Lecture Notes: Ray and Matter

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Contents

CHAPTER 1

Introduction

Short summary:

Focus on information gained from adsorption, reflection, or transmission of radiation of solid materials. How light propagate in linear media, what are absorption, dispersion and attenuation phenomena ? What is a structure factor and what is its relation to pair correlation functions ?

Long summary:

In the first part, I will focus on the problem of the propagation of an electromagnetic wave when the wavelength is large (UV, optical, etc.) compared to the interatomic distances. The problem of polarization of the medium in metals and in semiconductors (Drude, Lorentz, interband, etc.) will be discussed and surface plasmons which are longitudinal excitations at the SC-metal interface will be treated. Finally, we will discuss how we can localize light on length scales smaller than the wavelength (e.g. nanoparticles). This part will be completed by a section on the Kramers-Kronig relations that link reflectance to absorption. The second part of the course will focus on phenomena where the incident wavelength is much smaller, such that matter can be resolved to atomic scales. The problem of structure factors and their interpretation in terms of correlation functions (neutrons, X, etc.) will be discussed.

(1) Introduction : Microscopic approach to Maxwell's equations, properties of wave propagation in the vacuum
   (a) Wave propagation in the vacuum : Maxwell's equations;
   (b) Equations in Si and cgs units;
   (c) Canonical solutions: plane waves, spherical waves;
   (d) Polarization for monochromatic plane waves;
   (e) Energy;
   (f) Wave packet and group velocity.
(2) Electrodynamic of continuous media I : Propagation of electromagnetic waves in a medium, macroscopic Maxwell equations
   (a) Microscopic Maxwell equations;
   (b) Spatial and temporal averaging;
   (c) Averaged Maxwell equations and introduction to two auxiliary fields $\mathbf{P}$ and $\mathbf{H}$;
   (d) Matching conditions at interfaces;
(3) Electrodynamic of continuous media II:
   (a) Local response for non-magnetic, linear and homogeneous media (permitivity and and dialectric tensor);
   (b) The complex dialectric function and the refractive index N;
   (c) Boundary conditions.
(4) Semi-classical theory for ϵ
   (a) Drude absorption for free carriers in metals and semi-conductors;
      (i) Assumptions and components of the Drude model;

(ii) Real and imaginery parts of $\sigma(\omega)$ and $\epsilon(\omega)$;
(iii) Refractive index
(iv) Plasma frequency.
(b) Lorentz model for insulators;
(i) Dilute limits: the depolarizing field;
(ii) Real and imaginery parts of $\sigma(\omega)$ and $\epsilon(\omega)$;
(iii) Refractive index
(c) Surface plasmons at dialectric-metal interfaces.
(i) Bulk and surface plasmons;
(ii) Examples of nano-plasmonics.
(5) Introduction to Kramers-Kronig relations;
(a) Necessity for a relation between absorption and dispersion;
(b) Kramers-Kronig integrals in linear, isotropic media;
(c) Fourier transformation and frequency domain;
(d) The complex ω plane: The Lorentz oscillator;
(e) Use of the Cauchy theorem and Kramer-Kronig relations.
(6) Structure and scattering: Dynamic correlation and response.
(a) Elementary scattering theory - Bragg's law;
(b) Photons, neutrons or electrons;
(c) Correlation functions in liquids, gases and crystalline solid.

Why ray-matter interaction is important ?

(1) Can build new devices (mirrors, sensors, multi-fonctionnal particles ...) for a wealth of applications. This is trendy subject:
   (a) Fast commutable devices using multifunctional materials (i.e. materials where you can control properties by light) and nanostructured materials;
   (b) New tools for biomolecular manipulation : Optical tweezers (Nobel prize in chemistry, 2018);
   (c) New tools for labeling, detection, drug delivery, theranostics etc. using metallic nanoparticles (enhancement of the electromagnetic field intensities due to the coupling between the photons and an excitation called plasmon, see SERS effect).

(2) New insights about the low energy excitation which control and govern the properties of the materials. As shown below, everything depends on the wavelength. Typical excitations in Solid Stat physics are in the $1 - 10$ meV range. There are obvious exceptions. A typical band gap in a semiconductor is about 1 eV (1.1 for Si). The plasma frequency for Silver is about 3.8 eV. To understand why the plasma fgrequency is important, recall that Silver is good metal with a lot of conduction electrons. These electrons form a plasma which can oscillate (there are positive ions). This plasma is highly reflective below the plasma frequency. Silver is a very poor reflector in the UV range.

(3) Ray-Matter interaction also concerns rays whose wavelength is of the order of the interatomic distances.
   (a) X-ray diffraction (ESRF) is essential for determining structure factors;
   (b) Neutron scattering (thermal neutrons at the ILL have a wavelength of the order of 2 Å.). Ideal to probe optical phonons, spin and charge density waves etc.

References

To compose this course, I used the following references:

(1) Optical effects in Solids, D.B. Tanne, Cambridge Universiyt Press, 2019[9];
(2) Modern Electrodynamics, A. Zangwill, Cambridge University Press, 2012[11];
(3) Electrodynamique des milieux continus, E. M. Landau and E. Lifschitz, Mir, 2019[4];
(4) Principles of Condensed Matter, P.M. Chaikin and T.C. Lubensky, Cambridge University Press, 1995[2];
(5) Solid State Physics, N. Ashcroft and D. Mermin, Saunders College Publishing, 1976;
(6) Principles of Electronics Materials and Devices, SZ. Kasap, McGraw-Hill, 2018;
(7) Plasmonics: Fundamental and applications, S. Maier, Springer, 2007[5].

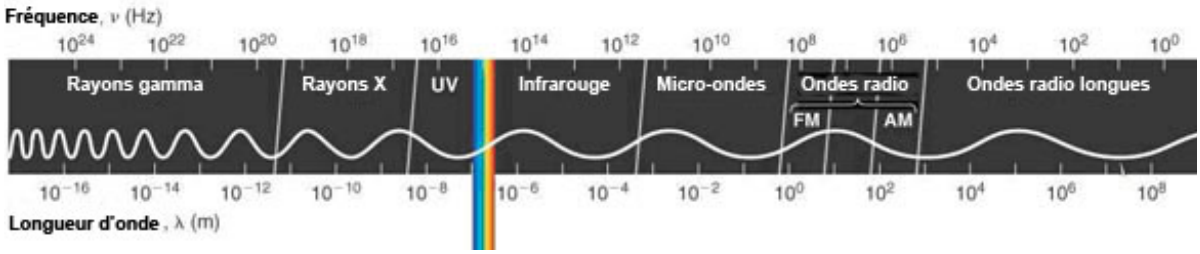

FIGURE 1. Electromagnetic spectrum.

