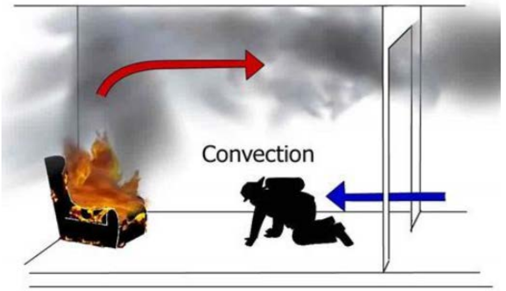
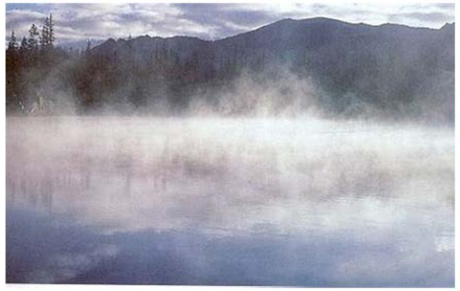
F. Thermodynamics

Thermodynamics is the study of two things mainly. One is the different ways that can manifest itself. Some of these ways you've studied in PHY 141 (mechanical energy). But we'll consider another one (internal energy):





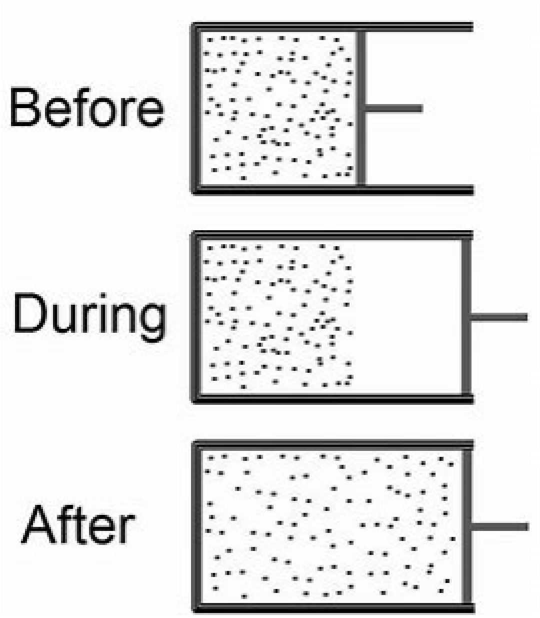
Associated with that is a study of the multifarious ways energy can be transferred, one of which being work, and the other, heat: We'll get to that later:

The 1^{st} **law of thermodynamics** will relate these two concepts.

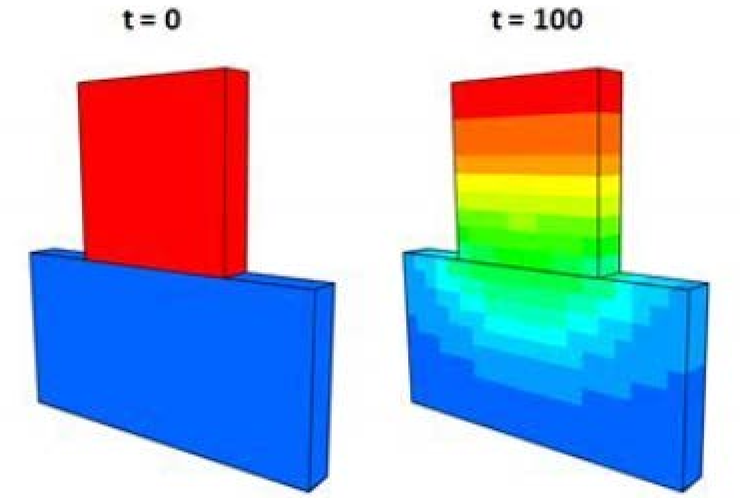
F. Thermodynamics

The other thing that thermodynamics studies is **entropy**, and the ways that it can be created, or transferred. This concept puts restrictions on the kinds of energy conversions allowed, and culminates in the **2nd law of thermodynamics**. It provides insight into things as varied as:

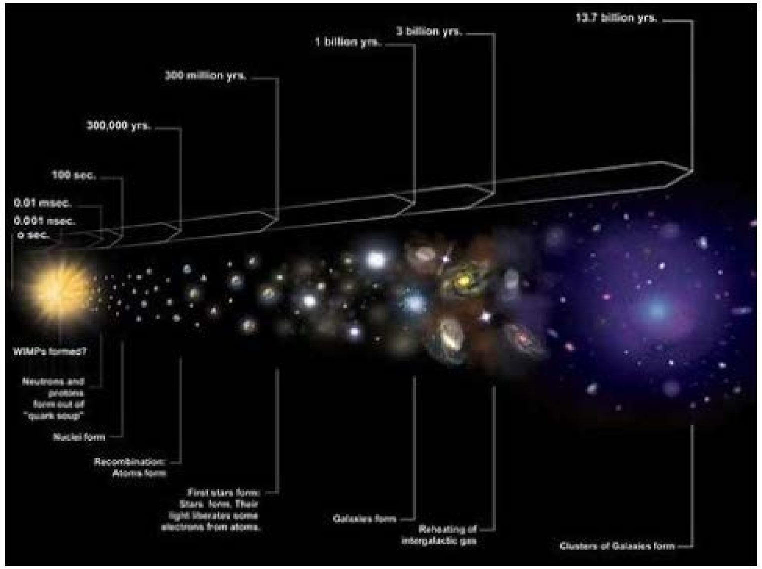
why gasses expand:



why heat transfers only from hot to cold, and not vice versa. and why they'll come to the same temperature



whether the universe has always existed, or instead began at some point in the distant past.



