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

Discussion for Lecture 8: Entropy and microstate multiplicity

Reading: Chapters 2.1-2.6 Record!!!

- 1. Micro and macro states; microstate multiplicity
- 2. Basic ideas of probability; large samples
- 3. Ideal gas example
- 4. Entropy and microstate multiplicity

Course schedule for Spring 2021

(Preliminary schedule -- subject to frequent adjustment.) Reading assignments are for the **An Introduction to Thermal Physics** 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			
10	Wed: 02/17/2021				
11	Fri: 02/19/2021				
12	Mon: 02/22/2021				
13	Wed: 02/24/2021				
14	Fri: 02/26/2021	Chap. 4.1			
15	Man. 02/04/2024				
10	Mon: 03/01/2021				

Your questions – Including some from last time --

From Kristen -- Could we discuss what we would use equation 2.41 in, is it important we know how to derive it or will we be given the values of the variables in the equation? I am confused when the book talks about free expansion what they mean by "we have manufactured new entropy, right here on the spot". How can you manufacture new entropy? Why is it important to know the macrostate multiplicity versus the microstate multiplicity? Why can you use the multiplicity to determine the entropy, what is this really telling us about how they are related? In the lecture from Wednesday, slide 21, why at the top is kB not multiplied by N but at the bottom it is?

From Parker -- The second law of thermodynamics states that the total entropy of the universe tends to increase, do we say it is not a fundamental law in one sense because of the probabilistic nature of it? The first law (that the change in internal energy is the work done on the system plus heat) is fundamental in the sense that it is a deterministic not probabilistic phenomenon. what sort of processed can be approximated as reversible on a macroscopic scale? Everyday life examples mostly, and why?

From Chao -- Can you explain more on the relationship between multiplicity function and area of momentum hypersphere? What does the volume of momentums stand for, and while we can calculate it, why it can use the area of a hypersphere to stand for it?

From Rich -- How do you distinguish between reversible and irreversible processes? For example, wouldn't melting ice increase entropy yet this is still reversible? I am still confused how processes that create entropy are irreversible? For example, melting ice increases entropy but this is not irreversible? Similar to the first question, I know the formula for Gibb's Free Energy is G=H-TS. Does this show entropy can be converted to enthalpy, and does this violate the second law of thermodynamics?

From Annelise -- Why does heat flow from warm to cold if the warmer something is the more entropy it has?

From Michael -- Is the reason that entropy is always increasing is because the universe is constantly increasing? When calculating the multiplicity of a gas such as we did for our homework, is the radius we are using always going to be sqrt(2mU). If so why/why not?

From Zezhong -- Is the reason that entropy is always increasing is because the universe is constantly increasing? I still get confused about the Gibbs Paradox, I wonder how this paradox works since the description in the textbook seems vague for me

From Leon -- Could we review a bit on the multiplicity of a monatomic ideal gas? I'm still a bit confused with the concept of momentum space and the sphere, and/other equations associated with / them ing 2021 -- Lecture 8

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

From last Friday's lecture --

Carnot invented a very efficient ideal cycle which Clausius further analyzed as "entropy" *S* which is related to heat according to S_f



 $Q_{ABCD} = Q_A + Q_B + Q_C + Q_D$ $Q_A = 0 \quad \text{(adiabatic at } S_1\text{)}$ $Q_B \text{ isothermal at } T_2$ $Q_C = 0 \quad \text{(adiabatic at } S_2\text{)}$ $Q_D \text{ isothermal at } T_1$ $Q_{ABCD} = (S_2 - S_1)(T_2 - T_1)$

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Some details

Ideal gas equation of state $PV = Nk_BT$

Ideal gas internal energy $U = \frac{Nk_BT}{\gamma - 1}$

First law of thermodynamics

 $\Delta U = Q + W$

For isothermal process $\Delta U = 0$ and Q = -W

$$Q_B = Nk_B T_2 \ln\left(\frac{V_3}{V_2}\right) \qquad Q_D = Nk_B T_1 \ln\left(\frac{V_1}{V_4}\right)$$

Also note that because of adiabatic ideal gas equations -- $V_1 T_1^{1/(\gamma-1)} = V_2 T_2^{1/(\gamma-1)}$ and $V_3 T_2^{1/(\gamma-1)} = V_4 T_1^{1/(\gamma-1)}$ $\Rightarrow \frac{V_3}{V_2} = \frac{V_4}{V_1} \Rightarrow Q_{ABCD} = Nk_B \ln \left(\frac{V_3}{V_2}\right) (T_2 - T_1)$ PHY 341/641 Spring 2021 -- Lecture 8

2/12/2021

Summary of results



From Wednesday's lecture --

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

Example-- Consider a system at fixed U and N expanding from $V_i \rightarrow V_f$:

$$S(N, V_f, U) - S(N, V_i, U) = Nk_B \ln\left(\frac{V_f}{V_i}\right)$$

From Carnot example

$$\frac{Q_B}{T_2} = Nk_B \ln\left(\frac{V_3}{V_2}\right) = -\frac{Q_D}{T_1} = S_2 - S_1$$

Some details from "derivation" of Sackur-Tetrode equation

Microstate: the "distribution" of particles in phase space:

$$\Rightarrow D(\{q_1\cdots q_{3N}\},\{p_1\cdots p_{3N}\},t)$$

Macrostate multiplicity based on total ("internal") energy U:

$$\Omega(N,U) = C \int d^{3N} q d^{3N} p D(\{q_i\},\{p_i\}) \delta(H(\{q_i\},\{p_i\})-U))$$

$$\square$$
Dirac delta
function
$$Hamiltonian$$

In practice, we will assume that *D* is uniform.

