3.21 Spring 2002: Lecture 1

- **Class Structure** (Described in Syllabus) Lectures will be mostly chalk on the board, supplemented by computer simulations and graphics. This is a 15 unit class. You are expected to spend 5 (waking) hours in lectures. The other ten hours should be occupied by reading the text or any supplementary materials, reviewing or recopying your lecture notes, and doing your homework. If you begin spending **significantly more** than 15 hours a week on this class, please confer with your classmates. The groups are designed to reduce the amount of time spent on homework—not to increase it. If the the class is generally spending more than 15 hours, let us know so we can adjust.

- **Grading**

  2 exams 25%/exam Two exams will be in-class during the lecture period.

  Homework 25% Class groups will be organized. Each group will turn in a joint homework and receive a single grade that is recorded for each member of the group. Everyone in the group receives the same grade.

  Class Participation 25% You will receive credit for asking good questions or making good comments during lectures and recitations—*if you state your name.* You will not receive credit for "showing off": a good question or a comment is one that benefits most of your classmates. There will be random questions to students during lectures. You should be prepared to answer simple questions succinctly or say that you honestly don't know–and call on a friend.

- **Lecture Notes** will often be found on the web. You can use them any way you wish. The lecture notes will supplement (and sometimes correct) the textbook.

- **The textbook (KPIM)** for this course is being printed at CopyTech. You should be able to buy a copy next week at CopyTech for a very modest price. You are expected to read the book and understand the concepts that are covered in the lecture. Because the book is still in revision, comments/corrections on the book in the form of writing will be very welcome and will be regarded as class participation.

- **Office hours** can be found on the website.

Thermodynamics and Kinetics

Joule/Kelvin

$$dU = \delta W + \delta Q \tag{1-1}$$

Carnot/Clausius For the limiting case of a reversible process,

$$dS = \frac{\delta Q}{T} \tag{1-2}$$

Boltzmann

$$S(U) = k \log \omega_U \tag{1-3}$$

Gibbs Rigorous and mostly complete foundation of equilibrium of materials.

Two fundamental results.

1. *If an extensive quantity can be exchanged between two bodies, then a necessary condition for equilibrium is that the associated potential, which is an intensive quantity, must have the same value in each body.*

2. *If a system is in equilibrium with reservoir that maintains a constant potential (e.g. P and T), then there exists a free energy function for that system (e.g., $G(P,T)$) that is minimized at equilibrium. Therefore, a necessary condition for equilibrium is that every small variation in G must be non-negative:*[1] $(\delta G)_{P=const.,T=const.} \geq 0$.

[1] For a closed system, i.e., one that has a fixed number of atoms.

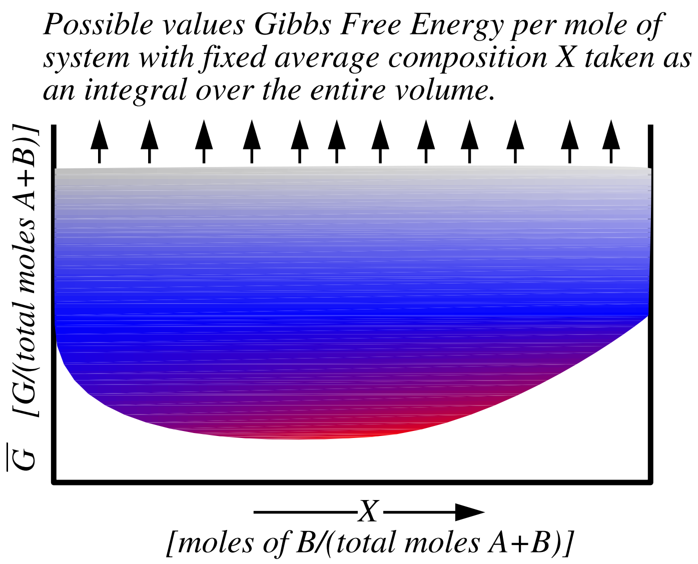

Figure 1-1: Representation of all possible values of the molar free energy function that is minimized at equilibrium.