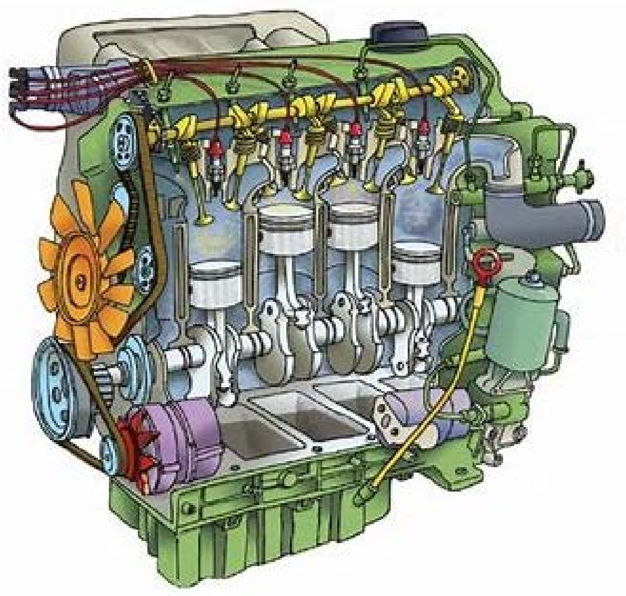
F. Thermodynamics

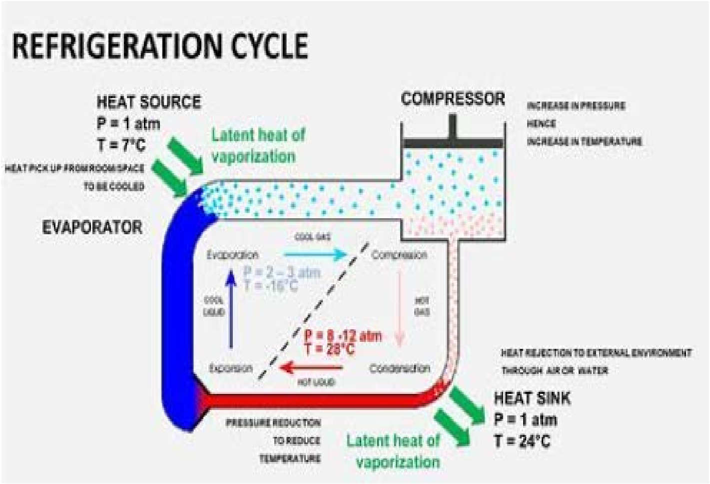
Apropos practical matters, we'll use the 1st and 2nd laws of thermodynamics to analyze the performance and efficiency of:

Heat Engines
(like internal combustion)

Metabolic Engines

and Refrigerators





F.1 Mechanical Energy

First up is energy. So in 141, you already examined mechanical energy, as (mostly) manifested in the ball here:

