Collective Effects

in

Equilibrium and Nonequilibrium Physics

Website: http://cncs.bnu.edu.cn/mccross/Course/

Caltech Mirror: http://haides.caltech.edu/BNU/

Today's Lecture: Hydrodynamics

- Systematic equations for the time evolution of systems near equilibrium
- Collective dynamics at low frequencies and long wavelengths of conserved quantities and broken symmetry variables
- Captures essential physics of new phases (Goldstone modes, etc.)
- Outline
    - ◇ Idea: two coupled systems
    - ◇ Continuum systems
    - ◇ Applications
        - ⋆ Spin wave hydrodynamics
        - ⋆ Equations of fluid dynamics and heat flow
    - ◇ Equilibrium, near equilibrium, and far from equilibrium

Equilibrium

Consider n macroscopic variables x_i and generalized forces X_i appearing in the thermodynamic identity as

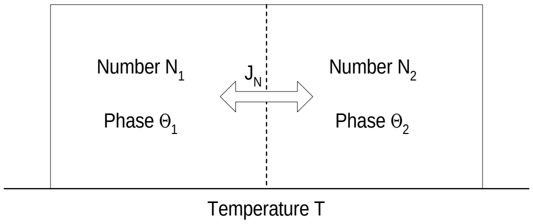
$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN + \sum_i \frac{X_i}{T}dx_i$$

- The x_i may be a quasi-conserved quantity (e.g. the partition of energy between two weakly coupled subsystems) or related to a broken symmetry "angle" variable
- The generalized force conjugate to the variable x_i is $X_i = T(\partial S/\partial x_i)_{E,x_{j\neq i},\ldots}$.
- The force can also be written $X_i = -(\partial E/\partial x_i)_{S,x_{j\neq i},\ldots} = -(\partial F/\partial x_i)_{T,x_{j\neq i},\ldots}$, etc.
- In the maximum entropy (microcanonical) or minimum free energy (canonical) state the conjugate fields are zero

  $$X_i = 0$$

  and there is no dynamics.

Example: Josephson Junction



Number N_1

Phase Θ_1

J_N

Number N_2

Phase Θ_2

Temperature T

$$TdS = \cdots - \Delta\mu dN + \Phi\Delta\Theta$$

with

$$\Phi = -dE_J/d\Delta\Theta$$

In the minimum free energy state $\Delta\mu = \Phi = 0$ and there is no phase dynamics or superflow

Near Equilibrium - Summary

- Near equilibrium the dynamics can be expanded in the small forces

$$\frac{dx_i}{dt} = \gamma_{ij} X_j$$

  with $\boldsymbol{\gamma}$ the *kinetic matrix*
- Kinetic matrix may have nondissipative (reactive) and dissipative components

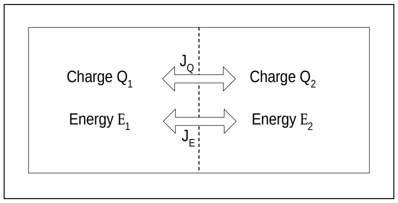
$$\boldsymbol{\gamma} = \boldsymbol{\gamma}^r + \boldsymbol{\gamma}^d$$

- Kinetic matrix satisfies *Onsager symmetry* relationships

$$\begin{array}{lll} \gamma_{ij} = \gamma_{ji} & \text{for } x_i, x_j \text{ same time reversal signature} & (\text{e.g. } N \text{ and } T) \\ \gamma_{ij} = -\gamma_{ji} & \text{for } x_i, x_j \text{ opposite time reversal signature} & (\text{e.g. } N \text{ and } \Theta) \end{array}$$

- Second law of thermodynamics places constraints on the matrix elements, e.g. $\gamma_{ii} \geq 0$.
- Kinetic matrix γ_{ij} can be related to correlation matrix $\langle \dot{x}_i(0)\dot{x}_j(t)\rangle$ via the fluctuation dissipation theorem

Example: Thermoelectric Effect



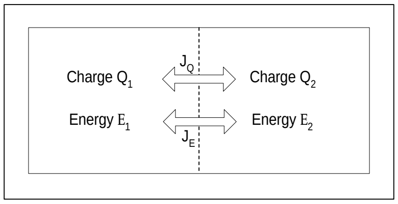
Two parts of an isolated system in contact via the exchange of energy E and charge Q.

