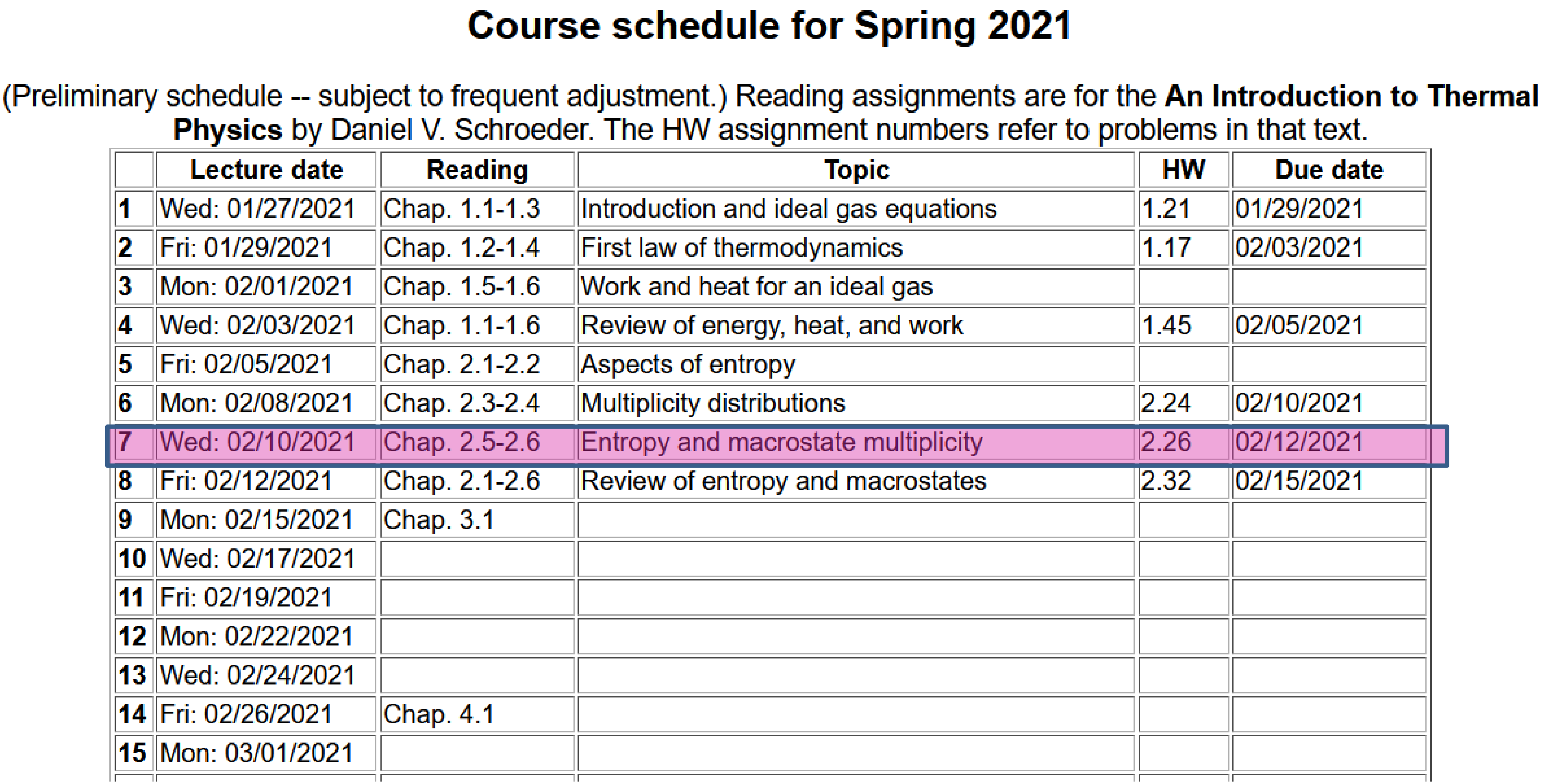
PHY 341/641 Thermodynamics and Statistical Mechanics
MWF: Online at 12 PM & FTF at 2 PM

Discussion for Lecture 7:
Entropy and microstate multiplicity

Reading: Chapters 2.5-2.6

1. **Micro and macro states of an ideal gas**
2. **Entropy and microstate multiplicity**

Record!!!



