Collective Effects in Equilibrium and Nonequilibrium Physics

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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.)
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• 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

$$dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN + \sum_i \frac{X_i}{T} dx_i$$
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- The force can also be written \( X_i = -(\partial E / \partial x_i)_{S,x_j \neq i,...} = -(\partial F / \partial x_i)_{T,x_j \neq i,...} \), etc.
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- 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

\[ TdS = \cdots - \Delta \mu dN + \Phi \Delta \Theta \]

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 \( \gamma \) the kinetic matrix.
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\gamma = \gamma^r + \gamma^d
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- Kinetic matrix satisfies Onsager symmetry relationships

\[ \gamma_{ij} = \gamma_{ji} \quad \text{for} \ x_i, x_j \ \text{same time reversal signature} \quad (e.g. \ N \ \text{and} \ T) \]

\[ \gamma_{ij} = -\gamma_{ji} \quad \text{for} \ x_i, x_j \ \text{opposite time reversal signature} \quad (e.g. \ N \ \text{and} \ \Theta) \]
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• Second law of thermodynamics places constraints on the matrix elements, e.g. \( \gamma_{ii} \geq 0 \).

• Kinetic matrix \( \gamma_{ij} \) 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

\[ TdS = -\left(\frac{\Delta T}{T}\right)dE - \Delta \Phi dQ \]

where $\Delta \Phi$ is the voltage difference $\Phi_2 - \Phi_1$ and $\Delta T = T_2 - T_1$. 
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- 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
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\[
H = \dot{E} = -\gamma_{EQ} \Delta \Phi - \gamma_{EE} \Delta T / T
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We would like to learn something about the coefficients $\gamma$
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 $k_B$).
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- 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.
**Fluctuations**

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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

\[ \langle x_i x_j \rangle = k_B (\beta^{-1})_{ij} \]
\[ \langle X_i X_j \rangle = k_B T^2 \beta_{ij} \]
\[ \langle x_i X_j \rangle = -k_B T \delta_{ij} \]

- The last result will be important below
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• 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)

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

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

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

\[ C_{ij}(-\tau) = \langle x_i(t)x_j(t - \tau) \rangle \quad \text{definition} \]

\[ = \langle x_i(t + \tau)x_j(t) \rangle \quad \text{add } \tau \text{ to } t \]

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

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• 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.
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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.
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- If $x_i, x_j$ have the same signature under time reversal

$$C_{ij}(\tau) = \langle x_i(-t)x_j(-t - \tau) \rangle \quad \text{time reversal}$$

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and all the components are even functions of $\tau$. 
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- If $x_i$, $x_j$ have opposite signatures under time reversal
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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 $\langle x_i \rangle = 0$)

$$C_{ij}(\tau) = \langle x_i(t)x_j(t + \tau) \rangle$$
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• Differentiating the two expressions w.r.t. $\tau$ and afterwards putting $\tau \to 0$ gives

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

• Using the Onsager regression hypothesis this can be written

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\gamma_{jk}\langle x_iX_k \rangle = \gamma_{ik}\langle X_kx_j \rangle
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• Using \( \langle x_i X_k \rangle \propto \delta_{ik} \) this gives

\[
\gamma_{ji} = \gamma_{ij}
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Onsager Symmetry Relation: Result
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• 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 $\gamma_{ji} = -\gamma_{ij}$. 
Onsager Symmetry Relation: Result

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- 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 $\gamma$ that arise from the requirement of the increase in entropy approaching equilibrium.
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- 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 $\gamma$ is antisymmetric (i.e. $x_i$ and $x_j$ of opposite time reversal signature) drop out from the sum—these are the reactive terms.
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- Summing over $i, j$ even and odd time reversal signature separately

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

\[ I = \dot{Q} = -\gamma_{QQ} \Delta \Phi - \gamma_{EQ} \Delta T / T \]
\[ H = \dot{E} = -\gamma_{EQ} \Delta \Phi - \gamma_{EE} \Delta T / T \]
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- *Seebeck effect*: voltage from a temperature difference with no current

\[ \Delta \Phi = -\left( \frac{1}{T} \frac{\gamma_{EQ}}{\gamma_{QQ}} \right) \Delta T \]
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- **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
  \[ H = \left( \frac{\gamma_{EQ}}{\gamma_{QQ}} \right) I \]
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

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

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- 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.
Collective Effects in Equilibrium and Nonequilibrium Physics:  April 21, 2006

Continuum Systems

Thermodynamic identity

\[ T \, ds = d \varepsilon - \mu \, dn + \sum_i X_i \, d \xi_i \]

or in terms of the free energy

\[ df = -sdT + \mu \, dn - \sum_i X_i \, d \xi_i \]

with \( s, \varepsilon, \xi_i \) 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 \( \mathbf{v}_s = (\hbar/m) \nabla \Theta \) and \( \mathbf{j}_s = n_s (\hbar/m) \nabla \Theta \) the supercurrent.
• In the maximum entropy (microcanonical) or minimum free energy (canonical) state the conjugate fields $T, \mu, X_i$ are spatially uniform and there is no dynamics.
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• For deviations from this state

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

• 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 $\mathbf{j}^r = \mathbf{g}$
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$$\mathbf{j}_i = j^r_i + j^d_i$$

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• The dissipative currents $j^d_i$ are zero in equilibrium and near equilibrium can be expanded in gradients of the conjugate fields

$$j^d_i = \sum_j \gamma_{ij} \cdot \nabla X_j$$
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For deviations from this state

