

Tutorial Lecture

The variational principle formulated by Onsager (1931)

Reciprocal relations for irreversible processes: Heat transport

The heat flux \mathbf{J} induced by temperature gradient ∇T is given by the constitutive equations

$$J_i = -\sum_{j=1}^3 \lambda_{ij} \nabla_j T \quad (i=1,2,3).$$

The λ_{ij} are coefficients of heat conductivity. The heat conductivity tensor is *symmetric* even in crystals of low symmetry (Stokes 1851).

Onsager's reciprocal relations derived from microscopic reversibility

For a *closed* system, consider the fluctuations of a set of (macroscopic) variables α_i ($i=1,\dots,n$) with respect to their most probable (equilibrium) values. The entropy of the system S has a maximum S_e at equilibrium so that $\Delta S = S - S_e$ can be written in the quadratic form

$$\Delta S(\alpha_1, \dots, \alpha_n) = -\frac{1}{2} \sum_{i,j=1}^n \beta_{ij} \alpha_i \alpha_j,$$

where β is symmetric and positive definite. The probability density at α_i ($i=1,\dots,n$) is given by

$$f(\alpha_1, \dots, \alpha_n) = f(0, \dots, 0) e^{\Delta S/k_B}$$

where k_B is the Boltzmann constant. The forces conjugate to α_i ($i=1,\dots,n$) are defined by

$$X_i = \frac{\partial \Delta S}{\partial \alpha_i} = -\sum_{j=1}^n \beta_{ij} \alpha_j$$

which are linear combinations of α_i ($i=1,\dots,n$) not far from equilibrium.

Following the above definition of the forces, the equilibrium average (over the distribution function $f(\alpha_1, \dots, \alpha_n)$) of $\alpha_i X_j$ is given by

$$\langle \alpha_i X_j \rangle = -k_B \delta_{ij}.$$

Microscopic reversibility leads to the equality

$$\langle \alpha_i(t) \alpha_j(t+\tau) \rangle = \langle \alpha_j(t) \alpha_i(t+\tau) \rangle$$

for time correlation functions. In a certain domain not far from equilibrium, the macroscopic variables α_i ($i=1,\dots,n$) satisfy the linear equations

$$\frac{d}{dt} \alpha_i(t) = -\sum_{k=1}^n M_{ik} \alpha_k(t) = \sum_{j=1}^n L_{ij} X_j(t).$$

Here the Onsager coefficient matrix L is related to the (rate) coefficient matrix M via the relation $L = M \beta^{-1}$.

Onsager's hypothesis is that fluctuations evolve in the mean according to the same macroscopic laws. Therefore, in evaluating the correlation function $\langle \alpha_i(t) \alpha_j(t + \tau) \rangle$ for a short time interval τ (a hydrodynamic time scale which is macroscopically short but microscopically long), $\alpha_j(t + \tau)$ is given by

$$\alpha_j(t + \tau) = \alpha_j(t) + \tau \frac{d}{dt} \alpha_j(t) = \alpha_j(t) + \tau \sum_{k=1}^n L_{jk} X_k(t).$$

It is worth pointing out that τ is macroscopically short for the linear expansion but microscopically long for the applicability of the macroscopic laws. It follows that $\langle \alpha_i(t) \alpha_j(t + \tau) \rangle$ is given by

$$\langle \alpha_i(t) \alpha_j(t + \tau) \rangle = \langle \alpha_i(t) \alpha_j(t) \rangle + \tau \sum_{k=1}^n L_{jk} \langle \alpha_i(t) X_k(t) \rangle = \langle \alpha_i(t) \alpha_j(t) \rangle - \tau k_B L_{ji}.$$

Similarly, $\langle \alpha_j(t) \alpha_i(t + \tau) \rangle$ is given by

$$\langle \alpha_j(t) \alpha_i(t + \tau) \rangle = \langle \alpha_j(t) \alpha_i(t) \rangle - \tau k_B L_{ij}.$$

Comparing the above two time correlation functions, we obtain the reciprocal relations

$$L_{ji} = L_{ij}$$

from microscopic reversibility. Note that $\langle \alpha_i(t) \alpha_j(t) \rangle = \langle \alpha_j(t) \alpha_i(t) \rangle$ by definition.