$$E_{mech.} = \frac{1}{2}mv^2 + \frac{1}{2}I\omega^2 + mgy + \frac{1}{2}kx^2$$

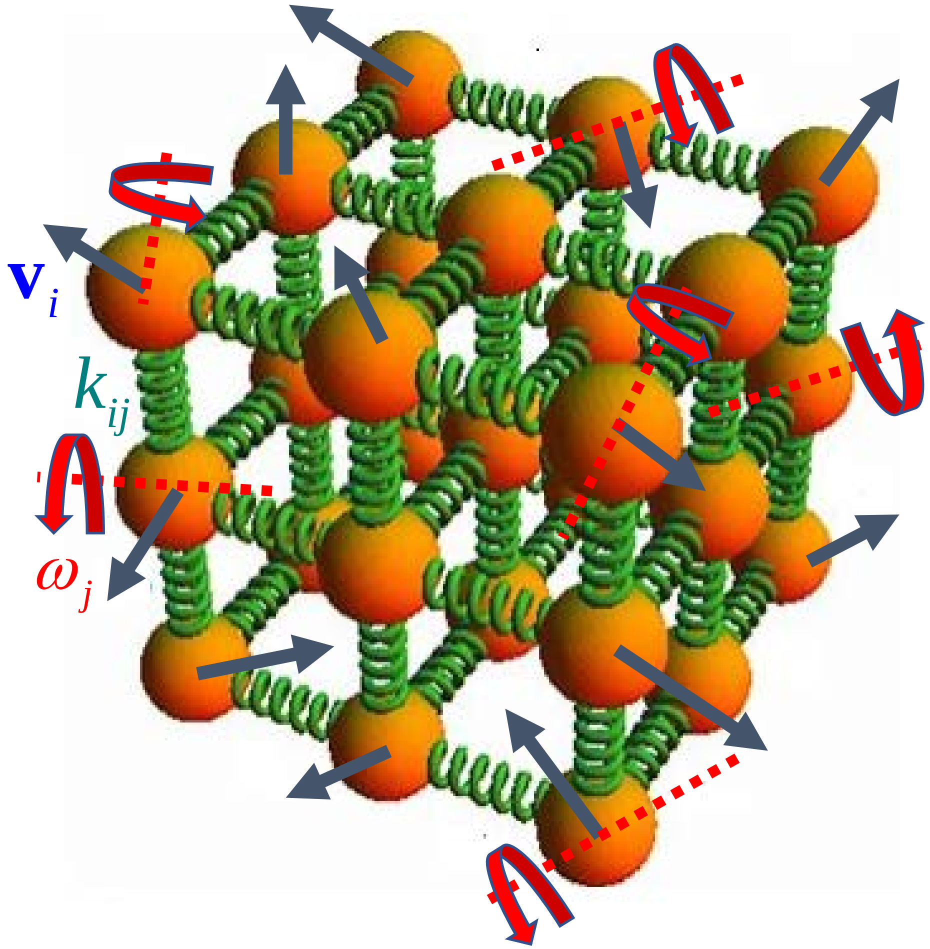
F.1 Internal (Thermal) Energy

If you zoom in on any object, though, you'll see more energy than was first apparent. For example consider this model of a solid. Even if it is completely at rest, and has no mechanical energy, we'd see that it does have *internal* energy.

- The atoms are rapidly oscillating back and forth with random velocities v_i
- The atoms are possibly rotating about their axes with random angular velocities ω_i
- By virtue of the chemical bonds holding them together, they also possess a spring-like potential energy.

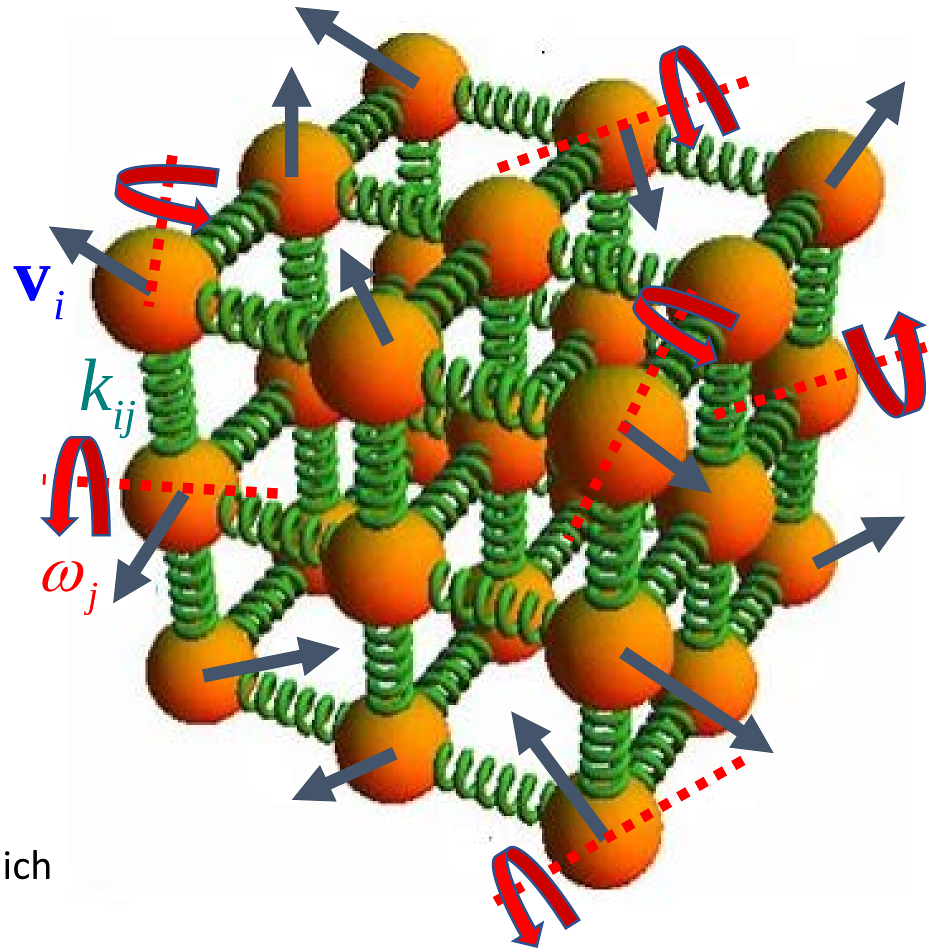
So we could say:

$$E_{int.} = \sum_i \left[\frac{1}{2} m_i v_i^2 + \frac{1}{2} I_i \omega_i^2 \right] + \sum_{ij} \frac{1}{2} k_{ij} (r_i - r_j)^2$$



F.1 Internal (Thermal) Energy

But although our formula is true, it doesn't help *practically*, because there are quintillions of atoms, and we cannot possibly calculate the energy of an object by taking each atom's own energy precisely into account.