The study of materials processes is a combination of Thermodynamics and Kinetics. Kinetics relies on thermodynamics as a rigorous foundation. Kinetics is less rigorous and more approximate; but, perhaps applicable to more real systems.

Materials Processes	
Relatively few variables	Complex interations involving a space and time continuum of variables.
Precise stratements about equilibrium states or quasistatic processes	Approximate statements or models for complex evolving systems
Powerful concepts and foundation, but limited to ideal systems	Approximate but predicitive statements for a wide range of phenomenae

Extending Thermodynamics to Kinetics

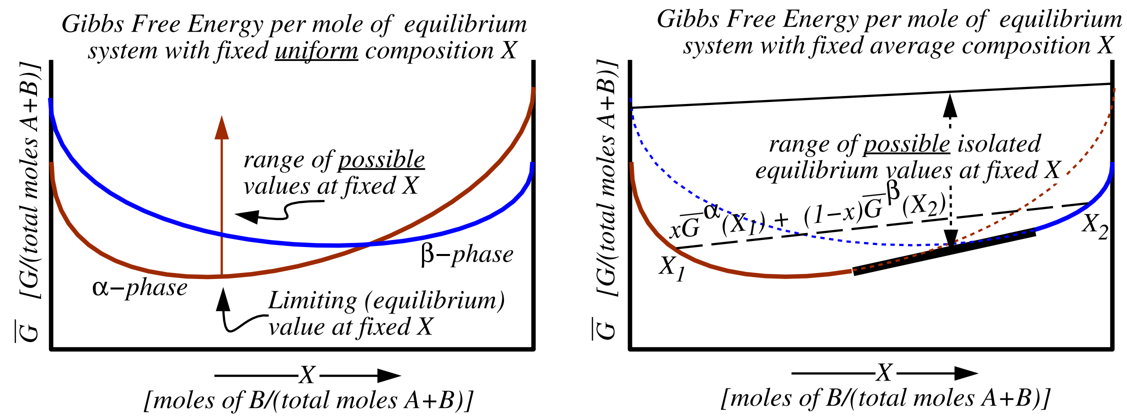

Figure 1-2: If the two curves on the left represent the lowest possible values of an appropriate thermodynamic function function that is minimized at equilibrium (such as $\overline{G}(P,T)$ at a fixed value of P, T) and if each phase constrained to have a homogeneous composition X, then these curves are *the equilibrium values of the appropriate free energy* as a function of X (i.e., $\overline{G}(P,T,X)$).

If the constraint that the system has a homogeneous composition is removed, then if any combination of compositions X_i—distributed among all possible phases in such a way that the average composition is $X_\circ$—has a lower free energy than any homogeneous system, then the equilibrium free energy curve is the convex hull from below of all the homogenous free energy curves (i.e., the single-phase compositions of the homogeneous molar free energy curves plus the common tangent).

The values of 'comparison' free energies of systems constructed from linear combinations of homogeneous equilibrium molar free energies is also bound from above—a set that is considerably smaller than non-equilibrium values of that function which is minimized during an approach to equilibrium.

Mathematical Background

Fields A field associates a physical quantity with a position, $\vec{x} = (x, y, z)$ at a time, t.[2] A field may also be a function of time: $f(\vec{x}, t)$ where f is the physical quantity that depends on

[2]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.

location and time.

