Physics 1021

Spring 2011, 18b

Thermal Physics
Describes and predicts the state of a system

What is a state?	Set of values that describe the current condition of a system, usually in equilibrium
Is this physics different than what we have learned?	No! At the microscopic level, the ideas of momentum and kinematics, forces and acceleration, energy conservation and Newton’s Laws still apply.
Why do we learn it?	This is very practical. We can connect the ideal laws we have learned to useful, realistic systems, most of which are composed of large numbers of atoms and molecules
How do we make the connection to what we have learned so far?	We do this through statistics. For example when we measure the pressure of a gas, we are measuring average impulsive force of a large number of molecules colliding with the walls of our container.

Thermal Physics
Describes and predicts the state of a system

What is a state?	Set of values that describe the current condition of a system, usually in equilibrium
What are state variables?	Accurate, accepted descriptors. Temperature, pressure, Volume, concentration, density
What are not?	Things that change the state but do not describe it, or cannot be quantified as a content. Work, heat are important examples

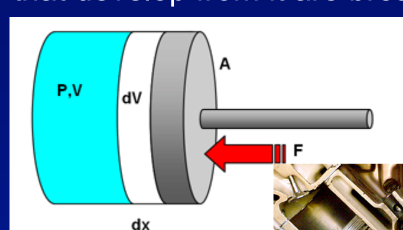
Today's agenda:

•Define and illustrate a number of important state variables.

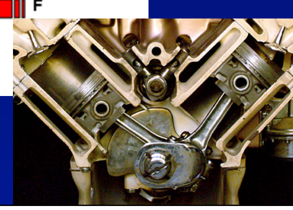
•We will make the connection between microscopic mechanism and the macroscopic state description whenever possible.

•We will focus on the non-interacting gas (ideal gas), because it is simple and the ideas that develop from it are broadly applicable.

•We will calculate heat and work.
Our favorite example: the ideal gas in a piston.



$dW = Fdx$
$= PAdx$
$= PdV$



Position and velocity ↓ mean free path and temperature

New Topic

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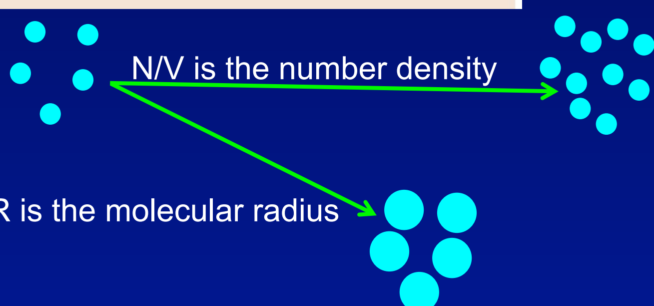
Mean Free Path

The **mean free path,** λ, is average distance a molecule travels before colliding with another molecule

$$\lambda = \frac{1}{4\sqrt{2}\pi(N/V)r^2} \qquad \text{(mean free path)}$$



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ConcepTest 18b.1 mean free path

The table shows the properties of four gases, each having the same number of molecules. Rank in order, from largest to smallest, the mean free paths λ_A to λ_D of molecules in these gases.

1. $\lambda_B > \lambda_A = \lambda_C > \lambda_D$
2. $\lambda_B > \lambda_A = \lambda_C = \lambda_D$
3. $\lambda_B = \lambda_C > \lambda_A = \lambda_D$
4. $\lambda_C > \lambda_D > \lambda_A = \lambda_B$
5. $\lambda_C > \lambda_A = \lambda_B = \lambda_D$

Gas	A	B	C	D
Volume	V	$2V$	V	V
Atomic mass	m	m	$2m$	m
Atomic radius	r	r	r	$2r$

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3. $\lambda_B = \lambda_C > \lambda_A = \lambda_D$
4. $\lambda_C > \lambda_D > \lambda_A = \lambda_B$
5. $\lambda_C > \lambda_A = \lambda_B = \lambda_D$

Bigger radius and smaller volume mean less room to move. Mass is irrelevant.

