# THERMAL PROPERTIES OF MATTER II

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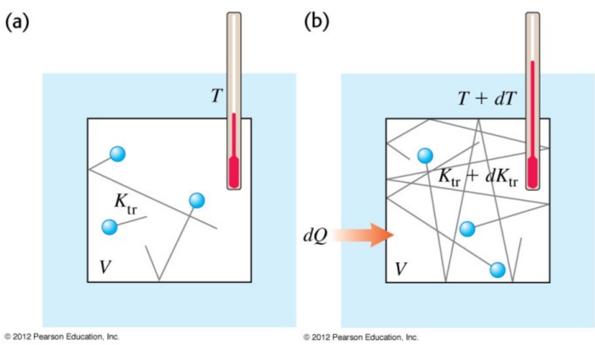
| Intended Learning Outcomes – after this lecture you will learn:<br>1. heat capacity of gases, experimental and theoretical aspects<br>2. distribution function as a statistical tool to describe the microscopic aspects of a gas<br>Textbook Reference: Ch 18.4 – 18.5 |

**Heat Capacity of Ideal Gas**

At constant volume, i.e., no expansion, $C_V$ **molar heat capacity at constant volume**




heat needed to raise temperature by $dT$

$$dQ = nC_V dT$$

increase in KE of gas

$$dK_{\text{tr}} = \frac{3}{2}nRdT$$

$$nC_V dT = \frac{3}{2}nRdT$$

$$\Rightarrow \boxed{C_V = \frac{3}{2}R} = 12.47\ \text{J/mol·K}$$

Interpretation: consider the KE of a single molecule

For monoatomic gas (point particle), already know (from kinetic theory) that KE of a particle is $\frac{3}{2}kT$,

Each molecule, treated as a point particle, $E = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$, 3 quadratic terms in $E$, we say that its **degree of freedom** is 3

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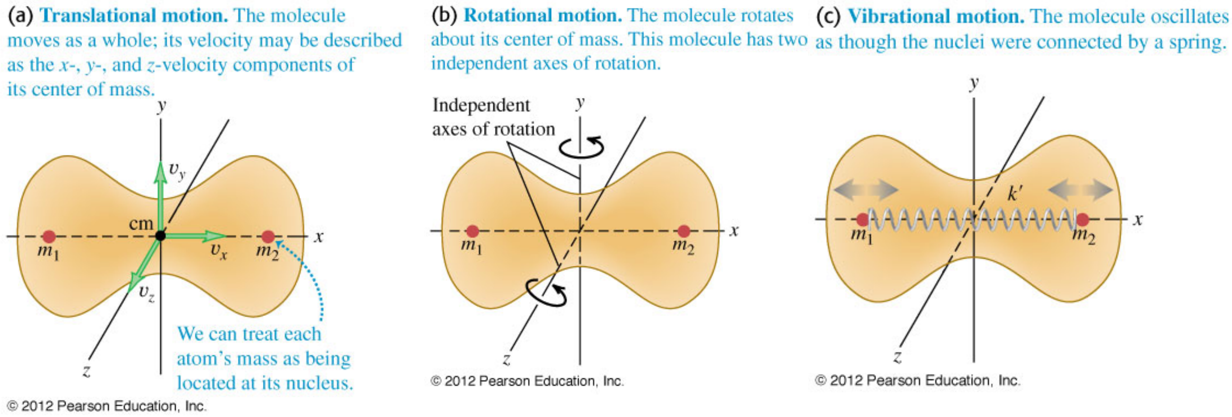
| **Principle of equipartition of energy**: each degree of freedom (quadratic term in $E$) carries an amount of energy $\frac{1}{2}kT$ (to be proved in PHYS 4050) |

If the degree of freedom of a molecule is $f$,

$$nC_V dT = \frac{f}{2}NkdT = \frac{f}{2}nRdT \quad \Rightarrow \quad \boxed{C_V = \frac{f}{2}R}$$

For diatomic molecules




**translation** of CM

$$E = \frac{1}{2}m\left(v_{CMx}^2 + v_{CMy}^2 + v_{CMz}^2\right)$$

degrees of freedom is **3** ($x$, $y$, $z$ directions)

