PHY 341/641 Thermodynamics and **Statistical Mechanics** MWF: Online at 12 PM & FTF at 2 PM

Discussion for Lecture 9: Entropy and microstate multiplicity Record!!!

Reading: Chapters 3.1-3.2

- 1. Temperature and entropy
- 2. Heat and entropy

Course schedule for Spring 2021

schedule -- subject to frequent adjustment.) Reading assignments are for the An Introduction to Therm by Daniel V. Schroeder. The HW assignment numbers refer to problems in that text.

	Lecture date	Reading	Торіс	HW	Due date
1	Wed: 01/27/2021	Chap. 1.1-1.3	Introduction and ideal gas equations	1.21	01/29/2021
2	Fri: 01/29/2021	Chap. 1.2-1.4	First law of thermodynamics	1.17	02/03/2021
3	Mon: 02/01/2021	Chap. 1.5-1.6	Work and heat for an ideal gas		
4	Wed: 02/03/2021	Chap. 1.1-1.6	Review of energy, heat, and work	1.45	02/05/2021
5	Fri: 02/05/2021	Chap. 2.1-2.2	Aspects of entropy		
6	Mon: 02/08/2021	Chap. 2.3-2.4	Multiplicity distributions	2.24	02/10/2021
7	Wed: 02/10/2021	Chap. 2.5-2.6	Entropy and macrostate multiplicity	2.26	02/12/2021
8	Fri: 02/12/2021	Chap. 2.1-2.6	Review of entropy and macrostates	2.32	02/15/2021
9	Mon: 02/15/2021	Chap. 3.1-3.2	Temperature, entropy, heat	3.10a-b	02/17/2021
10	Wed: 02/17/2021	Chap. 3.3-3.4	Temperature, entropy, heat	3.23	02/19/2021
11	Fri: 02/19/2021	Chap. 3.5-3.6	Temperature, entropy, heat	3.28	02/22/2021
12	Mon: 02/22/2021	Chap. 3.1-3.6	Temperature, entropy, heat	3.38	02/24/2021
4.0					

Your questions –

From Parker -- Is there much significant difference between the classical definition of entropy dS=Q/T and the microscopic Boltzman view S=k In omega? Are they equivalent in some sense, or not? Doesn't the classical view not say anything about what entropy actually is, but does the microscopic view?

From Rich -- What are some examples of systems that operate with increasing or negative dS/dU graphs, what the book would call "Miserly" or "Enlightened" Systems? -When is it best to use dS= Q/T and when is it best to use dS=(integral of dT)? **From Annelise** -- This means that if a bit of energy passes from solid B to solid A, the entropy gained by A will be greater than the entropy lost by B". How is this possible? Later in section 3.3 the book says that sometimes the entropy will increase as it goes from one object to the next, but how is that possible? Where does that entropy come from?

From Kristen -- 1. Why is it that for a S versus U graph (Figure 3.1) a steep slope must correspond to a low temperature and a shallow slope to a high temperature? 2. Could you explain how the author used equation 3.6 to get to 3.7, I cannot follow his work. 3. Why does Cv go to zero when T goes to zero?

From Zezhong -- I wonder if there is a formal equation to transform epsilon/k to regular temperature units, also, I wonder if there is another way to understand temperature except entropy vs energy graph.

From Noah -- Does the residual entropy of a solid increase as the complexity of the solid increases, e.g. would a metal organic framework have a higher residual entropy than a diamond crystal?

Variables of thermodynamics

- **Temperature** $-T \ge 0$ in Kelvin scale
- \Box Volume V in units of m³
- □ Pressure P in units of Pascals (Newtons/m²)
- □ Entropy S in units of Joules/K
- □ Mass M in units of kg
- □ Number of particles N
- Energies of thermodynamics (in units of Joules)
 - □ Internal energy U
 - Enthalpy H
 - Helmholtz free energy F
 - Gibbs free energy G

Example of monoatomic ideal gas with energy U, volume V, N atoms:

$$S(N,V,U) \approx Nk_B \left(\ln \left(\frac{V}{N} \left(\frac{4\pi MU}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right)$$

Your book suggests that

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{NV}$$

Does this make sense?

$$\left(\frac{\partial S}{\partial U}\right)_{NV} = Nk_B \frac{3}{2U} = \frac{1}{T}$$

$$U = \frac{3}{2} N k_{B} T$$

Example of monoatomic ideal gas with energy U, volume V, N atoms: -- continued

$$S(N,V,U) \approx Nk_{B} \left(\ln \left(\frac{V}{N} \left(\frac{4\pi MU}{3Nh^{2}} \right)^{3/2} \right) + \frac{5}{2} \right)$$
$$\left(\frac{\partial S}{\partial U} \right)_{NV} = Nk_{B} \frac{3}{2U} = \frac{1}{T} \qquad U = \frac{3}{2} Nk_{B}T$$

How is this related to heat and heat capacity?