A vast simplification is afforded if we just focus on what the substance's energy is on average (meaning average over small interval of time). This only depends on three variables: T, V, N.

$$E_{\text{int.}} = E_{\text{int.}}(T, V, N)$$

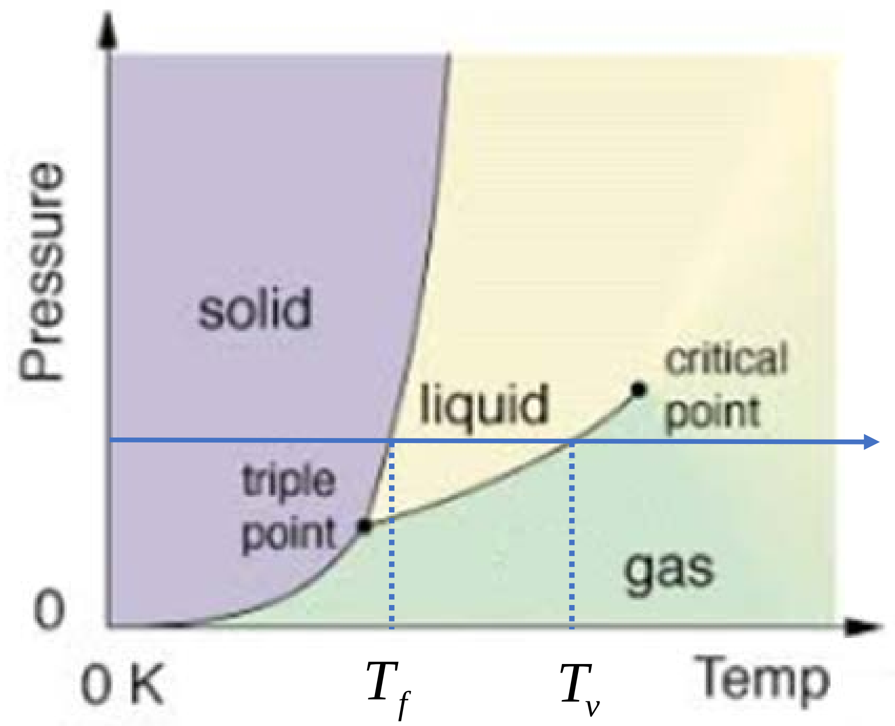
T = Temperature (in Kelvin). It measures mainly an atom's KE. But also takes some account of its PE, since high velocities means larger amplitudes of oscillations, which means greater separation between atoms, which means greater PE too.

V = Volume. It gives average space between atoms and is what predominantly accounts for their PE.

N = Number of particles. More particles means more energy.

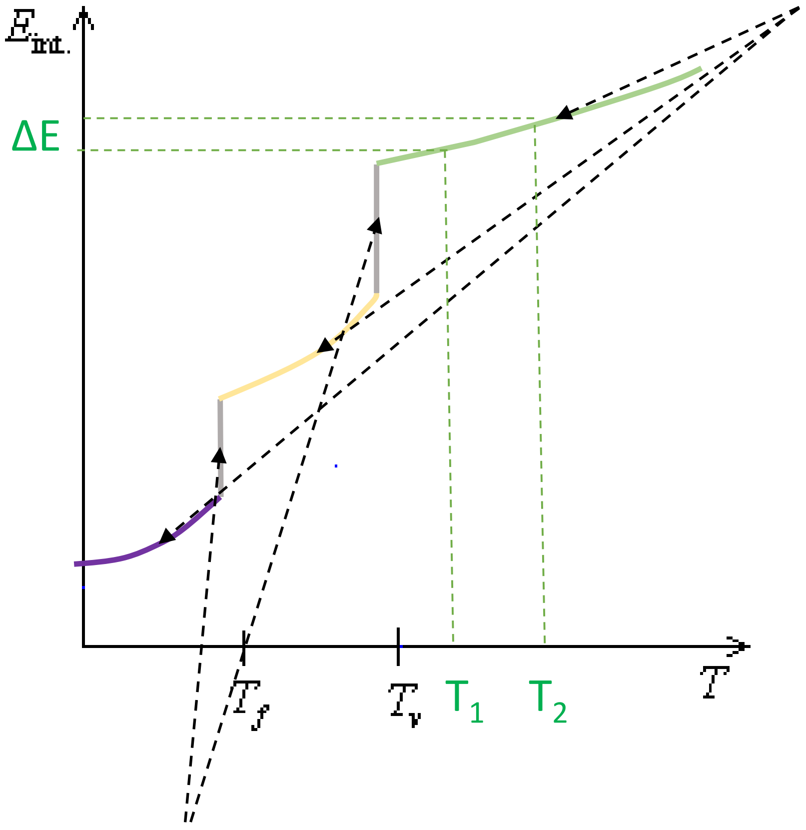
F.1 $E_{int.}$(T,V,N)'s dependence on T

Now we want to figure out what $E_{int.}$(T,V,N) is for various substances. Turns out even *this* gets complicated pretty quickly. So we'll temper our ambitions, and focus, for now, on just the T-dependence of $E_{int.}$. This is the *most* important aspect for practical applications.