- Thermodynamic identity

$$T\,dS = -(\Delta T/T)\,dE - \Delta\Phi\,dQ$$

  where $\Delta\Phi$ is the voltage difference $\Phi_2 - \Phi_1$ and $\Delta T = T_2 - T_1$.
- Conjugate thermodynamic forces are $-\Delta T/T$ and $-\Delta\Phi$.
- Equilibrium is given by the equality of temperature and electric potential, $\Delta T = \Delta\Phi = 0$.

Example: Thermoelectric Effect



Relaxation of small perturbations from equilibrium is described by the equations for the electric current I and energy (heat) current H

$$I = \dot{Q} = -\gamma_{QQ}\Delta\Phi - \gamma_{QE}\Delta T/T$$
$$H = \dot{E} = -\gamma_{EQ}\Delta\Phi - \gamma_{EE}\Delta T/T$$

We would like to learn something about the coefficients $\boldsymbol{\gamma}$

Onsager Symmetry Relations

- Derivation of the Onsager relationships depends on the relationship between fluctuations and dissipation.
- First review fluctuations from a thermodynamic point of view.

Fluctuations

- Microcanonical ensemble: probability $p(x_i)$ of a fluctuation of x_i away from equilibrium is given by the exponential of the entropy (divided by k_B).
- For macroscopic variables the fluctuations will be small, and we can expand the entropy about its maximum. For ease of notation redefine x_i so that its mean is zero.

$$S \approx S_0 - \frac{1}{2}\sum_{i,j=1}^{n} \beta_{ij} x_i x_j$$

  and then

$$p(\{x_i\}) = A \exp\left[-\frac{1}{2k_B}\sum_{ij} \beta_{ij} x_i x_j\right]$$

  a Gaussian probability distribution.
- The conjugate force is given by

$$\frac{X_i}{T} = (\partial S/\partial x_i) = -\sum_{j} \beta_{ij} x_j$$

Equal Time Correlations

- The equal time correlations are

$$\begin{aligned}\langle x_i x_j\rangle &= k_B(\beta^{-1})_{ij}\\ \langle X_i X_j\rangle &= k_B T^2 \beta_{ij}\\ \langle x_i X_j\rangle &= -k_B T \delta_{ij}\end{aligned}$$

- The last result will be important below
- The same results would be obtained by considering the free energy in the canonical ensemble, etc.

Correlation Functions: General Properties

The *correlation function* tells us how the fluctuations decay in time (putting $\langle x_i \rangle = 0$ again)

$$C_{ij}(t, t') = \langle x_i(t) x_j(t') \rangle.$$

- For time independent external conditions $C_{ij}(t, t')$ only depends on the time difference $\tau = t' - t$

$$C_{ij}(\tau) = \langle x_i(t) x_j(t + \tau) \rangle = \langle x_i(0) x_j(\tau) \rangle.$$

- Also we have

$$C_{ij}(0) = \langle x_i x_j \rangle$$

- Diagonal correlations $C_{ii}(\tau)$ are always less for nonzero τ than for $\tau = 0$. This is deduced from the inequality

$$\langle [x_i(t) \pm x_i(t + \tau)]^2 \rangle \geq 0$$

- Typically we expect the deviations from the mean to become uncorrelated at long times

$$C_{ij}(\tau \to \pm\infty) \to 0.$$

- By *shifting* the time coordinate we can relate the correlation function for negative times to the values for positive times

$$\begin{aligned} C_{ij}(-\tau) &= \langle x_i(t) x_j(t - \tau) \rangle && \text{definition} \\ &= \langle x_i(t + \tau) x_j(t) \rangle && \text{add } \tau \text{ to } t \end{aligned}$$

giving

$$C_{ij}(-\tau) = C_{ji}(\tau)$$

- In particular the diagonal correlation functions are *even* functions of time

$$C_{ii}(\tau) = C_{ii}(-\tau)$$

- This result does *not* depend on issues of *time reversibility* of the dynamical equations.

Correlation Functions: Time Reversal Symmetry

For the common case in thermodynamics that the microscopic equations are time reversible we can use time reversal symmetry to get further relationships.

