

2.57 Nano-to-Macro Transport Processes
Fall 2004
Lecture 21

Last time we talked about the current density as

$$J_e = L_{11} 'q \left(\frac{d\Phi}{dx} \right) + L_{12} \left(\frac{dT}{dx} \right),$$

For electrons, $q = -e$ and $\Phi = \varphi_e - \frac{\mu}{e}$. Here φ_e is electrostatic potential, which is related to the electrical field. Chemical potential μ is related to diffusion. Their combination Φ is electrochemical potential, indicating the total driving force of charges. The current density can be rewritten as

$$J_e = L_{11} \left(-\frac{d\Phi}{dx} \right) + L_{12} \left(\frac{dT}{dx} \right).$$

Note: The second term $L_{12} \left(\frac{dT}{dx} \right) = L_{12} T \left(\frac{1}{T} \frac{dT}{dx} \right)$ is similar to $\Delta S = \frac{dQ}{T}$ and may be compared with entropy flux.

The heat transferred is

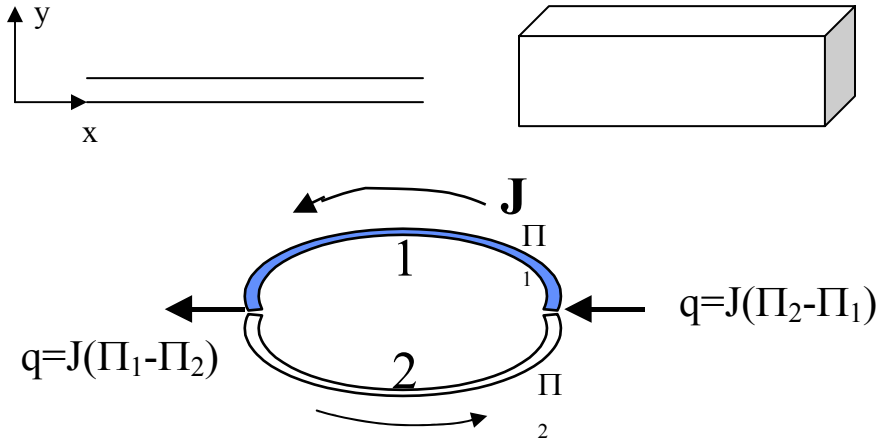
$$J_q = \frac{2}{V} \sum_{k_x} \sum_{k_y} \sum_{k_z} v_x (E - \mu) f = L_{21} \left(-\frac{d\Phi}{dx} \right) + L_{22} \frac{dT}{dx}$$

For open circuits, $J_e=0$. We obtain

$$-S = \frac{d\Phi / dx}{dT / dx} = \frac{V}{T_h - T_c} = \frac{L_{12}}{L_{11}},$$

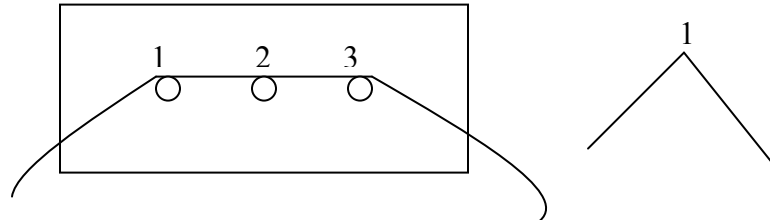
where S is called the seebeck coefficient.

Note: (1) S is dependent on the density of states. Therefore, it can be enhanced by using nanostructures such as thin films or nanowires. This effect is also the principle of thermal couples. (2) In the summation, we cannot use integral for quantized directions.



(2) In $S = -\frac{d\Phi/dx}{dT/dx}$, T should be the electron temperature T_e . In equilibrium cases, T_e is close to phonon T_p and we can use this effect to measure T_p . However, for extreme cases such as laser ablation, the two temperatures are not in equilibrium. Cautions should be taken.

(3) For an on-chip thermocouple, the measured temperature does not correspond to the junction point, but closer to the average temperature from 1 to 3. This is different from the normal thermocouples.



When $dT/dx=0$, we have

$$J_q = L_{21} \left(-\frac{d\Phi}{dx} \right) = \frac{L_{21}}{L_{11}} J_e = \Pi J_e,$$

where the Peltier coefficient $\Pi = TS$, $L_{21} = TL_{12}$. Note one thermoelectric coefficient (S here) can be used to express all other coefficients. This is a requirement of the “time reversal invariance” of the mechanical equations of motion, i.e., the particles retrace their former paths if all velocities are reversed. Based on this principle, Onsager (1931) derived the famous **Onsager reciprocity relations**. The flux of any extensive variable, J_k , of a system (such as energy flux, particle flux) or at a local point of a system can be expressed as a linear combination of all the generalized driven forces F_j ,

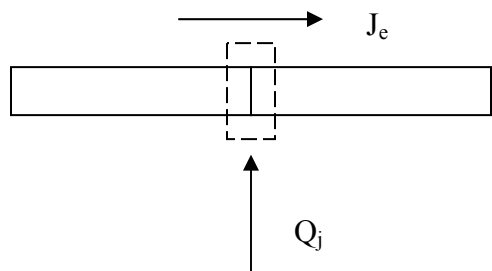
$$J_k = \sum_j L_{jk} F_j.$$

Onsager got a Nobel Prize for his work.