Temperature of fusion, where solid becomes liquid.

Temperature of vaporization, where liquid becomes gas.



$$\Delta E = mL$$

L = latent heat: is phase dependent

$$\frac{dE}{dT} = mc$$

m = mass

c = specific heat capacity: is T-dependent, and phase-dependent.

integrating, we get:

$$\Delta E = \int_{T_1}^{T_2} mc\,dT$$

e.g. for water...

$$c_s \approx 2.03 \frac{\text{kJ}}{\text{kg}\cdot\text{K}} \qquad L_f = 333 \frac{\text{kJ}}{\text{kg}}$$

$$c_l \approx 4.18 \frac{\text{kJ}}{\text{kg}\cdot\text{K}} \qquad L_v = 2256 \frac{\text{kJ}}{\text{kg}}$$

$$c_g \approx 1.98 \frac{\text{kJ}}{\text{kg}\cdot\text{K}}$$

F.1 $E_{int.}(T,V,N)$'s dependence on T

Say we put 2kg of steam at 130°C in the freezer. How much energy must it extract from the steam to condense it to water, and then halfway to ice?

$$\Delta E_{\text{int.}} = \int_{T_1}^{T_v} mcdT - mL_v + \int_{T_v}^{T_f} mcdT - (m/2)L_f$$

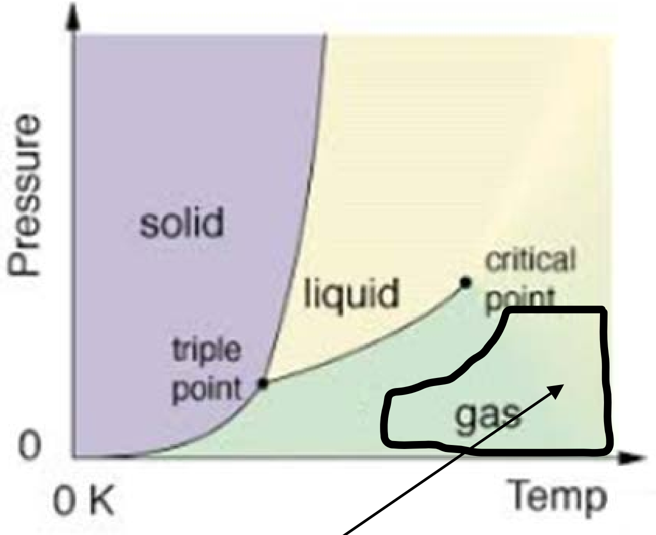
$$= \int_{130}^{100} (2\,\text{kg})\left(1.98\frac{\text{kJ}}{\text{kg K}}\right)dT - (2\,\text{kg})\left(2256\frac{\text{kJ}}{\text{kg}}\right) + \int_{100}^{0} (2\,\text{kg})\left(4.18\frac{\text{kJ}}{\text{kg K}}\right)dT - (1\text{kg})\left(333\frac{\text{kJ}}{\text{kg}}\right)$$

$$= (2\,\text{kg})\left(1.98\frac{\text{kJ}}{\text{kg K}}\right)(-30\text{K}) - (2\,\text{kg})\left(2256\frac{\text{kJ}}{\text{kg}}\right) + (2\,\text{kg})\left(4.18\frac{\text{kJ}}{\text{kg K}}\right)(-100\text{K}) - (1\text{kg})\left(333\frac{\text{kJ}}{\text{kg}}\right)$$

$$= -119\text{kJ} - 4510\text{kJ} - 836\text{kJ} - 333\text{kJ}$$

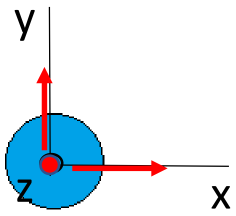
$$= -5800\,\text{kJ}$$

F.1 General $E_{int.}$(T,V,N) formula for Ideal Gas



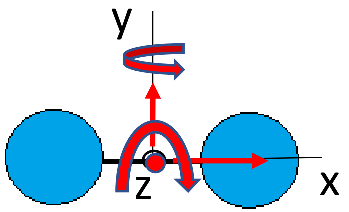
If we restrict ourselves to the high temperature region of a gas, where its KE dominates its PE, we can develop an explicit formula for the internal energy function. The formula breaks down into three different cases:

