

Thermal Physics = Thermodynamics + Statistical Mechanics

- conceptually, the *most difficult* subject of the undergraduate physics program.

Thermodynamics provides a framework of relating the *macroscopic* properties of a system to one another. It is concerned only with macroscopic quantities and ignores the microscopic variables that characterize individual molecules (both strength and weakness).

Statistical Mechanics is the bridge between the microscopic and macroscopic worlds: it links the laws of thermodynamics to the statistical behavior of molecules.

* Lecture notes: Originally written by Prof. Gershenson *

Macroscopic Description is Qualitatively Different!

Why do we need to consider macroscopic bodies as a special class of physical objects?

For a single particle: all equations of classical mechanics, electromagnetism, and quantum mechanics are **time-reversal invariant** (Newton's second law, $F = dp/dt$, looks the same if the time t is replaced by $-t$ and the momentum p by $-p$).

For macroscopic objects: the processes are often **irreversible** (a time-reversed version of such a process never seems to occur).

Examples: (a) living things grow old and die, but never get younger, (b) if we drop a basketball onto a floor, it will bounce several times and eventually come to rest - **the arrow of time** does exist.

“More is different”, Phil Anderson, *Science*, **177**, 393 (1972)

The Main Idea of the Course

Statistical description
of a large system
of identical (mostly,
non-interacting) particles

all microstates of an isolated
system occur with the same
probability, the concepts of
multiplicity (configuration
space), **Entropy**



Equation of state
for macrosystems
(how macroparameters of the
system and the temperature
are interrelated)



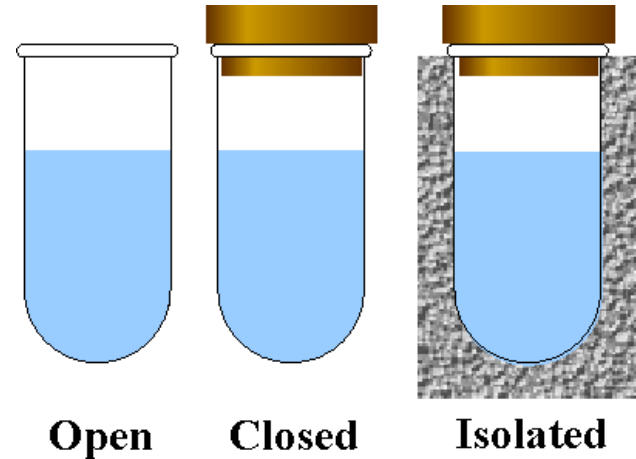
Irreversibility of
macro processes,
the 2nd Law of Thermodynamics

Thermodynamic Systems, Macroscopic Parameters

Open systems can exchange both matter and energy with the environment.

Closed systems exchange energy but not matter with the environment.

Isolated systems can exchange neither energy nor matter with the environment.



Internal and external macroscopic parameters: temperature, volume, pressure, energy, electromagnetic fields, etc. (average values, fluctuations are ignored).

No matter what is the initial state of an isolated system, eventually it will reach **the state of thermodynamic equilibrium** (no macroscopic processes, only microscopic motion of molecules).

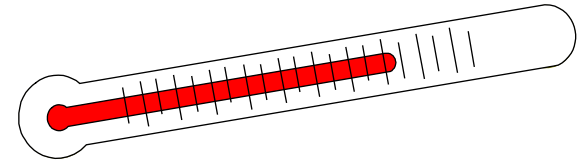
A very important macro-parameter: Temperature

Temperature is a property associated with **random motion of many particles**.

Introduction of the concept of temperature in thermodynamics is based on the **the zeroth law of thermodynamics**:

A well-defined quantity called **temperature** exists such that two systems will be in thermal equilibrium if and only if both have the same temperature.