The relationships depend on the time signature of the variable x_i: positions, energies, number… are unchanged under time reversal; momentum, superfluid phase… change sign.

- If x_i, x_j have the *same* signature under time reversal

  $$\begin{aligned} C_{ij}(\tau) &= \langle x_i(-t)x_j(-t-\tau)\rangle \quad \text{time reversal} \\ &= \langle x_i(t)x_j(t-\tau)\rangle \quad \text{time shift by } 2t \end{aligned}$$

  giving

  $$C_{ij}(\tau) = C_{ij}(-\tau)$$

  and all the components are even functions of τ.

- If x_i, x_j have *opposite* signatures under time reversal

  $$C_{ij}(\tau) = -C_{ij}(-\tau)$$

From the fluctuation-dissipation theorem we can expect that this gives symmetry results for the kinetic matrix (dissipation)

Onsager Symmetry Relation: Derivation

- Consider the correlation function of the fluctuations about equilibrium (remember we have set things up so $\langle x_i\rangle = 0$)

  $$C_{ij}(\tau) = \langle x_i(t)x_j(t+\tau)\rangle$$

- For variables x_i have the same symmetry under time reversal we have shown $C_{ij}(\tau) = C_{ij}(-\tau)$

  $$\langle x_i(t)x_j(t+\tau)\rangle = \langle x_i(t+\tau)x_j(t)\rangle$$

- Differentiating the two expressions w.r.t. τ and afterwards putting $\tau \to 0$ gives

  $$\langle x_i(t)\dot{x}_j(t)\rangle = \langle \dot{x}_i(t)x_j(t)\rangle$$

- Using the Onsager regression hypothesis this can be written

  $$\gamma_{jk}\langle x_i X_k\rangle = \gamma_{ik}\langle X_k x_j\rangle$$

- Using $\langle x_i X_k\rangle \propto \delta_{ik}$ this gives

  $$\gamma_{ji} = \gamma_{ij}$$

Onsager Symmetry Relation: Result

- We have proved that the kinetic matrix is *symmetric*. This is known as the Onsager symmetry relation.
- This result applies if x_i and x_j have the *same* behavior under time reversal; if they have the *opposite* behavior, e.g., one a velocity and one a displacement, a similar argument gives $\gamma_{ji} = -\gamma_{ij}$.
- Another way to get this result is from the fluctuation dissipation theorem proved in lecture 5. From those results it can be shown

  $$\gamma_{ij} = \frac{1}{k_B T} \int_{-\infty}^{0} \langle \dot{x}_i(t) \dot{x}_j(t+\tau) \rangle d\tau$$

  and the Onsager relation follows.

Other Constraints

There are other constraints on the kinetic matrix γ that arise from the requirement of the increase in entropy approaching equilibrium.

- The rate of change of entropy is given by

  $$T\dot{S} = \sum_i X_i \dot{x}_i = \sum_{ij} X_i \gamma_{ij} X_j$$

  The ij terms such that γ is antisymmetric (i.e. x_i and x_j of opposite time reversal signature) drop out from the sum—these are the reactive terms.
- Summing over i, j even and odd time reversal signature separately

  $$T\dot{S} = \sum_{i,j \text{ even}} X_i \gamma_{ij}^{(e)} X_j + \sum_{i,j \text{ odd}} X_i \gamma_{ij}^{(o)} X_j .$$

- Positive entropy production for any X_i places *constraints* on the $\gamma^{(e)}$, $\gamma^{(o)}$ matrices

  $$\gamma_{ii}^{(e)} \geq 0$$
  $$\gamma_{ij}^{(e)} \leq \sqrt{\gamma_{ii}^{(e)} \gamma_{jj}^{(e)}}$$

  and similar results for $\boldsymbol{\gamma}^{(o)}$

Thermoelectric Effect: Results

$$I = \dot{Q} = -\gamma_{QQ}\Delta\Phi - \gamma_{EQ}\Delta T/T$$

$$H = \dot{E} = -\gamma_{EQ}\Delta\Phi - \gamma_{EE}\Delta T/T$$

- *Seebeck effect:* voltage from a temperature difference with no current

$$\Delta\Phi = -\left(\frac{1}{T}\frac{\gamma_{EQ}}{\gamma_{QQ}}\right)\Delta T$$

- *Peltier effect*: heat current from an electric current with no temperature difference

$$H = \left(\frac{\gamma_{EQ}}{\gamma_{QQ}}\right) I$$

- Onsager relation provides a simple relationship between the Seebeck and Peltier coefficients.
- Second law requires $\gamma_{EQ} \leq \sqrt{\gamma_{QQ}\gamma_{EE}}$ so that the electrical and thermal conductances limit the magnitude of the thermoelectric effects.