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	Topic	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	Mon: 03/01/2021				

Your questions –

From Kristen -- 1. 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? 2. 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?

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.

From Chao -- Can you explain more on the relationship between multiplicity function and area of momentum hypersphere?

From Rich -- How do you distinguish between reversible and irreversible processes? For example, wouldn't melting ice increase entropy yet this is still reversible?

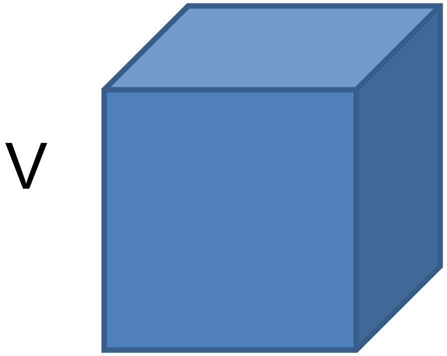
From Annelise -- Why does heat flow from warm to cold if the warmer something is the more entropy it has?

From Michael -- Is the reason that entropy is always increasing is because the universe is constantly increasing?

From Zezhong -- Is the reason that entropy is always increasing is because the universe is constantly increasing?

Estimating the multiplicity function for a monoatomic ideal gas.

From classical mechanics, assuming each atom is labeled ("distinguishable")



Suppose there are N atoms within volume V, each having coordinates and momenta --

$$x_i, y_i, z_i, p_{xi}, p_{yi}, p_{zi}$$

$$i = 1, 2, \ldots .N$$

In fact, these $6N$ variables that characterize each particle each vary in time according to Newton's laws -- $x_i(t), y_i(t), z_i(t), p_{xi}(t), p_{yi}(t), p_{zi}(t)$

This *6N* dimensional space is called phase space

Phase space

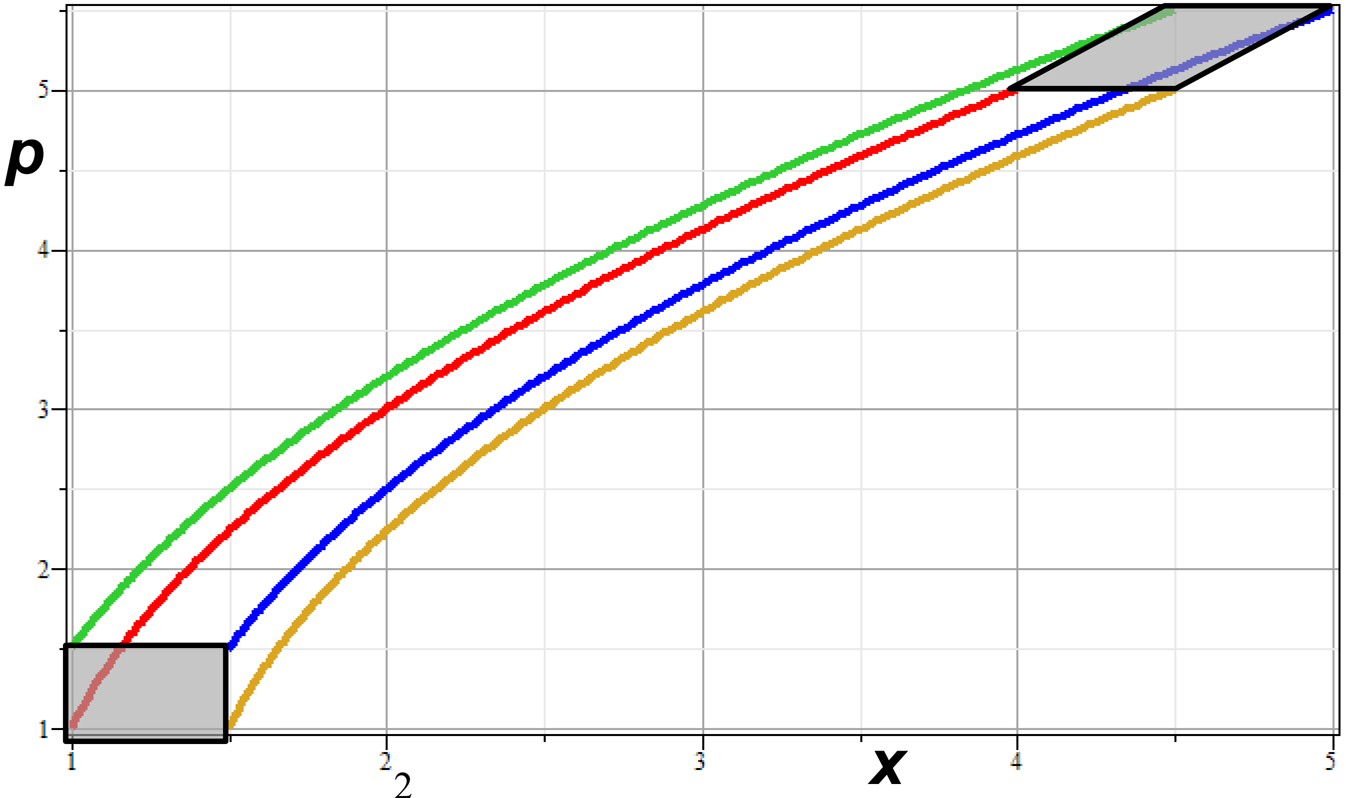
Phase space is defined at the set of all coordinates and momenta of a system:

