



# **Thermodynamics**

## **The Kinetic Theory of Gases**

### **Molecular Model**

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## Last time

- heat transfer mechanisms
- conduction over a distance
- convection
- heat transfer: radiation and Stefan's law

# Overview

- a little more about radiative heat transfer
- modeling an ideal gas at the microscopic level
- pressure and temperature from microscopic model

## Reminder: Radiation

Heat can also be transferred across a vacuum by **radiation**.

This radiation takes the form of electromagnetic (em) radiation, or light. However, most of this radiation is not in the range of wavelengths that are visible to us.

Light carries energy, so this an energy transfer.

## Reminder: Stefan's Law

How fast does a hot object radiate away energy?

$$P = \sigma A e T^4$$

where

- $P$  is power
- $\sigma = 5.6696 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$
- $A$  is the surface area of the object
- $e$  is the emissivity ( $0 \leq e \leq 1$  always)
- $T$  is temperature

The net rate of energy change depends on the difference in temperature  $\Delta T$ , between an object and its environment.

$$P_{\text{net}} = \sigma A e (T_o^4 - T_e^4)$$

# Light (Electromagnetic Radiation)

Light travels at this fixed speed,  $c = 3.00 \times 10^8 \text{ m s}^{-1}$ .

For any wave, if  $v$  is the wave propagation speed:

$$v = f\lambda$$

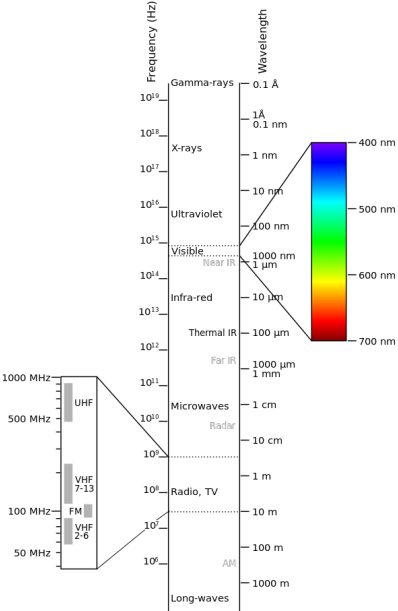
For light:

$$c = f\lambda$$

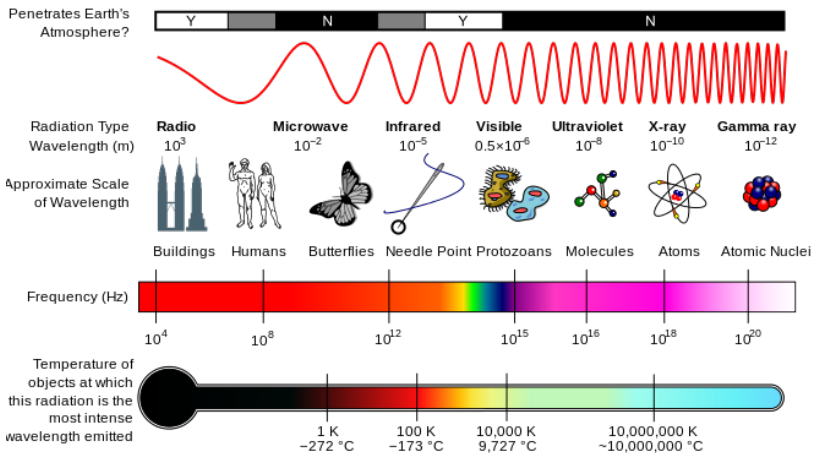
So, if the frequency of the light is given, you also know the wavelength, and vice versa.

$$\lambda = \frac{c}{f} ; \quad f = \frac{c}{\lambda}$$

# Electromagnetic spectrum



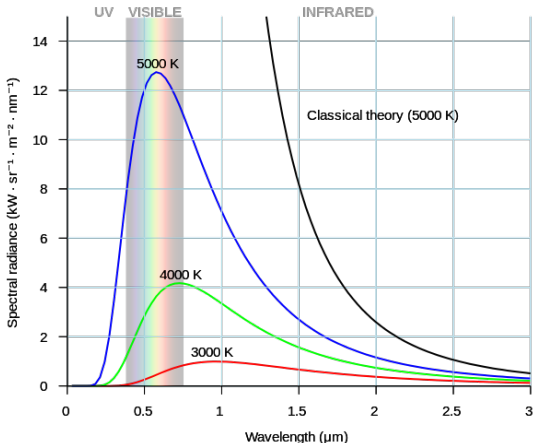
# Electromagnetic spectrum





# Blackbody Radiation

All objects radiate light with characteristic wavelengths depending on the object's temperature.



