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

# Discussion for Lecture 10: Entropy and microstate multiplicity Reading: Chapters 3.3-3.4 Record!!!

- 1. Entropy and pressure for ideal gas example
- **2.** Entropy for a spin  $\frac{1}{2}$  system

Online Colloquium: "A Tale of Seven Scientists and a New Philosophy of Science" — February 18, 2021 at 4 PM

Dr. Eric Scerri Faculty and Lecturer Department of Chemistry and Biochemistry University of California, Los Angeles Thursday, February 18, 2021, 4 PM EST Via Video Conference (contact wfuphys@wfu.edu for link information)

### **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 --**should we think of the Thermodynamic identity dU=T dS - P dV as a consequence of the laws of thermodynamics? Also does it apply to both the macroscopic and microscopic views, or just the macroscopic view?

**From Kristen --** 1. How can a temperature be infinite, as in the paramagnet example when U=0? 2. How can we apply the idea of paramagnets to the real world? I am having trouble visualizing 3. Could you define quasistatic and isentrophic in more detail? 4. In the last part of section 3.4, it talks about how since the thermodynamic identity applies there is a positive change in the entropy. Why is that?

**From Annelise** --Does the Cv of something change based on the mass of whatever you are calculating? I am assuming that it does and that is what J/(K\*Kg) means, but I just want to make sure. My discussion question for today is: why is the entropy highest when the U=0? I am confused when the book said that the temperature is infinite (meaning the system will gladly give up energy to any other system whose temperature is finite).

**From Rich** -- How do you derive the equations for change in entropy for a constant pressure process from the thermodynamic identity equation?

Your questions – continued

From Chao -- how does the formula 3.30 derived from the result of 3.29 and 3.28?

From Michael -- Can you give us an example of a realworld isentropic process that is both adiabatic and quasistatic? Recall for the mono atomic ideal gas:

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

Previously we have shown that

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

What if we consider the volume derivative of the entropy for a mono atomic ideal gaw?

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

Evaluting V derivative:



from the ideal gas law, this corresponds to  $\frac{P}{T}$ 

What all of this tell us?

While we have derived these results for a mono atomic ideal gas, perhaps we can assume that the functional dependences are more general.

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

In the following assume the particle number N is fixed. Suppose that the entropy can be written: S(V,U)This means that the differential can be written:

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V} dU + \left(\frac{\partial S}{\partial V}\right)_{U} dV$$

 $dS = \frac{1}{T}dU + \frac{P}{T}dV$ or: dU = T dS - P dV

Looks a lot like the first law of thermodynamics.

$$dU = Q + W$$
$$dU = TdS - PdV$$

$$Q \Leftrightarrow TdS \qquad \qquad W \Leftrightarrow -PdV$$

Note that this analysis implies that we should consider the internal energy U = U(S, V)

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V} dS + \left(\frac{\partial U}{\partial V}\right)_{S} dV = TdS - PdV$$
$$\Rightarrow T = \left(\frac{\partial U}{\partial S}\right)_{V} \qquad P = -\left(\frac{\partial U}{\partial V}\right)_{S}$$

Mathematical consistency

Suppose f(x, y) such that df = a(x, y)dx + b(x, y)dy

where 
$$a(x, y) = \left(\frac{\partial f}{\partial x}\right)_{y}$$
 and  $b(x, y) = \left(\frac{\partial f}{\partial y}\right)_{x}$ 

Check that second derivatives are consistent ---

$$\frac{\partial^2 f}{\partial y \partial x} = \frac{\partial}{\partial y} \left( \left( \frac{\partial f}{\partial x} \right)_y \right)_x = \frac{\partial^2 f}{\partial x \partial y} \qquad \Rightarrow \left( \frac{\partial a}{\partial y} \right)_x = \left( \frac{\partial b}{\partial x} \right)_y \qquad \text{Maxwell's relations}$$

For example: 
$$U = U(S, V)$$
  
 $dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV = TdS - PdV$   
 $\Rightarrow T = \left(\frac{\partial U}{\partial S}\right)_V P = -\left(\frac{\partial U}{\partial V}\right)_S$ 

Maxwell's relations show that

$$\left(\frac{\partial T}{\partial V}\right)_{S} = -\left(\frac{\partial P}{\partial S}\right)_{V}$$

Consider a system of spin 1/2 particles in a magnetic field B



Figure 3.6. A two-state paramagnet, consisting of N microscopic magnetic dipoles, each of which is either "up" or "down" at any moment. The dipoles respond only to the influence of the external magnetic field B; they do not interact with their neighbors (except to exchange energy). Copyright ©2000, Addison-Wesley.

Note that in this model, the spins only interact with the magnetic field B and do not interact with each other.

Which of these real systems in a constant magnetic field is better represented by this model?