Gas	A	B	C	D
Volume	V	$2V$	V	V
Atomic mass	m	m	$2m$	m
Atomic radius	r	r	r	$2r$

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Temperature in a Gas

- The thing we call *temperature* measures the average translational kinetic energy of molecules in a gas.
- A higher temperature corresponds to a larger value of ϵ_{avg} and thus to higher molecular speeds.
- By definition, $\epsilon_{avg} = \frac{1}{2} m v_{rms}^2$, and in a gas, $\epsilon_{avg} = 3/2\, k_B T$ and …

$$v_{rms} = \sqrt{\frac{3k_B T}{m}}$$

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State variables

New Topic

PHYS 1021: Chap. 18, Pg 10

State Variables and their relationships

What do you need to know?

- P, V, N, T are almost all you need to know about a gas
- Relation between state variables: $PV = nRT$ or $PV = Nk_BT$
Ideal gas law – always keep this in your back pocket to fill in gaps
  - $k_B = 1.38 \times 10^{-23}$ J/K
  - R = 8.314 J/mole*K
- STP = standard temperature and pressure; (T,P) = (0C, 1atm) = (273.15 K, 101,325 Pa) in standard units.

Example: Molar volume

What is the volume occupied by 1 mole of O_2 at STP?

$V_{STP} = 22.4$ L

Ponderable: Molecular Speeds and Collisions

The density of air at STP is about one thousandth the density of water. How does the average distance between air molecules compare to the average distance between water molecules? Explain.

Solids and liquids resist being compressed. They are not totally incompressible, but it takes large forces to compress them even slightly. If it is true that matter consists of atoms, what can you infer about the microscopic nature of solids and liquids from their incompressibility -- hint: think about the connection between total energy and PV?

Gases, in contrast with solids and liquids, are very compressible. What can you infer from this observation about the microscopic nature of gases?

Can you think of any everyday experiences or observations that would suggest that the molecules of a gas are in constant, random motion? (Note: The existence of "wind" is not such an observation. Wind implies that the gas as a whole can move, but it doesn't tell you anything about the motions of the individual molecules in the gas.)

Helium has atomic mass number A = 4. Neon has A = 20 and argon has A = 40. Rank in order, from largest to smallest, the mean free paths of He, Ne, and Ar at STP. Explain.

Pressure in a Gas

The pressure on the wall of a container due to all the molecular collisions is

$$p = \frac{F}{A} = \frac{1}{3}\frac{N}{V}mv_{\text{rms}}{}^{2}$$

This expresses the macroscopic pressure in terms of the microscopic physics. The pressure depends on the density of molecules in the container and on how fast, on average, the molecules are moving.

Ponderable: Molecular Speeds pressure and temperature

•Two gases have the same number density and the same distribution of speeds. The molecules of gas 2 are more massive than the molecules of gas 1.

•Do the two gases have the same pressure? If not, which is larger?

•Do the two gases have the same temperature? If not, which is larger?

•Consider a gas at at absolute zero?

•What is its average kinetic energy? Explain.

•Can a molecule have negative kinetic energy? Explain.

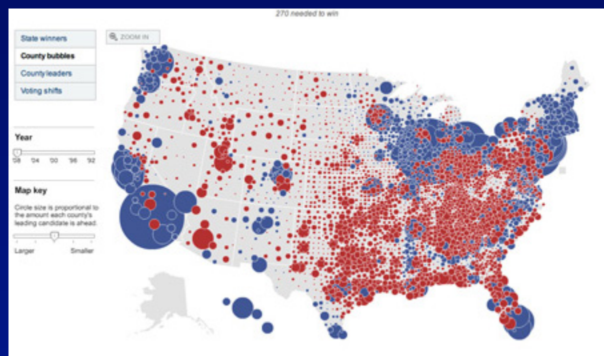
•Based on your answers to parts above, what is the kinetic energy of every molecule in the gas at absolute zero?

State diagrams

New Topic

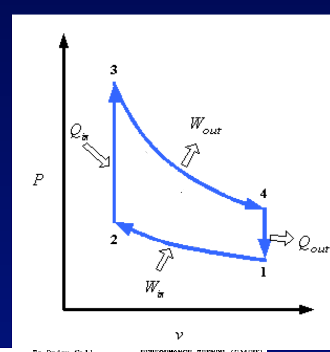
State diagrams

- Ahem, I don’t think so …



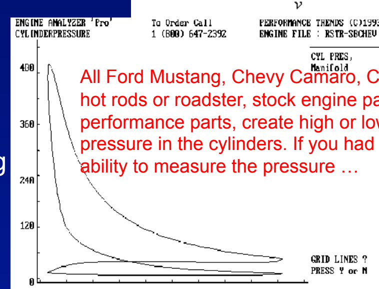
State diagrams

- These are more typical:
  - •P on y-axis, V on x-axis
  - •Lines that show the path taken from state A to state B
  - •Type of process is labeled
  - •Q and W in/out are added as arrows



- All points on the PV diagram must conform to PV = nRT.
  - •At any point, T can be calculated

•Many state variables are independent of the path taken, e.g. T, U, S, but along some Q and W are easier to calculate than along others.