Continuum Systems

Thermodynamic identity

$$T ds = d\varepsilon - \mu dn + \sum_i X_i d\xi_i$$

or in terms of the free energy

$$df = -s dT + \mu dn - \sum_i X_i d\xi_i$$

with s, ε, ξ_i the corresponding densities of conserved quantities or gradients of angle variables, e.g. for the superfluid

$$T ds = d\varepsilon - \mu dn + \mathbf{j}_s \cdot d\mathbf{v}_s$$

with $\mathbf{v}_s = (\hbar/m)\boldsymbol{\nabla}\Theta$ and $\mathbf{j}_s = n_s(\hbar/m)\boldsymbol{\nabla}\Theta$ the supercurrent.

- In the maximum entropy (microcanonical) or minimum free energy (canonical) state the conjugate fields T, μ, X_i are spatially uniform and there is no dynamics.
- For deviations from this state

$$\partial \xi_i / \partial t + \nabla \cdot \mathbf{j}_i = 0 \qquad \xi_i \text{ conserved quantity or gradient of angle}$$

- Currents $\mathbf{j}_i$ may have nondissipative (reactive) component and dissipative components

$$\mathbf{j}_i = \mathbf{j}^r + \mathbf{j}^d$$

  e.g. for the supercurrent in a superfluid $\mathbf{j}^r = -\mu/m$ and for the density in a normal fluid $\mathbf{j}^r = \mathbf{g}$
- The dissipative currents $\mathbf{j}^d$ are zero in equilibrium and near equilibrium can be expanded in gradients of the conjugate fields

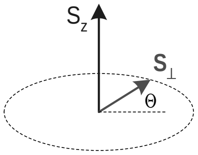
$$\mathbf{j}_i^d = \sum_j \boldsymbol{\gamma}_{ij} \cdot \nabla X_j$$

- Physical symmetries of the system restrict which terms in $\boldsymbol{\gamma}$ may be nonzero
- Kinetic matrix $\boldsymbol{\gamma}$ satisfies the *Onsager symmetry* conditions
- Positive entropy production places *constraints* on the coefficients $\boldsymbol{\gamma}$

Examples of Applications

1. Hydrodynamic theory of spin waves
2. Heat and mass flow in a fluid

Hydrodynamics Theory of Spin Waves



Thermodynamic identity

$$T ds = d\varepsilon - \mu_z ds_z - \mathbf{\Phi} \cdot d(\nabla\Theta) \text{ with } \mathbf{\Phi} = K\nabla\Theta$$

Phase dynamics

$$\dot{\Theta} = \mu_z + h_z^d \text{ with } h_z^d = 0 \text{ in uniform state}$$

- Form time derivative of entropy density, using conservation laws and phase dynamics

$$\frac{ds}{dt} = -\frac{1}{T}\nabla \cdot \mathbf{j}^\varepsilon + \frac{\mu_z}{T}\nabla \cdot \mathbf{j}^{s_z} - \frac{\mathbf{\Phi}}{T}\cdot\nabla(\mu_z + h_z^d)$$

- Entropy production equation

$$\frac{ds}{dt} = -\nabla\cdot\mathbf{j}^s + R \qquad \text{with} \qquad R \geq 0$$

with the entropy current and production

$$\mathbf{j}^s = T^{-1}(\mathbf{j}^\varepsilon - \mu_z \mathbf{j}^{s_z} + \mathbf{\Phi} h_z^d)$$
$$RT = -T^{-1}\mathbf{j}^s \cdot \nabla T - (\mathbf{j}^{s_z} + \Phi)\cdot\nabla\mu_z + h_z^d \, \nabla \cdot \mathbf{\Phi}$$