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  $\xi_i$ conserved quantity or gradient of angle

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• Positive entropy production places constraints on the coefficients $\gamma$
Examples of Applications

1. Hydrodynamic theory of spin waves

2. Heat and mass flow in a fluid
Hydrodynamics Theory of Spin Waves

Thermodynamic identity

\[ T ds = d\varepsilon - \mu_z ds_z - \Phi \cdot d(\nabla \Theta) \] with \( \Phi = K \nabla \Theta \)

Phase dynamics

\[ \dot{\Theta} = \mu_z + h^d_z \] with \( h^d_z = 0 \) in uniform state
Hydrodynamics Theory of Spin Waves

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

\[ \frac{ds}{dt} = -\frac{1}{T} \nabla \cdot \mathbf{j}^\epsilon + \frac{\mu_z}{T} \nabla \cdot \mathbf{j}^s_z - \frac{\Phi}{T} \cdot \nabla (\mu_z + h^d_z) \]
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• Entropy production equation

\[ \frac{ds}{dt} = -\nabla \cdot J^s + R \quad \text{with} \quad R \geq 0 \]

with the entropy current and production

\[ J^s = T^{-1}(j^\varepsilon - \mu_z j^{s_z} + \Phi h^d_z) \]

\[ RT = -T^{-1}j^s \cdot \nabla T - (j^{s_z} + \Phi) \cdot \nabla \mu_z + h^d_z \cdot \nabla \cdot \Phi \]
Dynamics

Entropy Production

\[ RT = -T^{-1} \mathbf{j}^s \cdot \nabla T - (\mathbf{j}^{sz} + \Phi) \cdot \nabla \mu_z + h^d_z \nabla \cdot \Phi \]
Dynamics

Entropy Production

\[ RT = -T^{-1} \mathbf{j}^s \cdot \nabla T - (\mathbf{j}^{s_z} + \Phi) \cdot \nabla \mu_z + h^d_z \nabla \cdot \Phi \]

Expand dissipative parts of \( \mathbf{j}^s, \mathbf{j}^{s_z}, h^d_z \) in gradients of conjugate fields \( \nabla T, \nabla \mu_z, \nabla \cdot \Phi \)

\[ \mathbf{j}^{s_z} = -\Phi - D \nabla \mu_z \]
\[ h^d_z = \zeta \nabla \cdot \Phi \]
\[ \mathbf{j}^s = -T^{-1} K \nabla T \]

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

Entropy Production

\[ RT = -T^{-1} \mathbf{j}^s \cdot \nabla T - (\mathbf{j}^{s_z} + \Phi) \cdot \nabla \mu_z + h^d_z \nabla \cdot \Phi \]

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\[ \mathbf{j}^s = -T^{-1} K \nabla T \]

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

For positive entropy production \( D, \zeta, K \) must be positive
Spin Waves

Coupled $S_z$, $\Theta$ equations

\[
\dot{S}_z = K \nabla^2 \Theta + \chi^{-1} D \nabla^2 S_z \\
\dot{\Theta} = \chi^{-1} S_z + K \zeta \nabla^2 \Theta
\]
Spin Waves

Coupled $S_z$, $\Theta$ equations

\[
\begin{align*}
\dot{S}_z &= K \nabla^2 \Theta + \chi^{-1} D \nabla^2 S_z \\
\dot{\Theta} &= \chi^{-1} S_z + K \zeta \nabla^2 \Theta
\end{align*}
\]

The dispersion relation now gives a damped wave

\[
\omega = \pm ck - \frac{1}{2} i \gamma k^2 + O(k^4)
\]

with $c = \sqrt{K/\chi}$ and $\gamma = \chi^{-1} D + K \zeta$
Equations of Fluid Motion and Heat Transfer

Thermodynamic identity ($\varepsilon$, $s$ are per mass)

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

Mass conservation (LL1.2)

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

Momentum conservation (LL15.1)

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

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)

$$\frac{\partial (\rho s)}{\partial t} + \nabla \cdot (\rho s \mathbf{v} - \frac{K}{T} \nabla T) = \frac{K (\nabla T)^2}{T^2} + \eta \frac{2}{2T} \left( \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} - \frac{2}{3} \delta_{ij} \frac{\partial v_i}{\partial x_i} \right)^2 + \frac{\zeta}{T} \left( \frac{\partial v_i}{\partial x_i} \right)^2$$
Equilibrium, Near Equilibrium, and Far from Equilibrium
Equilibrium v. Nonequilibrium

Equilibrium
Equilibrium v. Nonequilibrium

Equilibrium
Equilibrium v. Nonequilibrium

Nonequilibrium
Equilibrium v. Nonequilibrium

Equilibrium
Equilibrium v. Nonequilibrium

Nonequilibrium
Equilibrium - Far From Equilibrium

\[ \Delta T \]

Driving

Perturbations
decay

Equilibrium
Equilibrium - Far From Equilibrium

\[ \Delta T \]

- Perturbations grow
- Perturbations decay

\[ \Delta T_c \]

Equilibrium
Equilibrium - Far From Equilibrium

- Perturbations grow
- Perturbations decay
- 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
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• Such a system may be treated with the systematic hydrodynamic equations that can be derived from basic thermodynamics with Onsager’s extensions
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Far From Equilibrium

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• 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.