Scalar Fields

Vector Fields

Tensor Fields

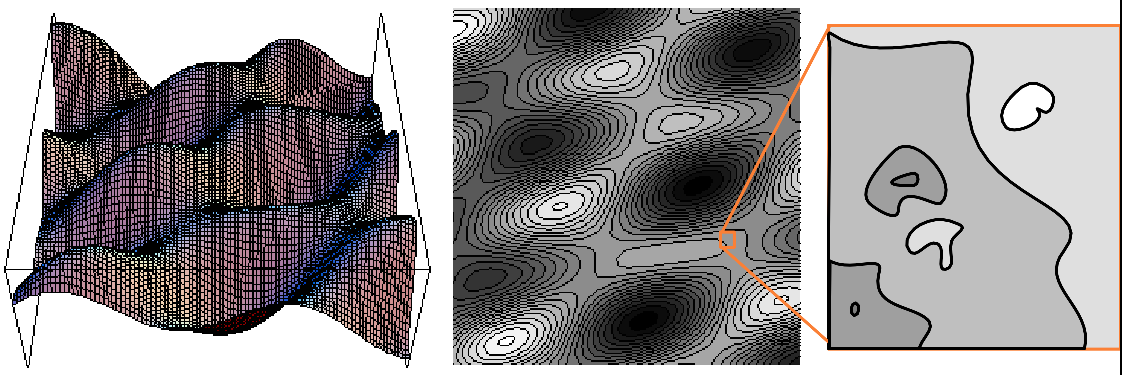

Figure 1-3: Two representations of a scalar field in two-dimensions are illustrated in the left and middle figures.

Every sufficiently smooth scalar field has a natural vector field associated with it: the gradient field.

Consider a stationary scalar field $c(\vec{x})$ such as the one illustrated in Figure 2-1.

$$c(\vec{x} + \vec{v}t) = c(\vec{x}) + \nabla c \cdot \vec{v} \Big|_{t=0} \Delta t + \ldots \tag{1-4}$$

The instantaneous rate of change of c with respect to t is therefore:

$$\frac{dc}{dt} = \nabla c \cdot v \tag{1-5}$$

The gradient is parallel to the direction of steepest ascent.

This can be generalized even further by considering a time-dependent field $c(\vec{x}, t)$, the instantaneous rate of change of c with velocity $\vec{c}(\vec{x})$ is

$$\frac{dc}{dt} = \nabla c \cdot v + \frac{\partial c}{\partial t} \tag{1-6}$$

- Continuum Limits Nature is fundamentally discrete, how is that we can discuss things like derivates?

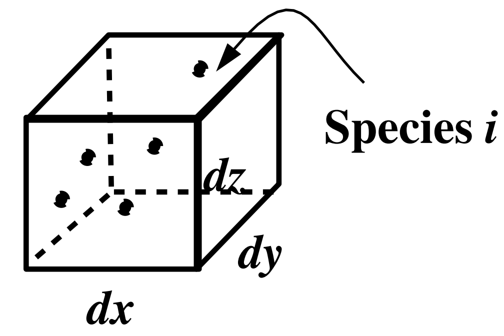

Figure 1-4: Infinitesimal volume with dimensions dx, dy, and dz located at $\vec{x}$.

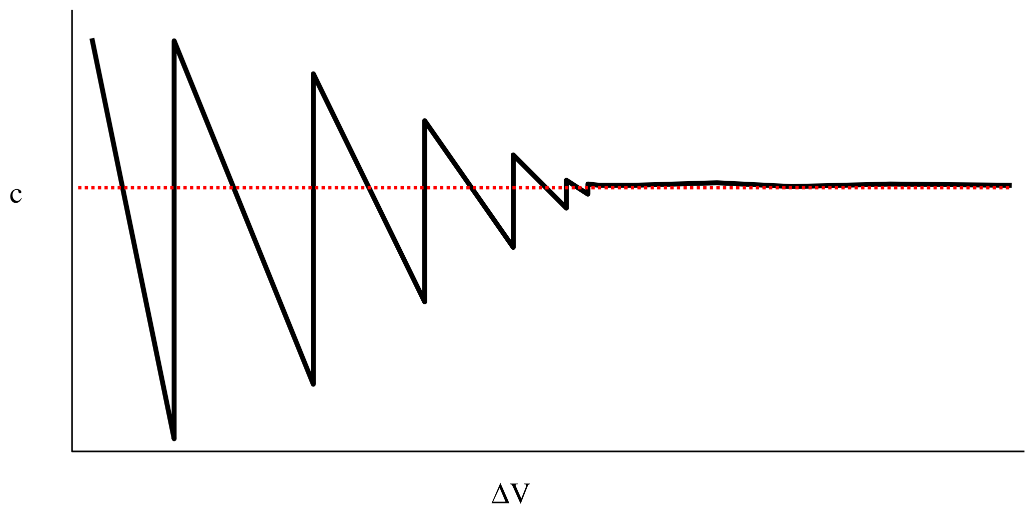

Figure 1-5: Behavior of the concentration at a point $c(\Delta V(\vec{x}))$ as the volume shrinks towards the point $\vec{x}$.

