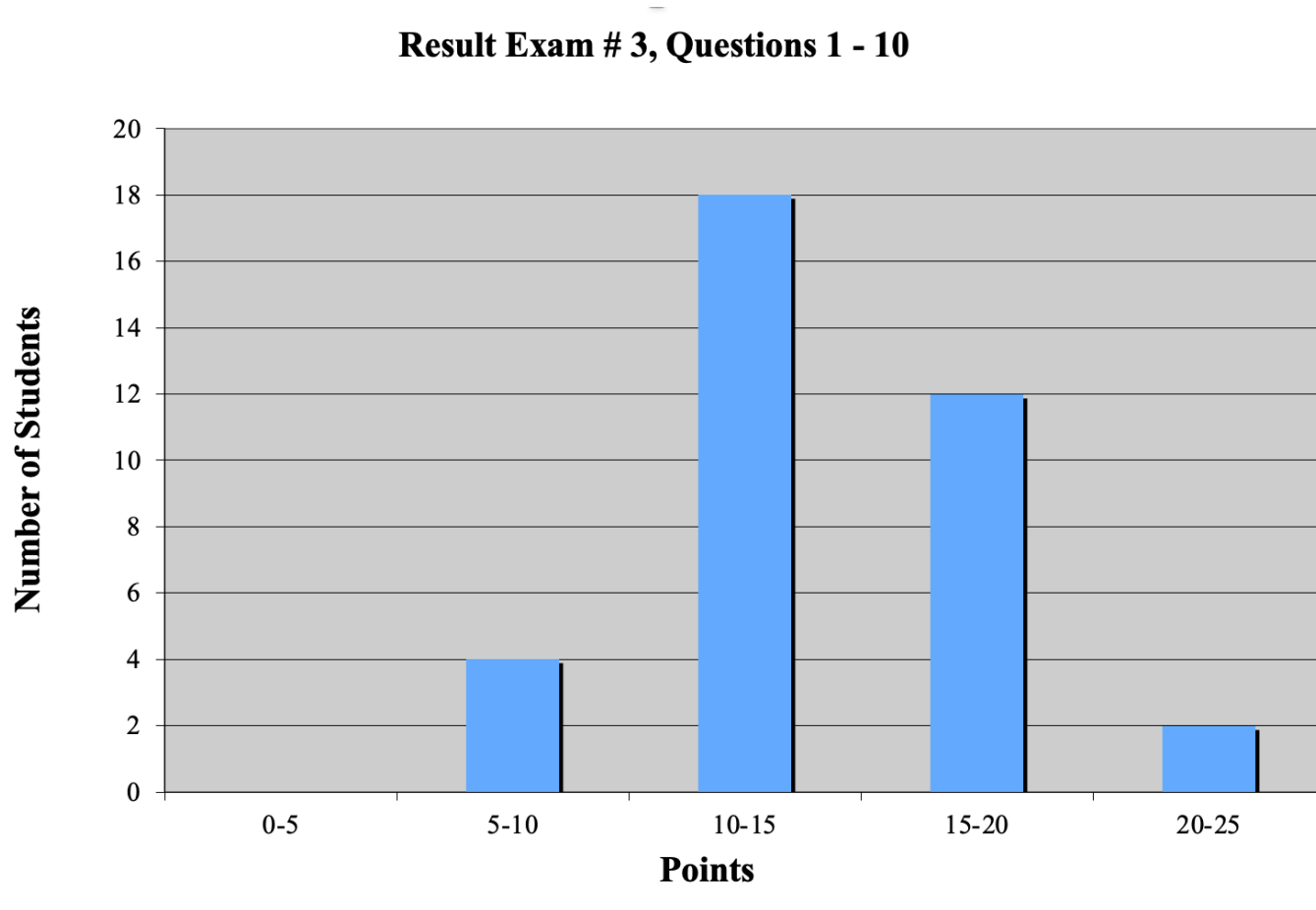# Physics 141.
Lecture 22.

Carry-on Luggage.

Physics 141.
Lecture 22.

- Course Information.

- Entropy.

  - Quick review of topics discussed during our last lecture.

  - Heat capacity.

  - The Maxwell-Boltzmann velocity distribution of gas molecules.

First result from Exam # 3.

Result Exam # 3, Questions 1 - 10

Analysis of experiment # 5.
Updated Timeline.

- ✔11/14: collisions in the May room
- ✔ 11/18: analysis files available.
  - https://www.pas.rochester.edu/~tdimino/phy141/lab05/
- 11/25: each student has determined his/her best estimate of the velocities before and after the collisions (analysis during regular lab periods).
- 11/25: complete discussion and comparison of results with colliding partners and submit final results (velocities and errors).
- 11/27: results will be compiled, linear momenta and kinetic energies will be determined, and results will be distributed.
- 12/2: office hours by lab TA/TIs to help with analysis and conclusions.
- 12/6: students submit lab report # 5.
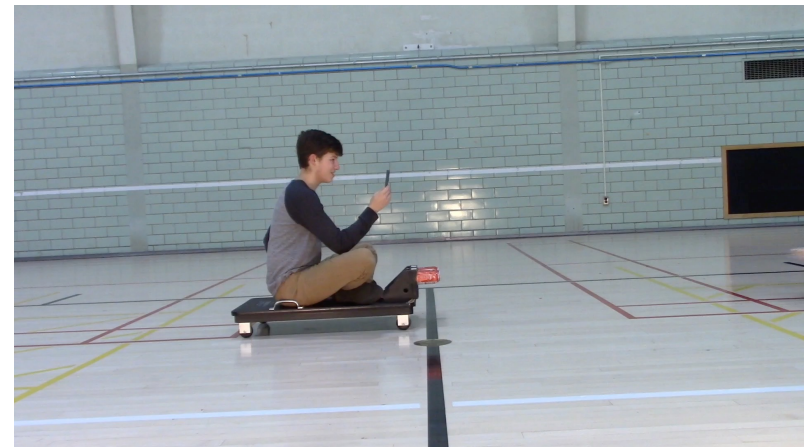
Distributing 4 units of energy among three degrees of freedom.

- Consider an atom with three degrees of freedom; each degree of freedom has a vibrational character with the same characteristic frequency.

- For this system we find:
  - 3 ways: 4:0:0 configuration.
  - 6 ways: 3:1:0 configuration.
  - 3 ways: 2:2:0 configuration.
  - 3 ways: 1:1:2 configuration.

- What is the probability to see the different configurations?
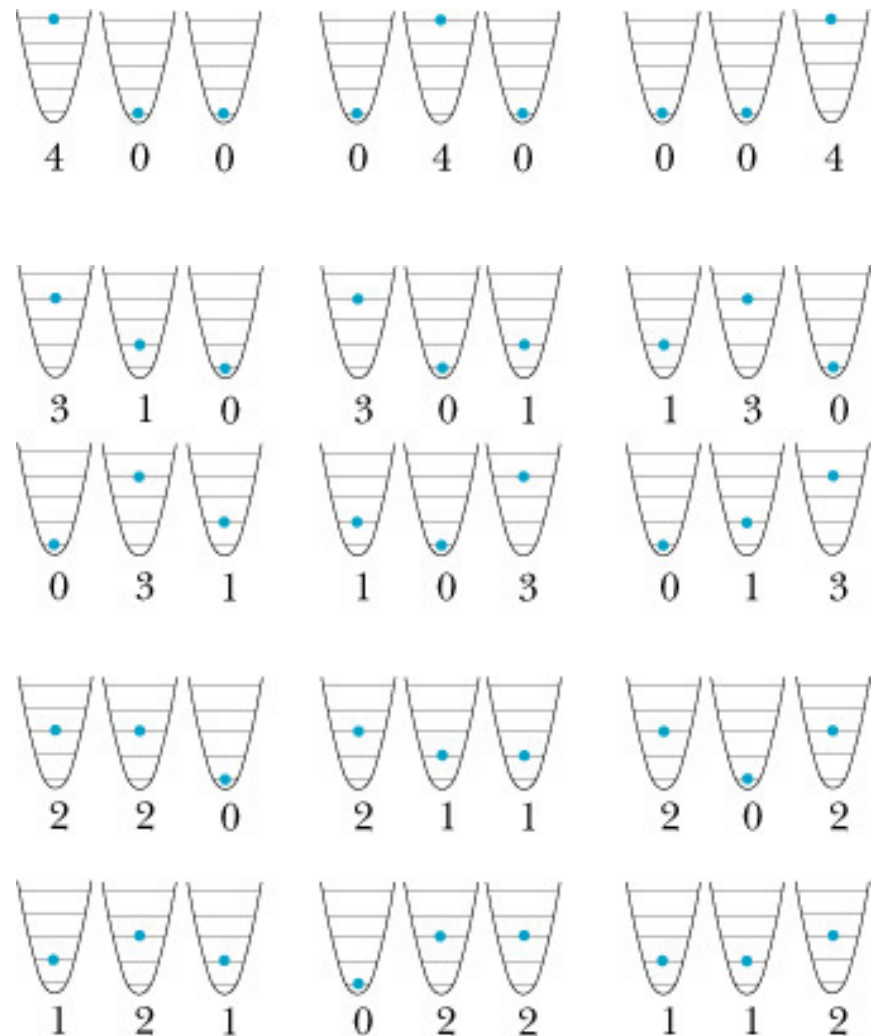
Distributing energy.
The fundamental assumption.

