

# Physics 170: Statistical Mechanics and Thermodynamics

## Lecture 5B

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Varian 238

# Midterm

When: Monday, October 30, 1:30 pm

Where: here (PAB 102-103)

You may bring **1 sheet** of handwritten notes.

Review opportunities

- Review problems (+ solutions)
- Course contents list on Canvas
- My office hours **Monday, 9:30 AM**

**EXERCISE 5B: FREE EXPANSION AND ENTROPY OF MIXING****Objectives:**

- Review how we derive **Maxwell relations**
- Compare examples of **irreversible** and **reversible** processes in thermodynamics
- Calculate the **entropy of mixing** between ideal gases

1. *Heat Capacity of a Gas of Diatomic Molecules* (continued from last time).

- a. Figure 1 shows the heat capacity  $C_V$  of a gas of  $H_2$ . Explain this graph as completely as possible. Label the values of the plateaus on the vertical scale.

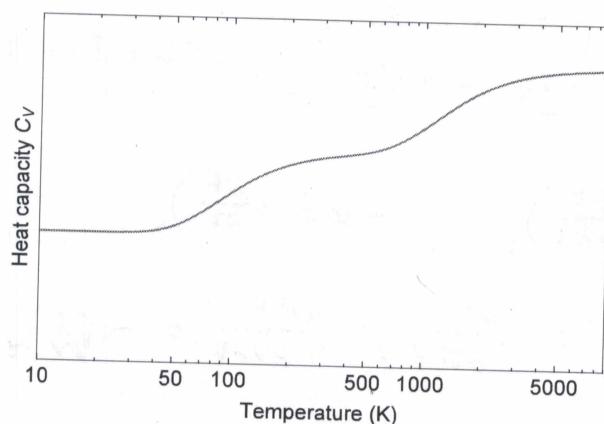


FIG. 1. Heat capacity of an  $H_2$  molecule in the gas phase as a function of temperature  $T$ .

See notes from last time (on next page).

- Q1. Figure 1 shows the heat capacity  $C_V$  of a gas of  $H_2$ . Explain this graph as completely as possible. Label the values of the plateaus on the vertical scale.

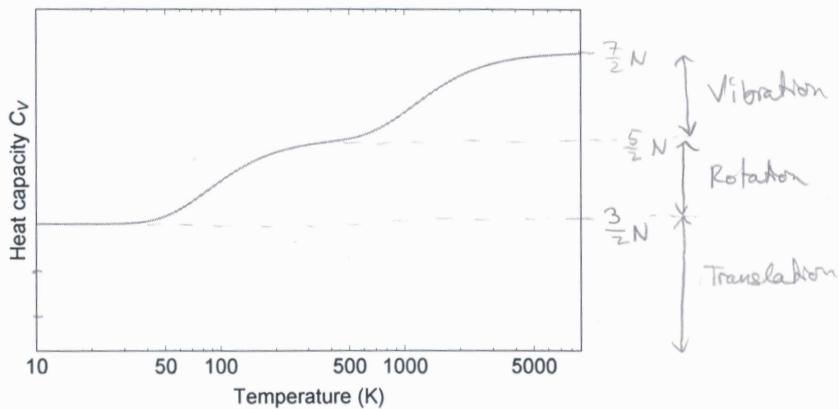


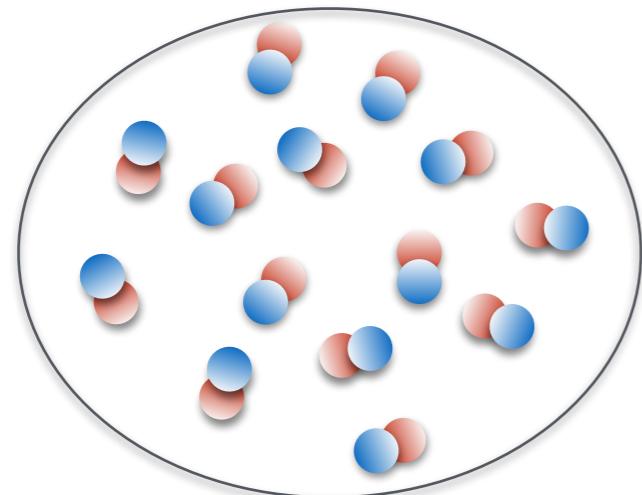
FIG. 1. Heat capacity of  $H_2$  gas as a function of temperature  $T$ .