$$c(\vec{x}) = \lim \Delta V \rightarrow 0 \frac{\int_{\Delta V} \xi(\vec{x})(\delta(\vec{x_1} + \vec{x_2} + \ldots + \vec{x_N})dV}{\delta V} \tag{1-7}$$

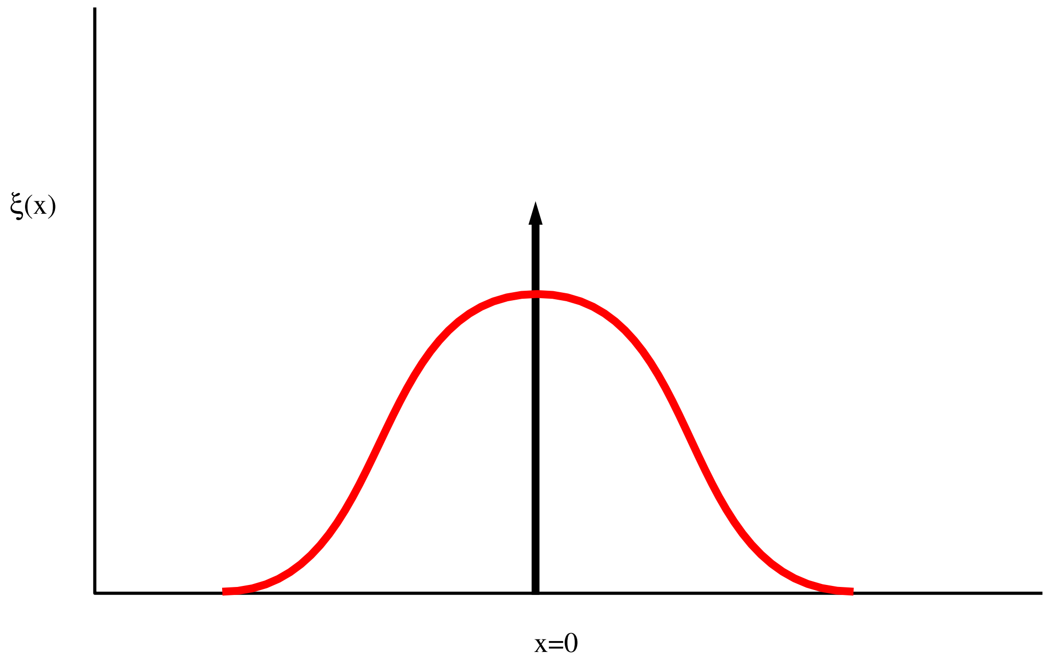

Figure 1-6: The function $\xi(\vec{x})$ performs a weighted sampling of points near $\vec{x} = 0$.

