

Techniques Spectroscopiques

Applications à l'étude des biomolécules et de leurs assemblages

C. Sanchez

Décembre 2024

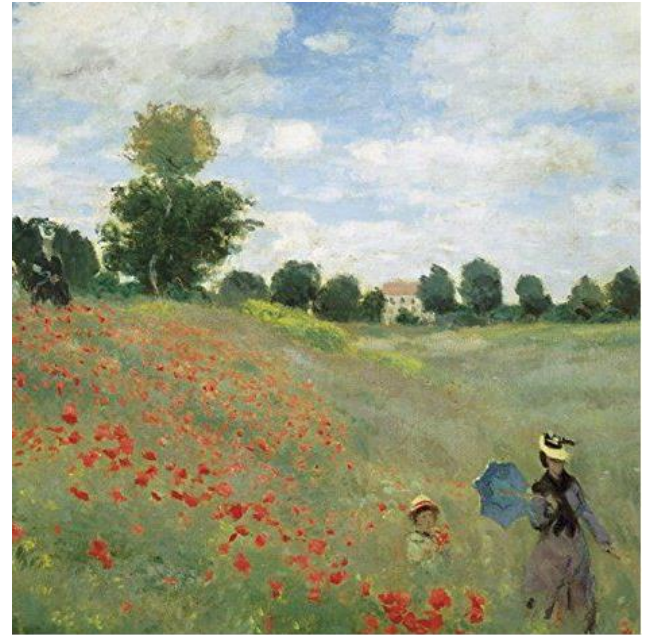
1. Nature de la matière et des interactions (Introduction)
2. Méthodes de diffusion de la lumière
3. Spectroscopie d'absorption moléculaire

Méthodes spectroscopiques :

Etude des interactions lumière – matière

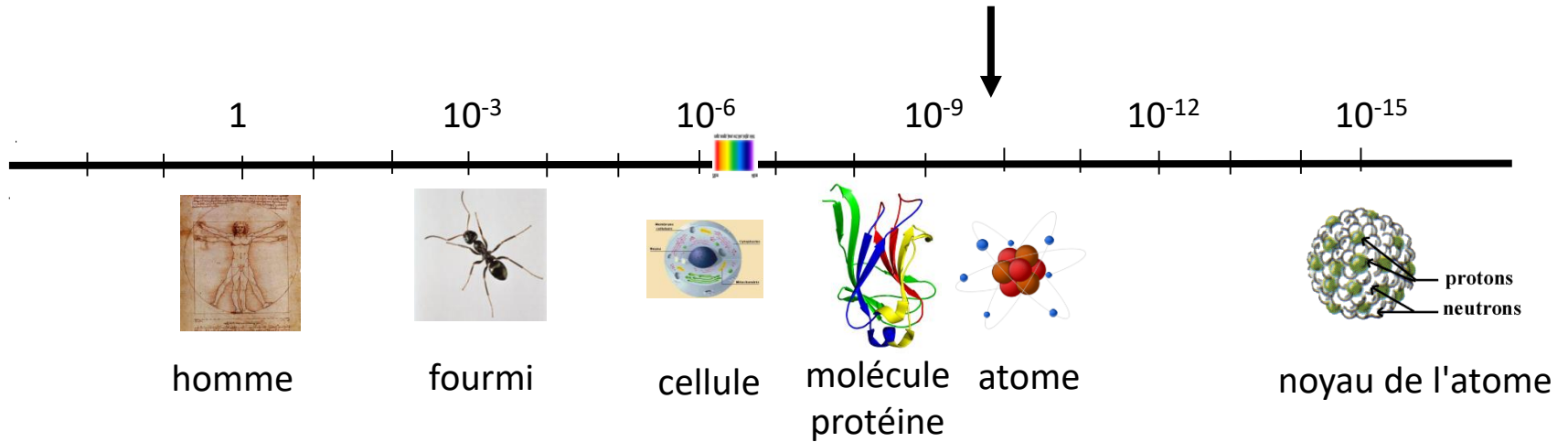
Voir le visible et l'invisible

Voir le mouvement

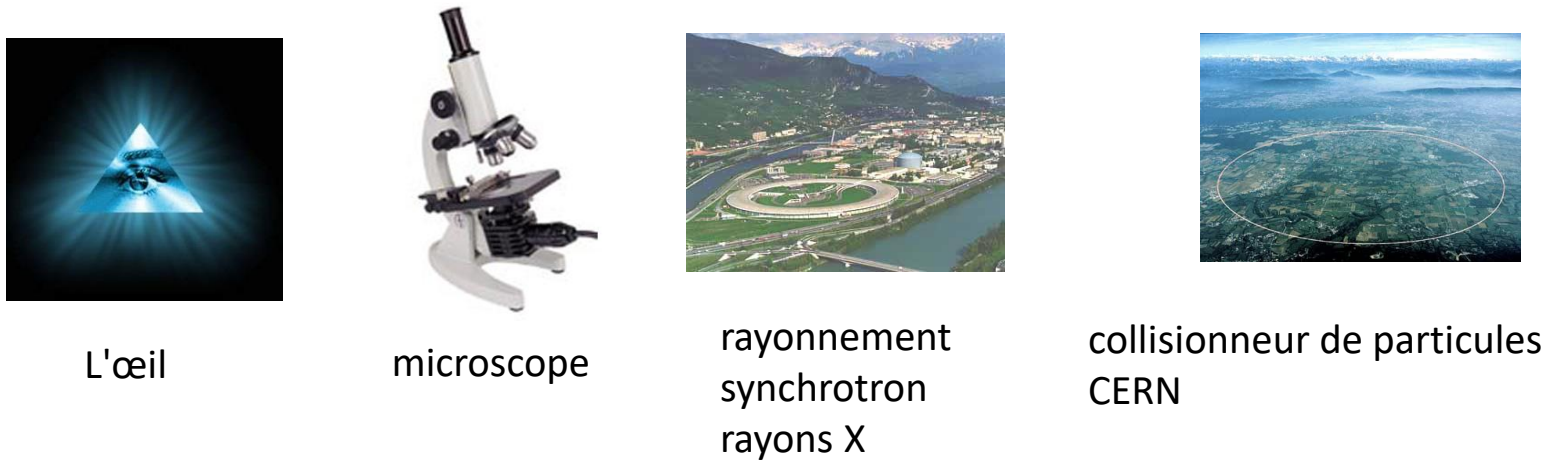


Claude Monet (Coquelicots, 1873)

La structure : une question d'échelle

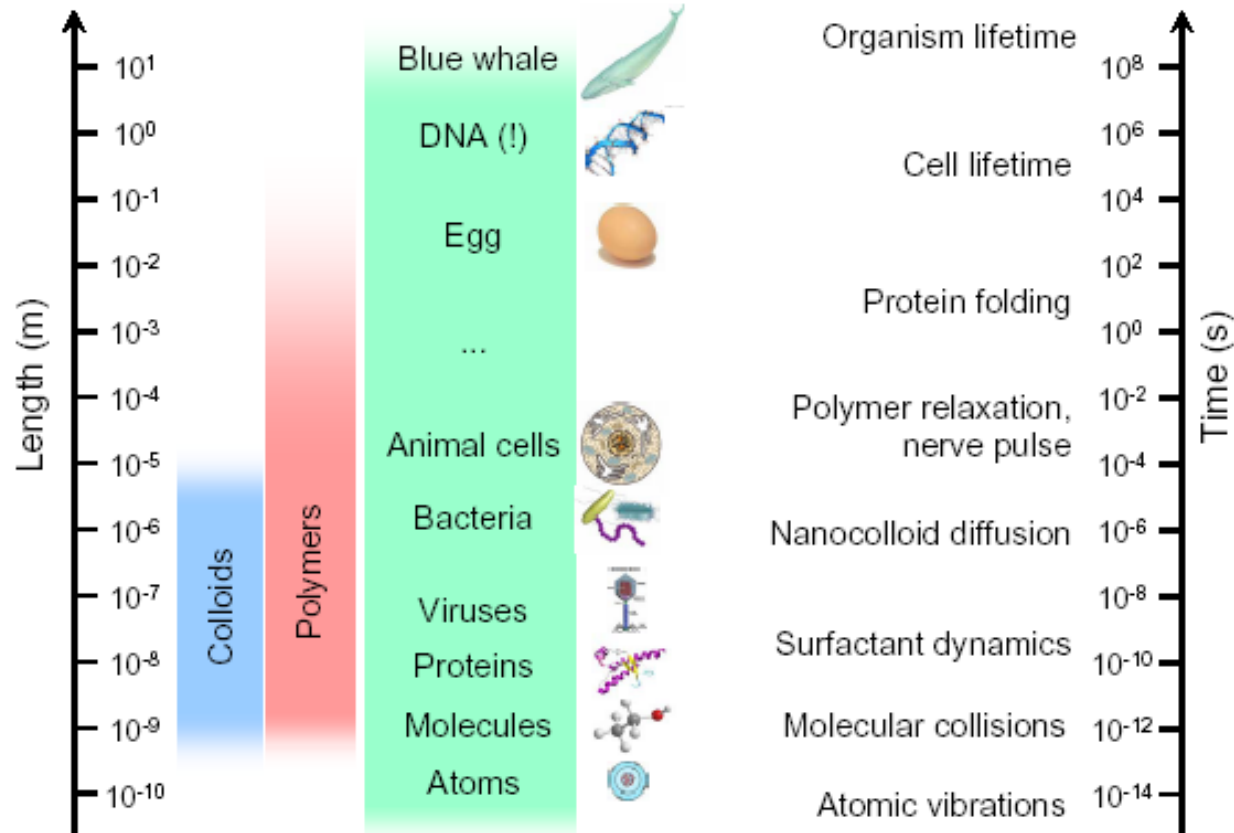


Les outils d'observation



Plus on veut voir petit, plus l'instrument est grand

Exemples d' échelles de longueur et de temps



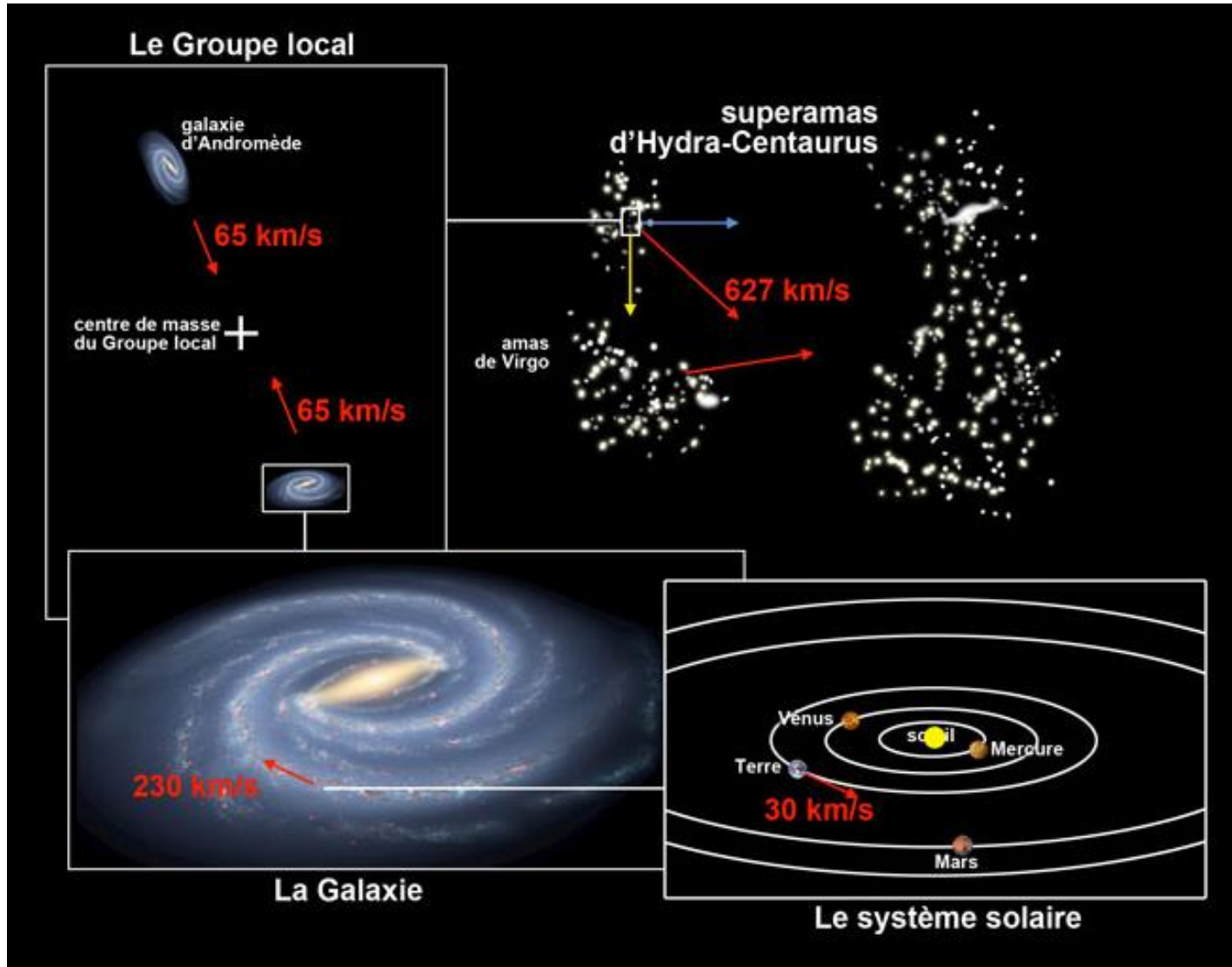
« *Dans le vide infini s'agite la matière* »

(Lucrece, *De Rerum Natura*, -100 bc)

« *Le mouvement est le mode d'existence de la matière* »

(F. Engels, *Dialectique de la Nature*, 1883)

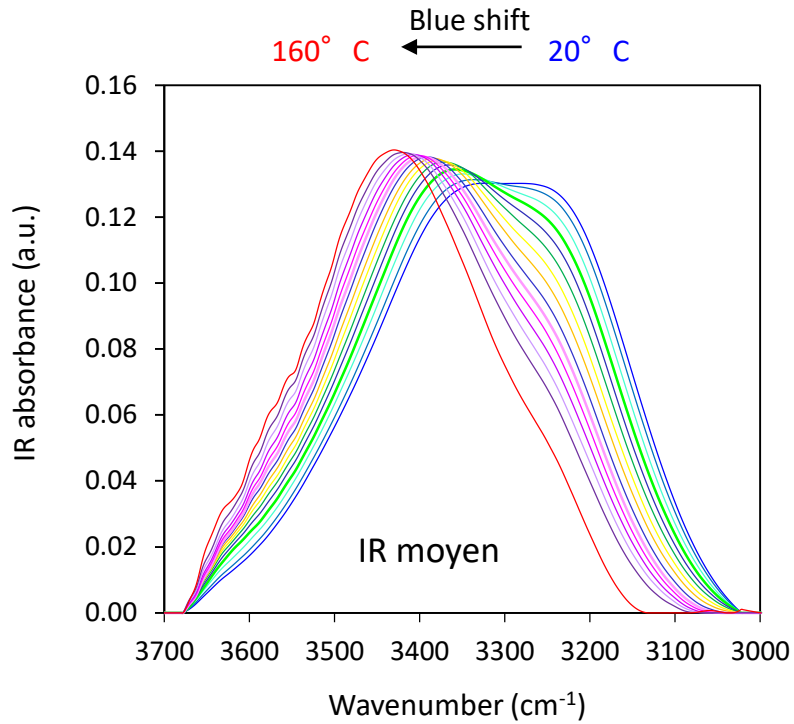
Velocity of cosmic bodies (ex.)



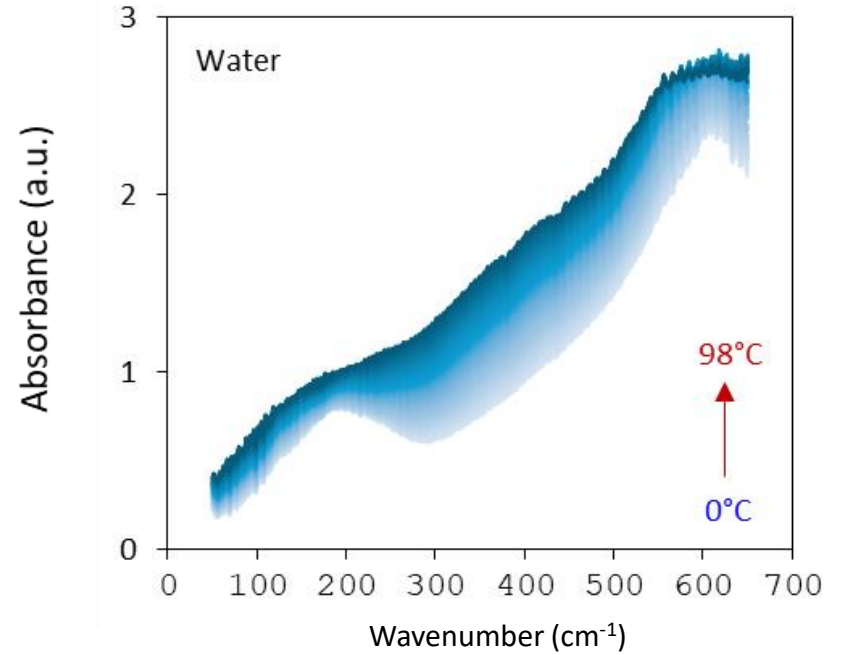
(828 000 km/h)

Spectres infrarouge de l'eau en fonction de la température

IR moyen



IR lointain (THZ)



$$\Delta E_{\text{Hb}} = -0.00060264 \times \nu_{\text{OH}}^2 + 0.34809 \times \nu_{\text{OH}} + 463.92.$$

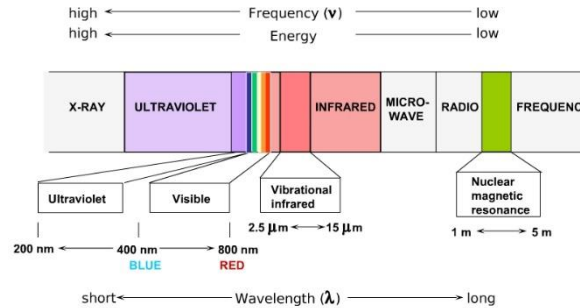
T. Shimoaka, T. Hasegawa, K. Ohno, Y. Katsumoto, Correlation between the local OH stretching vibration wavenumber and the hydrogen bonding pattern in a condensed phase : Quantum chemical approach to analyze the broad OH band, J. Mol. Struct. 1029, 2012, 209-216.

Physique classique

Physique quantique

Anciens
grecs

Aristote, Leucippe, Democrite,
Epicure
Lucreèce



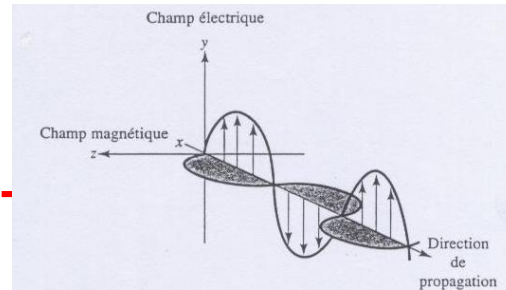
-400 / -200

-1

1400
1500
1600
1700
1800

non Relativiste

Copernic, Bruno
Galilée
Newton
Huygens
J.C. Maxwell
(notion d'éther)



1900

Relativiste

K. Lorentz
R. Poincaré
A. Einstein

M. Plank
M. Curie
W. Heisenberg
W. Pauli
N. Bohr
L. De Broglie
E. Schrödinger
P. Dirac
R. Feynman
A. Aspect

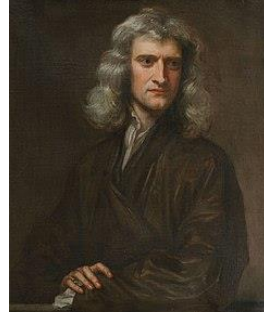
1925

1950

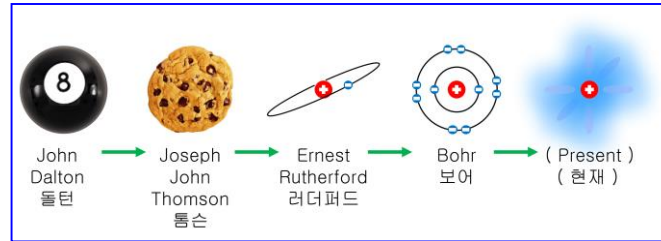
1980

What is matter?

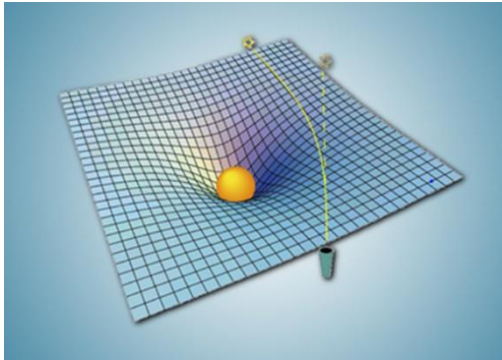
Newtonian Mechanics



Sir I. Newton

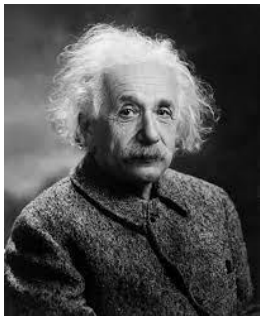


General Relativity Theory



$$G_{\mu\nu} + \Lambda g_{\mu\nu} = \kappa T_{\mu\nu}$$

Einstein Field Equations

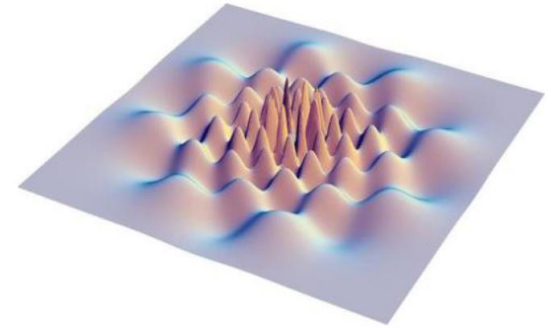


Gravity
 Strong Nuclear Interaction
 Weak Nuclear Interaction
 Electromagnetic Interaction



L. de Broglie

Quantum Mechanics



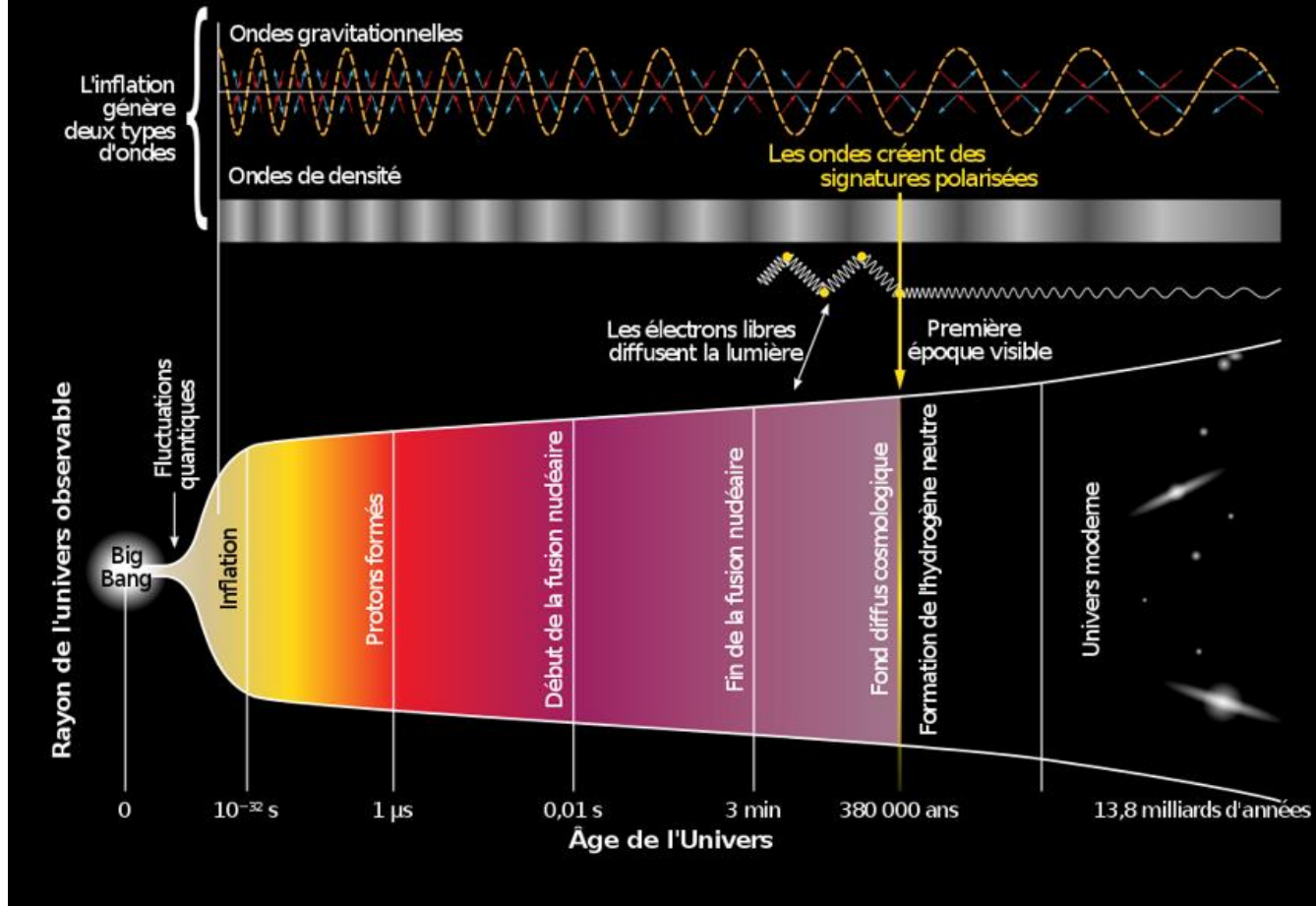
$$\frac{\hat{\mathbf{p}}^2}{2m} |\Psi(t)\rangle + V(\hat{\mathbf{r}}, t) |\Psi(t)\rangle = i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle$$

Schrödinger Equation



E. Schrödinger

Histoire de l'Univers



10^{-44} s : Fluctuations quantiques (mousse)

10^{-43} s : Echelle de Planck

10^{-38} s : Inflation

Taux d'expansion de l'Univers : $\times 10^{50} - 10^{10^{12}}$?

