

Physical Chemistry

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origin

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study

Equilibrium + Structure + Change

Introduction

- Mass of proton = $2000 \times$ mass of electron
- Electrons contribute very little to the total mass of the atom, but occupy an appreciable volume, and are responsible for the atomic bulk.

The Quantum Rules:

“The energy of an object cannot be changed by an arbitrary amount.”

Consider a pendulum.

$$0, h\nu, 2h\nu, 3h\nu, \dots$$

h = Planck's constant

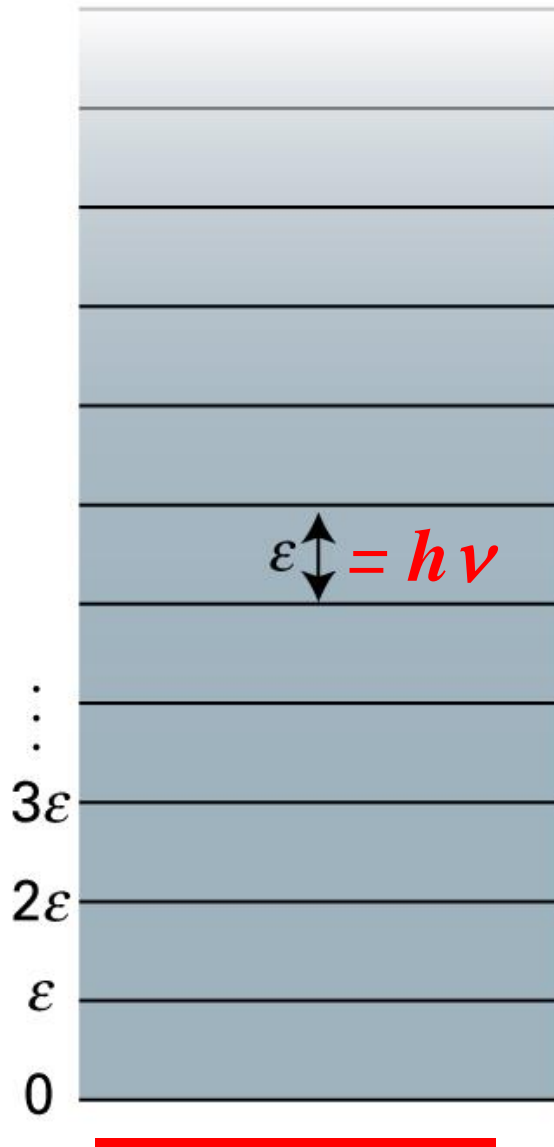
ν = natural frequency



pendulum or spring

$$\nu = \frac{1}{2\pi} \sqrt{\frac{g}{l}} = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

Reference Point



Figs. 8B.1 and 8B.2

Fig. 15B.11. Harmonic Oscillator

The array of molecular energy levels used to calculate the **molecular partition function**.

Chap. 15

Phonon = Lattice Vibration

Reference Point ?

Pendulums of different natural frequencies accept and give up quanta of different sizes, and the higher the natural frequency the larger the quantum energy.

$$h = 4.1357 \times 10^{-15} \text{ eV}\cdot\text{s}$$

if $\nu = 1 \text{ Hz}$, $h\nu = 4.1357 \times 10^{-15} \text{ eV} \longrightarrow$ too small to be detected.

Only when very high-frequency motions are involved, the quantum energy $h\nu$ becomes large enough to give rise to significant effects.

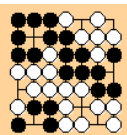
A mass on a spring oscillating with simple harmonic motion:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

Phonon

$\nu \approx 10^{13} \text{ Hz}$

\therefore When the mass is that of an atom, the frequency is extremely high ($\nu \approx 10^{13} \text{ Hz}$), and so we must be prepared for the significant quantum effects in vibrating molecules.