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

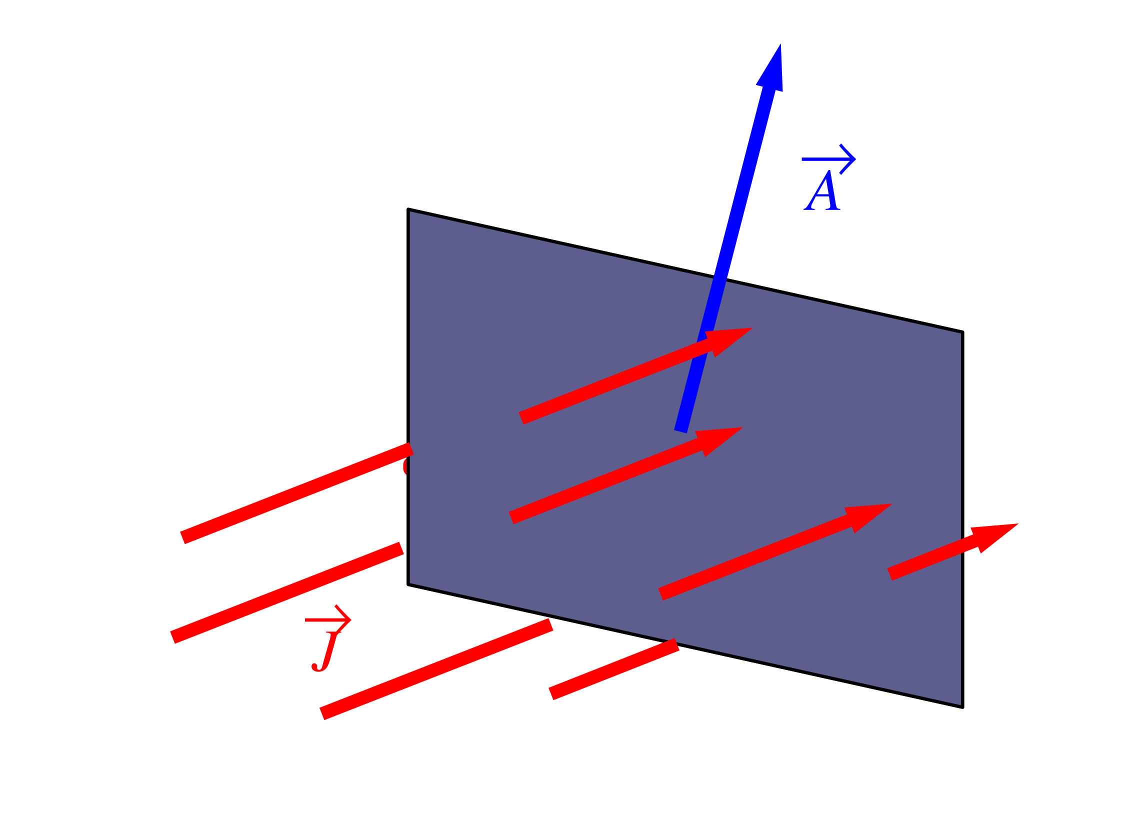

Figure 1-7: The vector $\Delta\vec{A}$.

$$\dot{M}_i(\Delta\vec{A}) \propto |\Delta\vec{A}| \tag{1-8}$$

The proportionality factor must be a vector field:

$$\dot{M}_i(\Delta\vec{A}) = \vec{J}_i \Delta\vec{A} \tag{1-9}$$

This defines the local flux as the continuum limit of:

$$\frac{\dot{M}_i(\Delta\vec{A})}{\Delta A} = \vec{J}_i(\vec{x}) \cdot \hat{n} \tag{1-10}$$

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

$$\Delta M_i = (i \text{ Flowing in }) - (i \text{ Flowing out }) + (\text{Rate of Production of} i) \tag{1-11}$$

$$\begin{aligned} \delta M_i = \; & -\vec{J}(x + dx/2, 0, 0) \cdot \hat{i} dydz \Delta t + \\ & \vec{J}(x - dx/2, 0, 0) \cdot \hat{i} dydz \Delta t - \\ & \ldots + \\ & \ldots + \\ & \vec{J}(0, 0, z - dz/2) \cdot \hat{k} dxdy \Delta t \\ & + \dot{\rho}_i(\vec{x}) \Delta t \Delta V \end{aligned} \tag{1-12}$$

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,

$$\frac{\partial c}{\partial t} = -\nabla \cdot \vec{J} + \dot{\rho}_m \tag{1-13}$$

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. 2-10 could have been derived directly from:

$$\begin{aligned} \dot{M}_i &= -\int_{\mathcal{B}(\Delta V)} \vec{J}_i \cdot d\vec{A} + \int_{\Delta V} \dot{\rho}_i dV \\ &= -\int_{\mathcal{B}(\Delta V)} \vec{J}_i \cdot \hat{n} dA + \int_{\Delta V} \dot{\rho}_i dV \\ &= \int_{\Delta V} (-\nabla \cdot \vec{J}_i + \dot{\rho}_i) dV \end{aligned} \tag{1-14}$$

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