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3.205 Thermodynamics and Kinetics of Materials—Fall 2006

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Lecture 1: Fields and gradients; fluxes; continuity equation; entropy production; driving forces and fluxes

Lecture References

1. Balluffi, Allen, and Carter, *Kinetics of Materials*, Chapters 1 and 2.
2. Hildebrand, F. B., *Advanced Calculus for Applications*, Prentice-Hall, (1976). QA303.H642, or other applied math book of your choice.

Key Concepts

- Thermodynamics is precise about equilibrium states, but real materials are rarely at equilibrium.
- The concept of *local equilibrium* is applicable to real materials on a micro-scale.
- The rates of approach to equilibrium in real materials are found experimentally to depend on gradients of thermodynamic potentials.
- A *scalar field* associates a physical quantity with position—e.g., a composition field $c(\vec{x})$.
- The *gradient* of a scalar field is a vector that quantifies how rapidly the field changes with position.
- The *flux* of a substance quantifies the rate at which that substance flows through a unit area. The flux is a vector that is parallel to the local direction of the flow.
- The *rate of accumulation* of a the density of an extensive quantity is *minus* the divergence of the flux of that quantity, plus the rate of production of the substance.
- For conserved quantities like the number of moles of a component in a solution there are no sources or sinks and hence no production of the substance. For non-conserved quantities like entropy there can be production of the quantity during the course of a spontaneous process.
- The local entropy production can be expressed as a sum of terms, each of which is a product of a flux and a conjugate “force” (see KOM Eq. 2.15).
- Familiar empirical laws are linear relationships between fluxes and their conjugate forces: Fourier’s law of heat conduction, Fick’s law for diffusion, and Ohm’s law for electrical conduction (see KOM Table 2.1).
- The basic postulate of irreversible thermodynamics is that, near equilibrium, the local entropy production is non-negative (see KOM Eq. 2.16).
- When more than one force is active, each force will generally cause a flux of its corresponding quantity. There are both *direct* couplings between forces and conjugate fluxes, and *cross* terms that may also contribute to fluxes (see KOM Eqs. 2.20–21).
- When several forces are active, the flux of a given quantity is postulated to be linearly related to *all* of the forces. Furthermore, the matrix of coupling coefficients $L_{\alpha\beta}$ in the system of linear equations $J_\alpha = L_{\alpha\beta}X_\beta$ is postulated to be symmetric, that is, $L_{\alpha\beta} = L_{\beta\alpha}$.
- The potential which appears in the total conjugate force acting on a component in a material is called the *diffusion potential*,Φ (see KOM Eqs. 2.40–41).