Onsager's variational principle governing irreversible processes

Consider the heat transport in a crystal. The “forces” and “rates” (“velocities”) are related by the constitutive equations

$$-\frac{1}{T} \nabla_i T = X_i = \sum_{j=1}^3 R_{ij} J_j,$$

where X_i ($i=1,2,3$) are the forces and the components of the heat flux J_j ($j=1,2,3$) are the rates. Here the matrix R is the inverse of the Onsager coefficient matrix L , which is also symmetric. The dissipation function $\phi(\mathbf{J}, \mathbf{J})$ is introduced in the form of

$$\phi(\mathbf{J}, \mathbf{J}) \equiv \frac{1}{2T} \sum_{i,j=1}^3 R_{ij} J_i J_j.$$

It is worth emphasizing that ϕ can be defined in this quadratic form because of the symmetry in the matrices R and L . It is observed that substituting the constitutive equations into the quadratic expression for ϕ yields

$$2\phi(\mathbf{J}, \mathbf{J}) \equiv \frac{1}{T} \sum_{i,j=1}^3 R_{ij} J_i J_j = \frac{1}{T} \sum_{i=1}^3 J_i X_i = \sum_{i=1}^3 J_i \nabla_i \left(\frac{1}{T} \right),$$

which equals the rate of entropy production per unit volume due to heat transport.

Let s denote the local entropy density in the system. Then, under the assumption of local equilibrium, the rate of change of s is given by

$$\frac{ds}{dt} = \frac{1}{T}(-\nabla \cdot \mathbf{J}),$$

where $-\nabla \cdot \mathbf{J}$ is the rate of local accumulation of heat. The rate of change of the total entropy S is the volume integral

$$\dot{S} = \int \frac{ds}{dt} dV = \int \left(-\frac{1}{T} \nabla \cdot \mathbf{J} \right) dV.$$

The rate of the entropy given off to the surrounding environment is given by the surface integral

$$\dot{S}^* = \int \left(\frac{J_n}{T} \right) dA,$$

where J_n is the *outward* normal component of the heat flux at the boundary. It follows that

$$\dot{S} + \dot{S}^* = \int \left(-\frac{1}{T} \nabla \cdot \mathbf{J} \right) dV + \int \left(\frac{J_n}{T} \right) dA = \int \left(-\frac{1}{T} \nabla \cdot \mathbf{J} \right) dV + \int \nabla \cdot \left(\frac{\mathbf{J}}{T} \right) dV = \int \mathbf{J} \cdot \nabla \left(\frac{1}{T} \right) dV.$$

It can be shown that the constitutive equations for heat transport can be derived from the variational principle

$$\Phi(\mathbf{J}, \mathbf{J}) - [\dot{S}(\mathbf{J}) + \dot{S}^*(J_n)] = \text{minimum},$$

where the temperature distribution is prescribed, and the rates, i.e., the heat flux \mathbf{J} , are varied. Here $\Phi(\mathbf{J}, \mathbf{J})$ is defined by

$$\Phi(\mathbf{J}, \mathbf{J}) \equiv \int \phi(\mathbf{J}, \mathbf{J}) dV \equiv \int \left(\frac{1}{2T} \sum_{i,j=1}^3 R_{ij} J_i J_j \right) dV,$$

$\dot{S}(\mathbf{J})$ is defined by

$$\dot{S}(\mathbf{J}) \equiv \int \left(-\frac{1}{T} \nabla \cdot \mathbf{J} \right) dV,$$

and $\dot{S}^*(J_n)$ is defined by

$$\dot{S}^*(J_n) \equiv \int \left(\frac{J_n}{T} \right) dA,$$

with

$$\dot{S}(\mathbf{J}) + \dot{S}^*(J_n) \equiv \int \mathbf{J} \cdot \nabla \left(\frac{1}{T} \right) dV.$$

