in the integration so that we can define  $F(t)$  with an  $F(\mathbf{q}^N, \mathbf{p}^N, t)$  that is even in  $\mathbf{p}^N$ .

For example, the phase space volume  $\Gamma(\alpha)$  defined in (10.83b) are even in  $\mathbf{p}^N$ . Hence, (10.84a) gives

$$\begin{aligned}
 f(\alpha) P(\alpha, t \mid \alpha', t') &= \frac{1}{\Omega_{\Delta E}(E)} \Gamma(\alpha', t) \cap \Gamma(\alpha, t') \\
 &= f(\alpha') P(\alpha', t \mid \alpha, t') \quad (10.85) \\
 &= f(\alpha') P(\alpha', t' \mid \alpha, t) \quad [\text{see (10.76-a)}]
 \end{aligned}$$

(10.75c) then gives

$$\begin{aligned}
 \langle \alpha_j(t) \alpha_k(t') \rangle &= \int d^n \alpha \int d^n \alpha' f(\alpha) P(\alpha, t \mid \alpha', t') \alpha_j \alpha_k' \\
 &= \int d^n \alpha \int d^n \alpha' f(\alpha') P(\alpha', t \mid \alpha, t') \alpha_j \alpha_k' \\
 &= \langle \alpha_k(t) \alpha_j(t') \rangle
 \end{aligned}$$

or

$$\begin{aligned} \langle \alpha_j \alpha_k(\tau) \rangle &= \langle \alpha_k \alpha_j(\tau) \rangle = \langle \alpha_j(\tau) \alpha_k \rangle \\ \langle \boldsymbol{\alpha} \boldsymbol{\alpha}^T(\tau) \rangle &= \langle \boldsymbol{\alpha}(\tau) \boldsymbol{\alpha}^T \rangle \quad [ \text{Consequence of time-reversal invariant.} ] \end{aligned} \quad (10.75)$$

which should be compared with (10.76b)

$$\langle \boldsymbol{\alpha} \boldsymbol{\alpha}^T(\tau) \rangle = \langle \boldsymbol{\alpha}(-\tau) \boldsymbol{\alpha}^T \rangle \quad [ \text{Consequence of equilibrium averaging.} ]$$

### 10.D.1.2. Regression of Fluctuations

As usual, we define

$$\frac{d \boldsymbol{\alpha}(t)}{d t} = \lim_{\tau \rightarrow 0} \frac{\boldsymbol{\alpha}(t + \tau) - \boldsymbol{\alpha}(t)}{\tau} \quad (10.89)$$

where  $\tau \rightarrow 0$  is taken to mean  $\tau$  is microscopically long (as compared to the **collision time**  $T_0$  between molecular collisions) but macroscopically short (as compared to the **relaxation time**  $T$  required for fluctuations to decay to equilibrium), i.e.,

$$T_0 \ll \tau \ll T \quad (10.90)$$

which defines the **hydrodynamic limit** so that all “points” in the system are at local thermodynamic equilibrium at all “instants” of time.

Assuming the usual exponential decay, we have

$$\frac{d \boldsymbol{\alpha}(t)}{d t} = -\mathbf{M} \cdot \boldsymbol{\alpha}(t) \quad (10.87)$$

with solution

$$\boldsymbol{\alpha}(t) = e^{-\mathbf{M}t} \cdot \boldsymbol{\alpha} \quad \boldsymbol{\alpha}(0) = \boldsymbol{\alpha} \quad (10.88)$$

For short times, (10.88) gives

$$\boldsymbol{\alpha}(t) = \boldsymbol{\alpha} - t \mathbf{M} \cdot \boldsymbol{\alpha} + O(t^2) \quad (10.89)$$

Thus, keeping only 1st order terms, (10.75) becomes

$$\begin{aligned} &\langle (\boldsymbol{\alpha} - t \mathbf{M} \cdot \boldsymbol{\alpha}) (\boldsymbol{\alpha} - t' \mathbf{M} \cdot \boldsymbol{\alpha})^T \rangle \approx \langle (\boldsymbol{\alpha} - t' \mathbf{M} \cdot \boldsymbol{\alpha}) (\boldsymbol{\alpha} - t \mathbf{M} \cdot \boldsymbol{\alpha})^T \rangle \\ \rightarrow &-t \langle (\mathbf{M} \cdot \boldsymbol{\alpha}) \boldsymbol{\alpha}^T \rangle - t' \langle \boldsymbol{\alpha} (\mathbf{M} \cdot \boldsymbol{\alpha})^T \rangle \approx -t \langle \boldsymbol{\alpha} (\mathbf{M} \cdot \boldsymbol{\alpha})^T \rangle - t' \langle (\mathbf{M} \cdot \boldsymbol{\alpha}) \boldsymbol{\alpha}^T \rangle \\ \therefore &\langle (\mathbf{M} \cdot \boldsymbol{\alpha}) \boldsymbol{\alpha}^T \rangle = \langle \boldsymbol{\alpha} (\mathbf{M} \cdot \boldsymbol{\alpha})^T \rangle \\ &\mathbf{M} \cdot \langle \boldsymbol{\alpha} \boldsymbol{\alpha}^T \rangle = \langle \boldsymbol{\alpha} \boldsymbol{\alpha}^T \rangle \cdot \mathbf{M}^T \end{aligned} \quad (10.92)$$

Using [see (7.27)],

$$\langle \boldsymbol{\alpha} \boldsymbol{\alpha}^T \rangle = k_B \mathbf{g}^{-1}$$

we get

$$\mathbf{M} \cdot \mathbf{g}^{-1} = \mathbf{g}^{-1} \cdot \mathbf{M}^T \quad (10.93)$$

Since  $\mathbf{g}^T = \mathbf{g}$ , setting the **transport coefficient matrix** as

$$\mathbb{L} \equiv \mathbf{M} \cdot \mathbf{g}^{-1} \quad (10.94)$$

turns (10.93) into

$$\mathbb{L} = \mathbb{L}^T \quad \text{or} \quad L_{ij} = L_{ji} \quad (10.95)$$

which is known as the **Onsager's relations**.

(10.87) thus becomes

$$\frac{d \boldsymbol{\alpha}(t)}{d t} = -\mathbb{L} \cdot \mathbf{g} \cdot \boldsymbol{\alpha}(t)$$

$$\begin{aligned} &= -\frac{1}{T} \mathbb{L} \cdot \mathbf{F}(t) && [ (10.79) \text{ used. } ] && (10.96) \\ &= \mathcal{J}(t) && [ (10.80) \text{ used. } ] \end{aligned}$$

Owing to its resemblance to the Ohm's law

$$\mathbf{J} = \boldsymbol{\kappa} \cdot \mathbf{E}$$

where  $\mathbf{J}$  is the current density,  $\boldsymbol{\kappa}$  the conductivity tensor &  $\mathbf{E}$  the electric field, (10.96) is called the **generalized Ohm's law**.