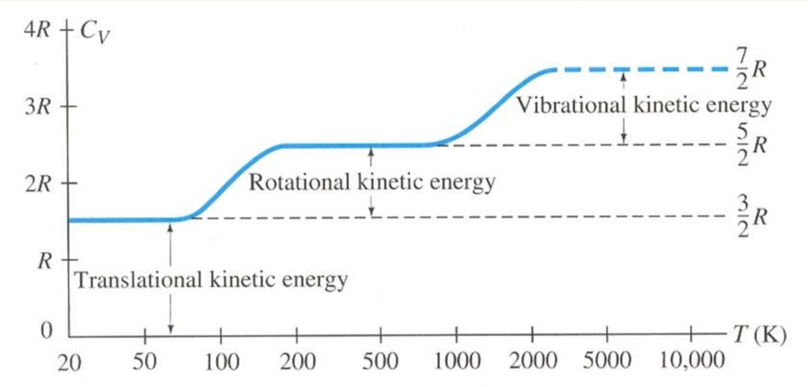
PHAS1000 – THERMAL PHYSICS

Lecture 10

Equipartition



Mid-term survey

Thermal Physics Prof Alison Voice

Mid-term Feedback

Comment on all things about Thermal physics:

- Lectures
- Slides
- Workshops
- etc

Overview

This lecture covers:

- Molar heat capacity at constant volume c_v'
- Degrees of freedom
- Equipartition theorem
- Quantum explanation of heat capacity
- Dulong-Petit law for solids

Molar Heat capacity

Molar heat capacity (c') is the heat needed to raise the temperature of *1 mole* by 1K

$$Q = nc'\Delta T$$

UNITS: J/mol.K

Heat capacity $C = mc = nc'$

$$c' = \frac{mc}{n} = Mc$$

M = molar mass

Most materials have approximately the same value of c'. WHY?

Molar heat capacity of gases

Molar Heat Capacities in J/mol·K of Various Gases at 25°C

Gas	c'_v	c'_v/R
Monatomic		
He	12.52	1.51
Ne	12.68	1.52
Ar	12.45	1.50
Kr	12.45	1.50
Xe	12.52	1.51
Diatomic		
N_2	20.80	2.50
H_2	20.44	2.46
O_2	20.98	2.52
CO	20.74	2.49
Polyatomic		
CO_2	28.17	3.39
N_2O	28.39	3.41
H_2S	27.36	3.29

c'_v is the molar heat capacity for a substance heated at constant volume, i.e. in a rigid container.