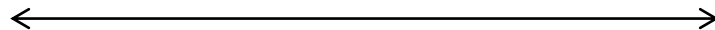
A la fin de l'inflation (10^{-32} s)

10^{94} kg/m^3

$10^{26} - 10^{28} \text{ K}$

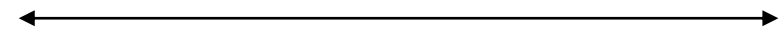
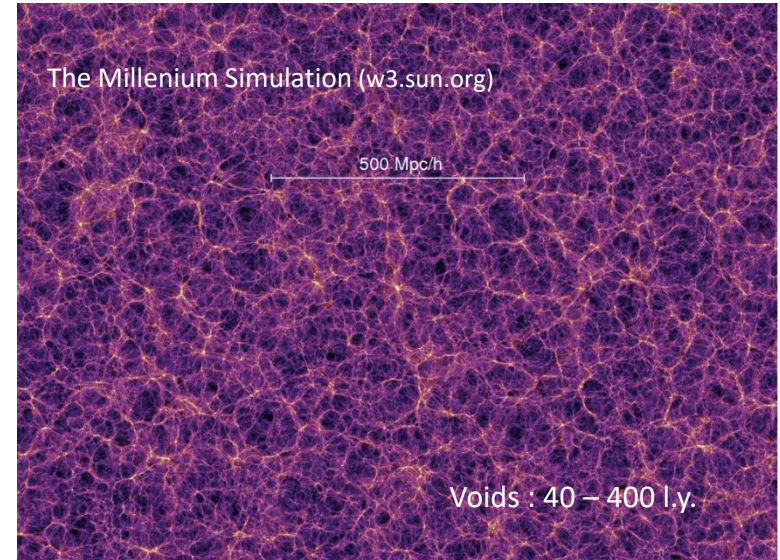
The Universe : An unthinkable volume

Superstructures of Universe



23 trillions light-year (pour dire)

10^{40} km



6,7 milliards d'années-lumière

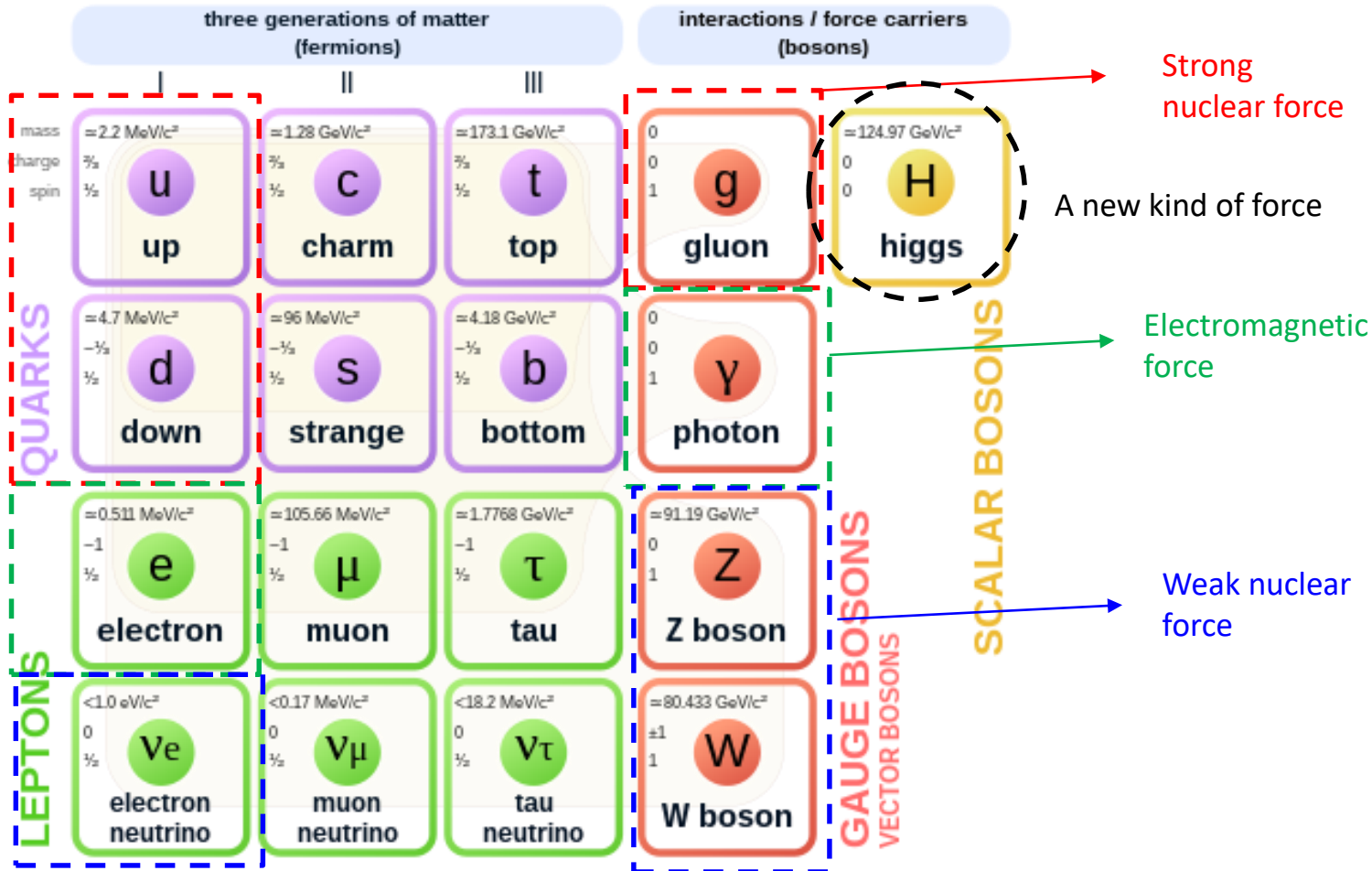
L'univers n'est pas dans un espace, il contient la matière et c'est au voisinage de la matière que l'espace existe. L'espace absolu et le temps absolu indépendamment de la matière n'existent pas.



Standard Model of Particle Physics : Quantum Field Theory

(i.e. + Classical Field theory + Special Relativity + Quantum mechanics)

Standard Model of Elementary Particles



The matter we believe to understand

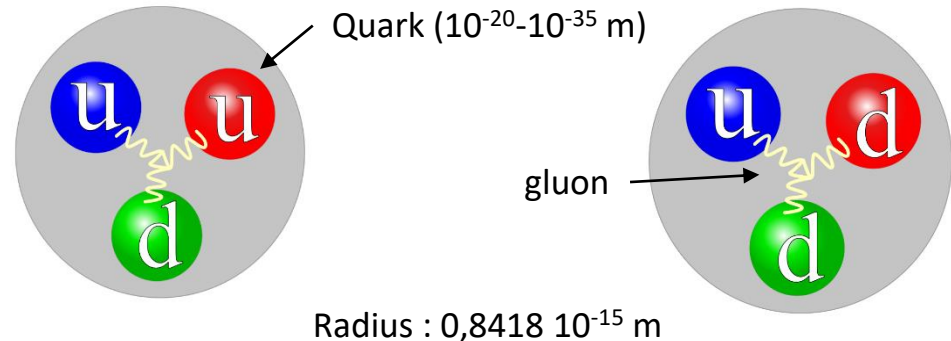
Baryonic matter : Protons, neutrons, the components of the nuclei (nucleons)

Nobel Prize 2004

Gross, Politzer, Wilczek

quark masses make up only **2%**
of the mass of the proton or
neutron

Mass would be an emerging property !!!



Free proton representation
(lifetime mini: $2,1 \times 10^{29}$ years)

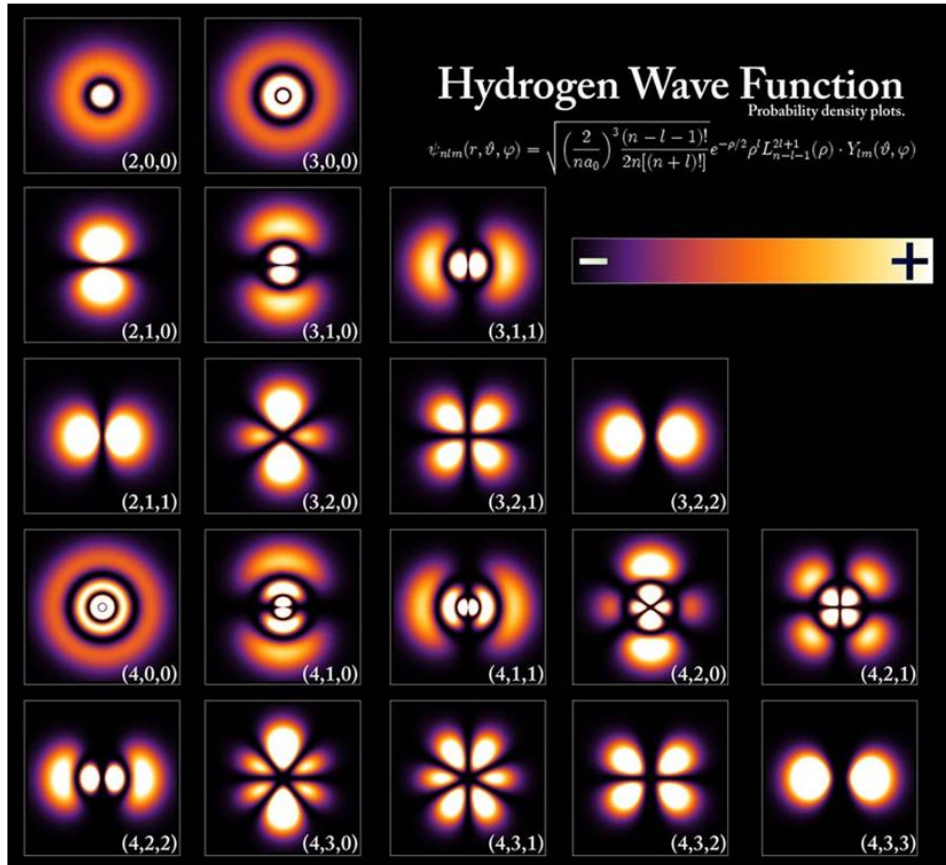
Proton mass : $(1,672\ 62 \times 10^{-27}$ kg

Representation of a free
Neutron (lifetime < 15 min)

Neutron mass : $1,675 \times 10^{-27}$ kg

Atoms, in the sense of modern physics and chemistry, are a convenient point of departure. An atom consists of its nucleus, wherein is concentrated all the positive electric charge and overwhelmingly most of the mass ($> 99.9\%$, in all cases), surrounded by a cloud of much lighter electrons. So the first order of business is to understand the origin of the mass of atomic nuclei.

Premières orbitales électroniques de l'atome d'hydrogène

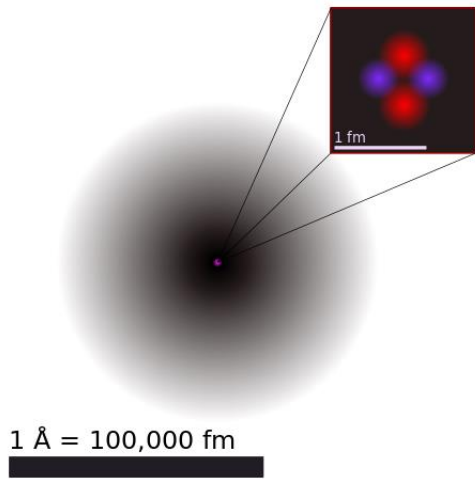


n = nombre quantique principal
(niveau d'énergie de l'électron)

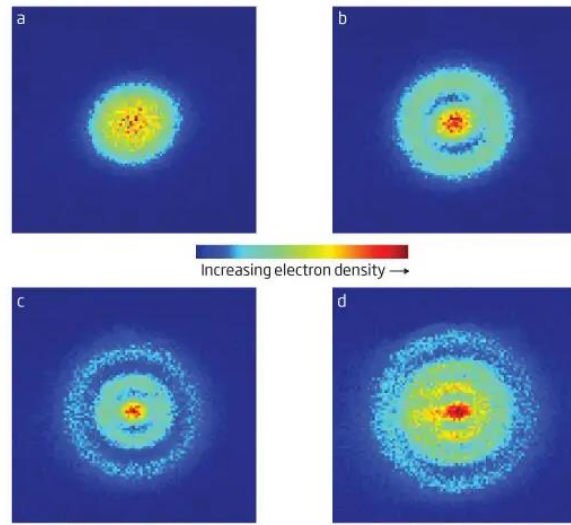
+ m (n.q. tertiaire ou
magnétique,
orientation des
orbitales)

+ s (n.q. de spin,
moment cinétique
intrinsèque de
l'électron)

l = s, p, d, f,
g, h, i, k, (moment angulaire)



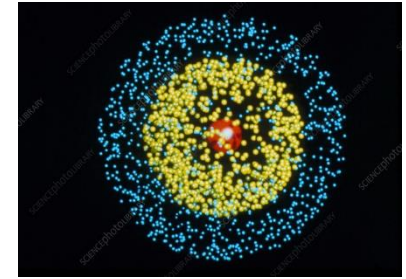
Quantum picture of the Helium atom



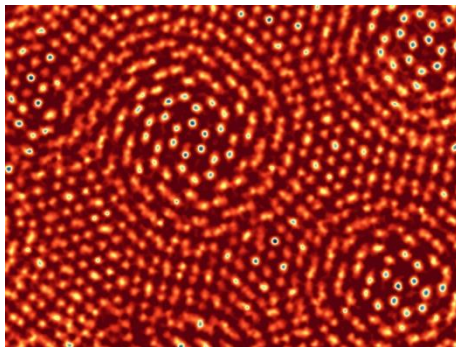
First « picture » of the hydrogen atom

$R : 25 \times 10^{-12} \text{ m}$ $M : 1.67 \times 10^{-24} \text{ kg}$

Stodolna et al. (2013). Hydrogen atoms under Magnification:
Direct observation of the nodal structure of Stark state. PRL 110, 213001.

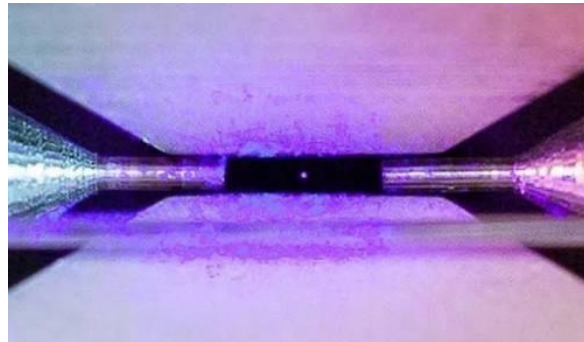


Computed electronic structure of Lithium

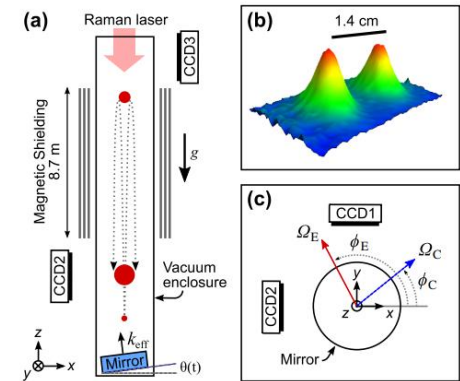


Molybdenum or sulfur atoms
(each dot is an atom)

DAVID MULLER/CORNELL UNIVERSITY



Photograph of Single Strontium Atom Wins
National Science Photography Competition 2018
D. Nadlinger)



Atom interferometry.

S.M. Dickerson, J.M. Hogan, A. Sugarbaker, D.S. Johnson, and M.A. Kasevich. Multi-axis Inertial Sensing with Long-Time Point Source Atom Interferometry. PRL 111, 083001 (2013).

Atoms are produced upon interactions of quantum fields

An example of pair production : the Electron – Positron pair

If the photon is near an atomic nucleus, the energy of a photon can be converted into an electron–positron pair:

$$(Z^+) \gamma \rightarrow e^- + e^+$$

The photon's energy is converted to particle mass in accordance with Einstein's equation, $E = m \cdot c^2$. The photon must have higher energy than the sum of the rest mass energies of an electron and positron ($2 \cdot 511 \text{ keV} = 1.022 \text{ MeV}$, resulting in a photon-wavelength of 1.2132 picometer) for the production to occur.

(Wikipedia)

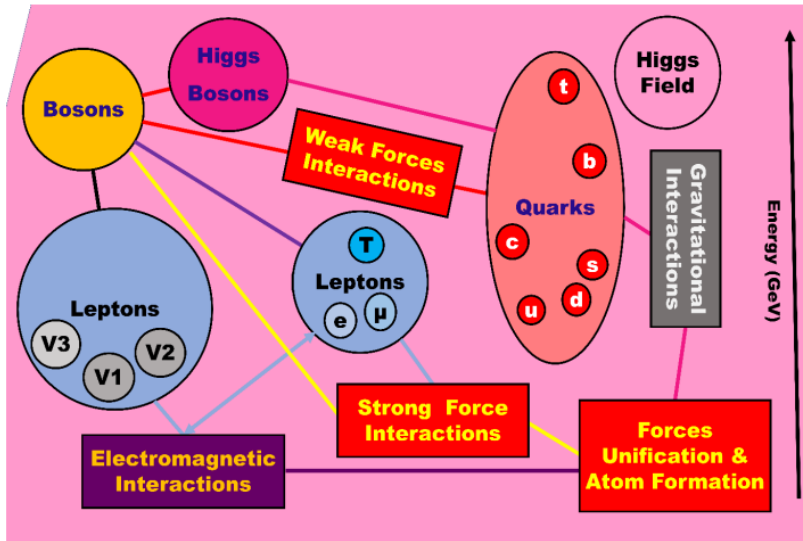


Figure 5. Elemental mass formation and forces interaction unification.

A. Hussain, M.M. Abbas. A Review of Elemental Mass Origin and Fundamental Forces Unification for Nuclear and Aerospace Industries. J Mod Nanotechnol 1, 2021, 2

G. Voisin, F. Mottez, S. Bonazzola. Electron-positron pair production by gamma rays in an anisotropic flux of soft photons, and application to pulsar polar caps. Monthly Notices of the Royal Astronomical Society, 474, 2018, 1436–1452.

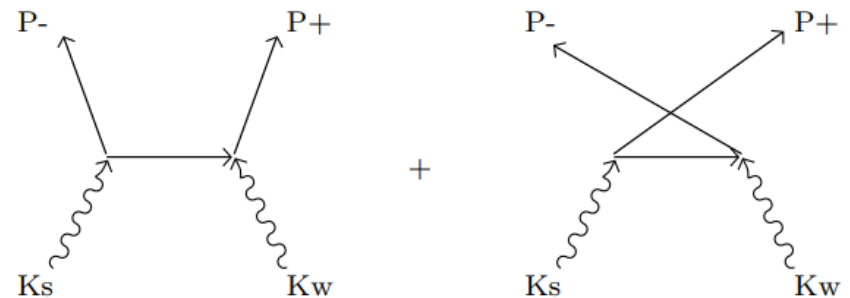


Figure 1. Reaction of electron-positron pair creation from a pair of photons represented to first order by Feynman diagrams. Photons have 4-momenta K_s and K_w while electron and positron have respectively P_- and P_+ .

To describe electromagnetic interactions

(Dynamics of energy and momentum, mass is a consequence)

Electrodynamics

(from Maxwell's Field Equations ;
Electromagnetic theory of light)

$$\nabla \cdot \mathbf{E} = \frac{\rho_v}{\epsilon} \quad (\text{Gauss' Law})$$

$$\nabla \cdot \mathbf{H} = 0 \quad (\text{Gauss' Law for Magnetism})$$

$$\nabla \times \mathbf{E} = -\mu \frac{\partial \mathbf{H}}{\partial t} \quad (\text{Faraday's Law})$$

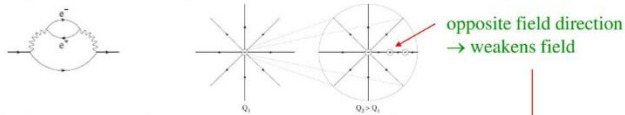
$$\nabla \times \mathbf{H} = \mathbf{J} + \epsilon \frac{\partial \mathbf{E}}{\partial t} \quad (\text{Ampere's Law})$$

Quantum Electrodynamics

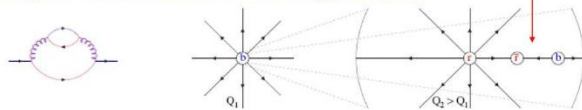
$$S_{\text{QED}} = \int d^4x \left[-\frac{1}{4} F^{\mu\nu} F_{\mu\nu} + \bar{\psi} (i\gamma^\mu D_\mu - m) \psi \right]$$

Running couplings: QED vs QCD

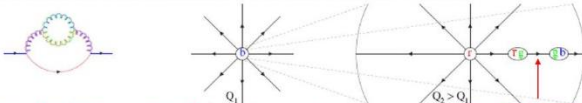
QED: Quantum fluctuations polarise vacuum and *screen* electron charge at large dist.



QCD: Quark vacuum fluctuation -> screening (as in QED)



QCD: Gluon vacuum fluctuation -> anti-screening (not in QED)



Gluons dominate -> net result is *anti-screening*

same field direction
-> strengthens field

Quantum Chromodynamics

Quantum fluctuations of vacuum

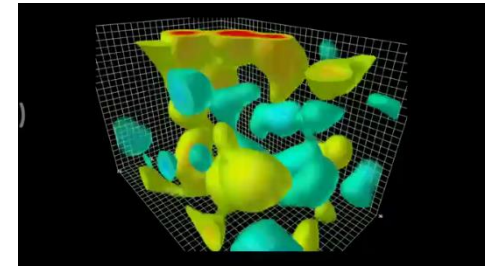
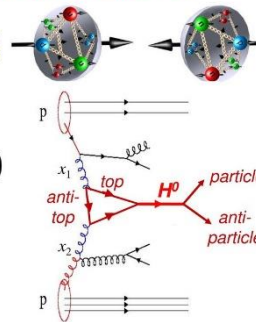
How create & find Higgs boson at LHC ?

Proton-proton collisions gives quark-gluon processes where energy create mass, $E=mc^2$

-> probability to create H^0

$$\sigma(pp \rightarrow H^0 \dots) = g(x_1) g(x_2) \sigma(gg \rightarrow H^0)$$

Higgs boson decays to particle-antiparticle pair
 $q\bar{q}, \ell\bar{\ell}, W^+W^-, Z^0Z^0$
and is reconstructed from decay products

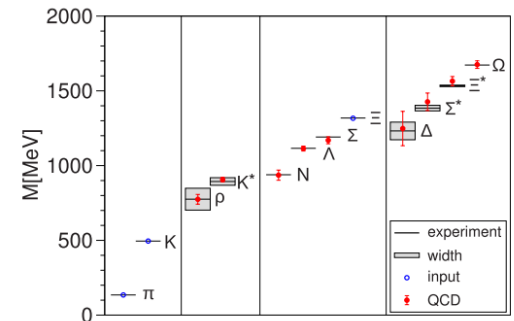


Simulation box: some fm side (D. Leinweber)
Fluctuations of energy density of quantum field

All fundamental properties of matter are predicted by QCD

$E = mc^2$
confirmed
experimentally

Fig. 3. The light hadron spectrum of QCD. Horizontal lines and bands are the experimental values with their decay widths. Our results are shown by solid circles. Vertical error bars represent our combined statistical (SEM) and systematic error estimates. π, K , and Ξ have no error bars, because they are used to set the light quark mass, the strange quark mass and the overall scale, respectively.



S. Dürr, Z. Fodor, J. Frison, C. Hoelbling, R. Hoffmann, D. Katz, S. Krieg, T. Kurth, L. Lellouch, T. Lippert, K. K. Szabo, G. Vulvert. *Ab Initio Determination of Light Hadron Masses. Science 322, 2008, 1224-1227.*



Monsieur le Duc (Louis Victor) de Broglie

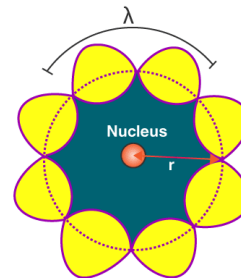
Matter is Particle AND Wave

« À toute particule matérielle de masse m et de vitesse v doit être associée une onde réelle »

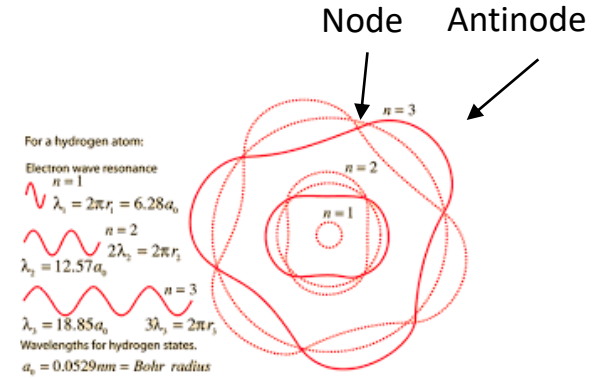
De Broglie Wavelength

$$\lambda = \frac{h}{p} \quad p = mv$$

$$\lambda = \frac{h}{mv}$$



Quantization of Angular Momentum of Electron

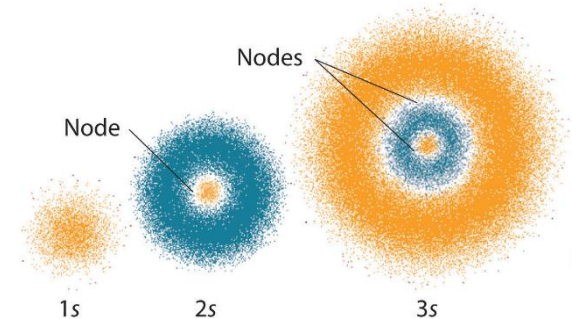


Orbitals

The quantum theory of Electron

The quantum de Broglie – Bohm pilot wave theory

The thermodynamic pilot wave theory



What is the origin of the wave ?

« On peut donc concevoir que par suite d'une **grande loi de la Nature**, à chaque morceau d'énergie de masse propre m , soit lié un phénomène périodique de fréquence ν_0 telle que l'on ait $h\nu_0 = mc^2$, étant mesurée dans le système lié au morceau d'énergie. Cette hypothèse est la base de notre système : elle vaut, comme toutes les hypothèses, ce que valent les conséquences qu'on en peut déduire. »

« Ce qui caractérise l'électron comme atome d'énergie, ce n'est pas la petite place qu'il occupe dans l'espace, **je répète qu'il l'occupe tout entier**, c'est le fait qu'il est insécable, non subdivisible, qu'il forme une unité »

$$E = mc^2 = h\nu = k_B T$$

A Law of Nature

At thermodynamic equilibrium

One of the consequences of the revised SI is that the conversion factors among the energy units J, kg, m⁻¹, Hz, K, and eV are now exact based on $E = mc^2 = \hbar c/\lambda = h\nu = kT$. The conversion factor between

Rydberg frequency $\alpha_{\infty} c R_{\infty}$	α_{∞}	$1.0973731568508(6) \times 10^7 \text{ m}^{-1}$	Hz	exact
Boltzmann constant	k	1.380649×10^{-23}	J K ⁻¹	exact
Avogadro constant	N_A	$6.02214076 \times 10^{23}$	mol ⁻¹	exact
molar gas constant $N_A k$	R	$8.314462618 \dots$	J mol ⁻¹ K ⁻¹	exact
Faraday constant $N_A e$	F	$96485.33212 \dots$	C mol ⁻¹	exact
Stefan-Boltzmann constant $(\pi^2/60)k^4/\hbar^3c^2$	σ	$5.670374419 \dots \times 10^{-8}$	W m ⁻² K ⁻⁴	exact
Non-SI units accepted for use with the SI				
electron volt (e/C)J	eV	$1.602176634 \times 10^{-19}$	J	exact

E. Tiesinga, P.J. Mohr, D.B. Newell, B.N. Taylor. CODATA Recommended Values of the Fundamental Physical Constants: 2018. J. Phys. Chem. Ref. Data 50, 033105 (2021)

Since the 2019 redefinition of SI base units,[1] which took effect on 20 May 2019, the Faraday constant has the exactly defined value given by the product of the elementary charge e and Avogadro constant NA:

$$F \equiv e \times N_A = 1.602179934 \times 10^{-19} \text{ C} \times 6.02214076 \times 10^{23} \text{ mol}^{-1} \\ = 9.64853321233100184 \times 10^4 \text{ C} \cdot \text{mol}^{-1}$$

Wikipedia

One Faraday is the amount of electric charges carried by one mole of particles

i.e. $9.64853321233100184 \times 10^4 * 6,24150907446076\text{E}+18$ point charges per Coulomb = $6.02214076 \times 10^{23}$

The particle – wave duality of matter : The walking droplets

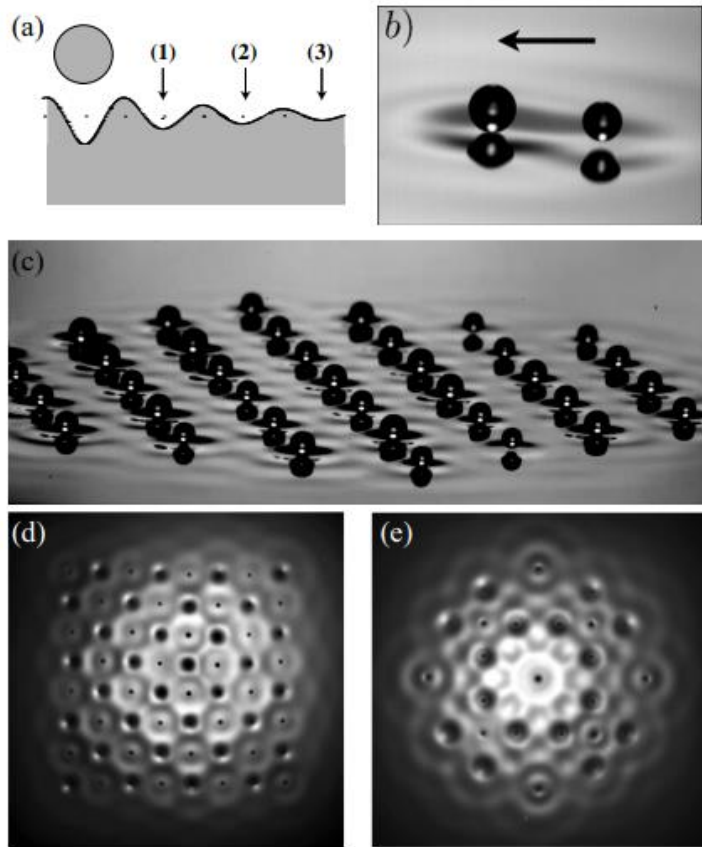


FIGURE 1.6 – (a) Positions d'équilibre pour une goutte placée dans le champ d'ondes créé par une autre goutte. (b) Duo asymétrique se déplaçant spontanément à la surface du bain. D'après [31]. (c) Vue de côté d'un réseau triangulaire de gouttes. (d) Vue de dessus d'un réseau carré. (e) Vue de dessus d'un réseau formé de carrés et d'octogones. D'après [29].

