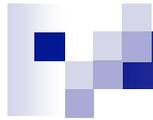
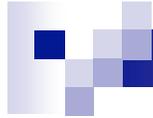


Irreversible Thermodynamics



Thermodynamics and Kinetics

- Thermodynamics is precise about what cannot happen.
- How can thermodynamics be applied to systems that are away from equilibrium?
- How are concepts from thermodynamics useful for building kinetic models?



A few math concepts

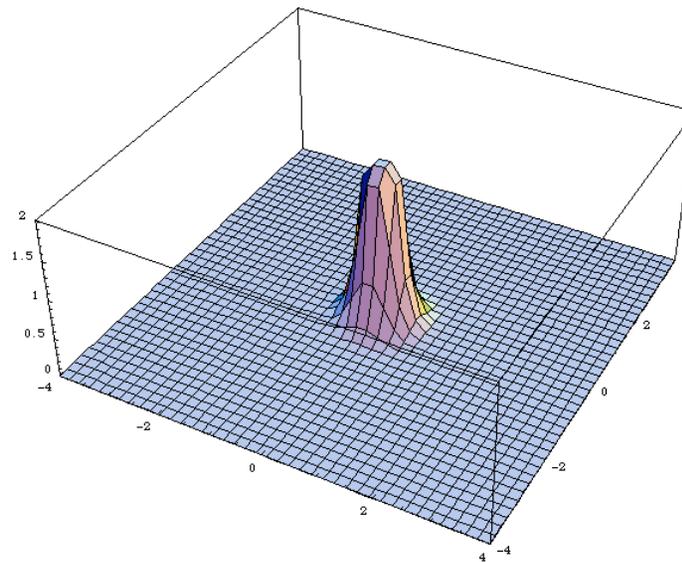
- Fields, scalar
- Fields, vector
- Fields, tensor
- Variations of scalar fields

■ Fields, scalar

Values of something are specified as a function of position,

$$\vec{r} = x\hat{i} + y\hat{j} + z\hat{k}, \text{ and (in kinetics) time.}$$

Example: composition field $c(\vec{r}, t)$ from a point source diffusing into a body

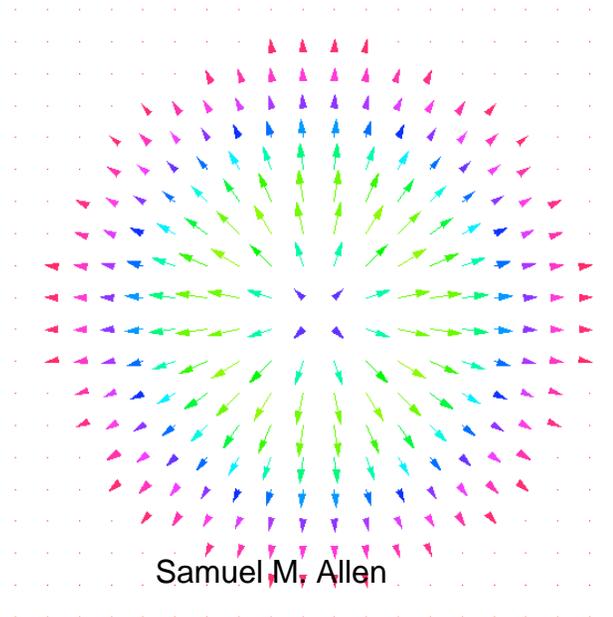


■ Fields, vector

Values of a vector quantity are specified as a function of position and (in kinetics) time

Example: velocity is a vector field, e.g. in a flow field

$$\vec{v}(\vec{r}, t)$$





- Fields, tensor

A second-rank tensor called the *stress tensor*

$\sigma_{ij}(\vec{r})$ relates force \vec{F} at a point to an oriented area \hat{A}

at that point



■ Variations of scalar fields

- Stationary field, moving point \vec{r} (a bug on a surface...)

$$c(\vec{r} + \vec{v} dt) = c(\vec{r}) + \vec{\nabla} c \cdot \vec{v} dt$$

$$\frac{dc}{dt} = \vec{\nabla} c \cdot \vec{v}$$

- Evolving field, moving point \vec{r} (a bug on a surface in an earthquake...)

$$\frac{dc}{dt} = \vec{\nabla} c \cdot \vec{v} + \frac{\partial c}{\partial t}$$



■ Continuum limits

Is it possible to define a *local* value for concentration in the limit $\Delta V \rightarrow 0$?

Figures removed due to copyright restrictions.

See Figures 1.5 and 1.6 in Balluffi, Robert W., Samuel M. Allen, and W. Craig Carter.

Kinetics of Materials. Hoboken, NJ: J. Wiley & Sons, 2005. ISBN: 0471246891.

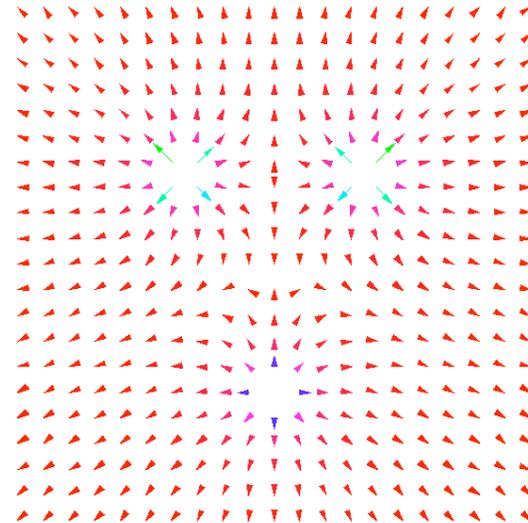
It is, with suitable care.

