Last Time

Mathematical Background: Types of Fields

Fluxes and Accumulation

Conserved and Non-conserved Quantities

Fundamental Postulate: Entropy Production Density is Non-Negative

Assumption of Local Equilibrium

Form of the Entropy Production Density

Conjugate Forces, Fluxes and Empirical Flux Laws for Unconstrained Components				
Quantity	Flux	Conjugate Force	Empirical Flux Law	
Heat	$\vec{J}_Q$	$-\frac{1}{T}\nabla T$	Fourier's	$\vec{J}_Q = -\kappa\nabla T$
Mass	$\vec{J}_i$	$-\nabla\mu_i$	*Modified*[6] Fick's form	$\vec{J}_{c_i} = -M_i c_i \nabla\mu_i$
Charge	$\vec{J}_q$	$-\nabla\phi$	Ohm's	$\vec{J}_q = -\rho\nabla\phi$

3.21 Spring 2002: Lecture 3

Entropy Production for Simple Cases

If heat is the only quantity that is flowing:

$$T\dot{\sigma} = \frac{k|\nabla T|^2}{T} \tag{3-1}$$

If diffusion is the only operating process:

$$T\dot{\sigma} = M_i c_i |\nabla\mu_i|^2 \tag{3-2}$$

In general, the entropy production is the sum of all operating fluxes dotted into (minus) the gradient of the associated potential.[7]

[7] If this is to be generalized to non-conserved quantities, then another term is included to account for the local production of that non-conserved quantity,

$$T\dot{\sigma} = -\frac{\vec{J}_Q}{T}\cdot\nabla T - \vec{J}_i\cdot\nabla F_i - \mathcal{P}(A) \tag{3-3}$$

where $\mathcal{P}(A)$ is a positive definite operator, e.g.,

$$T\dot{\sigma} = -\frac{\vec{J}_Q}{T}\cdot\nabla T - \vec{J}_i\cdot\nabla F_i - \alpha A\dot{A} \tag{3-4}$$

$$T\dot{\sigma} = -\frac{\vec{J}_Q}{T}\cdot\nabla T - \vec{J}_i\cdot\nabla F_i - \frac{\alpha}{2}\dot{A}^2 \tag{3-5}$$

Generalized Coupling for the Near-Equilibrium Case

Let $\vec{\Gamma_i} \equiv -\nabla F_i$ represent the generalized driving forces for a system near equilibrium. A system near equilibrium is one where the driving forces are all small, therefore we can expand the fluxes in terms of these small driving forces:

$$
\begin{aligned}
J_Q(\Gamma_Q, \Gamma_q, \Gamma_i, \ldots, \Gamma_N) &= \frac{\partial J_Q}{\partial \Gamma_Q}\Gamma_Q + \frac{\partial J_Q}{\partial \Gamma_q}\Gamma_q + \ldots + \frac{\partial J_Q}{\partial \Gamma_N}\Gamma_N \\
J_q(\Gamma_Q, \Gamma_q, \Gamma_i, \ldots, \Gamma_N) &= \frac{\partial J_q}{\partial \Gamma_Q}\Gamma_Q + \frac{\partial J_q}{\partial \Gamma_q}\Gamma_q + \ldots + \frac{\partial J_q}{\partial \Gamma_N}\Gamma_N \\
&\vdots \\
J_N(\Gamma_Q, \Gamma_q, \Gamma_i, \ldots, \Gamma_N) &= \frac{\partial J_N}{\partial \Gamma_Q}\Gamma_Q + \frac{\partial J_N}{\partial \Gamma_q}\Gamma_q + \ldots + \frac{\partial J_N}{\partial \Gamma_N}\Gamma_N
\end{aligned} \tag{3-6}
$$

or,

$$J_\alpha = L_{\alpha\beta}\Gamma_\beta \tag{3-7}$$

It is important to remember the origin of the L_{ij}. They are derived as the linear coefficients of driving forces around the equilibrium state–i.e. the case of condition of small driving forces. Remember that if a function, $f(x, y, z)$ is expanded around a particular point up to linear terms:

$$
\begin{aligned}
&\Delta f(x - x_\circ, y - y_\circ, z - z_\circ) = \\
&\left(\frac{\partial f}{\partial x}\Big|_{x=x_\circ,\ y=y_\circ,\ z=z_\circ} \right)\Delta x + \left(\frac{\partial f}{\partial y}\Big|_{x=x_\circ,\ y=y_\circ,\ z=z_\circ} \right)\Delta y + \left(\frac{\partial f}{\partial z}\Big|_{x=x_\circ,\ y=y_\circ,\ z=z_\circ} \right)\Delta z
\end{aligned} \tag{3-8}
$$

The values of the linear terms are functions of the point about which they are expanded $(x_\circ,\ y_\circ,\ z_\circ)$, so in the expansion in Eq. 3-7, the linear coefficients $L_{\alpha\beta}$ are also functions of the particular equilibrium state about which the system is expanded. In other words, we should *expect* the $L_{\alpha\beta}$ to be functions of temperature, equilibrium chemical potential, pressure, etc.