All Ford Mustang, Chevy Camaro, Corvette, hot rods or roadster, stock engine parts or performance parts, create high or low pressure in the cylinders. If you had the ability to measure the pressure …

ConcepTest 18b.2 Energy

Which system has the largest average translational kinetic energy per molecule?

A. 2 mol of He at p = 2 atm, T = 300 K
B. 2 mol of N_2 at p = 0.5 atm, T = 450 K
C. 1 mol of He at p = 1 atm, T = 300 K
D. 1 mol of N_2 at p = 0.5 atm, T = 600 K
E. 1 mol of Ar at p = 0.5 atm, T = 450 K

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Internal energy depends only upon temperature. The gas with the highest T wins!

Ponderable: Molecular Speeds and pressure

•According to kinetic theory, the pressure of a gas depends on the number density and the rms speed of the gas molecules. Consider a sealed container of gas that is heated at constant volume.

•Does the number density of the gas increase or stay the same? Explain.

•According to the ideal gas law, does the pressure of the gas increase or stay the same? Explain.

•What can you infer from these observations about a relationship between the gas temperature (a macroscopic parameter) and the rms speed of the molecules (a microscopic parameter)?

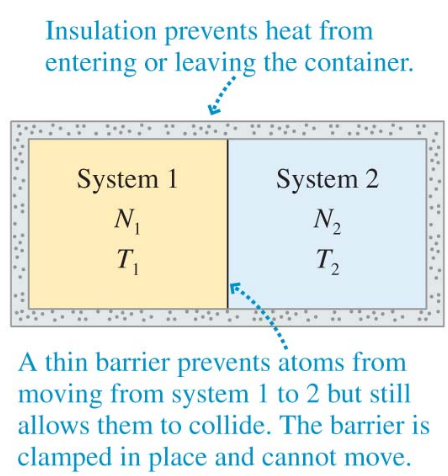
•Suppose you could suddenly increase the speed of every molecule in a gas by a factor of 2.

•Would the rms speed of the molecules increase by a factor of $2^{1/2}$, 2, or 2^2? Explain.

•Would the gas pressure increase by a factor of $2^{1/2}$, 2, or 2^2? Explain.

Thermal Interactions and Heat

FIGURE 18.14 Two gases can interact thermally through a very thin barrier.



Thermal Interactions and Heat

The condition for thermal equilibrium is that the average translational kinetic energies of the atoms in both systems are equal.

$$(\epsilon_1)_{avg} = (\epsilon_2)_{avg} \qquad \text{(thermal equilibrium)}$$

Because the average energies are directly proportional to the final temperatures, thermal equilibrium is characterized by the macroscopic condition as follows:

$$T_{1f} = T_{2f} = T_f \qquad \text{(thermal equilibrium)}$$

The final thermal energies of the two systems are

$$E_{1f} = \frac{n_1}{n_1 + n_2} E_{tot}$$

$$E_{2f} = \frac{n_2}{n_1 + n_2} E_{tot}$$

Entropy

New Topic

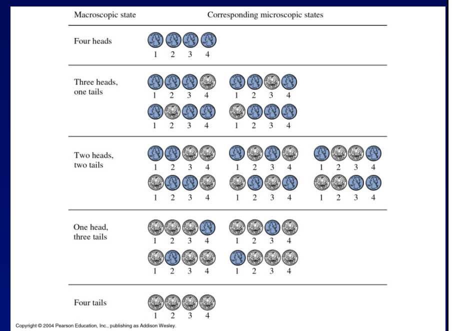
Entropy

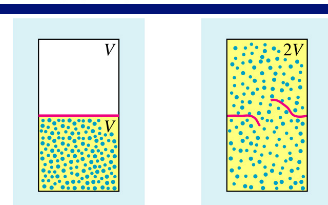
- Statistical definition of entropy:
  - $S=k_B \ln w$
- where w is the number of microstates corresponding to a given macrostate.
  - For any system, the most probable macroscopic state is the one with the greatest number of corresponding microscopic states, which is also the macroscopic state with the greatest ~~disorder~~ entropy.