A. Eddi. *Marcheurs, dualité onde-particule et Mémoire de chemin. Dynamique des Fluides. [physics.flu-dyn]. Université Paris-Diderot - Paris VII, 2011.*

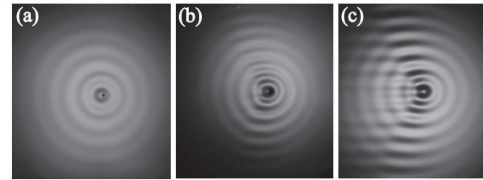


FIGURE 4.1 – Photographies des ondes générées par un marcheur de diamètre $D = 760 \mu\text{m}$ dans de l'huile de viscosité $\mu = 20 \cdot 10^{-3} \text{ Pa}\cdot\text{s}$. (a) L'écart au seuil $\Gamma = 17\%$ est important, le marcheur est lent et les ondes quasiment axisymétriques. (b) Pour $\Gamma = 7\%$, le champ d'ondes est distordu et un sillage se met en place à l'arrière du marcheur. (c) Pour $\Gamma = 1.8\%$, le sillage est très développé et présente une forme de fer à cheval

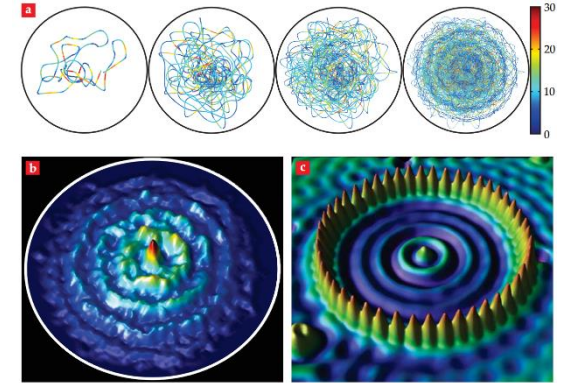
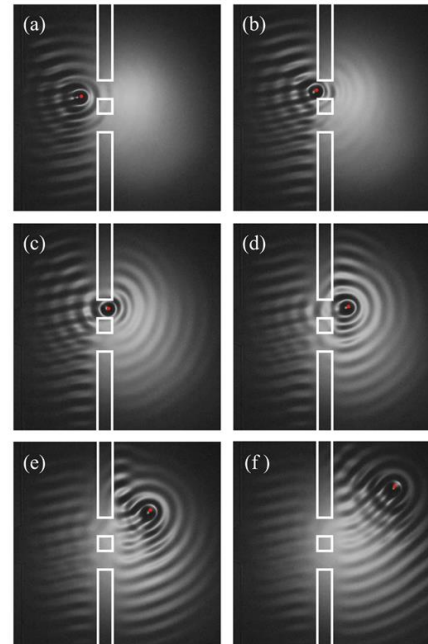
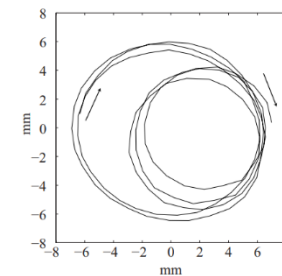


Fig. 2. A walker in a circular corral. The high-memory trajectories of increasing length depicted in (a) are color coded according to droplet speed in millimeters per second. (b) The histogram of the walker's position corresponds roughly to the amplitude of the corral's most unstable Faraday mode. The emerging statistics of the confined walker are reminiscent of (c) the statistics of electrons in a quantum corral. Figure adapted with permission from Harris et al. (2013). Copyright 2013, AIP Publishing LLC.

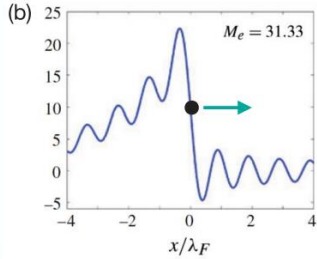
The walking droplet double-slit experiment



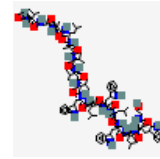
Trajectoire du marcheur lors d'une transition entre les plateaux $n = 1$ et $n = 0$. La goutte passe instantanément d'un plateau à l'autre, sans décrire d'orbites de rayon intermédiaire.

The particle – wave duality of matter : A Law of Nature

Hydrodynamic quantum pilot wave theory

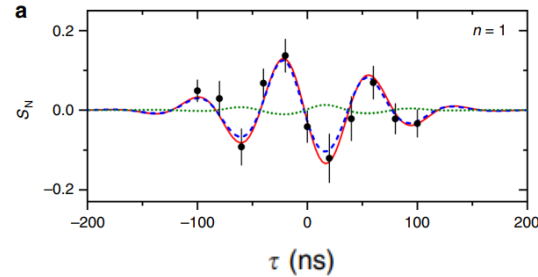


Y. Dagan, J.W.M. Bush. Hydrodynamic quantum field theory: the free particle. *Comptes Rendus Mécanique*, 348, 2020, 555-571.

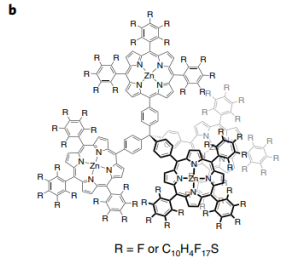


Gramicidin

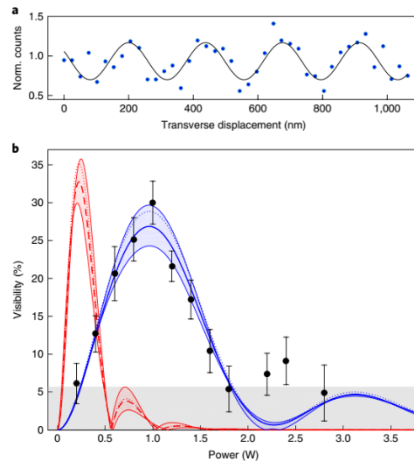
$1.9 \text{ kg}\cdot\text{mol}^{-1}$



A. Shayeghi, P. Rieser, G. Richter, U. Sezer, J.H. Rodewald, P. Geyer, T.J. Martinez, M. Arndt. Matter-wave interference of a native polypeptide. *Nature Com.*, 11, 2020, 1447.

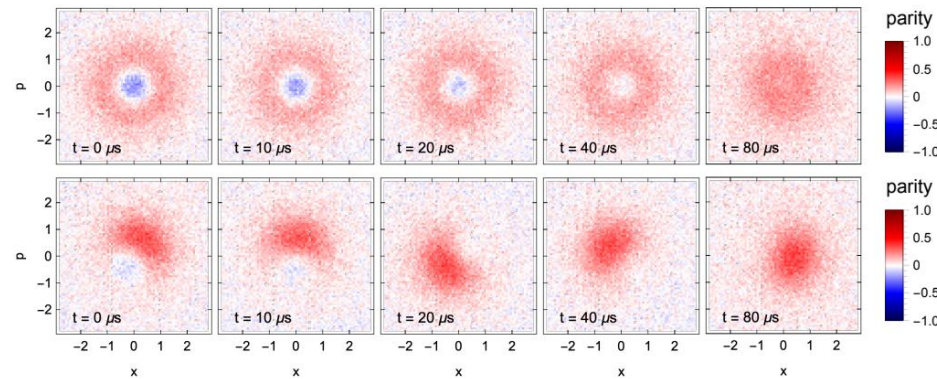


$> 25 \text{ kg}\cdot\text{mol}^{-1}$



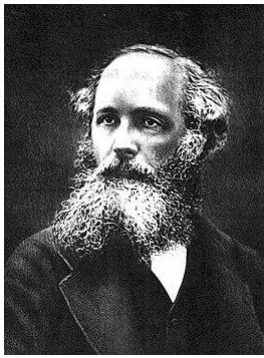
Y.Y. Fein, P. Geyer, P. Zwick, F. Kiałka, S. Pedalino, M. Mayor, S. Gerlich, M. Arndt. Quantum superposition of molecules beyond 25 kDa. *Nature Physics*, 15, 2019, 1242–1245.

Wigner Functions



μg amount

B. Schrinski, Y. Yang, U. von Lupke, M. Bild, Y. Chu, K. Hornberger, S. Nimmrichter, M. Fadel. Macroscopic quantum test with bulk acoustic wave resonators, *arXiv:2209.06635v1 [quant-ph]* 14 Sep 2022.



Another Law of Nature

Law of Conservation of Total Current

From Maxwell's Equations and de Broglie – Bohm quantum pilot wave theory

$$\frac{\partial}{\partial t} (\epsilon_0 \nabla \cdot \mathbf{e}) + \nabla \cdot \mathbf{j}_Q = \nabla \cdot \left(\epsilon_0 \frac{\partial \mathbf{e}}{\partial t} + \mathbf{j}_Q \right) = 0$$

$$\nabla \cdot (\mathbf{J}_{total}) = 0 \quad \nabla \cdot \left(\underbrace{\mathbf{j}_Q}_{\text{Property of matter}} + \underbrace{\overbrace{\epsilon_0 \frac{\partial \mathbf{E}}{\partial t}}^{\mathbf{j}_D}}_{\text{Property of space}} \right) = 0$$

$$\nabla \cdot \mathbf{j}_Q = -\frac{\partial}{\partial t} \rho_Q$$



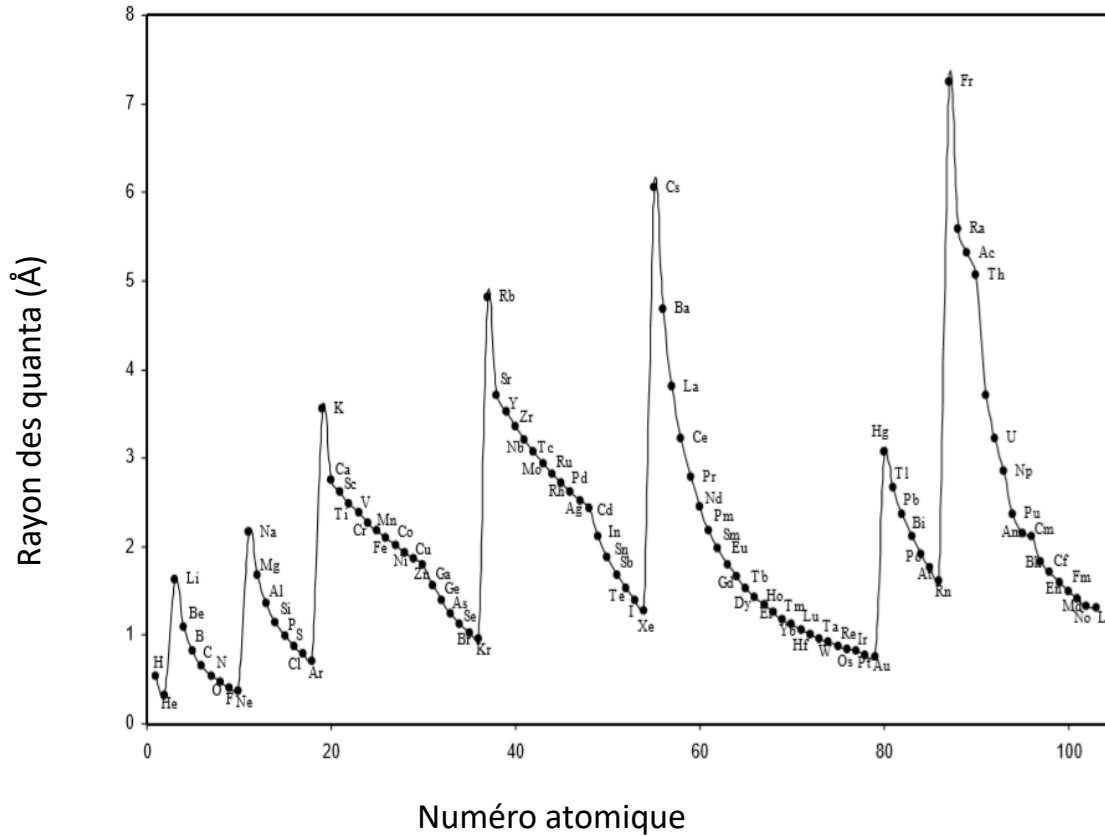
B. Eisenberg, X. Oriols, and D. Ferry. Dynamics of Current, Charge and Mass. Mol. Based Math. Biol. 5, 2017, 78–115.

Tableau périodique des éléments chimiques

Groupe	I A	II A											III B	IV B	V B	VI B	VII B	O	
Période	1	2											13	14	15	16	17	18	
1	Hydrogène 1 H 1,007975																		Hélium 2 He 4,002602
2	Lithium 3 Li 6,9395	Béryllium 4 Be 9,0121831	← nom de l'élément (gaz, liquide ou solide à 0°C et 101,3 kPa) ← numéro atomique ← symbole chimique ← masse atomique relative [ou celle de l'isotope le plus stable] ⊕ [CIAAW "Atomic Weights 2013" + rev. 2015]										Bore 5 B 10,8135	Carbone 6 C 12,0106	Azote 7 N 14,006855	Oxygène 8 O 15,99940	Fluor 9 F 18,99840316	Néon 10 Ne 20,1797 (u)	
3	Sodium 11 Na 22,98976928	Magnésium 12 Mg 24,3055	III A	IV A	V A	VIA	VII A	VIII			IB	II B	Aluminium 13 Al 26,9815385	Silicium 14 Si 28,085 (u)	Phosphore 15 P 30,97376200	Soufre 16 S 32,0675	Chlore 17 Cl 35,4515	Argon 18 Ar 39,948 (u)	
4	Potassium 19 K 39,0983 (u)	Calcium 20 Ca 40,078 (u)	Scandium 21 Sc 44,955908 (u)	Titane 22 Ti 47,867 (u)	Vanadium 23 V 50,9415 (u)	Chrome 24 Cr 51,9961 (u)	Manganèse 25 Mn 54,938044	Fer 26 Fe 55,845 (u)	Cobalt 27 Co 58,933194	Nickel 28 Ni 58,6934 (u)	Cuivre 29 Cu 63,546 (u)	Zinc 30 Zn 65,38 (u)	Gallium 31 Ga 69,723 (u)	Germanium 32 Ge 72,630 (u)	Arsenic 33 As 74,921595	Sélénium 34 Se 78,971 (u)	Brome 35 Br 79,904	Krypton 36 Kr 83,798 (u)	
5	Rubidium 37 Rb 85,4678 (u)	Strontium 38 Sr 87,62 (u)	Yttrium 39 Y 88,90584	Zirconium 40 Zr 91,224 (u)	Niobium 41 Nb 92,90637	Molybdène 42 Mo 95,95 (u)	Technétium 43 Tc [98]	Ruthénium 44 Ru 101,07 (u)	Rhodium 45 Rh 102,90550	Palladium 46 Pd 106,42 (u)	Argent 47 Ag 107,8682 (u)	Cadmium 48 Cd 112,414 (u)	Indium 49 In 114,818 (u)	Étain 50 Sn 118,710 (u)	Antimoine 51 Sb 121,760 (u)	Tellure 52 Te 127,60 (u)	Iode 53 I 126,90447	Xénon 54 Xe 131,293 (u)	
6	Césium 55 Cs 132,905452	Baryum 56 Ba 137,327 (u)	Lanthanides 57–71	Hafnium 72 Hf 178,49 (u)	Tantale 73 Ta 180,94788	Tungstène 74 W 183,84 (u)	Rhénium 75 Re 186,207 (u)	Osmium 76 Os 190,23 (u)	Iridium 77 Ir 192,217 (u)	Platine 78 Pt 195,084 (u)	Or 79 Au 196,966569	Mercure 80 Hg 200,592 (u)	Thallium 81 Tl 204,3835	Plomb 82 Pb 207,2 (u)	Bismuth 83 Bi 208,98040	Polonium 84 Po [209]	Astato 85 At [210]	Radon 86 Rn [222]	
7	Francium 87 Fr [223]	Radium 88 Ra [226]	Actinides 89–103	Rutherfordium 104 Rf [267]	Dubnium 105 Db [268]	Seaborgium 106 Sg [269]	Bohrium 107 Bh [270]	Hassium 108 Hs [277]	Meitnérium 109 Mt [278]	Darmstadtium 110 Ds [281]	Roentgenium 111 Rg [282]	Copernicium 112 Cn [285]	Nihonium 113 Nh [286]	Flerovium 114 Fl [289]	Moscovium 115 Mc [289]	Livermorium 116 Lv [293]	Tennessee 117 Ts [294]	Oganesson 118 Og [294]	
	Lanthane 57 La 138,90547	Cérium 58 Ce 140,116 (u)	Praséodyme 59 Pr 140,90766	Néodyme 60 Nd 144,242 (u)	Prométhium 61 Pm [145]	Samarium 62 Sm 150,36 (u)	Europium 63 Eu 151,964 (u)	Gadolinium 64 Gd 157,25 (u)	Terbium 65 Tb 158,92535	Dysprosium 66 Dy 162,500 (u)	Holmium 67 Ho 164,93033	Erbium 68 Er 167,259 (u)	Thulium 69 Tm 168,93422	Ytterbium 70 Yb 173,045	Lutécium 71 Lu 174,9668				
	Actinium 89 Ac [227]	Thorium 90 Th 232,0377	Protactinium 91 Pa 231,03688	Uranium 92 U 238,02891	Neptunium 93 Np [237]	Plutonium 94 Pu [244]	Americium 95 Am [243]	Curium 96 Cm [247]	Berkélium 97 Bk [247]	Californium 98 Cf [251]	Einsteinium 99 Es [252]	Fermium 100 Fm [257]	Mendelevium 101 Md [258]	Nobelium 102 No [259]	Lawrencium 103 Lr [260]				

Métaux						Non métaux							
Alcalins	Alcalino-terreux	Lanthanides	Actinides	Métaux de transition	Métaux pauvres	Métalloïdes	Autres non-métaux	Halogènes	Gaz nobles	Non classés	primordial	désintégration d'autres éléments	synthétique

Size of atoms



Atoms	Orbital Exponent	Atomic Radii (Å)
H	1	0.5292
He	1.7	0.3113
Li	0.65	1.6282
Be	0.975	1.0855
B	1.3	0.8141
C	1.625	0.6513
N	1.95	0.5427
O	2.275	0.4652

(rayon de Bohr)

(Ghosh & Biswas, 2002)

Van der Waals radius of atoms

Table 1. Crystallographic van der Waals radii of nonmetals

Author, year	$R, \text{Å}$								
	H	F	Cl	Br	I	O	S	N	C
Pauling, 1939	1.2	1.35	1.80	1.95	2.15	1.40	1.85	1.5	1.70
Bondi, 1964	1.20	1.47	1.75	1.85	1.98	1.52	1.80	1.55	1.70
Zefirov, 1974	1.16	1.40	1.90	1.97	2.14	1.29	1.84	1.50	1.71
Gavezzotti, 1983–1999	1.17	1.35	1.80	1.95	2.10	1.40	1.85	1.50	1.70
Batsanov, 1995			1.80	1.90	2.10	1.51	1.80		1.68
Wieberg, 1995		1.5	1.8	1.9	2.1	1.5	1.8	1.6	1.7
Rowland, 1996	1.10	1.46	1.76	1.87	2.03	1.58	1.81	1.64	1.77

(It takes into account attractive/repulsive forces
Relation with atom polarizability)

Electronegativity increases

Electronegativity decreases

1 Group 1A	2 Group 2A
Li 1.0	Be 1.5
Na 0.9	Mg 1.2
K 0.8	Ca 1.0
Rb 0.8	Sr 1.0
Cs 0.7	Ba 0.9

H
2.1

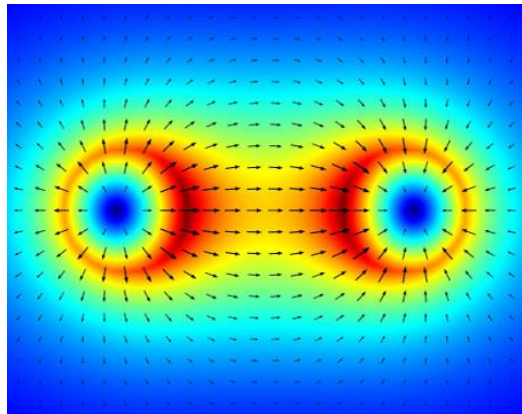
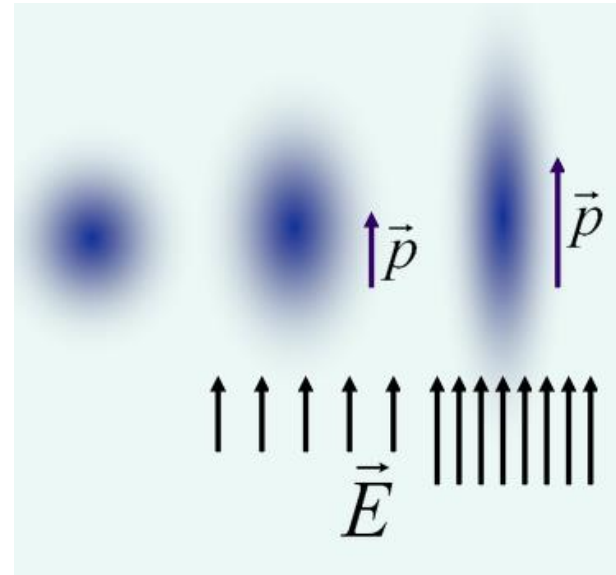
13 Group 3A	14 Group 4A	15 Group 5A	16 Group 6A	17 Group 7A	18 Group 8A
B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	
Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	
Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	
In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	
Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.1	

Polarizability of atoms

Microscopic property (atom, molecule, matter in general)

$$\vec{p} = \alpha \vec{E}$$

Deformability of electron cloud
in response to an electric field



A dipole in an electric field
(positive charge (left)
Negative charge (right))

The Clausius-Mosetti or Lorentz-Lorenz equation

Clausius-Mosetti equation

$$R_M = \frac{4\pi\rho_N\alpha_{el}}{3} = \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2}$$

Molar Refractivity

ρ_N Number density (nber/m³) (N_a/V_m)

α_{el} Static average electronic polarizability (m³)

ϵ_∞ High frequency static permittivity ($\approx n^2$)

$$\alpha_{el}(\text{\AA}^3) = \frac{10^{30}}{4\pi\epsilon_0} \alpha(\text{C}\cdot\text{m}^2\cdot\text{V}^{-1}) = \frac{fe^2}{m\omega_e^2}$$

with f the number of oscillating electrons and ω_e the electron vibration frequency

and *Ionization energy* ($\text{kJ}\cdot\text{mol}^{-1}$) = $IE = h\omega_e$

Dielectric permittivity

Macroscopic collective property

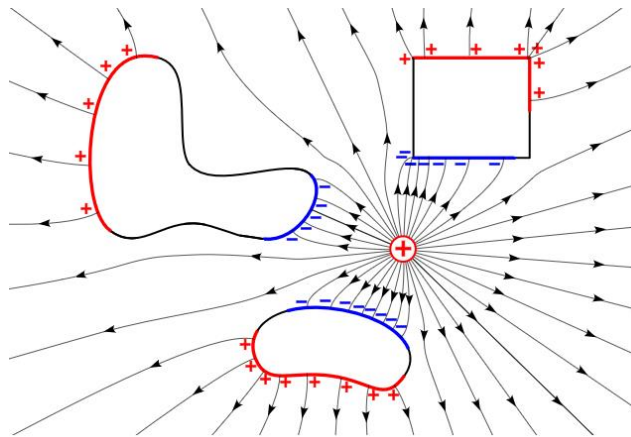
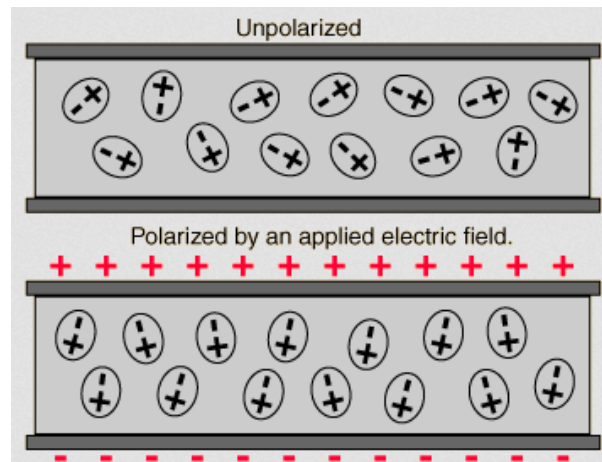


Figure : Distribution of electronic charges induced in Conducting bodies the electric field of a close Positive charge, due to electrostatic induction

Induction Electric Field →

$$\vec{D} = \epsilon \vec{E}$$

$$\epsilon_r = \frac{\epsilon}{\epsilon_0}$$



Material	Complex Permittivity
Water	78
Methanol	25
DMSO	46
Quartz sand	2.5
Granular Paraffin	1.7
Milk powder	2

Total interaction energy

Old school

$$\begin{aligned}
 E_T &= E_{\text{repulsive}} + E_{\text{attractive}} \\
 &= E_{\text{rep}} + E_{\text{el}} + E_{\text{vdW}} \\
 &= E_{\text{rep}} + E_{\text{el}} + E_{\text{Keesom}} + E_{\text{Debye}} + E_{\text{London}}
 \end{aligned}$$

We keep the E_{el} term to comply with textbooks

$$\begin{aligned}
 \mathcal{L} &= \frac{1}{4g^2} G_{\mu\nu}^a G_{\mu\nu}^a + \sum_j \bar{\psi}_j (i\gamma^\mu D_\mu + m_j) \psi_j \\
 \text{where } G_{\mu\nu}^a &\equiv \partial_\mu A_\nu^a - \partial_\nu A_\mu^a + if_{bc}^a A_\mu^b A_\nu^c \\
 \text{and } D_\mu &\equiv \partial_\mu + it^a A_\mu^a \\
 &\text{That's it!}
 \end{aligned}$$

QCD

F. Wilczek. QCD made simple. *Physics Today*, august 2000, 22-28.

Born multipole repulsion energy

$$U_{\text{rep}(ij)}(R) = K_i K_j \frac{1}{R} \frac{q_i q_j (8\pi)^2}{(8\pi)^2 \alpha^6} \left(1 + \frac{1}{2} \alpha R + \frac{1}{12} (\alpha R)^2 \right)^2 e^{-\alpha R}$$

Number of electrons involved

Relative atom size

Relative atom shape

For water

where R is the internuclear distance, i, j refers to hydrogen and oxygen atoms, K is the relative atom size, α describes the width of the electron density (a kind of index of the atom shape) and q is the maximum number of electrons that are involved in overlap for a particular atom.

THE GENERAL THEORY OF MOLECULAR FORCES.

BY F. LONDON (*Paris*).

Received 31st July, 1936.

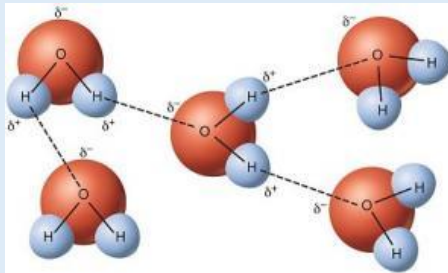
F. London. The general theory of molecular forces. Trans. Faraday Soc., 1937,33, 8-26

On the nature of intermolecular forces

Van der Waals, a firm advocate of the molecular theory, ascribed critical phenomena to the attraction between molecules, but never speculated on the nature of intermolecular interactions. In the early 20th century, two young Dutch physicists, Willem Hendrik Keesom (1876–1956)^[30] and Peter Debye (1884–1966)^[31] suggested that molecules might behave as electrical dipoles and that cohesive forces could have therefore an electrostatic nature.

Keesom forces

Permanent dipole – permanent dipole



Water : hydrogen-bond interaction

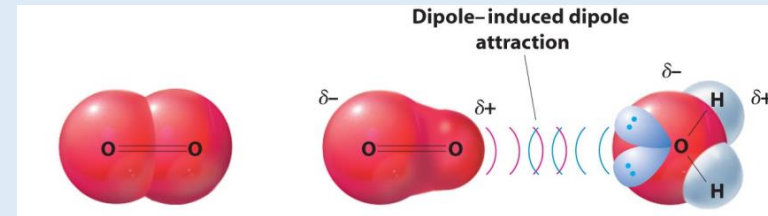
The Keesom force can be attractive (dipole antiparallel) or repulsive (dipole parallel), but vanishes as temperature increases, because thermally induced motions of the permanent dipoles disorder their mutual alignment.

Very important :

The three forces have different characteristic time (from fs for London dispersion forces to ps for Keesom forces)

Debye forces

Permanent dipole – induced dipole

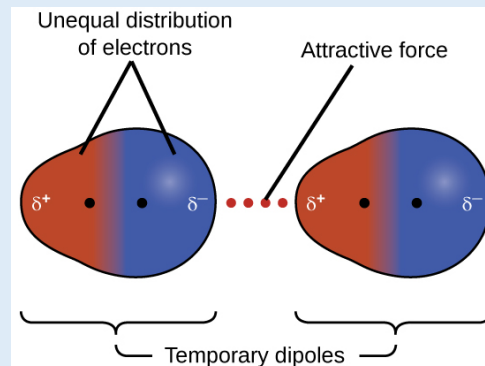


The Debye force does not disappear at high temperature (*it increases*) and is always attractive.