Photon

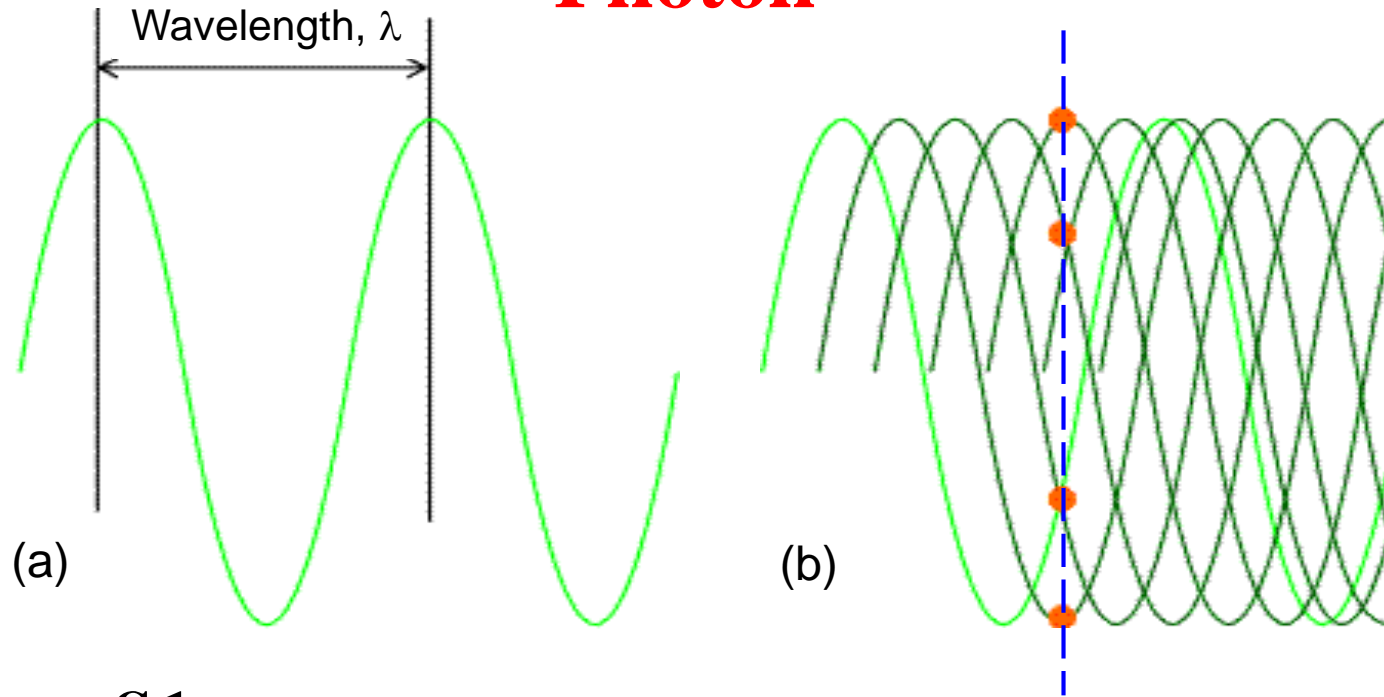


Figure C.1

The wave is shown travelling to the right at a speed c .

Wavelength and frequency are related by $\lambda \nu = c$.

Figures C.5 and C.6

Plane-polarized and circularly-polarized waves.

