Last Time

Thermodynamics as a Foundation for Kinetics

Gibbs Results for Equilibrium of Heterogenous Substances

Began Mathematical Background

3.21 Spring 2002: Lecture 2

Mathematical Background, cont'd

Fields

A field associates a physical quantity with a position, $\vec{x} = (x, y, z)$ at a time, t.[1] A field may also be a function of time: $f(\vec{x}, t)$ where f is the physical quantity that depends on location and time.

[1] Other (i.e., $\vec{r} = (r, \theta, \phi)$, etc.) or lower dimensional (i.e., $\vec{x} = (x, y)$, etc.) coordinate systems will be employed when appropriate.

Scalar Fields

Vector Fields

Tensor Fields Sometimes an external (laboratory) coordinate system must be specified as well as an internal (material) coordinate system, especially in those cases for which the material coordinate system refers to a symmetry direction or the orientation of a plane in the material. Tensors represent ways of connecting quantities to coordinate systems. A vector is a simple tensor—-called a rank 1 tensor—-that connects a single value (i.e. a magnitude) to a coordinate frame. A rank two tensor connects two coordinate systems—for instance the stress σ_{ij} represents the magnitude of the total force in a particular direction (the i-direction) distributed over a plane with a particular area (magnitude) oriented with a particular normal vector in the j-direction.[2]

Fluxes

Flux is an important vector field quantity in kinetics and it is important to understand it. It represents the rate at which "stuff" flows through a specified unit of area—an area is oriented in space.

[2]For the stress tensor, the two coordinate systems (material and laboratory) are usually chosen to the identical. This is the typical case for tensors in engineering applications, but it is not necessary.