$$\left(\{q_\sigma(t)\},\{p_\sigma(t)\}\right)$$

For a d dimensional system with N particles, the phase space corresponds to $2dN$ degrees of freedom.

The notion of density of particles in phase space is simply the ratio of the number of particles per unit phase space volume. It seems reasonable that under conditions where there are no sources or sinks for the particles, that the density should remain constant in time.

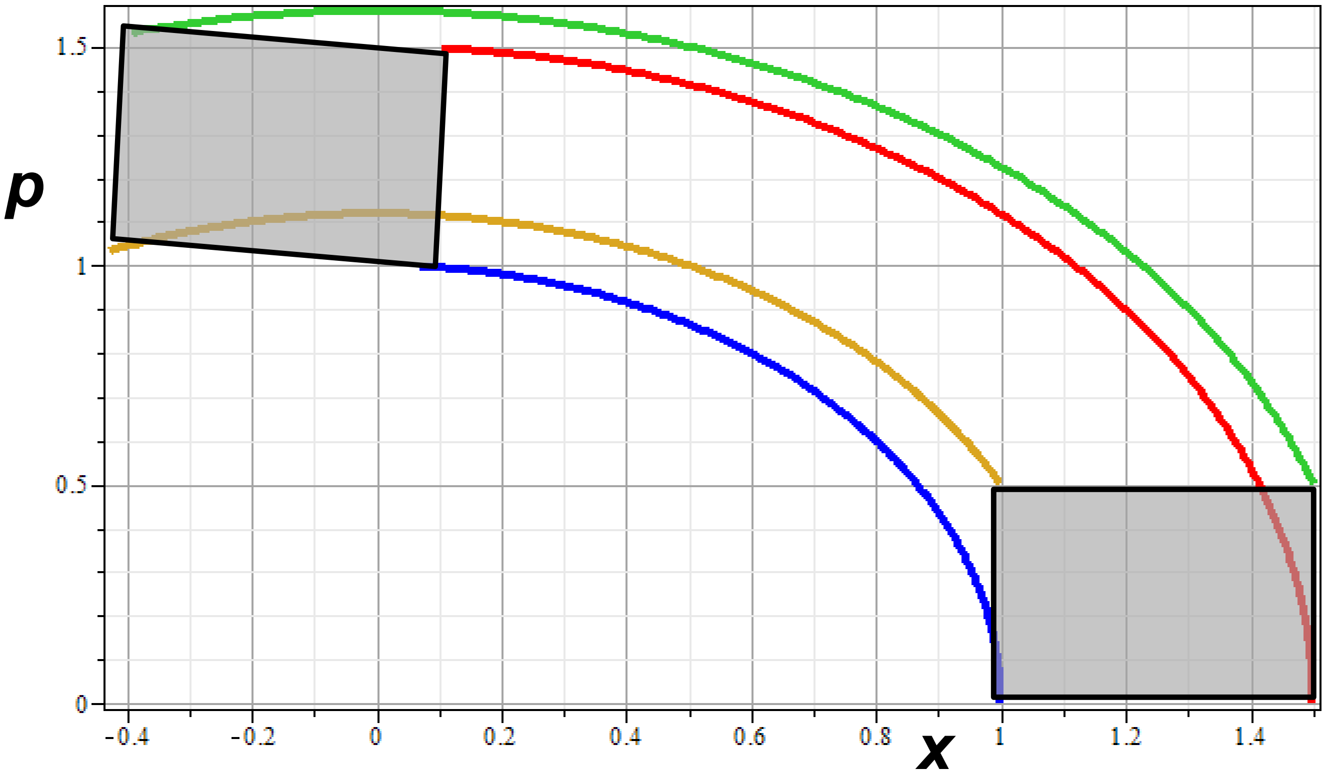
Phase space diagram for one-dimensional motion due to constant force



