Problem Solving

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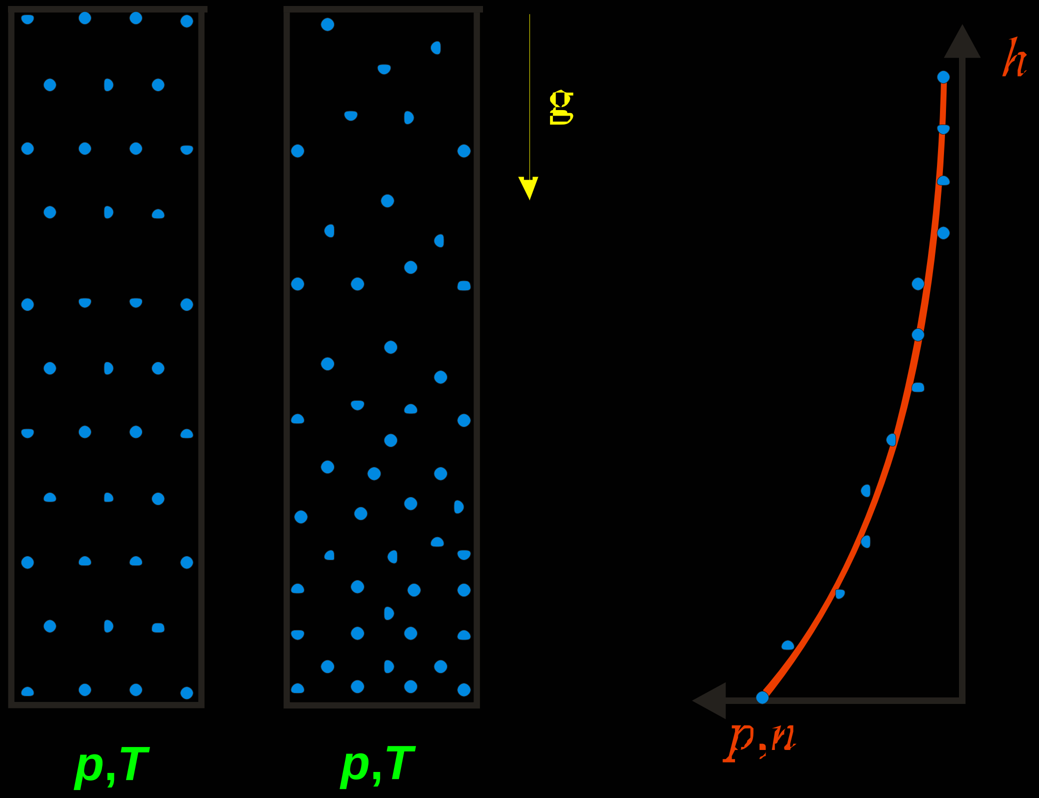
Problem Solving

- The Earth's atmosphere is just the air we breathe. It's also a buffer that keeps us from meteorites, a screen against deadly radiation, and the reason radio waves can be bounced for long distances around the planet.
- The atmosphere of Earth is a layer of gases surrounding our planet. It is a gas system which is not in thermodynamic equilibrium: its temperature is not uniform and the amounts of its chemical constituents (N_2, O_2, Ar, CO_2, etc.) are maintained at a nonequilibrium value through the complex physical and chemical processes and interactions involved.

Problem Solving

- We will define and calculate the most important physical properties of the atmosphere: thickness, mass and atmospheric escape (dissipation) time.
- We will also analyze the nonradiative processes in the Earth's atmosphere as a responsible processes for the efficiency of global warming. Our analysis will be based on the fundamentals of collisional (scattering) processes that occur among all constituents of the atmosphere, contributing to the energy transfer responsible for the air heating around us.