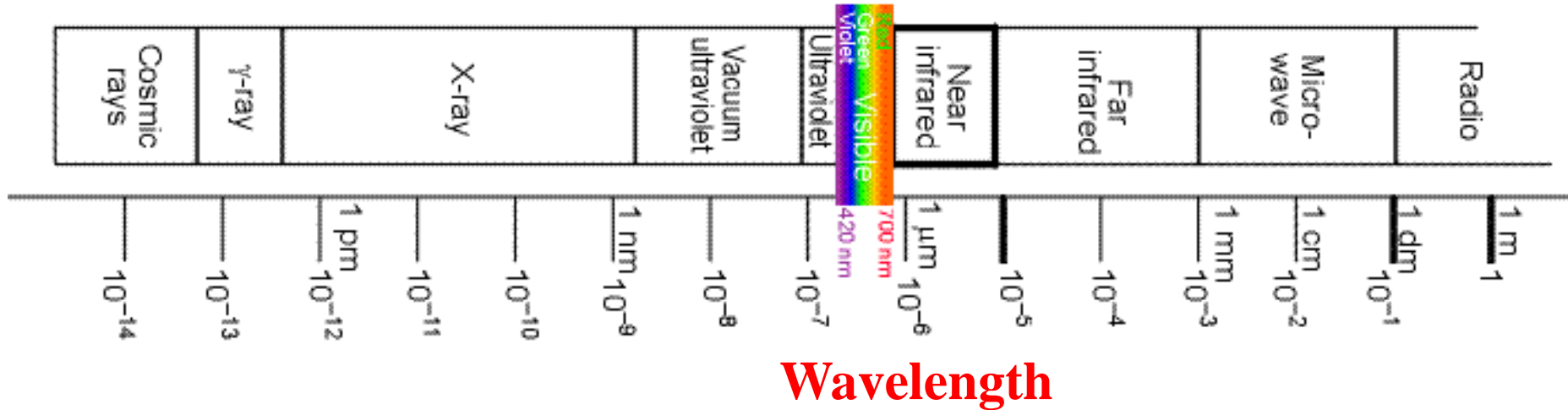
Nuclear
excitation

Core-electron
excitation

Electronic
excitation

Molecular
vibration

Molecular
rotation



Wavelength

Figure C.4

The regions of the electromagnetic spectrum and the types of excitation that give rise to each region.