London forces

(purely quantum effect ; predicted by QED)

Induced dipole – induced dipole



The London force is stronger at low temperature and may be attractive or repulsive (always attractive for similar molecules)

The only force that is retarded at long distance

van der Waals interaction energy (microscopic theory)

$$E_{vdW} = E_{\text{Keesom}} + E_{\text{Debye}} + E_{\text{London}} \quad (+E_{\text{Casimir-Polder}})$$

Orientational Induction Dispersion

$$E_{vdw} = -\frac{C_{vdw}}{r^6} = \frac{C_{orient} + C_{induct} + C_{disp}}{r^6} \quad (\text{non-retarded})$$

with C_{vdW} the C6 parameter of the Lennard-Jones potential

Similar molecules *in vacuo*

$$C_{orient} = \frac{u^4}{3k_B T (4\pi\epsilon_0)^2} \quad C_{ind} = \frac{2u^2\alpha_{el}}{(4\pi\epsilon_0)^2} \quad C_{disp} = \frac{3\alpha_{el}^2 h\nu_{IE}}{(4\pi\epsilon_0)^2}$$

where u and α_{el} are, respectively, the dipole moment (Debye unit) and the electronic polarizability, ϵ_0 the vacuum permittivity, $h\nu_e$ the ionization energy and ν_e is the main electronic absorption frequency (UV region), Please note the $(1/\pi\epsilon_0)$ ratio is the Coulomb constant k_e .

Israelachvili, J. (2011). *Intermolecular & Surface forces*, Ch. 4-6, Third Edition, Academic Press, London, p. 71-130.

Parsegian, V. A. (2006). *Van der waals forces*, Cambridge University Press, New York, p. 77.

Leite, F.L., Bueno, C.C., Da Róz, A.L., Ziemath, E.C. and Oliveira Jr., O.N. (2012). *Theoretical models for surface forces and adhesion and their measurement using Atomic Force Microscopy*. *Int. J. Mol. Sci.* 13, 12773-12856.

Mohebifar, M. and Rowley, C. N. (2020). *An efficient and accurate model for water with an improved non-bonded potential*, *J. Chem. Phys.* 153, 134105.

Van der Waals Energy Coefficients C (10^{-79} J m⁶)

Total VDW Energy C_{VDW}

Similar Molecules

Interacting Molecules	Electronic Polarizability $\frac{\alpha_0}{4\pi\epsilon_0}$ (10^{-30} m ³)	Permanent Dipole Moment μ (D) ^a	Ionization Potential $I = h\nu_1$ (eV) ^b	Van der Waals Energy Coefficients C (10^{-79} J m ⁶)			Theoretical Eq. (6.17)	From Gas Law Eq. (6.14)	Dispersion Energy Contribution to Total (Theoretical) (%)
				C_{ind} $\frac{2\mu^2\alpha_0}{(4\pi\epsilon_0)^2}$	C_{orient} $\frac{\mu^4}{3kT(4\pi\epsilon_0)^2}$	C_{disp} $\frac{3\alpha_0^2 h\nu_1}{4(4\pi\epsilon_0)^2}$			
Ne–Ne	0.39	0	21.6	0	0	4	4	4	100
CH ₄ –CH ₄	2.60	0	12.6	0	0	102	102	101	100
HCl–HCl	2.63	1.08	12.7	6	11	106	123	157	86
HBr–HBr	3.61	0.78	11.6	4	3	182	189	207	96
HI–HI	5.44	0.38	10.4	2	0.2	370	372	350	99
CH ₃ Cl–CH ₃ Cl	4.56	1.87	11.3	32	101	282	415	509	68
NH ₃ –NH ₃	2.26	1.47	10.2	10	38	63	111	162	57
H ₂ O–H ₂ O	1.48	1.85	12.6	10	96	33	139	175	24

Dissimilar Molecules

Dissimilar Molecules	Van der Waals Energy Coefficients C (10^{-79} J m ⁶)			Theoretical Eq. (6.17)	From Gas Law Eq. (6.14)	Dispersion Energy Contribution to Total (Theoretical) (%)
	$\frac{\mu_1^2\alpha_{02} + \mu_2^2\alpha_{01}}{(4\pi\epsilon_0)^2}$	$\frac{\mu_1^2\mu_2^2}{3kT(4\pi\epsilon_0)^2}$	$\frac{3\alpha_{01}\alpha_{02}h\nu_1\nu_2}{2(4\pi\epsilon_0)^2(\nu_1 + \nu_2)}$			
Ne–CH ₄	0	0	19	19 ^c	—	100
HCl–HI	7	1	197	205	—	96
H ₂ O–Ne	1	0	11	12	—	92
H ₂ O–CH ₄	9	0	58	67	—	87

^a1 D = 3.336 × 10⁻³⁰ Cm.

^b1 eV = 1.602 × 10⁻¹⁹ J.

^cThis approximate value may be compared with the ab initio calculation by Fowler et al., (1989) that gives 23 × 10⁻⁷⁹ J m⁶.

McLachlan's generalized theory for van der Waals forces

For similar molecules in condensed phase

$$E_{vdw} = C_{\nu=0} + C_{\nu>0} = - \left[3k_B T \left(\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} \right)^2 + \frac{\sqrt{3} h \nu_e (n_1^2 - 1)^2}{4 (n_1^2 + 2)^{\frac{3}{2}}} \right] \frac{a_1^6}{r^6} - \frac{C_8}{r^8} \dots$$

Keesom-Debye
London

where ε_1 and n_1 are, respectively, the static permittivity of body and refractive index in the visible range, k_B and T are the Boltzman constant and the temperature, respectively, h is the Planck constant, ν_e is the main electronic absorption frequency (UV region), depends on ionization energy, a_1 is the molecule radius and r is the distance between interacting bodies. C_8 is the octupole-octupole interaction term. Higher terms may be required. (for similar molecules and $r \gg a_1$)

NB: This equation is in theory only applicable with hydrophobic molecules because it does not consider local dipole – dipole interactions (no scaling in R^3). However, using for a_1 the molecular radius instead of the hard sphere radius and taking into account anisotropy allow to find reasonable values for TOTAL interaction energy for water.

van der Waals interaction energy (macroscopic theory)

Dzyaloshinskii-Lifshitz-Pitaevskii (DLP) theory

Non retarded and retarded

$$A_{v=0} = \frac{3k_bT(\epsilon_1 - \epsilon_m)(\epsilon_2 - \epsilon_m)}{4(\epsilon_1 + \epsilon_m)(\epsilon_2 + \epsilon_m)} = \frac{3k_bT(\epsilon_1 - 1)^2}{4(\epsilon_1 + 1)^2}$$

$$A_{v>0}(r) = \frac{3\hbar c}{32\sqrt{2}n_m r} \left(\frac{n_1^2 - n_m^2}{n_1^2 + n_m^2} \frac{n_2^2 - n_m^2}{n_2^2 + n_m^2} \right) \left[\left(2 + \frac{3}{2}v_T r \right) e^{-v_T r} - (2 + v_\infty r) e^{-v_\infty r} \right]$$

$$v_T = \frac{4\pi k_b T n_m}{c\hbar} \text{ and } v_\infty = 4n_m \frac{(n_1^2 + n_m^2)^{1/2} (n_2^2 + n_m^2)^{1/2}}{(n_1^2 + n_m^2)^{1/2} + (n_2^2 + n_m^2)^{1/2}} \frac{v_e}{c}$$

McDowell, L.C. (2019). Surface van der Waals forces in a nutshell. *J. Chem. Phys.* 150, 081101.

van der Waals
interaction potential

$$U_{vdW} = -\frac{A(r)}{12\pi r^2}$$

Takes into account Keesom-
Debye

A(r) : Hamaker constant

Quantum electrodynamics of van der Waals interactions

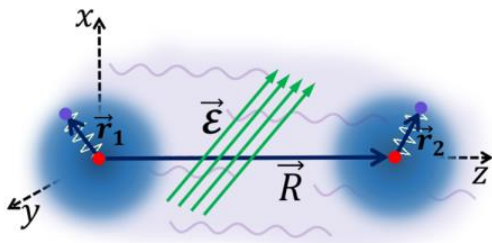


Figure 1. Two interacting quantum Drude oscillators under the influence of both the fluctuating vacuum electromagnetic field and an applied uniform static electric field $\mathcal{E} = (\mathcal{E}_x, \mathcal{E}_y, \mathcal{E}_z)$.

Two coupled Quantum Drude Oscillators

$$\Delta \mathcal{U}(R) = -\frac{3\alpha_1\alpha_2\hbar\omega_1\omega_2}{2(4\pi\epsilon_0)^2(\omega_1 + \omega_2)R^6} + \frac{\alpha_1\alpha_2(\mathcal{E}_x^2 + \mathcal{E}_y^2 - 2\mathcal{E}_z^2)}{4\pi\epsilon_0 R^3} - \frac{\alpha_1\alpha_2(\alpha_1 + \alpha_2)(\mathcal{E}_x^2 + \mathcal{E}_y^2 + 4\mathcal{E}_z^2)}{2(4\pi\epsilon_0)^2 R^6}$$

Keesom

which is the same as the second term of eq 9. Considering the QDO states in $|I\rangle$, this interaction energy corresponds to the situation when both QDOs couple to the vacuum field via their static field-induced dipoles and exchange one virtual photon, indicating the electrostatic nature of this interaction term. Taking into account the R^{-3} scaling, this term corresponds to a field-induced (dipole–dipole) electrostatic interaction.

$$\Delta \mathcal{U}_1^{(4)}(R) = \begin{cases} -\frac{3\alpha_1\alpha_2\omega_1\omega_2\hbar}{2(4\pi\epsilon_0)^2(\omega_1 + \omega_2)R^6} & R \ll c/\omega \\ -\frac{23\hbar c\alpha_1\alpha_2}{4\pi(4\pi\epsilon_0)^2 R^7} & R \gg c/\omega \end{cases}$$

London

*Casimir – Polder
(London counterpart
for the retarded regime)*

When both atoms couple to the vacuum field via their fluctuating dipoles, the treatment of eq 17 as in refs 36 and 37 delivers⁶⁵ the known London and Casimir–Polder dispersion energies

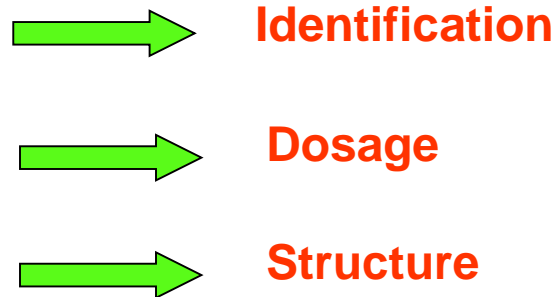
effectively “sees” another one as a static object. Finally, when one of the species couples to the vacuum field via its static dipole moment and the other one by its fluctuating dipole, the resulting interaction energy is

unaffected by retardation. These features allow us to identify the term of eq 19 as the field-induced polarization energy.

Debye

Propriétés du rayonnement électromagnétique :
étude de l'interaction d'une onde avec la matière

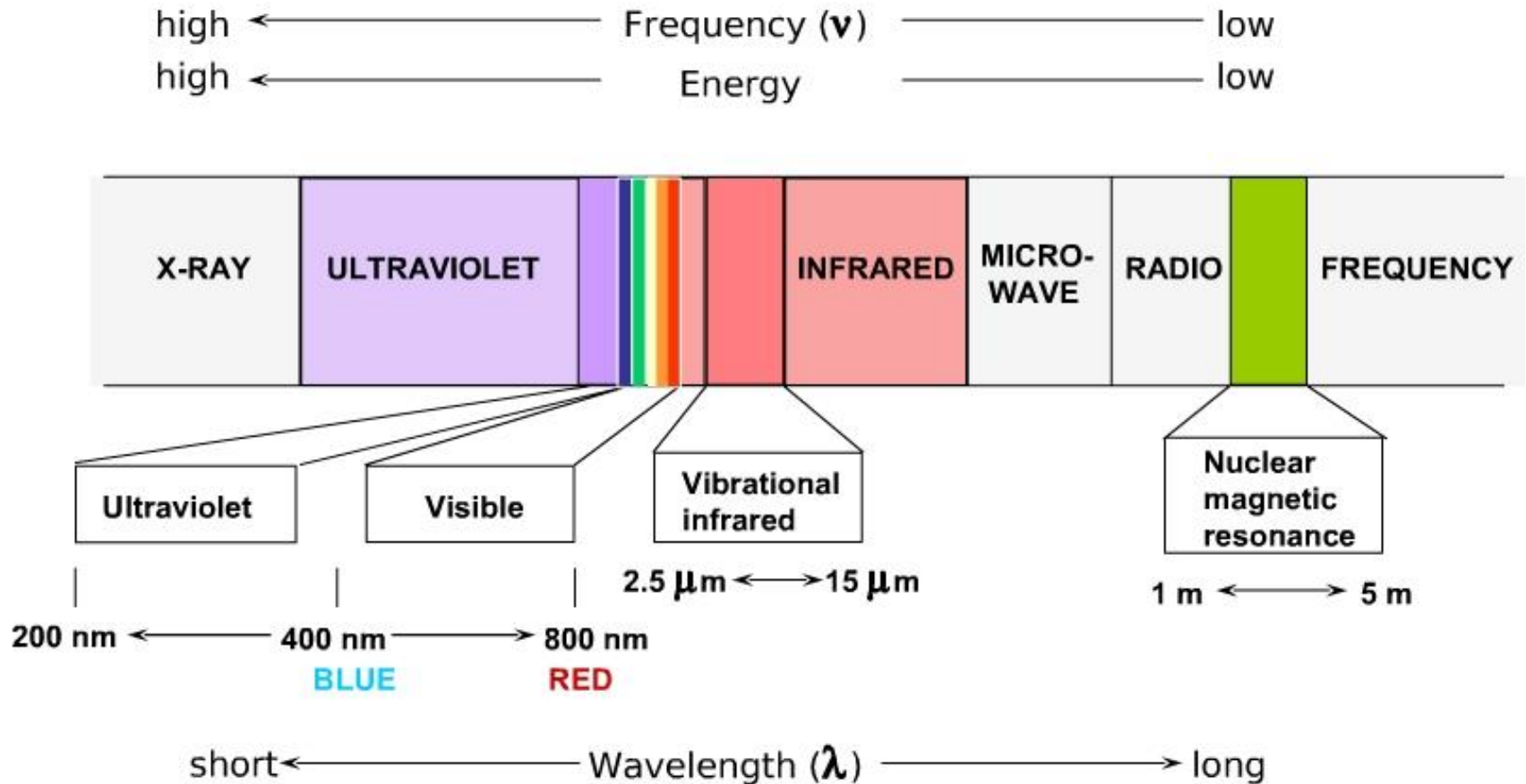
Les méthodes optiques ou spectrométriques regroupent toutes les méthodes relevant des phénomènes d'**absorption**, d'**émission**, de **diffusion de radiations** électromagnétiques **par la matière** que ce soit d'un point de vue **atomique ou moléculaire**.



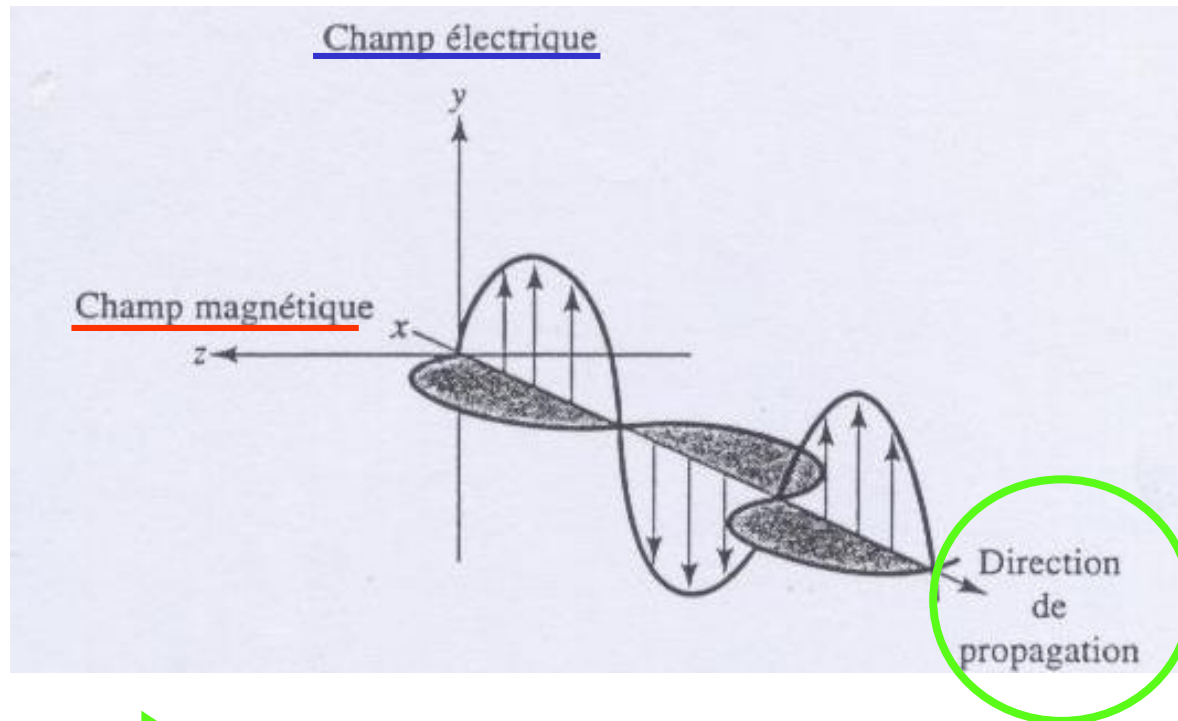
Nature et propriétés des ondes électromagnétiques (lumière)

Un rayonnement électromagnétique est un type d'énergie qui prend de nombreuses formes, les plus facilement reconnaissables étant la **lumière visible** et la **chaleur rayonnante** alors que les rayons γ , X, UV, micro-ondes ou ondes radio en sont des manifestations moins évidentes.

Le spectre électromagnétique



Toute radiation lumineuse (lumière) est constituée de deux composantes : un vecteur **champ magnétique** et un vecteur **champ électrique** qui sont **perpendiculaires** et varient de façon **sinusoïdale**. La vibration lumineuse se propage dans une direction perpendiculaire aux deux vecteurs pour former une onde lumineuse



Caractère ondulatoire de la lumière

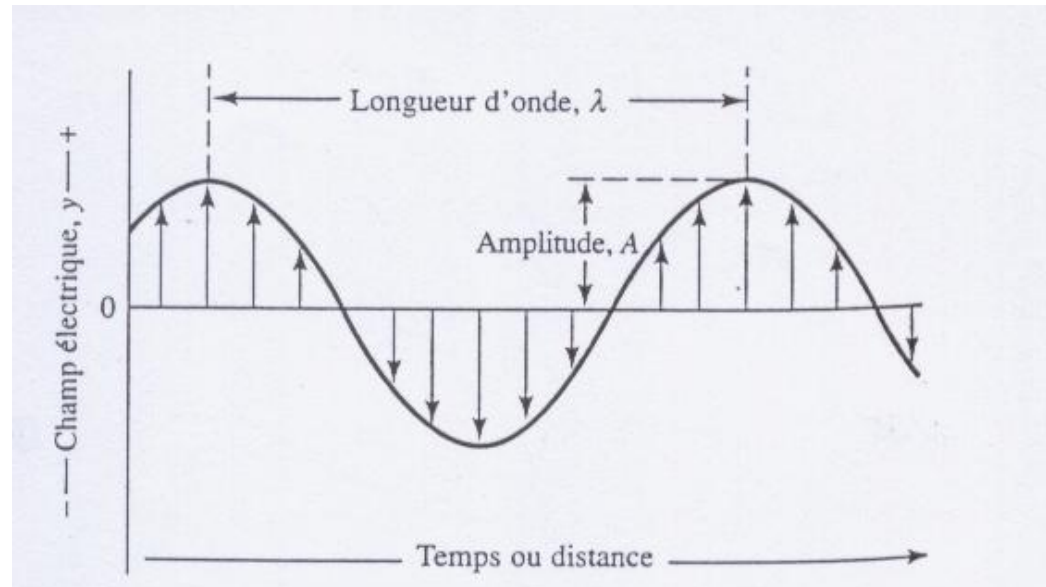
Les paramètres de l'onde

Sa **période p** : temps qui sépare le passage entre deux maxima ou deux minima successifs. Elle est exprimée en **seconde**.

Sa **fréquence ν** : nombre d'oscillations du champ par seconde et vaut $1/p$. Elle est exprimée en **hertz ou s^{-1}** . Paramètre fixé par la source lumineuse.

Sa **longueur d'onde λ_i** : distance entre deux maxima ou deux minima successifs d'une onde. Elle est exprimée en **nm** (10^{-9} m) ou **μm** (10^{-6} m). L'indice i signale que la longueur d'onde dépend du milieu traversé.

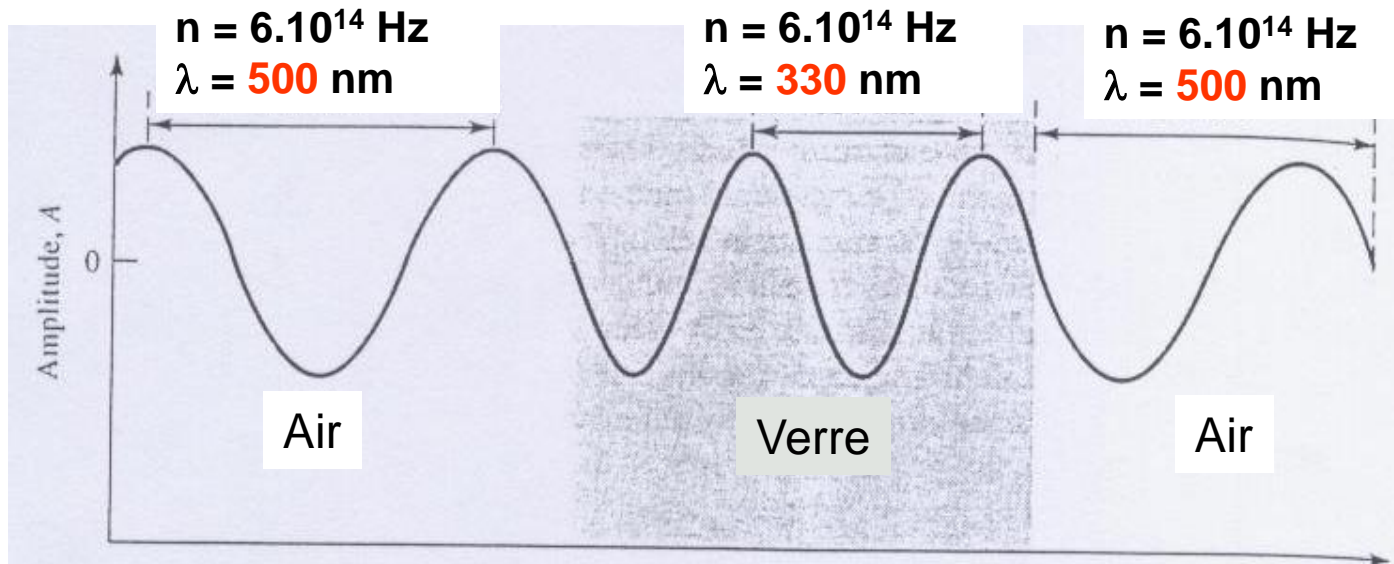
Son **nombre d'onde $\bar{\nu}_i$** : nombre d'ondes contenues dans l'intervalle de 1 cm et vaut $1/\lambda$. Il est exprimé en **cm^{-1}** ou kayzer.



Sa **vitesse de propagation (célérité) c_i** : produit de la fréquence par la longueur d'onde. Elle est exprimée en $m.s^{-1}$ et dépend comme la longueur d'onde du milieu traversé. Dans le vide, elle vaut $2,998.10^8 m.s^{-1}$. Dans un milieu d'indice de réfraction n , la vitesse du rayonnement est **$v = c/n$** .

Air $n = 1,0003$; eau $n=1,333$; 50% saccharose $n = 1,420$

Dans tout milieu matériel, la propagation est ralentie par les interactions entre le champ électromagnétique du rayonnement et les électrons liés aux atomes ou molécules présentes. Comme la fréquence est constante, la λ diminue



L'énergie d'un photon E (en joules) dépend de la fréquence du rayonnement.

$$E = h \cdot \nu \quad (\text{en J})$$

$$E = h \cdot \nu = h \cdot c / \lambda = h \cdot c \cdot \bar{\nu}$$

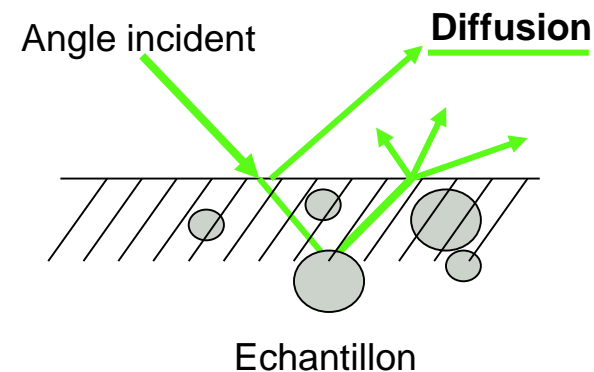
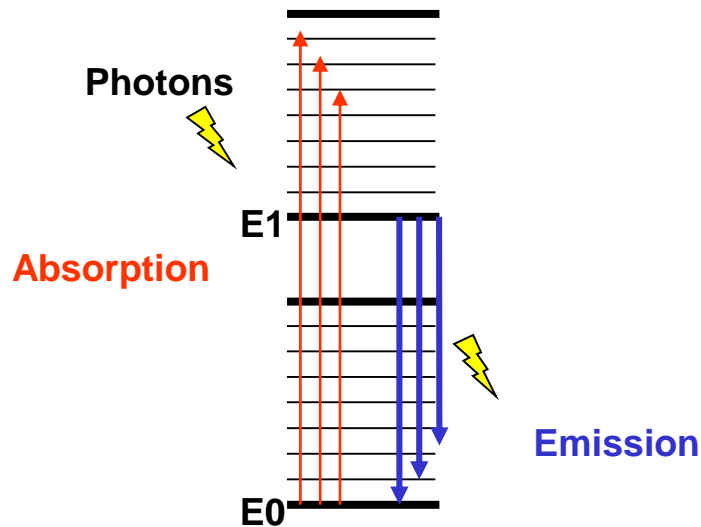
Avec $h = 6,62 \cdot 10^{-34}$ (constante de Planck), ν = fréquence cycle/s ou hertz,
 c = vitesse rayonnement = $3 \cdot 10^8$ m.s⁻¹

La fréquence ν et le nombre d'onde $\bar{\nu}$ sont tous les deux proportionnels à l'énergie du photon.

$$E = h \cdot \nu \cdot N \quad (\text{en J/mol})$$

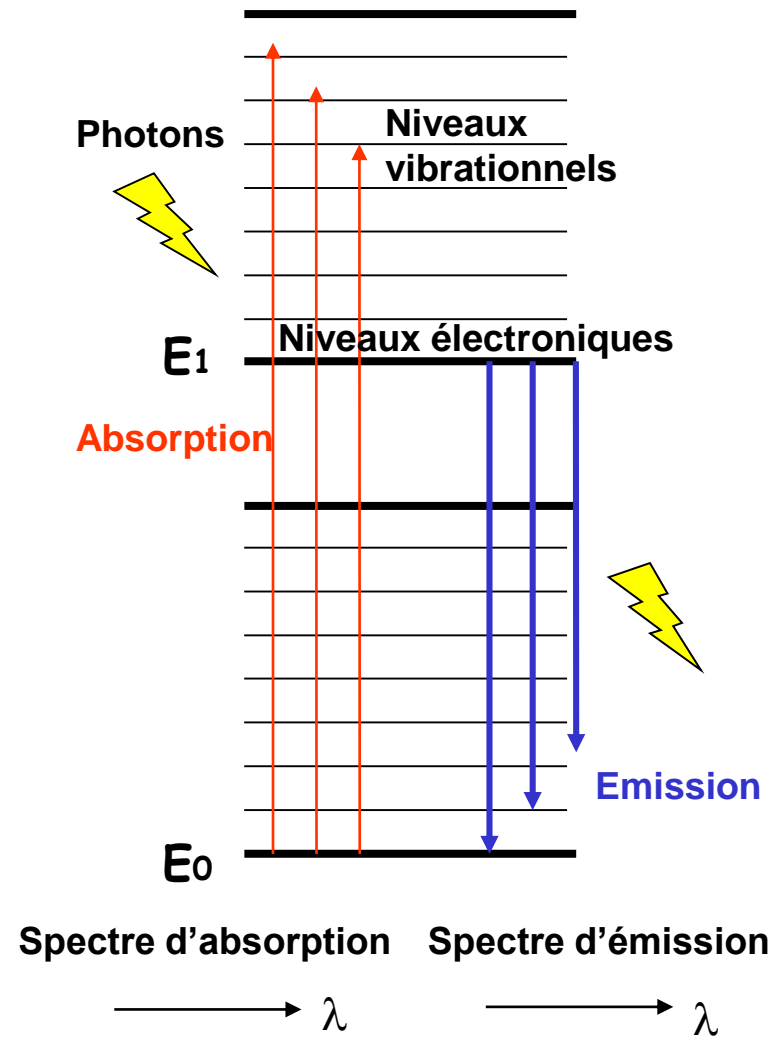
Avec $N = 6.023 \cdot 10^{23}$ (nombre d'Avogadro)

Le modèle ondulatoire ne peut expliquer les propriétés optiques de la lumière, il faut aussi considérer cette radiation comme une **série discontinue de photons** ou **quanta d'énergie**. C'est le caractère **quantique de la lumière**. Les interactions entre la matière et la lumière correspondent à l'absorption ou l'émission ou encore la diffusion par la matière de l'un de ces quanta d'énergie.



