

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

Plan for Lecture 2:

Reading: Chapters 1.2-1.4

- 1. Ideal gas equation of state**
- 2. Notion of degrees of freedom**
- 3. Work**
- 4. First law of thermodynamics**

1/29/2021

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In this lecture, we will review the ideal gas equation of state and then start discussing energy measures for ideal gasses.

<http://users.wfu.edu/natalie/s21phy341/homework/>

PHY 341/641 Thermodynamics and Statistical Mechanics

MWF 12 and 2 Online and face-to-face <http://www.wfu.edu/~natalie/s21phy341/>

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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 |
| 3 | Mon: 02/01/2021 | | | | |
| 4 | Wed: 02/03/2021 | | | | |

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The homework for this time is a bit more involved and will be due by the time of lecture 4.

Your questions – unanswered questions from last time --

Chao --Is there any relations between the number of atoms composing the molecules and the molecules' degrees of freedom? How does $f=6$ for atoms in crystalline solid being derived?

Can we derive a formula for thermal energy of diatomic gas in class?

Rich -- -Is there any theoretical definition or practical use for temperature in a single dimension (ie T_x , T_y , T_z) ? Why is rotation down the length of a diatomic molecules not considered?

Kristen -- After doing the assigned reading I would love to discuss why it is that many of the equations of thermodynamics are correct only when measured on the kelvin scale. Additionally, in the text specifically with Equation 1.17, the term translational kinetic energy is used, I was hoping you could clarify how this is different from simple kinetic energy.

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Here are some of the questions from last time, that we did not yet cover. Please continue to pose your questions and suggestions for class discussion.h

Parker --And as the book states instead of $PV=NRT$, do you recommend we remember the conversion factor $nR=Nk$? What is the reason for this?

Annelise --how come in the average pressure equation we only take into consideration the velocity in the x direction? I see that in the next theorem about kinetic energy we can conclude that the y, z, and x equations are all equal- is this true for the pressure equation as well?

Leon --My question for tomorrow's lecture material focus on degrees of freedom. I still have a blurred definition of it. I first thought it's like coordinates and then find it wrong. So is it defined like all possible forms of energy a molecule could have? And how to know the exact number of df for different molecules.

Noah -- One of the footnotes says that a decrease in the temperature by a factor of e is a more precise definition. Why is this?
2. I am curious to learn more about how some vibrational degrees of freedom do not contribute to temperature, and what types of modes these would be.

Comment on the ideal gas equation of state

$$PV = Nk_B T$$

$k_B \equiv$ Boltzmann's constant

$$\mathbf{1.380649 \times 10^{-23} \text{ J K}^{-1}}$$

Note that it is sometimes more convenient to represent this equation in terms of the number “ n ” of moles of particles (1 mole = 6.0224076×10^{23} particles)

$$PV = nRT$$

$$\mathbf{R = 8.314462618 \text{ J mol}^{-1} \text{ K}^{-1}}$$

You can use either and both forms as convenient.

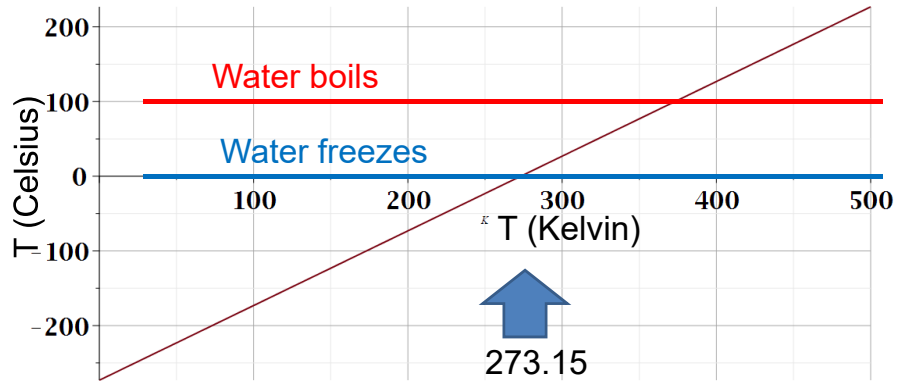
More comments on the ideal gas equation of state

$$PV = Nk_B T$$

Why must we use T measured on the Kelvin scale?

The Celsius and Fahrenheit scales were invented on the basis of human experience without a recognition of the properties of matter. The experimental analysis leading to the ideal gas equation of state lead to the notion that the correlation of temperature and matter is best described by a temperature scale for which $T \geq 0$.

Temperature scales



History of ideal gas equation of state – short article from department of energy --

<https://www.energy.gov/ne/articles/empirical-math-model-ideal-gas-law-0>

Multiple scientists over ~ 200 years starting in 1663

Boyle

Charles

Guy-Lussac

Avogadro

Limitations of ideal gas equation of state

1. Assume gas particles are points (do not account for particle size) which particularly limits validity at high density
2. Assume gas particles do not interact with each other
3. Other?

Your homework problem for this and Monday's lecture will explore some of these issues.

Microscopic analysis of ideal gas equation of state.

$$PV = Nk_B T$$

Figure from your textbook:

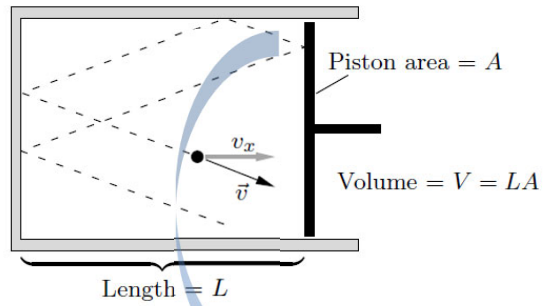


Figure 1.4. A greatly simplified model of an ideal gas, with just one molecule bouncing around elastically. Copyright ©2000, Addison-Wesley.