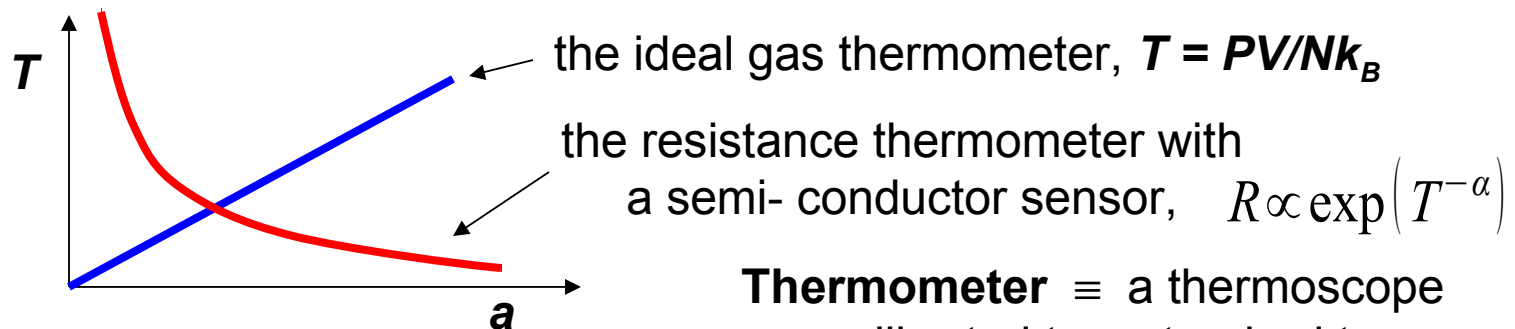
Temperature Measurement



Properties of a **thermoscope** (any device that quantifies temperature):

1. It should be based on an easily measured macroscopic quantity **a** (volume, resistance, etc.) of a common macroscopic system.
2. The function that relates the chosen parameter with temperature, **$T = f(a)$** , should be monotonic.
3. The quantity should be measurable over as wide a range of **T** as possible.

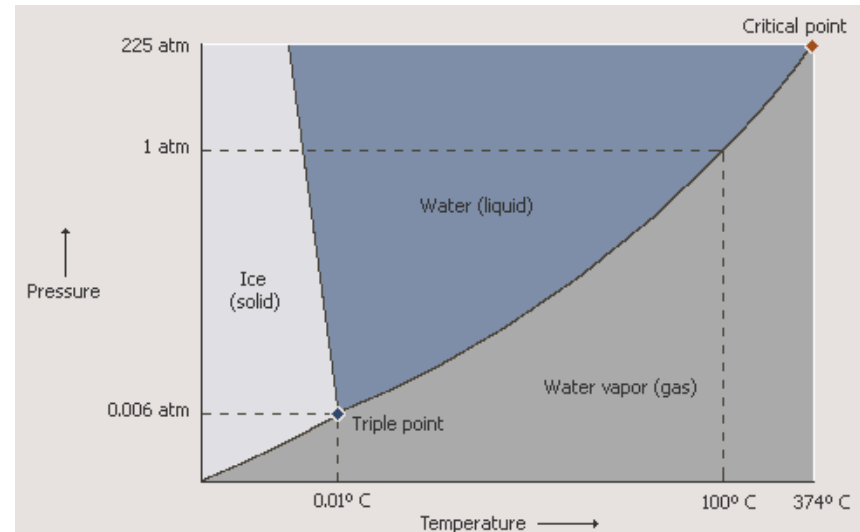
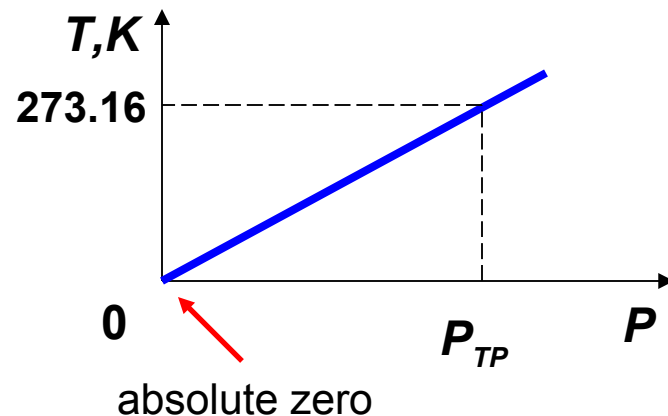
The simplest case – linear dependence **$T = Aa$** (e.g., for the ideal gas thermometer, **$T = PV/Nk_B$**).



Thermometer \equiv a thermoscope
calibrated to a standard temp. scale

The Absolute (Kelvin) Temperature Scale

The absolute (Kelvin) temperature scale is based on fixing T of the triple point for water (a specific $T = 273.16 \text{ K}$ and $P = 611.73 \text{ Pa}$ where water can coexist in the solid, liquid, and gas phases in equilibrium).