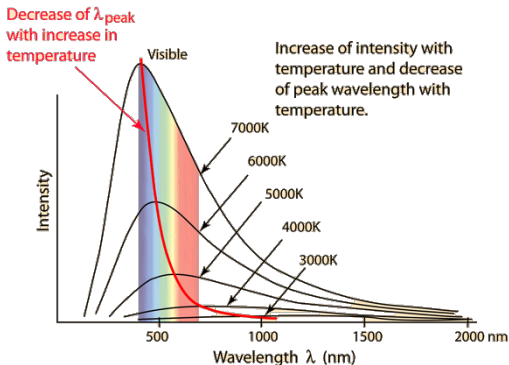
Hotter objects emit light with shorter wavelengths (on average).

<sup>1</sup>Graph from Wikipedia, created by user Darth Kule.

# Blackbody Radiation: Wien's Law

**Wien's (Displacement) Law** relates the peak wavelength emitted by a blackbody to its temperature:

$$\lambda_{\max} = \frac{b}{T}$$



$b = 2.898 \times 10^{-3} \text{ m K}$  is a constant.

<sup>1</sup>Figure from HyperPhysics.

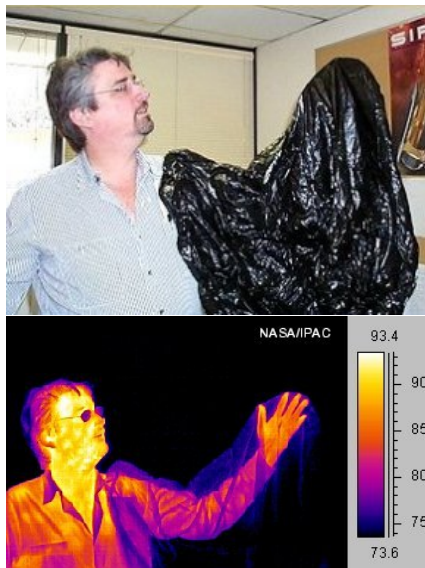
# Radiation

People emit light as well, but the wavelengths corresponding to our body temperature are longer than what we can see with the naked eye.

Humans and warm-blooded animals radiate **infrared radiation**. (“below red”)



## Visible vs. Infrared radiation



# Radiation

Objects much hotter than the human body will radiate at shorter wavelengths that are visible to us.



# The Greenhouse Effect

Gardeners use greenhouses, huts made of glass or transparent plastic, to keep plants warm.

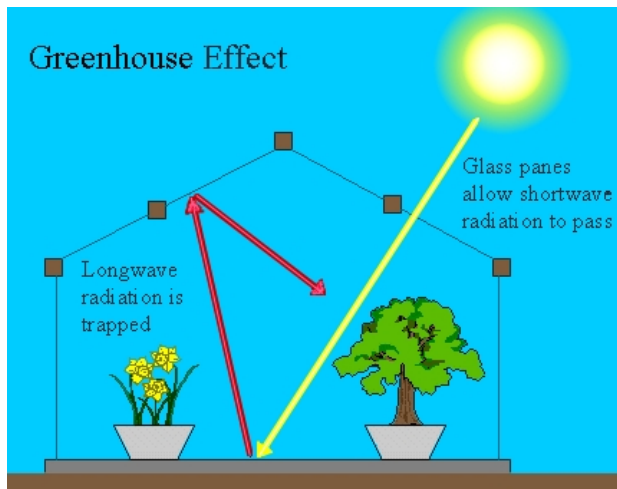
The effect that causes this to work is called the greenhouse effect.