Difference in entropy:
$\Delta S=S_2-S_1=k_B \ln (w_2/w_1)$

For free expansion (with volume double):
$\Delta S=k_B \ln (w_2/w_1)=nR\ln 2$

Coin toss:





(a) Gas occupies volume V; number of microstates $= w_1$

(b) Gas occupies volume $2V$; number of microstates $= w_2 = 2^N w_1$

Entropy changes require heat

$dQ = TdS$

If entropy increases, then heat must be input:

$\Delta Q = T\Delta S$ (constant T)

ConcepTest 18b.3 entropy

When you toss three coins, which outcome has the most entropy?

A) 3 heads
B) 3 tails
C) 1 head, 2 tails
D) 1 tail, 2 heads
E) both C and D

ConcepTest 18b.3 entropy

When you toss three coins, which outcome has the most entropy?

A) 3 heads
B) 3 tails
C) 1 head, 2 tails
D) 1 tail, 2 heads
E) both C and D

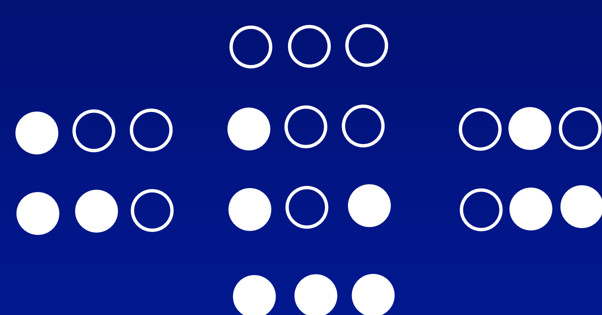
S=k ln w, where w is the number of microstates corresponding to the same macrostate. C) and D) are equally likely, thus the same entropy.

3 tails:

1 head, 2 tails:

1 tail, 2 heads:

3 heads:



ConcepTest 18b.4 entropy

Two identical boxes each contain 1,000,000 molecules. In box A, 750,000 molecules happen to be in the left half the box while 250,000 are in the right half. In box B. 499,900 molecules happen to be in the left half the box while 500,100 are in the right half. At this instant of time,

1. The entropy of box A is smaller than the entropy of box B.
2. The entropy of box A is equal to the entropy of box B.
3. The entropy of box A is larger than the entropy of box B.

ConcepTest 18b.4 entropy

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3. The entropy of box A is larger than the entropy of box B.

We can assume that the left right assignment is totally random, so there are $2^{1,000,000}$ possible states. We know from coin flips that the closer the state is to 50/50, the higher is the multiplicity and $S = k_B \ln w$, where w is the number of microstates

How do you calculate 1,000,000!/500,100! *499,900! ?

Stirling's approximation:

$$\ln n! = n \ln n - n + \frac{1}{2}\ln(2\pi n)$$

ConcepTest 18b.5 entropy

A 1 kg block of ice in a freezing lake (T = 0 C) melts. What happens to the entropy?

1. The entropy decreases.
2. The entropy increases.
3. The entropy is unchanged

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ConcepTest 18b.5 entropy

A 1 kg block of ice in a freezing lake (T = 0 C) melts. What happens to the entropy?

1. The entropy decreases.
2. The entropy increases.
3. The entropy is unchanged

The water molecule are freed from being locked in one state to being able to diffuse throughout the lake. Therefore W and S increase.

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ConcepTest 18b.6 entropy

A 1 kg block of ice in a freezing lake (T = 0 C) melts. What happens to the temperature of the surrounding air?

1. The temperature decreases.
2. The temperature increases.
3. The temperature is unchanged

ConcepTest 18b.6 entropy

A 1 kg block of ice in a freezing lake (T = 0 C) melts. What happens to the temperature of the surrounding air?

1. The temperature decreases.
2. The temperature increases.
3. The temperature is unchanged

It takes heat to increase entropy (and to melt ice!). That comes from the surrounding air, so the air cools

Do you calculate the heat removed from the air, and thus the change in entropy?


Time's up…
…see you next time.
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