EQUIPARTITION THEOREM: QUALITATIVE TREATMENT

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Each translational degree of freedom in a molecule has an associated average kinetic energy of $\frac{1}{2}kT$, so for the molecules in a gas the total kinetic energy due to translational motion is $\frac{3}{2}kT$. It turns out that, in general, any energy component with a quadratic dependence on its associated position or velocity contributes $\frac{1}{2}kT$ to the total thermal energy. This includes rotational degrees of freedom, since the energy is $\frac{1}{2}I\omega^2_i$, where $I$ is the moment of inertia about axis $i$ and $\omega_i$ is the angular velocity about that same axis. Chemical bonds also act approximately like springs, so two bonded atoms can vibrate relative to each other, giving rise to another kinetic energy term and a potential energy term given by $\frac{1}{2}k_xx^2$ where $k_x$ is the spring constant and $x$ is the molecular separation.

The total number of degrees of freedom $f$ for a given molecule can be tricky to calculate for more complex molecules, but once $f$ is found, the equipartition theorem says that the thermal energy of a collection of $N$ molecules is

$$U_{\text{thermal}} = \frac{1}{2}kT \times Nf$$

(1)

**Example 1.** A monatomic gas such as helium is the simplest case, as it has only the three translational degrees of freedom, so for a collection of $N$ atoms

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

(2)

A litre ($10^{-3}$ m$^3$) of helium at $T = 293$ K (room temperature) and a pressure of 1 atm $= 1.01325 \times 10^5$ Pa has a thermal energy of

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

(3)

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

(4)

$$= 152 \text{ J}$$

(5)
For air, if we neglect argon (which accounts for about 1% of air), all the molecules are diatomic ($\text{N}_2$ and $\text{O}_2$). At room temperature, the vibrational modes don’t contribute, since these diatomic molecules have to be hit very hard to get a vibration going, so the only extra degrees of freedom are the two rotational degrees of freedom that we get by rotating a dumbbell shape about the two axes that are perpendicular to the bond joining the two atoms. (A rotation about the axis of the bond isn’t counted as such a rotation doesn’t change the position of the molecule.) So in this case $f = 5$ and we have

$$U = \frac{5}{2}NkT = \frac{5}{2}PV = 253 \text{ J}$$  \hspace{1cm} (6)

**Example 2.** In an elemental solid such as lead, each atom has 6 vibrational degrees of freedom (3 kinetic and 3 potential, as described above). Since the atoms are fixed in their positions in the lattice, there are no translational degrees of freedom, and there are no rotational degrees of freedom for a single atom. For 1 gram of lead, we have

$$N = \frac{10^{-3}}{(207.2 \text{ amu})(1.66 \times 10^{-27} \text{ kg amu}^{-1})} = 2.91 \times 10^{21}$$  \hspace{1cm} (7)

The thermal energy at $T = 293 \text{ K}$ is

$$U = \frac{6}{2}NkT = 35.3 \text{ J}$$  \hspace{1cm} (8)

**Example 3.** In a water molecule, the two hydrogen atoms are not in a straight line with the oxygen atom, so water has 3 rotational degrees of freedom in addition to the 3 translational degrees of freedom. [A linear molecule such as carbon dioxide has only 2 rotational degrees of freedom since the rotation about the O-C-O axis doesn’t count.] Each O-H bond can vibrate like a spring, so that would add 4 more degrees of freedom. The total number is therefore $f = 3 + 3 + 4 = 10$. [Actually, come to think of it, there could be other vibrational modes as well. The H-O-H angle could change without the length of either H-O bond changing, so there’s probably another vibrational mode there. However, that’s not really a spring-type vibration, so I’m not sure if it counts in the equipartition theorem.]

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