Recall the first law of thermo --

 $\Delta U = Q + W$

For a constant volume process, $\Delta U_V = Q_V$

Heat capacity at constant volume:

$$C_V = \frac{dQ_V}{dT} = \frac{d\Delta U_V}{dT} = \frac{3}{2}Nk_B$$

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$$\Rightarrow dU_V = dQ_V = dS_V T$$
 or $dS_V = \frac{dQ_V}{T}$

Question – is it reasonable to to use the entropy-heat relationship $dS = \frac{dQ}{T}$ (assuming "reversible" conditions)

Consider the monoatomic ideal gas:

 $PV = Nk_B T$ $S(N, V, U) = Nk_B \left(\ln \left(\frac{V}{N} \left(\frac{4\pi MU}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right)$

For constant volume process --

$$dU = dQ = \frac{3}{2}Nk_{B}dT$$
$$\Rightarrow dS = \frac{dQ}{T} = \frac{3}{2}Nk_{B}\frac{dT}{T}$$
$$\Rightarrow S_{f} - S_{i} = \frac{3}{2}Nk_{B}\ln\left(\frac{T_{f}}{T_{i}}\right)$$

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Question – is it reasonable to to use the entropy-heat relationship $dS = \frac{dQ}{T}$ (assuming "reversible" conditions)

Consider the monoatomic ideal gas:

 $PV = Nk_B T$ $S(N, V, U) = Nk_B \left(\ln \left(\frac{V}{N} \left(\frac{4\pi MU}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right)$

For isobaric process --

$$dQ = dU - dW = \frac{5}{2}Nk_B dT$$
$$\Rightarrow dS = \frac{dQ}{T} = \frac{5}{2}Nk_B \frac{dT}{T}$$
$$\Rightarrow S_f - S_i = \frac{5}{2}Nk_B \ln\left(\frac{T_f}{T_i}\right)$$

Does this really work?

Consider the isobaric case more carefully --

$$PV = Nk_B T$$
$$S(N, V, U) = Nk_B \left(\ln \left(\frac{V}{N} \left(\frac{4\pi MU}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right)$$

For isobaric process --

$$S_f - S_i = Nk_B \left(\ln\left(\frac{V_f}{V_i}\right) + \frac{3}{2} \ln\left(\frac{U_f}{U_i}\right) \right)$$

Previously we have shown that for the monoatomic ideal gas $-U = \frac{3}{2}Nk_BT$

$$\Rightarrow S_f - S_i = Nk_B \left(\ln\left(\frac{T_f}{T_i}\right) + \frac{3}{2}\ln\left(\frac{T_f}{T_i}\right) \right) = \frac{5}{2}Nk_B \ln\left(\frac{T_f}{T_i}\right)$$

Exercise: What is $S_f - S_i$ for an adiabatic or an isothermal process?

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More general expressions for heat capacity and entropy

$$dS_V = \frac{C_V dT}{T}$$

Example from your textbook.

Suppose that C_V for a cup of water is 840 J/K. What is the change of entropy when you heat the water from

$$T_i = 293$$
K to $T_f = 373$ K?
 $S_f - S_i = C_V \int_{293}^{373} \frac{dT}{T} = C_V \ln\left(\frac{T_f}{T_i}\right) = 203$ J/K

More examples -

Empirically we know of examples of matter changing phase at constant temperature and often with little change in volume. The heat involved with such a phase change is called the "latent" heat. The latent heat associated with the phase change of ice to water is 3.34 x 10⁵ J/kg at 273 K

The entropy change to when 1 kg of ice is melted at 273 K is:

$$S_f - S_i = \frac{3.34 \times 10^5 \text{ J}}{273 \text{ K}} = 1223 \text{ J/K}$$

More discussion about thermodynamic variables, particularly entropy.

Most of our discussion in class has focused on the behavior of an isolated system and the notions of the thermodynamic variables and measures assume that the system is in equilibrium. What happens when we have two systems?



What happens when the two systems can exchange energy?

N,V,P,
T,U,S
N,V,P,
T,U,S
N,V,P,
T,U,S
N,V,P,T,U,S
N,V,P,T,U,S
$$\bigcap_{AB} \Omega_{AB} \Omega_{AB}$$
At equilibrium, we expect the combined system
to have a new total internal energy U and the combined
multiplicity function

$$\Omega_{AB} = \sum_{i} \Omega_{A}(U_{Ai})\Omega_{B}(U - U_{Ai}) > \Omega_{A}(U_{A})\Omega_{B}(U_{B})$$

$$\Rightarrow S_{AB} = k_{B} \ln(\Omega_{AB}) > S_{isolated}$$

Summary of ideas on entropy and macrostate multiplicity

If an isolated system with many molecules is permitted to change, then, with overwhelming probability, the system will evolve to the macrostate of largest entropy and will subsequently remain in that macrostate.