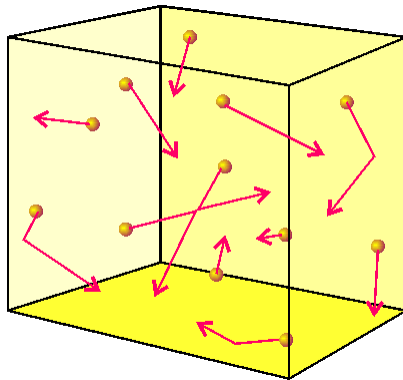


$$T \equiv 273.16 \text{ K} \left(\frac{P}{P_{TP}} \right) \quad \text{- for an ideal gas constant-volume thermoscope}$$

P_{TP} – the pressure of the gas in a constant-volume gas thermoscope at $T = 273.16 \text{ K}$

Our first model of a many-particle system: the Ideal Gas

Models of matter: **gas** models (random motion of particles)
 lattice models (positions of particles are fixed)



Air at normal conditions:

$\sim 2.7 \cdot 10^{19}$ molecules in 1 cm^3 of air (*Pr.* 1.10)

Size of the molecules $\sim (2-3) \cdot 10^{-10} \text{ m}$, distance between the molecules $\sim 3 \cdot 10^{-9} \text{ m}$

The average speed - 500 m/s

The mean free path - 10^{-7} m (0.1 micron)

The number of collisions in 1 second - $5 \cdot 10^9$

The ideal gas model - works well *at low densities* (diluted gases)

- all the molecules are identical, N is huge;
- the molecules are tiny compared to their average separation (point masses);
- the molecules do not interact with each other;
- the molecules obey Newton's laws of motion, their motion is random;
- collisions between the molecules and the container walls are elastic.

The Equation of State of Ideal Gases

An equation of state - an equation that relates macroscopic variables (e.g., P , V , and T) for a given substance *in thermodynamic equilibrium*.

In equilibrium (\equiv no macroscopic motion), just a *few macroscopic* parameters are required to describe the state of a system.

The ideal gas equation of state:

$$PV = nRT$$

P – pressure [Newtons/m²]

V – volume [m³]

n – number of moles of gas [mol]

T – the temperature in Kelvins [K]

R – a universal constant $R \approx 8.315 \frac{J}{mol \times K}$



The Ideal Gas Law

In terms of the total number of molecules, $N = n \cdot N_A$

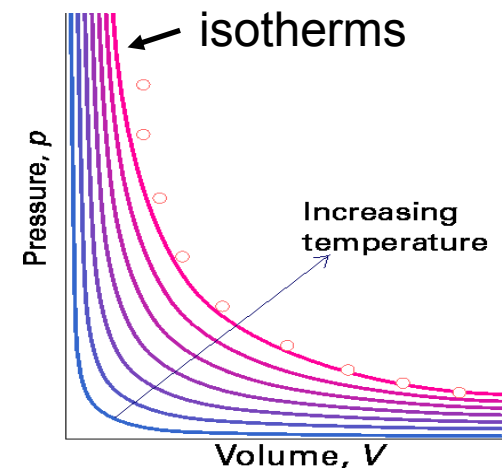
$$PV = Nk_B T$$

the Boltzmann constant $k_B = R/N_A \approx 1.38 \cdot 10^{-23} \text{ J/K}$
(introduced by Planck in 1899)

The equations of state cannot be derived within the frame of thermodynamics: they can be either considered as experimental observations, or “borrowed” from statistical mechanics.

Avogadro's Law: equal volumes of different gases at the same P and T contain the same amount of molecules.

The P - V diagram – the projection of the surface of the equation of state onto the P - V plane.

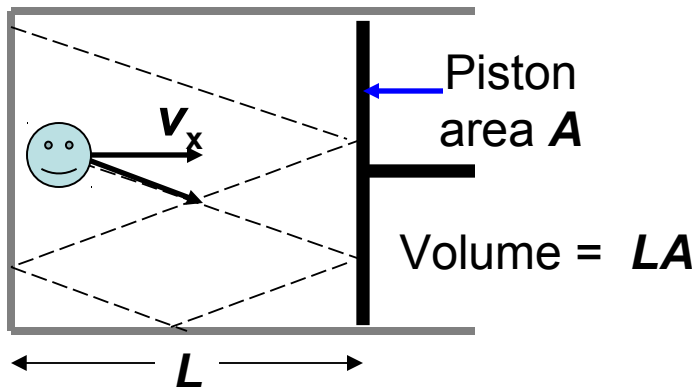


Connection between K_{tr} and T for Ideal Gases

T of an ideal gas \Leftrightarrow the kinetic energy of molecules

Pressure – the result of collisions between the molecules and walls of the container.