monatomic



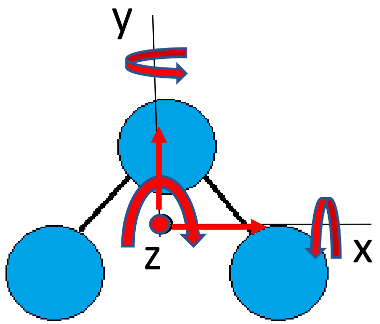
$$E_{molecule} = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \cancel{\frac{1}{2}I_x\omega_x^2} + \cancel{\frac{1}{2}I_y\omega_y^2} + \cancel{\frac{1}{2}I_z\omega_z^2}$$
$$= \frac{1}{2}k_BT + \frac{1}{2}k_BT + \frac{1}{2}k_BT + 0 + 0 + 0$$

diatomic



$$E_{molecule} = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \cancel{\frac{1}{2}I_x\omega_x^2} + \frac{1}{2}I_y\omega_y^2 + \frac{1}{2}I_z\omega_z^2$$
$$= \frac{1}{2}k_BT + \frac{1}{2}k_BT + \frac{1}{2}k_BT + \frac{1}{2}k_BT + \frac{1}{2}k_BT + 0$$

triatomic or more



$$E_{molecule} = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2 + \frac{1}{2}I_z\omega_z^2$$
$$= \frac{1}{2}k_BT + \frac{1}{2}k_BT + \frac{1}{2}k_BT + \frac{1}{2}k_BT + \frac{1}{2}k_BT + \frac{1}{2}k_BT$$

$$\boxed{E_{\text{int.}}(T,V,N) = \frac{f}{2}Nk_BT} \longleftarrow E_{molecule} = \frac{f}{2}k_BT$$

$f = \#$ of degrees of freedom $= 3, 5, 6$

$k_B =$ Boltzman constant $= 1.38 \times 10^{-23}$ J/K

F.1 General $E_{int.}$(T,V,N) formula for Ideal Gas

How fast is an O_2 molecule moving at room temperature (T = 30˚C)?

The mass of this molecule would be 16g per mole approximately, which works out to be:

$$m_{O_2} = \frac{m_{molarO_2}}{N_A} = \frac{2(0.016\,\text{kg})}{6.022\times10^{23}}$$
$$= 5.32\times10^{-26}\text{ kg}$$

The speed is a function of the translational kinetic energy. The average translational kinetic energy would be:

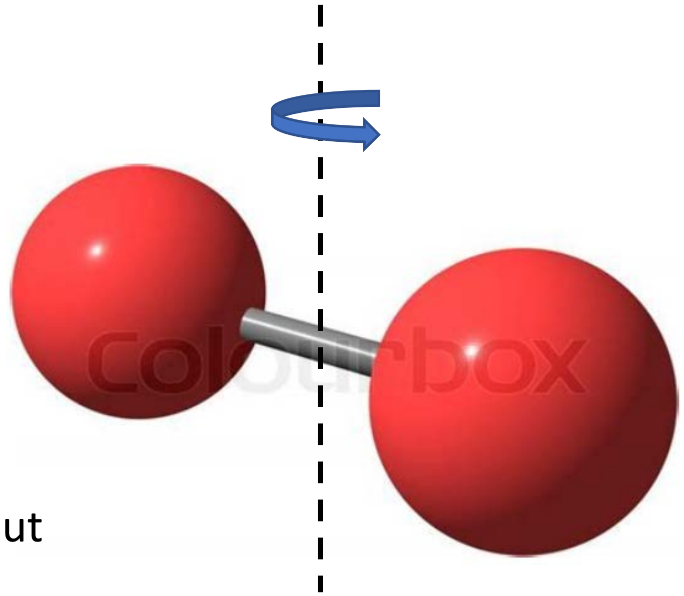
$$KE = \frac{1}{2}mv^2$$
$$= \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$$
$$= \frac{1}{2}k_BT + \frac{1}{2}k_BT + \frac{1}{2}k_BT$$
$$= \frac{3}{2}k_BT$$

$$\frac{1}{2}mv^2 = \frac{3}{2}k_BT$$
$$v = \sqrt{\frac{3k_BT}{m}}$$
$$= \sqrt{\frac{3(1.38\times10^{-23})(273+30)}{5.32\times10^{-26}}}$$
$$= 486\,\text{m/s} \sim 1100\text{mph}$$

purty fast

F.1 General $E_{int.}(T,V,N)$ formula for Ideal Gas

What is the frequency of rotation of an O_2 molecule about any particular axis, at room temperature (T =30˚C)? You can suppose that the molecule has a bond length of 0.1nm.