Problem Solving

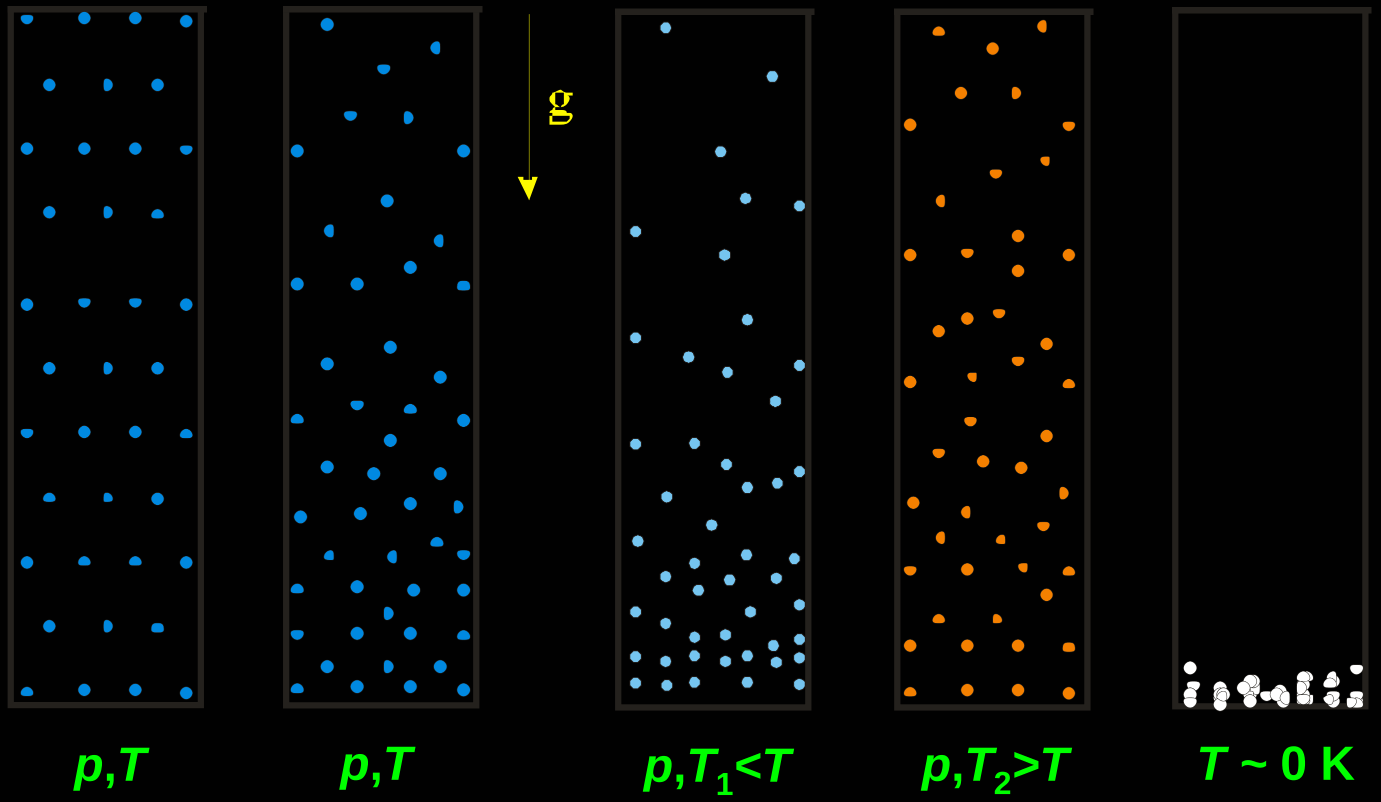


- Pressure and thickness

Problem Solving

$pV=\nu RT$

$p=nkT$



- Pressure and thickness

Problem Solving

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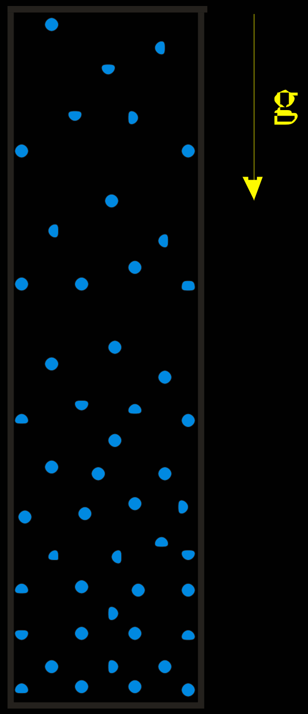
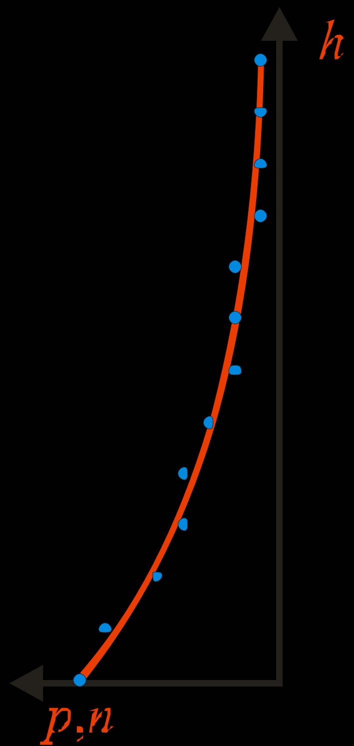


p,T



$$n = n_0 \exp\left(-\frac{mgz}{kT}\right).$$

$$p = p_0 \exp\left(-\frac{Mgz}{RT}\right),$$

- Pressure and thickness

Problem Solving

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p=nkT

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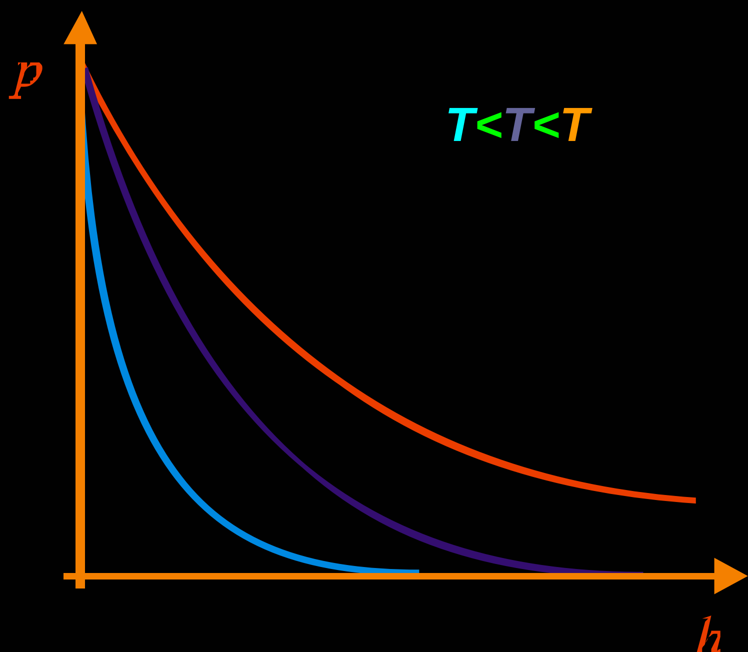