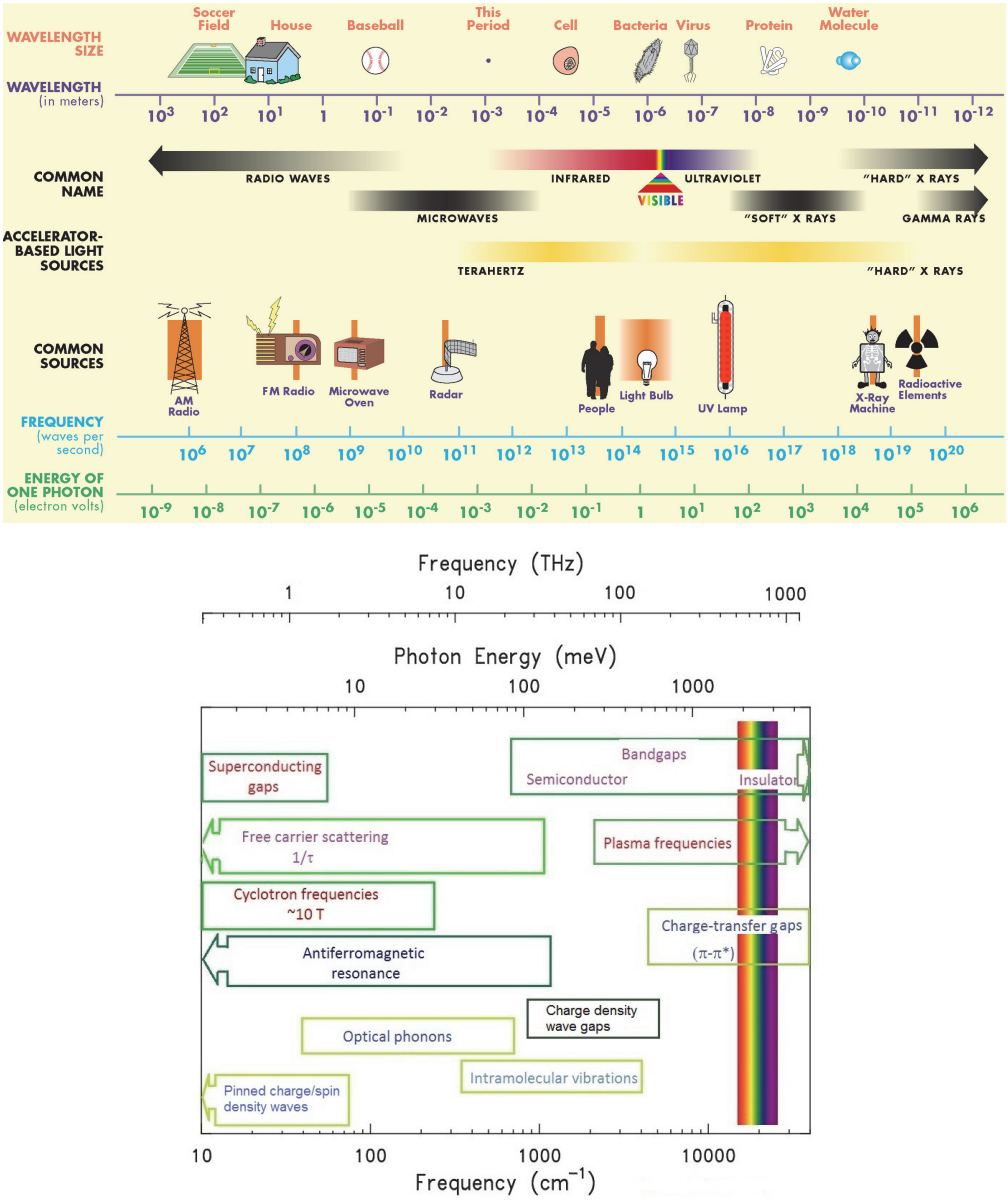

FIGURE 2. Chart for optical processes in solids, after Ref.[9].

CHAPTER 2

Maxwell equations in the vacuum

1. Summary

(1) Microscopic approach to Maxwell equations;
(2) Properties of waves in the vacuum;
(3) Polarisation.

2. Introduction

We are interested in cases where the distribution of electrical charges and electrical current are time dependent. As a result of theses variations, there is an electromagnetic wave. Since waves are not necessarily monochromatic, we use Fourier decomposition for the electrical field

$$\mathbf{E}(\mathbf{r},t)=\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}e^{-i\omega t}\tilde{\mathbf{E}}(\mathbf{r},\omega) \tag{1}$$

and for the magnetic field

$$\mathbf{B}(\mathbf{r},t)=\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}e^{-i\omega t}\tilde{\mathbf{B}}(\mathbf{r},\omega) \tag{2}$$

Using complex number is a mathematical commodity and both fields are real quantities

$$\mathbf{E}(\mathbf{r},t)\to \mathrm{Re}\left[\mathbf{E}(\mathbf{r})e^{-i\omega t}\right] \tag{3}$$

As discussed in the preceding chapter, the wave frequency

$$\nu=\frac{\omega}{2\pi} \tag{4}$$

and the wave length

$$\lambda=\frac{c}{\nu} \tag{5}$$

cover a very large spectrum from $10^{-16}m$ (gamma rays) to $10^{8}m$ (radiowaves).

REMARK 1. *This is a mathematical note. We will often use the $\delta(x-x')$ distribution. This δ can be understood as an operator in the space of well-behaved functions $f(x)$ such that for any $f(x)$*

$$\delta : f(x)\to f(0) \tag{6}$$

and this operation is always written as

$$\int dx\, f(x)\delta(x-x')=f(x') \tag{7}$$

The reason for this, is that the distribution $\delta(x)$ can be understood as the limit of a sequence of functions which become more and more highly peaked at the point where its argument vanishes. An example is

$$\delta(x)=\lim_{n\to\infty}\frac{n}{\sqrt{\pi}}\exp\left\{-n^2x^2\right\} \tag{8}$$

since we have for any $f(x)$

$$\lim_{n\to\infty}\frac{n}{\sqrt{\pi}}\int dx\, f(x)\exp\left\{-n^2x^2\right\}=f(0) \tag{9}$$

Using Fourier transform, we also have

$$\delta(x) = \frac{1}{2\pi}\int dk\, e^{ikx} \tag{10}$$

since, for any $f(x)$,

$$\int dx\, f(x)\delta(x) = \frac{1}{2\pi}\int dk \int dx\, e^{ikx} f(x) = \frac{1}{2\pi}\int dk \tilde{f}(k) = f(0) \tag{11}$$

where the last equality is simply the definition of the inverse Fourier transform of $f(x)$ taken at $x = 0$.