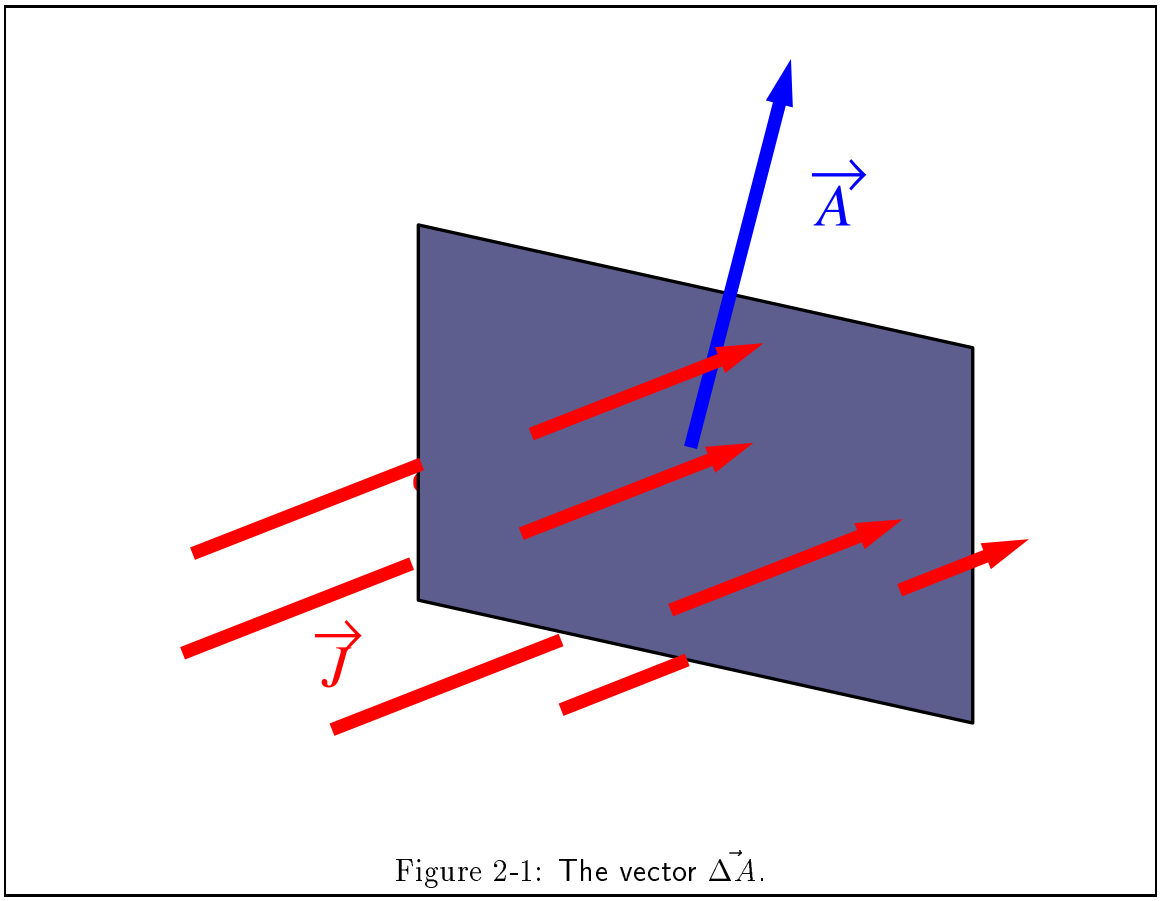

Figure 2-1: The vector $\Delta\vec{A}$.

Let $\Delta\vec{A}$ be an oriented patch of area, $\Delta\vec{A} = \hat{n}\Delta A = (A_x, A_y, A_z)$. If $\dot{M}_i$ is the rate at which i flows through a unit area, it follows that

$$\dot{M}_i(\Delta\vec{A}) \propto |\Delta\vec{A}| \tag{2-1}$$

The proportionality factor must be a vector field:

$$\dot{M}_i(\Delta\vec{A}) = \vec{J}_i \cdot \Delta\vec{A} \tag{2-2}$$

This defines the local flux as the continuum limit of:

$$\frac{\dot{M}_i(\Delta\vec{A})}{\Delta A} = \vec{J}_i(\vec{x}) \cdot \hat{n} \tag{2-3}$$

Accumulation

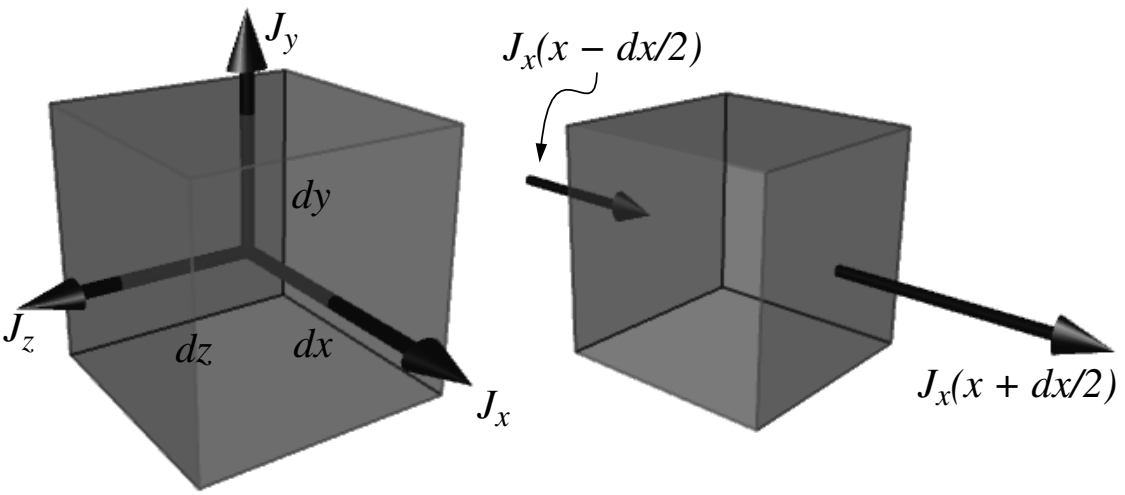

Figure 2-2: Illustration of limiting method of finding accumulation related to the divergence of the flux.

The rate at which i accumulates in a volume $\Delta V = dxdydz$ (with outward oriented normals) during time interval Δt is:

$$\Delta M_i = (i \text{ Flowing in }) - (i \text{ Flowing out }) + (\text{Rate of Production of } i) \tag{2-4}$$

$$\begin{aligned} \delta M_i = \quad & -\vec{J}(x + dx/2, 0, 0) \cdot \hat{i} dydz\Delta t + \\ & \vec{J}(x - dx/2, 0, 0) \cdot \hat{i} dydz\Delta t - \\ & \ldots + \\ & \ldots + \\ & \vec{J}(0, 0, z - dz/2) \cdot \hat{k} dxdy\Delta t \\ & + \dot{\rho}_i(\vec{x})\Delta t\Delta V \end{aligned} \tag{2-5}$$

where $\dot{\rho}_i(\vec{x})$ is the density of the rate of production of i in ΔV.