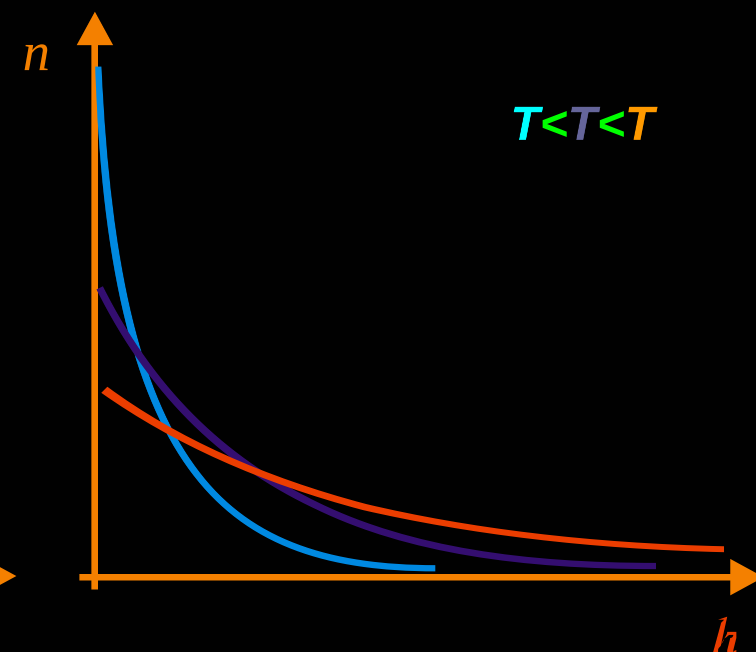

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Problem Solving

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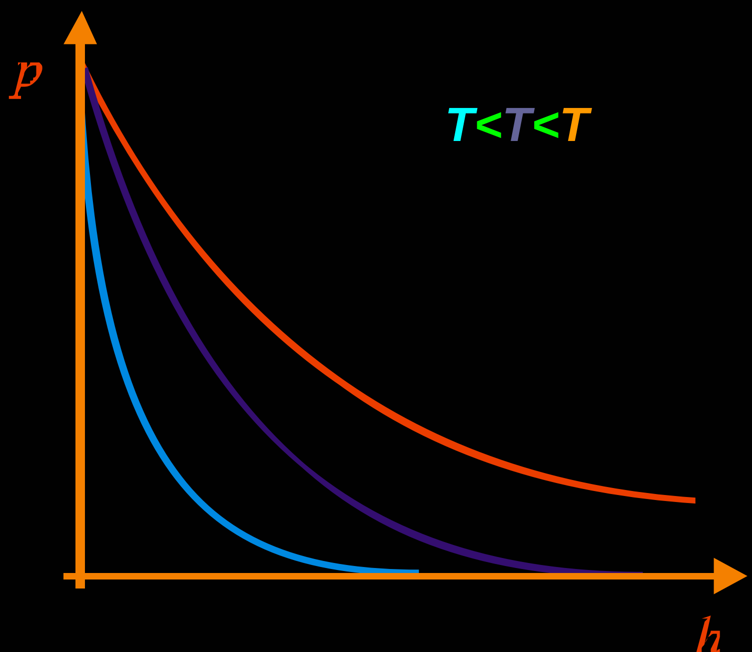

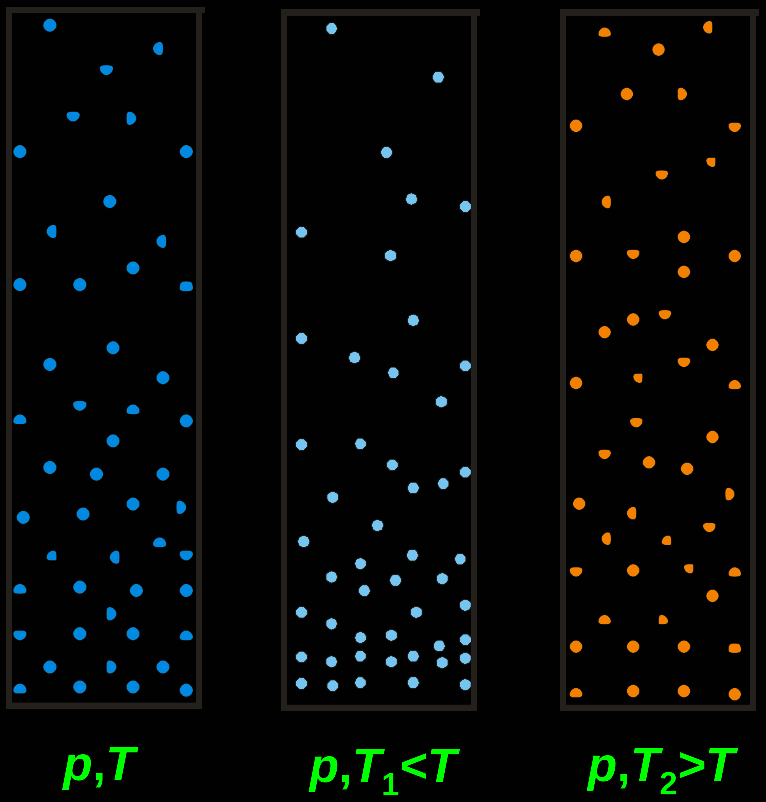

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Problem Solving

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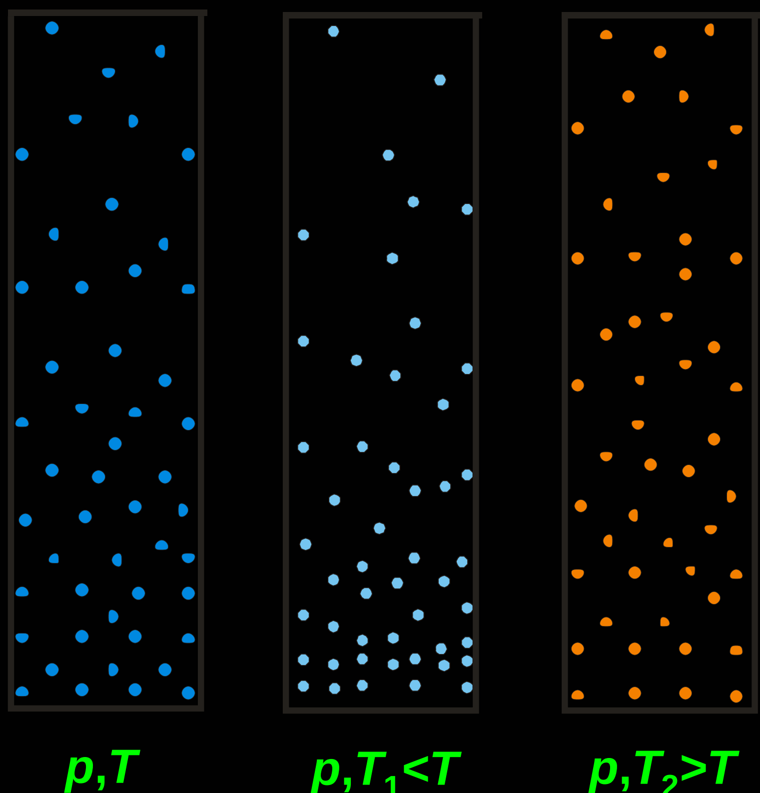