Dynamics

Entropy Production

$$RT = -T^{-1}\mathbf{j}^s \cdot \nabla T - (\mathbf{j}^{s_z} + \Phi)\cdot\nabla\mu_z + h_z^d \, \nabla \cdot \mathbf{\Phi}$$

Expand dissipative parts of $\mathbf{j}^s$, $\mathbf{j}^{s_z}$, h_z^d in gradients of conjugate fields ∇T, $\nabla\mu_z$, $\nabla \cdot \mathbf{\Phi}$

$$\mathbf{j}^{s_z} = -\Phi - D\nabla\mu_z$$
$$h_z^d = \zeta\nabla \cdot \mathbf{\Phi}$$
$$\mathbf{j}^s = -T^{-1}K\nabla T$$

(Off-diagonal terms are absent by mirror and time symmetries)

For positive entropy production D, ζ, K must be positive

Spin Waves

Coupled S_z, Θ equations

$$\dot{S}_z = K\nabla^2\Theta + \chi^{-1}D\nabla^2 S_z$$
$$\dot{\Theta} = \chi^{-1}S_z + K\zeta\nabla^2\Theta$$

The dispersion relation now gives a *damped* wave

$$\omega = \pm ck - \tfrac{1}{2}i\gamma k^2 + O(k^4)$$

with $c = \sqrt{K/\chi}$ and $\gamma = \chi^{-1}D + K\zeta$

Back Forward

Equations of Fluid Motion and Heat Transfer

Thermodynamic identity (ε, s are per mass)

$$d\varepsilon = T\,ds + \frac{p}{\rho^2}d\rho + \mathbf{v}\cdot d\mathbf{g}$$

Mass conservation (LL1.2)

$$\frac{\partial\rho}{\partial t} + \nabla\cdot\mathbf{g} = 0 \qquad \text{with} \qquad \mathbf{g} = \rho\mathbf{v}$$

Momentum conservation (LL15.1)

$$\frac{\partial(\rho\mathbf{v})}{\partial t} + \boldsymbol{\nabla}\cdot\boldsymbol{\Pi} = 0 \qquad \text{or} \qquad \frac{\partial(\rho v_i)}{\partial t} + \nabla_j \Pi_{ij} = 0$$

with (LL15.3)

$$\Pi_{ij} = p\delta_{ij} + \rho v_i v_j - \eta\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} - \frac{2}{3}\delta_{ij}\frac{\partial v_i}{\partial x_i}\right) - \zeta\delta_{ij}\frac{\partial v_i}{\partial x_i}$$

Entropy production (LL49.5-6)

$$\frac{\partial(\rho s)}{\partial t} + \nabla\cdot(\rho s\mathbf{v} - \frac{K}{T}\boldsymbol{\nabla}T) = \frac{K(\nabla T)^2}{T^2} + \frac{\eta}{2T}\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} - \frac{2}{3}\delta_{ij}\frac{\partial v_i}{\partial x_i}\right)^2 + \frac{\zeta}{T}\left(\frac{\partial v_i}{\partial x_i}\right)^2$$

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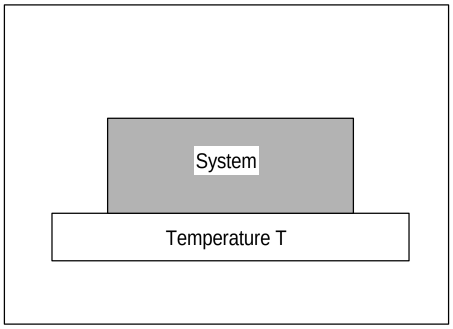
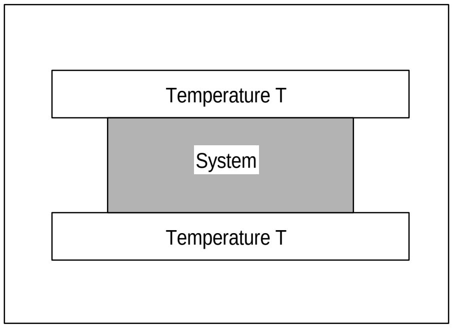
Equilibrium, Near Equilibrium, and Far from Equilibrium