- In order to determine the probability to observe a certain configuration, we rely on **the fundamental assumption of statistical mechanics** to make this determination:

  A fundamental assumption in statistical mechanics is that in our state of microscopic ignorance, each microstate (microscopic distribution of energy) corresponding to a given macrostate (total energy) is equally probable.

- For example $N = 3$:
  - 15 microstates; probability of each one is 1/15.
  - 3 ways: 4:0:0 configuration (20% probability).
  - **6 ways: 3:1:0 configuration (40% probability).**
  - 3 ways: 2:2:0 configuration (20% probability).
  - 3 ways: 1:1:2 configuration (20% probability).

Distributing energy.
Number of states: different representations.

- Since the number of states of a system is enormous (even for small system with a few hundred oscillators) it is often more convenient to look at the natural logarithm of the number of states.
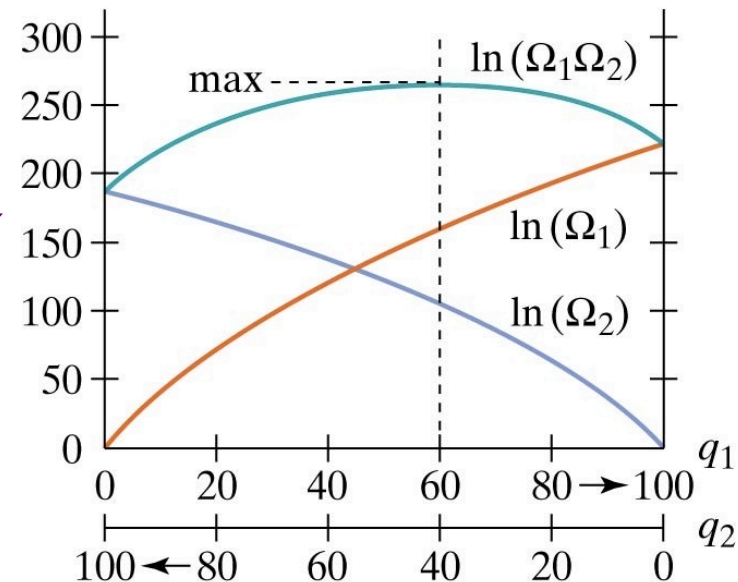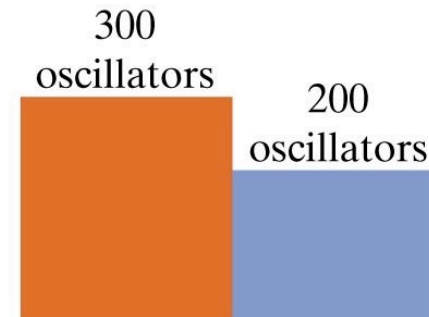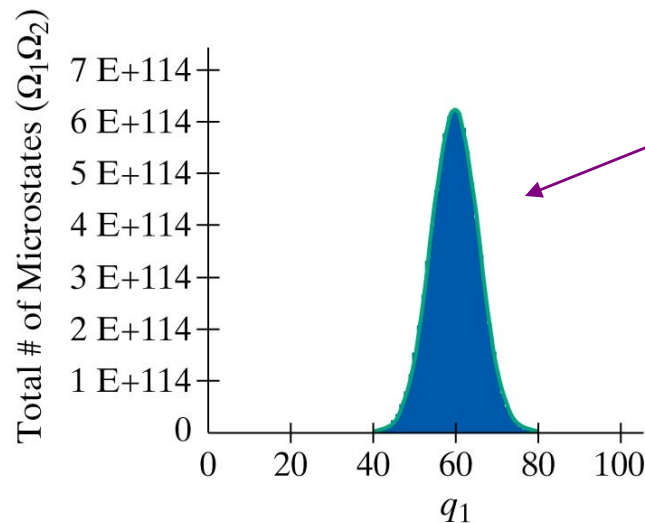
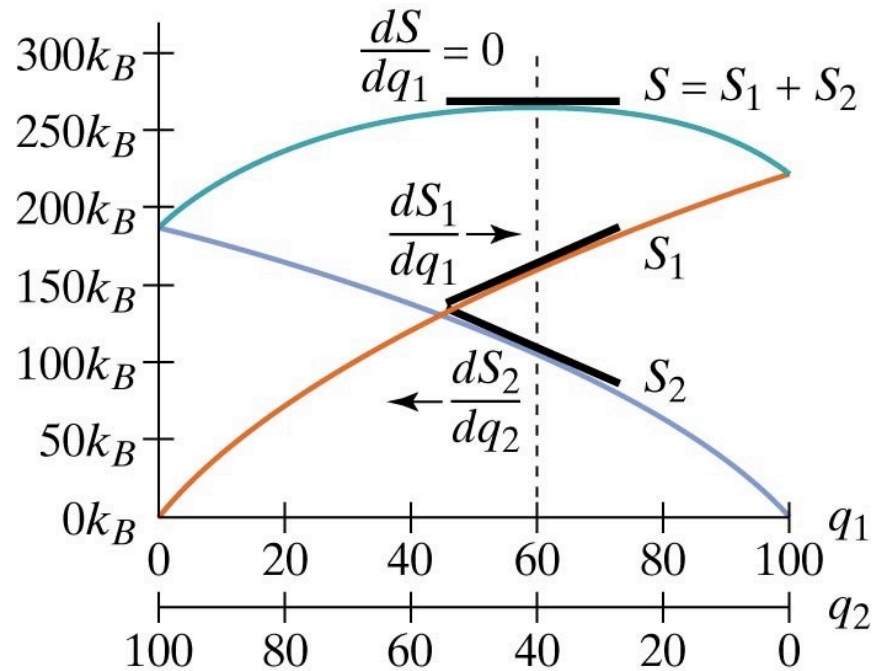# Entropy.

- Since the evolution of the system depends on the number of microstates, the concept of entropy is introduced.
- The entropy S of one of the blocks we have been discussing is defined as

$$S = k \ln(\Omega) = S_1 + S_2$$

  where k is the Boltzmann constant (1.4×10^{-24} J/K).
- The entropy of the total system is the sum of the entropy of the blocks that make up the system.
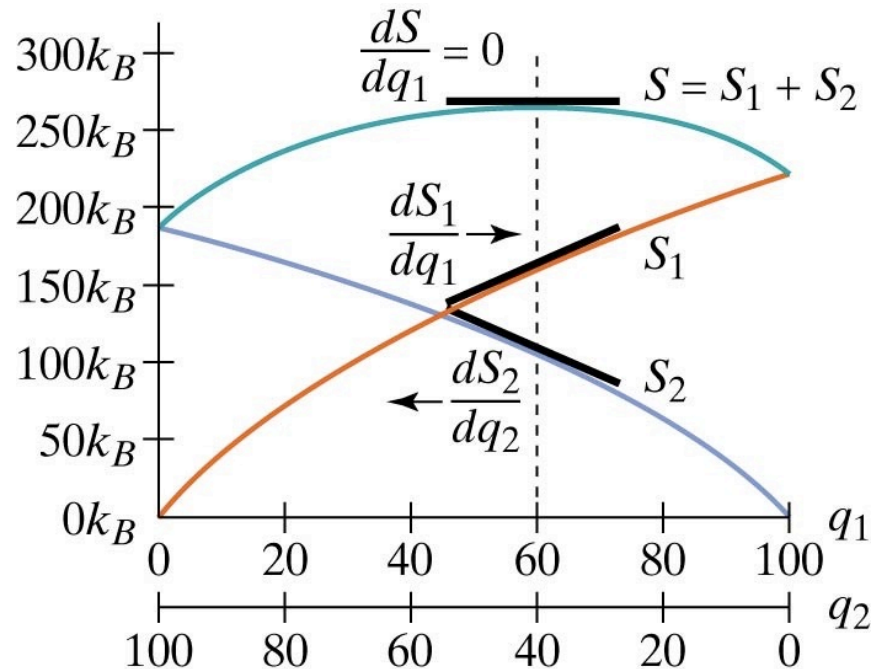
Entropy and the Second Law of Thermodynamics.

- To achieve thermal equilibrium, the system will maximize its entropy.
- The most likely evolution of the system is the focus of the **second law of thermodynamics**:

  If a closed system is not in equilibrium, the most probable consequence is that the entropy of the system will increase.