- \* At low- $T$ , only vibrational degrees of freedom are accessible.
- \* L is quantized in units of  $\hbar$ , so rotational degrees of freedom start to matter for  $\tau_{\text{rot}} \sim \frac{\hbar^2}{2MR^2} \sim 90 \text{ K}$   $[2R \sim 70 \text{ pm} = \text{bond length in } H_2]$
- \* Vibrational frequency is higher ( $\omega_v > \omega_{\text{rot}}$ ) — so additional degrees of freedom become accessible @ high temperature

Note: in context of equipartition theorem, we loosely use "degree of freedom" to refer to a quadratic term in the Hamiltonian. So e.g. a free particle in 1D contributes 1 term (1/2 of energy), but a 1D harmonic oscillator contributes 2 terms (x and p  $\Rightarrow$  1+1 of energy). For the free particle, x does not contribute because there is no potential; neither does  $\Theta$  in a free rotor.

# Statistical Mechanics

Microscopic  
description



- Quantum mechanics
- Mechanics
- E&M

*Probability  
& Statistics*  
→

← *experiments*

Macroscopic  
properties

*E.g.:*  
Temperature  
Pressure  
Entropy  
Magnetization

Response functions:

- Heat capacity
- Magnetic susceptibility
- Compressibility

+ phase transitions, etc.

## Probability & Statistics

binomial, Poisson, Gaussian

## Ensembles

microcanonical, canonical, grand canonical

Fundamental assumption  
⇒ *maximization of entropy* ★

## Equations of State

E.g.,  $M(T,B)$  or  $p(N,T,V)$

## Response Functions

heat capacity, magnetic susceptibility,  
polarizability, compressibility, ...

- ★ In microcanonical ensemble (fixed  $N, E$ ): entropy of system
- ★ In canonical ensemble (fixed  $N, T$ ), entropy of system + reservoir  
⇒ Boltzmann factor, partition function, & Helmholtz free energy
- ★ In grand canonical ensemble (variable  $N$ ), ...

Reality often works the other way:  
measuring response functions &  
inferring microscopics

## Probability & Statistics

binomial, Poisson, Gaussian

## Ensembles

microcanonical, canonical, grand canonical

Fundamental assumption  
⇒ *maximization of entropy* ★

## Equations of State

E.g.,  $M(T,B)$  or  $p(N,T,V)$

## Response Functions

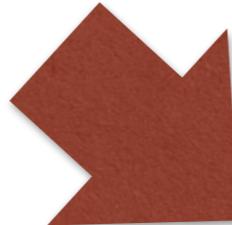
heat capacity, magnetic susceptibility,  
polarizability, compressibility, ...

*State functions*

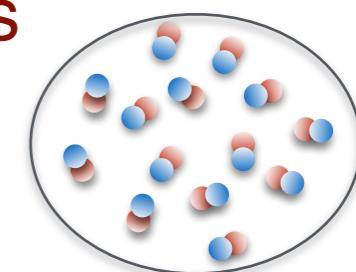
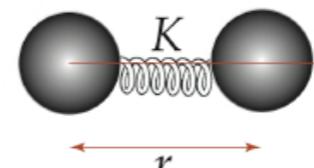
$p$ ,  $T$ ,  $V$ ,  $\sigma$ : redundant