The variation of $\Phi(\mathbf{J}, \mathbf{J}) - [\dot{S}(\mathbf{J}) + \dot{S}^*(J_n)]$ is given by

$$\delta \left\{ \Phi(\mathbf{J}, \mathbf{J}) - [\dot{S}(\mathbf{J}) + \dot{S}^*(J_n)] \right\} = \int \sum_k \left[\frac{\partial}{\partial J_k} \phi(\mathbf{J}, \mathbf{J}) - \nabla_k \left(\frac{1}{T} \right) \right] \delta J_k dV,$$

from which we have

$$\frac{\partial}{\partial J_k} \phi(\mathbf{J}, \mathbf{J}) = \nabla_k \left(\frac{1}{T} \right)$$

according to the variational principle. We note that these are exactly the constitutive equations

$$\frac{1}{T} \sum_j R_{kj} J_j = \nabla_k \left(\frac{1}{T} \right) = \frac{X_k}{T}.$$

As shown already, inserting the constitutive equations into the quadratic expression for ϕ yields the equality

$$2\phi(\mathbf{J}, \mathbf{J}) = \sum_k J_k \frac{\partial}{\partial J_k} \phi(\mathbf{J}, \mathbf{J}) = \sum_k J_k \nabla_k \left(\frac{1}{T} \right),$$

and hence the integral form

$$2\Phi(\mathbf{J}, \mathbf{J}) = \dot{S}(\mathbf{J}) + \dot{S}^*(J_n).$$

Note that $\dot{S}(\mathbf{J}) + \dot{S}^*(J_n)$ is the rate of change of the entropy in the system *and* the surrounding environment. Therefore, the rate of entropy production $2\Phi(\mathbf{J}, \mathbf{J})$ is equal to the rate of change of the entropy $\dot{S}(\mathbf{J}) + \dot{S}^*(J_n)$ in an irreversible process governed by the constitutive equations.

If the system is isothermal and in thermal equilibrium with the environment, then

$$\dot{S}^*(J_n) \equiv \int \left(\frac{J_n}{T} \right) dA = -\frac{1}{T} \dot{Q} = -\frac{1}{T} \dot{U},$$

where $\dot{Q} = -\int J_n dA$ is the rate of heat transfer from the environment into the system, \dot{U} is the rate of change of the energy of the system, and $\dot{Q} = \dot{U}$ according to the first law of thermodynamics. Note that the temperature distribution is uniform here. It follows that the variational principle becomes

$$\Phi(\mathbf{J}, \mathbf{J}) - [\dot{S}(\mathbf{J}) + \dot{S}^*(J_n)] = \Phi(\mathbf{J}, \mathbf{J}) + \frac{1}{T} [\dot{U}(\mathbf{J}) - T\dot{S}(\mathbf{J})] = \text{minimum},$$

where $\dot{U}(\mathbf{J}) = -T\dot{S}^*(J_n)$ has been used for the rate of change of the energy. As $\dot{U}(\mathbf{J}) - T\dot{S}(\mathbf{J})$ is the rate of change of the Helmholtz free energy $F \equiv U - TS$, the variational principle becomes

$$\Phi(\mathbf{J}, \mathbf{J}) + \frac{1}{T} \dot{F}(\mathbf{J}) = \text{minimum},$$

where $\dot{F}(\mathbf{J})$ is the rate of change of the Helmholtz free energy. Note that $\Phi(\mathbf{J}, \mathbf{J})$ is positive definite and quadratic in the rates while $\dot{F}(\mathbf{J})$ is linear in the rates. Minimizing $\Phi(\mathbf{J}, \mathbf{J}) + \dot{F}(\mathbf{J})/T$ with respect to the rates yields the equality

$$2T\Phi(\mathbf{J}, \mathbf{J}) = -\dot{F}(\mathbf{J}),$$

which shows that $2T\Phi(\mathbf{J}, \mathbf{J})$ is the rate of free energy dissipation in an irreversible process governed by the variational principle.