Strategy: Pressure = Force/Area = $\frac{\text{Momentum}}{\Delta t} / \text{Area}$



For each (elastic) collision: $\Delta p_x = 2 m v_x$

Intervals between collisions: $\Delta t = 2 L / v_x$

$$P_i = \frac{2 m v_x}{2 L / v_x} \frac{1}{A} = p_x v_x \frac{1}{V} = m v_x^2 \frac{1}{V}$$

no-relativistic motion

For N molecules - $PV = \sum_i^N m v_x^2 = N m \langle v_x^2 \rangle$

Connection between K_{tr} and T for Ideal Gases (cont.)

$$\left. \begin{aligned} PV &= \sum_i^N m v_x^2 = N m \langle v_x^2 \rangle \\ PV &= N k_B T \end{aligned} \right\} m \langle v_x^2 \rangle = k_B T$$

Average kinetic energy of the translational motion of molecules:

$$\langle K_{tr} \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{1}{2} m \langle v_x^2 + v_y^2 + v_z^2 \rangle = \frac{3}{2} m \langle v_x^2 \rangle$$

$$\langle K_{tr} \rangle = \frac{3}{2} k_B T \quad - \text{the temperature of a gas is a direct measure of the average translational kinetic energy of its molecules!}$$

$$U = K_{tr} = \frac{3}{2} N k_B T$$

The internal energy U of a monatomic ideal gas is independent of its volume, and depends only on **T** ($\Delta U = 0$ for an isothermal process, **$T = \text{const}$**).

$$PV = \frac{2}{3} U$$

- for an ideal gas of non-relativistic particles, kin. energy \propto (velocity)².

Comparison with Experiment

	$dU/dT(300K)$ (J/K·mole)
Monatomic	
Helium	12.5
Argon	12.5
Neon	12.7
Krypton	12.3
Diatomic	
H ₂	20.4
N ₂	20.8
O ₂	21.1
CO	21
Polyatomic	
H ₂ O	27.0
CO ₂	28.5

$$U = \frac{3}{2} N k_B T$$

- for a point mass
with three degrees
of freedom

Testable prediction: if we put a known dU into a sample of gas, and measure the resulting change dT , we expect to get

$$\frac{dU}{dT} = \frac{3}{2} N k_B$$

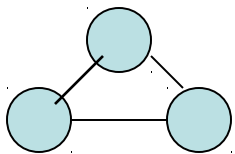
$$\frac{3}{2} (6 \cdot 10^{23} \text{ mole}^{-1}) (1.38 \cdot 10^{-23} \text{ J/K})$$

$$12.5 \text{ J/K} \cdot \text{mole}$$

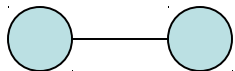
Conclusion: diatomic and polyatomic gases can store thermal energy in forms other than the translational kinetic energy of the molecules.

Degrees of Freedom

The degrees of freedom of a system are a collection of independent variables required to characterize the system.



Polyatomic molecules: **6** (transl. +rotat.) degrees of freedom



Diatomic molecules: **$3 + 2 = 5$** transl.+rotat. degrees of freedom

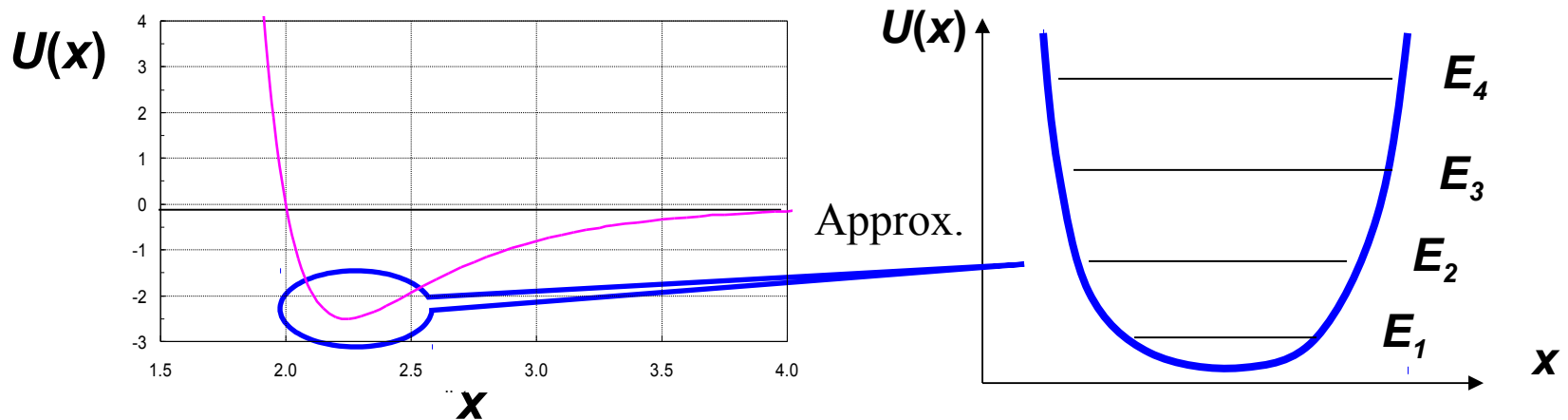
Degrees of Freedom (cont.)