**rotation** about CM

$$E = \frac{1}{2}\left(I_y\omega_y^2 + I_z\omega_z^2\right)$$

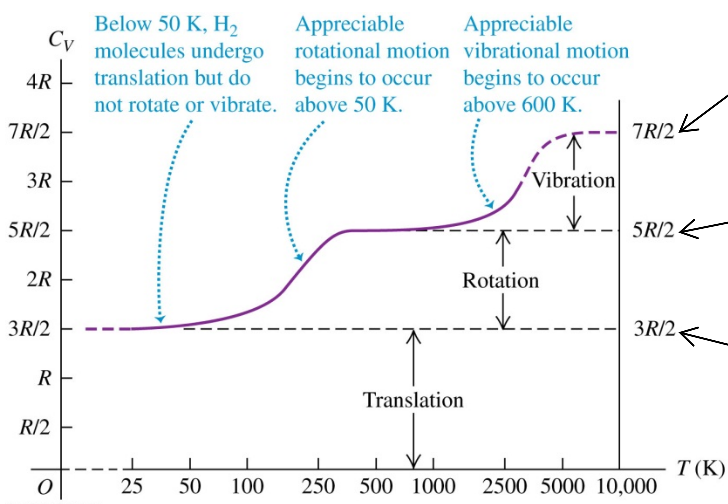
degrees of freedom is **2** (about $y$, $z$ axis)

**vibration** about CM (modeled as a 1D harmonic oscillator)

$$E = \frac{1}{2}mv'^2 + \frac{1}{2}kx^2$$

degrees of freedom is **2**

⚠ total degrees of freedom is 7, *but* from quantum mechanics, rotational and vibrational motions need minimum amount of energy to activate




translation, rotation and vibration activated, $f = 7$, $C_V = 7R/2$

$T$ not high enough to activate vibration, translation and rotation only, $f = 5$, $C_V = 5R/2$

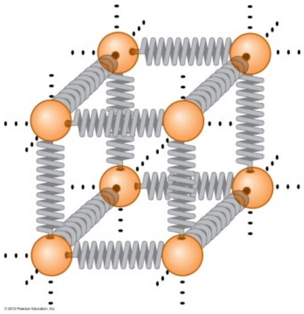
$T$ not high enough to activate rotation and vibration, translation only, $f = 3$, $C_V = 3R/2$

Question

a cylinder with a fixed volume contains $H_2$ gas at 25 K. You add heat to the gas at a constant rate until its temperature reaches 500 K. The temperature increase most rapidly near the (beginning / end) of this process?

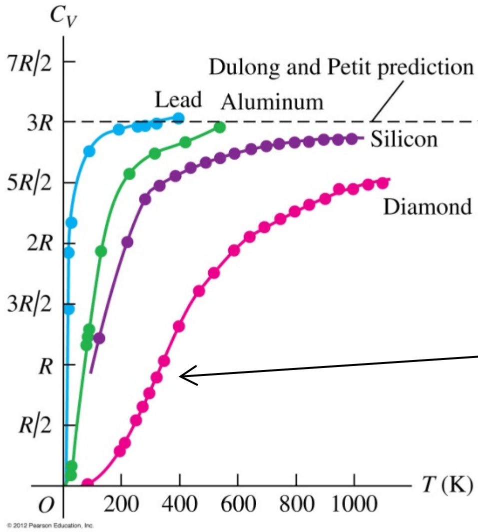
Answer: see inverted text on P. 625 of textbook

For a solid, inter-atomic vibration dominates, modelled as harmonic oscillators



each atom modeled as **3** independent 1D harmonic oscillators, total degree of freedom is $f = 3 \times 2 = 6$

$$C_V = \frac{f}{2}R = 3R$$ **Dulong and Petit rule**



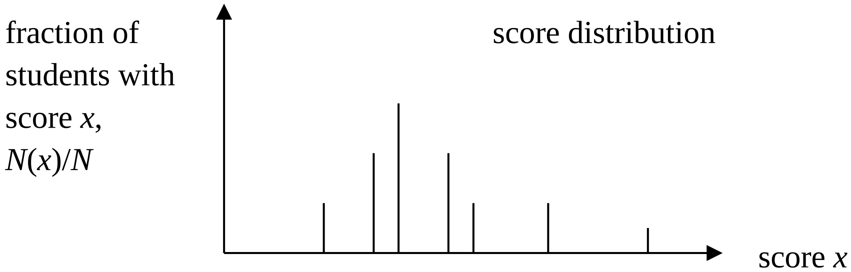

classical (high temperature) limit, as predicted by Dulong and Petit rule

low temperature region, dominated by quantum mechanical effects

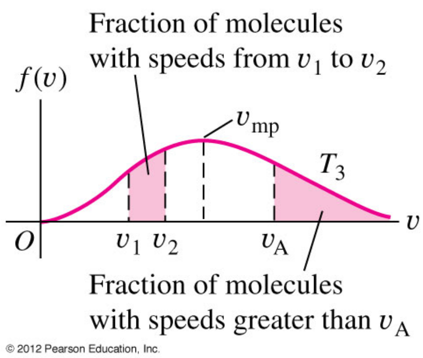
**Molecular speed**

Gas particles have different speeds, since they are identical and number is huge, need statistics