3. Maxwell equation

We assume that matter is simply the sum of point like particles in vacuum. If q_i is the charge of type i particle with position $\mathbf{r}_i(t)$, there is a charge density which depends on position, $\mathbf{r}$ and time, t, as:

$$\rho_m(\mathbf{r}, t) = \sum_i q_i \delta(\mathbf{r} - \mathbf{r}_i(t)) \tag{12}$$

where the δ-distribution of charges obeys the rule (the integral runs over a volume element $\Delta\Omega$)

$$\int_{\Delta\Omega} d^3r\, \delta(\mathbf{r} - \mathbf{r}_i(t)) = 1 \quad \text{iff} \quad \mathbf{r}_i(t) \in \Delta\Omega \tag{13}$$

Associated with density (13), there is a current density

$$\mathbf{j}_m(\mathbf{r}, t) = \sum_i q_i \mathbf{v}_i \delta(\mathbf{r} - \mathbf{r}_i(t)) \tag{14}$$

where $\mathbf{v}_i$ is the velocity of the charged particle of type i.

To describe the propagation of waves, we will use the following the ∇ (nabla) operator

(1) Gradient: If $V(x, y, z)$ is a scalar field, the gradient of V is a vector:

$$\boldsymbol{\nabla} V = \frac{\partial V}{\partial x}\hat{\mathbf{u}}_x + \frac{\partial V}{\partial y}\hat{\mathbf{u}}_y + \frac{\partial V}{\partial z}\hat{\mathbf{u}}_z \tag{15}$$

where $\hat{\mathbf{u}}_{x,y,z}$ are unit vectors.

(2) Divergence: If $\mathbf{A}$ is a vector with components $(A_x(x, y, z), A_y \ldots, A_z \ldots)$ all functions of (x, y, z), the divergence of $\mathbf{A}$ is a scalar:

$$\boldsymbol{\nabla} \cdot A = \frac{\partial A_x}{\partial x} + \frac{\partial A_y}{\partial y} + \frac{\partial A_z}{\partial z} \tag{16}$$

(3) Rotational If $\mathbf{A}$ is a vector with components $(A_x(x, y, z), A_y \ldots, A_z \ldots)$ all functions of (x, y, z), the rotational (curl) is a vector:

$$\boldsymbol{\nabla} \times \mathbf{A} = (\nabla_x, \nabla_y, \nabla_z) \wedge \mathbf{A} \tag{17}$$

Exercice 3.1. *Compute the normal vector $\hat{\mathbf{n}}$ to the ellipsoïdal surfaces defined by the constant values of*

$$V(x, y, z) = \frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} \tag{18}$$

Check your result for $a = b = c$.

A very useful identity to remember is as follows

(19)

Divergence (Rotational (of a vector field)) = Rotational(Gradient (of a Scalar))) = 0 or DRG = 0

For the best or/and the worse, the are two unit systems. The SI and the CGS (centimeter, gram, second). To make or lives as simple or complicated as possible, the former is generally

used for waves in the vacuum. The latter is always used to describe waves in media. We, therefore, have to get used to both unit systems.

The microscopic Maxwell equations read as (the subscript m stands for microscopic. This will be useful in the next chapter where we will introduce local averages of microscopic field).

(1) SI (international system) :

$$\begin{aligned} \boldsymbol{\nabla}\cdot\mathbf{E} &= \frac{\rho_m}{\epsilon_0} \quad \boldsymbol{\nabla}\times\mathbf{E} = -\frac{\partial\mathbf{B}}{\partial t} \\ \boldsymbol{\nabla}\cdot\mathbf{B} &= 0 \quad \boldsymbol{\nabla}\times\mathbf{B} = \mu_0\mathbf{j}_m + \epsilon_0\mu_0\frac{\partial\mathbf{E}}{\partial t} \end{aligned} \tag{20}$$

with the condition[1]

$$\epsilon_0\mu_0 c^2 = 1 \tag{21}$$

(2) Gaussian CGS

$$\begin{aligned} \boldsymbol{\nabla}\cdot\mathbf{E} &= 4\pi\rho_m \quad \boldsymbol{\nabla}\times\mathbf{E} = -\frac{1}{c}\frac{\partial\mathbf{B}}{\partial t} \\ \boldsymbol{\nabla}\cdot\mathbf{B} &= 0 \quad \boldsymbol{\nabla}\times\mathbf{B} = \frac{4\pi}{c}\mathbf{j}_m + \frac{1}{c}\frac{\partial\mathbf{E}}{\partial t} \end{aligned} \tag{22}$$

In CGS, $\mathbf{E}$ and $\mathbf{B}$ have the same units. In CGS, the unit of a force is a dyne ($1\,dyne = 10^{-5}\,N$), and energies are measured in erg ($1\,erg = 10^{-7}\,J$)

Let us also introduce the Laplacian operator for any vector field $\mathbf{E} = (E_x, E_y, E_z)$

$$\nabla^2\mathbf{E} = \nabla^2 E_x\hat{\mathbf{u}}_x + \nabla^2 E_y\hat{\mathbf{u}}_y + \nabla^2 E_z\hat{\mathbf{u}}_z \tag{23}$$

with the usual definition for the Laplacian for each coordinate E_x, E_y, E_z

$$\nabla^2 E_x = \frac{\partial^2 E_x}{\partial x^2} + \frac{\partial^2 E_x}{\partial y^2} + \frac{\partial^2 E_x}{\partial z^2} \tag{24}$$

For practical purposes, these equations are only useful if one wants to describe wave propagation outside the medium where the sources are located. It is indeed totally illusory and useless to describe the propagation of light in materials using these equations. In the next chapter, we will see how this problem can be overcome by performing local averaging. In the the vacuum $\rho_m = 0$ and $\mathbf{j}_m = \mathbf{0}$, so that the Maxwell equations can be further simplified using

$$\boldsymbol{\nabla}\times(\boldsymbol{\nabla}\times\mathbf{E}) = \boldsymbol{\nabla}\times\left(-\frac{\partial\mathbf{B}}{\partial t}\right) = -\frac{\partial}{\partial t}\left[\boldsymbol{\nabla}\times\mathbf{B}\right] = -\epsilon_0\mu_0\frac{\partial^2\mathbf{E}}{\partial t^2} \tag{25}$$

But

$$\boldsymbol{\nabla}\times(\boldsymbol{\nabla}\times\mathbf{E}) = \boldsymbol{\nabla}(\boldsymbol{\nabla}\cdot\mathbf{E}) - \nabla^2\mathbf{E} \tag{26}$$

so that

$$\nabla^2\mathbf{E} - \frac{1}{c^2}\frac{\partial^2\mathbf{E}}{\partial t^2} = 0 \tag{27}$$

In the same way, we have the symmetric equation for the magnetic field

$$\nabla^2\mathbf{B} - \frac{1}{c^2}\frac{\partial^2\mathbf{B}}{\partial t^2} = 0 \tag{28}$$

where the ∇^2 operator is often written as the Δ operator.