Plus all vibrational degrees of freedom. The one-dimensional vibrational motion counts as **two** degrees of freedom (kin. + pot. energies):

$$K + U(x) = \frac{1}{2} m \langle \dot{x}^2 \rangle + \frac{1}{2} k \langle x^2 \rangle$$

For a diatomic molecule (e.g., H_2), **5** transl.+rotat. degrees of freedom plus **2** vibrational degrees of freedom = total **7** degrees of freedom

Among **7** degrees of freedom, only **3** (translational) degrees correspond to a **continuous** energy spectrum (classical), the other **4** – to a **discrete** energy spectrum (Quantum).



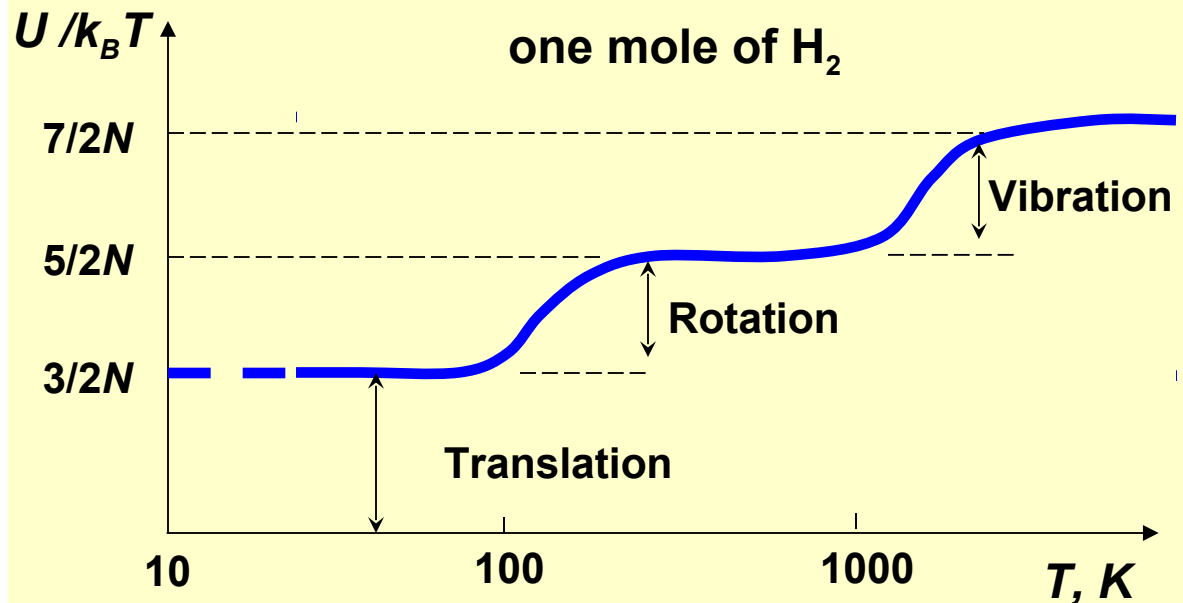
“Frozen” degrees of freedom

For an ideal gas

$$PV = Nk_B T$$

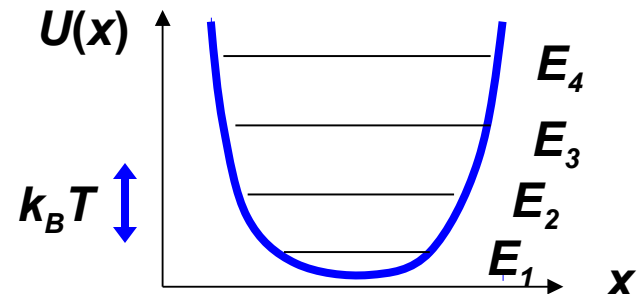
$$U = f/2 Nk_B T$$

Example of H_2 :



An energy available to a H_2 molecule colliding with a wall at $T=300$ K: $3/2 k_B T \sim 40$ meV. If the difference between energy levels is $\gg k_B T$, then a typical collision cannot cause transitions to the higher (excited) states and thus cannot transfer energy to this degree of freedom: it is “frozen out”.