Expanding to first order in dx, dy, dz, subtracting, and using the continuum limit,

$$\frac{\partial c}{\partial t} = -\nabla \cdot \vec{J} + \dot{\rho}_m \tag{2-6}$$

The rate of accumulation of the density of an extensive quantity is **minus** *the divergence of the flux of that quantity plus the rate of production*

Note that Eq. 2-6 could have been derived directly from:

$$\begin{aligned} \dot{M}_i \quad & = -\int_{\mathcal{B}(\Delta V)} \vec{J}_i \cdot d\vec{A} + \int_{\Delta V} \dot{\rho}_i dV \\ & = -\int_{\mathcal{B}(\Delta V)} \vec{J}_i \cdot \hat{n} dA + \int_{\Delta V} \dot{\rho}_i dV \\ & = \int_{\Delta V} (-\nabla \cdot \vec{J}_i + \dot{\rho}_i) dV \end{aligned} \tag{2-7}$$

where $\mathcal{B}(\Delta V)$ is the oriented surface around ΔV and the

Conserved and Unconserved Quantities

Conserved quantities are those that do not vanish from or spring into existence at any time or place. Therefore, the rate of production term in the accumulation must be identically equal to zero—for conserved quantities:

$$\frac{\partial C_i}{\partial t} = -\nabla \cdot \vec{J}_{N_i} \tag{2-8}$$

where C_i is the density (or concentration) of i, or the continuum limit of $N_i/\Delta V$ where N_i is the amount of i. The number of atoms of a particular type is conserved.[3]

Molecules are not conserved if chemical reactions take place.

Internal energy is conserved:

$$\frac{\partial u}{\partial t} = -\nabla \cdot \vec{J}_U \tag{2-9}$$

Examples of things that are *not* conserved include magnetization or spin density, atomic order, and polarization. Entropy is not conserved, thus there must be an expression:

$$\frac{\partial s}{\partial t} = -\nabla \cdot \vec{J}_S + \dot{\sigma}(\vec{x}, t) \tag{2-10}$$

where $\dot{\sigma}$ is the rate of entropy production per unit volume.

[3] Ignoring nuclear decay.

Introduction to Irreversible Thermodynamics

Equation 2-10 may seem sensible, but is it possible to form a physical picture of what is meant by the flux of entropy $\vec{J}_S$?