Collision of atom with piston exerts pressure

Slide from lecture 1.

From Lecture 1 analysis:

Pressure on piston from one collision

$$P = \frac{F_x}{A} \approx m \frac{\Delta v_x}{\Delta t} \frac{1}{A} \approx m \frac{2v_x}{2L/v_x} \frac{1}{A} = \frac{mv_x^2}{V}$$

Some questions about these equations

1. The time interval estimate $2L/v_x$ does not take into account particles near the boundary which may not travel a distance of $2L$. Comment, in general boundary effects are much smaller than the bulk contributions.
2. Why are we only considering pressure due to x direction motion? Comment, this is special to our setup, but it is assumed that the gas motion is isotropic.

$$P = \frac{N}{3V} m \langle v^2 \rangle_{average}$$

Note that v denotes the magnitude of the **translational velocity** and the average is over all gas particles in the sample.

Collision analysis + ideal gas equation of state

$$P = \frac{N}{3V} m \langle v^2 \rangle = \frac{Nk_B T}{V}$$

$$\Rightarrow k_B T = \frac{1}{3} m \langle v^2 \rangle = \frac{2}{3} \langle K_{translation} \rangle$$

This should work reasonably for mono atomic ideal gases.

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This was roughly the conclusion of Monday's lecture.

What about more complicated ideal gases composed of diatomic molecules such as O_2 or N_2 ?

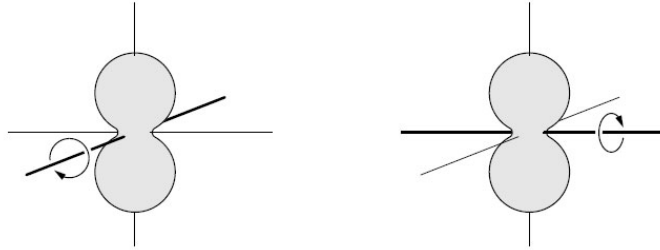


Figure 1.5. A diatomic molecule can rotate about two independent axes, perpendicular to each other. Rotation about the third axis, down the length of the molecule, is not allowed. Copyright ©2000, Addison-Wesley.

In this case, there is non-trivial energy associated with rotational motion in the two axes perpendicular to the molecular bond while rotation about the bond axis involves a trivial expenditure of energy.

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Having established that temperature is related to the translational kinetic energy of a monoatomic particle, what can we expect for the temperature relation to a diatomic or more complex molecule?

$$K = K_{translation} + K_{rotation} + K_{vibration} + \dots$$

Introduce the notion of “degrees of freedom” f

$$f = 3 + \text{rotations}$$

Here 3 represents the 3 translational degrees of freedom and “rotations” mean the number of nontrivial moments of inertia for the molecule (2 for a diatomic, 3 for CH₄, for example).

Equipartition theorem –

At temperature T each degree of freedom of the molecule on average takes the amount of energy $\frac{1}{2} k_B T$.

What do you think about the equipartition theorem

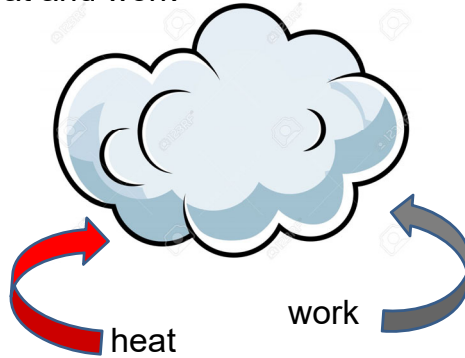
- a. Totally believable
- b. Somewhat skeptical
- c. Totally unconvinced

On the basis of the equipartition theorem, we can then deduce that the motional energy of an ideal gas containing N particles can be written

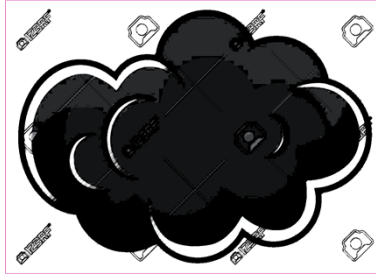
$$U_{thermal} = \frac{f}{2} N k_B T$$

Notions of heat and work

Initial system



Final system



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Heat: Q Heat added to the system is defined as positive if it flows from a higher temperature to a lower temperature

Work: W Work done on the system defined as positive if the system contracts.

Internal energy U of the system is its average motional energy

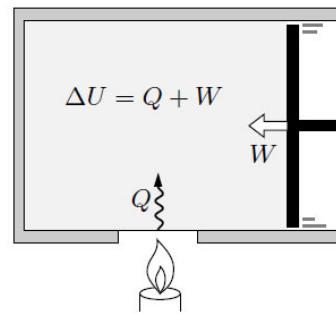
First "law" of thermodynamics

$$\Delta U = Q + W$$

First "law" of thermodynamics

$$\Delta U = Q + W$$

Figure 1.7. The total change in the energy of a system is the sum of the heat added to it and the work done on it. Copyright ©2000, Addison-Wesley.



We will study this law for our ideal gas system.