Equilibrium v. Nonequilibrium



Equilibrium

Equilibrium v. Nonequilibrium



Equilibrium

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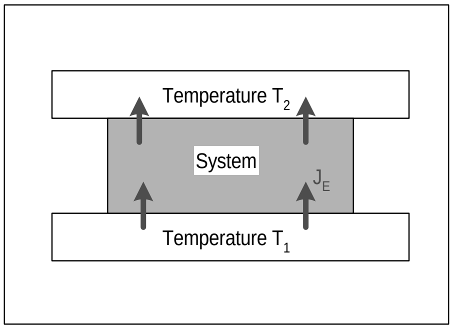
Equilibrium v. Nonequilibrium



Nonequilibrium

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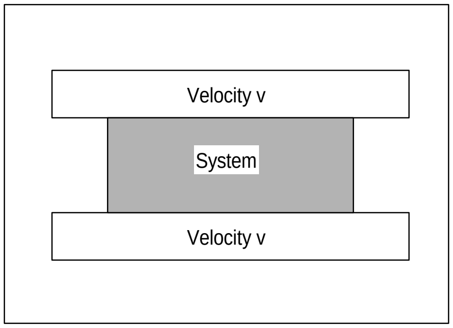
Equilibrium v. Nonequilibrium


Velocity v

System

Velocity v

Equilibrium

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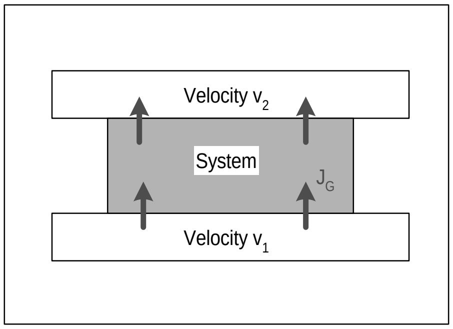
Equilibrium v. Nonequilibrium


Velocity v_2

System

J_G

Velocity v_1

Nonequilibrium

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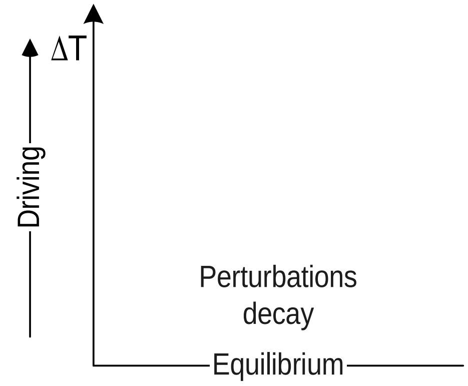
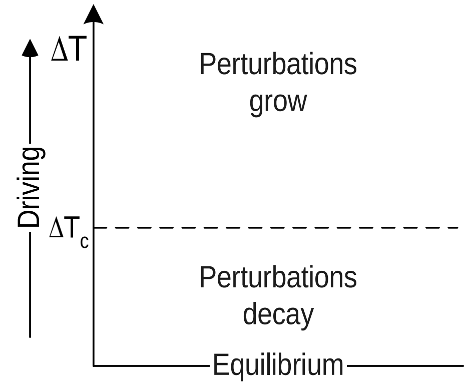
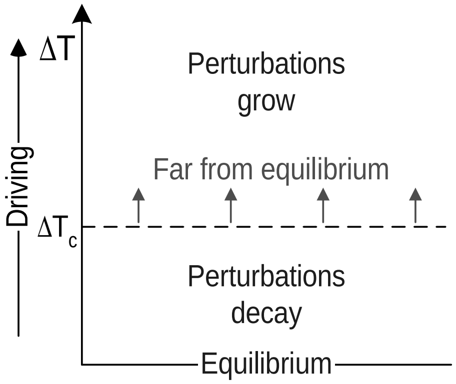
Equilibrium - Far From Equilibrium



Equilibrium - Far From Equilibrium



Equilibrium - Far From Equilibrium



Far From Equilibrium

- A macroscopic system may be globally far from equilibrium, but have small gradients of the thermodynamic fields so that locally it is near equilibrium
- Such a system may be treated with the systematic hydrodynamic equations that can be derived from basic thermodynamics with Onsager’s extensions
- These systems allow a quantitative understanding of phenomenon far from equilibrium
- Other systems far from equilibrium may not be near local equilibrium, e.g. biology, chemistry. For these quantitative descriptions are harder.