The Sun is very hot and emits a lot of radiation in the visible (shorter) wavelengths.

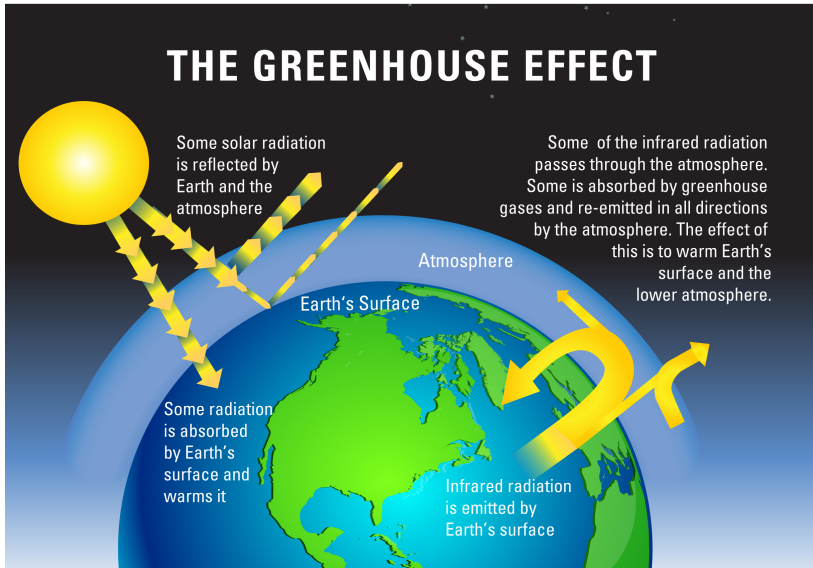
Objects on Earth absorb this radiation and emit their own. However, since objects on the Earth are substantially cooler than the Sun, the wavelengths re-emitted are longer.

The glass allows the shorter wavelengths through, but traps the longer wavelengths.

# The Greenhouse Effect



# The Greenhouse Effect



<sup>1</sup>Figure from the National Academy of Sciences, *America's Climate Choices*



# Kinetic Theory of Gases

We have already started to study what happens in thermodynamic systems to bulk properties in various transformations.

However, just from looking at macroscopic quantities it is not entirely clear how to interpret pressure, or what temperature or heat actually is.

# Kinetic Theory of Gases

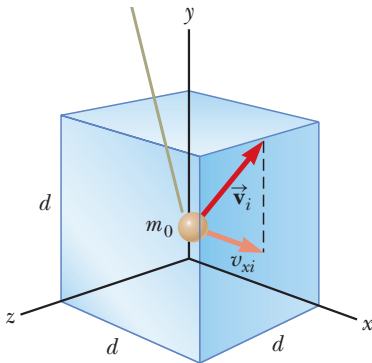
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However, just from looking at macroscopic quantities it is not entirely clear how to interpret pressure, or what temperature or heat actually is.

**Statistical thermodynamics** seeks to explain how these macroscopic quantities arise from the microscopic behavior of particles, *on average*.

We cannot model every the motion of every single particle in a substance, but we can say a lot about the **ensemble** of particles statistically.

# Molecular Model of an Ideal Gas



We model the particles of gas as small, identical, and obeying Newton's laws, with no long range interactions.

We assume all collisions are elastic.

For now, consider a single particle in a cubic box, of side length  $d$ .

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<sup>1</sup>Figure from Serway & Jewett.

# Molecular Model of an Ideal Gas

We start by considering the origin of pressure.

When a particle, mass  $m_0$ , rebounds off a wall, its momentum change is:

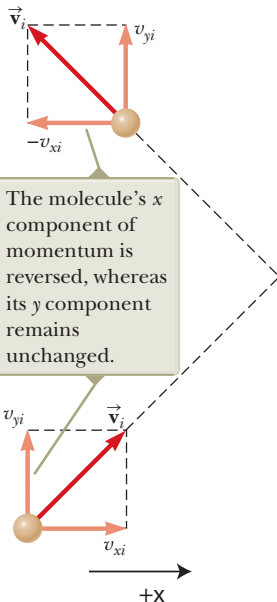
$$\Delta p = -2m_0 v_x$$

The average force on the particle is

$$\bar{F}_{\text{part}} = \frac{\Delta p}{\Delta t}$$

and by Newton III the force on the wall is:

$$\bar{F} = \frac{2m_0 v_x}{\Delta t} \mathbf{i}$$



# Molecular Model of an Ideal Gas

The gas particle bounces back and forth between the left and right walls.