⇒ thermodynamic relations

$$dE = -pdV + \tau d\sigma$$



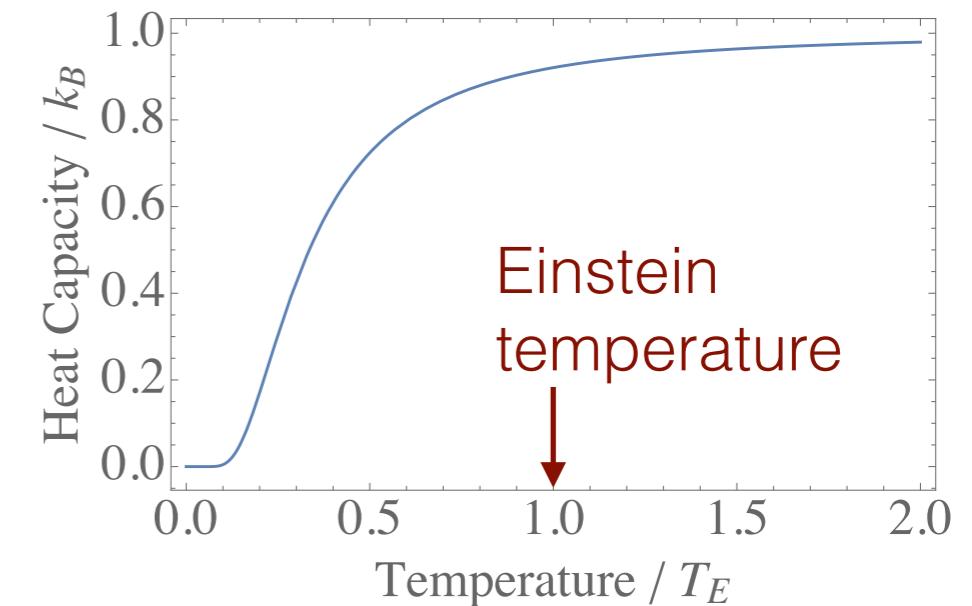
## Model Systems



↑↓↑↓↓↑↓↓↑↑

# Model Systems

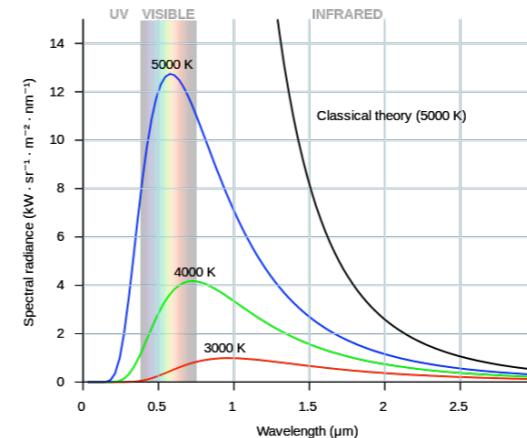
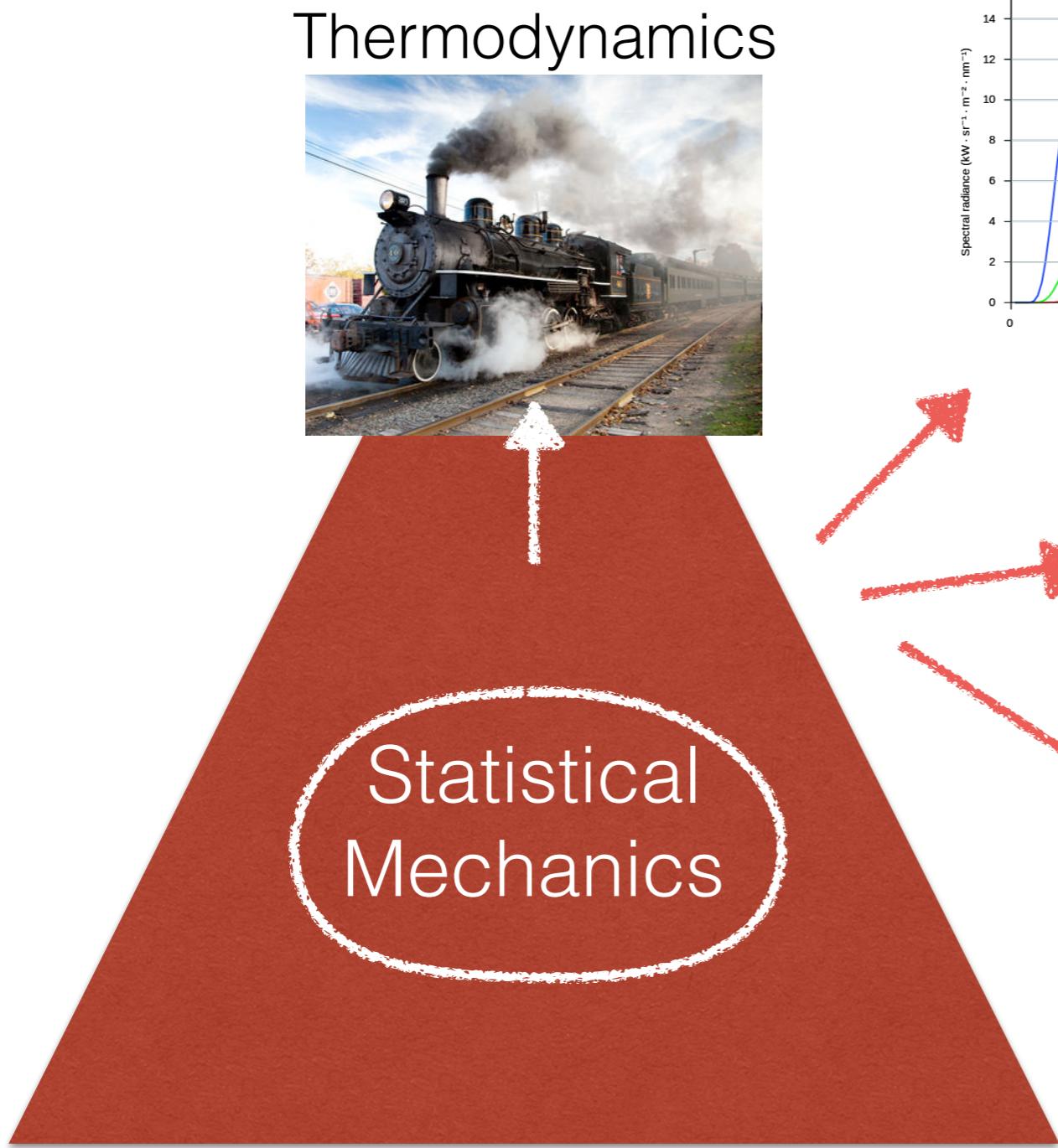
- Random walk  $\Rightarrow$  paramagnet, electric dipoles, polymer chain
- Harmonic oscillator
  - vibrations of molecules  
 $\Rightarrow$  heat capacities of solids & gases
  - photons & blackbody radiation
- Ideal (or non-ideal) gas
  - Classical thermodynamics: heat engines & refrigerators