Now apply the above equation to the small control volume shown in the following figure. The energy conservation yields

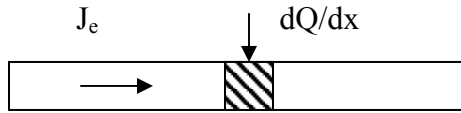
$$Q_j = J_{q2} - J_{q1} = (\Pi_2 - \Pi_1) J_e,$$

which is positive (absorbing heat from the ambient) for $\Pi_2 > \Pi_1$.



Another phenomenon is the Thomson effect. Along the following bar, we have

$$T \frac{dS}{dT} = \frac{1}{J_e} \frac{dq/dx}{dT/dx} = \beta.$$



The overall energy equation is

$$q = \frac{dJ_q}{dx} + J_e \frac{d\Phi}{dx} = \sigma J_e^2 + k \frac{dT}{dx} + \text{Thomson term}.$$

And thermal conductivity is

$$k_e = L_{12}L_{21} / L_{11} - L_{22}.$$

The Wiedemann-Franz law states

$$\frac{k_e}{\sigma T} = \text{const} = L = 2.45E-8 \text{ W}\Omega / K^2,$$

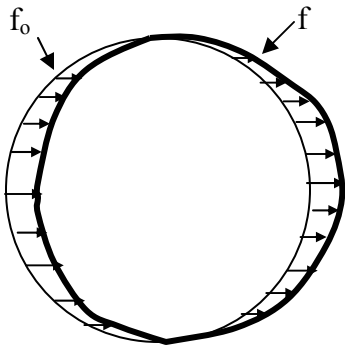
where the constant L is Lorenz number.

Now consider the Boltzmann equation under the relaxation time approximation

$$\frac{\partial g}{\partial t} + \frac{\partial f_o}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{r}} f_o + \mathbf{v} \cdot \nabla_{\mathbf{r}} g + \frac{\mathbf{F}}{m} \cdot \nabla_{\mathbf{v}} f_o + \frac{\mathbf{F}}{m} \cdot \nabla_{\mathbf{v}} g = -\frac{g}{\tau}, \quad g = f - f_o.$$

By neglecting some terms, we have obtained

$$g = -\tau \left(\mathbf{v} \cdot \nabla_{\mathbf{r}} f_o + \frac{\mathbf{F}}{m} \cdot \nabla_{\mathbf{v}} f_o \right).$$



(1) Assume that f only has small deviation from f_o , indicating local equilibrium. Now we have $g = f - f_o \ll f_o$. This yields

$$\tau \mathbf{v} \cdot \nabla_{\mathbf{r}} f_o \ll f_o$$

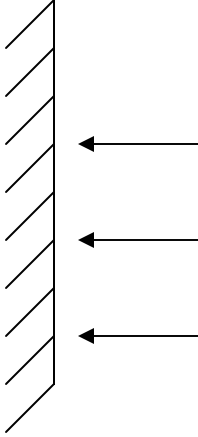
$$\text{or } \tau \mathbf{v} \frac{df_o}{dT} \frac{dT}{dx} \ll f_o \Rightarrow \frac{\Lambda}{T} \frac{dT}{dx} \ll 1 \Rightarrow \Lambda / L \ll 1, \quad \frac{dT}{dx} \text{ should not be too large.}$$

(2) Within $\mathbf{v} \cdot \nabla_{\mathbf{r}} f_o$, $\mathbf{v} \cdot \nabla_{\mathbf{r}} g$, we ignore the latter one. This implies

$$\nabla_{\mathbf{r}} f_o \gg \nabla_{\mathbf{r}} g$$

(3) We ignore $\frac{\partial f_o}{\partial t}$ on the LHS compared with $\frac{g}{\tau}$ on the RHS. This indicates

$$\frac{\partial f_o}{\partial t} \ll \frac{g}{\tau} \Rightarrow t \gg \tau.$$



Now consider the above transient process in which an infinite wall is heated suddenly.

The theoretical solution of $\frac{\partial T}{\partial t} = \frac{k}{\rho c} \frac{\partial^2 T}{\partial x^2}$ is $T = \exp(-x/\sqrt{at})$, which indicate that T is

nonzero at any long distance from the wall. Since the thermal wave propagates with a limited velocity (sound velocity), this is obviously impossible. To compensate for the error, the **Cattaneo equation** is introduced

$$\bar{\tau} \frac{\partial J_q}{\partial t} + J_q = -k \frac{\partial T}{\partial x}$$

where $\bar{\tau}$ is a weighed average of the relaxation time relative to the heat flux expression.