The entropy production for the near-equilibrium case is given by:

$$T\dot{\sigma} = L_{\alpha\beta}\Gamma_\alpha\Gamma_\beta \geq 0 \tag{3-9}$$

Because the term on the right hand side must be positive definite and because each term is real, it is necessary that the matrix $L_{\alpha\beta}$ is symmetric; this is Onsager's Symmetry Relation:

$$L_{\alpha\beta} = L_{\beta\alpha} \tag{3-10}$$

Example: Thermal and Ionic Conducting Bar

Consider heat transport in a bar that can conduct both heat and electricity via ionic conductivity:

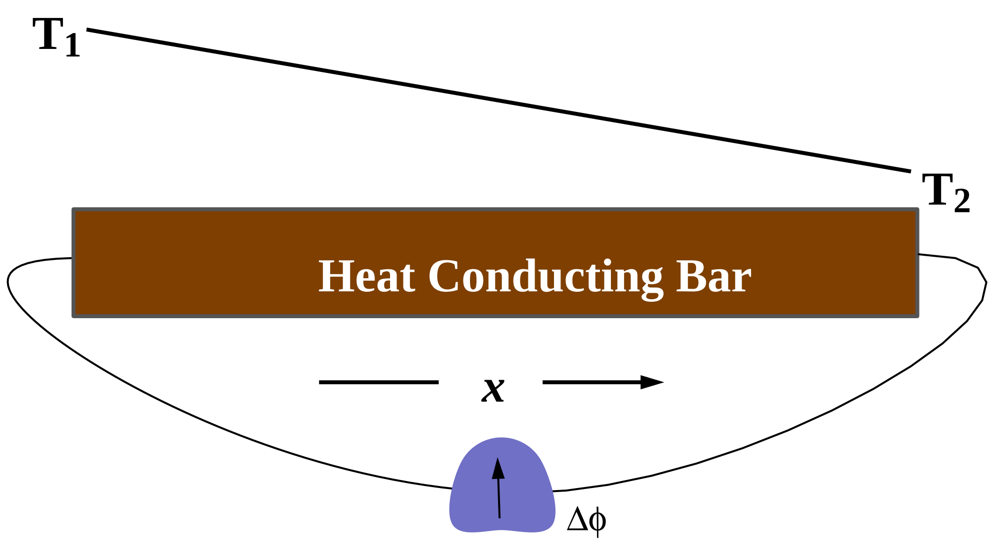

Figure 3-1: Thermal and ionic conducting bar with ends at two fixed temperatures.

$$\begin{aligned} J_Q &= L_{QQ}\frac{-\nabla T}{T} - L_{Qq}\nabla\phi \\ J_q &= L_{qQ}\frac{-\nabla T}{T} - L_{qq}\nabla\phi \end{aligned} \tag{3-11}$$

Suppose there is no electric current (perfect voltmeter), then

$$\nabla\phi = \frac{L_{qQ}}{L_{qq}}\left(\frac{-\nabla T}{T}\right) \tag{3-12}$$

thus for the case of no electric current density,

$$J_Q = \left(L_{QQ} - \frac{L_{qQ}^2}{L_{qq}}\right)\left(\frac{-\nabla T}{T}\right) \tag{3-13}$$

Therefore, the heat flux has two identifiable components, one that comes from the electrostatic potential difference and one the comes from temperature difference. The "kinetic coefficients" of the flux are related to combinations of the "direct effect coefficients" L_{QQ} and L_{qq} and the indirect coefficients L_{Qq} and L_{qQ}. Presumably, experiments could be performed on such a system to verify whether the Onsager symmetry relation applies, i.e. if $L_{Qq} = L_{qQ}$.

A set of such physical experiments is considered below.