- Note: even when the two blocks are in thermal equilibrium, there may still be exchange of energy between the blocks, but the time averaged energy exchange will be zero.
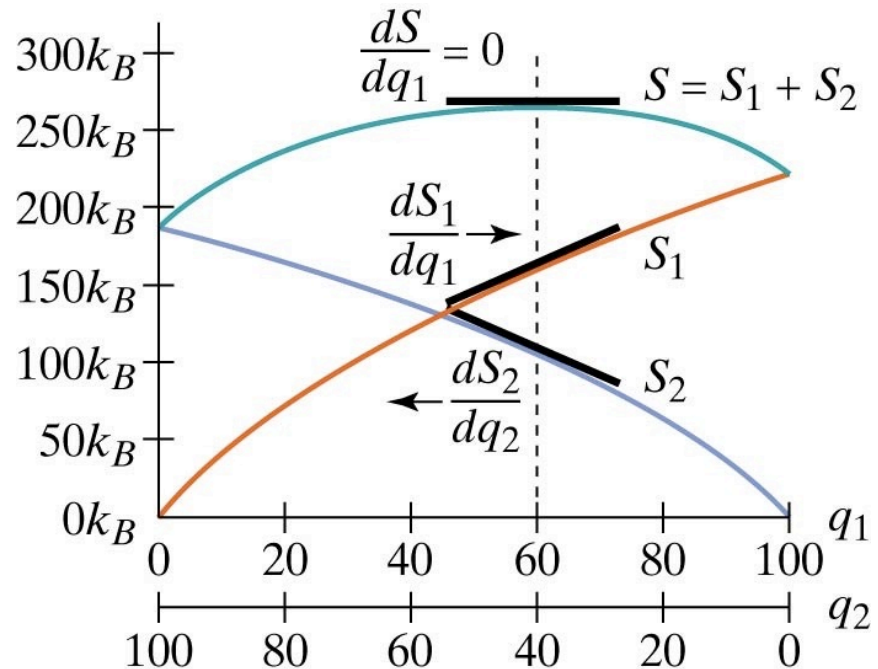
Entropy and the Second Law of Thermodynamics.

- If we know the entropy as function of for example the number of vibrational quanta of block 1, we can express the condition for equilibrium as

$$\frac{dS}{dq_1} = \frac{dS_1}{dq_1} + \frac{dS_2}{dq_1} = 0$$

or

$$\frac{dS_1}{dq_1} = -\frac{dS_2}{dq_1}$$

Entropy and the temperature.
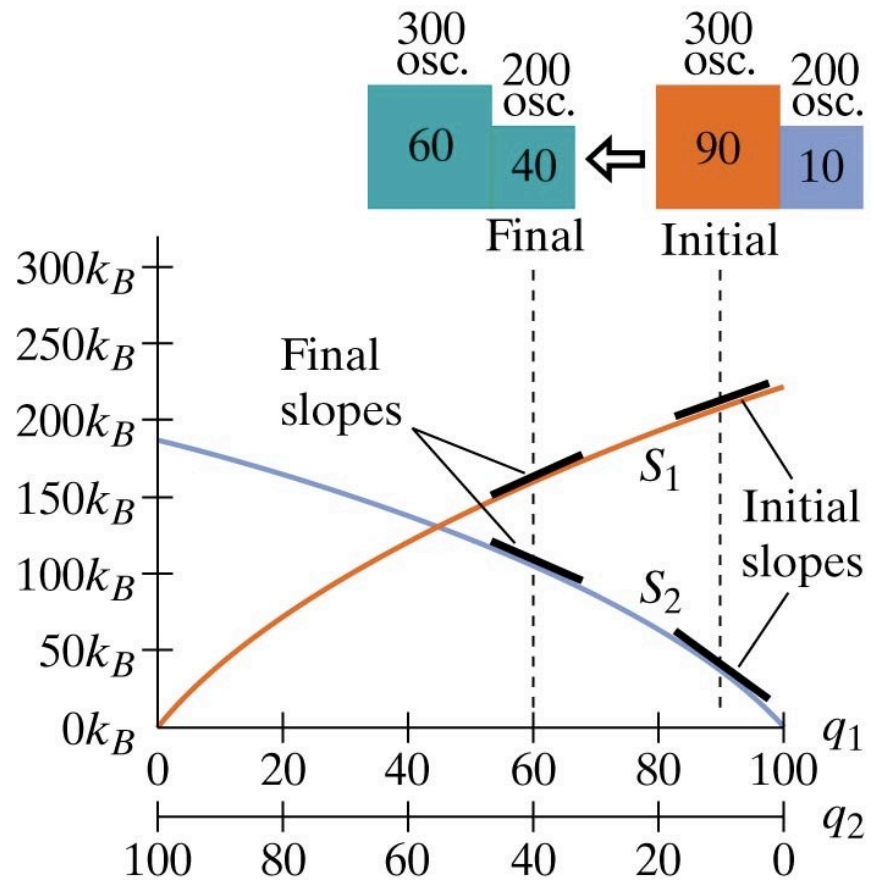
- Since $q_1 + q_2 = $ constant (assuming there is no exchange of energy with the environment surrounding the two blocks), the condition for equilibrium can be rewritten as

$$\frac{dS_1}{dq_1} = \frac{dS_2}{dq_2}$$

- Since thermal equilibrium is achieved when the temperature of the blocks are the same, **the slope of the entropy curves must be related to the temperature of the blocks**.

Entropy and the temperature.

- The temperature of a system is defined as

$$\frac{1}{T} = \frac{dS}{dE_{int}}$$

- The temperature defined in this manner is expressed in units of Kelvin (K) since the internal energy is measured in units of Joules and the entropy is measured in units of J/K.

- Using the definition of temperature, we conclude that block 1 initially has a higher temperature than block 2.
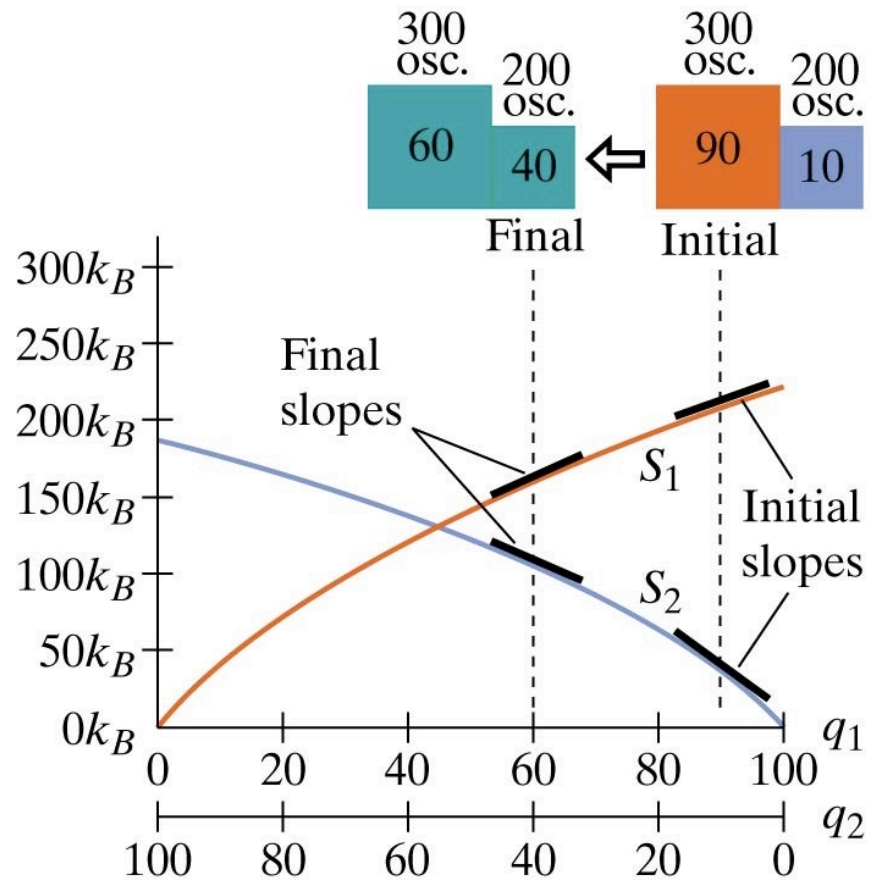
Entropy and temperature.

- The maximum entropy is reached when

$$\frac{dS_1}{dq_1} = \frac{dS_2}{dq_2}$$

- Assuming that each oscillator has the same energy quantization, this condition is equivalent to

$$\frac{1}{T_1} = \frac{1}{T_2}$$

or

$$T_1 = T_2$$

The Boltzmann distribution.