- A. Ferromagnetic iron
- B. Water

Figure 3.7. The energy levels of a single dipole in an ideal two-state paramagnet are  $-\mu B$  (for the "up" state) and  $+\mu B$  (for the "down" state). Copyright ©2000, Addison-Wesley.



$$U = -\mu B \sum_{i=1}^{N} s_i \quad \text{where } s_i = \begin{cases} +1 & \text{spin up} \\ -1 & \text{spin down} \end{cases}$$

Here  $\mu$  denotes the magnetic moment including 1/2 factor B denotes the magnetic field strength

#### Example for N=100

$N_{\uparrow}$	$U/\mu B$	$M/N\mu$	$\Omega$	S/k	$kT/\mu B$	C/Nk
100	-100	1.00	1	0	0	
99	-98	.98	100	4.61	.47	.074
98	-96	.96	4950	8.51	.54	.310
97	-94	.94	$1.6 imes 10^5$	11.99	.60	.365
÷	:	:	÷	:	:	:
52	-4	.04	$9.3 imes10^{28}$	66.70	25.2	.001
51	-2	.02	$9.9 imes10^{28}$	66.76	50.5	
50	0	0	$1.0 imes 10^{29}$	66.78	$\infty$	
49	2	02	$9.9 imes10^{28}$	66.76	-50.5	
48	4	04	$9.3 imes10^{28}$	66.70	-25.2	.001
÷	:	:	÷	:	:	:
1	98	98	100	4.61	47	.074
0	100	-1.00	1	0	0	

Table 3.2. Thermodynamic properties of a two-state paramagnet consisting of 100 elementary dipoles. Microscopic physics determines the energy U and total magnetization M in terms of the number of dipoles pointing up,  $N_{\uparrow}$ . The multiplicity  $\Omega$  is calculated from the combinatoric formula 3.27, while the entropy S is  $k \ln \Omega$ . The last two columns show the temperature and the heat capacity, calculated by taking derivatives as explained in the text. Copyright ©2000, Addison-Wesley.

$$U = -\mu B \sum_{i=1}^{N} s_i \quad \text{where } s_i = \begin{cases} +1 & \text{spin up} \\ -1 & \text{spin down} \end{cases}$$

Here  $\mu$  denotes the magnetic moment including 1/2 factor

B denotes the magnetic field strength

$$N_{\uparrow} = \sum_{i=1}^{N} \delta_{s_{i},+1} \qquad N_{\downarrow} = \sum_{i=1}^{N} \delta_{s_{i},-1}$$
$$\Rightarrow U = -\mu B \left( N_{\uparrow} - N_{\downarrow} \right)$$
Magnetization:  $M \equiv -\frac{\partial U}{\partial B} = \mu \left( N_{\uparrow} - N_{\downarrow} \right)$ 

Macrostate multiplicity:  $\Omega(N, N_{\uparrow}) = \frac{N!}{N_{\uparrow}! (N - N_{\uparrow})!}$ 

Note that there is something fishy about the sign;  $\mu$  can + or – depending on whether the particle is a proton or electron

Entropy: 
$$\frac{S}{k_B} = \ln \left( \Omega(N, N_{\uparrow}) \right)$$
$$\approx N \ln N - N - N_{\uparrow} \ln N_{\uparrow} + N_{\uparrow} - \left( N - N_{\uparrow} \right) \ln \left( N - N_{\uparrow} \right) + \left( N - N_{\uparrow} \right)$$
$$= N \ln N - N_{\uparrow} \ln N_{\uparrow} - \left( N - N_{\uparrow} \right) \ln \left( N - N_{\uparrow} \right)$$

Evaluating the energy derivative of the entropy to determine *T* :

$$\frac{S}{k_B} = \ln\left(\Omega(N, N_{\uparrow})\right) \approx N \ln N - N_{\uparrow} \ln N_{\uparrow} - \left(N - N_{\uparrow}\right) \ln\left(N - N_{\uparrow}\right)$$

$$U = -\mu B \left( N_{\uparrow} - N_{\downarrow} \right) = -\mu B \left( 2N_{\uparrow} - N \right) \qquad N_{\uparrow} = \frac{N}{2} - \frac{U}{2\mu B}$$
$$\left( \frac{\partial S}{\partial U} \right)_{N,B} = \left( \frac{\partial S}{\partial N_{\uparrow}} \right)_{N,B} \left( \frac{\partial N_{\uparrow}}{\partial U} \right)_{N,B} = \frac{k_{B}}{2\mu B} \ln \left( \frac{N - U / \mu B}{N + U / \mu B} \right) = \frac{1}{T}$$

Expressing the last results in terms of U as a function of T:

$$U = N\mu B \left( \frac{1 - e^{2\mu B/k_B T}}{1 - e^{-2\mu B/k_B T}} \right) = -N\mu B \tanh\left(\frac{\mu B}{k_B T}\right)$$

### Plot of entropy vs U in scaled units for N=100





Heat capacity of system at constant field --

$$U = -N\mu B \tanh\left(\frac{\mu B}{k_B T}\right)$$
$$C_B = \left(\frac{\partial U}{\partial T}\right)_B = Nk_B \left(\frac{\mu B}{k_B T}\right)^2 \frac{1}{\cosh^2\left(\mu B / k_B T\right)}$$

