Physics 170:
Statistical Mechanics and Thermodynamics

Lecture 4A

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Outline

Last time…
we defined the Helmholtz free energy $F = E - \tau\sigma$
$$= -\tau \ln Z$$

Today

- More intuition for meaning of *free energy* from gases
- Start derivation of ideal gas law from first principles
- **Starting point:** First Law of Thermodynamics
  $\Rightarrow$ Fundamental Thermodynamic Relation

First Law of Thermodynamics
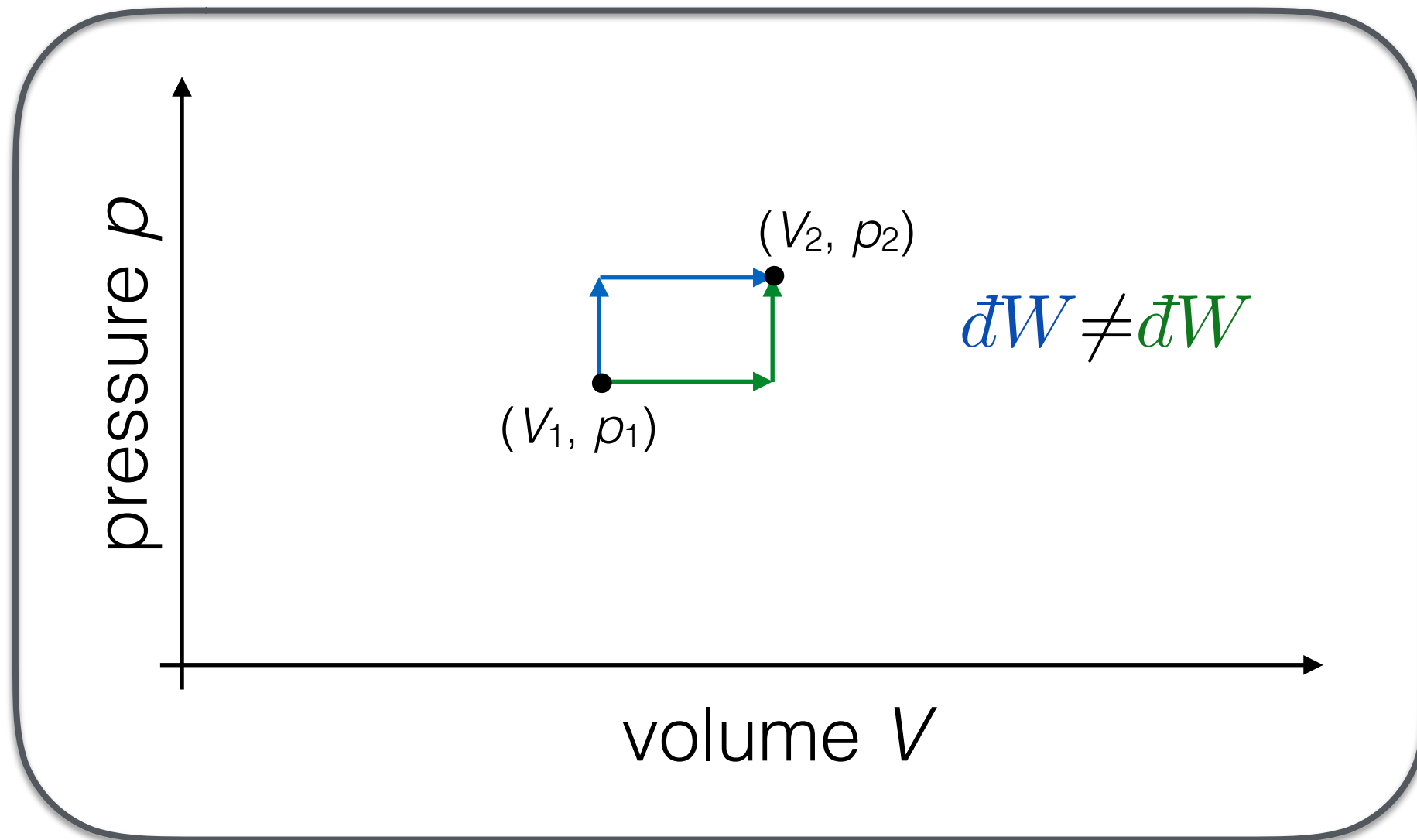
Energy is conserved:

work   heat

$$dE = đW + đQ$$

Why the $đ$ symbol?

- Changes $đ$ depend not only on initial & final states but on the path we take through parameter space

Inexact Differentials

$$dE = \dbar W + \dbar Q$$

"exact"   "inexact"

$\dbar W \neq \dbar W$

pressure p

volume V

(V_2, p_2)

(V_1, p_1)

First Law of Thermodynamics

Energy is conserved:

work   heat

$$dE = \text{\dj}W + \text{\dj}Q$$

Why the $\text{\dj}$ symbol?