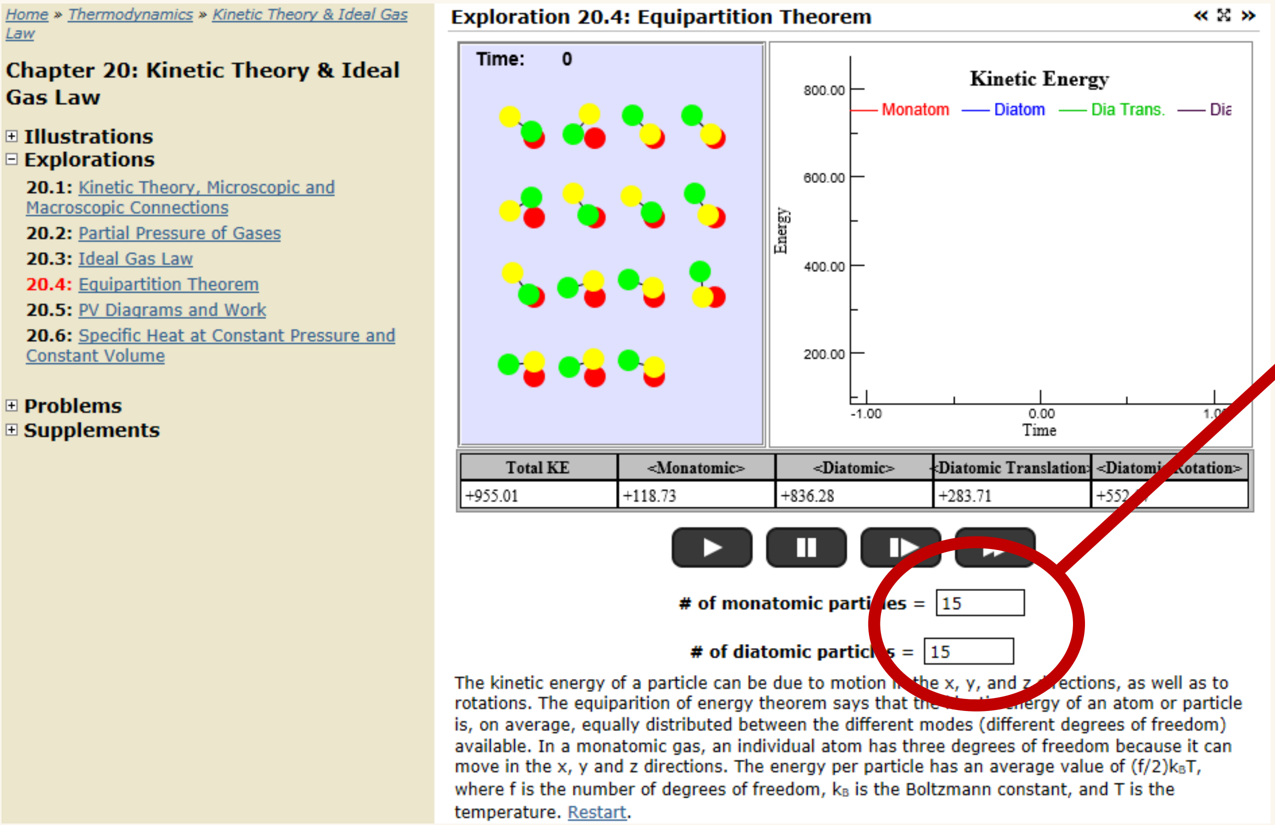
$c'_v \approx 1.5R$ For monatomic

$c'_v \approx 2.5R$ For diatomic

$c'_v > 2.5R$ For polyatomic

Monatomic and Diatomic

https://www.compadre.org/Physlets/thermodynamics/ex20_4.cfm

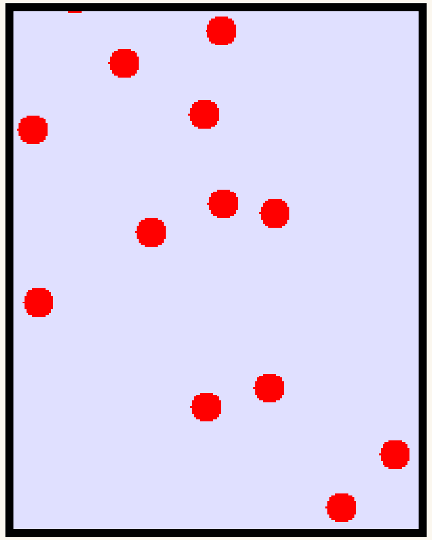


Click the URL (or the picture) to open the simulation website.

Set the number of monatomic particles to 15 and diatomic to zero. Press play. Observe the motion and collisions.

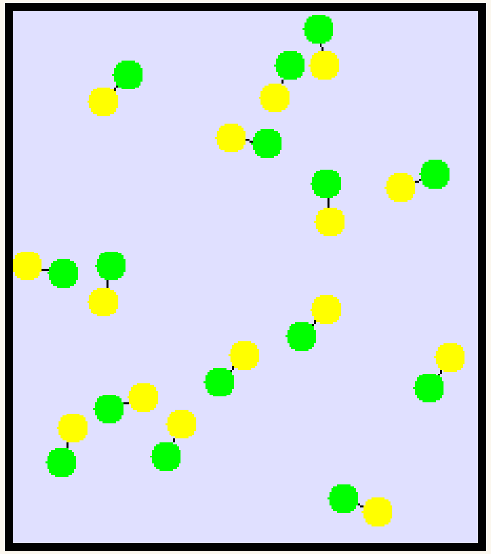
Set the number of monatomic particles to zero and diatomic to 15. Press play. Observe the motion and collisions.