L'**absorption** correspond à la capture de photons par les électrons des atomes, qui se trouvent ainsi portés à des niveaux excités ; ce qui peut se traduire, notamment, par l'échauffement d'une masse de matière ou par la production d'un courant électrique (effet photoélectrique). **UV – VIS – IR**

L'**émission** de lumière correspond à la libération de quanta d'énergie (sous forme de photons) par les électrons des atomes retournant à un niveau énergétique inférieur, après avoir été portés à un niveau supérieur par une action excitatrice fournissant l'énergie nécessaire ; suivant la nature de l'excitation, on observe les divers phénomènes d'incandescence ou de **luminescence** **Fluorescence, phosphorescence**.



Structure de la matière

L'énergie des molécules varie de façon discontinue et on considère qu'elle correspond à la somme de quatre termes

$$E_{\text{totale}} = E_n + E_e + E_v + E_r$$

E_n = énergie nucléaire correspond à l'énergie du noyau constitutif des atomes

E_e = énergie électronique qui concerne les électrons périphériques, puis les électrons des couches internes (divers états énergétiques des différents électrons de valence)

E_v = énergie de vibration qui correspond à une modification des mouvements de vibration des atomes d'une molécule

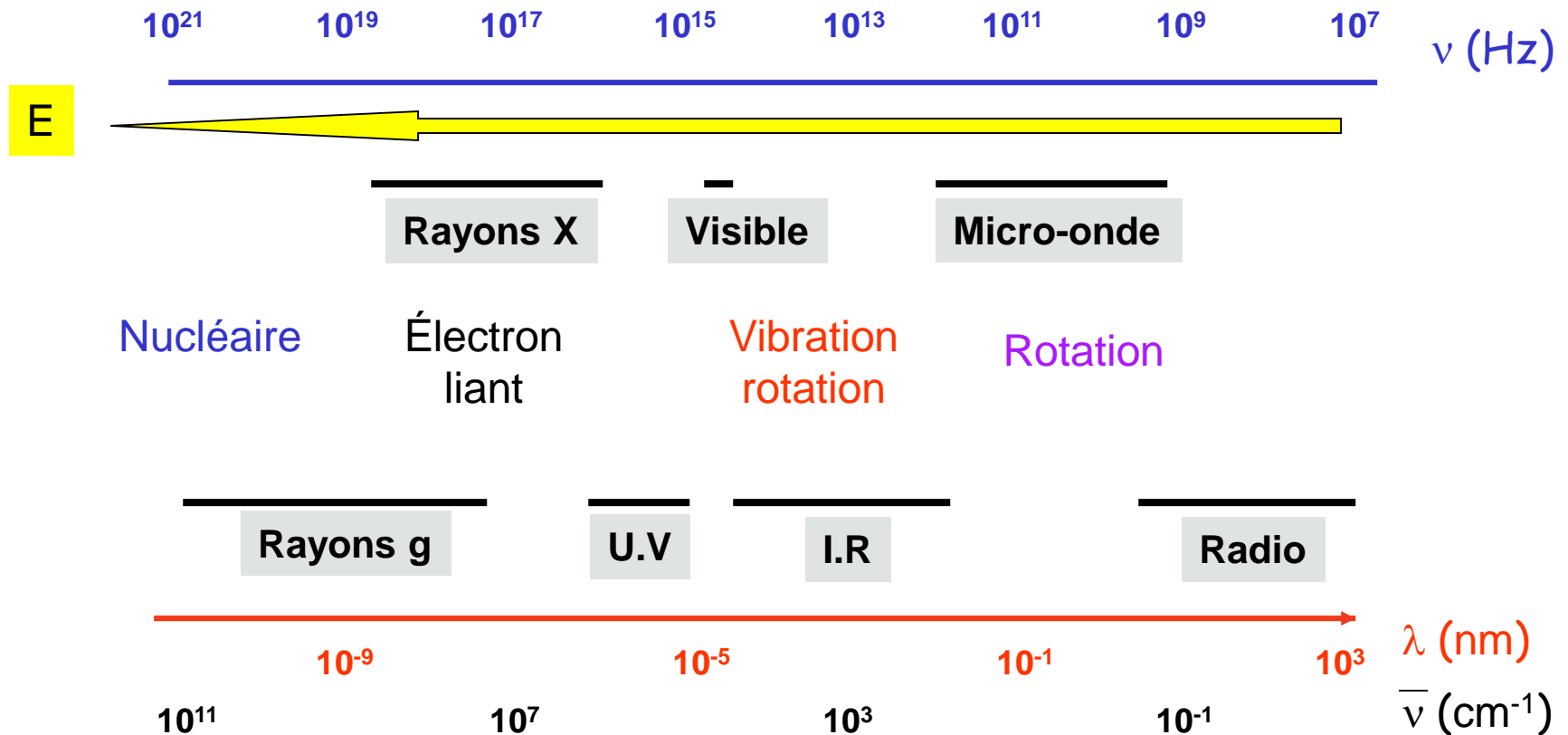
E_r = énergie de rotation qui correspond à une modification du mouvement de rotation de la molécule (rotation de la molécule autour de son centre d'inertie)

$$E_n \gg E_e \gg E_v \gg E_r$$

Pour un environnement énergétique donné, une molécule (ou un atome) occupe le niveau énergétique le plus bas ou de plus faible énergie
= **E fondamental**

Le spectre électromagnétique

Le spectre électromagnétique couvre un domaine extrêmement étendu de longueur d'onde et de fréquences, et donc d'énergie. Pour chaque région du spectre, une méthode spectroscopique y est associée.



Spectre électromagnétique et type de spectroscopie

Pour chaque région du spectre, une méthode spectroscopique y est associée

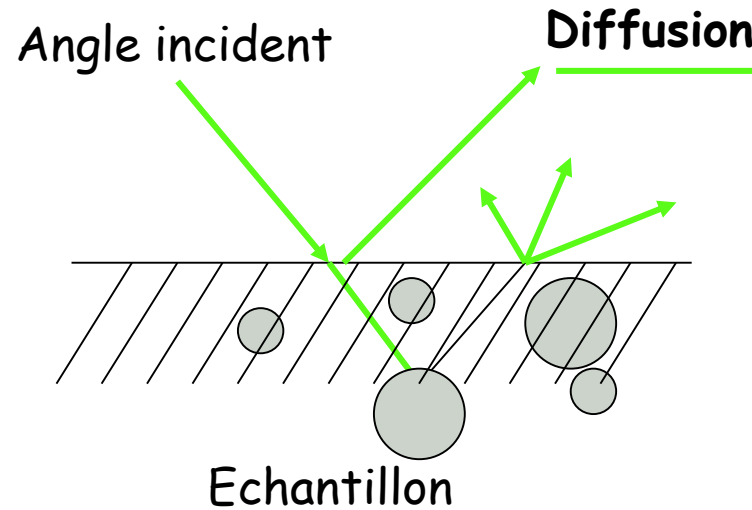
Type de spectroscopie	Domaine usuel de longueur d'onde*	Domaine usuel de nombre d'onde/cm ⁻¹	Type de transition quantique
Émission de rayons γ	0,005–1,4 Å	—	nucléaire
Absorption, émission, fluorescence et diffraction de rayons X	0,1–100 Å	—	électron interne
Absorption d'ultraviolet lointain	10–180 nm	1×10^6 à 5×10^4	électrons liants
Absorption, émission et fluorescence dans l'ultraviolet et le visible	180–780 nm	5×10^4 à $1,3 \times 10^4$	électrons liants
Absorption d'infrarouge et diffusion Raman	0,78–300 μm	$1,3 \times 10^4$ à $3,3 \times 10^1$	vibration-rotation de molécules
Absorption de micro-ondes	0,75–3,75 mm	13–2,7	rotation de molécules
Résonance paramagnétique électronique [†]	3 cm	0,33	spin électronique dans un champ magnétique
Résonance magnétique nucléaire [‡]	0,6–10 m	2×10^{-2} à 1×10^{-3}	spin nucléaire dans un champ magnétique

* 1 Å = 10^{-10} m = 10^{-8} cm
 1 nm = 10^{-9} m = 10^{-7} cm
 1 μm = 10^{-6} m = 10^{-4} cm

[†]N.d.tr. : En anglais : *Electron Spin Resonance (ESR)*.

[‡]N.d.tr. : En anglais : *Nuclear Magnetic Resonance (NMR)*.

Diffusion de rayonnement (IR, Lumière, Neutrons, R)



Diffusion : changement de direction de la lumière due à des interactions avec la matière

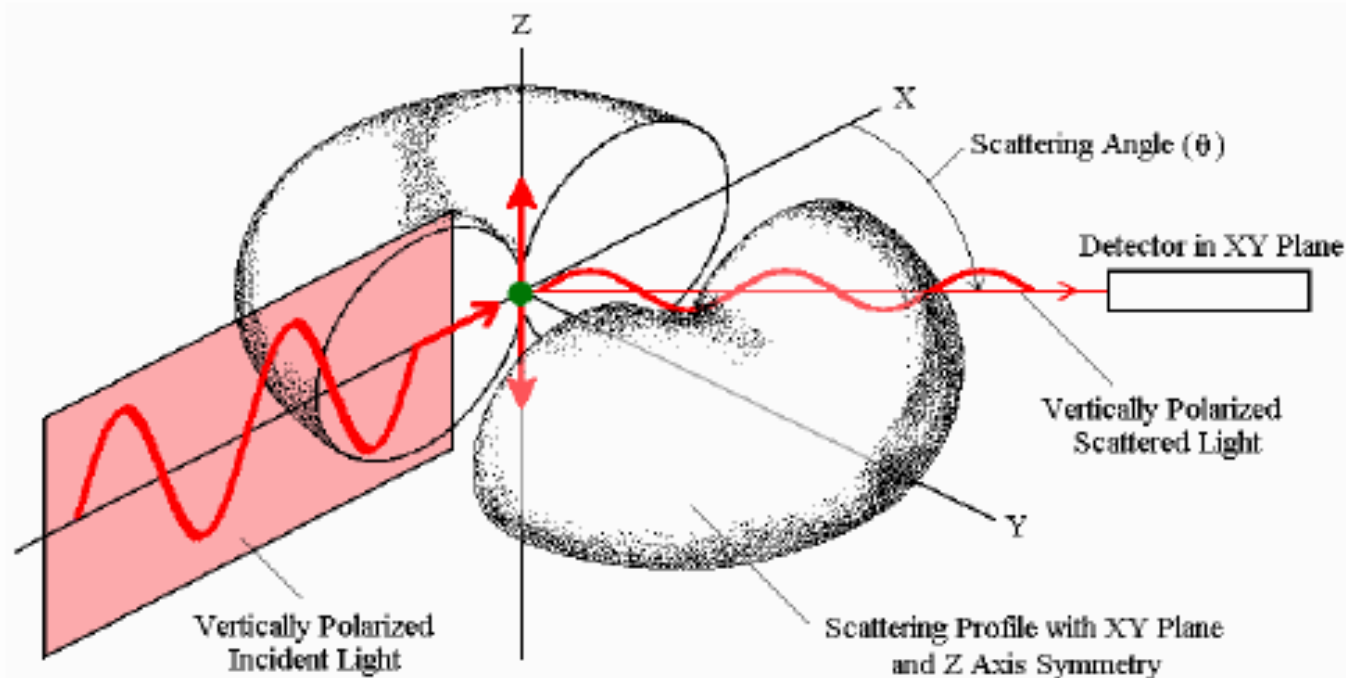
Elle peut se faire avec ou sans transfert d'énergie, avec ou sans changement de λ comparé au rayonnement incident

Méthodes de diffusion du rayonnement

Diffusion de la lumière (Light Scattering)

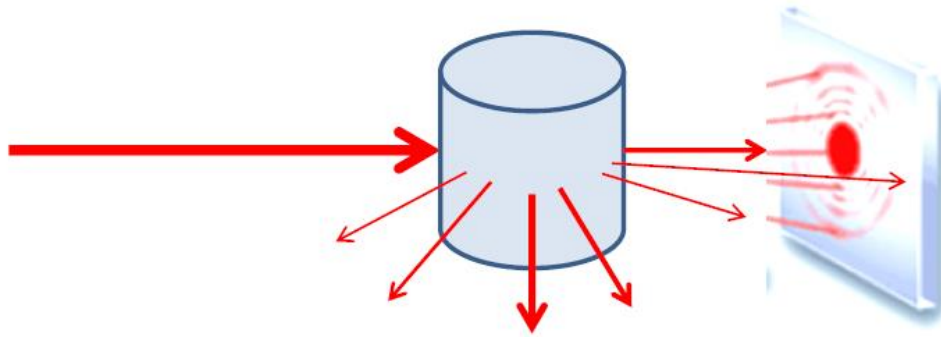
Light - Matter Interactions: Scattering

The incident photon induces an oscillating dipole in the electron cloud. As the dipole changes, energy is radiated or scattered in all directions.



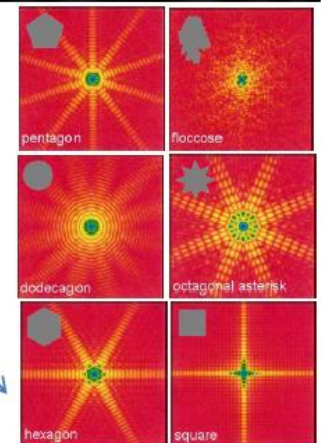
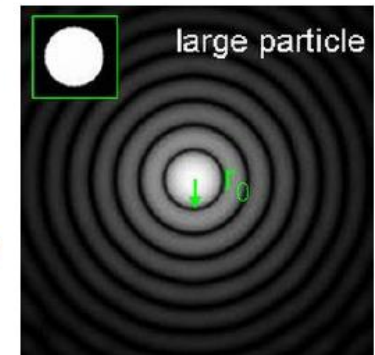
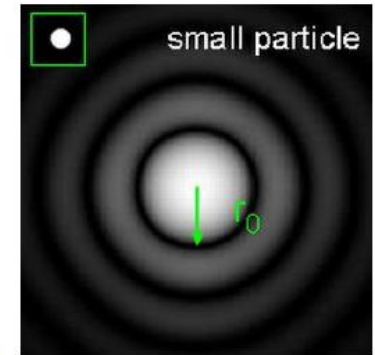
Le principe :

On envoi un faisceau de rayonnement sur un échantillon ...

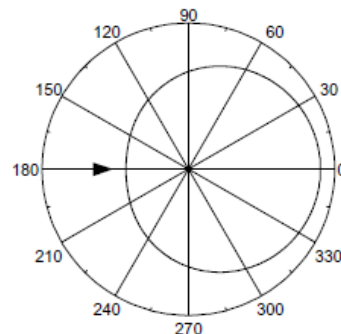
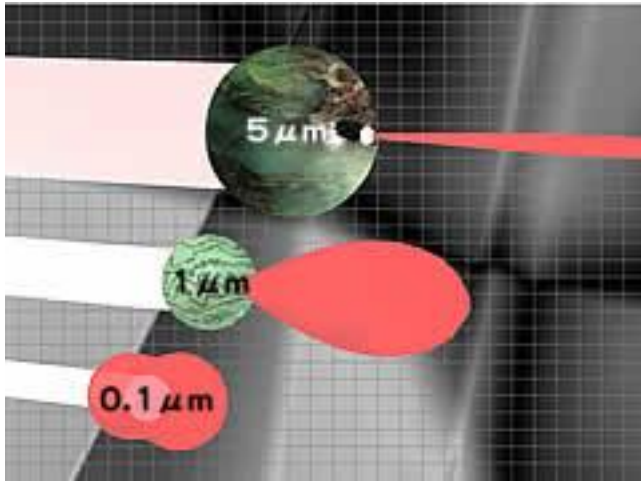


... et on regarde le profil de diffraction

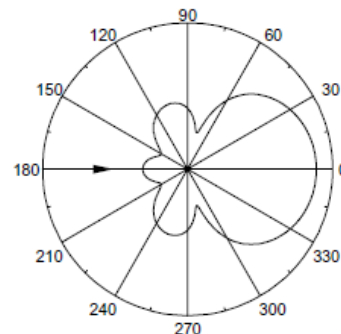
→ pour des échantillons dilués et parfaitement monodisperses, ça ressemble à ça ...



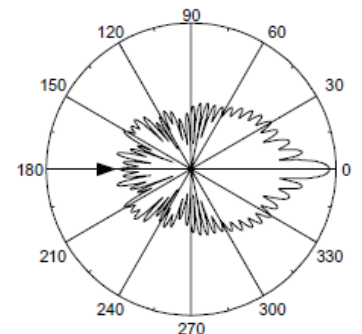
Diffusion angle and particle size



$$d_p \approx 0.2\lambda$$

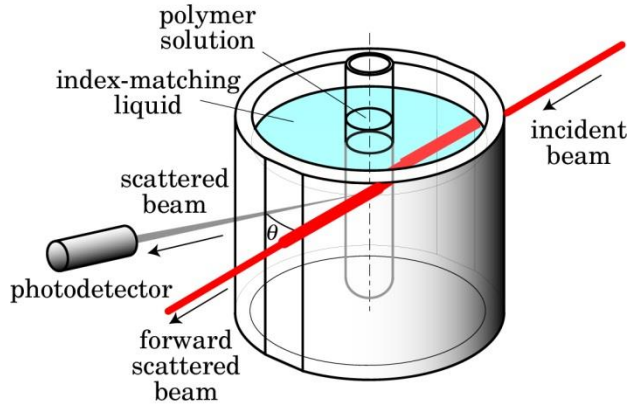


$$d_p \approx 1.0\lambda$$

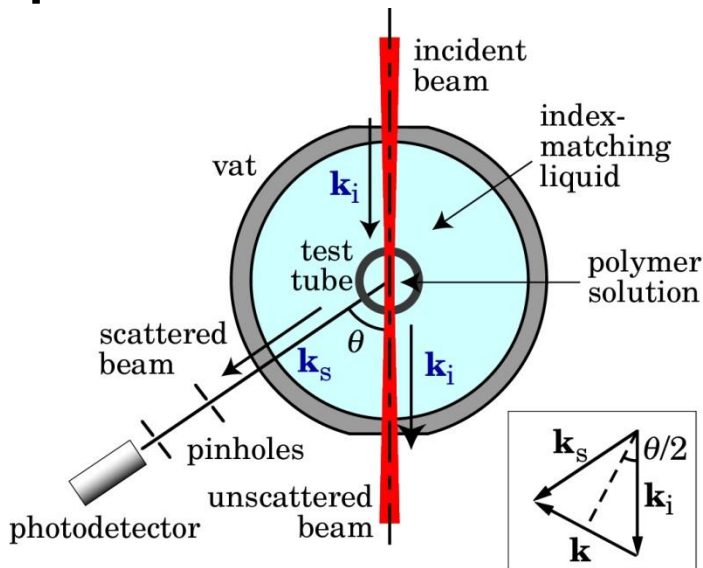


$$d_p \approx 10\lambda$$

Scattering wavevector



top view



wavevector

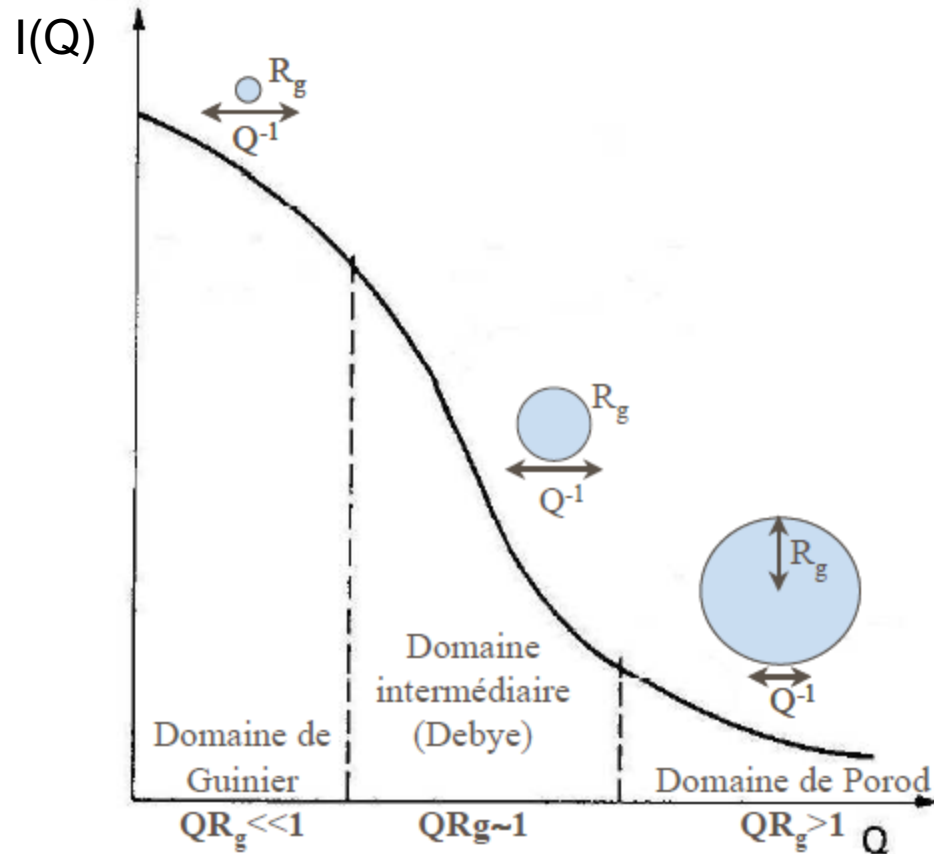
$$|\mathbf{k}_i| = |\mathbf{k}_s| = \frac{2\pi}{\lambda} \quad (\text{in vacuum})$$

$$= \frac{2\pi}{\lambda/n} \quad (\text{in solution})$$

scattering wavevector

$$k = |\mathbf{k}| = \frac{4\pi n}{\lambda} \sin \frac{\theta}{2}$$

Domaines du vecteur de diffusion (Lois d'échelle)



Solutions studied by light scattering

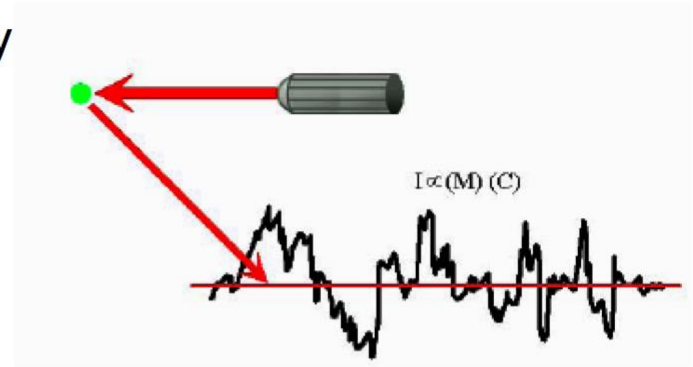
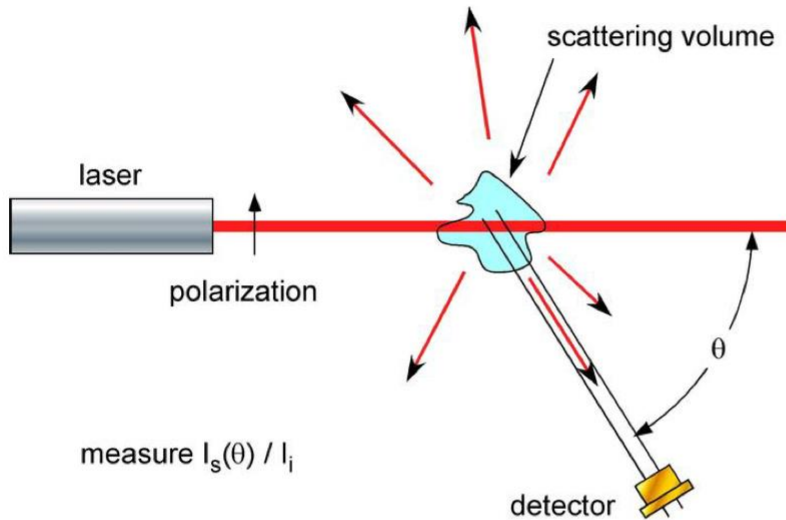
	X-rays	Neutrons	UV/Vis
λ	$\sim 1.5 \text{ \AA}$	$\sim 1-20 \text{ \AA}$	$\sim 5000 \text{ \AA}$
Energy	$\sim \text{keV}$	$\sim \text{meV}$	$\sim 10 \text{ eV}$
Source	Synchrotron 10^{12} to 10^{15} ph/cm ² /s	Reactor 10^4 to 10^8 n/cm ² /s	Laser 10^{22} ph/cm ² /s
k	$2 \cdot 10^{-4} - 3 \cdot 10^{-2}$	$2 \cdot 10^{-2} - 2$	$1 \cdot 10^{-2} - 4 \cdot 10^{-1}$
	Structure	Structure Dynamiques	Structure (SLS) Dynamiques (DLS)

The scattering signal may be analysed by several methods:

- ▶ Average signal strength: **static**, 'classic'
- ▶ Fluctuations of signal: **dynamic**, quasi-elastic
- ▶ Shift of the signal: **electrophoretic**

Static Light Scattering

Measurement of the average scattering intensity

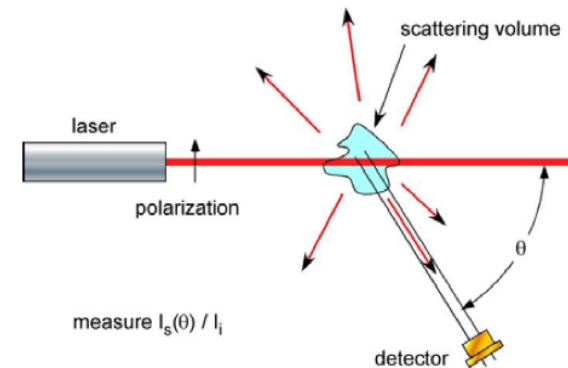
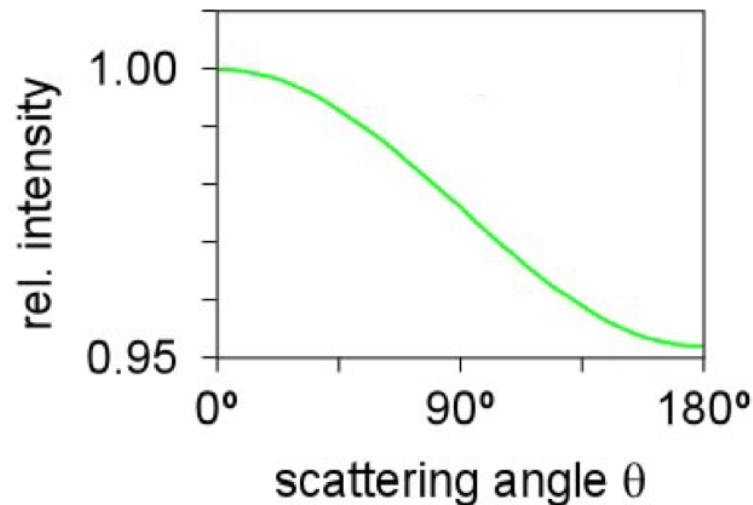


$$I(\theta)_{\text{scattered}} \propto Mc \left(\frac{dn}{dc} \right)^2 P(\theta)$$

The intensity is a function of the particle's molecular weight, its concentration, shape (form factor) and of the refractive index increment of the solution.

Form factor

In general, the scattered intensity varies with Θ , the angle between the incident beam and the detector.