First we need the moment of inertia of the O_2 molecule.
This would be:

$$\begin{aligned} I &= m_1 r_1^2 + m_2 r_2^2 \\ &= (2.66\times10^{-26}\,\mathrm{kg})(0.05\times10^{-9}\,\mathrm{m})^2 + (2.66\times10^{-26}\,\mathrm{kg})(0.05\times10^{-9}\,\mathrm{m})^2 \\ &= 1.33\times10^{-46}\,\mathrm{kg\cdot m^2} \end{aligned}$$

Then, from the equipartition theorem, the rotational kinetic energy about that axis would be:

$$\begin{aligned} KE &= \frac{1}{2} I\omega^2 \\ &= \frac{1}{2} k_B T \end{aligned}$$

$$\frac{1}{2} I\omega^2 = \frac{1}{2} k_B T$$

$$I\omega^2 = k_B T$$

$$\omega = \sqrt{\frac{k_B T}{I}}$$

$$\begin{aligned} \omega &= \sqrt{\frac{(1.38\times10^{-23})(292)}{1.33\times10^{-46}}} \\ &= 5.5\times10^{12}\,\frac{\mathrm{rad}}{\mathrm{s}} \end{aligned}$$

and so the frequency of rotation is: $f = \dfrac{\omega}{2\pi} = \dfrac{5.5\times10^{12}}{2\pi} = 8.8\times10^{11}\,\mathrm{Hz}$

F.1 General $E_{int.}(T,V,N)$ formula for Ideal Gas

Suppose we're sitting in a 7m×5m×3m room at atmospheric pressure (101kPa), and room temperature (30C). How much thermal energy resides in the air?

$$\begin{aligned}E_{gas} &= \frac{f}{2} N k_B T \\ &= \frac{5}{2} N k_B T \\ &= \frac{5}{2} pV \\ &= \frac{5}{2}(101\times10^3)(7\times5\times3) \\ &= 2.6\times10^7\,\mathrm{J}\end{aligned}$$

But note $pV = Nk_BT$, and so we can make the replacement:

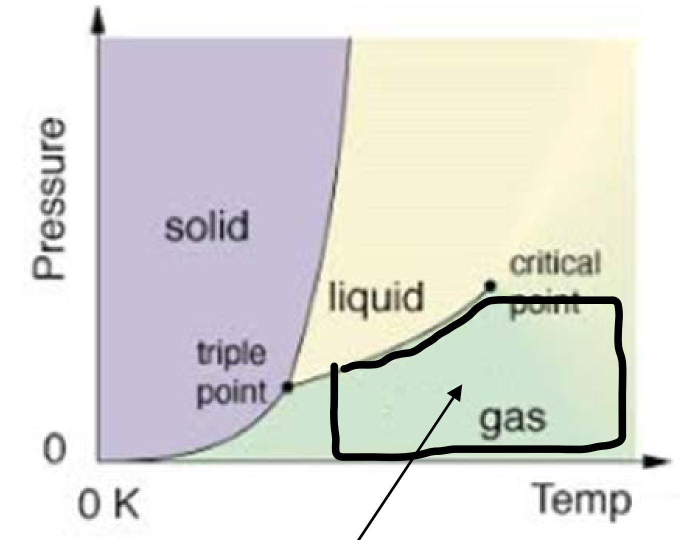
If a car with mass 2000kg had the same energy, how fast would it be moving?

$$2.6\times10^7 = \frac{1}{2} m v^2$$

$$2.6\times10^7 = \frac{1}{2}(2000) v^2 \longrightarrow v = \sqrt{\frac{2(2.6\times10^7)}{2000}} = 161\,\mathrm{m/s} \sim 360\,\mathrm{mph}$$

also purty fast. The goal of thermodynamics is to harness this internal/thermal energy

F.1 General $E_{int.}(T,V,N)$ formula for Van der Waals Gas



We can relax the condition that KE >> PE a bit. The Van der Waals model of a gas is a bit more general, and captures the most salient details of the interaction between the gas's molecules. As such it can make some predictions about when/how the gas condenses into a liquid.

$$E_{\text{int.}}(T,V,N)=\frac{f}{2}Nk_BT-\frac{aN^2}{V}$$

Kinetic energy

Potential energy term modeling the weak internal attractive forces between molecules.

a is parameter that quantifies the strength of the forces:

TABLE 5.3 Values of the van der Waals Constants for Some Common Gases

Gas	$a\left(\frac{\text{atm}\cdot\text{L}^2}{\text{mol}^2}\right)$	$b\left(\frac{\text{L}}{\text{mol}}\right)$
He	0.0341	0.0237
Ne	0.211	0.0171
Ar	1.35	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0511
H_2	0.244	0.0266
N_2	1.39	0.0391
O_2	1.36	0.0318
Cl_2	6.49	0.0562
CO_2	3.59	0.0427
CH_4	2.25	0.0428
NH_3	4.17	0.0371
H_2O	5.46	0.0305

F.1 General $E_{int.}$(T,V,N) formula for Van der Waals Gas

Say 2 mol of CO_2 gas is stored in a 750cm^3 container at T = 280K. Calculate the energy according to the ideal gas equation. And then according to the more accurate Van der Waals model.

$$E_{ideal} = \frac{f}{2} N k_B T \qquad \text{*note } nR = Nk_B$$

$$= \frac{6}{2}(nR)T$$

$$= (3)(2)(8.31)(280)$$

$$= 1.4 \times 10^4 \,\mathrm{J}$$

$$E_{Van} = \frac{f}{2} N k_B T - \frac{aN^2}{V}$$

$$= 1.4 \times 10^4 \,\mathrm{J} - \frac{(1\times10^{-48})(2\times6.022\times10^{23})^2}{750(0.01\mathrm{m})^3}$$

$$= 1.4\times10^4 \,\mathrm{J} - 1.9\times10^3 \,\mathrm{J}$$

$$= 1.2\times10^4 \,\mathrm{J}$$

$$a = 3.59 \frac{\mathrm{atm}\cdot\mathrm{L}^2}{\mathrm{mol}^2}$$

$$= 3.59 \frac{(101320\mathrm{Pa})\cdot(0.001\mathrm{m}^3)^2}{(6.022\times10^{23})^2}$$

$$= 1\times10^{-48} \,\mathrm{Pa}\cdot\mathrm{m}^6$$

So ideal is cloooose to accurate.