Differences in motion



Monatomic

Translation



Diatomic

Translation + Rotation

Degrees of Freedom

Each way in which a system can absorb energy is called a degree of freedom

Translation

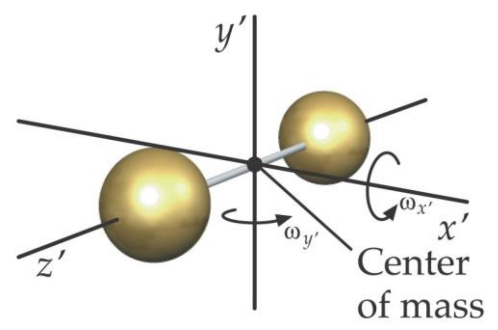
$$\frac{1}{2}mv_{av}^2 = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$$

3 possible degrees of freedom per molecule

Rotation

$$\frac{1}{2}I\omega^2 = \frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2 + \frac{1}{2}I_z\omega_z^2$$

3 possible degrees of freedom per molecule



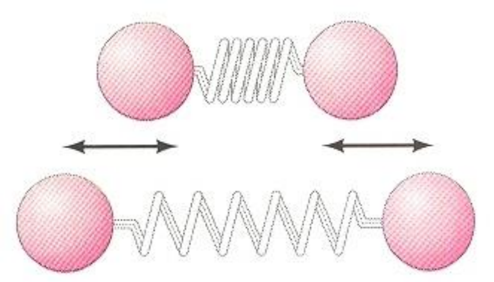
For diatomic molecule ignore rotation about bond axis.
(moment of inertia negligible)

Vibration

$$E_{vib} = KE_{vib} + PE_{vib}$$

$$E_{vib} = \frac{1}{2}\mu v^2 + \frac{1}{2}kx^2$$

2 possible degrees of freedom per bond



μ = reduced mass $\quad$ k = bond stiffness

Equipartition Theorem

When a substance is in thermal equilibrium there is an average energy of $\frac{1}{2}kT$ per molecule ($\frac{1}{2}RT$ per mole) associated with each degree of freedom.

Temperature

Translation

$$\frac{1}{2}mv_{av}^2 = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$$

Temperature

Function of translational kinetic energy of molecules

Translational kinetic energy per molecule

$$\frac{1}{2}m(v^2)_{av} = 3 \times \frac{1}{2}kT = \frac{3}{2}kT$$

Translational kinetic energy per mole

$$\frac{1}{2}M(v^2)_{av} = \frac{3}{2}RT$$

Heat Capacity and Internal Energy

$$Q = nc'\Delta T \qquad dQ = nc'dT \qquad c' = \frac{1}{n}\frac{dQ}{dT} \qquad c'_v = \frac{1}{n}\frac{dU}{dT}$$

When heated at constant volume, all the heat goes into internal energy (U).

This will be discussed in next lecture

Success of the Equipartition Theorem gases

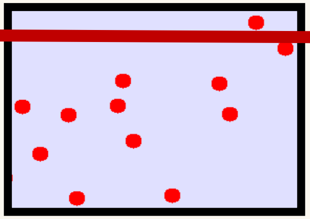
	Degrees of Freedom	U per mole	c_v'
monatomic	3	$\frac{3}{2}RT$	$\frac{3}{2}R$
diatomic	5	$\frac{5}{2}RT$	$\frac{5}{2}R$
polyatomic	6	$\frac{6}{2}RT$	$\frac{6}{2}R$

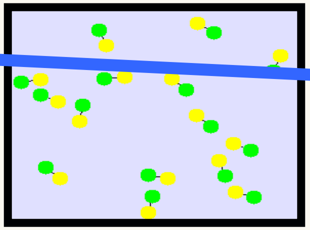
Ignoring vibration which does not contribute to heat capacity until high temps.

From Equipartition Theorem

$$c_v' = \frac{1}{n}\frac{dU}{dT}$$

The success of the Equipartition Theorem is that it predicts the experimental values of c_v'





c'_v	c'_v/R
12.52	1.51
12.68	1.52
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1 mole of monatomic gas and 1 mole of diatomic gas, are stored in identical rigid containers, both initially at room temperature. If the same amount of heat is added to each container, what can you say about their temperature rises?

