
Onsager's Reciprocal Relations

We have talked in class about the continuum description of the laws of thermodynamics. As a complementary discussion, we present here the notion of Onsager's Reciprocal Relations, a fundamental concept in close-to-equilibrium statistical mechanics. Though this is not directly related to continuum theory (i.e. they do not involve spatial degrees of freedom), they are crucial in understanding macroscopic response of thermodynamic systems, and we feel that no introductory course in non-equilibrium thermodynamics can be complete without it. These relations are derived within a linear response theory, i.e. close to thermal equilibrium. This is the simplest non-equilibrium case and later in the course we'll go nonlinear, which will be a whole lot of fun.

1 Transport coefficients (out of eq. properties)

Say there is a set of thermodynamic variables $\{A_i\}$ that describe our system. For simplicity we'll assume that $\langle A_i \rangle = 0$, otherwise we can always define $\alpha_i = A_i - \langle A_i \rangle$. We define the conjugate fluxes and forces to be

$$J_i \equiv \frac{dA_i}{dt} \; , \qquad\qquad X_i \equiv \frac{\partial S}{\partial A_i} \; , \tag{1}$$

where S is the system's entropy (but could equally as well be any thermodynamic potential). Note that by J_i we mean a steady change in A_i, not thermal fluctuations. These changes are maintained by fixing the forces X_i. Using (1), we can write the entropy production rate Σ as

$$\Sigma = \frac{dS}{dt} = \sum_i J_i X_i \tag{2}$$

The basic assumption of close-to-equilibrium thermodynamics is that the fluxes are linear functions of the forces. This is known by the name *linear response.* Explicitly, we write

$$J_i = \sum_j L_{ij} X_j \; . \tag{3}$$

The matrix L_{ij} is called the transport matrix, or the conductivity matrix. The meaning of "linear response" is that the coefficients L_{ij} *do not depend on* X_i. They may depend on state variables such as the temperature, but not on the forces.

Plugging (3) into (2) gives

$$\Sigma = \sum_{i,j} L_{ij} X_i X_j \; . \tag{4}$$

The 2^{nd} law of thermodynamics tells us that Σ is non-negative. We therefore see immediately that L_{ij} is a positive-definite matrix. This constraints the transport coefficient in a strong way. For example, for any pair of indices i, j we must have

$$L_{ii}, \; L_{jj} < 0 \tag{5}$$

$$\det \begin{pmatrix} L_{ii} & L_{ij} \\ L_{ji} & L_{jj} \end{pmatrix} = L_{ii}L_{jj} - L_{ij}L_{ji} < 0 \; . \tag{6}$$

But Onsager tells us even more, with further reasoning that goes beyond the 2^{nd} law.

2 Equilibrium properties

For Onsager's relation to hold, we need to assume microscopic time-reversibility. Thus, the equilibrium correlations must satisfy

$$C_{ij}(\tau) = \langle A_i(t)A_j(t+\tau)\rangle = \langle A_i(t)A_j(t-\tau)\rangle = C_{ij}(-\tau)\ . \tag{7}$$

Also, in equilibrium we have stationarity so we can shift the time by τ and get

$$\langle A_i(t)A_j(t+\tau)\rangle = \langle A_i(t+\tau)A_j(t)\rangle\ . \tag{8}$$

Close to equilibrium, we can approximate that

$$S = S_{eq} + \Delta S(A_1,\ldots,A_n) \approx S_{eq} - \frac{1}{2}\sum_{i,j} g_{ij}A_iA_j\ , \qquad g_{ij} \equiv -\frac{\partial^2 S}{\partial A_i \partial A_j}\ . \tag{9}$$

The linear term vanishes because in equilibrium S is maximal, and the minus sign makes g_{ij} positive definite. g_{ij} is also clearly symmetric. In particular, we see that

$$X_i = \frac{\partial S}{\partial A_i} = \frac{\partial \Delta S}{\partial A_i} \approx -\sum_j g_{ij}A_j \tag{10}$$

From the definition of the entropy, the probability measure for fluctuations is

$$f(A_1,\ldots,A_n) = e^{S(A_1,\ldots,A_n)/k_B} \approx \frac{e^{\Delta S(A_1,\ldots,A_n)/k_B}}{\text{normalization}} \tag{11}$$

The matrix g_{ij} quantifies the fluctuations in the system - one can immediately calculate the instantaneous correlation $\langle A_iA_j\rangle$ by simple Gaussian integration with the measure f. However, it does not tell us anything about dynamics.