$$H(x,p)=\frac{p^2}{2m}-F_0x \qquad \dot{p}=F_0 \qquad \dot{x}=\frac{p}{m}$$

$$p_i(t)=p_{0i}+F_0t \qquad x_i(t)=x_{0i}+\frac{p_{0i}}{m}t+\frac{1}{2}F_0t^2$$

Phase space diagram for one-dimensional motion due to spring force



$$H(x,p)=\frac{p^2}{2m}+\frac{1}{2}m\omega^2x^2 \qquad \dot{p}=-m\omega^2x \qquad \dot{x}=\frac{p}{m}$$

$$p_i(t)=p_{0i}\cos\left(\omega t+\theta_{0i}\right) \qquad x_i(t)=\frac{p_{0i}}{m\omega}\sin\left(\omega t+\theta_{0i}\right)$$

Liouville’s Theorem (1838)

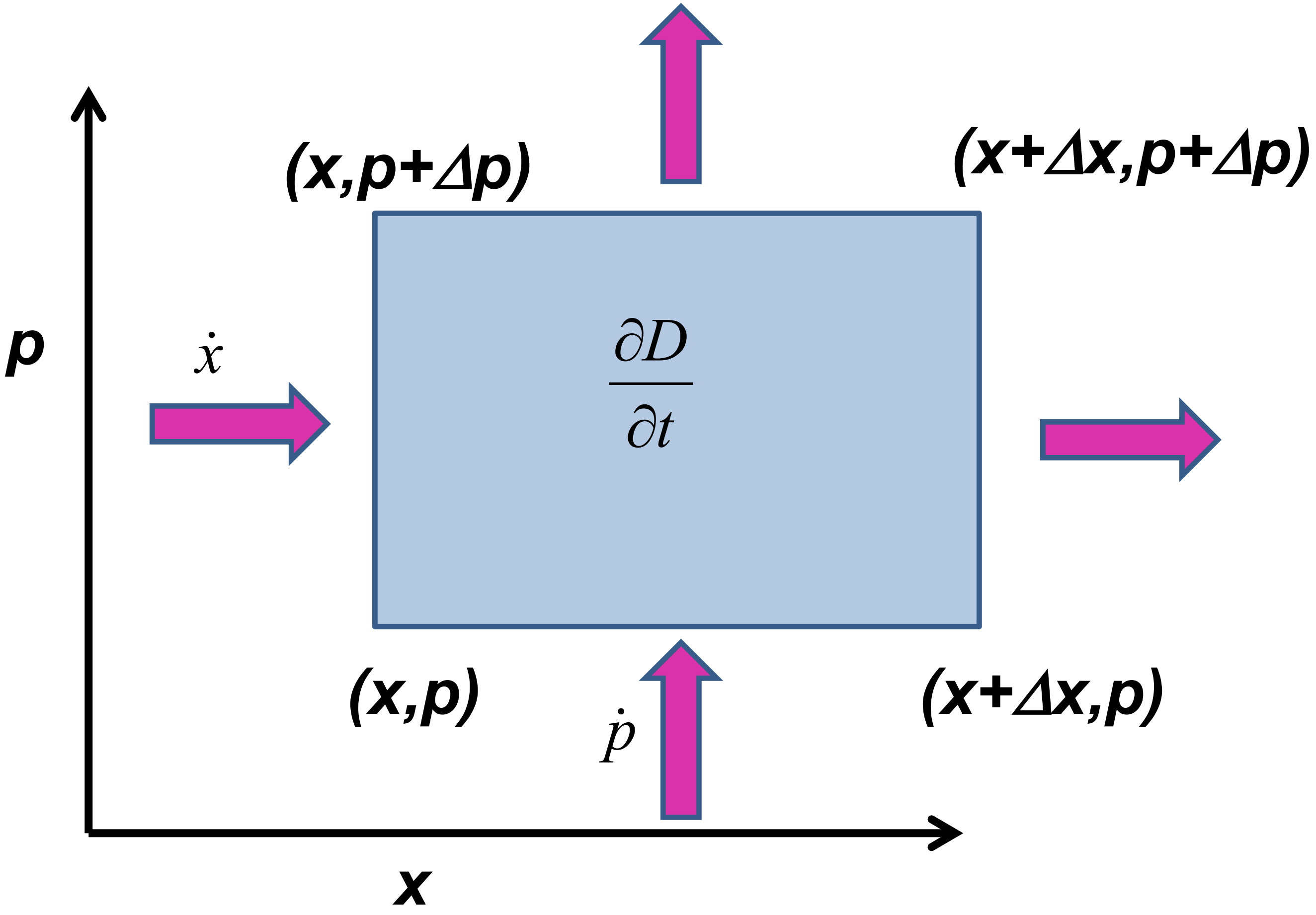
The density of representative points in phase space corresponding to the motion of a system of particles remains constant during the motion.