A Both gases have the same temp rise

B The monatomic gas has the greatest temperature rise

C The diatomic gas has the greatest temperature rise

D The temperature rise depends on molar mass

A Both gases have the same temp rise

##.##%

B The monatomic gas has the greatest temperature rise

##.##%

C The diatomic gas has the greatest temperature rise

##.##%

D The temperature rise depends on molar mass

##.##%

Answer Q1

1 mole of monatomic gas and 1 mole of diatomic gas, are stored in identical rigid containers, both initially at room temperature. If the same amount of heat is added to each container, what can you say about their temperature rises?

A Both gases have the same temp rise

B The monatomic gas has the greatest temperature rise

C The diatomic gas has the greatest temperature rise

D The temperature rise depends on molar mass

rigid container $\equiv$ constant volume

monatomic $c_v' = \frac{3}{2}R$

diatomic $c_v' = \frac{5}{2}R$

$Q = nc'\Delta T$

$\therefore \Delta T = \frac{Q}{nc'}$

both have 1 mole and same heat

$\therefore \Delta T \propto \frac{1}{c'}$

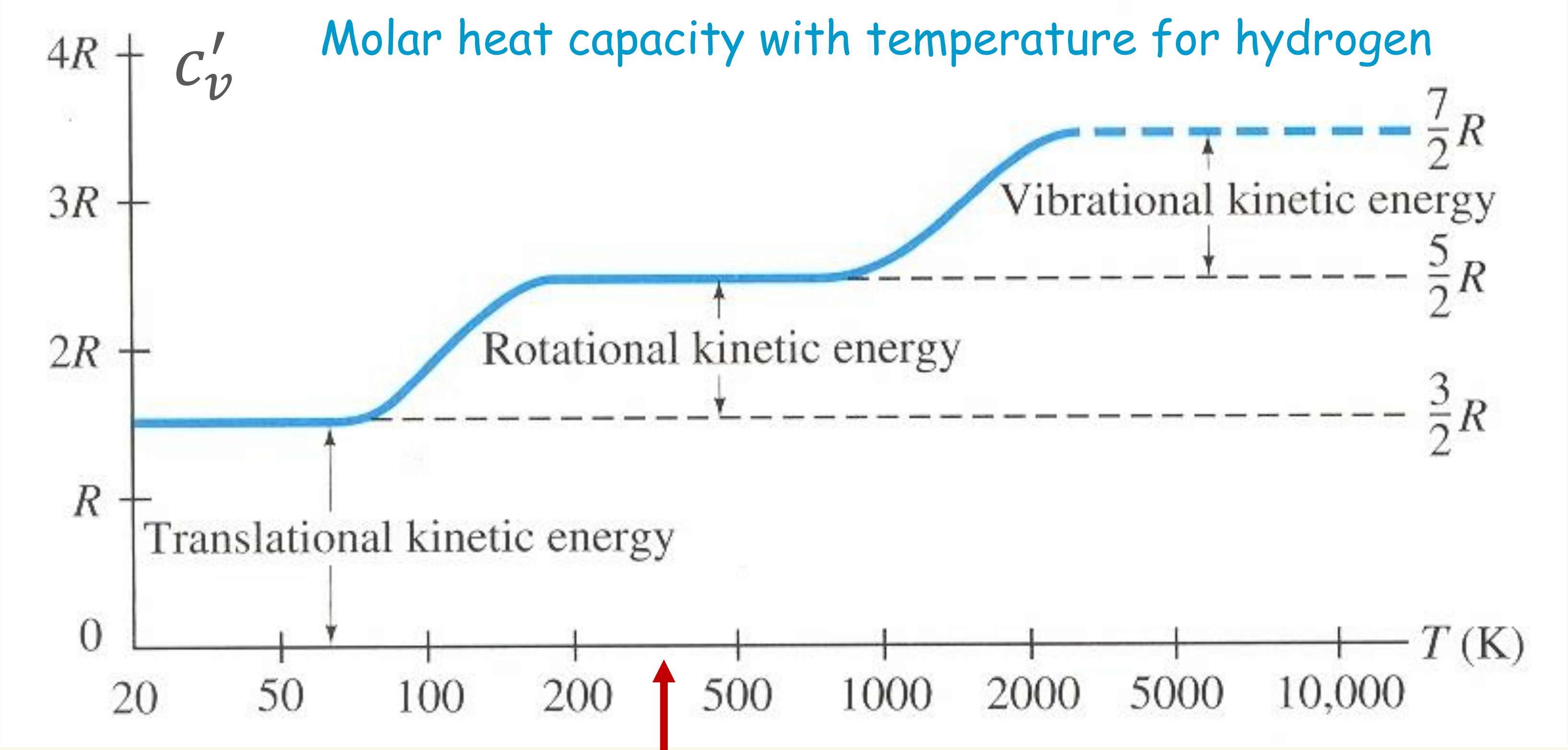
$\therefore$ biggest ΔT for smallest c'