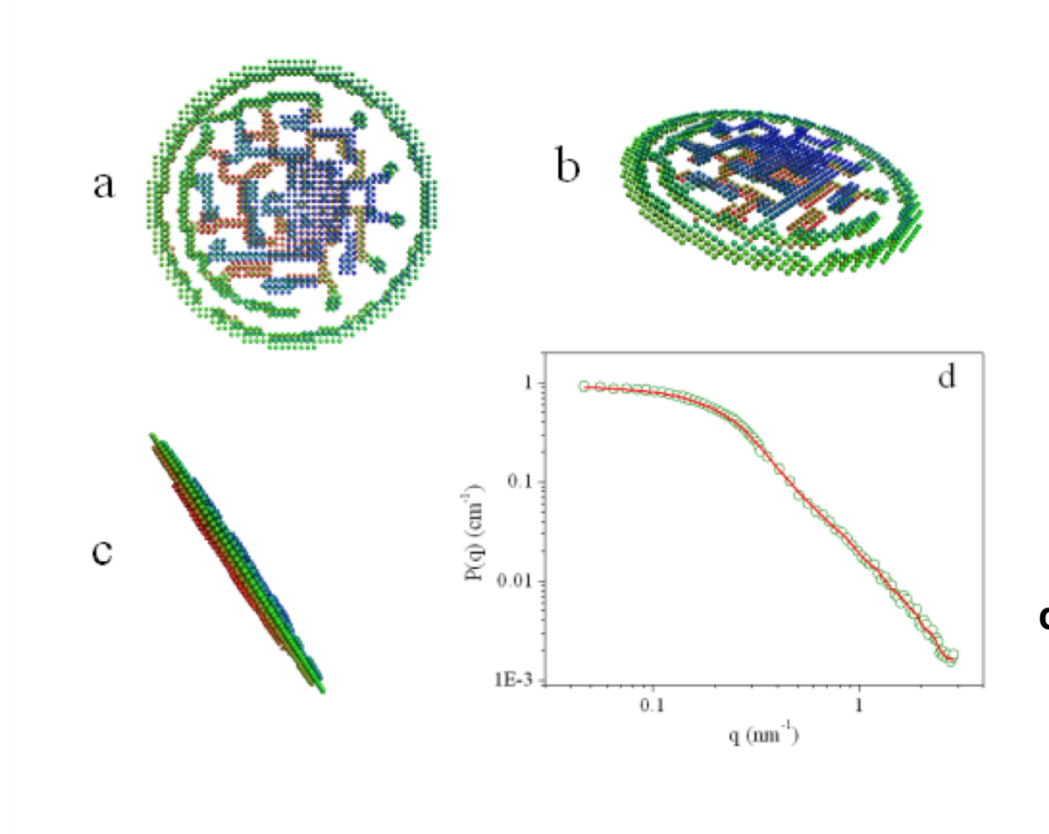
$$I(\theta)_{\text{scattered}} \propto Mc \left(\frac{dn}{dc} \right)^2 P(\theta)$$

The form factor, which accounts for this dependence is also a function of the wavelength and of the dimensions of the particule.

$$P(\theta) = 1 - \frac{16\pi^2 n_0^2}{3\lambda_0^2} \sin^2 \left(\frac{\theta}{2} \right) \langle r_g^2 \rangle + \dots$$

Structure de l'AG-peptide

Differentes vues du modèle 3D le plus probable

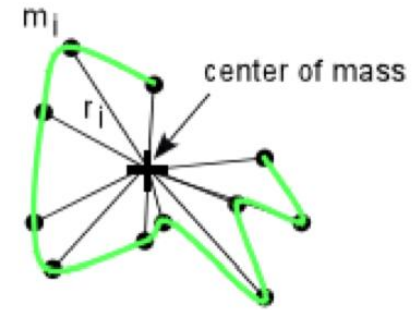


Disque plat
 $D=19.2$ nm
 $e = 2.0$ nm

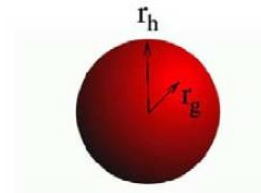
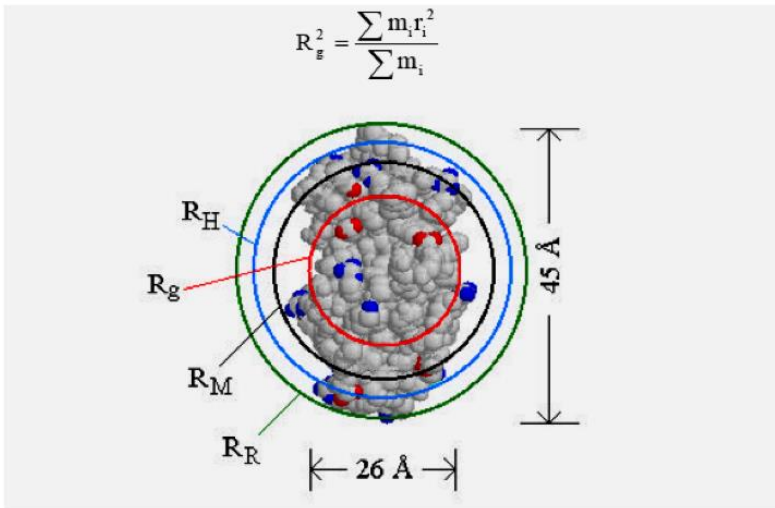
Structure interne
dense et fortement
branchée

Rayons des particules

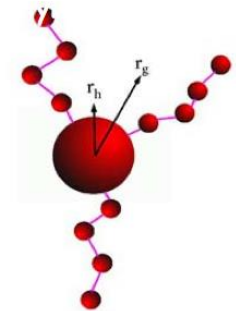
R_g est la moyenne des distances de chaque motif par rapport au centre de gravité G de la molécule. Plus la molécule est grande et plus le rayon de giration est élevé. Racine carrée de l'écart quadratique moyen des distances entre les atomes et le centre de gravité de la chaîne



$$\langle r_g^2 \rangle = \frac{\sum r_i^2 m_i}{M}$$



$$\rho = \frac{r_g}{r_h} = 0.77$$



$$\rho = \frac{r_g}{r_h} \approx 1.4$$

Equation de Rayleigh (Rayleigh-Debye-Zimm formalism)

$$\frac{KC}{R_\theta} = \left(\frac{1}{M} + 2A_2C \right) \frac{1}{P_\theta}$$

Facteur
de Forme

$$K = \frac{2\pi^2}{\lambda_o^4 N_A} \left(n_o \frac{dn}{dc} \right)^2$$

λ_o = laser wavelength
 N_A = Avogadro's number
 n_o = Solvent RI
 dn/dc = differential RI increment

$$P_\theta = 1 + \frac{16\pi^2 n_o^2 R_g^2}{3\lambda_o^2} \sin^2\left(\frac{\theta}{2}\right)$$

R_g = Radius of gyration
 θ = Measurement angle

Constante

$$R_\theta = \frac{I_A n_o^2}{I_T n_T^2} R_T$$

I_A = Intensity of analyte (sample I – solvent I)
 n_o = Solvent RI
 I_T = Intensity of standard (toluene)
 n_T = Standard (toluene) RI
 R_T = Rayleigh ratio of standard (toluene)

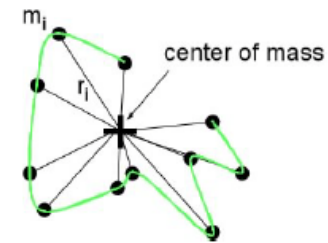
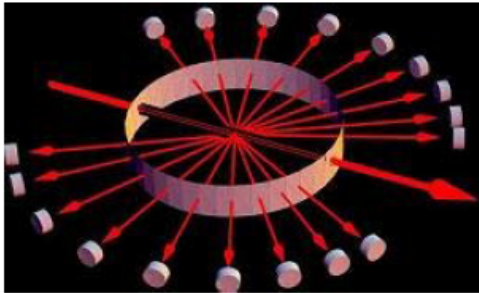
Rapport de
Rayleigh

A_2 (mol.mL.g⁻²): 2nd coefficient du viriel (non idéalité)

Objects smaller than the wavelength of light

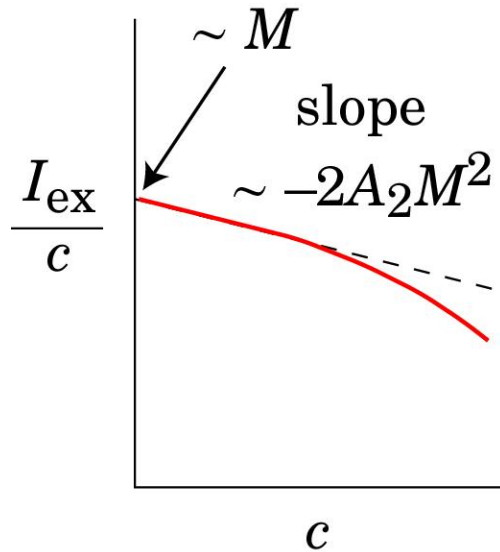
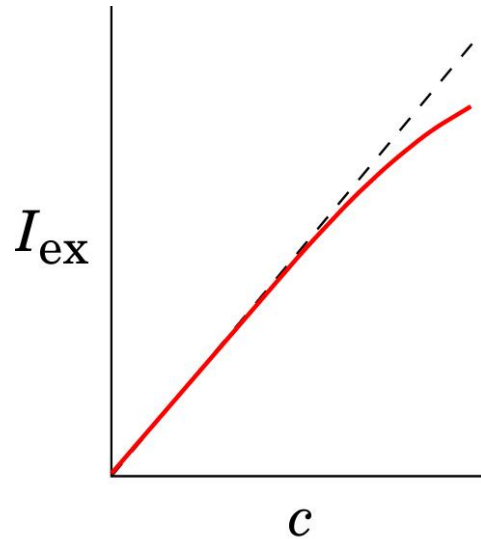
The form factor does not depend on Θ if $r_g \ll \lambda$ and diffusion is isotropic.

$$P(\theta) = 1 - \frac{16\pi^2 n_0^2}{3\lambda_0^2} \sin^2\left(\frac{\theta}{2}\right) \langle r_g^2 \rangle + \dots \approx 1$$

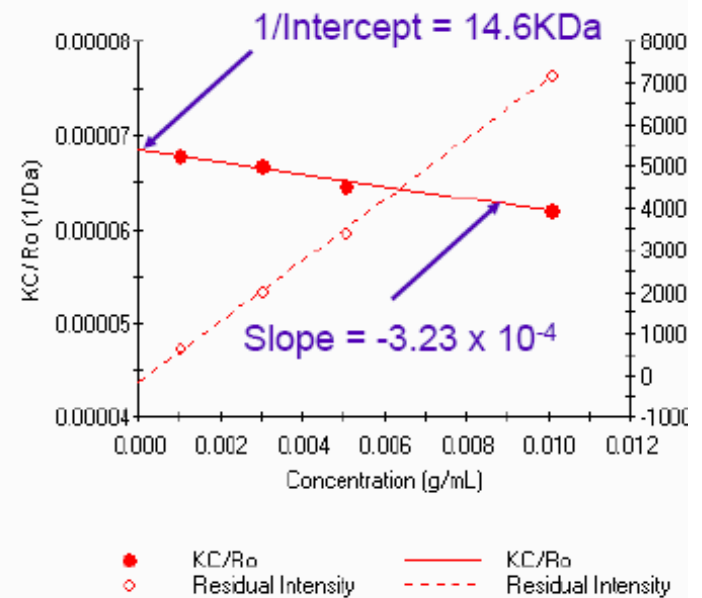


$$\frac{KC}{\Delta R_\theta} = \left(\frac{1}{M} + 2A_2C \right) P_\theta = \left(\frac{1}{M} + 2A_2C \right)$$

Debye plot

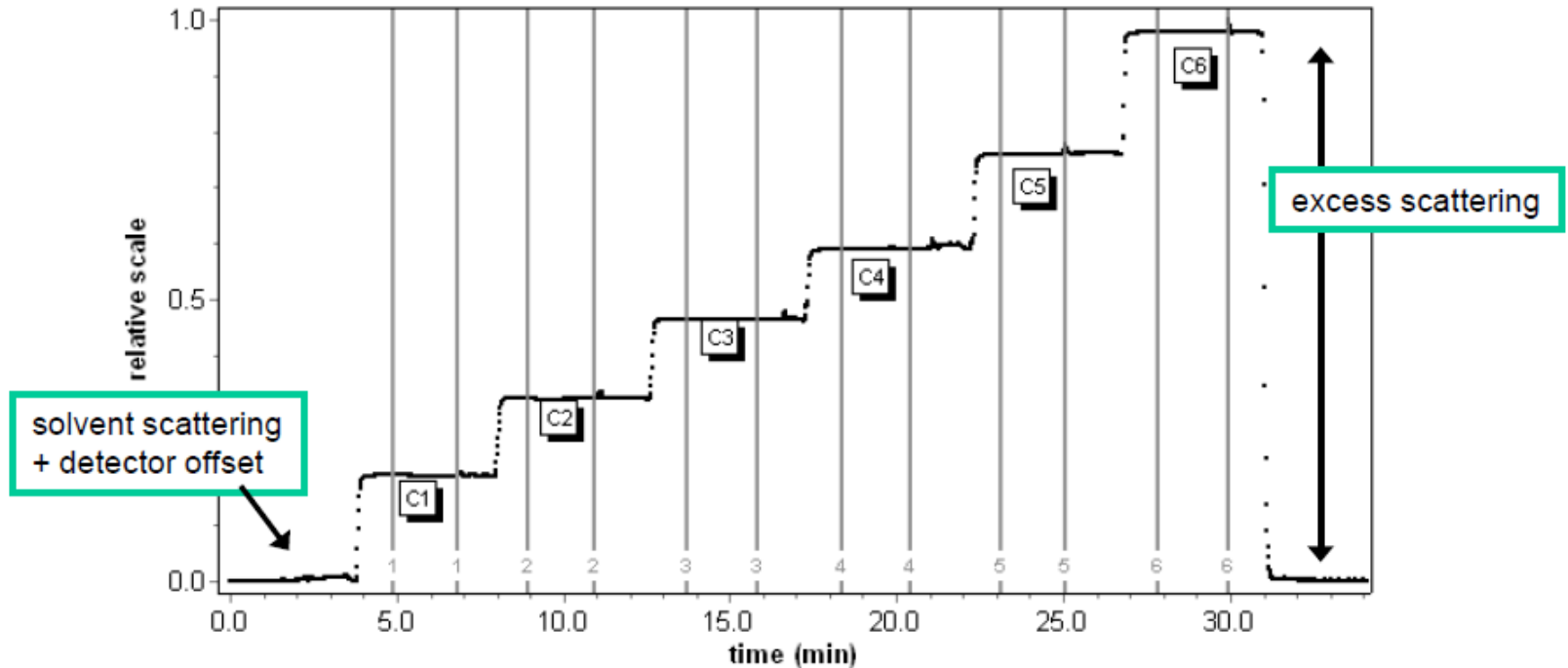


Molecular Weight Example (Lysozyme in PBS)



Zimm analysis

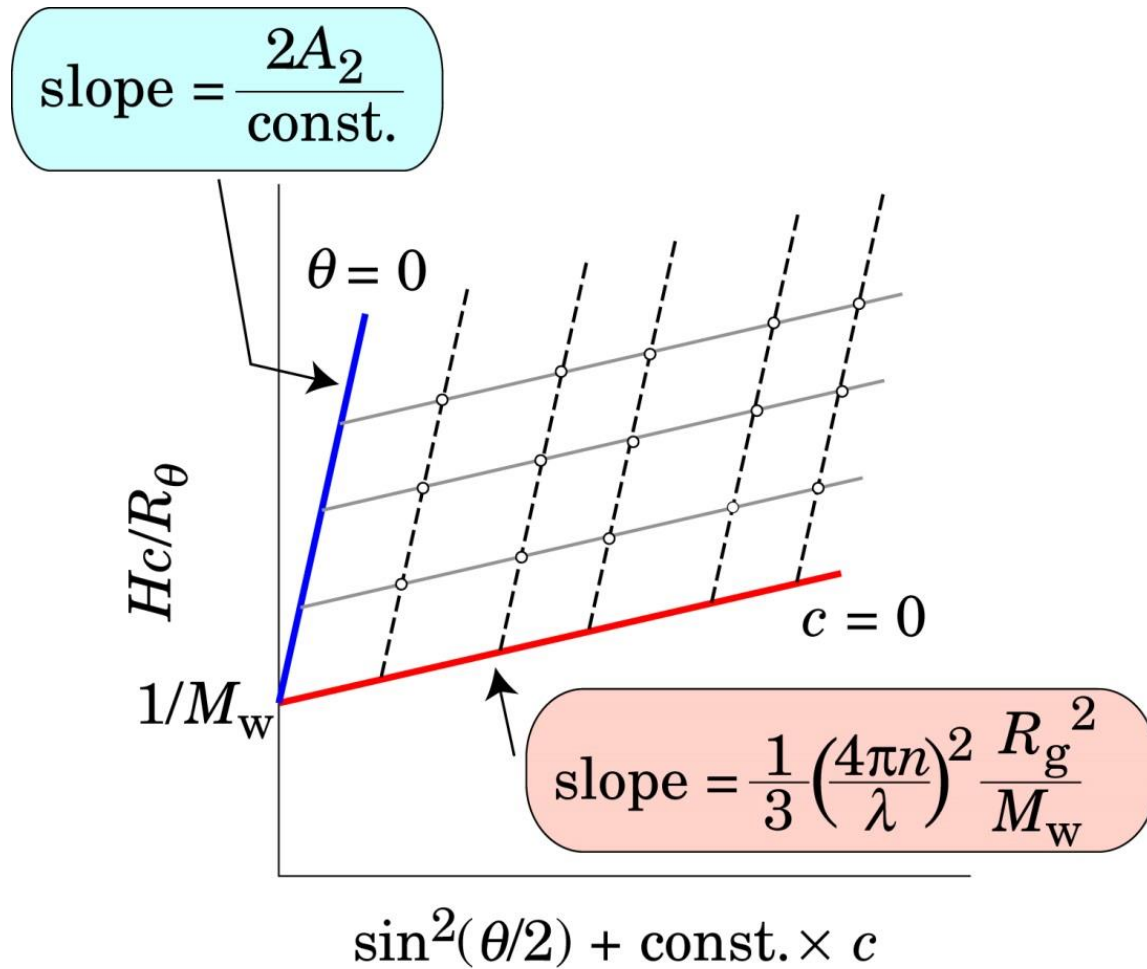
When R_g is large enough



Record Rayleigh ratio varying

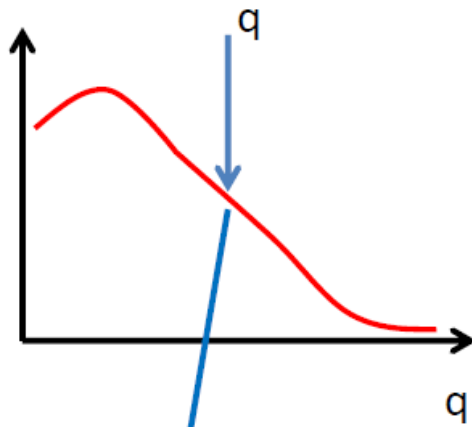
- angle (3 or 18 angles)
- concentration (multiple injections of known c).

Perform global fit of data to light scattering equation to retrieve M , A_2 and R_g



Dynamic light scattering

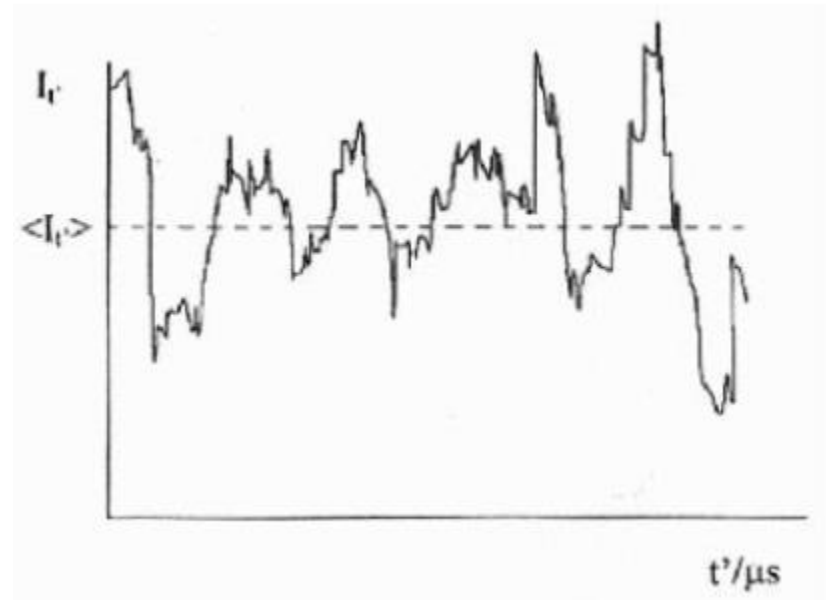
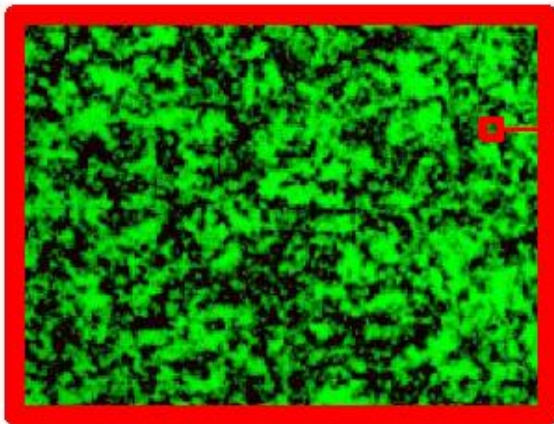
Intensité



En diffusion dynamique de la lumière, on se met à une valeur d'angle de diffusion (q constant) et on regarde l'évolution temporelle des fluctuations d'intensité qui reflète les fluctuations de concentration

Au cours du temps elle fluctue de manière très faible autour de sa valeur moyenne

La vitesse des fluctuations dépend de la taille des particules/macromolécules

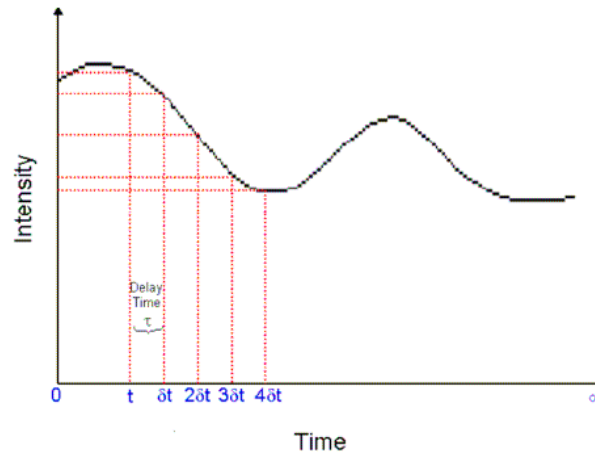


On parle de « speckle » = scintillement

Notion de corrélation

Corrélateur: comparateur de signal. Conçu pour mesurer le degré de similarité entre deux signaux, ou un signal avec lui-même à différents intervalles de temps.

Si l'intensité d'un signal est comparé avec lui-même à un point particulier à un temps t et un temps δt plus tard, alors pour un signal fluctuant de manière aléatoire (ex: mouvement brownien) il apparaît que les deux intensités ne sont pas reliées entre elles, i.e. il n'y a aucune corrélation entre les deux signaux.



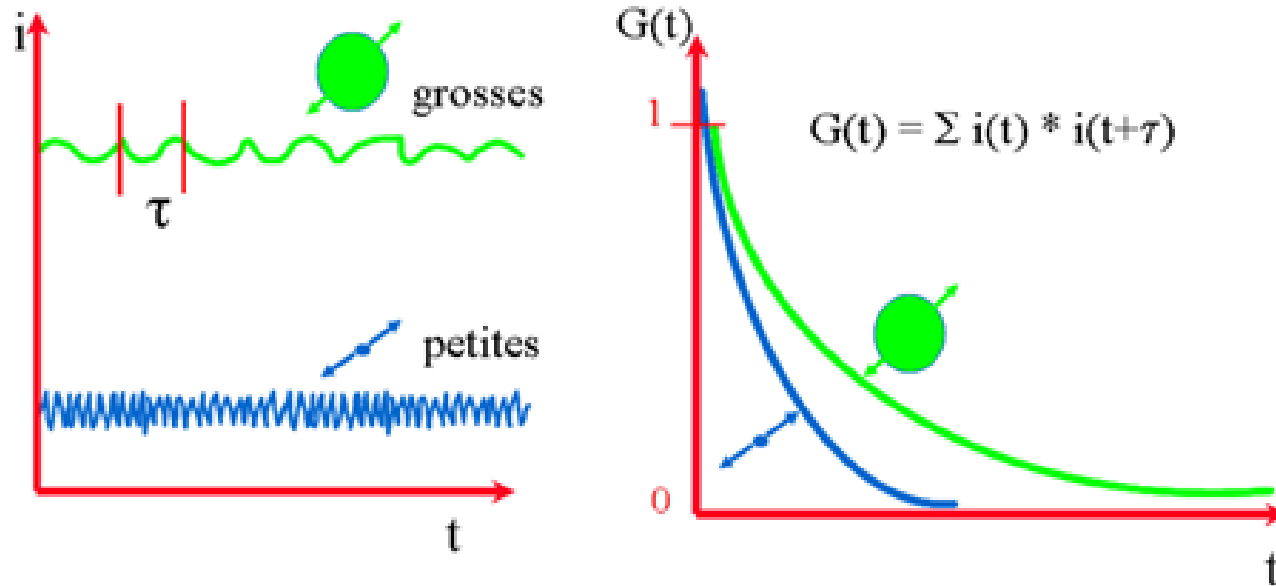
Cependant si l'intensité du signal au temps t est comparé à un temps $(t+\delta t)$ très court, Il y a dans ce cas une forte relation ou corrélation entre les deux signaux. La corrélation diminue aux temps $(t+2\delta t)$, $(t+3\delta t)$, $(t+4\delta t)$, etc.. jusqu'à disparaître pour des temps longs.

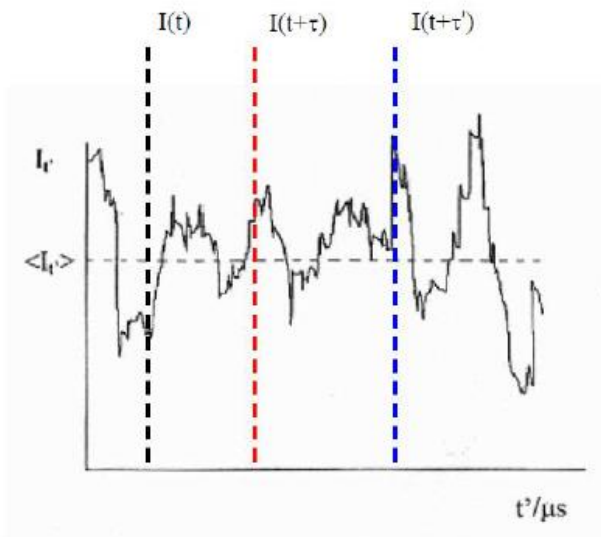
Temps d'échantillonnage (sample time): période de temps δt , de l'ordre de la nanoseconde ou microseconde. Un corrélateur possède une fenêtre de temps comprise entre $1 \mu s$ et $10 s$ (en général)

Fonction d'auto-corrélation (corrélogramme)

Fonction matérialisant la perte de corrélation du signal avec le temps.

Si les particules sont grandes, le signal change lentement et la corrélation persiste Longtemps. Si les particules sont petites et bougent rapidement, la corrélation est réduite plus rapidement.