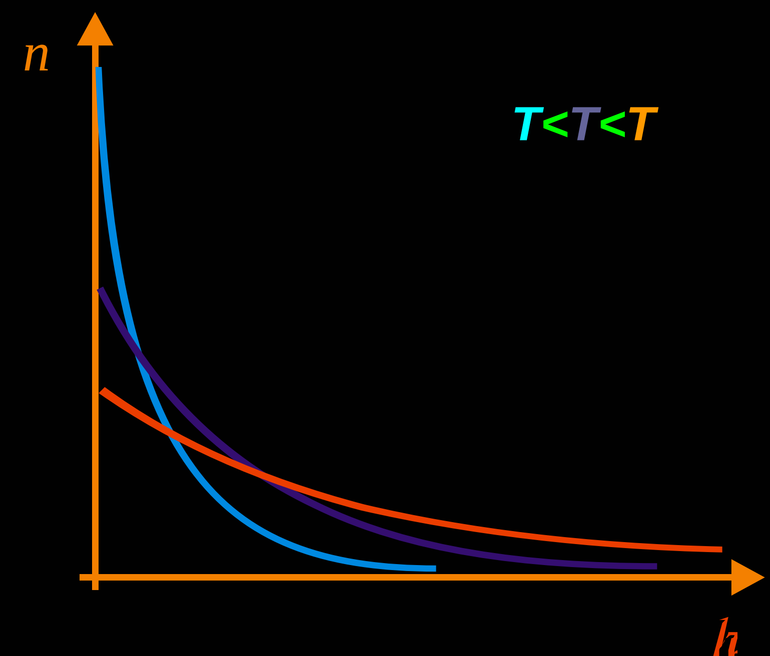

- Pressure and thickness

Problem Solving

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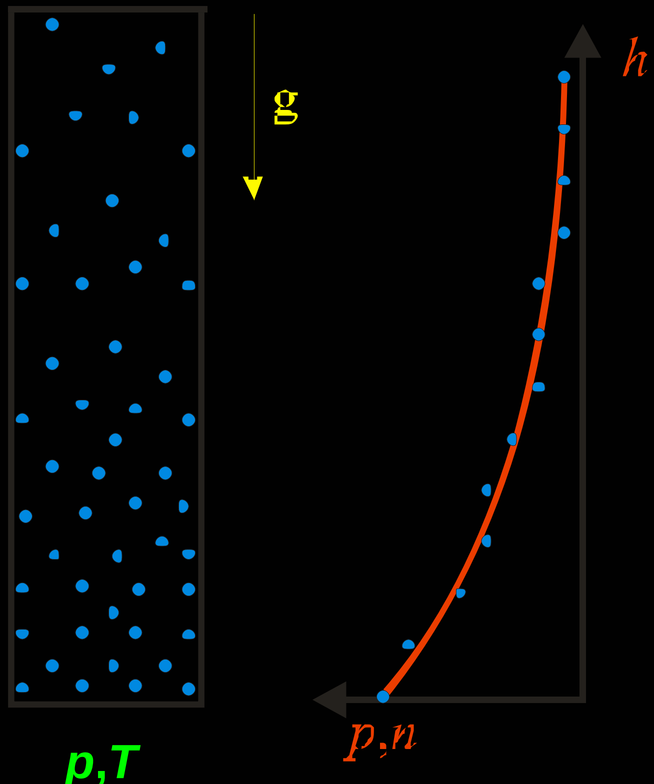


$$p = p_0 \exp(-z/h_e)$$

$$h_e = RT/Mg$$

$$M = 20\ \mathrm{g/mol}$$

$$T = 280\ \mathrm{K}$$

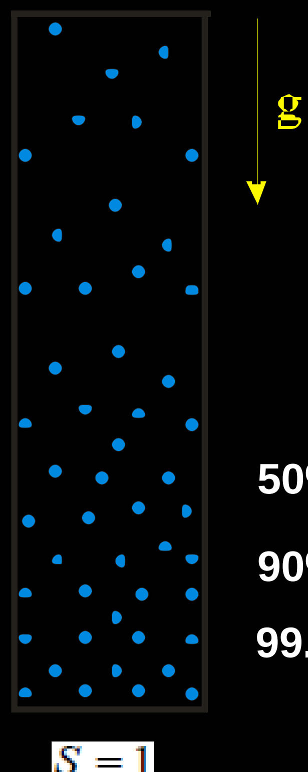
$$h_e \approx 8\ \mathrm{km}$$

- Pressure and thickness

Problem Solving

- Pressure and thickness

Problem Solving



$$dN = n_0 \exp\left(-\frac{mgz}{kT}\right)dz \quad \Big|_0^{\infty}$$

$$N = n_0 kT / mg$$

$$M_{атм} = Nm \cdot 4\pi R^2 = \frac{n_0 kT}{g} \cdot 4\pi R^2 = \frac{p_0}{g} \cdot 4\pi R^2 = 5{,}3 \times 10^{18}\ \text{kg}$$