Since the atoms are in a box of volume *V*:

$$\int d^{3N}q \Longrightarrow V^N$$

For an ideal gas with *N* atoms of mass *M*:

$$H(\{q_i\},\{p_i\}) = \frac{1}{2M} \sum_{i=1}^{3N} p_i^2$$

Impose constraint that the only non-trivial contributions

come from $\frac{1}{2M} \sum_{i=1}^{3N} p_i^2 = U$. In order simplify the mathematics,

first perform an intermediate calculation for

$$X(N,U) \equiv \int d^{3N} p \Theta \left(U - H\left(\{q_i\}, \{p_i\} \right) \right)$$



Define a radial variable for the 3N momentum space

Using
$$C = \frac{1}{h^{3N}N!}$$

When the dust clears --
 $\Omega(N,V,U) = \frac{V^N 2\pi M}{h^{3N}N!} \frac{(2\pi MU)^{3N/2-1}}{\Gamma\left(\frac{3N}{2}\right)}$
 $\approx \frac{V^N}{h^{3N}N!} \frac{\pi^{3N/2}}{(3N/2)!} \left(\sqrt{2MU}\right)^{3N}$

Boltzmann's idea was to use the multiplicity function to calculate the entropy --

 $S = k_B \ln(\Omega(N, V, U))$

$$\Omega(N,V,U) \approx \frac{V^{N}}{h^{3N}N!} \frac{\pi^{3N/2}}{(3N/2)!} \left(\sqrt{2MU}\right)^{3N}$$
$$\approx \left(\frac{V}{N} \left(\frac{4\pi MU}{3Nh^{2}}\right)^{3/2} e^{5/2}\right)^{N}$$

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

Sackur-Tetrode equation --

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

Example-- Consider a system at fixed U and N expanding from $V_i \rightarrow V_f$:

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Digression on δ and Θ functions

Properties of δ function : $\delta(x) = \begin{cases} 0 & \text{for } x \neq 0 \\ \infty & \text{for } x = 0 \end{cases}$ $\int_{-\epsilon}^{\epsilon} \delta(x) dx = 1$ $\int_{a-\epsilon}^{a+\epsilon} \delta(x-a) f(x) dx = f(a) \quad \text{for any reasonable function } f(x)$ Properties of Θ function :



Volume and surface integrals --

Example "hypersphere" for three dimensions --

r

volume
$$\rightarrow X(r) \equiv \int_{\text{sphere}} \sin\theta d\theta d\varphi s^2 ds = \int (\text{angular}) \int_{0}^{r} s^2 ds = 4\pi \frac{1}{3}r^3$$

surface $\rightarrow \frac{dX(r)}{dr} \equiv 4\pi r^2$

Other points to remember Basic ideas of probability theory mean (average) value and variance.

For continous variables -- continuous probability function P(x)

for
$$-\infty \le x \le \infty$$
 $\int_{-\infty}^{\infty} P(x) dx = 1$

Mean value:
$$\mu = \int_{-\infty}^{\infty} x P(x) dx$$
 Variance: $\sigma^2 = \int_{-\infty}^{\infty} (x - \mu)^2 P(x) dx$

For discrete variables -- continuous probability function P(n)

for
$$0 \le n \le \infty$$

$$\sum_{n=0}^{\infty} P(n) = 1$$

Mean value: $\mu = \sum_{n=0}^{\infty} nP(n)$ Variance: $\sigma^2 = \sum_{n=0}^{\infty} (n-\mu)^2 P(n)$

Some ideas about the second law of thermodynamics

- **Kelvin-Planck**: It is impossible to construct an engine which, operation in a cycle, will produce no other effect than the extraction of energy from a reservoir and the performance of an equivalent amount of work.
- **Clausius**: No process is possible whose sole result is cooling a colder body and heating a hotter body.
- Gould-Tobochnik: There exists an additive function of state known as the entropy S that can never decrease in an isolated system.
- Schoeder: Any large system in equilibrium will be found in the microstate with the greatest multiplicity (aside from fluctuations that are normally too small to measure.)

Up to now, we have focused on describing a single isolated sample. What happens when we have 2 samples that are somehow related to eachother?



Figure 2.3. Two Einstein solids that can exchange energy with each other, isolated from the rest of the universe. Copyright ©2000, Addison-Wesley.

$$\begin{split} \Omega_{total} &= \Omega_A \Omega_B \\ \frac{S_{total}}{k_B} &= \ln \Omega_A + \ln \Omega_B = \frac{S_A}{k_B} + \frac{S_B}{k_B} \\ & \text{PHY 341/641 Spring 2021 -- Lecture 8} \end{split}$$

Mixing of two gases, initially partitioned --



Figure 2.15. Two different gases, separated by a partition. When the partition is removed, each gas expands to fill the whole container, mixing with the other and creating entropy. Copyright ©2000, Addison-Wesley.