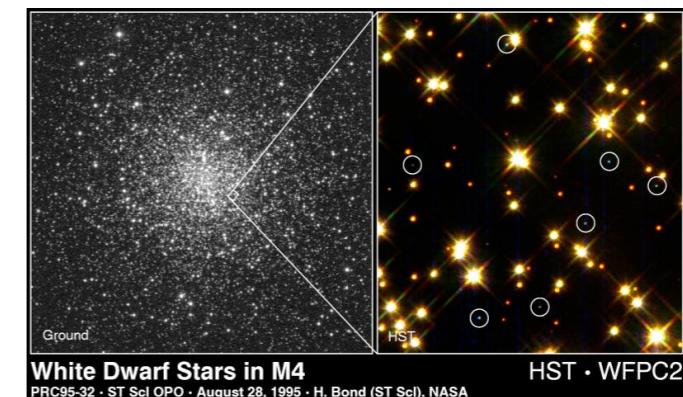
*When are our simple descriptions valid?*

*Where do they break down (e.g. classical vs. quantum gas)?*

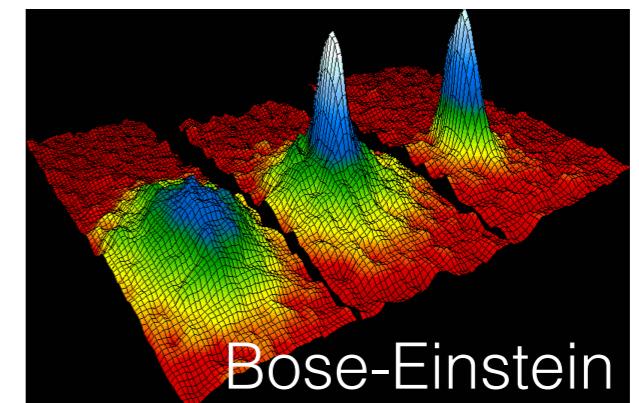
# Post-Midterm Topics



blackbody  
radiation



white dwarf  
stars  
(fermions)



Bose-Einstein  
condensate

# Laws of Thermodynamics

**Zero<sup>th</sup>:** If two systems are in equilibrium with a third system, they must be in thermal equilibrium with each other.

**First:** Heat is a form of energy, and energy is conserved.

**Second:** The entropy of a closed system tends to remain constant or to increase when a constraint internal to the system is removed.

**Third:** The entropy of a system approaches a constant value as the temperature approaches zero.

2. A useful Maxwell relation for calculating changes in entropy. Since the state functions  $\tau, \sigma, p, V$  form an overcomplete description of a gas, you can derive a number of relations between them and their derivatives. Starting from the fundamental thermodynamic relation, derive a Maxwell relation of the form:

$$\left( \frac{\partial \sigma}{\partial V} \right)_{\tau} = \left( \frac{\partial A}{\partial B} \right)_{V} \quad (1)$$

What are  $A$  and  $B$ ?

$$dE = -pdV + \tau d\sigma$$

$$dF = -p\underline{dV} - \sigma \underline{d\tau} \quad \text{← Use } F(N, \tau, V)$$

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

$$-\left( \frac{\partial p}{\partial \tau} \right)_{V} = \left( \frac{\partial^2 F}{\partial \tau \partial V} \right) = \left( \frac{\partial^2 F}{\partial V \partial \tau} \right) = -\left( \frac{\partial \sigma}{\partial V} \right)_{\tau}$$

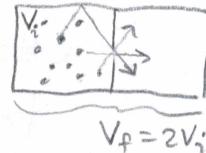
$$\therefore \left( \frac{\partial p}{\partial \tau} \right)_{V} = \left( \frac{\partial \sigma}{\partial V} \right)_{\tau}$$

$$[\text{so } A=p, B=\tau]$$

3. *Sudden expansion of an ideal gas.* Consider an ideal gas initially confined in a volume  $V_i$  at temperature  $T_1$ . We open a partition that allows the gas to expand to fill a volume  $V_f = 2V_i$ .