TABLE 5.3 Values of the van der Waals Constants for Some Common Gases

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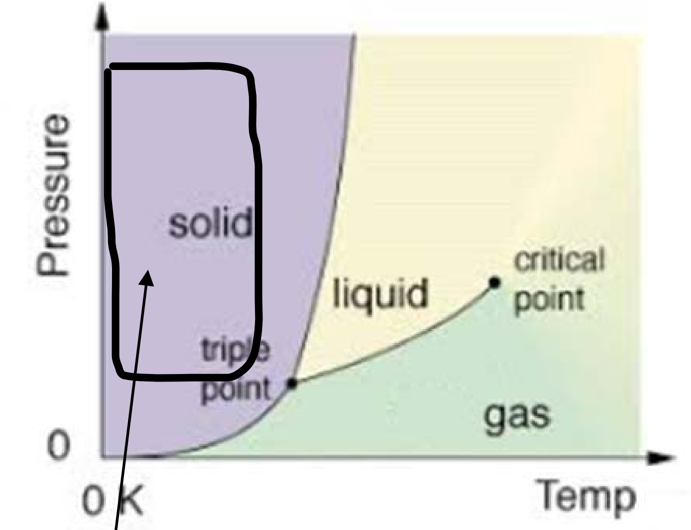
Cl_2	6.49	0.0562
CO_2	3.59	0.0427
CH_4	2.25	0.0428
NH_3	4.17	0.0371
H_2O	5.46	0.0305

F.1 General $E_{int.}$(T,V,N) formula for Ideal Solid



Another substance we can model fairly well is a solid, under conditions far from where it is close to a phase transition.

$$E_{\text{int.}}(T,V,N) = \frac{f}{2}Nk_BT + \frac{1}{2}\frac{B}{\upsilon}(V-\upsilon)^2$$

Kinetic energy. but also a portion of the spring-like potential energy binding the atoms together. *f = 6*

Potential energy term that models the majority of the spring-like potential energy binding the atoms together. Note the similarity to the spring potential energy $(1/2)k(x-\ell)^2$.

B = bulk modulus (measures solid's stiffness)

υ = volume at 0 temperature, pressure

Values for the Bulk Modulus of Solid and Liquid

Material	Bulk Modulus B (N/m^2)
Solids	
Aluminum	7.1×10^{10}
Brass	6.7×10^{10}
Copper	1.3×10^{11}
Lead	4.2×10^{10}
Nylon	6.1×10^{9}
Pyrex glass	2.6×10^{10}
Steel	1.4×10^{11}
Liquids	
Ethanol	8.9×10^{8}
Oil	1.7×10^{9}
Water	2.2×10^{9}

F.1 General $E_{int.}(T,V,N)$ formula for Ideal Solid

On Earth, where the temperature is 25°C, a steel weather satellite has volume $4.2m^3$, and is launched into space, its volume expands (due to lack of compressive atmospheric pressure) to $4.3m^3$. What was its energy on Earth, and what is its energy in space? We can suppose T = p = 0 in space, the density of steel is roughly that of its main component, iron, and its molar mass is also roughly that of iron.

So $\upsilon = 4.3m^3$, and $B = 1.4\times10^{11} N/m^2$. So in space,

$$E_{space}(T,V,N) = \frac{6}{2}Nk_B(0) + \frac{1}{2}\frac{1.4\times10^{11}}{4.3}(4.3-4.3)^2$$
$$= 0$$

And on Earth,

$$E_{earth}(T,V,N) = \frac{6}{2}Nk_B(272+25) + \frac{1}{2}\frac{1.4\times10^{11}}{4.3}(4.2-4.3)^2$$
$$= \frac{6}{2}(4.9\times10^6)(272+25) + \frac{1}{2}\frac{1.4\times10^{11}}{4.3}(4.2-4.3)^2$$
$$= 4.4\times10^9\,\mathrm{J} + 1.6\times10^8\,\mathrm{J}$$
$$= 4.6\times10^9\,\mathrm{J}$$

$$Nk_B = nR = \frac{m}{m_{molar}}R = \frac{\rho_{Fe}V}{m_{molar\,Fe}}R$$
$$= \frac{(7860\,\mathrm{kg/m^3})(4.2\mathrm{m}^3)}{0.0558\,\mathrm{kg}}(8.31\,\mathrm{J/mol\cdot K})$$
$$= 4.9\times10^6\,(\mathrm{J/K})$$