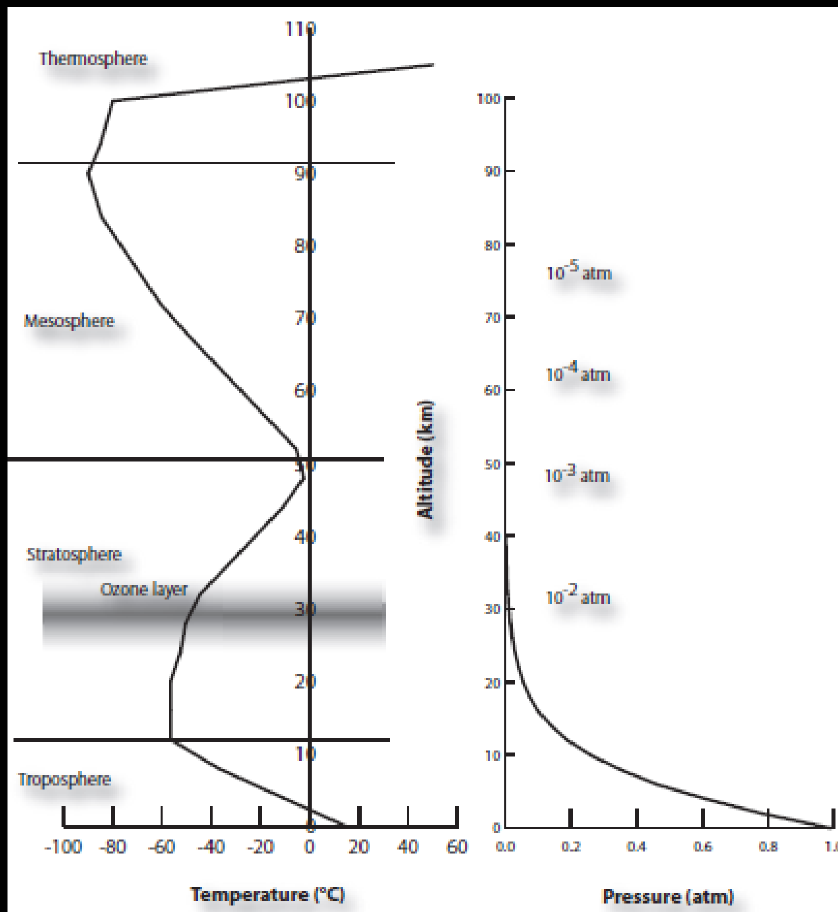
50% of the atmosphere by mass is below an altitude of 5.6 km

90% of the atmosphere by mass is below an altitude of 16 km

99.99997% of the atmosphere by mass is below 100 km

- Atmospheric mass

Problem Solving



1) Temperature is not uniform but is well defined locally at every point of altitude.

2) $g=g(h)+g(\omega)$.

We obtain that : $n \to \infty$ $p \to \infty$

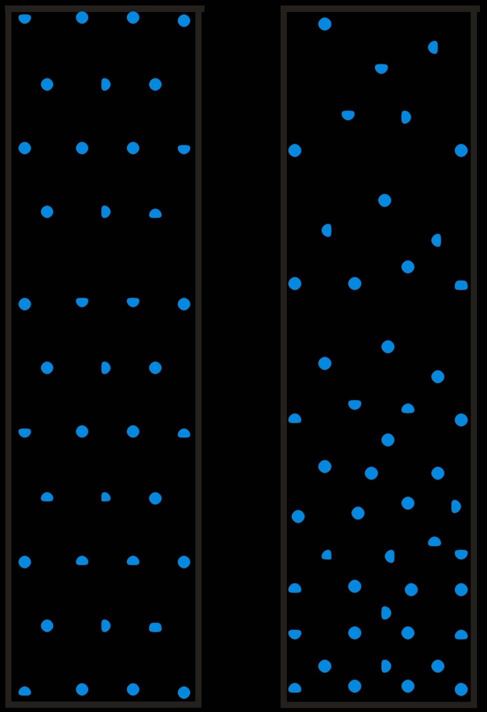
if $z \to \infty$

This conclusions are in contrary to the obtained experimental results but support the idea of the atmosphere as a system which is not in equilibrium.

- Nonequilibrium system

Problem Solving

- How we recognize that the Earth's atmosphere is in nonequilibrium state?
- When a system is not in equilibrium, processes such as chemical reactions, conduction of heat and transport of matter take place so as to drive the system towards equilibrium.
- Nonequilibrium systems usually exchange the matter with the surroundings to reach the equilibrium.



- Atmospheric dissipation

Problem Solving

- One of these processes is, so called, ***atmospheric dissipation*** **or** ***atmospheric escape*****. Its something like evaporation - if the kinetic energy of a molecule is high enough that its velocity is above the escape velocity (and it doesn't hit another molecule on its way out), it escapes. Lighter molecules will be more likely to have the velocity they need to escape. That is why there isn't much hydrogen in the atmosphere.**

- Atmospheric dissipation

Problem Solving

- If you want to calculate the average time for all molecules to escape from the Earth's atmosphere, you must use the Maxwell velocity distribution law.