Denote the density of particles in phase space: $D = D(\{q_\sigma(t)\}, \{p_\sigma(t)\}, t)$

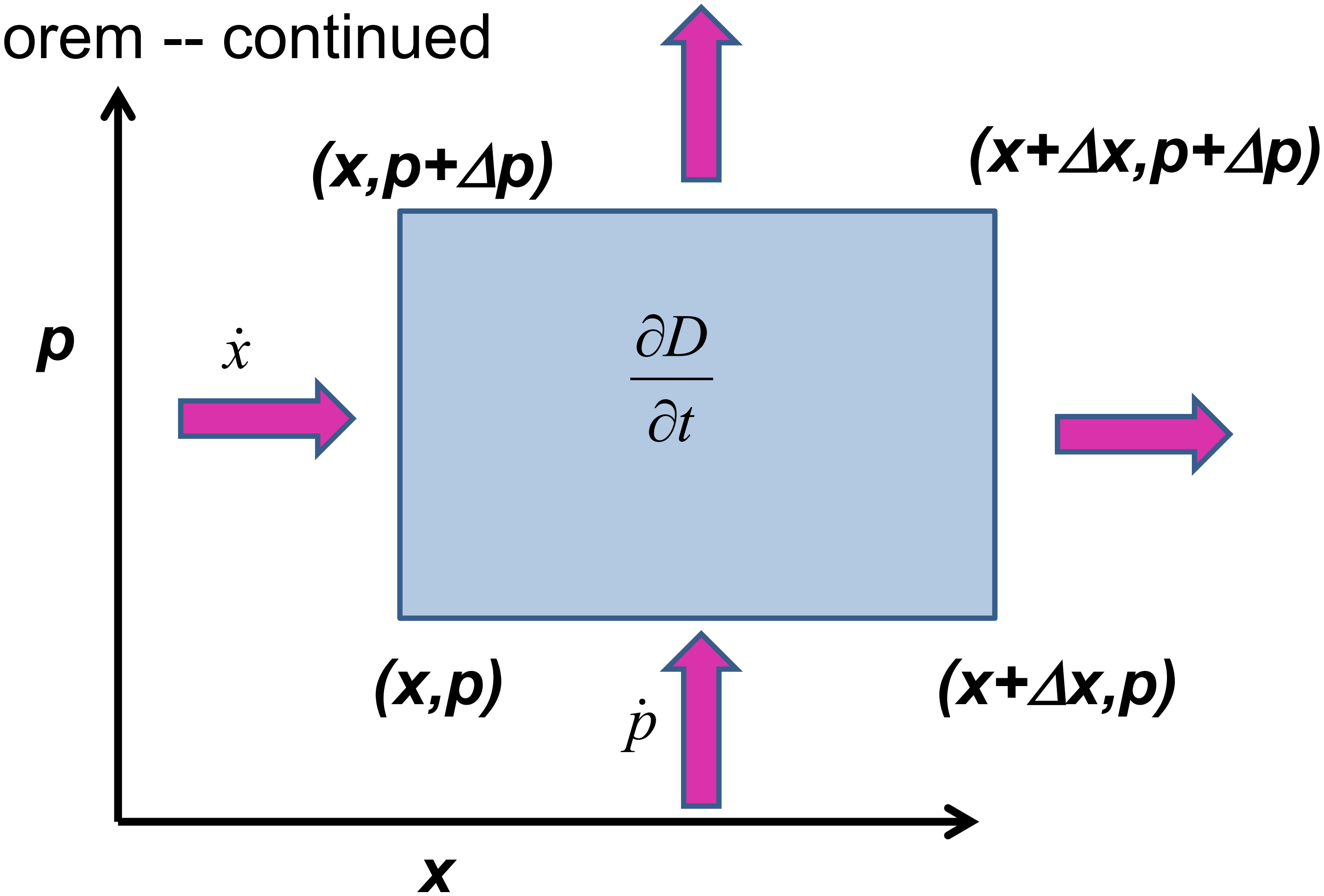
$$\frac{dD}{dt} = \sum_\sigma \left(\frac{\partial D}{\partial q_\sigma} \dot{q}_\sigma + \frac{\partial D}{\partial p_\sigma} \dot{p}_\sigma \right) + \frac{\partial D}{\partial t}$$