Combining this equation with the energy conservation equation (no heat generation considered),

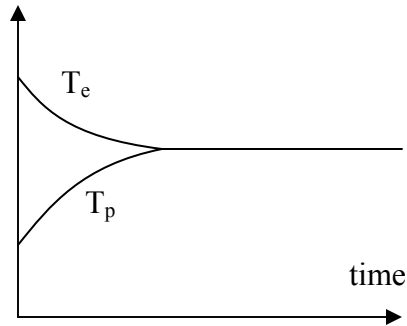
$$-\nabla \cdot \mathbf{J}_q = \rho c \frac{\partial T}{\partial t}$$

and eliminating J_q , we arrive at the following governing equation for the temperature distribution,

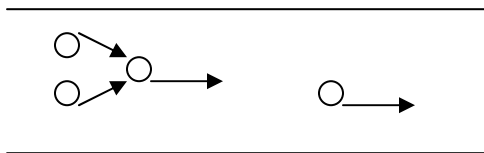
$$\bar{\tau} \frac{\partial^2 T}{\partial t^2} + \frac{\partial T}{\partial t} = \frac{k}{\rho c} \frac{\partial^2 T}{\partial x^2},$$

which is a **hyperbolic** type of equation.

However, the Cattaneo equation is not applicable in most experimental situations. Under fast heating, the temperature gradient is usually very large, and thus the condition that $(\Lambda/T) dT/dx$ cannot be satisfied. There is no convincing experimental data showing the validity of the hyperbolic equation. In femto-laser heating, the temperature of electrons is raised much higher than that of the phonons and after the relaxation time electrons exchange energy with phonons (the following figure).

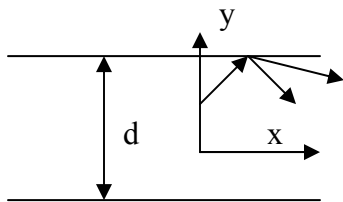


An experiment that is often cited as the proof for the validity of the hyperbolic equation is the second sound, which is encountered in low-temperature physics. However, the second sound is due to a different physical mechanism. At low temperatures, the umklap scattering is weak and normal scattering is strong, such that phonons have a nonzero average momentum (velocity). Equations for phonon hydrodynamics can be developed and the second sound can be described by these equations rather than the hyperbolic equation.



The derivations so far are for constitutive equations. We can also derive conservative equations from the Boltzmann equation. I will not go to details. Such conservative equations can be developed for gas molecules (Navier-Stokes equations), for electrons and phonons. Note: (1) In the 80s, people also conducted research based on Navier-Stokes type of equations for electron transport. However, it is not valid at nanoscale because just as Newton's shear stress law is not valid for rarefied gas flow, the drift-diffusion equation is not applicable to electrons.

Chapter 7 Classical Size Effects



When the electron and/or phonon mean free paths are comparable to or larger than the thin film thickness, they will collide more with the boundaries. The previous requirement $\Lambda/L \ll 1$ is not satisfied in this case. Most reflection on the wall is elastic. Two possibilities occur here: specular reflection, diffuse reflection.

First we have the Boltzmann equation

$$\mathbf{v} \cdot \nabla_{\mathbf{r}} f + \frac{\mathbf{F}}{m} \cdot \nabla_{\mathbf{v}} f = -\frac{f - f_0}{\tau}$$

or

$$\mathbf{v} \cdot \nabla_{\mathbf{r}} f_0 + \mathbf{v} \cdot \nabla_{\mathbf{r}} g + \frac{\mathbf{F}}{m} \cdot \nabla_{\mathbf{v}} f_0 + \frac{\mathbf{F}}{m} \cdot \nabla_{\mathbf{v}} g = -\frac{g}{\tau}.$$

Ignore $\frac{\mathbf{F}}{m} \cdot \nabla_{\mathbf{v}} g$. Magnitude comparison suggests that $v_y \frac{\partial g}{\partial y} \gg v_x \frac{\partial g}{\partial x}, v_z \frac{\partial g}{\partial z}$. Therefore,

we obtain

$$v_x \frac{df_0}{dx} + \frac{\mathbf{F}}{m} \cdot \nabla_{\mathbf{v}} f_0 = -\frac{g}{\tau} - v_y \frac{\partial g}{\partial y},$$

$$\tau v_x \frac{df_0}{dx} + \tau \frac{F_x}{m} \frac{df_0}{dv_x} = -g - \tau v_y \frac{\partial g}{\partial y}.$$

Note: For boundary scattering, the function $g(\mathbf{v})$ is unchanged but $g(\mathbf{r})$ is changed by scattering. For statistical calculation, caution needs to be taken when summation is conducted.