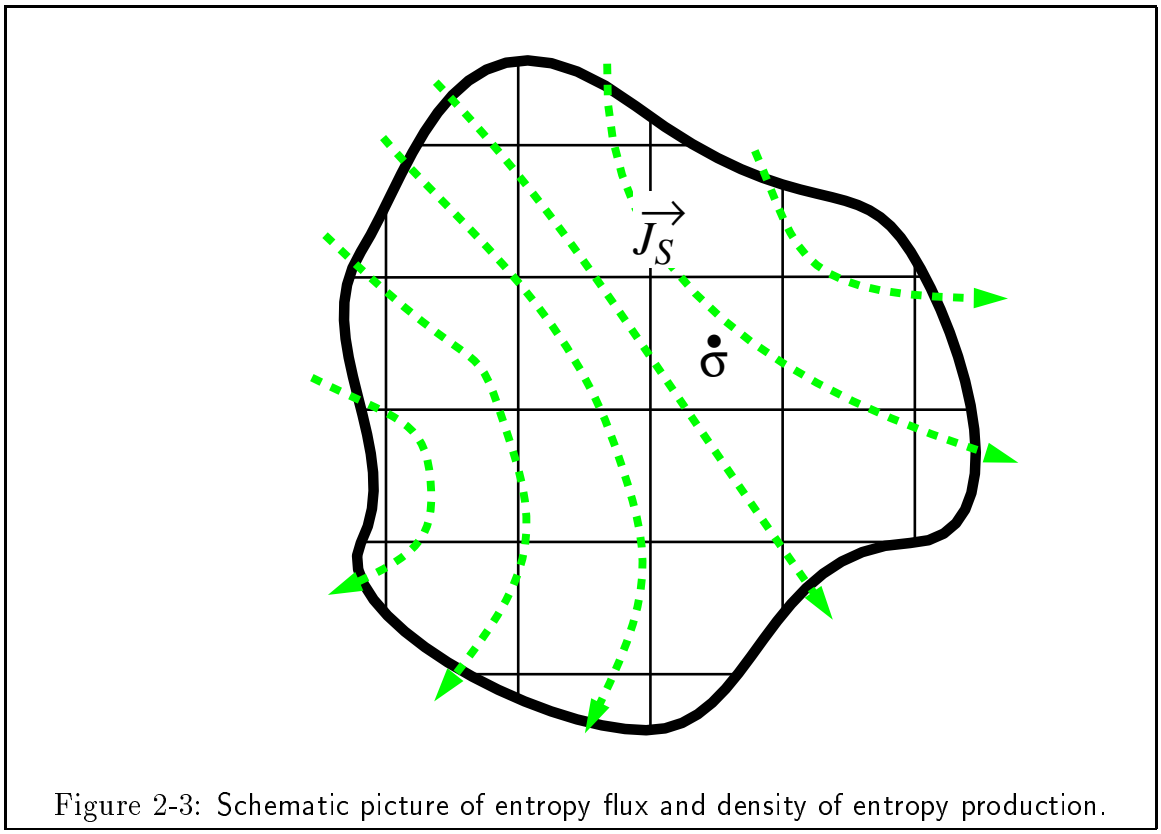

Figure 2-3: Schematic picture of entropy flux and density of entropy production.

What is meant by the continuum limit of the entropy density, s?

One way to find a meaningful picture of the entropy density is to *assume that equilibrium thermodynamics applies locally.* Then, the expression for equilibrium changes,

$$dU = TdS - PdV + \sum_i \mu_i dN_i \tag{2-11}$$

can be rearranged to find an expression for entropy in terms of more intuitive quantities. It is useful to write the above in terms of densities (dividing every extensive quantity by a reference unit volume $V_\circ$

$$Tds = du + Pdv - \sum_i \mu_i dc_i \tag{2-12}$$

It is useful to generalize this to other thermodynamic systems of interest and write the above equation as

$$Tds = du - \sum_i F_i dx_i \tag{2-13}$$

where the F_i are generalized potentials and the x_i are generalized displacements.

To illustrate how the assumption of local equilibrium will be used, consider *a closed system that does or receives no work from its surroundings*—i.e. a system where entropy can only increase according to the second law.

$$\frac{\partial}{\partial t}\int_{V_{closed}} sdV = \int_{V_{closed}} \dot{\sigma} dV - \int_{\mathcal{B}(V_{closed})} \vec{J}_S \cdot \hat{n} dA \tag{2-14}$$

where $\mathcal{B}(V_{closed})$ is the surface of the closed volume V_{closed} and $\hat{n}$ is the outward normal of that surface.

Supposing that the system does no work, only heat contributes to $\vec{J}_S = \vec{J}_U/T = \vec{J}_Q/T$ at the surface:

$$\frac{\partial}{\partial t}\int_{V_{closed}} sdV = \int_{V_{closed}} \dot{\sigma} dV - \int_{\mathcal{B}(V_{closed})} \frac{\vec{J}_Q \cdot \hat{n}}{T} dA \tag{2-15}$$

The last term is (minus) the total heat that enters the system:

$$\frac{\partial Q_{in}}{\partial t} = -\int_{\mathcal{B}(V_{closed})} \frac{\vec{J}_Q \cdot \hat{n}}{T} dA = -\int_{V_{closed}} \frac{\nabla \cdot \vec{J}_Q}{T} dV \tag{2-16}$$

(It is minus because if the $\vec{J}_Q$ is in the same general direction a $\hat{n}$ then heat is leaving the system.)

If the surface is uniformly at constant temperature, then

$$\frac{\partial S_{total}}{\partial t} - \frac{1}{T}\frac{\partial Q_{in}}{\partial t} = \int_V \dot{\sigma} dV \tag{2-17}$$

The term on the right of Eq. 2-17 is a measure of the irreversibility.