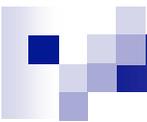
■ Fluxes

The flux vector \vec{J}_i represents mass flow of component i at a point per unit oriented area at that point

$$\lim_{\Delta A \rightarrow 0} \frac{\dot{M}_i(\Delta \vec{A})}{\Delta A} = \vec{J}_i \cdot \hat{n}$$

Example: swimming fish





■ Accumulation

Flow field, $\vec{J}(\hat{r})$

Rate of production in dV , $\dot{\rho}_i$

Accumulation of species i $\frac{\partial c_i}{\partial t} = -\nabla \cdot \vec{J}_i + \dot{\rho}_i$

For a conserved quantity like internal energy $\frac{\partial u}{\partial t} = -\nabla \cdot \vec{J}_u$

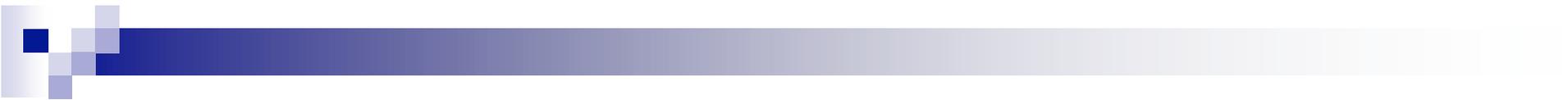
and for a non-conserved quantity like entropy

$$\frac{\partial S}{\partial t} = -\nabla \cdot \vec{J}_S + \dot{\rho}_i$$



System at Equilibrium

- Characterized by *uniform* values of various “potentials” throughout the system e.g. T, P, μ_i
- Densities of conjugate extensive quantities e.g. S, V, N_i can be inhomogeneous at equilibrium
- S is maximized in a system at constant U
- For an isolated system $dS \geq \frac{q}{T}$



System away from Equilibrium

- Kinetics concerns the path, mechanisms, and rates of spontaneous and driven processes.
- *Irreversible thermodynamics* attempts to apply thermodynamics principles to systems that are not in equilibrium and to suggest principles by which they relax toward equilibrium or steady state.



Postulate 1

- It is generally possible to use principles of the continuum limit to define meaningful, useful, *local* values of various thermodynamics quantities, e.g., chemical potential μ_i .
- Useful kinetic theories can be developed by assuming a functional relationship between the *rate* of a process and the *local* departure from equilibrium (“driving force”).



Postulate 2

- For any irreversible process the rate of entropy production is *everywhere* ≥ 0 .

$$\dot{\sigma} = \frac{\partial S}{\partial t} + \nabla \cdot \vec{J}_S \geq 0$$

- More restrictive than $dS^{\text{tot}} \geq 0$ for isolated system.



Postulate 3

- Assume linear coupling between fluxes J and forces X

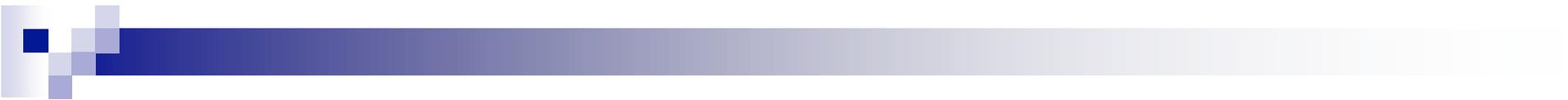
$$J_{\alpha} = L_{\alpha\beta} X_{\beta} \quad \alpha, \beta = Q, q, I, \dots, N_c$$

$$J_{\alpha} = \sum_{\beta} \sum_{\alpha} L_{\alpha\beta} X_{\alpha} X_{\beta}$$

- Electrical + heat conduction

$$J_q = L_{qq} X_q + L_{qQ} X_Q \quad \text{Direct coefficients, } L_{qq} \ L_{QQ}$$

$$J_Q = L_{Qq} X_q + L_{QQ} X_Q \quad \text{Coupling coefficients, } L_{qQ} \ L_{Qq}$$



Postulate 4

- Onsager symmetry postulate

- $L_{\alpha\beta} = L_{\beta\alpha}$ (microscopic reversibility).

$$L_{\alpha\beta} = L_{\beta\alpha} \Rightarrow \frac{\partial J_q}{\partial X_Q} = \frac{\partial J_Q}{\partial X_q}$$

Similar to Maxwell's relations in thermodynamics

Force/Flux Pairs

Flux	Conjugate Force	Empirical law
Heat \vec{J}_Q	$-\frac{1}{T}\nabla T$	$\vec{J}_Q = -K\nabla T$ Fourier
Charge \vec{J}_q	$-\nabla\phi$	$\vec{J}_q = -\rho\nabla\phi$ Ohm
Mass \vec{J}_i	$-\nabla\mu_i$	$\vec{J}_i = -M_i c_i \nabla\mu_i$ Fick



Multiple forces and fluxes

Consider simultaneous flow of heat and charge

$$\begin{aligned}\vec{J}_Q &= -L_{QQ}X_Q - L_{Qq}X_q \\ \vec{J}_q &= -L_{Qq}X_Q - L_{qq}X_q\end{aligned}$$

Compare heat flow in an electrical insulator
with heat flow in an electrical conductor