- Question:

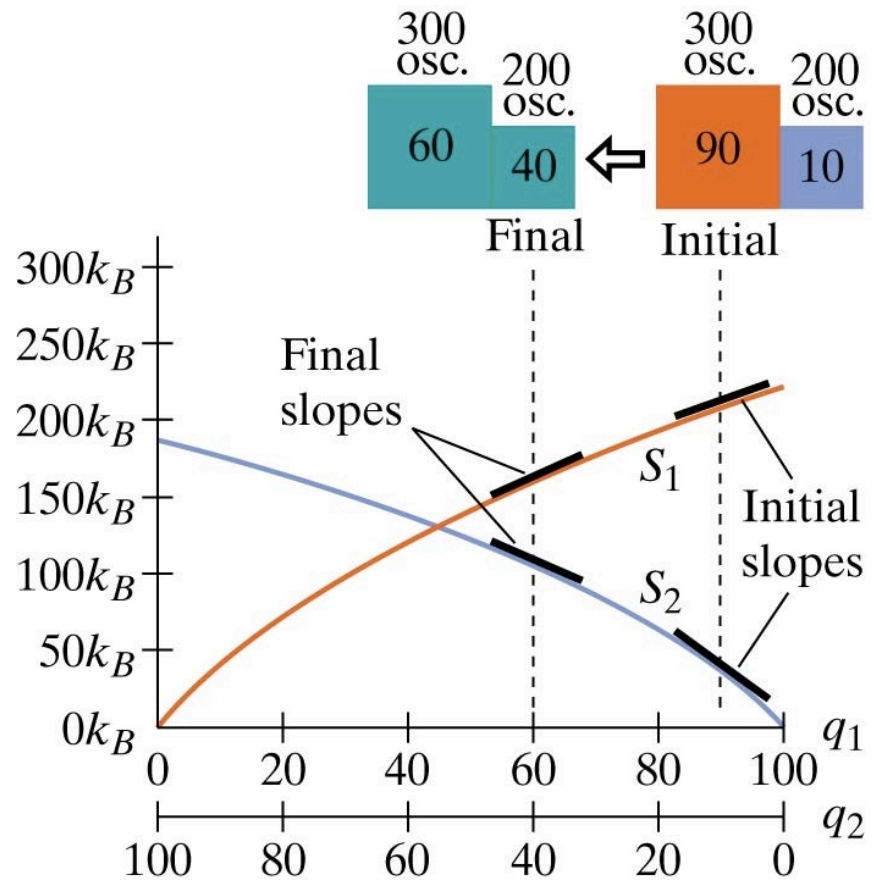 What does the fundamental theory of statistical mechanics tell us about the probability to see a single atom with a specific energy?

- Answer:

  A lot.

- Consider a single oscillator in contact with 300 other oscillators.

- The entropy of this system is equal to the entropy of the 300 oscillators.

- If the energy of the single oscillator increases, the number of states decreases.

$S_{res} = k_B \ln (\Omega_{res})$

E_{res}

$E = E_{tot} - E_{res}$

$S_{res} = k_B \ln (\Omega_{res})$

Energy of 300 oscillators

Energy of 1 oscillator

Expanded scale

E_{res}

$E = E_{tot} - E_{res}$
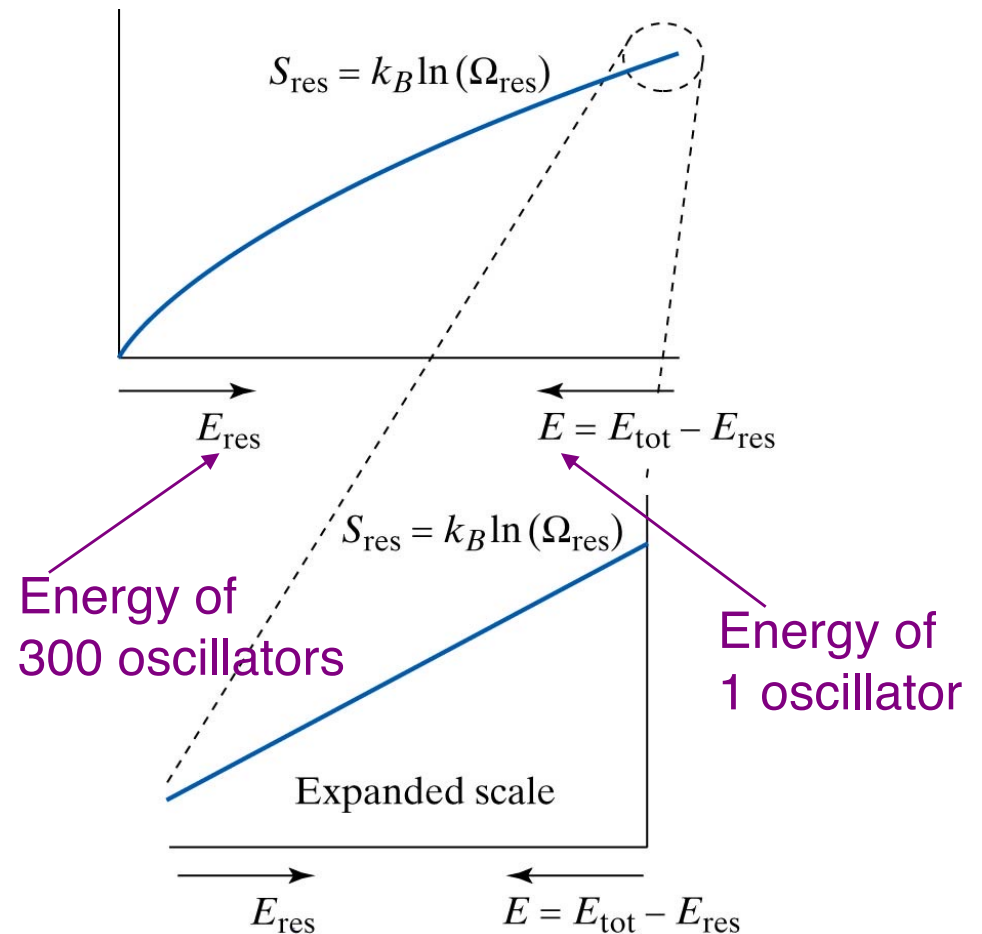
The Boltzmann distribution.

- The entropy curve is close to linear at small ΔE and its slope is equal to dS/dE_1.

- We can approximate the dependence of the entropy on ΔE in the following manner:

$$S = A - \frac{dS}{dE}\Delta E = A - \frac{\Delta E}{T}$$

- The number of states of the system, as function of ΔE, can now be determined:

$$\Omega = e^{\ln(\Omega)} = e^{S/k} = e^{A/k}e^{-\Delta E/kT}$$

$S_{res} = k_B \ln(\Omega_{res})$

E_{res} $E = E_{tot} - E_{res}$

$S_{res} = k_B \ln(\Omega_{res})$

Energy of 300 oscillators

Energy of 1 oscillator

Expanded scale

E_{res} $E = E_{tot} - E_{res}$
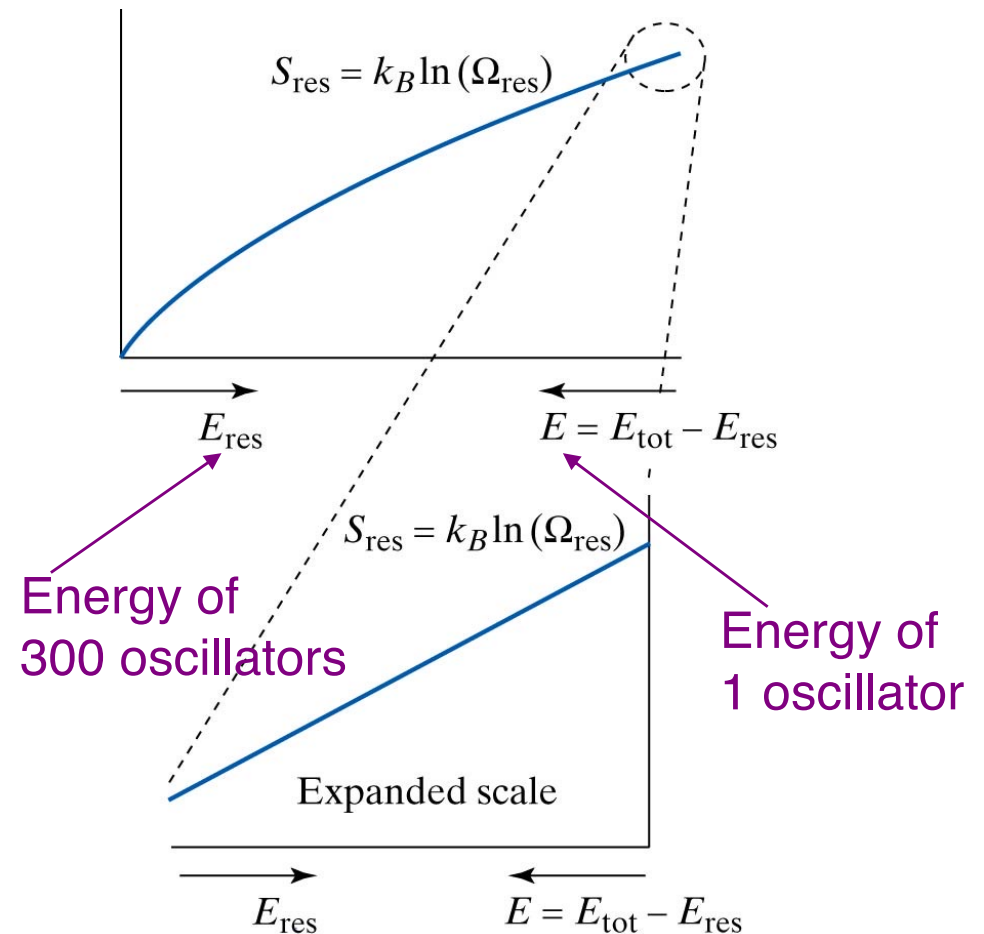
The Boltzmann distribution.

- Since the probability is proportional to the number of states, we conclude that:

    the probability of finding a microscopic system to be in a state with energy ΔE above the ground state of the system is proportional to $e^{-\Delta E/kt}$.