- a. How much work is done in the expansion? Explain.

No work is done in the expansion. The change in volume does not involve the particles exerting any force.



- b. What is the temperature after the expansion? Explain.

The temperature of the ideal gas depends only on (kinetic) energy  $E = \frac{3}{2} NT$ . Puncturing the wall (or removing partition) does not change the energy  $\Rightarrow$  gas equilibrates to same temperature after the expansion.

- c. What is the change of entropy in the expansion? Let  $\sigma_i$  denote the entropy of the gas before the expansion and  $\sigma_f$  the entropy after expansion. Calculate  $\sigma_f - \sigma_i$ .  
Hint: Use the relation you found in problem 2.

$$\left(\frac{\partial \sigma}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = \frac{N}{V}$$

$\curvearrowleft pV=NT$

$$\sigma_f - \sigma_i = \int_{V_i}^{V_f} \frac{N}{V} dV = N \ln(V_f) - N \ln(V_i) = N \ln(V_f/V_i)$$

$$\xrightarrow{V_f=2V_i} N \ln 2$$

- d. Was the process we considered **quasistatic** or not? Was it **reversible** or **irreversible**?

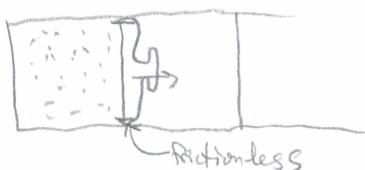
\* Not quasistatic - system is not in equilibrium throughout expansion.  
[We were still able to apply thermodynamic relations b/c we know equation of state & we know initial & final states ( $N, T, V$ ).]

\*  $\Delta T > 0 \Rightarrow$  irreversible.

- Returning the partition will not return the system to original configuration
- We could recompress the gas, but that requires coupling to another system, in which case the combined entropy will go up (2nd law).

- e. How would you change the manner in which the gas is allowed to expand in order to change the (ir)reversibility of the process, compared with the case considered above?

Let the gas expand by pushing against the wall, or slowly pull piston.



- \* can do @ const  $T$  or const  $P$
- important that state is well defined throughout.

4. *Entropy of mixing.* Two low-density gases of different species, each initially occupying the same volume  $V_i$  and at the same temperature  $\tau$ , are separated by a partition. The partition is punctured, allowing the gases to mix.

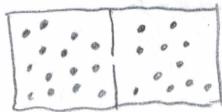
- a. Calculate the change in entropy  $\sigma_f - \sigma_i$  resulting from the mixing of the two gases, assuming there are  $N_1$  particles of species 1 and  $N_2$  particles of species 2.



- \* Each gas expands from  $V_i$  to  $V_f = 2V_i$ .
- \* This is just two simultaneous free expansions (in dilute limit).

$$\therefore \tau_f - \tau_i = (N_1 + N_2) N \ln 2$$

- b. Now suppose that the two species allowed to mix were the same. Would the change  $\sigma_f - \sigma_i$  be the same or different from your result in a.? Explain.



The result would be different,

For example, if  $N_1 = N_2$ , then  
the system is already in equilibrium.

In this case:  $\tau_f - \tau_i = 0$ .

- c. *Gibbs paradox.* Suppose that two gases of  $N_1$  and  $N_2$  **distinguishable particles** are allowed to mix. What is the change in entropy in this case? Explain.

We will come back to this another time.

- d. Which, if any, of the mixing processes considered above are **reversible**? Explain.

Removing the barrier between gases of  $N_1 = N_2$  identical particles is reversible. No increase in entropy. We could put the barrier back, and system would return to same macrostate.

Why should the situation be different if the particles are microscopically distinguishable? (See note on Gibbs paradox.)

- e. Are all of your results consistent with the ~~fundamental thermodynamic~~ relation? Explain.

$$dE = dW + dQ$$

$\Delta E \stackrel{?}{=} \Delta W + T \Delta S$  — Not true if  $\Delta S$  arises from a process that is not quasistatic.

**So, to be clear: yes, the results are consistent with the 1st Law. In the irreversible processes considered above, no work is done and there is no heat flow, but entropy nevertheless changes.**