$$j = \frac{1}{4} n_0 \sqrt{\frac{8kT}{\pi m}} \exp\left(-\frac{m v_{\mathrm{II}}^2}{2kT} \right) = 3 \times 10^{-296}\ \mathrm{s^{-1} m^{-2}}$$

$$J = j 4\pi R^2, \quad J = -\mathrm{d}N / \mathrm{d}t, \quad N = 4\pi R^2 h_{\mathrm{e}} n$$

$$j = \frac{1}{4} n_0 \sqrt{\frac{8kT}{\pi m}} \exp\left(-\frac{m v_{\mathrm{II}}^2}{2kT} \right) = -h_{\mathrm{e}} \frac{\mathrm{d}n}{\mathrm{d}t}$$

$$m = 5 \times 10^{-26}\ \mathrm{kg}$$

$$n_0 = 3 \times 10^{19}\ \mathrm{m^{-3}}$$

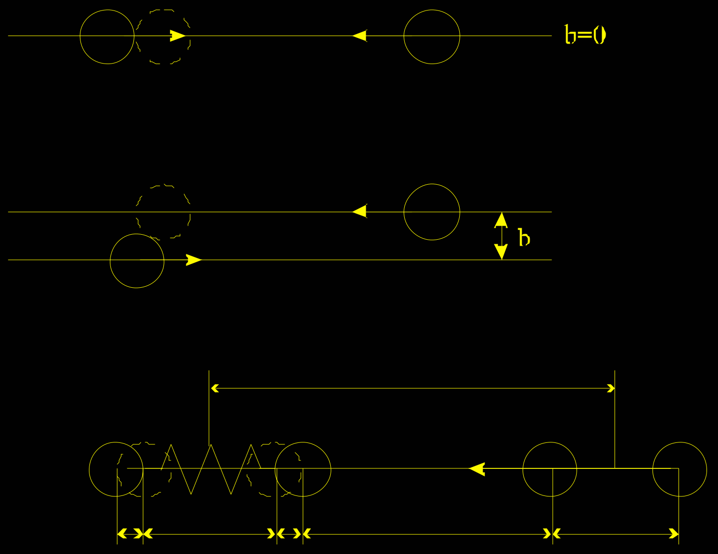
$$v_{\mathrm{II}} \approx 11\ \mathrm{km/s}$$

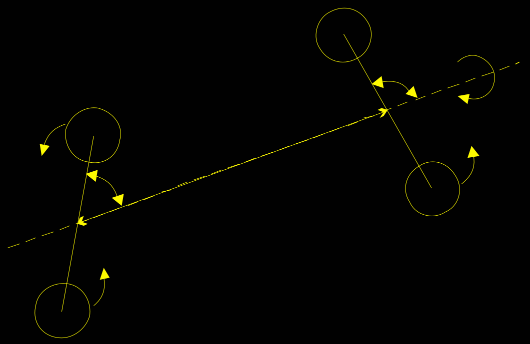
$$\tau = 4 h_{\mathrm{e}} \sqrt{\frac{\pi m}{8kT}} \exp\left(\frac{m v_{\mathrm{II}}^2}{2kT} \right) \approx 10^{319}\ \mathrm{s}.$$

- Atmospheric dissipation

Problem Solving

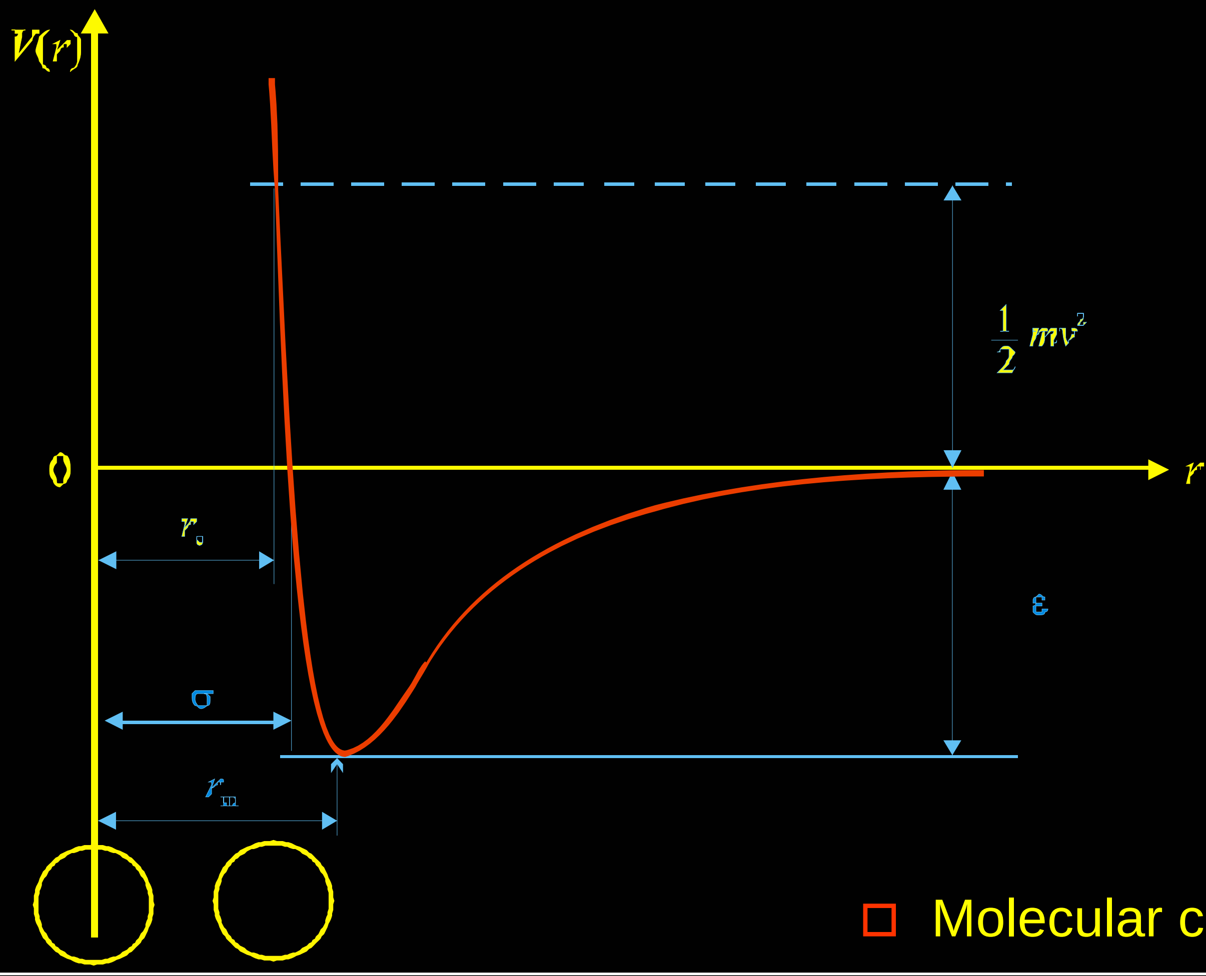
- Elastic and inelastic collisions can be recognized among the molecules in the atmosphere.
- Head-on collisions with or without vibrational and/or rotational energy transfer.