We do not know how long it interacts with the wall for each time, but what we can know, and is more useful, is what is the average force on the wall over a long period of time.

The time between the particle hitting the right wall once and hitting it again is

$$\Delta t = \frac{2d}{v_x}$$

So the average force on the wall from the one particle over long periods of time is

$$\bar{\mathbf{F}} = \frac{m_0 v_x^2}{d} \mathbf{i}$$

## Molecular Model of an Ideal Gas

In a gas, there will be many particles (assume each has mass  $m_0$ ) interacting with each wall in this way.

The  $i$ th particle exerts a force on the wall:

$$\bar{\mathbf{F}}_i = \frac{m_0 v_{xi}^2}{d} \mathbf{i}$$

(we ignore collisions between particles, since they are small and density is low)

The magnitude of the *total* force on the wall is:

$$F = \frac{m_0}{d} \sum_{i=1}^N v_{xi}^2$$

where  $N$  is the number of particles.

# Molecular Model of an Ideal Gas

We can re-write the sum  $\sum_{i=1}^N v_{xi}^2$  in terms of the average of the  $x$ -component of the velocity squared:

$$F = \frac{m_0}{d} N \overline{v_x^2}$$

We can already relate this force to a pressure, but first, let's relate it to the average translational kinetic energy of a particle.

# Molecular Model of an Ideal Gas

For a particle in 3-dimensions:

$$v_i^2 = v_{xi}^2 + v_{yi}^2 + v_{zi}^2$$

If this is true for each individual particle, it is true for averages over many particles automatically:

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$$



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No! We assume **isotropy**: the gas behaves the same way in each direction.

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$$

and

$$\overline{v^2} = 3\overline{v_x^2}$$

# Molecular Model of an Ideal Gas

$$F = \frac{m_0}{d} N \overline{v_x^2}$$

becomes:

$$\begin{aligned} F &= \frac{1}{3} \frac{m_0}{d} N \overline{v^2} \\ &= \frac{2}{3} \frac{N}{d} \bar{K}_{\text{trans}} \end{aligned}$$

where  $\bar{K}_{\text{trans}} = \frac{1}{2} m_0 \overline{v^2}$  is the average translational kinetic energy of a particle.

## Pressure from the Molecular Model

Using  $P = F/A$ , the pressure at the wall and throughout the gas is

$$P = \frac{2}{3} \frac{N}{Ad} \bar{K}_{\text{trans}}$$

which, since  $V = Ad = d^3$  we can write as:

$$P = \frac{2}{3} \frac{N}{V} \bar{K}_{\text{trans}}$$

This relates the pressure in the gas to the average translational kinetic energy of the particles.

More K.E., or less volume  $\Rightarrow$  higher pressure.

## Relation to Macroscopic view of an Ideal Gas

Ideal gas equation:

$$PV = nRT$$

or equivalently:

$$PV = Nk_B T$$

If we put our new expression for pressure into this equation:

$$\frac{2}{3} N \bar{K}_{\text{trans}} = Nk_B T$$

We can cancel  $N$  from both sides and re-arrange:

$$\bar{K}_{\text{trans}} = \frac{1}{2} m_0 \overline{v^2} = \frac{3}{2} k_B T$$

# Temperature from the Molecular Model

We can also relate temperature to molecular motion!

$$T = \frac{2}{3k_b} \bar{K}_{\text{trans}}$$

Temperature is directly proportional to the translational kinetic energy of the particles.

# Summary

- molecular model of an ideal gas
- pressure from collisions

**Test** ~~tomorrow~~ Wednesday.

## Homework

- full solution HW, due Fri
- WebAssign, due today