[1]We have :

$$\epsilon_0 = 8.85410^{-12} F\,m^{-1}$$
$$\mu_0 = 4\pi 10^{-7} H\,m^{-1}$$

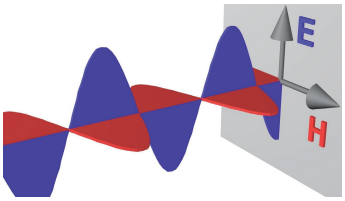

FIGURE 1. EM wave in vacuum.

EXERCICE 3.2. *Consider a plane wave*

$$\mathbf{E}(\mathbf{r},t) = \mathrm{Re}\left[e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}\mathbf{E}_0\right] \tag{29}$$

Show:

(1) $\boldsymbol{\nabla}\cdot\mathbf{E} = \mathrm{Re}\left[i\mathbf{k}\cdot\mathbf{E}_0 e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}\right]$;
(2) $\boldsymbol{\nabla}\times\mathbf{E} = \mathrm{Re}\left[i\mathbf{k}\wedge\mathbf{E}_0 e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}\right]$.
(3) Conclude that the Maxwell equations in the vacuum read as

$$\begin{aligned} \omega\mathbf{B} &= \mathbf{k}\wedge\mathbf{E} \quad ; \quad \mathbf{k}\cdot\mathbf{B} = 0 \\ -\omega\mathbf{E} &= c^2\mathbf{k}\wedge\mathbf{B} \quad ; \quad \mathbf{k}\cdot\mathbf{E} = 0 \end{aligned} \tag{30}$$

From this, one concludes:

(1) $\mathbf{E}$ *and* $\mathbf{B}$ *are perpendicular to each other and they are both perpendicular to* $\mathbf{k}$*. This is a TEM (transverse electromagnetic mode) mode;*
(2) ($\mathbf{E}$, $\mathbf{B}$, $\mathbf{k}$) *form a direct frame;*
(3) $\mathbf{E}$ *and* $\mathbf{B}$ *have the same phase.*

4. Canonical solutions in the vacuum

4.1. Plane waves. Consider an equation of the form

$$\nabla^2 w - \frac{1}{c^2}\frac{\partial^2 w}{\partial t^2} = 0 \tag{31}$$

and look for a solution which depends on a single variable, say z. We, therefore, look for a solution of

$$\frac{\partial^2 w}{\partial z^2} - \frac{1}{c^2}\frac{\partial^2 w}{\partial t^2} = 0 \tag{32}$$

The last equation can be written as

$$\left[\frac{\partial}{\partial z} + \frac{1}{c}\frac{\partial}{\partial t}\right]\left[\frac{\partial}{\partial z} - \frac{1}{c}\frac{\partial}{\partial t}\right] w = 0 \tag{33}$$

Let us change variables and define

(1) $\xi = z + ct$;
(2) $\eta = z - ct$.

Using the chain rules, one obtains:

$$\begin{aligned} \frac{\partial}{\partial \xi} &= \frac{1}{2}\left[\frac{\partial}{\partial z} + \frac{1}{c}\frac{\partial}{\partial t}\right] \\ \frac{\partial}{\partial \eta} &= \frac{1}{2}\left[\frac{\partial}{\partial z} - \frac{1}{c}\frac{\partial}{\partial t}\right] \end{aligned} \tag{34}$$

with

$$\frac{\partial^2 w}{\partial \xi \partial \eta} = \frac{\partial^2 w}{\partial z^2} - \frac{1}{c^2}\frac{\partial^2 w}{\partial t^2} = 0 \tag{35}$$

The general solution of this equation is of the form

$$g(\eta) + f(\xi) = g(z-ct) + f(z+ct) \tag{36}$$

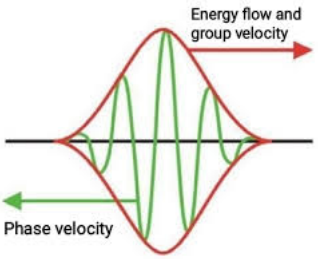

FIGURE 2. Group and phase velocity.

where $g(\eta)$ and $f(\xi)$ are two arbitrary functions.

By definition, a plane wave is a solution which can we written as

$$\mathbf{E}(z,t) = \mathbf{E}^+(z-ct) + \mathbf{E}^-(z+ct) \tag{37}$$

where the $+$ sign refers to a wave propagating towards the $z>0$ half-space at speed c, and the $-$ sign refers to a wave which propagates towards the $z>0$ half-space at a speed c.

For monochromatic waves, we retain only one Fourier component

$$\mathbf{E}^+(z-ct) = \mathbf{E_0} e^{i(kz-\omega t)} \tag{38}$$

which is a solution iff $\omega = ck$. The wave vector is defined as $\mathbf{k} = k\hat{\mathbf{u}}_z$ and we see from $\boldsymbol{\nabla}\cdot\mathbf{E}^+ = i\mathbf{k}\cdot\mathbf{E}^+ = 0$ that $\mathbf{E}^+$ is perpendicular to $\mathbf{k}$.

For a planar wave, the phase is given by

$$\phi = kz - \omega t \tag{39}$$

and is a constant in the plane $z = \omega/kt$. From dz/dt, this plane move at velocity $\omega/k = c$. In general, the ratio ω/k defines the phase velocity.

5. Group velocity

We have already defined what we mean by phase velocity. To go further, we consider a wave packet. A wave packet is constructed from an overall envelope function inside which one has an oscillating pattern.

One observes, see Fig. 2:

(1) The envelope can move to left or to the right;
(2) The oscillating pattern inside the envelope can move to the right or to the left even if the envelope is at rest.

The speed at which the oscillating pattern moves inside the envelope is the phase velocity we have already defined. To define the speed at which the envelope is moving (ie the group velocity), one has first to define what we mean by a wave packet.

A wave packet is the sum of monochromatic waves where $\omega(k)$ is not necessarily a linear function of k as in the vacuum (we will encounter this situation when we will study dispersive media). We assume, however, that $\omega(k)$ is smooth We write

$$u(\mathbf{r},t) = \frac{1}{(2\pi)^3}\int d^3k \hat{u}(k) e^{i(\mathbf{k}\cdot\mathbf{r}-\omega(k)t)} \tag{40}$$

where $\hat{u}(k)$ is peaked around some value. The usual choice is to take a Gaussian

$$\hat{u}(k_x) = \frac{1}{\sqrt{\pi\Delta k_x^2}} e^{-(k_x-k_{0,x})^2/\Delta k_x^2} \tag{41}$$

Using

$$\int ds e^{as-bs^2} = \sqrt{\frac{\pi}{b}} e^{a^2/4b} \tag{42}$$

one finds a Gaussian envelope in the physical space with:

$$u(x,0) = e^{ik_{0,x}} e^{-x^2/(\Delta x)^2} \quad \text{with} \quad \Delta x = 2/\Delta k_x \tag{43}$$