Visible Light: $\sim 400 - 700$ nm

$\sim 2 - 3$ eV

$\sim 10^{15}$ Hz

$$\lambda \text{ (nm)} = 1240 / h\nu \text{ (eV)}$$

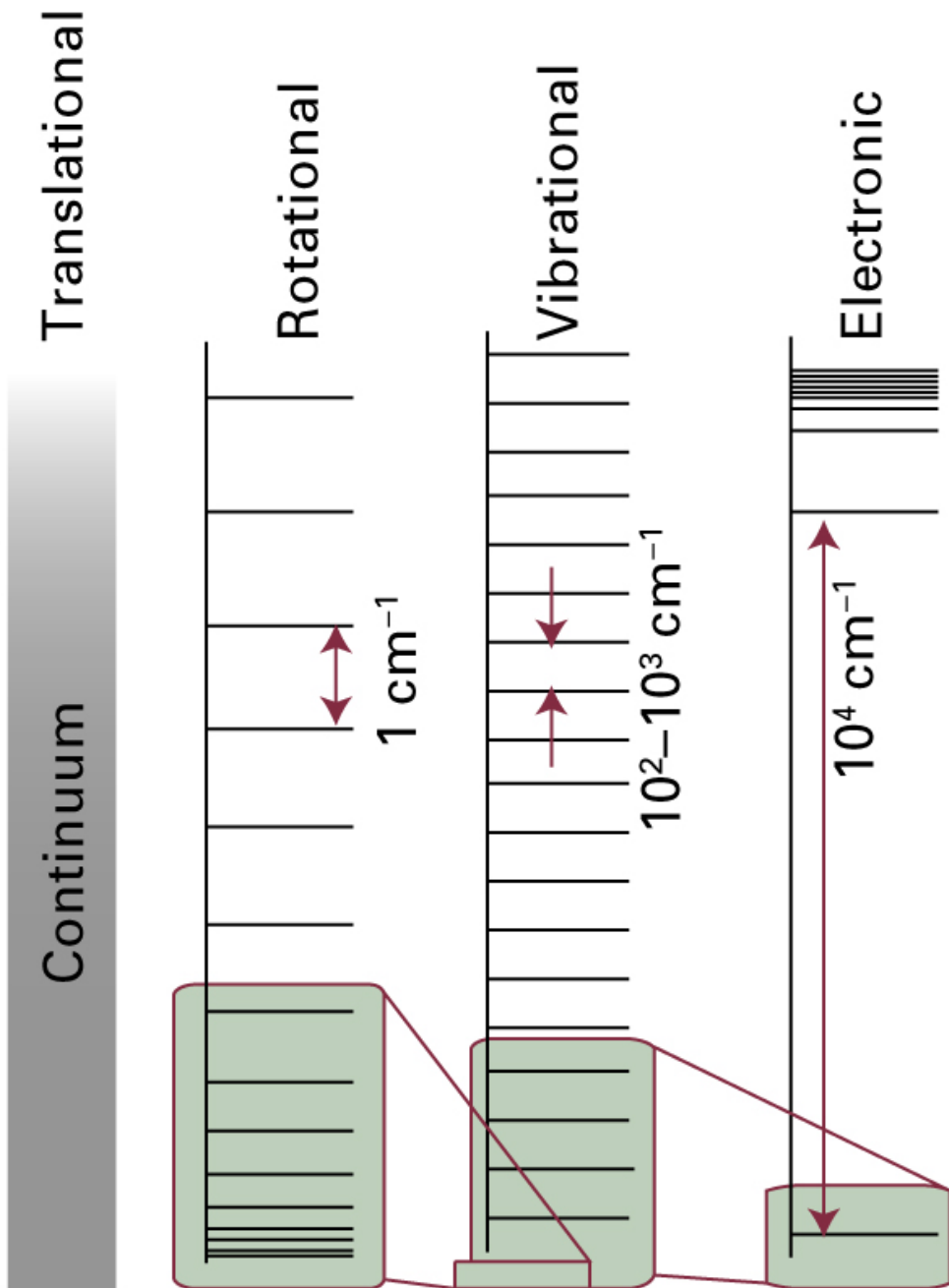


Figure B.3

Quantization of the energy of different types of motion.

Free **translational** motion in an infinite region looks not quantized, and the permitted energy levels form a continuum.

Rotation is quantized, and the separation increases as the state of excitation increases (moment of inertia of the molecule).

Vibrational motion is quantized, but note the change in scale between the ladders.

Electronic energy levels are quantized, and the separations are typically very large (of the order of 1 eV).