- This probability distribution is called the **Boltzmann distribution**.

High temperature

$k_B T$ E_1 $k_B T > E_1$
May find in excited state

Low temperature

E_1 $k_B T << E_1$
Unlikely to find in excited state

$k_B T$
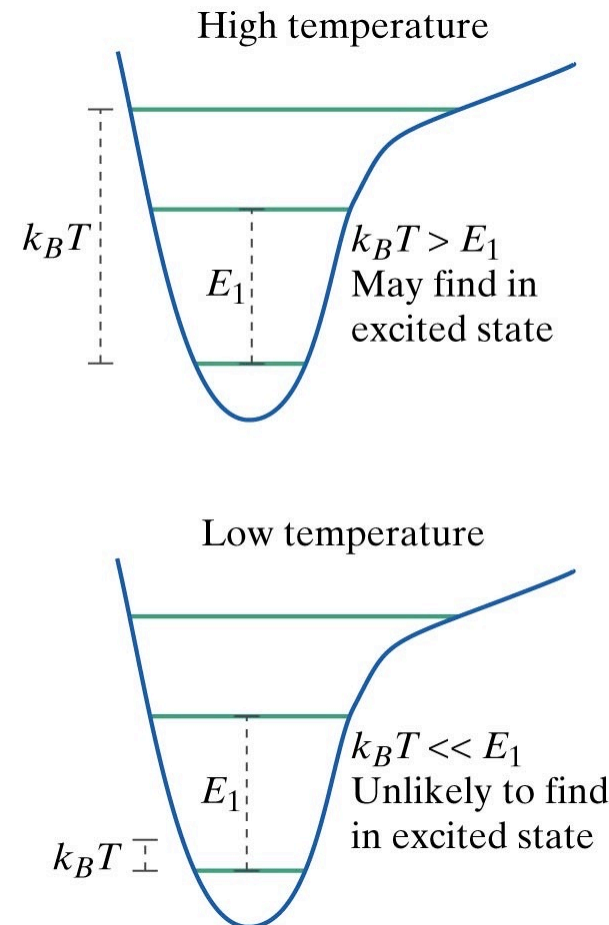
3 Minute 03 Second Intermission.

- Since paying attention for 1 hour and 15 minutes is hard when the topic is physics, let's take a 3 minute 03 second intermission.

- You can:
  - Stretch out.
  - Talk to your neighbors.
  - Ask me a quick question.
  - Enjoy the fantastic music.
  - Solve a WeBWorK problem.

The Boltzmann distribution.

- The energy of a gas molecule can have various components:
  - Translational
  - Vibrational
  - Rotational
  - Gravitational

- For each component, the probability will show an exponential dependence on energy.

- I will first focus on the translational component.

The Boltzmann distribution.

$$P\left(v_x\right)dv_x \propto e^{-\left(\frac{1}{2}Mv_x^2\right)/kT}\,dv_x$$
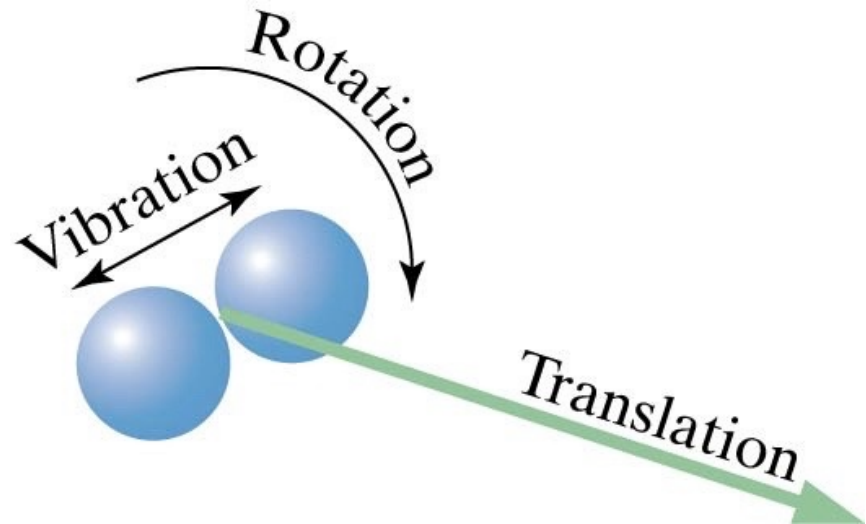
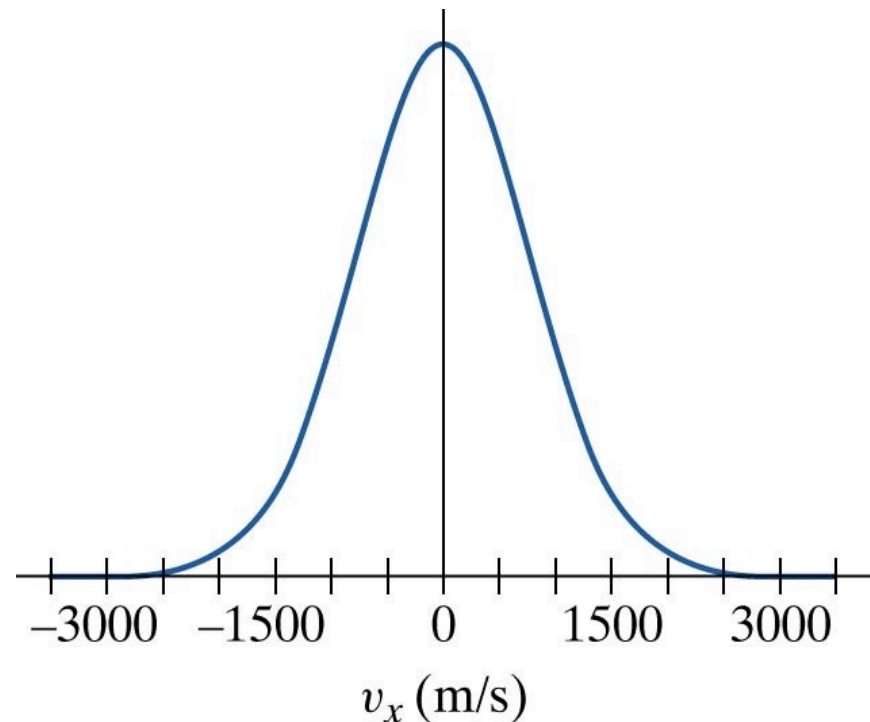- Consider that the gas molecule is moving with a velocity v_x along the x axis.
- The energy of the gas molecule, associated with its motion along the x axis, will be $(1/2)Mv_x^2$.
- The probability of finding the gas molecule with a velocity between v_x and $v_x + dv_x$ is equal to

$$P(v_x)dv_x \propto e^{-\frac{\frac{1}{2}Mv_x^2}{kT}}dv_x$$

v_x (m/s) axis: −3000   −1500   0   1500   3000

The Boltzmann distribution.

- We can do the same calculation for the *y* and *z* velocity distributions :

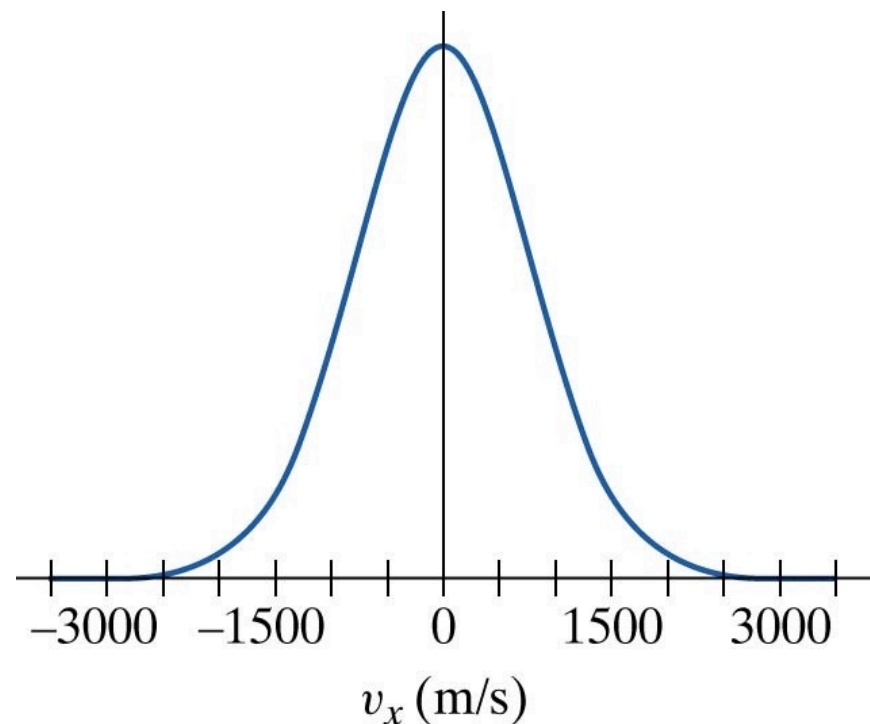$$P(v_y)dv_y \propto e^{-\frac{\frac{1}{2}Mv_y^2}{kT}}dv_y$$

$$P(v_z)dv_z \propto e^{-\frac{\frac{1}{2}Mv_z^2}{kT}}dv_z$$

- These equations can be combined to determine the dependence of the probability on *v*:

$$P(v)dv \propto e^{-\frac{\frac{1}{2}Mv^2}{kT}}dv_x dv_y dv_z$$

or

$$P(v)dv \propto 4\pi v^2 e^{-\frac{\frac{1}{2}Mv^2}{kT}}dv$$

The Maxwell-Boltzmann speed distribution.