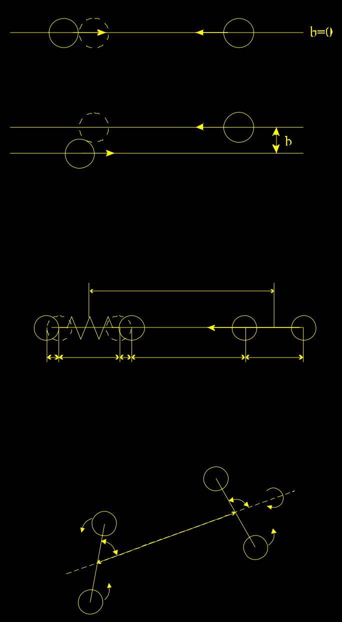




- Molecular collisions

Problem Solving





- Molecular collisions

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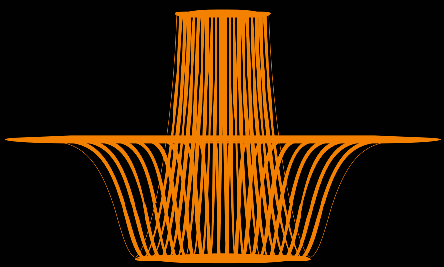
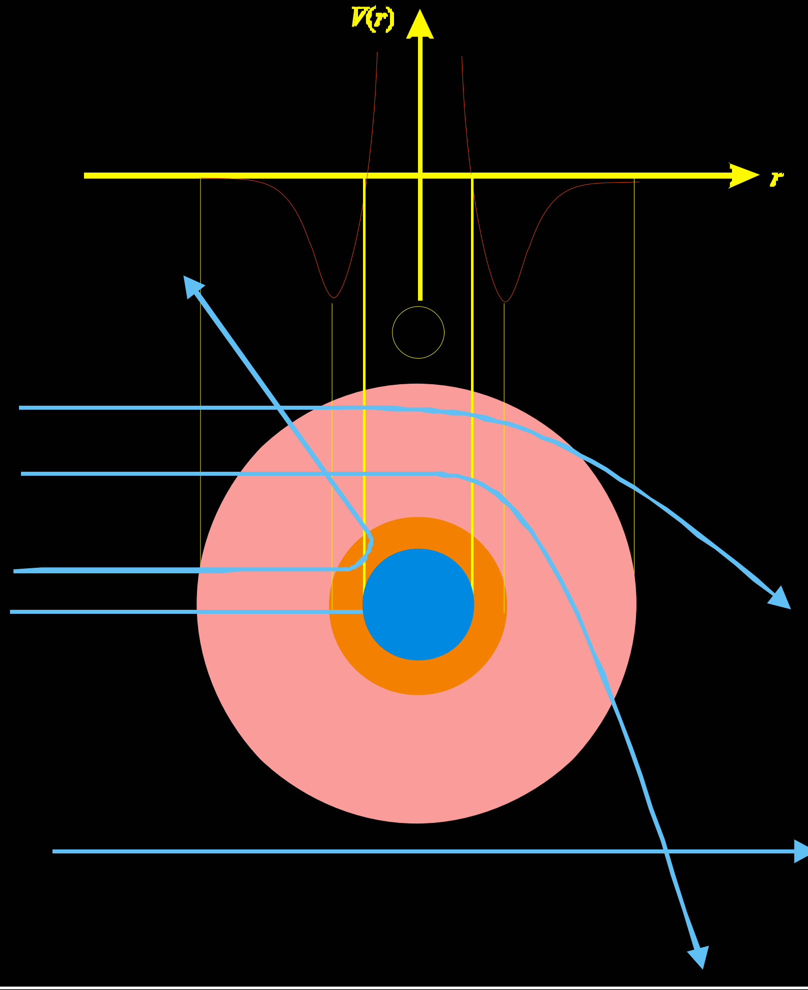
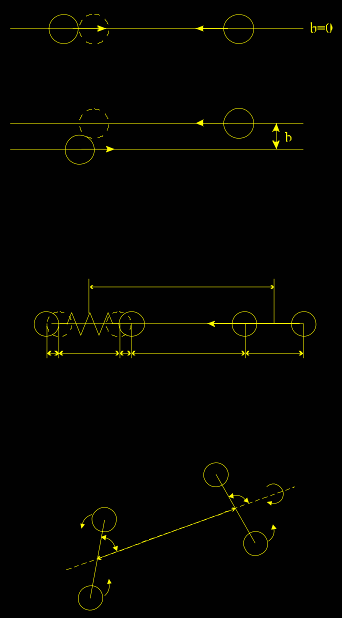


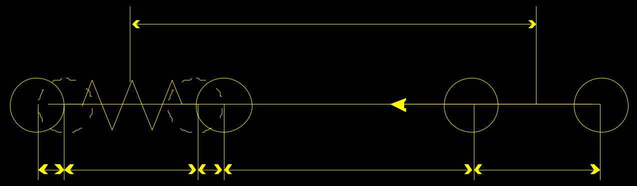




- Molecular collisions

Problem Solving

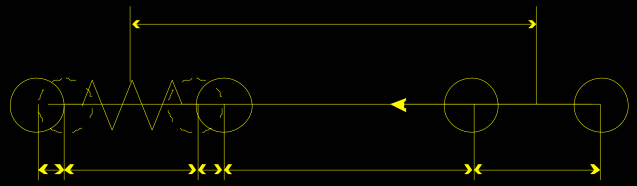
- Molecules usually gain and lose vibrational energy in collisions.
- They can be activated or deactivated by absorption or emission of IR radiation, but their radiative lifetime is so long that radiative deactivation may be neglected in most cases.
- They usually deactivate in nonradiative way due to collisions transforming all (or one part) of their vibrational energy to the translational energy of their collisional partner.