A **histogram** – number of occurrence of each value, e.g. your (hypothetical) midterm score



A **distribution function** $f(v)$ is like a histogram, except that the variable $v$ is continuous




Interpretation:
*fraction of particles* having speed between $v$ and $v + dv$ is $f(v)dv$, or
*probability* of a particles having speed between $v$ and $v + dv$ is $f(v)dv$

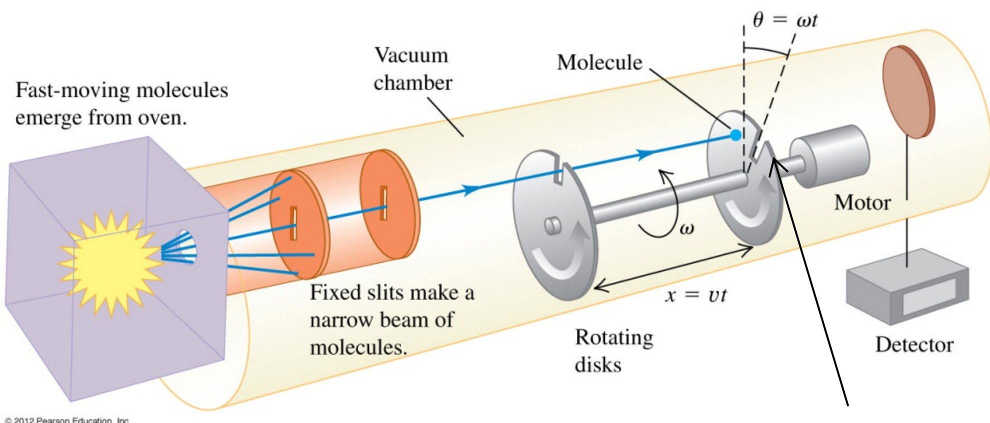
- ⚠ $f(v)$ is not a probability, it is a *probability density*, i.e., probability per unit $v$
- ⚠ What is the probability of a particle having speed $v$ exactly? Ans: zero!

Most probable speed $v_{\text{mp}}$ corresponds to maximum $f(v)$, $v_{\text{av}}$ and $v_{\text{rms}}$ are weighed averages

$$v_{\text{av}} = \int_0^\infty v f(v) dv$$

$$v_{\text{rms}}^2 = (v^2)_{\text{av}} = \int_0^\infty v^2 f(v) dv$$

How to measure $f(v)$?




only those with speed $v = \omega x/\theta$ can go through

$f(v)$ for an ideal gas can be derived using the method of statistical mechanics (PHYS 4050)

**Maxwell-Boltzmann distribution**

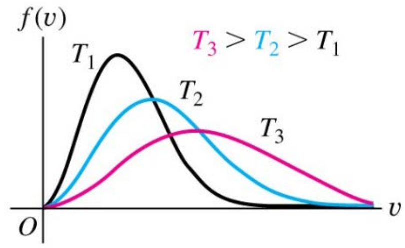
$$f(v) = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}$$

$$\frac{df}{dv} = 0 \Rightarrow \quad v_{mp} = \sqrt{\frac{2kT}{m}}$$

By carrying out the integrals we get

$$v_{\text{av}} = \sqrt{\frac{8kT}{\pi m}}, \quad v_{\text{rms}} = \sqrt{\frac{3kT}{m}}$$

agree with kinetic theory + ideal gas law (empirical)




at higher $T$

1. overall speed is higher
2. larger range of speed

## Clicker Questions

Q18.7

You have 1.00 mol of an ideal monatomic gas and 1.00 mol of an ideal diatomic gas whose molecules can rotate. Initially both gases are at room temperature. If the same amount of heat flows into each gas, which gas will undergo the greatest increase in temperature?

A. the monatomic gas

B. the diatomic gas

C. Both will undergo the same temperature change.

D. The answer depends on the molar masses of the gases.

E. The answer depends on whether or not the diatomic molecules can also vibrate.

Q18.8

The molar heat capacity at constant volume of diatomic hydrogen gas ($H_2$) is $5R/2$ at 500 K but only $3R/2$ at 50 K. Why is this?