This leads to a fundamental postulate of irreversible thermodynamics: $\boxed{\dot{\sigma} \geq 0 \text{ everywhere.}}$ or

$$\dot{\sigma} \equiv \frac{\partial s}{\partial t} + \nabla \cdot \vec{J}_S \geq 0 \tag{2-18}$$

Rewrite Eq. 2-18 using the assumption of local equilibrium (2-13):

$$\dot{\sigma} = \frac{1}{T}\frac{\partial u}{\partial t} - \sum_i \frac{F_i}{T}\frac{\partial X_i}{\partial t} + \nabla \cdot \vec{J}_s \tag{2-19}$$

To simplify writing, it is useful to introduce the "summation convention" where any repeated index becomes an implied sum. For instance, the dot-product can be written as $\vec{a} \cdot \vec{b} = \sum_i^3 a_i b_i = a_i b_i$ where in the final term the repeated index i is summed over all of its possible values; for instance, $Tds = du - F_i dX_i = dU - \sigma_{ij} d\epsilon_{ij} - \phi dq - H_i dB_i - \mu_i dc_i$ where σ_{ij} are the nine (3×3) components of the stress tensor, ϵ_{ij} are the nine components of the strain tensor,[4] ϕ is the electrostatic potential and q is charge density, H_i and B_i are the three (i.e., x, y, z) components of the applied and induced magnetic fields, and μ_i and c_i are the N chemical potentials and concentrations of the i independent chemical species.

Therefore, using the summation convention:

$$\dot{\sigma} = \frac{1}{T}\frac{\partial u}{\partial t} - \frac{F_i}{T}\frac{\partial X_i}{\partial t} + \nabla \cdot \vec{J}_s \tag{2-20}$$

Using a version of the vector chain rule: $\nabla \cdot A\vec{B} = \nabla A \cdot \vec{B} + A\nabla \cdot \vec{B}$:

[4] For a discussion of stress and strain (and the number of their independent components) in this thermodynamic discussion, refer to the addendum to this lecture.

$$\frac{F_i}{T}\frac{\partial X_i}{\partial t} = \nabla \cdot \left(\frac{\vec{J}_i F_i}{T}\right) - \vec{J}_i \cdot \nabla\left(\frac{F_i}{T}\right) \tag{2-21}$$

and

$$\frac{1}{T}\nabla \cdot \vec{J}_U = \nabla \cdot \left(\frac{\vec{J}_U}{T}\right) - \vec{J}_i \cdot \nabla\left(\frac{1}{T}\right) \tag{2-22}$$

in Eq. 2-20:

$$\dot{\sigma} = \vec{J}_u \cdot \nabla\left(\frac{1}{T}\right) - \vec{J}_i \cdot \nabla\left(\frac{F_i}{T}\right) + \nabla \cdot \left(\vec{J}_s - \frac{\vec{J}_u - F_i\vec{J}_i}{T}\right) \tag{2-23}$$

Define:

$$\vec{J}_s \equiv \frac{\vec{J}_u - F_i\vec{J}_i}{T} = \frac{\vec{J}_Q}{T} \tag{2-24}$$

so that,

$$\begin{aligned} \dot{\sigma} &= \vec{J}_u \cdot \nabla\left(\tfrac{1}{T}\right) - \vec{J}_i \cdot \nabla\left(\tfrac{F_i}{T}\right) \\ &= -\tfrac{\vec{J}_u}{T^2} \cdot \nabla T - \tfrac{\vec{J}_i}{T} \cdot \nabla F_i + \tfrac{F_i \vec{J}_i}{T^2} \cdot \nabla T \\ T\dot{\sigma} &= \tfrac{F_i \vec{J}_i - J_u}{T} \cdot \nabla T - \vec{J}_i \cdot \nabla F_i \\ &= -\tfrac{\vec{J}_Q}{T} \cdot \nabla T - \vec{J}_i \cdot \nabla F_i \geq 0 \end{aligned} \tag{2-25}$$

Because T is always positive, this implies a relation between the fluxes and the gradients of the potentials: **Naively (but not necessarily), $\vec{J}_Q$, must be antiparallel to ∇T; $\vec{J}_i$, must be antiparallel to ∇F_i for the entropy production to be everywhere positive.**

Consider quantity on the right-hand-side of Eq. 2-25 term-by-term:

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*[5] Fick's form	$\vec{J_{c_i}} = -M_i c_i \nabla\mu_i$
Charge	$\vec{J_q}$	$-\nabla\phi$	Ohm's	$\vec{J_q} = -\rho\nabla\phi$