Seebeck, Peltier Effects and Thomson's Second Relation

Consider the following experimental set-up:

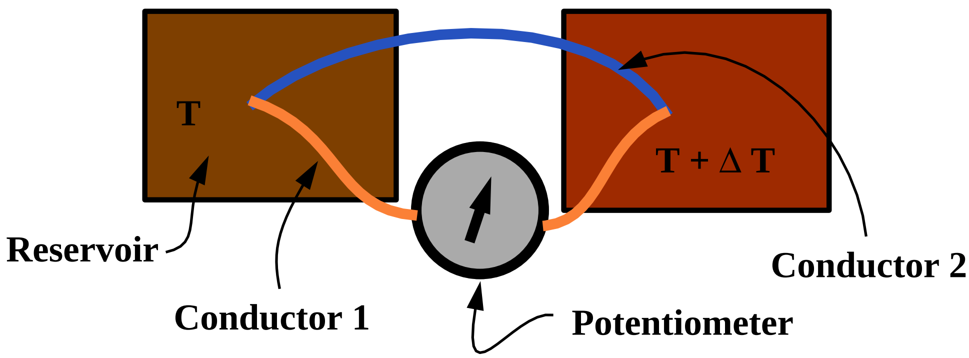

Figure 3-2: Experimental set-up for the Seebeck effect. A potentiometer measures the potential difference, $\Delta\phi$, between two conductor couples each at a different temperature.

In the Seebeck a potential difference is set up in response to the flow of heat between two reservoirs.

The thermoelectric power is a relation between the potential difference and the temperature difference:

$$\epsilon_{\text{Seebeck}} = \left(\frac{\Delta\phi}{\Delta T}\right)_{J_q=0} \tag{3-14}$$

The $J_q = 0$ indicates that the potentiometer is ideal. This quantity can be calculated using equations 3-11 using an approximation for the gradients $\nabla T \approx \Delta T/L$, etc.

$$\epsilon_{\text{Seebeck}} = \frac{-L_{qQ}}{TL_{qq}} \tag{3-15}$$

For the Peltier effect, the experimental set up is illustrated by:

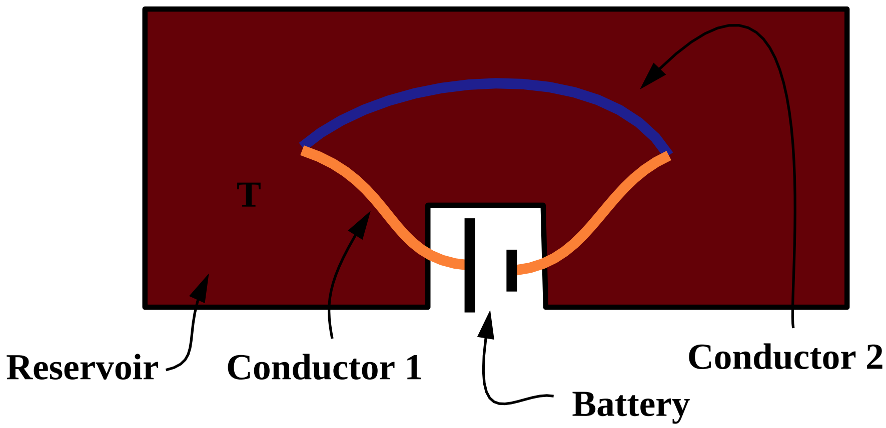

Figure 3-3: Experimental set-up for the Peltier effect. A perfect battery sets up a specified potential potential difference, $\Delta\phi$. As current, J_q, crosses the thermocouples, heat is produced and consumed depending on which material has a higher Fermi energy. Heat, J_Q, flows between the two junctions to maintain a constant temperature.

The Peltier coefficient is related to the ratio of the heat flux to the electric current:

$$\Pi_{\text{Peltier}} = \left(\frac{J_Q}{J_q}\right)_{\Delta T=0} \tag{3-16}$$

Using equations 3-11, the Peltier coefficient can be calculated in terms of the Onsager coefficients:

$$\Pi_{\text{Peltier}} = \left(\frac{L_{Qq}}{L_{qq}}\right) \tag{3-17}$$

If Onsager's symmetry relation holds ($L_{qQ} = L_{Qq}$), then there must be a relation between the Peltier and Seebeck coefficients:

$$\Pi_{\text{peltier}} = -\epsilon_{\text{Seebeck}} T \tag{3-18}$$

This relation is called Thomson's second relation and has been repeatedly experimentally verified and this can be considered experimental verification of Onsager's symmetry relation.

One Independent Mobile Species

Consider the case of one chemical species that can diffuse independently of all the others, such as an interstitial carbon atom diffusing in BCC iron, or the case where a gaseous species is diffusing through a quiescent gas mixture.