Since the Gaussian is strongly peaked around k_0, we can Taylor expand the dispersion relation $\omega(k)$ (dispersion means changes as a a function of $|k|$)

$$\omega(k) = \omega(k_0) + \left.\frac{d\omega}{dk}\right|_{k_0} (k - k_0) \tag{44}$$

and define the group velocity

$$\mathbf{v}_g = \left.\frac{d\omega}{dk_x}\right|_{k_{0,x}} \hat{\mathbf{u}}_{k_x} + \left.\frac{d\omega}{dk_y}\right|_{k_{0,y}} \hat{\mathbf{u}}_{k_y} + \left.\frac{d\omega}{dk_z}\right|_{k_{0,z}} \hat{\mathbf{u}}_{k_z} \tag{45}$$

We see that

$$u(x,t) = e^{i(k_0 x - \omega(k_0)t)} \frac{1}{(2\pi)^3} \int d^3k \hat{u}(k) e^{i((\mathbf{k}-\mathbf{k_0})\cdot(\mathbf{r}-v_g t)} \tag{46}$$

or

$$u(x,t) = e^{i(k_0 x - \omega(k_0)t)} \psi(x - v_g t) \tag{47}$$

is the product of two terms. The first is the usual monochromatic wave at $k = k_0$. The second does not change if we imagine that $x = v_g t$, or $dx/dt = v_g$. In vacuum $v_g = c$ and is equal to the phase velocity. In dispersive matter, this is not true.

5.1. Spherical waves. Another canonical solution is the spherical wave which only depend on the radial distance $r = |\mathbf{r}|$ and on t. The wave equation imposes a solution in the form

$$\mathbf{E}(r,t) = \frac{1}{r}\mathbf{E}^+(t - rc) + \frac{1}{r}\mathbf{E}^-(t + rc) \tag{48}$$

where the first is a divergent spherical wave (the other is a convergent one). For a divergent wave in the vacuum

$$\mathbf{E}(r,t) = \frac{1}{r} \operatorname{Re}\left[E_0 e^{i(kr-\omega t)}\right] \hat{\mathbf{u}}_r \tag{49}$$

6. Polarisation

The most general form for a propagating wave in the z-direction is

$$\begin{aligned} E_x &= E_x^0 e^{i(kz-\omega t+\phi_x)} \\ E_y &= E_y^0 e^{i(kz-\omega t+\phi_y)} \\ E_z &= 0 \end{aligned} \tag{50}$$

If the light is emitted by a natural source (star, light bubbles, etc.), there is no relation between the phases ϕ_x and ϕ_y. In that case, the difference $\phi_x - \phi_y$ is a stochastic variable which varies from time to time.

However, if $\phi_x - \phi_y$ is constant in time, on says that light is polarized. We have:

- If $\phi_x - \phi_y = p\pi$, with p integer, then we says that light is linearly polarized;
- If $\phi_x - \phi_y = \pm\pi/2$ and $E_x^0 = E_y^0$, the polarization is said to be circular;
- Otherwise, for constant $\phi_x - \phi_y$, the polarisation is said to be elliptical.

REMARK 2. *Ellipsometry measures a change in polarization as light reflects or transmits from a material structure. The measured response depends on optical properties and thickness of individual materials. Thus, ellipsometry is primarily used to determine film thickness and optical constants. Since the 1960s, as ellipsometry developed to provide the sensitivity necessary to measure nanometer-scale layers used in microelectronics, interest in ellipsometry has grown steadily. This widespread use is explained by increased dependence on thin films in many*

areas and the flexibility of ellipsometry to measure most material types: dielectrics, semiconductors, metals, superconductors, organics, biological coatings, and composites of materials (see: https://www.jawoollam.com/resources/ellipsometry-tutorial/what-is-ellipsometry).

7. Gauge fields

In Electrodynamics one introduces a scalar potentiel $V(x,y,z,t)$ and a vector potential $\mathbf{A}(x,y,z,t)$

$$\begin{aligned}\mathbf{E} &= -\boldsymbol{\nabla} V - \frac{\partial \mathbf{A}}{\partial t}\\ \mathbf{B} &= +\boldsymbol{\nabla}\times\mathbf{A}\end{aligned} \tag{51}$$

To understand why it may be useful, recall DRG = 0 !

(1) If $\boldsymbol{\nabla}\cdot\mathbf{B}=0$, then this equation is automatically satisfied if $\mathbf{B}=+\boldsymbol{\nabla}\times\mathbf{A}$;
(2) From $\boldsymbol{\nabla}\times\mathbf{E}=-\partial\mathbf{B}/\partial t$, we have $\boldsymbol{\nabla}\times(\mathbf{E}+\partial\mathbf{A}/\partial t)=0$ which is automatically satisfied if $\mathbf{E}+\partial\mathbf{A}/\partial t$ is a gradient.

These two conditions do not specify what are V and $\mathbf{A}$ and one has to introduce a condition (called a gauge condition). The popular choice is the Coloumb jauge

$$\boldsymbol{\nabla}\cdot\mathbf{A}+\epsilon_0\mu_0\frac{\partial V}{\partial t}=0 \tag{52}$$

8. Energy - Poynting vector

In electrostatics $1/(2\epsilon_0)\mathbf{E}$ is the energy density for the electrical field $\mathbf{E}$. The magnetic energy density is $1/(2\mu_0)\mathbf{B}^2$. We establish a conservation law for the total energy density of an EM wave.

Assume no current. From

$$\boldsymbol{\nabla}\times\mathbf{B}=\epsilon_0\mu_0\frac{\partial\mathbf{E}}{\partial t} \tag{53}$$

which implies

$$\mathbf{E}\cdot(\boldsymbol{\nabla}\times\mathbf{B})=\epsilon_0\mu_0\mathbf{E}\cdot\frac{\partial\mathbf{E}}{\partial t} \tag{54}$$

But

$$\boldsymbol{\nabla}\cdot(\mathbf{E}\wedge\mathbf{B})=\mathbf{B}\cdot(\boldsymbol{\nabla}\times\mathbf{E})-\mathbf{E}\cdot(\boldsymbol{\nabla}\times\mathbf{B}) \tag{55}$$

which means

$$-\frac{1}{\mu_0}\boldsymbol{\nabla}\cdot(\mathbf{E}\wedge\mathbf{B})=\epsilon_0\mathbf{E}\cdot\frac{\partial\mathbf{E}}{\partial t}+\mathbf{B}\cdot\frac{\partial\mathbf{B}}{\partial t} \tag{56}$$

This equation can be interpreted as a continuity equation. To see this, recall that if a quantity is conserved (for example the concentration of some molecules)

$$\frac{\partial c}{\partial t}+\boldsymbol{\nabla}\cdot\mathbf{j}=0 \tag{57}$$

where $\mathbf{j}$ is the current of particules. We try to write down an equation like this one in vacuum (when light propagates in matter, energy is not conserved).