$\therefore$ monatomic has greatest temp rise

ANS B

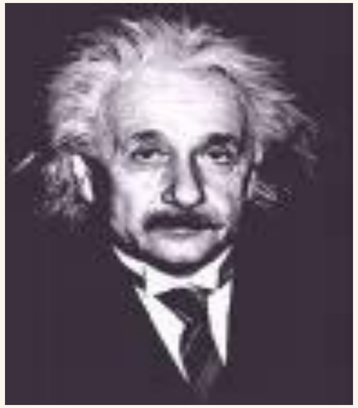
Failure of the Equipartition Theorem

gases

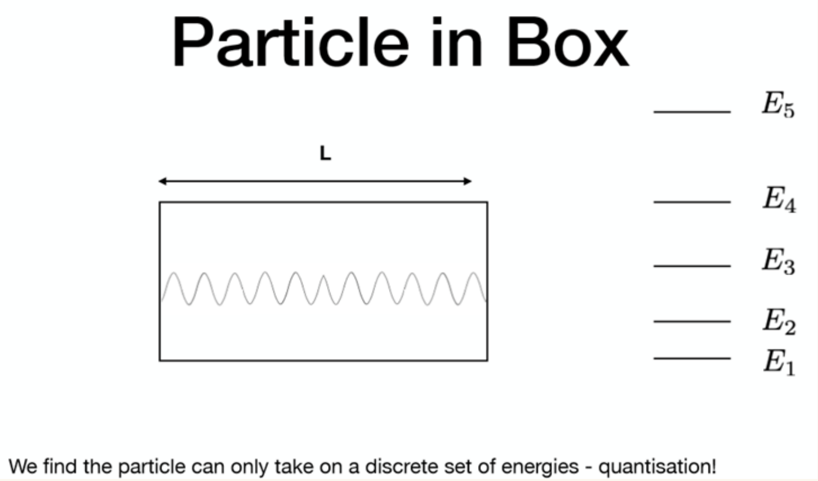


Room temp
~ 300 K

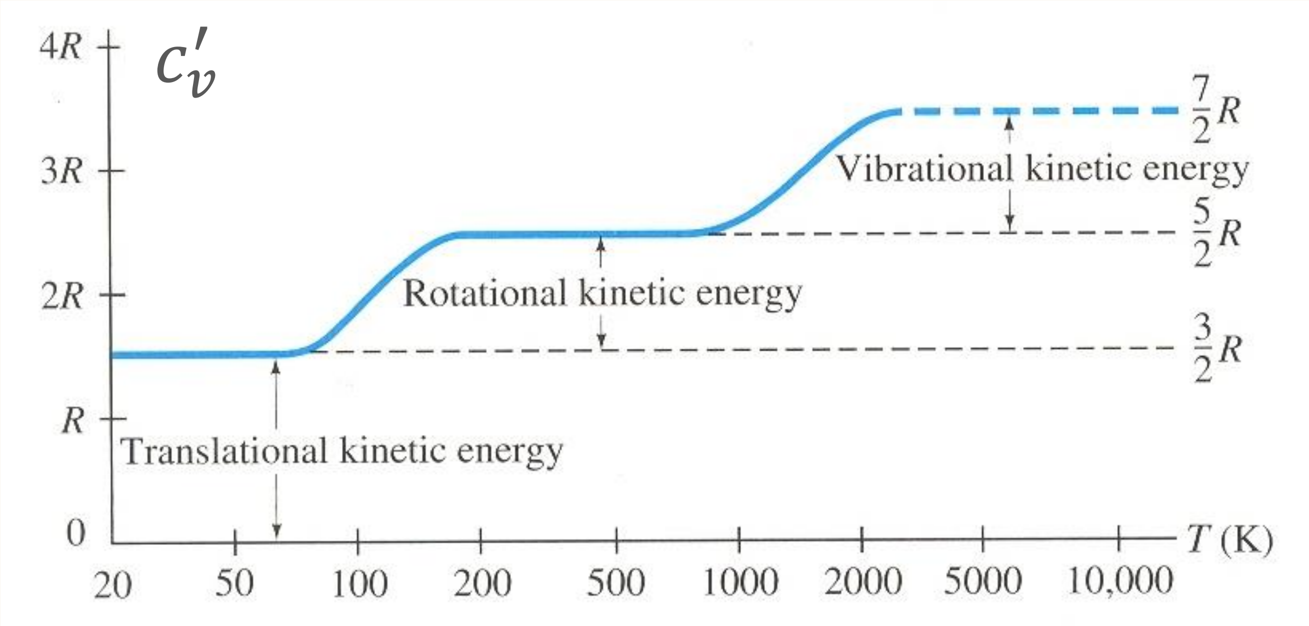
Notice logarithmic temp scale

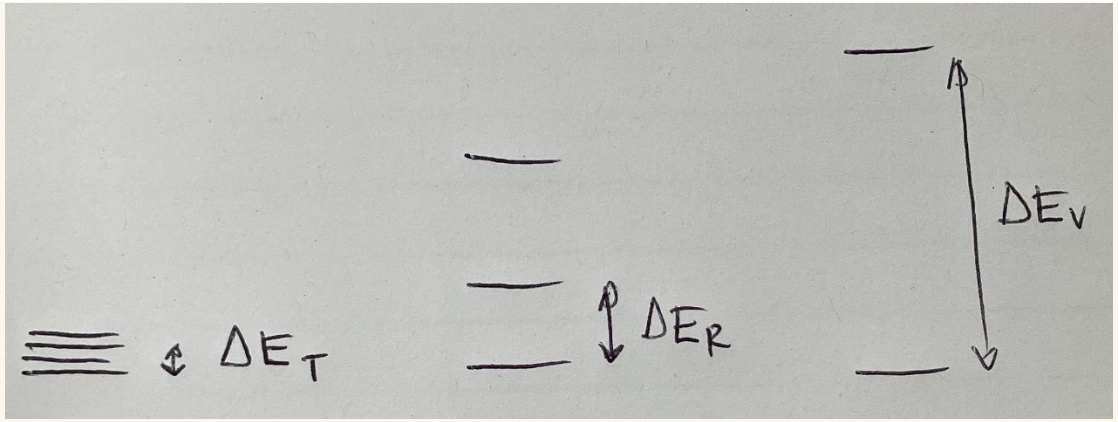


Albert Einstein
1879-1955



Quantum explanation





translation rotation vibration