- Changes $\text{\dj}$ depend not only on initial & final states but on the path we take through parameter space
- Work and heat are not **state functions**

EXERCISE 4A: FUNDAMENTAL THERMODYNAMIC RELATION

Objectives:

- Derive the **fundamental thermodynamic relation** from laws of thermodynamics
- Understand what it means for a physical process to be **(ir)reversible**
- Work towards calculating the **equation of state** of the **ideal gas**

Reading: Kittel & Kroemer, Ch. 3

Last time:

- We defined the **Helmholtz Free Energy** $F = E - \tau\sigma$
- We showed that $F = -\tau \ln Z$

1. *Fundamental thermodynamic relation.*
   The *First Law of Thermodynamics* is that energy is conserved. If one system is allowed to interact with another, energy can be exchanged in the form of either **work** W or **heat** Q. These two possible forms of energy exchange are summarized by the relation

$$dE = đW + đQ, \tag{1}$$

   where W represents work done on the system and Q represents heat absorbed by the system.

   a. The symbol $đ$ emphasizes that neither W nor Q is a **state function**: the differences $đW$ and $đQ$ depend not only on the initial and final macrostates but also on the path taken between them. By contrast the energy E is a state function. List at least three other state functions that you have encountered so far in this course.

   Temperature τ, entropy σ, magnetization M, spin excess X

   Today: pressure p, volume V

   b. The work $đW = -\mathbf{J} \cdot d\mathbf{x}$ arises from a displacement $d\mathbf{x}$ of an external parameters (i.e., a parameters of the Hamiltonian) resisted by a generalized force $\mathbf{J}$ exerted by the system. By "generalized," we mean that x_i need not have dimensions of length, and correspondingly J_i may not have dimensions of force, but the product $J_i x_i$ is always an energy.

      i. Perhaps the most familiar example of an external parameter is the volume V of a gas. What is the corresponding generalized force? Justify your answer with the aid of a sketch. (There is space on the next page.)
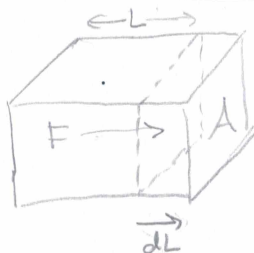
$$dV = A\,dL$$

$$p = F/A$$

$$dW = -F\,dL = -A \cdot p\,(dV/A)$$

$$= -p\,\underset{\underset{\text{generalized displacement}}{\llcorner}}{dV}$$

$W = $ work done $\underline{\underline{\text{on}}}$ system

$\therefore$ pressure p is the generalized force J

More generally:

$$J_i = -\frac{\partial E}{\partial x_i}$$

$\underset{\text{displacement}}{\llcorner}$

change in energy due to an external parameter (vs. heat: internal energy)

ii. If the external parameter we vary is a magnetic field $\mathbf{x} = \mathbf{B}$, what is the corresponding generalized force?

$$E = -\vec{M} \cdot \vec{B}$$

$$J_i = -\frac{\partial E}{\partial B_i} = M_i \quad \Longrightarrow \quad \boxed{\vec{J} = \vec{M}} \quad \text{Magnetization}$$

Slightly counterintuitive because it may seem that B is a force and M a displacement. But by definition, the displacement is a parameter in the Hamiltonian that we control—hence B.

c. In classical mechanics, work is the *only* way of changing a frictionless system's energy. The analog in statistical mechanics is an **adiabatic** process ($dQ = 0$).

   i. From a quantum mechanical perspective, an adiabatic process is one where the probability of occupying each eigenstate remains unchanged even while the associated energy eigenvalues may be changed by controlling external system parameters (e.g., magnetic field; volume). What macroscopic property (state function) then remains constant?
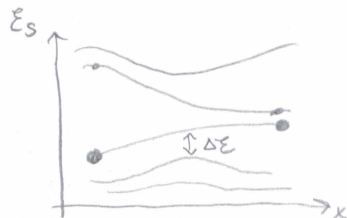

Entropy $\sigma - -\langle \ln P \rangle$ remains constant.

ii. Qualitatively, for a given change in system parameters (e.g., doubling the volume of a gas), how should one effect the change to ensure that the process is adiabatic?

- Fast enough to avoid heat exchange (thermal equilibration) with outside world.