- The probability to find a molecule with a speed between v and $v + dv$ is thus proportional to

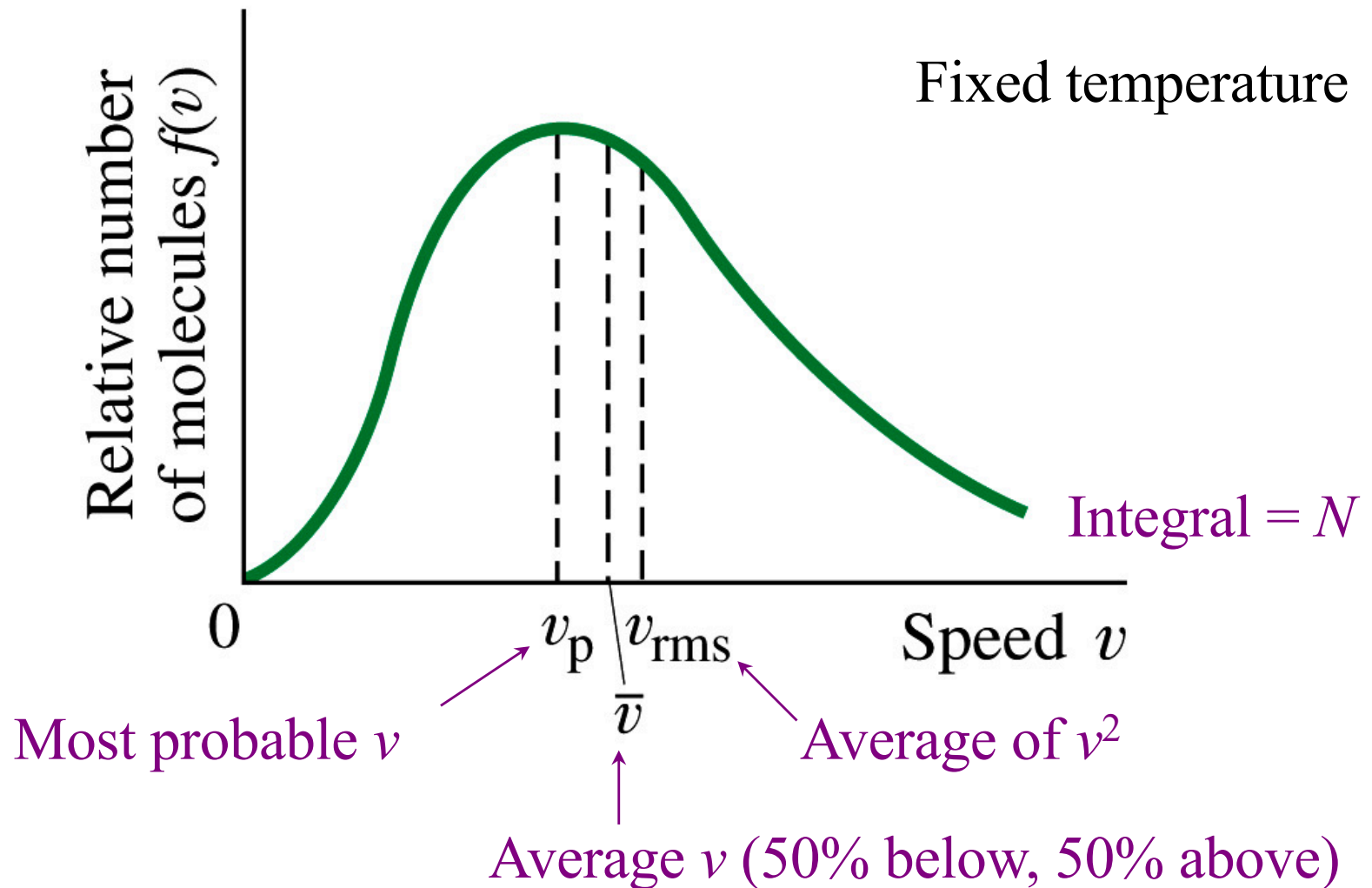$$P(v)dv \propto 4\pi v^2 e^{-\frac{\frac{1}{2}Mv^2}{kT}} dv$$

- But the probability to find the molecule with a speed between 0 and infinity is equal to 1. Thus:

$$1 = \int_0^\infty P(v)dv = 4\pi C \int_0^\infty v^2 e^{-\frac{1}{2}Mv^2/(kT)} = C \left(\frac{2\pi kT}{M}\right)^2$$
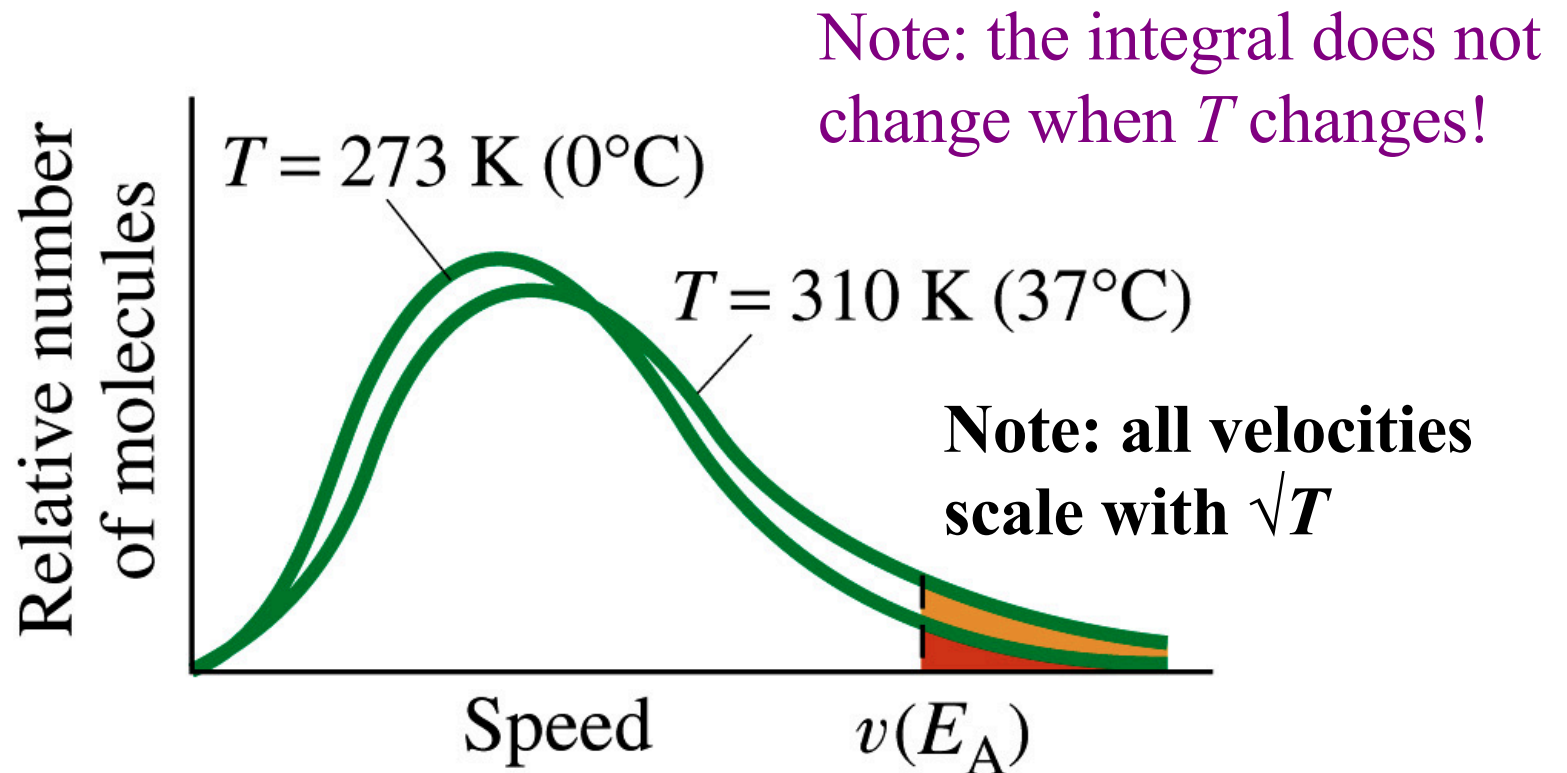
- The velocity distribution is thus equal to

$$P(v) = 4\pi \left(\frac{2\pi kT}{M}\right)^2 v^2 e^{-\frac{\frac{1}{2}Mv^2}{kT}}$$

The Maxwell-Boltzmann speed distribution.