Eq. (11) tells us that

$$\log(f) = -\frac{1}{2k_B} g_{ij}A_iA_j + const \tag{12}$$

$$k_B\frac{\partial \log f}{\partial A_i} = -g_{ij}A_j = X_i \tag{13}$$

We therefore get the orthogonality criterion:

$$\begin{aligned}\langle A_iX_j\rangle &= \int A_iX_jf(A_1,\ldots,A_n)dA_1\ldots dA_n\\ &= k_B\int A_i\frac{\partial \log f}{\partial A_j} f dA_1\ldots dA_n = k_B\int A_i\frac{\partial f}{\partial A_j}dA_1\ldots dA_n\\ &= k_B\int\left(\frac{\partial}{\partial A_j}(A_if) - f\frac{\partial A_i}{\partial A_j}\right)dA_1\ldots dA_n = -k_B\delta_{ij}\ .\end{aligned} \tag{14}$$

The first term vanishes as it is a boundary term, and the second term is δ_{ij} because f is normalized and $\{A_i\}$ are independent.

3 The regression hypothesis and symmetry of L_{ij}

Eq. (3) describes the dynamics of equilibrium fluctuations of $\{A_i\}$. Onsager assumed that when we take the system out of equilibrium by applying external forces, the dynamics will still be governed by Eq. (3), although the Hamiltonian has changed. That is, Onsager assumed that the relaxation ("regression") towards equilibrium follows the same dynamics as equilibrium fluctuations do. This is called "the regression hypothesis". We therefore have

$$J_i(t) = \sum_j L_{ij} X_j(t) \tag{15}$$

With this at hand, we can differentiate Eq. (8) with respect to τ. The LHS gives

$$\frac{\partial}{\partial \tau} \langle A_i(t) A_j(t+\tau) \rangle |_{\tau=0} = \langle A_i(t) J_j(t) \rangle = \sum_k \langle A_i(t) L_{jk} X_k(t) \rangle = -k_B \sum_k L_{jk} \delta_{ik} = L_{ji} \tag{16}$$

Where we used Eq. (14) to obtain the δ. Similarly, the RHS gives

$$\frac{\partial}{\partial \tau} \langle A_i(t+\tau) A_j(t) \rangle |_{\tau=0} = \langle J_i(t) A_j(t) \rangle = \sum_k \langle L_{ik} X_k(t) A_j(t) \rangle = -k_B \sum_k L_{ik} \delta_{kj} = L_{ij} \tag{17}$$

Equating (16) and (17) gives the famous Onsager Reciprocal Relations:

$$L_{ij} = L_{ji} \tag{18}$$

3.1 Remarks

3.1.1 Assumptions

Note that we needed:

- Time reversibility.
- Regression hypothesis.
- Independece of A_i, and conjugacy of A_i to J_i through ΔS.
- Linearity.

4 Relaxation to equilibrium

Why do systems relax toward equilibrium? One can see this by using Onsager Relations, as we will now show. Since g_{ij} is symmetric positive definite, we can choose to work with rotated and scaled variables A'_i for which $g_{ij} = \delta_{ij}$. Thus, the relation (10) takes the simple form $X_i = -A_i$. The evolution of A_i is then

$$\partial_t A_i = J_i = \sum_j L_{ij} X_j = -\sum_j L_{ij} A_j \ , \tag{19}$$

or, in compact form,

$$\partial_t \vec{A} = -\boldsymbol{L}\vec{A} \tag{20}$$

Since L_{ij} is positive definite (by the 2^{nd} law) we see that all the eigenvalues of L_{ij} have positive real parts, and therefore the system cannot explode, but we are not guaranteed that we'll have decay towards equilibrium ($\vec{A} = 0$). Onsager tells us that since L_{ij} is symmetric, it is diagonalizable with real eigenvalues, and therefore must decay towards equilibrium without oscillations. For example, suppose we had

$$\boldsymbol{L} = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \tag{21}$$

This $\boldsymbol{L}$ does not violate the 2^{nd} law, but what will the dynamics look like? Let's say we start with the initial condition $A_1 = 1,\ A_2 = 0$. The solution of the ODE (20) is

$$\begin{pmatrix} A_1(t) \\ A_2(t) \end{pmatrix} = \exp\left[\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} t\right] \begin{pmatrix} A_1(t=0) \\ A_2(t=0) \end{pmatrix} = \begin{pmatrix} \cos t & -\sin t \\ \sin t & \cos t \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} \cos t \\ \sin t \end{pmatrix} \tag{22}$$

The solutions are oscillatory and do not decay towards equilibrium. This is because the eigenvalues of $\boldsymbol{L}$ are ±i, which could not have been the case if $\boldsymbol{L}$ were symmetric.