- Molecular collisions

Problem Solving

- The problem which interests us is whether the collision is likely to result in a transfer of energy between vibration and translation.
- If we do not have some energy transfer it will be an adiabatic collision. Otherwise we have an inelastic nonadiabatic collision, because translational energy after and before the collision will be different.



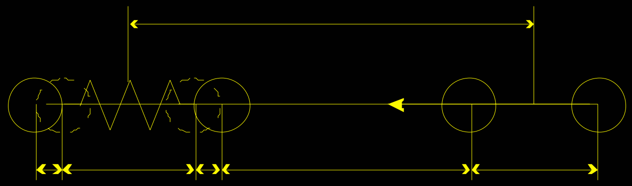
- Molecular collisions

Problem Solving

- A simple physical explanation could is given by Ehrenfest's Adiabatic Principle.
- This may be expressed by defining an adiabatic parameter:

$$\zeta = \frac{\tau_c}{t_v},$$

- Non-adiabatic collisions corresponds to the $\zeta < 1$
- The criterion for a non-adiabatic collisions with efficient energy transfer is now $\tau_c < t_v$.



- Molecular collisions

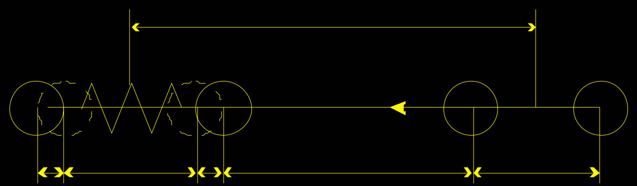
Problem Solving

- The duration of a collision may be regarded as $\tau_c = a / < v >$
- Now the criterion for efficient transfer becomes

$$\frac{a}{< v >} < \frac{1}{\nu} \quad \text{or} \quad < v > \; > a \cdot \nu.$$

- Taking the usual expression for the average velocity, this becomes

$$\langle v \rangle = \sqrt{\frac{8kT}{\pi m}} > a\nu \, .$$



- Molecular collisions

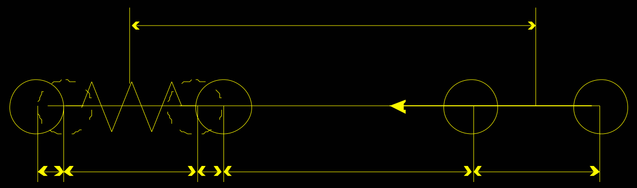
Problem Solving

- It is interesting to make a rough estimate for some diatomic molecule whose vibrational mode is active at 300 K. In his case *a* = 2x10^{-8} cm, <*v*>=2.8x10^4 cm/s, so

$$\tau_c = a / < v > = 7.15 \times 10^{-13}\ \mathrm{s}$$

- The fundamental vibrational frequency is $556\ \mathrm{cm}^{-1} = 1.7 \times 10^{13}\ \mathrm{Hz}$
- And the period of oscillation will be $t_v = \nu^{-1} = 5.88 \times 10^{-14}\ \mathrm{s}$
- We can see that $\tau_c > t_v$

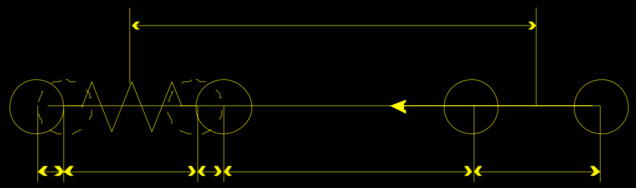
so one can conclude that for this molecule adiabatic collisions without energy transfer are dominant at room temperature.



- Molecular collisions

Problem Solving

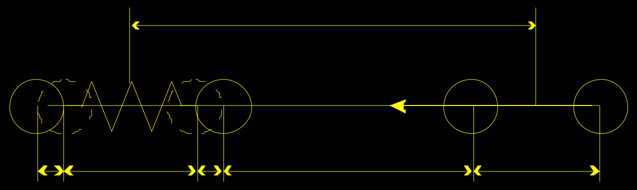
- Experiments shows that for some molecules whose vibrational modes are active at 300 K, the radius of influence is equal to a = 1.8x10^{-9} cm, while the mean velocity at the same temperature is $\langle v \rangle$=3.6x10^{4} cm/s. The vibrational frequency of this active modes is ν = 673 cm^{-1}.
- Calculate the adiabatic parameter for this molecule.
- What kind of collisions (adiabatic or non-adiabatic) are dominant for this molecule at room temperature?



- Homework

Problem Solving

- Experiments shows that, for one molecule whose vibrational mode is active at 300 K, the radius of influence is equal to *a* = 2.3x10^{-9} cm, while the mean velocity at the same temperature is $<v>$=2.7x10^{4} cm/s. The vibrational frequency of this active mode is ν = 404 cm^{-1}.
- Calculate the adiabatic parameter for this molecule.
- What kind of collisions (adiabatic or non-adiabatic) are dominant for this molecule at room temperature?



- Homework