Fixed temperature

Relative number of molecules $f(v)$

v_{p} v_{rms}

$\bar{v}$

0

Speed v

Integral $= N$

Most probable v

Average of v^2

Average v (50% below, 50% above)

The Maxwell-Boltzmann speed distribution.

Note: the integral does not change when T changes!

$T = 273$ K (0°C)

$T = 310$ K (37°C)

Note: all velocities scale with $\sqrt{T}$

Relative number of molecules

Speed

$v(E_A)$

Increasing T increases the fraction of molecules above a certain velocity.

The Boltzmann distribution and internal energy.

- The root-mean-square velocity associated with one degree of freedom (for example, motion in the x direction) is equal to

$$v_{x,rms}^2 = \frac{\int_0^\infty v_x^2 e^{-\frac{1}{2}Mv_x^2/(kT)}dv_x}{\int_0^\infty e^{-\frac{1}{2}Mv_x^2/(kT)}dv_x} = \frac{2}{M}\frac{\int_0^\infty \omega^2 e^{-\omega^2/(kT)}d\omega}{\int_0^\infty e^{-\omega^2/(kT)}d\omega} = \frac{1}{M}kT$$

- The root-mean-square kinetic energy associated with this degree of freedom is thus equal to

$$\overline{K}_{x,rms} = \frac{1}{2}Mv_{x,rms}^2 = \frac{1}{2}kT$$
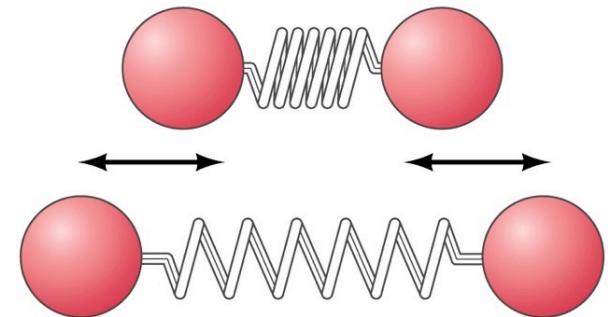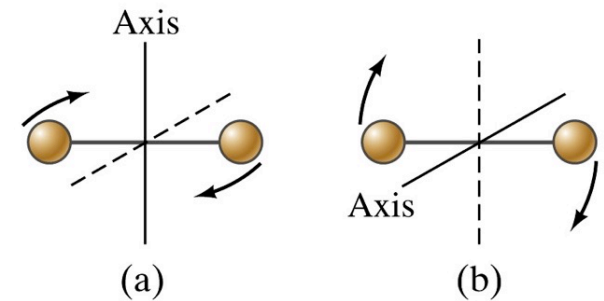
The Boltzmann distribution and internal energy.

- The root-mean-square kinetic energy associated with the three translational degrees of freedom is thus equal to

$$\overline{K}_{rms} = \overline{K}_{x,rms} + \overline{K}_{y,rms} + \overline{K}_{z,rms} = \frac{3}{2}kT$$

- It turns out that the average energy associated with each degree of freedom, including vibrational and rotational degrees of freedom, is $(1/2)kT$.

- Note:
    - The internal energy only depends on the temperature; it does **not** depend on the mass of the gas molecules.
    - At a given temperature, the rms velocity of heavier molecules will be smaller than the rms velocity of lighter molecules.

# The Boltzmann distribution and internal energy.

- Up to now we have assumed that the internal energy U of a gas is equal to $(3/2)kT$.
- This is correct for a monatomic gas, but is not correct for diatomic or triatomic gases.
- Predictions for a diatomic molecule:
  - Linear motion (3 degrees of freedom): $U = (3/2)kT$.
  - Rotational motion (2 degrees of freedom): $U = kT$.
  - Vibrational motion (2 degrees of freedom): $U = kT$.
- The number of degrees of freedom excited depend on the temperature.

The Boltzmann distribution and internal energy.

Remember: $Q = C\Delta T$

But: $K = \dfrac{1}{2}nkT$ and $\Delta K = \dfrac{1}{2}nk\Delta T = C\Delta T$
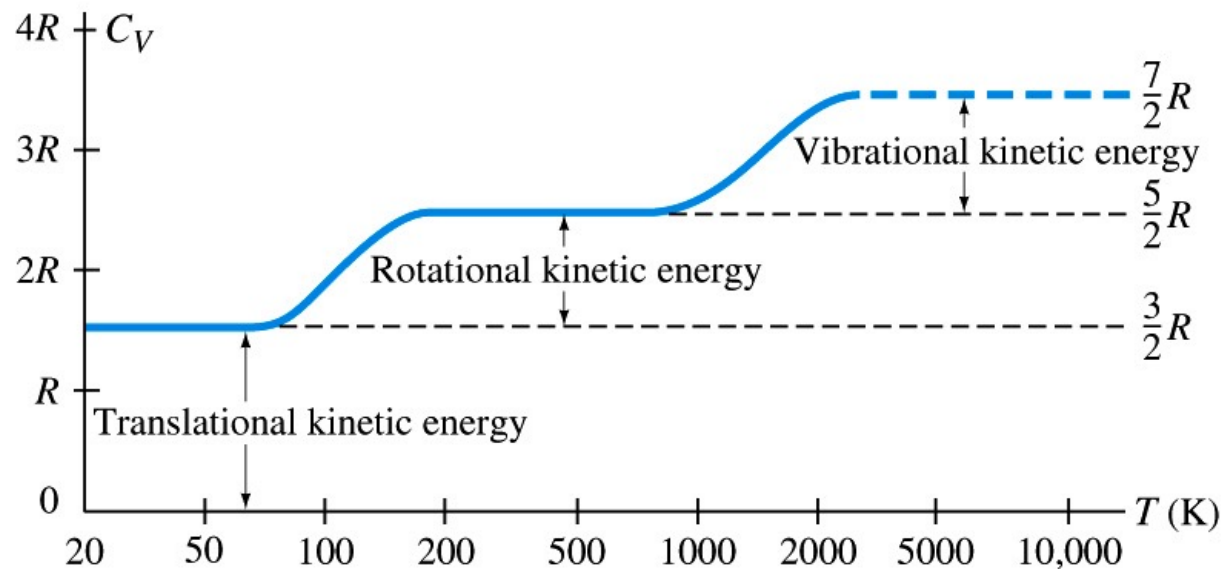
Molecular speed and its consequences.
The mean-free path.

- The RMS velocities of individual gas molecules are large. For example, for hydrogen at room temperature, the RMS velocity is 1920 m/s.

- Despite the large RMS velocity, the average diffusion velocity is much smaller and is largely determined by the mean-free path of the molecules.

- We expect that the mean-free path is inversely proportional to the cross-sectional area of the molecules and inversely proportional to the density.
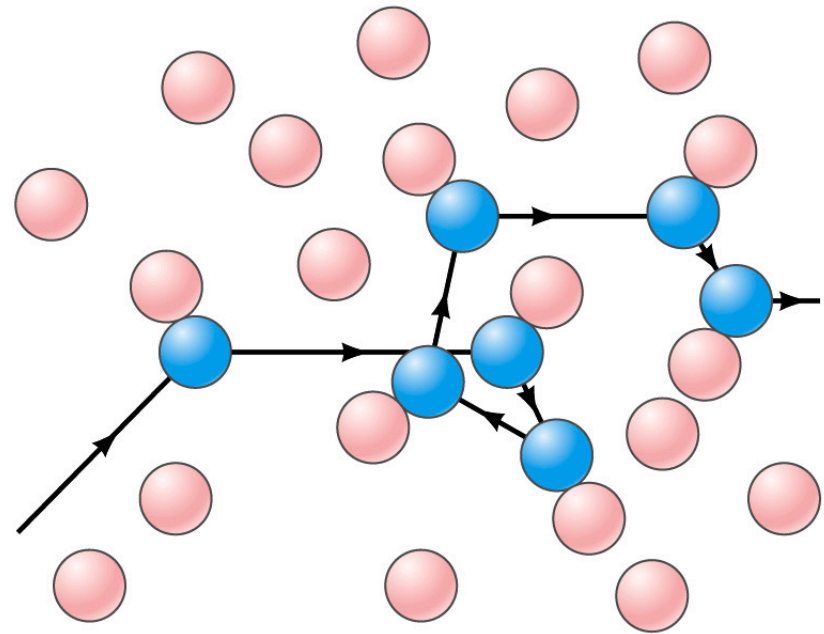
Typical values of the mean-free path are between 10^{-8} and 10^{-7} m

Probing molecular speeds in liquids.