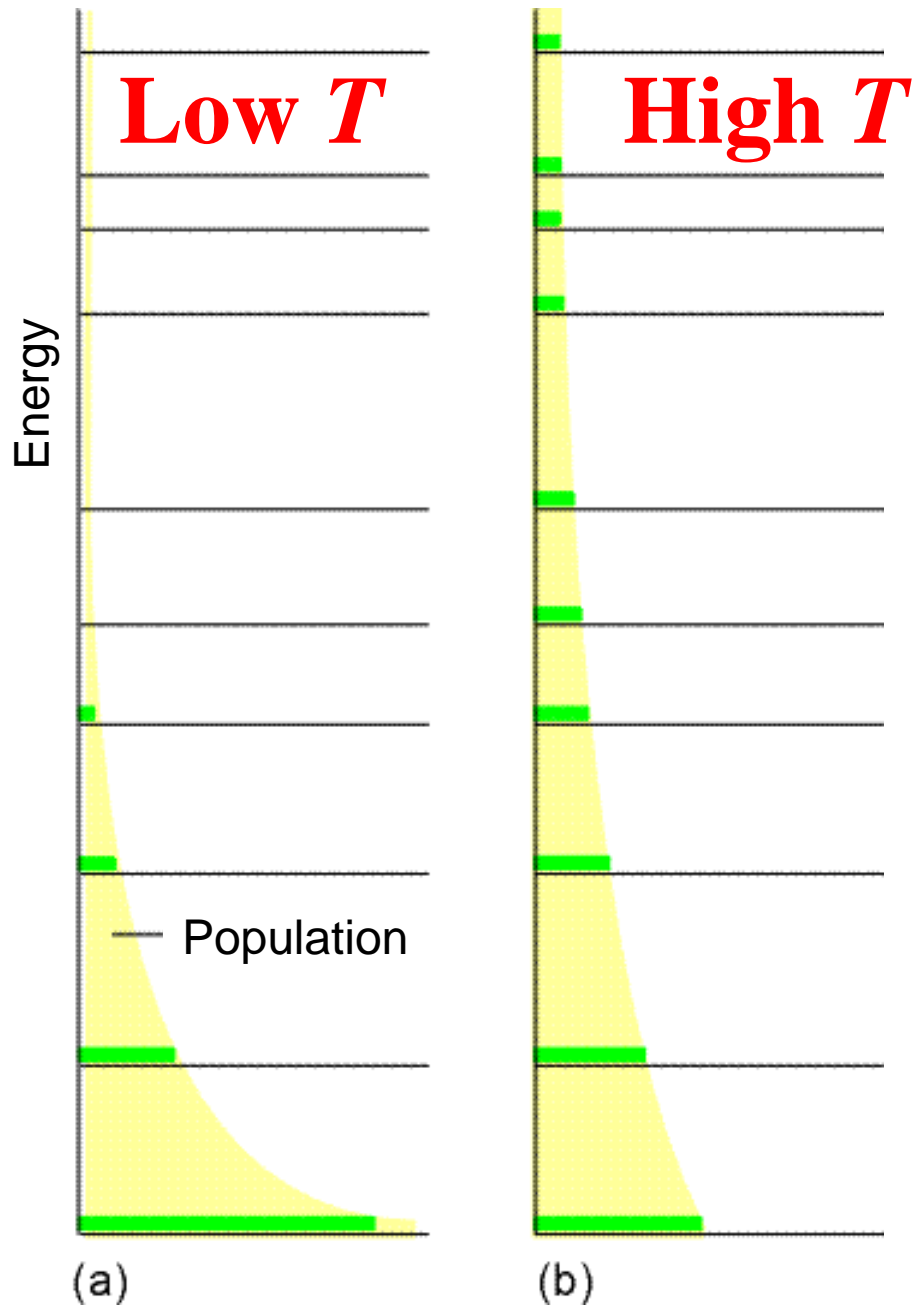


Figure B.4

The Boltzmann distribution predicts that the population of a state decreases exponentially with the energy of the state.

- (a) At low temperatures, only the lowest states are significantly populated.
- (b) At high temperatures, there is significant population in high-energy states as well as in low-energy states. At infinite temperature (not shown), all states are equally populated.