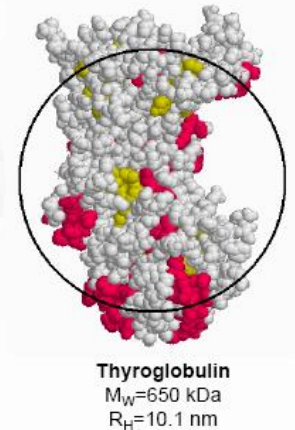
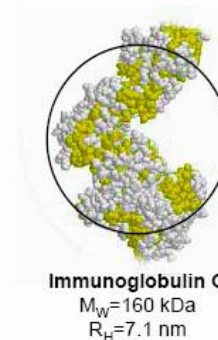
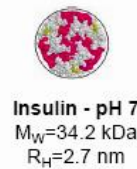
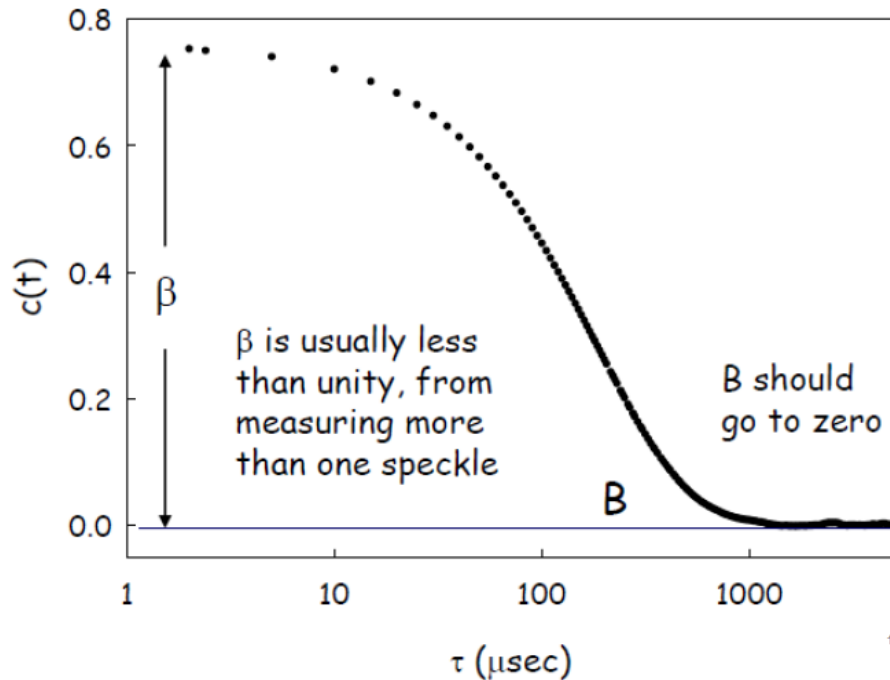
$G_2(\tau)$: Fonction de corrélation d'intensité

$$\Rightarrow G_2(\tau) = \frac{1}{T} \int_0^T I(t)I(t+\tau) d\tau$$

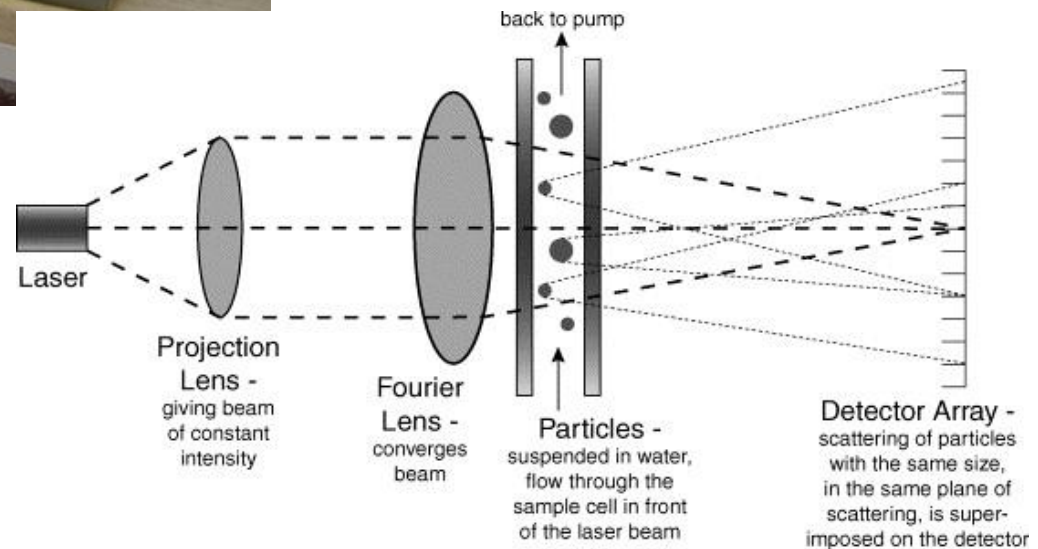
$$\Rightarrow C(\tau) = \frac{G_2(\tau) - B}{B} = \beta e^{-2\Gamma\tau}$$

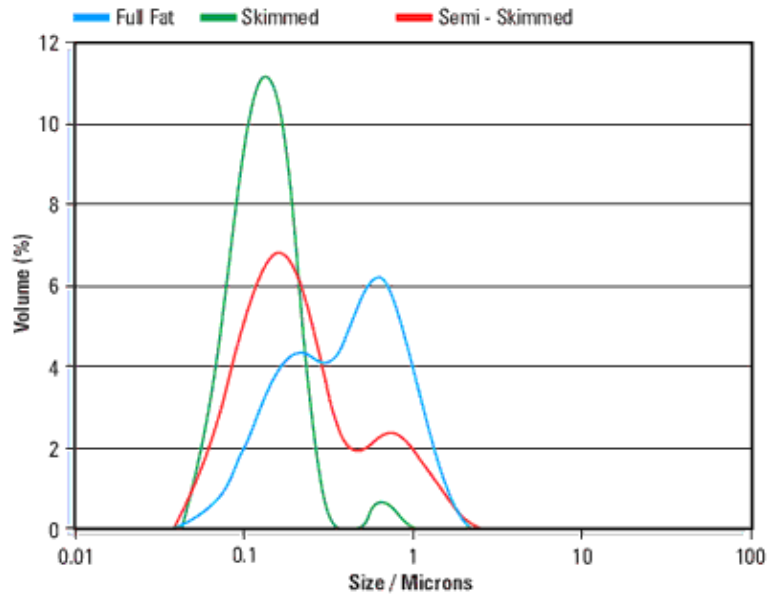
$$\Rightarrow D = \frac{\Gamma}{q^2}$$

$$r_H = \frac{kT}{6\pi\eta D}$$



Laser granulometry



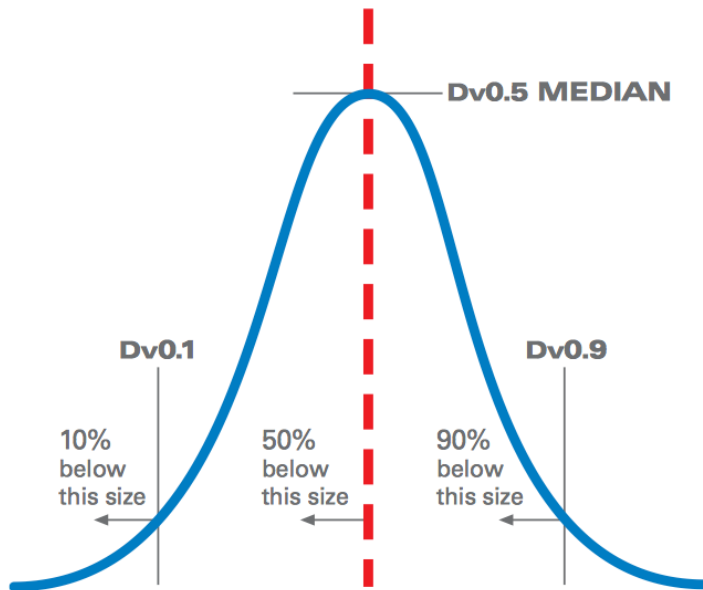


$$D[4,3] = \frac{\sum_1^n D_i^4 v_i}{\sum_1^n D_i^3 v_i}$$

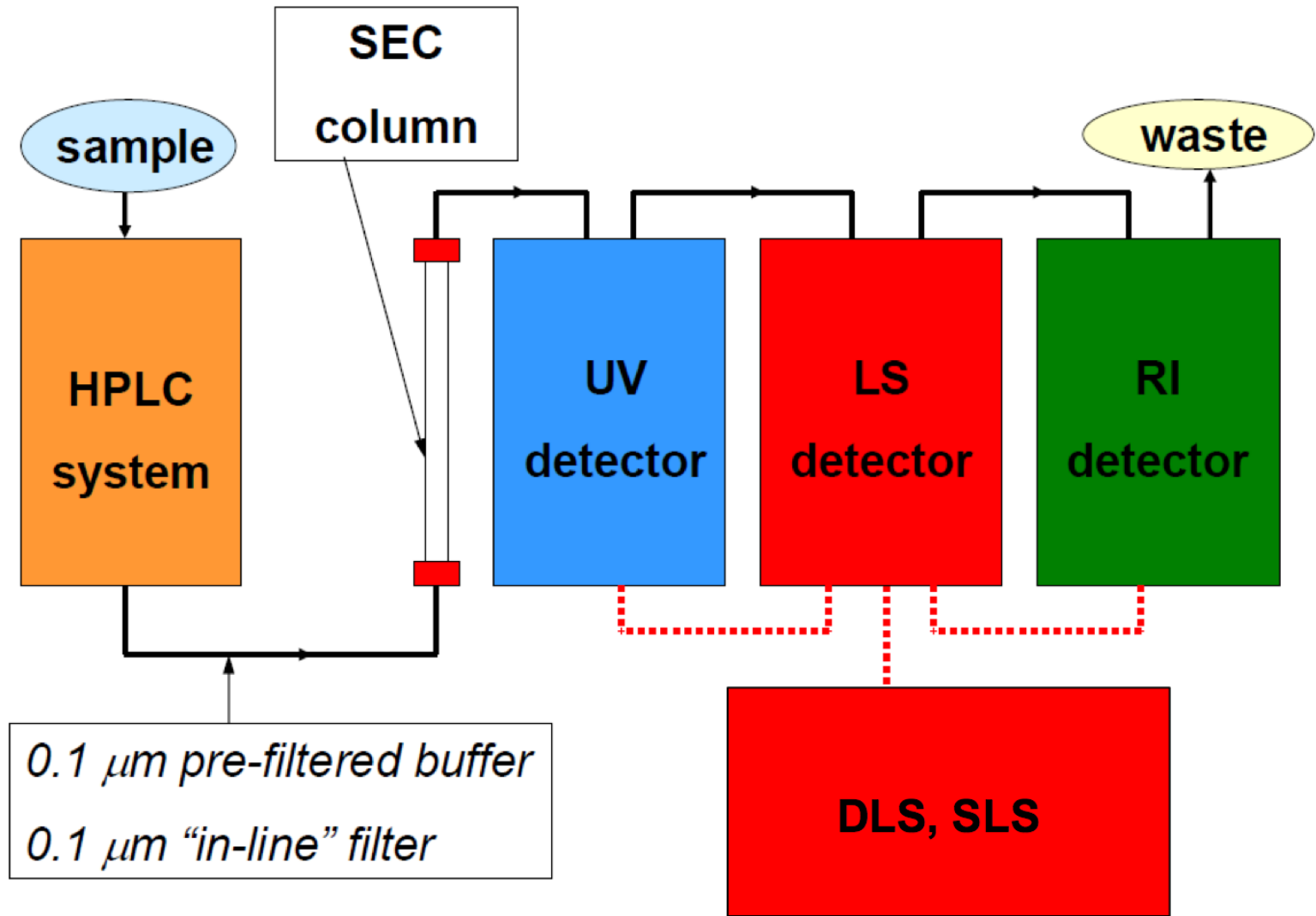
$$D[3,2] = \frac{\sum_1^n D_i^3 v_i}{\sum_1^n D_i^2 v_i}$$

$$\bar{D}_{pq}^{(p-q)} = \frac{\sum D_i^p}{\sum D_i^q}$$

$$Span = \frac{D_{v0.9} - D_{v0.1}}{D_{v0.5}}$$

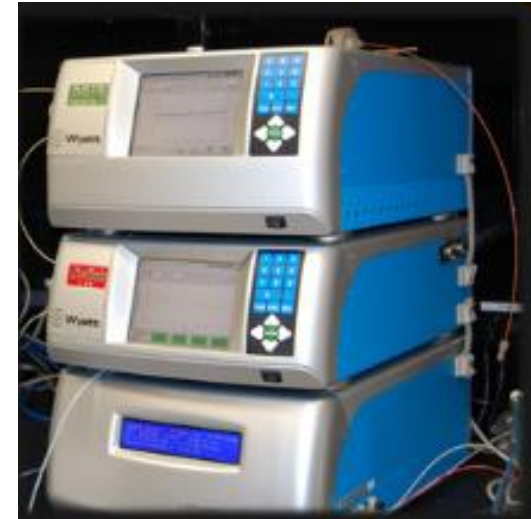
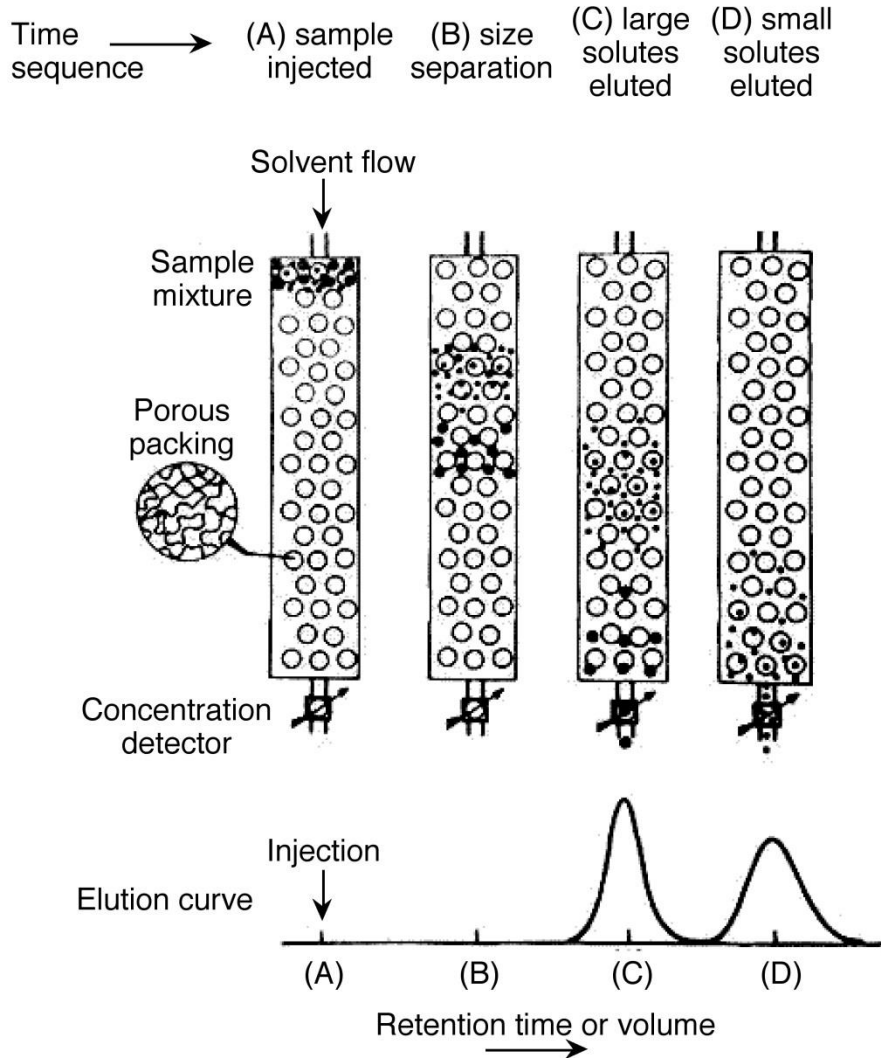


SEC-MALLS



SEC-MALLS

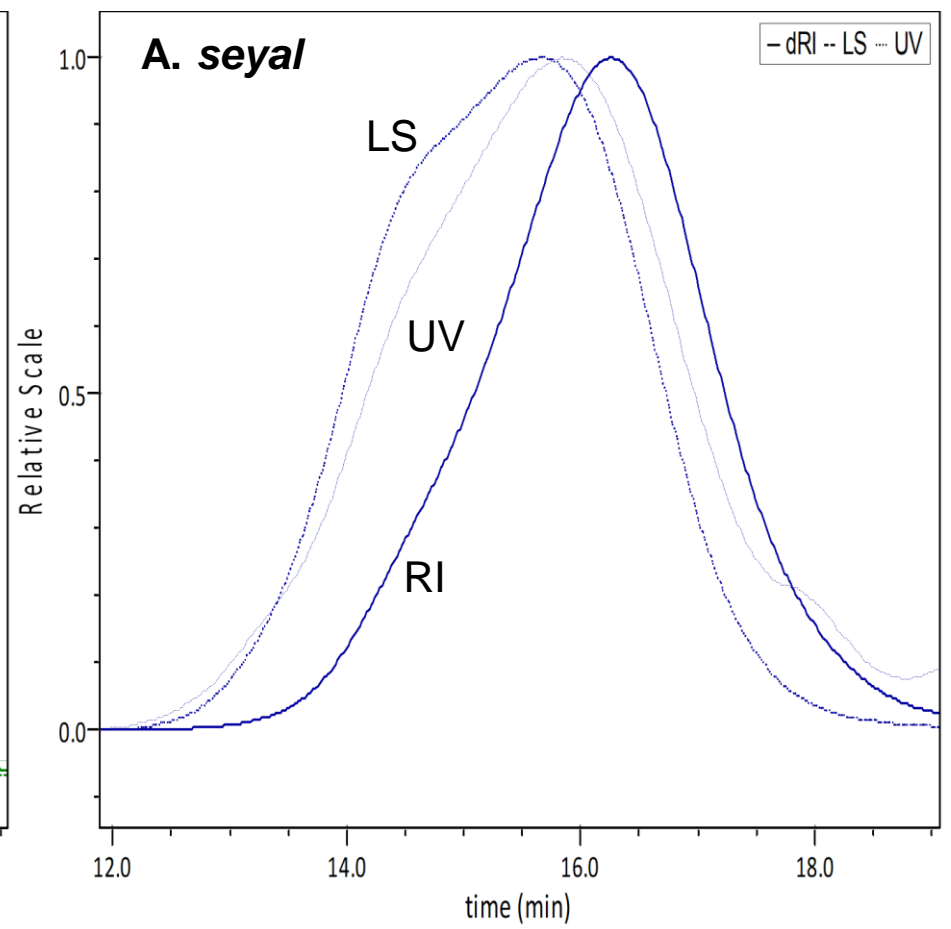
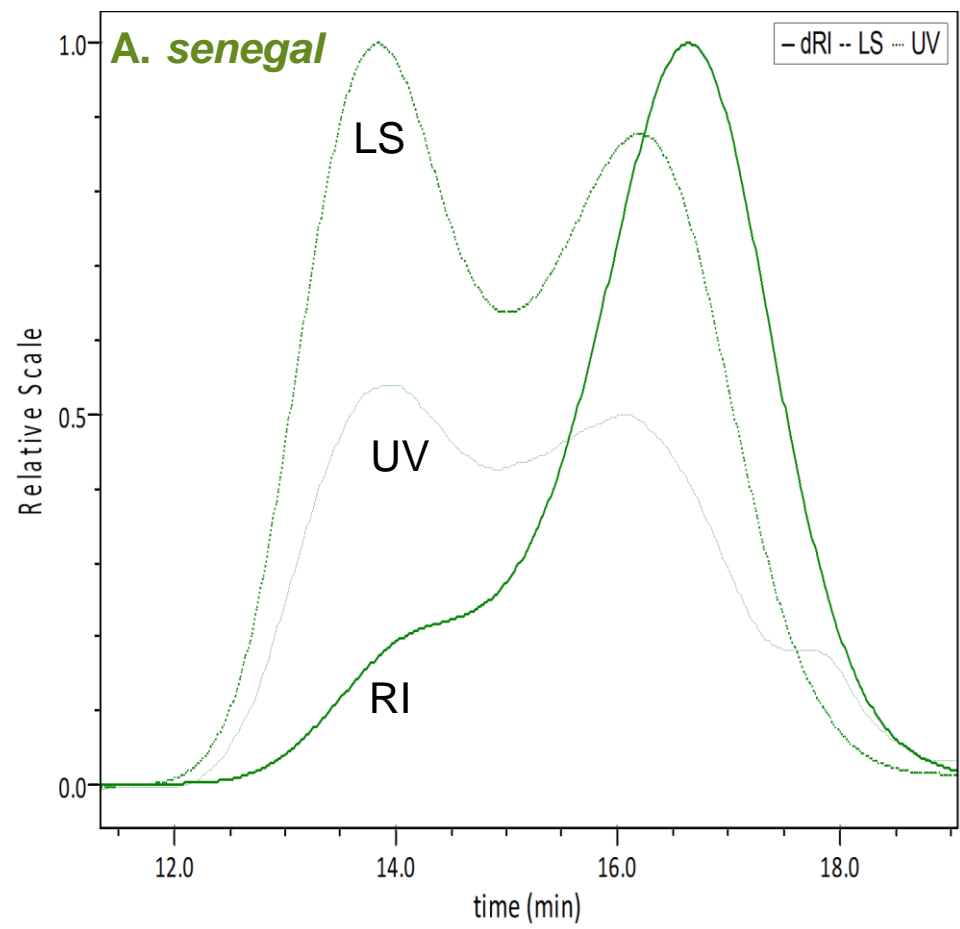
Size Exclusion Chromatography-Principle



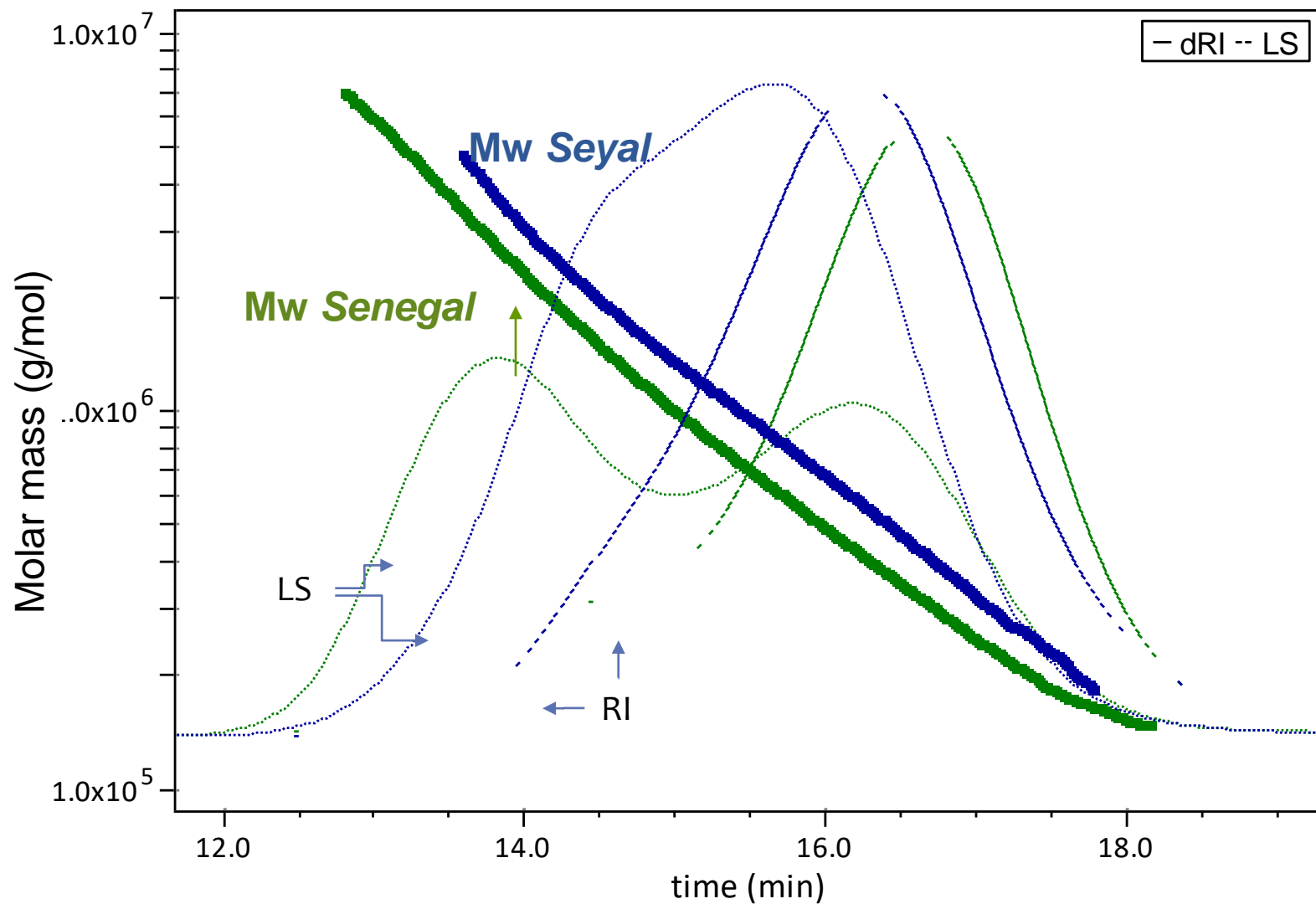
Quadruple détection

- UV
- RI
- Viscosimétrie capillaire
- Diffusion statique de la lumière multi-angles

Exemple: Complexité des gommes arabiques



Mw distribution of Acacia gums



Production

raw gum



grinding
1 à 5 mm

Dissolution

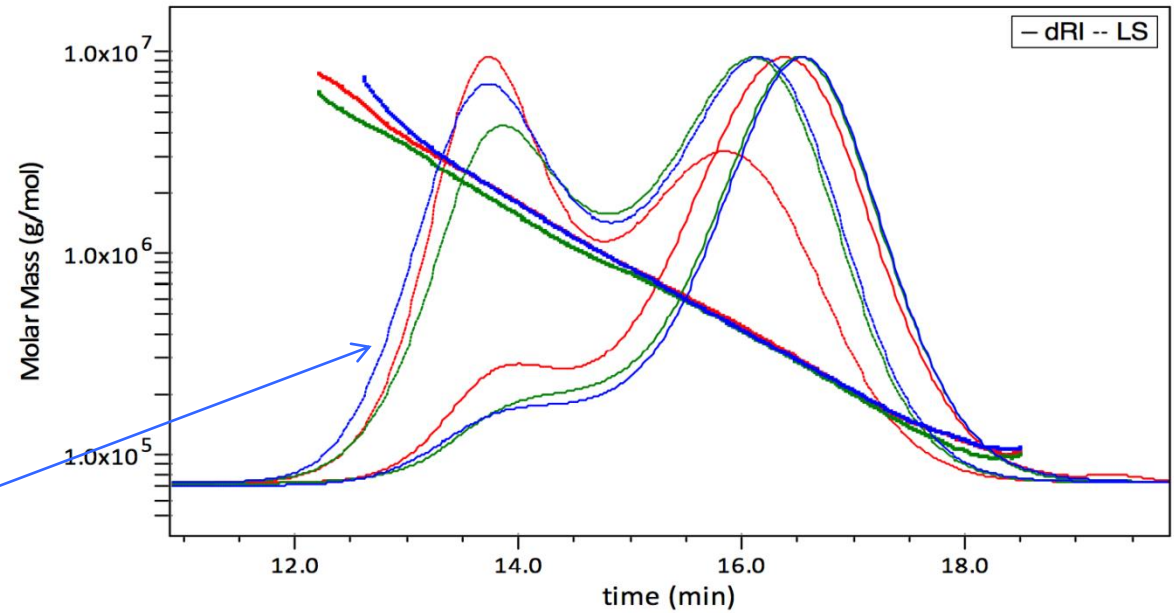
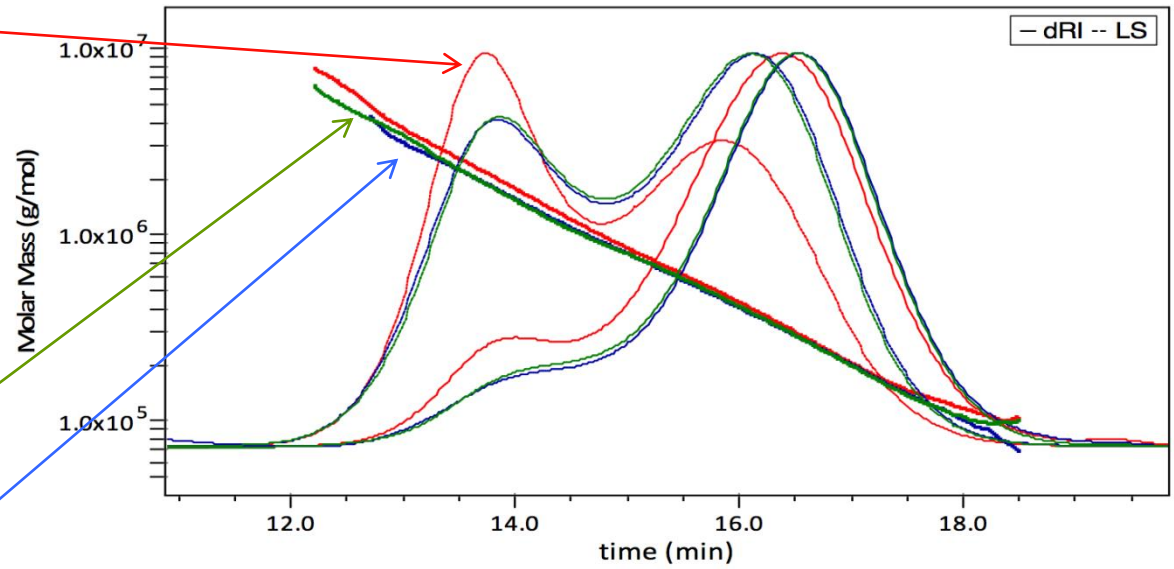
Decantation