- Slow enough to avoid diabatic transitions to other eigenstates

$$\left[\frac{d}{dt}\Delta\varepsilon \lesssim \frac{1}{2}\left(\frac{\Delta\varepsilon}{\hbar}\right)^2\right] \quad \text{c.f. Landau-Zener problem}$$

$\Rightarrow$ Need good thermal isolation; temperature of system may change.
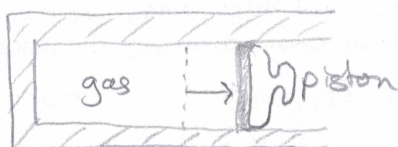
iii. If the occupations of eigenstates change, the corresponding change in the system's energy is the **heat** $đQ$. Assume that the process leading to this change is **quasi-static**, i.e., slow enough that the system is always in a well-defined equilibrium macrostate. Use the definition of temperature to find an expression for $đQ$.

Example

$\tau \leftarrow$ Energy

Energy changes due to both work **and** heat.

$$\frac{1}{\tau} = \frac{\partial\sigma}{\partial E}\Big|_x \quad\Longleftrightarrow\quad \tau = \frac{\partial E}{\partial\sigma}\Big|_x \quad\Longrightarrow\quad dE\Big|_x = \boxed{\tau\, d\sigma \equiv đQ}$$

Starting point: $dE = \frac{\partial E}{\partial \vec{x}}\Big|_\sigma \cdot d\vec{x} + \frac{\partial E}{\partial\sigma}\Big|_x \cdot d\sigma$

$\underbrace{\qquad}_{\substack{-\vec{J}\cdot d\vec{x} \\ \text{Work}}}$ $\underbrace{\qquad}_{\substack{\tau \\ \text{Heat}}}$

d. Based on Eq. 1, write down the **fundamental thermodynamic relation** between dE, dV, and $d\sigma$ for a system at pressure p and temperature τ.

$$dE = đW + đQ = -p\,dV + \tau\,d\sigma$$

2. *Relations between state functions.* Next class, we will derive from first principles the **equation of state** of the ideal gas, i.e., the relationship between its pressure, volume, and temperature. First, let us derive some useful general relations between the state functions.

   a. Following are some of the state functions that could be used to describe a homogeneous gas of N particles in thermal equilibrium:
      - Volume V
      - Pressure p
      - Temperature τ
      - Entropy σ
      - Energy E
      - Free energy F

      If I gave you the values of all of these quantities, the system would be overconstrained. How many are necessary to specify the macrostate of the gas?

      ✳ If I have a microscopic model (e.g., monatomic gas, non-interacting particles), it suffices to give V and τ ⟹ occupations of states ⟶ Everything else follows
      ⟶ Energy spectrum

      ✳ If I don't have such a model (e.g., effects of interactions?), I may learn something about the microscopics by measuring relations between state functions, e.g. $p(N, V, \tau)$ ⟵ equation of state

      ✳ Because in principal everything follows from V and τ, there are many relations between the state functions... eg:

   b. Based on the fundamental thermodynamic relation, the pressure is given by

      $$dE = -p\,dV + \tau\,d\sigma \implies \qquad p = -\left(\frac{\partial E}{\partial V}\right)_\sigma \qquad\qquad (2)$$

      However, we typically control the temperature and not the entropy. Derive an alternate expression for the <u>pressure</u> in terms of the Hemholtz free energy F and temperature τ.

      $$F = E - \tau\sigma$$

      $$dF = dE - \tau\,d\tau - \sigma\,d\tau = -p\,dV - \sigma\,d\tau$$

      $$\implies \boxed{p = -\left(\frac{\partial F}{\partial V}\right)_\tau}$$

c. Derive a similar differential relation for the entropy σ in terms of the Helmholtz free energy.

$$dF = -pdV - \sigma d\tau$$

$$\Rightarrow \boxed{\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V}$$

→ These relations are very useful, because we know how to calculate $F(N, \tau, V)$ from the partition function Z and can thence derive $p(N, \tau, V)$ and $\sigma(N, \tau, V)$.

d. Explain in words why the Helmholtz free energy $F(N, V, \tau)$ is useful for describing systems whose volume and temperature we control.

Based on the fundamental thermodynamic relation $dE = -pdV + \tau d\sigma$, we can relate changes $dF = -pdV - \sigma d\tau$ in free energy to changes in volume and temperature. So if we know dependence of F on V and τ, we can determine the state functions (p, σ) that we are not directly controlling.

e. Suppose that we slowly change the volume of a gas at constant temperature. Give a physical interpretation for the resulting change in the free energy of the gas.

$$dF|_\tau = -pdV$$

$$\Delta F|_\tau = \Delta W = \text{work done on the gas}$$

(or $-\Delta F$ is work done by the gas.)

⇒ Hence "free energy" — that portion of the total energy that is available to do work in an isothermal process.