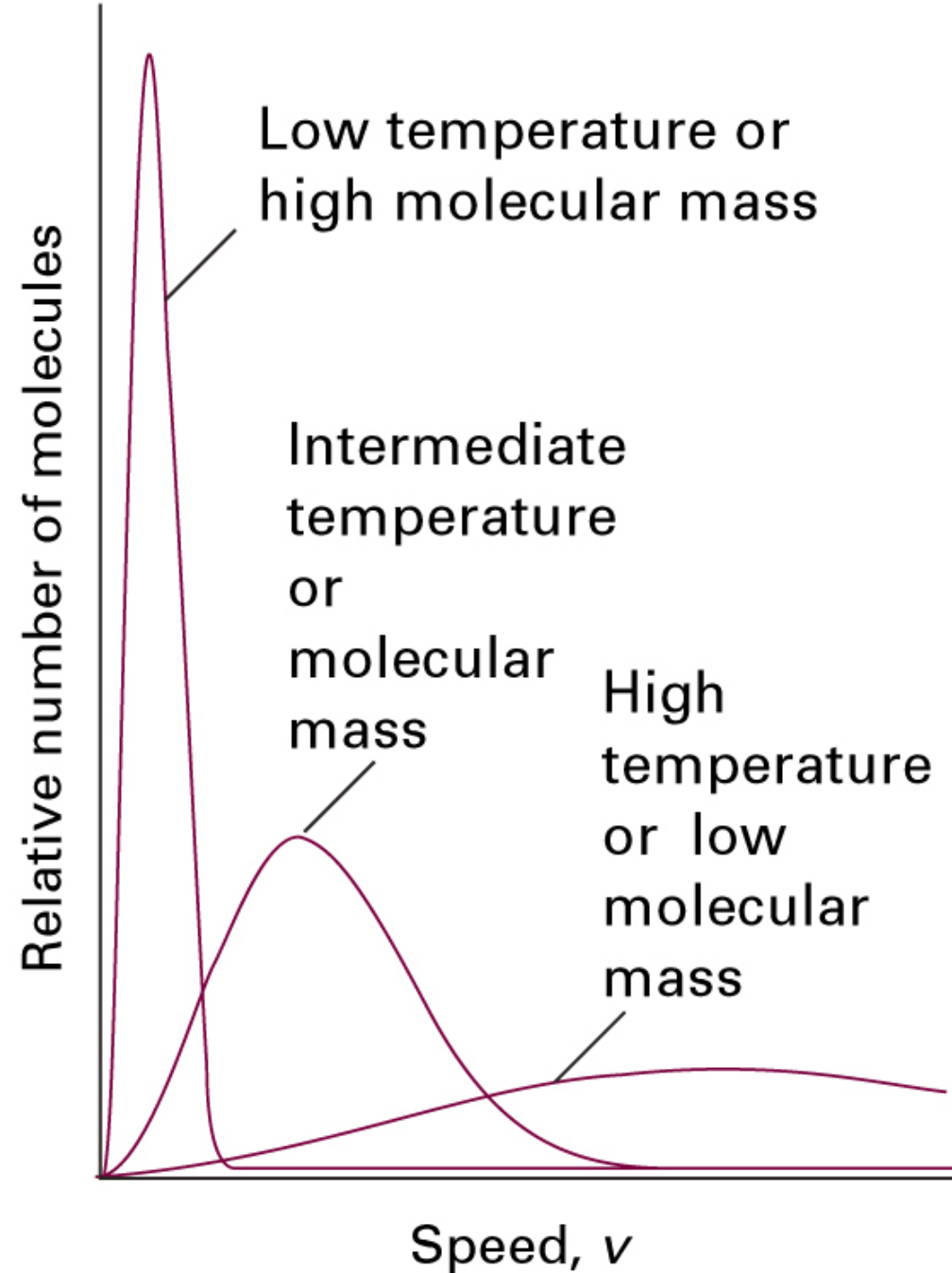
Figure B.6

The essential content of the

Maxwell-Boltzmann
distribution of
molecular speeds.

Note how the maximum in the distribution moves to higher speeds as the temperature is increased or, at constant temperature, we consider species of decreasing mass.

The distribution also becomes wider as its peak moves to higher speeds.



The average kinetic energy of one particle from the Maxwell-Boltzmann distribution = $\frac{3}{2} k_B T$.

B.3(b)
Chapter 15C

Equipartition theorem of classical physics:

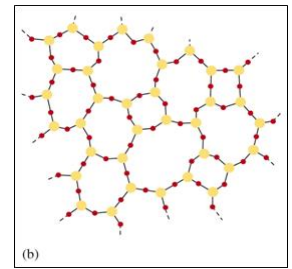
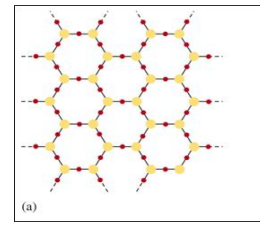
average energy of different modes of motion = $\frac{1}{2} k_B T$.

∴ three dimensional translational modes = $3 \times \frac{1}{2} k_B T$

Association of Atoms and Molecules

1. Covalent bond
2. Metallic bond: an assembly of cations (Li^{1+}) immersed in a sea of electrons
3. Ionic bond
4. van der Waals force: (a) due to polar attraction
(b) due to instantaneous electric dipoles
(c) due to **hydrogen bonding**

A.3. The State of Matter



Solid State: Crystal or Amorphous (Glass)

1. Morphology: crystal's external appearance
2. Crystal **defects**: the breaks in the uniformity of array
3. Liquid crystals: van der Waals attraction is so weak that the crystals possess virtually no rigidity.

Solid State vs. Liquid State

The Ordered Structure of Solid

~ δ -function atomic correlations



Less-Ordered Liquid (Fluid)

Diffuse atomic correlations



Melting Point

The Ability to Flow

The number of molecules with enough energy to move follows a **Boltzmann distribution**.

$$\text{Fluidity} \propto \exp(-\Delta E_a / RT)$$

where ΔE is the energy to be overcome.

$$\text{Viscosity} \propto \exp(+\Delta E / RT)$$

where ΔE is of the same order as the intermolecular binding energy.