Without electrical current current, the total energy density of the EM wave

$$u=\frac{1}{2}\epsilon_0\mathbf{E}^2+\frac{\mathbf{B}^2}{2\mu_0} \tag{58}$$

is obviously conserved. We expect, therefore, an equation of motion of the form

$$\frac{\partial u}{\partial t}+\boldsymbol{\nabla}\cdot\boldsymbol{\Pi}=0 \tag{59}$$

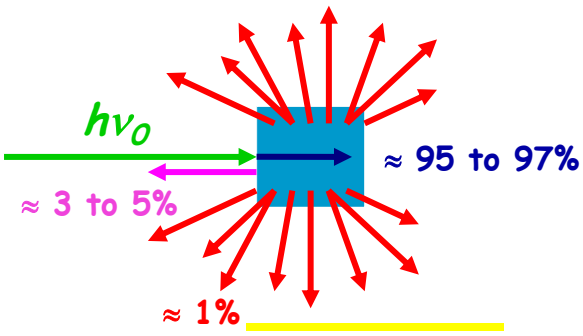

FIGURE 3. Rayleigh scattering.

Comparing with (56) gives

$$\mathbf{\Pi} = \frac{1}{\mu_0}\mathbf{E} \wedge \mathbf{B} \tag{60}$$

as a solution. The vector $\mathbf{\Pi}$ is called the Poynting vector.

REMARK 3. *Using the divergence theorem, this conservation equation can written as (for all surfaces S enclosing a volume V)*

$$\iint_S \mathbf{\Pi} \cdot \hat{\mathbf{n}}\, dS + \frac{dU}{dt} = 0 \qquad with \qquad U = \int_V u\, dv \tag{61}$$

EXERCICE 8.1. *Rayleigh scattering: Shine at frequency ν_0. Show $I_{scattered} \propto \nu_0^4$.*

9. Appendix : Mathematical Intermezzo

9.1. The divergence theorem.

From calculus, we know

$$\int_a^b f(x)dx = F(b) - F(a) \tag{62}$$

where $f(x)$ is the derivative of $F(x)$. The following theorem generalizes this formula when the integral is taken over a 3D-volume element.

THEOREM 9.1. *Let $\mathbf{F}(\mathbf{r})$ be a vector function defined in a volume V enclosed by a surface S. The surface S is not part of the volume but is tangent to V at all points. Then,*

$$\iiint_V d^3r\, \boldsymbol{\nabla} \cdot \mathbf{F}(\mathbf{r}) = \iint_S dS\, \hat{\mathbf{n}} \cdot \mathbf{F}(\mathbf{r}) \tag{63}$$

where the unit vector $\hat{\mathbf{n}}$ is the outward normal.

EXERCICE 9.1. *Let S be surface that bounds a volume V. Shows*

$$\iint dS\, \hat{\mathbf{n}} \cdot \hat{\mathbf{u}}_r = 0 \qquad \frac{1}{3}\iint dS\, \hat{\mathbf{n}} \cdot \mathbf{r} = V \tag{64}$$

9.2. The Stokes theorem.

THEOREM 9.2. *Consider a vector function $\mathbf{F}(\mathbf{r})$ defined on a closed surface bounded by a closed curve $\mathcal{C}$. The curve and the surface are oriented by the corkscrew rule. Then,*

$$\iint dS\, \hat{\mathbf{n}} \cdot \boldsymbol{\nabla} \times \mathbf{F}(\mathbf{r}) = \oint_{\mathcal{C}} \mathbf{dl} \cdot \mathbf{F}(\mathbf{r}) \tag{65}$$

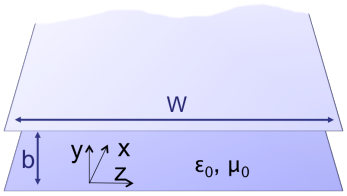

FIGURE 4. Geometry for a simple wave guide.

10. Waveguides

We have certainly all been familiar with the interruption of a radio broadcast while driving through a short tunnel, the end of the tunnel being visible. Why does this tunnel let electromagnetic waves pass at optical frequencies and not at radio frequencies?

EXERCICE 10.1. *We consider a monochromatic wave propagation along the* $\hat{\mathbf{u}}_z$ *direction (where* $W \gg d$*), see Fig. 4. We assume that the two metallic plates are perfect conductors and that they are separated by vacuum. Then,*

$$\Delta \mathbf{E} + \frac{\omega^2}{c^2}\mathbf{E} = 0 \tag{66}$$

with the boundary conditions

$$\mathbf{E}_{\parallel}(y = \pm b/2) = 0 \tag{67}$$

(1) Show that the transverse electric mode

$$\mathbf{E} = E_0 \cos(ky) e^{i\gamma z} e^{-i\omega t} \hat{\mathbf{u}}_z \tag{68}$$

is solution if γ *and* k *obeys some conditions.*

(2) we have seen that the TE propagation modes are fully characterized by a single integer p*. Give the phase velocity for each mode.*

(3) Show that there is a cutoff frequency ω_c *below which* γ *is a pure imaginary number. Can we have a propagating mode bellow this frequency ? In a gas station, the distance between the ground and the roof is about 5m. The cut-off frequency is then ? 30MHz. So the FM frequencies pass but the longwave ones do not.*

CHAPTER 3

Electrodynamic of continuous media - I

1. Summary

We write MACROSCOPIC Maxwell equations to understand how light propagates in linear media. What are dispersion, attenuation and absorption phenomena ?

2. Local averaging

Recall the Maxwell equations, see (98) or (100). The microscopic fields $\mathbf{E}_m$, $\mathbf{B}_m$ experience huge variations on the atomic or molecular scales. We are not interested in these short distance features but only in the long wave length limit. To get rid of these spurious variations, we use a procedure to perform local spatial averages.

At each point, consider a surrounding domain with size l such that

(1) $l \gg$ interatomic distances;
(2) $l \ll$ wavelength of the light used to probe the sample.

Call Ω the volume of the surrounding domain of a point P. Typically, the size l of Ω is of the order of a few tenth of nm.

If $F(\mathbf{r}, t)$ is a scalar field, define the average

$$< F(\mathbf{r}, t) >= \frac{1}{\Omega} \int_{\Omega} d^d r \, F(\mathbf{r}, t) \tag{69}$$

where the integral weights only the neighborhood of P in the volume Ω. Since the volume of the domain where we perform the integral is not infinite, the local average quantities depend on the position $\mathbf{r}$ of P. As a result of this averaging which eliminate all short distance fluctuations, one expects $< F(\mathbf{r}, t) >$ to be also a smooth function.