Typical energy transferred between molecules in collision = kT (thermal energy).

If $kT > \Delta E$ energy can be transferred

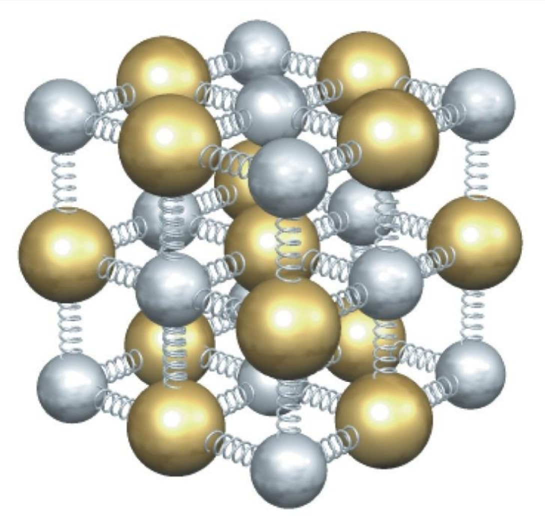
If $kT < \Delta E$ no energy transferred

Validity of Equipartition Theorem

If the spacing of the allowed energy levels is large compared with kT, then energy cannot be transferred by collisions and the classical equipartition theorem is not valid.