A. At 500 K the molecules can vibrate, while at 50 K they cannot.

B. At 500 K the molecules cannot vibrate, while at 50 K they can.

C. At 500 K the molecules can rotate, while at 50 K they cannot.

D. At 500 K the molecules cannot rotate, while at 50 K they can.

E. At 500 K the molecules can both vibrate and rotate, while at 50 K they cannot.



Q18.9

A quantity of gas containing $N$ molecules has a speed distribution function $f(v)$. How many molecules of this gas have speeds between $v_1$ and $v_2 > v_1$?

A. $\int_0^{v_1} f(v)dv - \int_0^{v_2} f(v)dv$

B. $N\left[\int_0^{v_1} f(v)dv - \int_0^{v_2} f(v)dv\right]$

C. $\int_0^{v_2} f(v)dv - \int_0^{v_1} f(v)dv$

D. $N\left[\int_0^{v_2} f(v)dv - \int_0^{v_1} f(v)dv\right]$

E. none of these



Ans: Q18.7) A, Q18.8) C, Q18.9) D

# James Clerk Maxwell

From Wikipedia, the free encyclopedia

**James Clerk Maxwell** FRS FRSE (13 June 1831 – 5 November 1879) was a Scottish[1] mathematical physicist.[2] His most prominent achievement was formulating classical electromagnetic theory. This unites all previously unrelated observations, experiments, and equations of electricity, magnetism, and optics into a consistent theory.[3] Maxwell's equations demonstrate that electricity, magnetism and light are all manifestations of the same phenomenon, namely the electromagnetic field. Subsequently, all other classic laws or equations of these disciplines became simplified cases of Maxwell's equations. Maxwell's achievements concerning electromagnetism have been called the "second great unification in physics",[4] after the first one realised by Isaac Newton.

Maxwell demonstrated that electric and magnetic fields travel through space in the form of waves and at the constant speed of light. In 1865, Maxwell published *A Dynamical Theory of the Electromagnetic Field*. It was with this that he first proposed that light was in fact undulations in the same medium that is the cause of electric and magnetic phenomena.[5] His work in producing a unified model of electromagnetism is one of the greatest advances in physics.

Maxwell also helped develop the Maxwell–Boltzmann distribution, which is a statistical means of describing aspects of the kinetic theory of gases. These two discoveries helped usher in the era of modern physics, laying the foundation for such fields as special relativity and quantum mechanics.

Maxwell is also known for presenting the first durable colour photograph in 1861 and for his foundational work on the rigidity of rod-and-joint frameworks (trusses) like those in many bridges.

Maxwell is considered by many physicists to be the 19th-century scientist having the greatest influence on 20th-century physics. His contributions to the science are considered by many to be of the same magnitude as those of Isaac Newton and Albert Einstein.[6] In the millennium poll—a survey of the 100 most prominent physicists—Maxwell was voted the third greatest physicist of all time, behind only Newton and Einstein.[7] On the centennial of Maxwell's birthday, Einstein himself described Maxwell's work as the "most profound and the most fruitful that physics has experienced since the time of Newton."[8] Einstein kept a photograph of Maxwell on his study wall, alongside pictures of Michael Faraday and Newton.[9]

## Life

### Early life, 1831–39

James Clerk Maxwell was born 13 June 1831 at 14 India Street, Edinburgh, to John Clerk, an advocate, and Frances Cay.[10] Maxwell's father was a man of comfortable means, of the Clerk family of Penicuik, Midlothian, holders of the baronetcy of Clerk of Penicuik; his brother being the 6th Baronet.[11] He had been born **John Clerk**,[12] adding the surname Maxwell to his own after he inherited a country estate in Middlebie, Kirkcudbrightshire from connections

**James Clerk Maxwell**

James Clerk Maxwell (1831–1879)

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| **Born** | 13 June 1831<br>Edinburgh, Scotland |
| **Died** | 5 November 1879 (aged 48)<br>Cambridge, England |
| **Citizenship** | United Kingdom |
| **Nationality** | Scottish |
| **Fields** | Physics and Mathematics |
| **Institutions** | Marischal College, Aberdeen<br>King's College London<br>University of Cambridge |
| **Alma mater** | University of Edinburgh<br>University of Cambridge |
| **Academic advisors** | William Hopkins |
| **Notable students** | George Chrystal |
| **Known for** | Maxwell's equations<br>Maxwell distribution<br>Maxwell's demon<br>Maxwell's discs<br>Maxwell speed distribution<br>Maxwell's theorem<br>Maxwell material<br>Generalized Maxwell model<br>Displacement current |
| **Notable awards** | Smith's Prize (1854)<br>Adams Prize (1857)<br>Rumford Medal (1860)<br>Keith Prize (1869–71) |

**Signature**

See http://en.wikipedia.org/wiki/James_Clerk_Maxwell for more detail.