0.5 μm particles in water, 50/50 glycerol-water, 75/25 glycerol-water, glycerol

http://www.physics.emory.edu/~weeks/squishy/BrownianMotionLab.html
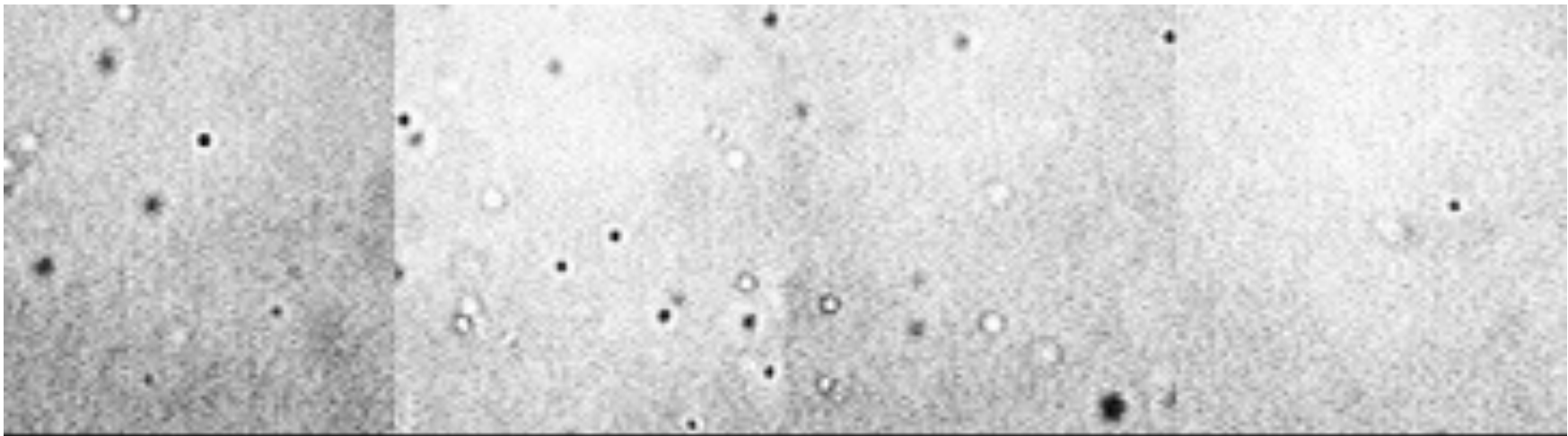
Molecular speed and its consequences.
The propagation of sound.

- Typical values for v_{rms}:

  - For H at 300 K: v_{rms} = 1,920 m/s.
  - For N at 300 K: v_{rms} = 517 m/s.

- The speed of sound in these two gases is 1,350 m/s for H and 350 m/s for N.
- Note: The speed of sound in a gas will always be less than v_{rms} since the sound propagates through the gas by disturbing the motion of the molecules. The disturbance is passed on from molecule to molecule by means of collisions; a sound wave can therefore never travel faster than the average speed of the molecules. Since v_{rms} increases with T, we expect v_{sound} to increase with T.

Molecular speed and its consequences.
The composition of the atmosphere.

- Typical values for v_{rms}:

    - For H at 300 K: v_{rms} = 1,920 m/s.
    - For N at 300 K: v_{rms} = 517 m/s.

- A significant fraction of the H molecules in the atmosphere have a velocity that exceeds the escape velocity of the earth. This is one of the reasons that our atmosphere contains virtually no hydrogen and helium.
- Since the escape velocity decreases with decreasing planetary mass, the escape velocity of the moon is so low that it has no atmosphere (even the heavier gas molecules would quickly escape).

Molecular speed and its consequences. Evaporation.

- Evaporation: transformation from the liquid to the gas phase.
- A microscopic view of evaporation:
  - Molecules with high velocity moving close to the surface can overcome the strong attractive forces between the molecules and escape from the liquid (evaporation).
  - The average velocity of the molecules left behind in the liquid will be lowered.
  - Since the average velocity is proportional to the temperature, the temperature of the liquid is lowered when evaporation takes place.
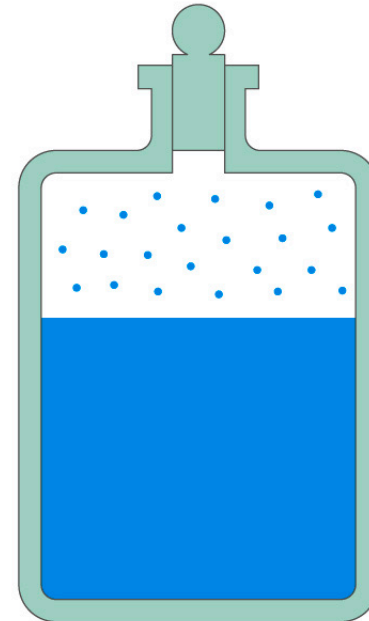
Next week: Chapter 13.
Aka Supplement S1.

SUPPLEMENT
S1
Gases and Heat Engines
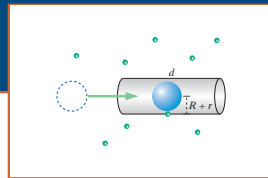
OBJECTIVES

After studying this supplement, you should be able to

- Determine the flow rate of a gas through a hole, given microscopic information about the gas
- Determine the change in temperature and pressure of a gas undergoing compression or expansion
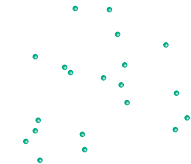- Determine the efficiency of a heat engine

S1.1 GASES, SOLIDS, AND LIQUIDS

In contrast to a solid, a gas has no fixed structure. The gas molecules are not bound to each other but move around very freely, which is why a gas does not have a well-defined shape of its own; it fills whatever container you put it in (Figure S1.1). Think, for example, of the constantly shifting shape of a cloud, or the deformability of a balloon, in contrast with the rigidity of a block of aluminum. On average, gas molecules are sufficiently far apart that most of the time they hardly interact with each other. This low level of interaction is what makes it feasible to model a gas in some detail, using relatively simple concepts.

In a gas the molecular motion must be sufficiently violent that molecules can't stay stuck together. At high enough temperatures, any molecules that do manage to bind to each other temporarily soon get knocked apart again by high-speed collisions with other molecules. However, at a low enough temperature, molecules move sufficiently slowly that collisions are no longer violent enough to break intermolecular bonds. Rather, more and more molecules stick to each other in a growing mass as the gas turns into a liquid or, at still lower temperatures, a solid.

Figure S1.1 Molecules in a gas.

Liquids Are More Complex

A liquid is intermediate between a solid and a gas. The molecules in a liquid are sufficiently attracted to each other that the liquid doesn't fly apart like a gas (Figure S1.2), yet the attraction is not strong enough to keep each molecule near a fixed equilibrium position as in a solid. The molecules in a liquid can slide past each other, giving liquids their special property of fluid flow (unlike solids) with fixed volume (unlike gases).

The analysis of liquids in terms of atomic, microscopic models is quite difficult compared with gases, where the molecules only rarely come in contact with other atoms, or compared with solids, where the atoms never move very far away from their equilibrium positions. For this reason, in

Figure S1.2 Molecules in a liquid.

S1-1

this introductory textbook with its emphasis on atomic-level description and analysis we concentrate mostly on understanding gases and solids.

An active field of research, called "molecular dynamics," models liquids, gases, and solids by computational modeling using the Momentum Principle and appropriate forces between the molecules. The difference between this work and the computational models you have made is that sophisticated programming techniques are required to deal with very large numbers of molecules, sometimes as many as a million, in a reasonable amount of computer time.

S1.2 GAS LEAKS THROUGH A HOLE

In Chapter 12 we used statistical mechanics to determine the average speed of a gas molecule. Here we'll see some interesting phenomena in which the average speed plays a role. We will model the gas molecules as little balls that don't attract each other and interact only in brief elastic collisions.

We will frequently use the symbol $n = N/V$ to stand for the number of gas molecules per unit volume, which we will express in SI units as number per cubic meter:

NUMBER DENSITY: NUMBER PER CUBIC METER

$$\text{Definition: } n \equiv \frac{N}{V}$$

N is the number of gas molecules in the volume V. The units of n are molecules per cubic meter.

Warning: You may be familiar from chemistry with the ideal gas law written in the form $PV = nRT$, where n is the number of moles. Here n means something else—the number of molecules per cubic meter, N/V.

EXAMPLE **n at Standard Temperature and Pressure**

Standard Temperature and Pressure (or STP) is defined for a gas to be 0 °C = 273 K and the average air pressure at sea level. Under STP conditions the ideal gas law can be used to show that one mole of a gas will occupy a volume of 22.4 liters $= 22.4 \times 10^3 \text{ cm}^3 = 22.4 \times 10^{-3} \text{ m}^3$. What is the number density n of a gas at STP?

Solution One mole consists of 6.02×10^{23} molecules, so

$$n = \frac{6.02 \times 10^{23} \text{ molecules}}{22.4 \times 10^{-3} \text{ m}^3}$$
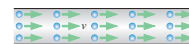$$= 2.68 \times 10^{25} \text{ molecules/m}^3$$

Figure S1.3 Side view of molecules all traveling to the right with speed v inside a tube. There are n molecules per cubic meter inside the tube.

Cross-sectional area A

Figure S1.4 End view of molecules all traveling the same direction in a tube of cross-sectional area A.

One-Directional Gas

We will calculate the leakage rate of a gas through a small hole in a container filled with the gas. First we'll consider a simplified one-directional example, in order to understand the basic issues before stating the results for a real three-dimensional gas.

The chain of reasoning that we follow is basically geometric. Consider a situation in which many gas molecules are all traveling to the right inside a tube. For the moment, temporarily assume that they all have the same speed v (Figure S1.3). The cross-sectional area of the tube is A (Figure S1.4).

Enough physics for this week!