We have the following properties

$$\begin{aligned} < \partial_t F(\mathbf{r}, t) > &= \partial_t < F(\mathbf{r}, t) > \\ < \partial_x F(\mathbf{r}, t) > &= \partial_x < F(\mathbf{r}, t) > \end{aligned} \tag{70}$$

EXERCICE 2.1. *Mathematically, this procedure amounts to integrating with some weight function, say $w(x)$. In one dimension:*

$$< F(x, t) >= \int_{-\infty}^{+\infty} w(x - x') F(x', t) \tag{71}$$

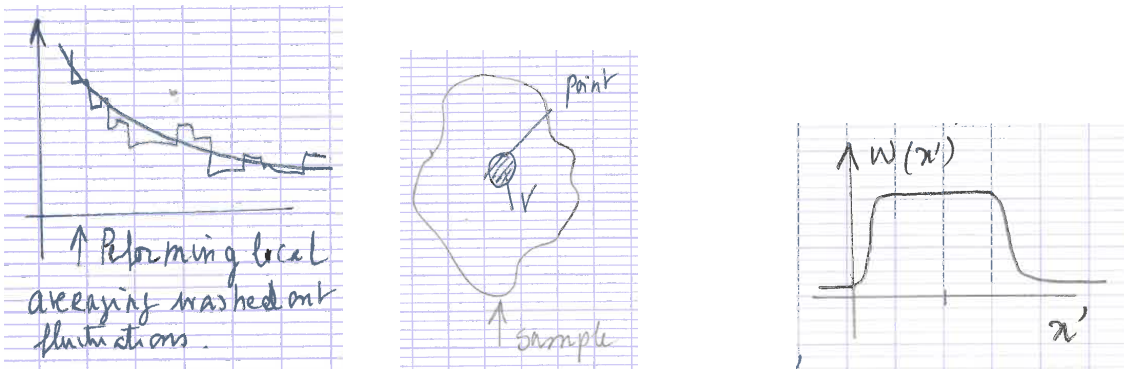

FIGURE 1

By integrating by parts, show the last equality in (70).

What we want to do is to write down the Maxwell equations for local averaged fields $\mathbf{E}(\mathbf{r},t) =< \mathbf{E}_m(\mathbf{r},t) >$ and $\mathbf{B}(\mathbf{r},t) =< \mathbf{B}_m(\mathbf{r},t) >$.

$$\begin{aligned} &\boldsymbol{\nabla}\cdot\mathbf{E} = \frac{<\rho_m>}{\epsilon_0} \qquad \boldsymbol{\nabla}\times\mathbf{E} = -\frac{\partial\mathbf{B}}{\partial t} \\ &\boldsymbol{\nabla}\cdot\mathbf{B} = 0 \qquad \boldsymbol{\nabla}\times\mathbf{B} = \mu_0 <\mathbf{j}_m> +\epsilon_0\mu_0\frac{\partial\mathbf{E}}{\partial t} \end{aligned} \tag{72}$$

3. Performing $< \rho_m >$: How the polarization P emerges

We assume electrical neutrality, meaning

$$\int d^3r < \rho_m >= \int d^3r\rho_m = 0 \tag{73}$$

where the integral is over the whole sample. Outside the sample, $\rho_m = 0$. If $< \rho_m >$ obeys (73), then there exists some vector field (to be determined) $\mathbf{P}$ such that

$$< \rho_m >= -\boldsymbol{\nabla}\cdot\mathbf{P} \tag{74}$$

where the $-$ signe is pure convenience. Outside the sample, $\mathbf{P} = 0$. Indeed, we have

$$\int d^3r < \rho_m >= -\int_{Boundary} d^2r\,\hat{\mathbf{n}}\cdot\mathbf{P} = 0 \tag{75}$$

since $\mathbf{P} = \mathbf{0}$ on the boundary because of continuity.

To understand why the vector $\mathbf{P}$ may be useful, consider the total dipolar moment

$$\mathbf{p} = \int d^3r\,\rho_m\mathbf{r} = \int d^3r\ <\rho_m>\mathbf{r} \tag{76}$$

Write

$$\mathbf{r} = x\hat{\mathbf{u}}_x + y\hat{\mathbf{u}}_y + z\hat{\mathbf{u}}_z = \sum_\alpha \alpha\hat{\mathbf{u}}_\alpha \tag{77}$$

We have

$$\mathbf{p} = -\sum_\alpha \hat{\mathbf{u}}_\alpha \int d^3r\,\alpha\boldsymbol{\nabla}\cdot\mathbf{P} \tag{78}$$

and

$$\boldsymbol{\nabla}\cdot(\alpha\mathbf{P}) = \alpha\boldsymbol{\nabla}\cdot\mathbf{P} + \mathbf{P}\cdot\boldsymbol{\nabla}\alpha \quad \alpha = x,y,z \tag{79}$$

with

$$\boldsymbol{\nabla}\alpha = \hat{\mathbf{u}}_\alpha \quad \alpha = x,y,z \tag{80}$$

Using the divergence theoreme and the continuity of $\mathbf{P}$ (which implies that $\mathbf{P}$ is zero on the boundary), we have

$$\mathbf{p} = \int d^3r\,\mathbf{P} \tag{81}$$

which implies tat $\mathbf{P}$ is nothing but the dipolar moment per unit volume.

Our first conclusion runs, therefore, as follows. Even for the case of electrical neutrality, an electrical field makes the distribution of $\pm$ charges no more homogeneous. We have a gradient of charges, and this gradient induces a polarization that we call $\mathbf{P}$.

What happens now if the material is not electrically neutral ? This means that we have introduced by hand an ion in an initially neutral material. Before, we had $< \rho_m >= -\boldsymbol{\nabla}\cdot\mathbf{P}$. We have now

$$< \rho_m > -\rho_{ext} = -\boldsymbol{\nabla}\cdot\mathbf{P} \tag{82}$$

where ρ_{ext} is the density of charges we have introduced inside the sample by hand.

EXERCICE 3.1. *Do the conduction electrons in a metal contribute to ρ_{ext} ? The answer is no, since there are compensated by the ions.*

Finally, we can write

$$\boldsymbol{\nabla} \cdot \mathbf{E} = \frac{\rho_{ext}}{\epsilon_0} - \boldsymbol{\nabla} \cdot \mathbf{P} \tag{83}$$

where $\mathbf{E}$ has still the meaning of a mesoscopic average.

For practical purpose, we can define the new vector $\mathbf{D}$ (electrical displacement) by

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P} \tag{84}$$

and $\mathbf{D}$ is a new macroscopic variable which contains the effect of polarizing the medium. From this definition, we have

$$\boldsymbol{\nabla} \cdot \mathbf{D} = \rho_{ext} \tag{85}$$

To conclude, we note that this definition still holds in the dynamic regime (there is no time derivative in the corresponding Maxwell equation).