The rotational energy levels are ~ 15 meV apart, the difference between vibrational energy levels ~ 270 meV. Thus, the rotational degrees start contributing to U at $T > 200$ K, the vibrational degrees of freedom - at $T > 3000$ K.

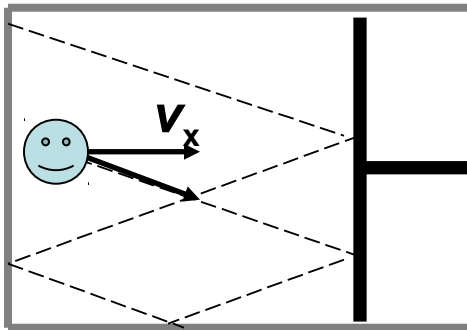


Equipartition of Energy

“Quadratic” degree of freedom – the corresponding energy = $f(x^2, v_x^2)$
[translational motion, (classical) rotational and vibrational motion, etc.]

Equipartition Theorem: At temperature T , the average energy of any “quadratic” degree of freedom is $\frac{1}{2}k_B T$.

- holds **only** for a system of particles whose kinetic energy is a quadratic form of x^2, v_x^2 (e.g., the equipartition theorem does not work for photons, $E = cp$)



Piston – a mechanical system with one degree of freedom. Thus,

$$\frac{m \langle v_x^2 \rangle}{2} = \frac{M \langle u^2 \rangle}{2} = \frac{1}{2} k_B T$$

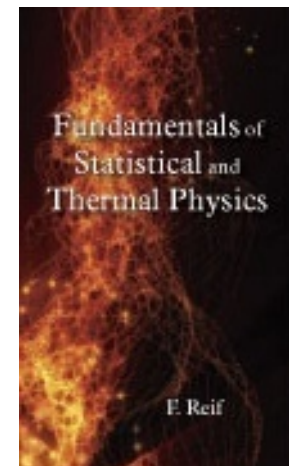
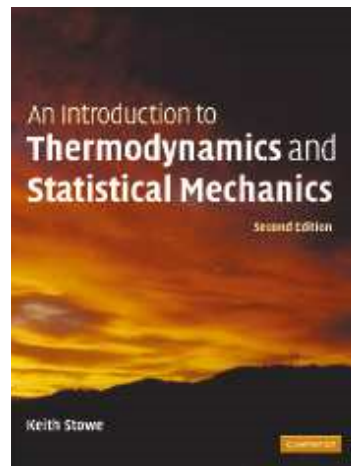
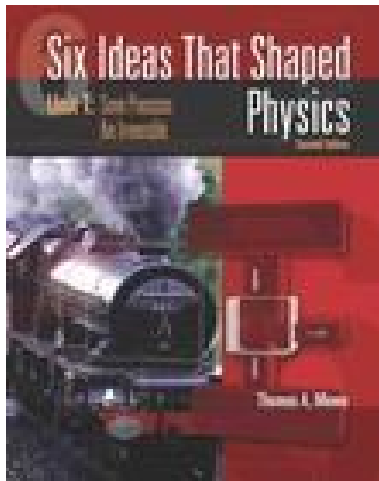
M – the mass of a piston, $\langle u^2 \rangle$ the average u^2 , where u is the piston's speed along the x -axis.

Thus, the energy that corresponds to the one-dimensional translational motion of a macroscopic system is the same as for a molecule (in this respect, a macrosystem behaves as a giant “molecule”).

For the “next” lecture:

Recall the ideal gas laws, look at the ideal gas problems (some problems are posted on the course Web page).

reference books



The root-mean-square speed

$$v_{rms} \equiv \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3k_B T}{m}} \quad \text{- not quite the average speed, but close...}$$

For H_2 molecules ($m \sim 2 \cdot 1.7 \cdot 10^{-27}$ kg) at 300K: $v_{rms} \sim 1.84 \cdot 10^3$ m/s

For N_2 – v_{rms} (Pr. 1.18), for O_2 – $v_{rms} = 461$ m/s

This speed is close to the speed of sound in the gas – the sound wave propagates due to the thermal motion of molecules.