According to Liouville's theorem: $\dfrac{dD}{dt} = 0$

Liouville's theorem



Liouville's theorem -- continued

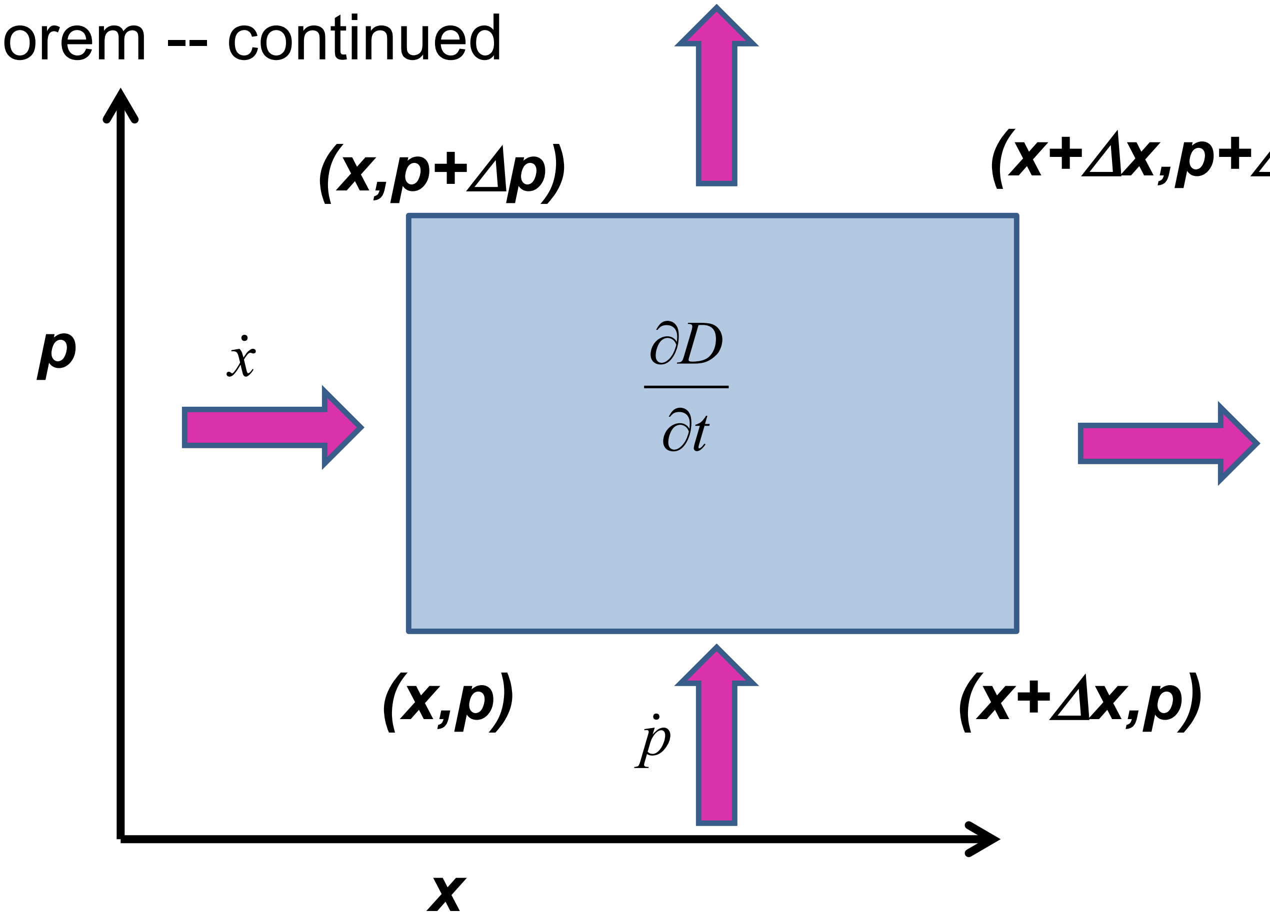


$$\frac{\partial D}{\partial t} \Rightarrow \text{time rate of change of particles within volume}$$

$$= \text{ time rate of particle entering minus particles leaving}$$

$$= -\frac{\partial D}{\partial x}\dot{x} - \frac{\partial D}{\partial p}\dot{p}$$

Liouville's theorem -- continued



$$\frac{\partial D}{\partial t} = -\frac{\partial D}{\partial x}\dot{x} - \frac{\partial D}{\partial p}\dot{p}$$

$$\frac{\partial D}{\partial t} + \frac{\partial D}{\partial x}\dot{x} + \frac{\partial D}{\partial p}\dot{p} = 0 = \frac{dD}{dt}$$

Review:
Liouville’s theorem:

Imagine a collection of particles obeying the Canonical equations of motion in phase space.

Let D denote the "distribution" of particles in phase space:

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

Liouville's theorm shows that:

$$\frac{dD}{dt} = 0 \qquad \Rightarrow D \text{ is constant in time}$$

Note that we are assuming that no particles are created or destroyed in these processes.

Why is the Liouville theorem significant?

We are about to analyze the microstates of an ideal gas by enumerate the possible coordinates and momenta independent of their time dependence. The Liouville theorem suggests that is a good thing to do.

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

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

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

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

constant

Dirac delta function

Hamiltonian

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

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