Suppose that the only driving force is the gradient in chemical potential of the interstitial species, then

$$J_1 = -L_{11}\nabla\mu_1 \tag{3-19}$$

The chemical potential can be related to local concentration through the activity coefficient γ_1:

$$\mu_1 = \mu_1^o + kT\ln\gamma_1 c_1 \tag{3-20}$$

Therefore, $\nabla\mu$ can be related to ∇c:

For the ideal case, the activity coefficient is independent of concentration, so

$$J_1 = -L_{11}\frac{kT}{c_1}\nabla c_1 \tag{3-21}$$

One would expect this relation to hold for very dilute alloys (Henry's law) or self-interstitial diffusion in a very pure alloy (Raoult's law).

For the case of a non-ideal solution:

$$J_1 = -L_{11}\frac{kT}{c_1}\left(\frac{\partial\ln\gamma_1}{\partial\ln c_1}+1\right)\nabla c_1 \tag{3-22}$$

If this is compared to the most simple version of Fick's first law, $J_1 = -D_1 \nabla c_1$, D_1 is called the intrinsic diffusivity and it is related to the Onsager coefficient as:

$$D_1 = L_{11} \frac{kT}{c_1} \left(\frac{\partial \ln \gamma_1}{\partial \ln c_1} + 1 \right) \tag{3-23}$$

The atomic mobility be defined by the the Einstein relation between the average drift velocity and the driving force, $\langle v \rangle = -M_1 \nabla \mu_1$.

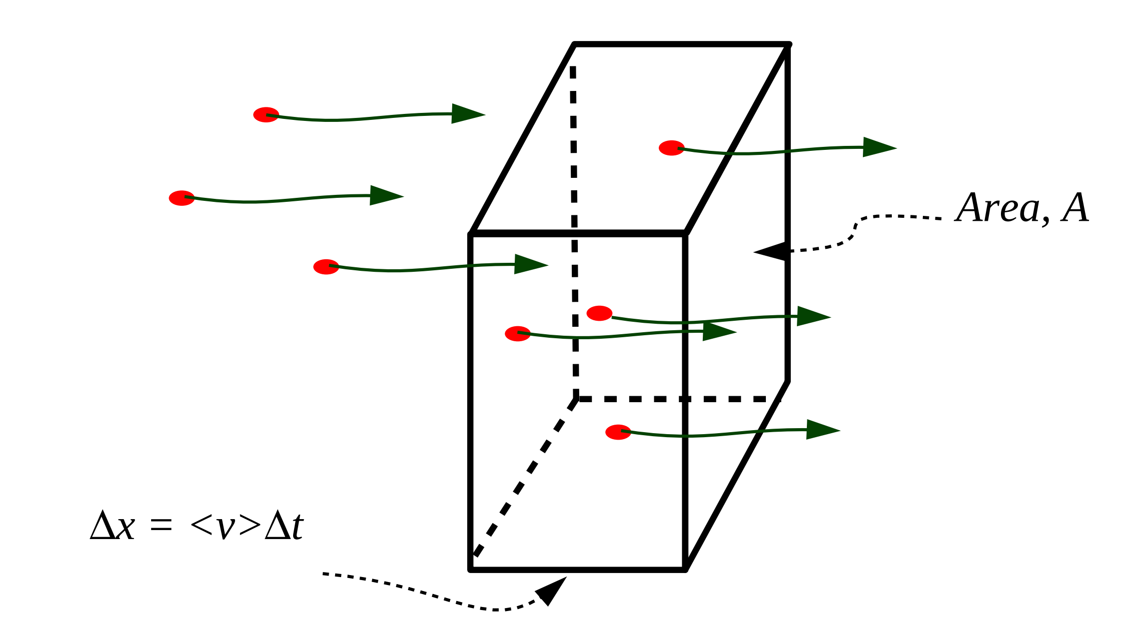

Figure 3-4: The number of atoms that cross through a plane in a time Δt is the concentration c multiplied by the volume $A \langle v \rangle \Delta t$.

$$\langle N_{\text{pass-thru}} \rangle = A \Delta x c_1 = A \langle v \rangle \Delta t c_1 \tag{3-24}$$

Using the above equation, the flux must be related to the average velocity through the relation,

$$J_1 = \langle v \rangle c_1 \tag{3-25}$$

Therefore, using the Einstein drift velocity,

$$L_{11} = c_1 M_1 \tag{3-26}$$

and the relation between intrinsic diffusivity and mobility is

$$D_1 = kT \left(\frac{\partial \ln \gamma_1}{\partial \ln c_1} + 1 \right) M_1 \tag{3-27}$$

If the solution is ideal—as in the case of mixture of radioisotopes of an otherwise identical atomic species—then the diffusivity is called the self-diffusivity D_1^* and since the activity coefficient is constant:

$$D_1^* = kTM_1 \tag{3-28}$$