If the spacing of energy levels is much smaller than kT, energy quantization will not be noticed and the equipartition theorem holds.

Solids



Each atom in a crystalline solid can vibrate about its equilibrium position.

Number of degrees of freedom = 3 KE + 3 PE per atom = 6

Thus $c_v' = \frac{6}{2}R = 3R = 3 \times 8.31 \approx 25\, J/mol.K$

Dulong-Petit Law

Dulong-Petit Law: All solids have $c_v' = 3R$

Discovered in 1819

Pierre Louis Dulong
1785 - 1838

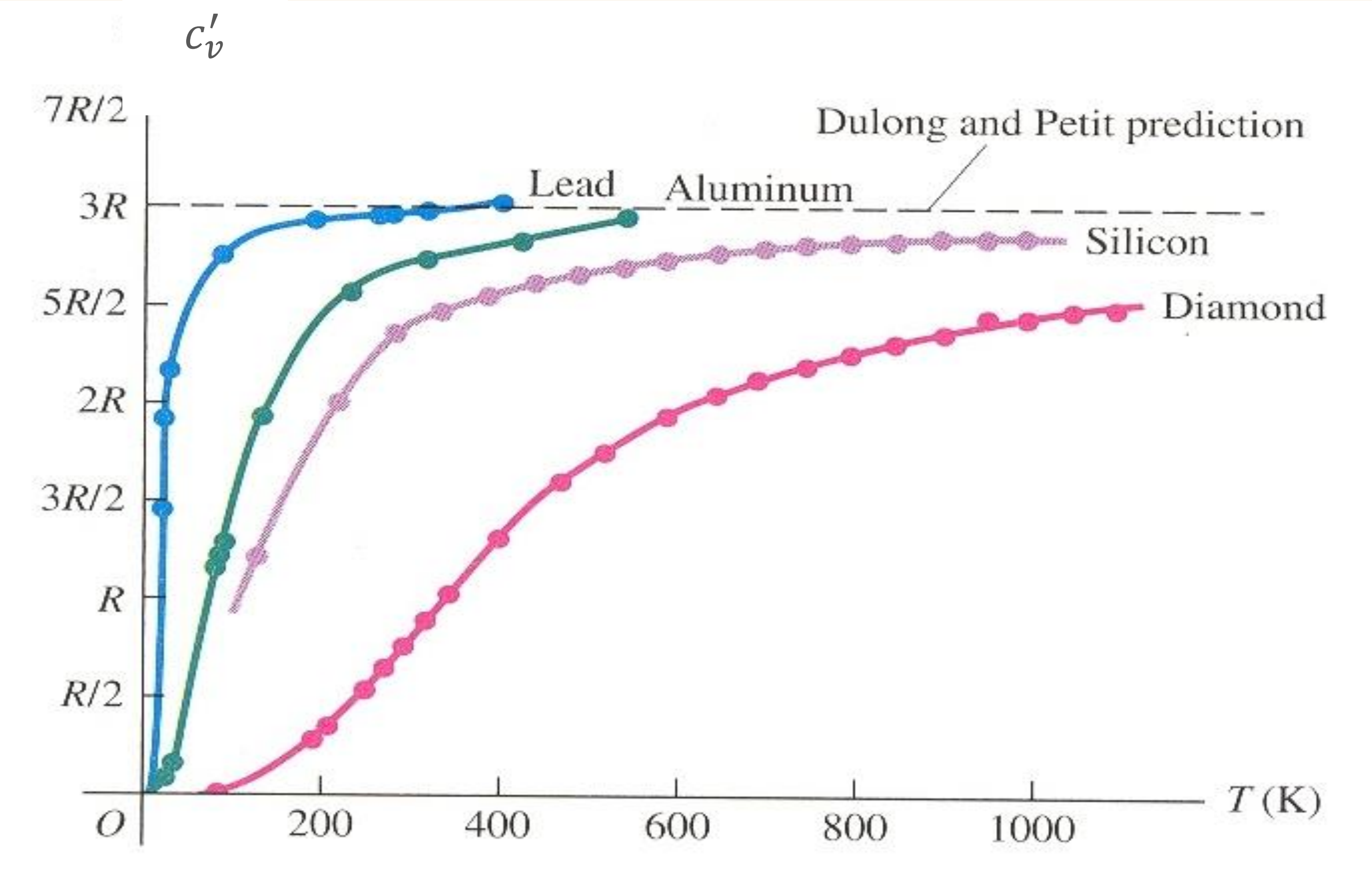
Alexis Therese Petit
1791 - 1820

Specific Heats and Molar Specific Heats of Some Solids and Liquids

Substance	c, kJ/kg·K	c′, J/mol·K
Aluminum	0.900	24.3
Bismuth	0.123	25.7
Copper	0.386	24.5
Glass	0.840	—
Gold	0.126	25.6
Ice (−10°C)	2.05	36.9
Lead	0.128	26.4
Silver	0.233	24.9
Tungsten	0.134	24.8
Zinc	0.387	25.2
Alcohol (ethyl)	2.4	111
Mercury	0.140	28.3
Water	4.18	75.2

Dulong-Petit Law

Valid at high temperature, when all DoF are active