Centrifugation

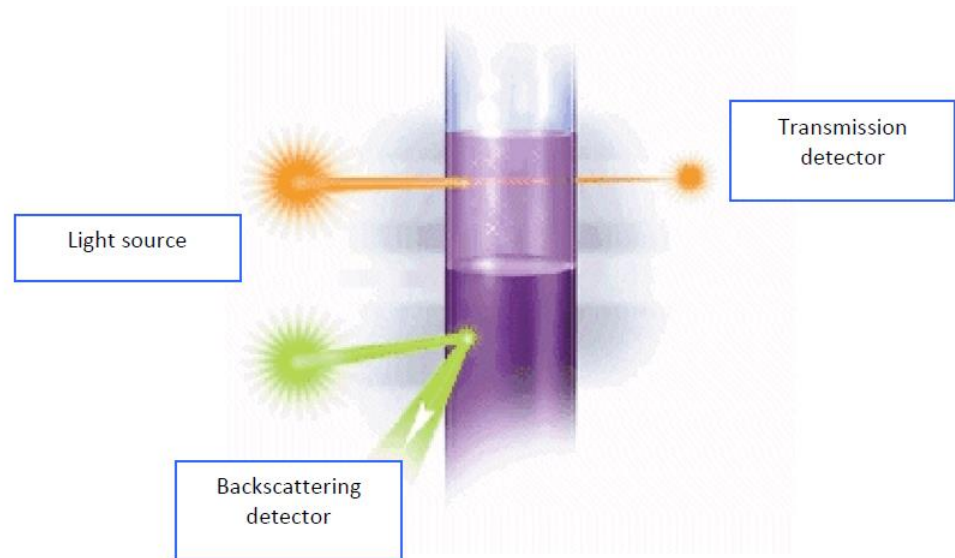
Filtrations

Pasteurisation

Atomisation

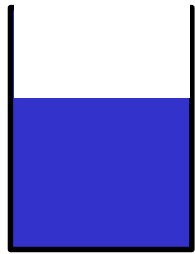
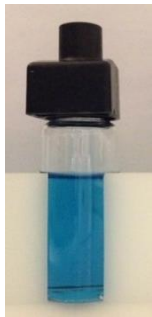


Turbiscan et stabilité des dispersions/suspensions colloïdales



Test d'efficacité de la gomme d'Acacia

Détermination de la dose de gomme arabique nécessaire pour empêcher la floculation d'une solution colloïdale d'hexacyanoferrate(II) de fer(III) en milieu hydro-alcoolique par un sel de calcium

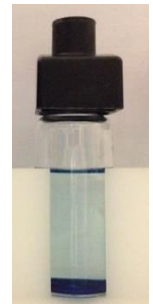


Matrice hydro-alcoolique – minérale
(pH 3.1)

CaCl₂ à 22 g/L (
V = 1 ml)



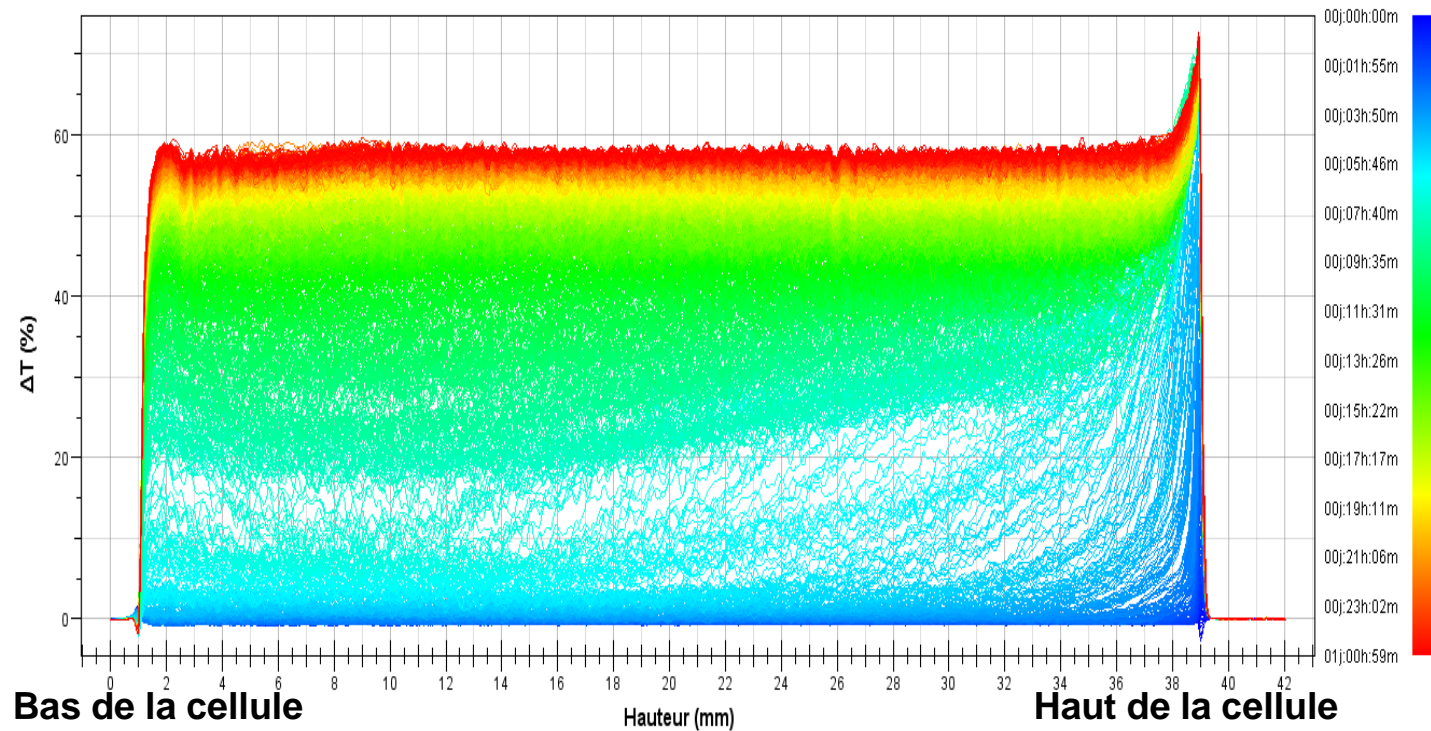
Après 24h à 25° C dans
l'obscurité



Déstabilisation de
la fraction minérale

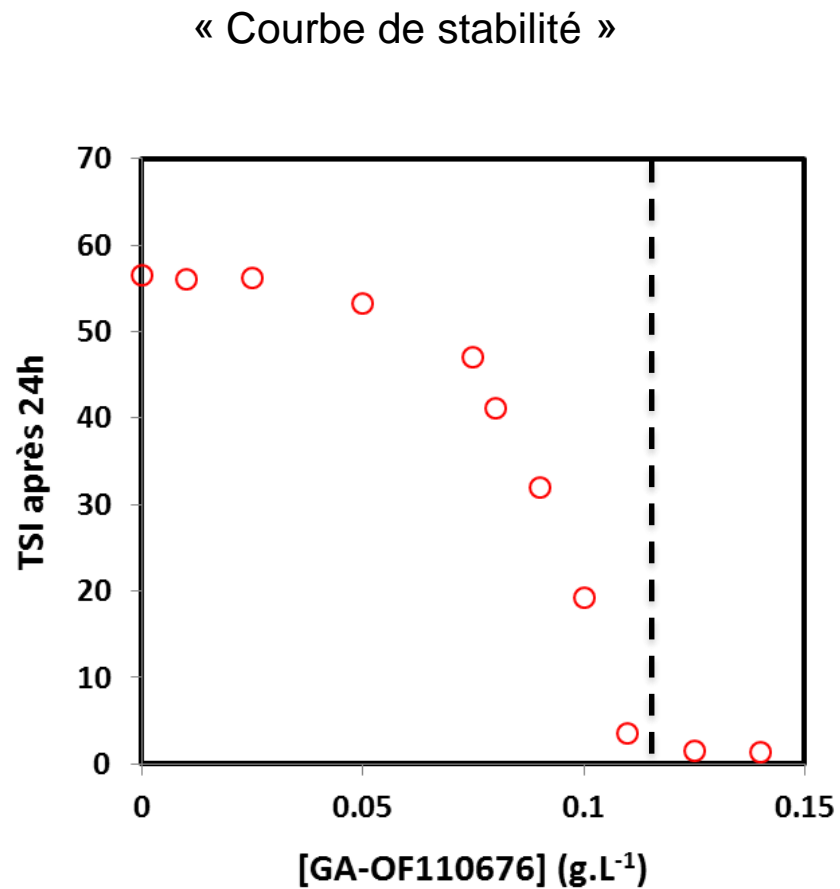
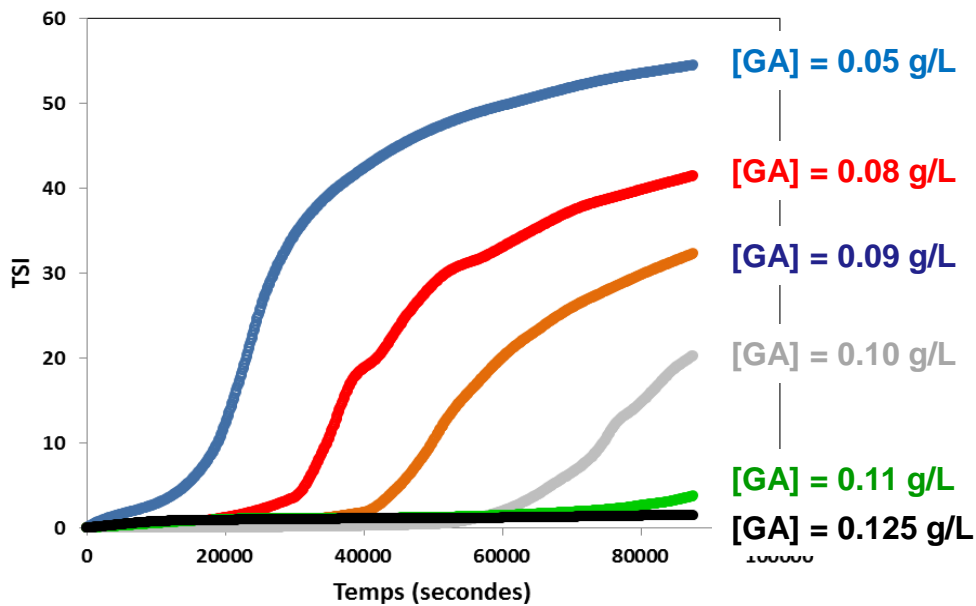
Cinétique de déstabilisation de la fraction minérale

Solution hydro-alcoolique + hexacyanoferrate de fer + CaCl_2



$$TSI = \sum_i \frac{\sum h |scan_i(h) - scan_{i-1}(h)|}{H}$$

Déstabilisation de la fraction minérale et concentration en gomme d'Acacia



Structure des fractions macromoléculaires de la gomme d'Acacia

Composition

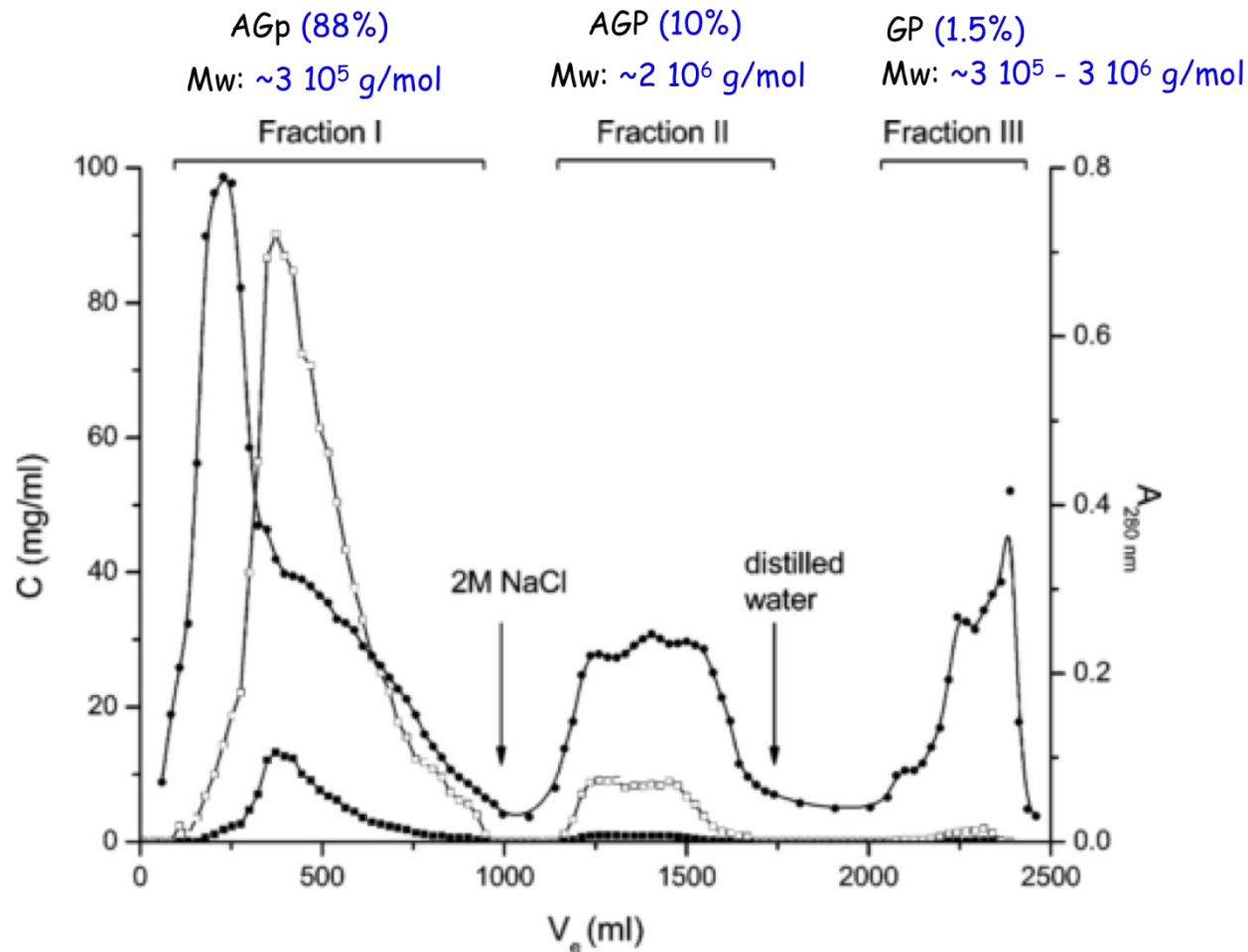
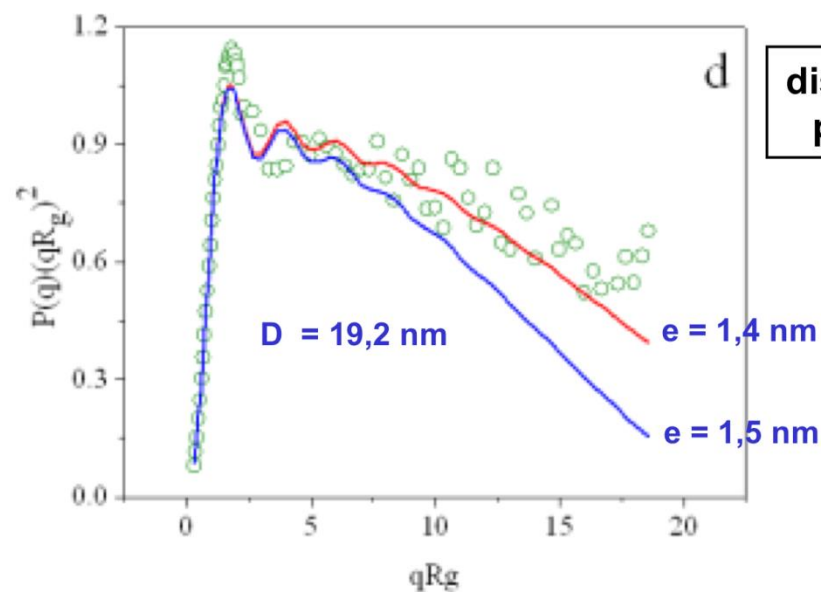
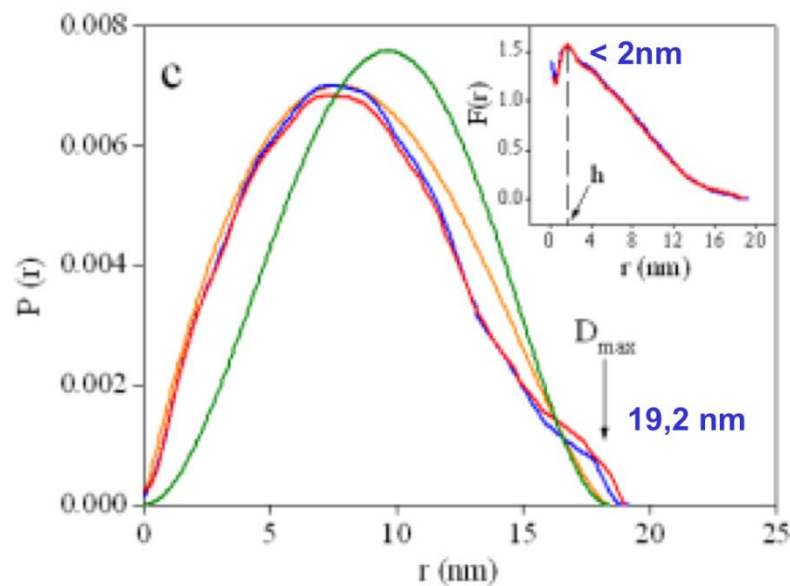
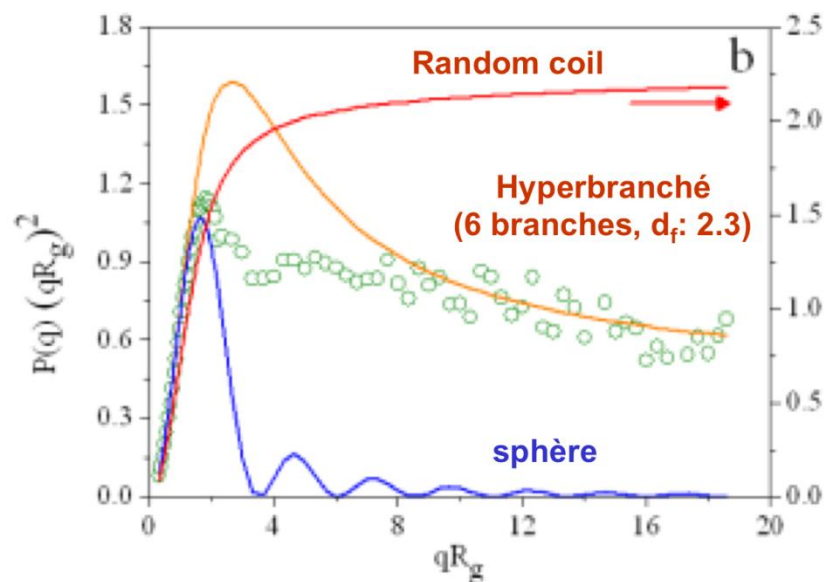
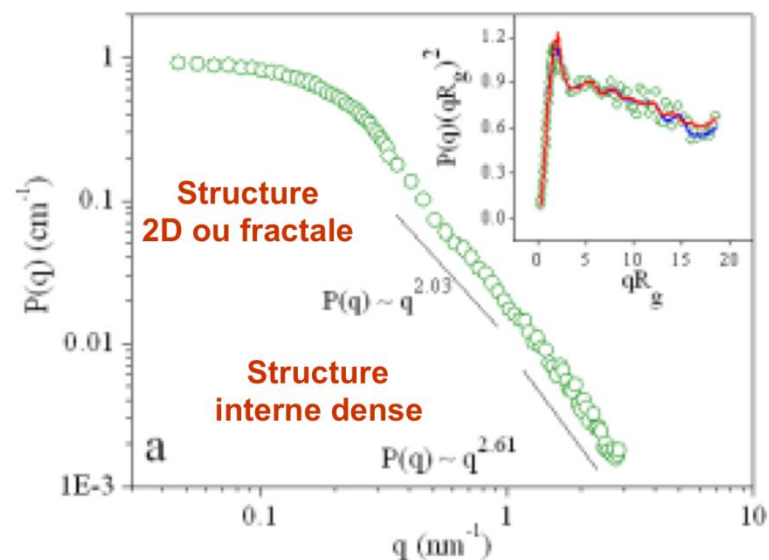


Figure 1. Elution curve of Acacia gum (25 g in 225 mL of 4.2 M NaCl) following fractionation by hydrophobic interaction chromatography on Phenyl-Sepharose CL-4B. Molecular fractions were eluted using 4.2 M NaCl (808 mL), 2 M NaCl (808 mL), and distilled water (1215 mL). Left traces: neutral sugars (\square) and uronic acids (\blacksquare) concentration C (mg/mL). Right trace: $A_{280\text{ nm}}$ (\bullet).

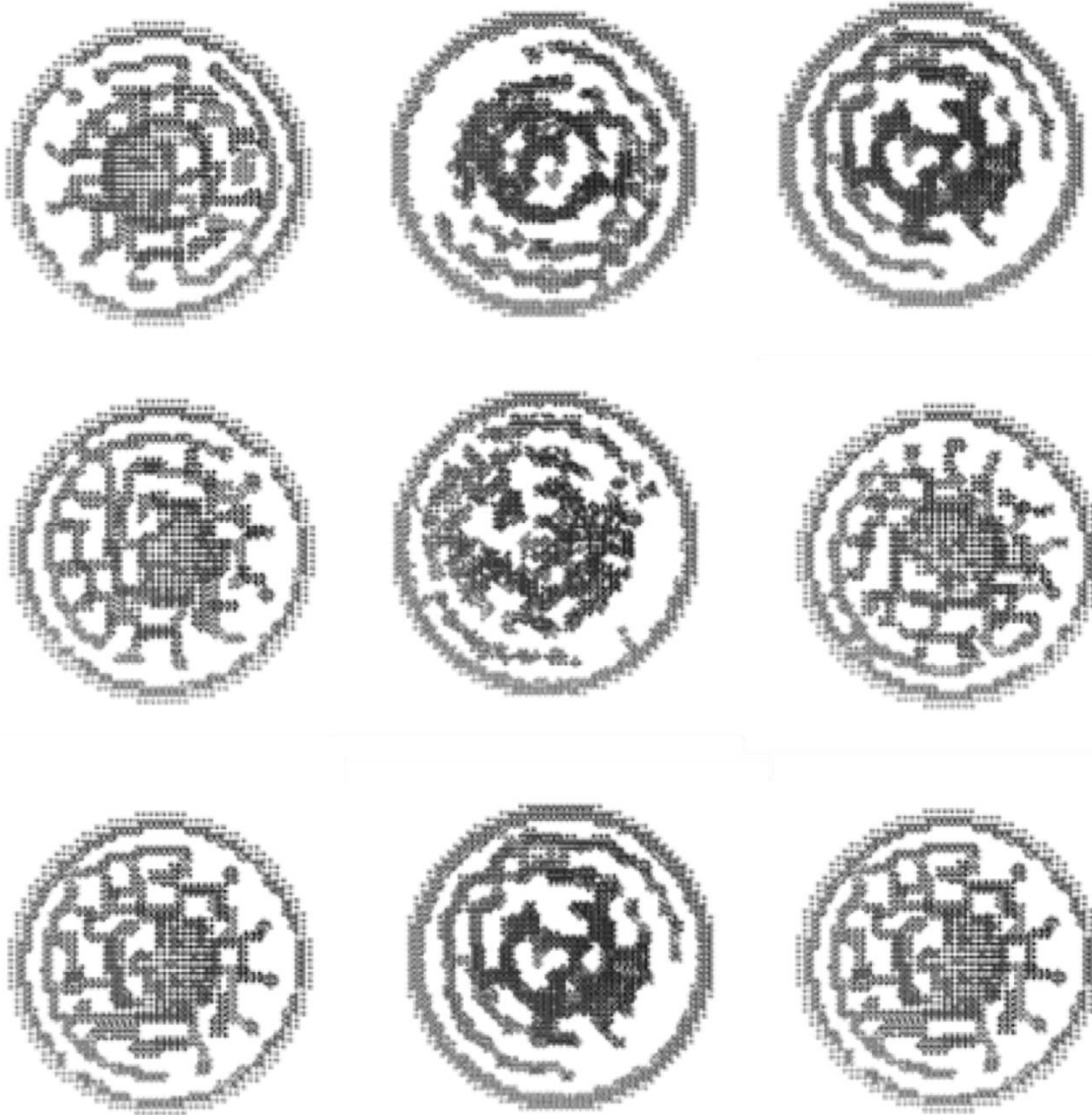
Structure 3D de l'arabinogalactan-peptide (fraction majeure – $M_w \sim 300\,000$ g/mol)

IFT

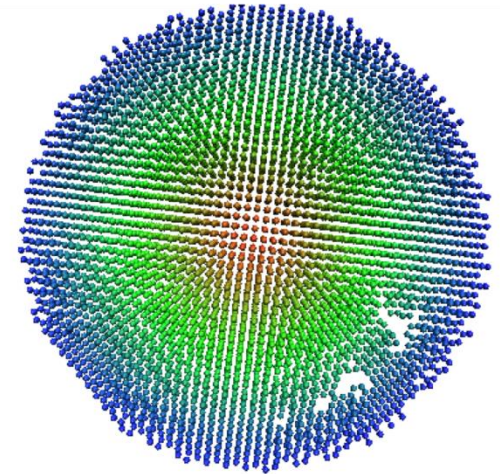


Structure de l'AG-peptide

Différents runs

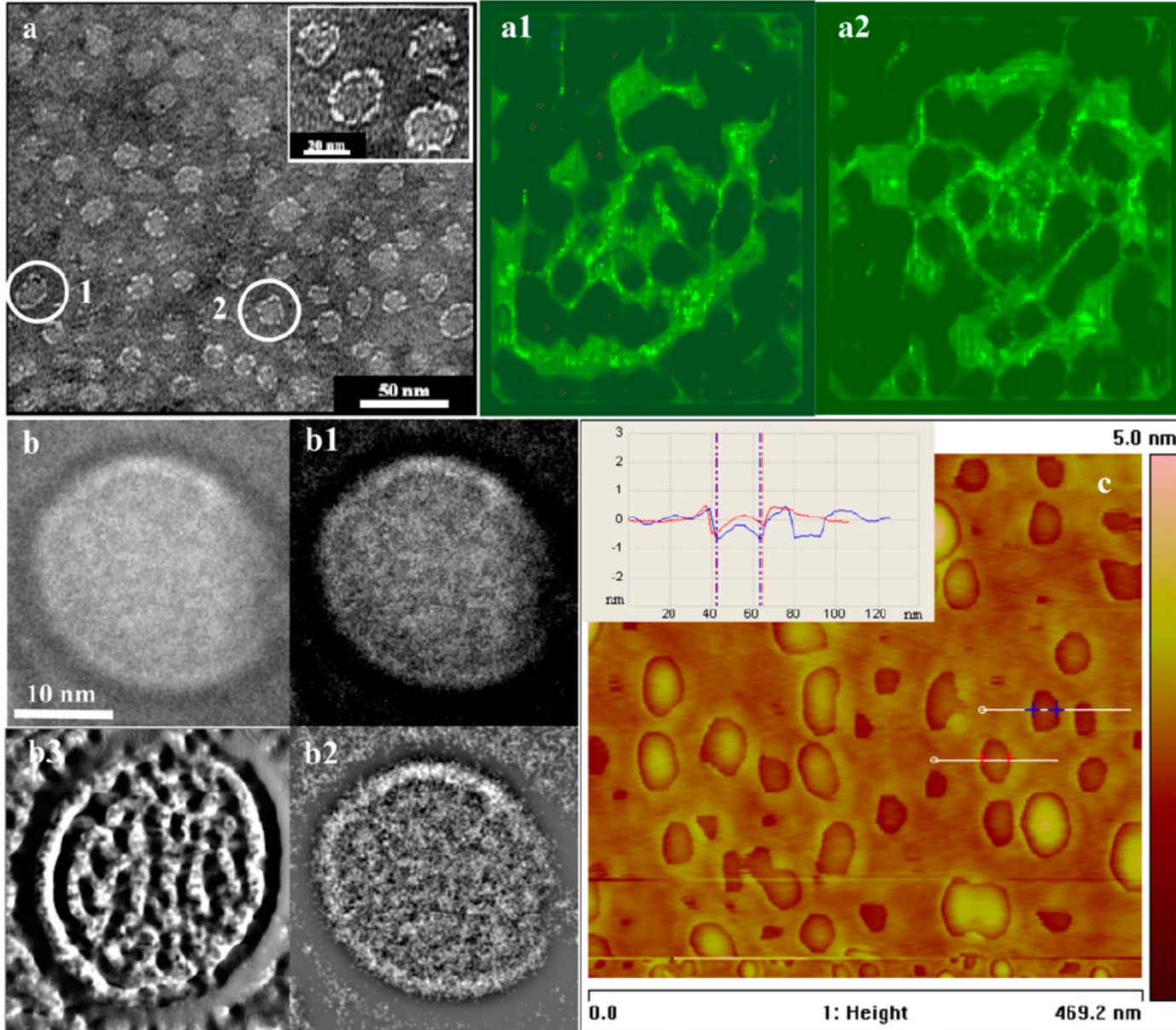


Modèle moyenné



Structure de l'AG-peptide

Comparaison modèle 3D model - microscopie



AFM

$e = 1 \text{ nm}$

$D = 20 \text{ nm}$

Pas de propriétés
viscoélastiques

(Images de phase et
Topologiques
similaires)

Structure de l'AG-peptide

Comparaison modèle 3D model - microscopie