Activation Energy

Activation Enthalpy

~2-3 eV

Gas Phase

The average distance between molecules is normally large relative to their diameter. At low pressure, the intermolecular interactions are likely to be negligible, and the gas satisfies **the ideal gas (perfect gas) law**:

$$pV = nRT \quad p: \text{pressure} \quad (\text{A.5})$$

n : amount of gas

T : absolute temperature

V : volume

The mean kinetic energy of 1 mol of gas = $\frac{3}{2} RT$

The kinetic energy of 1 mol of gas = $\frac{1}{2} m \langle v^2 \rangle N_A$

N_A : Avogadro's number

$\langle v^2 \rangle$: average value of v^2

$$\frac{3}{2} RT = \frac{1}{2} m \langle v^2 \rangle N_A$$

$$\underline{\underline{\frac{3}{2} k_B T = \frac{1}{2} m \langle v^2 \rangle}}$$

$$\langle v^2 \rangle = \frac{3RT}{mN_A}$$

$$\sqrt{\langle v^2 \rangle} = \sqrt{\frac{3RT}{mN_A}} = \sqrt{\frac{3k_B T}{m}} : \text{Root mean square speed}$$

$$k_B = \frac{R}{N_A}$$

Transformations of Matter

- Can it occur? **Thermodynamics**
- How fast does it occur? **Kinetics**

The probability that, when the collision occurs, it does so with sufficient energy to react will be determined by **the Boltzmann distribution**.

E_a : necessary energy (**activation energy** of the reaction)

Chapter 20D

Rate of reaction \propto (rate of collision) \times (probability that collision carries enough energy)

$$\propto Z(T) \exp\left(-\frac{E_a}{RT}\right) \quad \text{Arrhenius equation}$$

Phonon $\nu \approx 10^{13}$ Hz

International System of Units (SI) CGS (cgs) or MKS

Table F.1 The SI base units

Physical quantity	Symbol for quantity	Base unit
Length	l	metre, m
Mass	m	kilogram, kg
Time	t	second, s
Electric current	I	ampere, A
Thermodynamic temperature	T	kelvin, K
Amount of substance	n	mole, mol
Luminous intensity	I_v	candela, cd

cm g s A K mol

Table F.2 A selection of derived units

Physical quantity	Derived unit*	Name of derived unit
Force	1 kg m s^{-2}	newton, N
Pressure	$1 \text{ kg m}^{-1} \text{ s}^{-2}$ 1 N m^{-2}	pascal, Pa
Energy	$1 \text{ kg m}^2 \text{ s}^{-2}$ 1 N m 1 Pa m^3	joule, J
Power	$1 \text{ kg m}^2 \text{ s}^{-3}$ 1 J s^{-1}	watt, W

$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J} = 1.602 \times 10^{-12} \text{ erg}$

* Equivalent definitions in terms of derived units are given following the definition in terms of base units.

$$\Delta t \Delta E \geq h$$

Table F.3 Common SI prefixes

Prefix	y	z	a	<u>f</u>	p	n	μ	m	c	d
Name	yocto	zepto	atto	femto	pico	nano	micro	milli	centi	deci
Factor	10^{-24}	10^{-21}	10^{-18}	10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}
Prefix	da	h	<u>k</u>	M	G	T	P	E	Z	Y
Name	deca	hecto	kilo	mega	giga	tera	peta	exa	zeta	yotta
Factor	10	10^2	10^3	10^6	10^9	10^{12}	10^{15}	10^{18}	10^{21}	10^{24}

$$h = 4.1357 \times 10^{-15} \text{ eV}\cdot\text{s}$$

Table F.4 Some common units

Physical quantity	Name of unit	Symbol for unit	Value*
Time	minute	min	60 s
	hour	h	3600 s
	day	d	86 400 s
	year	a	31 556 952 s
Length	ångström	Å	10^{-10} m
Volume	litre	L, l	1 dm^3
Mass	tonne	t	10^3 kg
Pressure	bar	bar	10^5 Pa
	atmosphere	atm	101.325 kPa
Energy	electronvolt	<u>eV / atom</u>	$1.602\ 176\ 53 \times 10^{-19}$ J
		<u>eV / molecule</u>	$96.485\ 31 \text{ kJ mol}^{-1}$
			$\approx 10^5 \text{ J/mol}$

* All values in the final column are exact, except for the definition of 1 eV, which depends on the measured value of e , and the year, which is not a constant and depends on a variety of astronomical assumptions.

Problems from Chap. Foundations

A.1(b) A.2(b) A.3(b) A.10(b) A.19(b)

B.2 B.4 B.6

B.4(b) B.8(b) B.9(b) B.14(b) B.15(b)

B.17(b) B.19(b) B.20(b) B.23(b) B.24(b)

C.1(b) C.2(b)