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

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

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

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

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

$$\delta(x-a) \leftrightarrow \frac{d\Theta(x-a)}{dx}$$

delta function

step function

Define a radial variable for the $3N$ momentum space

$$\rho = \sqrt{\sum_{i=1}^{3N} p_i^2}$$

$$X(N,U) = \int d^{3N}p\ \Theta\Big(H\big(\{q_i\},\{p_i\}\big) - U\Big)$$

$$= \int (\text{angular part}) \int_0^{\sqrt{2MU}} d\rho\ \rho^{3N-1}$$

$$= \frac{(2\pi MU)^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)}$$

Special mathematical function

$\Gamma(M) = (M-1)!$ for integer M

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

When the dust clears --

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

$$\approx \frac{V^N}{h^{3N} N!} \frac{\pi^{3N/2}}{\left(3N/2\right)!} \left(\sqrt{2MU}\right)^{3N}$$

Multiplicity function for an ideal gas in volume V and internal energy U:

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

So what?


S = k. log W
LVDWIG
BOLTZMANN
1844 – 1906
DR PHIL. PAULA
BOLTZMANN
GEB. CHIARI
1891 – 1977
ARTHUR
BOLTZMANN
DIPL. ING. DR PHIL. HOFRAT
1881 – 1952
LVDWIG
BOLTZMANN
1923 – 1943
ZTER MÄNNLICHER NACHKOMME.
GEFALLEN BEI SMOLENSK
HENRIETTE
BOLTZMANN
EB. EDLE VON AIGENTLER
1854 – 1938

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 --

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

Does it make any sense?

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

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

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.)