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Question

If the Dulong Petit law holds, which would you expect to have a higher specific heat capacity, lead or copper?

Molar masses: lead = 207 g   copper = 63.5 g

Answer

If the Dulong Petit law holds, which would you expect to have a higher specific heat capacity, lead or copper?

Molar masses: lead = 207 g copper = 63.5 g

$c' = Mc$ so $c = \frac{c'}{M}$

for all solids $c' = 3R$ gives $c = \frac{3R}{M}$

$\therefore$ highest c is for lowest M

$\therefore$ copper

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Summary

Equipartition theorem

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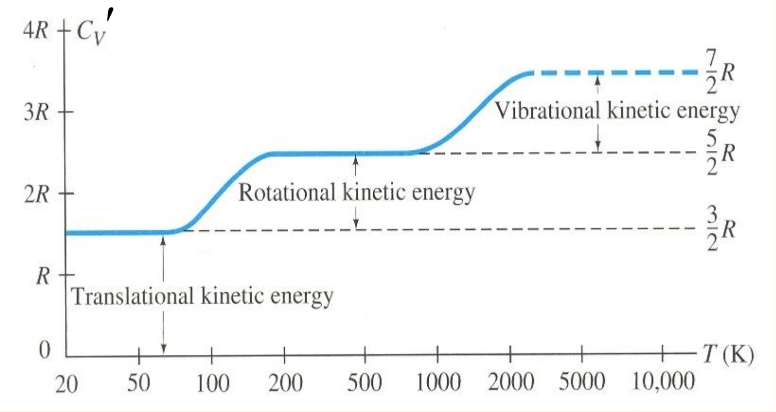
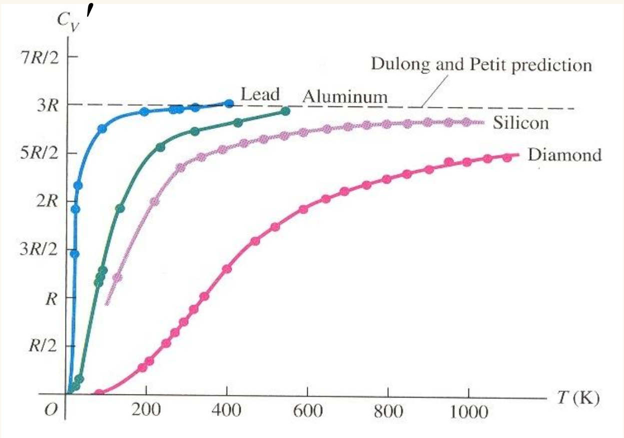
Gases



Solids



Gases have $c_v' = DoF \times \frac{1}{2}R$

Valid when all DoF active, i.e. when kT >> ΔE

Dulong-Petit Law: All solids have $c_v' = 3R$

Valid at high temperatures when all DoF active

$$c_v' = \frac{1}{n}\frac{dU}{dT}$$