4. Performing $< j_m >$

(1) First, consider the case of an insulator in the time independent regime. The total current is zero, meaning that there is an exact compensation of the in-and-out-current. So, for any arbitrary cross-section

$$\iint_{dS} dS \; < \mathbf{j}_m > \cdot \hat{\mathbf{n}} = 0 \tag{86}$$

We use for any vector field $\mathbf{M}$

$$\oint_{\mathcal{C}} \mathbf{M} \cdot \mathbf{dl} = \iint dS \, \boldsymbol{\nabla} \times \mathbf{M} \cdot \hat{\mathbf{n}} \tag{87}$$

By analogies with what we have done before, define the magnetization $\mathbf{M}$ through the local average of $\mathbf{j}_m$

$$< \mathbf{j}_m >= \boldsymbol{\nabla} \times \mathbf{M} \tag{88}$$

with $\mathbf{M} = \mathbf{0}$ outside the sample. We are going to see that $\mathbf{M}$ is nothing but the magnetization density. To see this, write the dipolar magnetic moment as

$$m = \frac{1}{2} \int_{Sample} d^3 r \, \mathbf{r} \wedge \mathbf{j}_m \tag{89}$$

we have (and this calculation is not trivial)

$$\mathbf{m} = \int_{Sample} d^3 r \, \mathbf{M} \tag{90}$$

Just as before, a non-uniform magnetization with $\boldsymbol{\nabla} \times \mathbf{M} \neq \mathbf{0}$ contributes to a current density.

(2) Second, consider now the case of a conductor (or an electrolyte) where an external current is driven into the system (still in the time independent regime). We add this external current $\mathbf{j}_{free}$ to the magnetization current

$$\boldsymbol{\nabla} \times \mathbf{B} = \mu_0 \mathbf{j}_{free} + \mu_0 \boldsymbol{\nabla} \times \mathbf{M} \tag{91}$$

We can always define

$$\mathbf{H} = \frac{\mathbf{B}}{\mu_0} - \mathbf{M} \tag{92}$$

so that

$$\boldsymbol{\nabla} \times \mathbf{H} = \mathbf{j}_{free} \tag{93}$$

By definition, and to be sure sure to mislead everybody, **H** is called the magnetic field and **B** is the magnetic induction.

What happens now in the time dependent regime ? Assume that we introduce charges in the system. If these charges move, there is a current. But electrical charges are conserved, meaning

$$\boldsymbol{\nabla}\cdot\mathbf{j}_{free}+\frac{\partial\rho}{\partial t}=0 \tag{94}$$

But,

$$\boldsymbol{\nabla}\cdot\mathbf{D}=\rho_{ext} \tag{95}$$

so that

$$\boldsymbol{\nabla}\cdot\left[\mathbf{j}_{free}+\frac{\partial\mathbf{D}}{\partial t}\right]=0 \tag{96}$$

Use now the DRG theorem. Define the magnetic field **H** through

$$\boldsymbol{\nabla}\times\mathbf{H}=\mathbf{j}_{free}+\frac{\partial\mathbf{D}}{\partial t} \tag{97}$$

which agrees with the one above in the time independent regime. To conclude, we have indeed define a new vector field **H** so that

(1) $\mathbf{H}=\mathbf{B}/\mu_0$ outside the sample;
(2) $\mathbf{H}=\mathbf{B}/\mu_0-\mathbf{M}$ inside the sample.

The upshot of all of this is as follows. The Maxwell equations are now relatively simple

(1) In SI:

$$\begin{aligned}\boldsymbol{\nabla}\cdot\mathbf{D}=\rho_{ext}\quad\boldsymbol{\nabla}\times\mathbf{E}=-\frac{\partial\mathbf{B}}{\partial t}\\ \boldsymbol{\nabla}\cdot\mathbf{B}=0\quad\boldsymbol{\nabla}\times\mathbf{H}=\mathbf{j}_{ext}+\frac{\partial\mathbf{D}}{\partial t}\end{aligned} \tag{98}$$

with the definitions (in SI)

$$\begin{aligned}\mathbf{D}&=\epsilon_0\mathbf{E}+\mathbf{P}\\ \mathbf{H}&=\frac{\mathbf{B}}{\mu_0}-\mathbf{M}\end{aligned} \tag{99}$$

This result obtained at the expense of having introduced two new fields **D** and **H** which are only defined through macroscopic averages. We did not solve the problem (yet), and this is a rewriting of the microscopic Maxwell equation. As before, the number of unknowns is the same as the number of equations.

(2) In Gaussian CGS

$$\begin{aligned}\boldsymbol{\nabla}\cdot\mathbf{D}=4\pi\rho_{ext}\quad\boldsymbol{\nabla}\times\mathbf{E}=-\frac{1}{c}\frac{\partial\mathbf{B}}{\partial t}\\ \boldsymbol{\nabla}\cdot\mathbf{B}=0\quad\boldsymbol{\nabla}\times\mathbf{H}=\frac{4\pi}{c}\mathbf{j}_{free}+\frac{1}{c}\frac{\partial\mathbf{D}}{\partial t}\end{aligned} \tag{100}$$

with the definitions (in CGS)

$$\begin{aligned}\mathbf{D}&=\mathbf{E}+4\pi\mathbf{P}\\ \mathbf{H}&=\mathbf{B}-4\pi\mathbf{M}\end{aligned} \tag{101}$$

5. Energy

From the Maxwell equation

$$\boldsymbol{\nabla} \times \mathbf{H} = \mathbf{j}_{free} + \frac{\partial \mathbf{D}}{\partial t} \tag{102}$$

we have (after taking the scalar product with $\mathbf{E}$)

$$\mathbf{E} \cdot \boldsymbol{\nabla} \times \mathbf{H} = \mathbf{j}_{free} \cdot \mathbf{E} + \frac{\partial \mathbf{D}}{\partial t} \cdot \mathbf{E} \tag{103}$$

Using the identity

$$\boldsymbol{\nabla} \cdot (\mathbf{E} \wedge \mathbf{H}) = \mathbf{H} \cdot \boldsymbol{\nabla} \times \mathbf{E} - \mathbf{E} \cdot \boldsymbol{\nabla} \times \mathbf{H} \tag{104}$$

with

$$\boldsymbol{\nabla} \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \tag{105}$$

we get

$$\frac{\partial \mathbf{D}}{\partial t} \cdot \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} \cdot \mathbf{H} = -\boldsymbol{\nabla} \cdot \mathbf{E} \wedge \mathbf{H} - \mathbf{j}_{ext} \cdot \mathbf{E} \tag{106}$$

Define the instantaneous Poynting vector

$$\boldsymbol{\Pi} = \mathbf{E} \wedge \mathbf{H} \tag{107}$$

Here I want to show

$$\boldsymbol{\nabla} \cdot \boldsymbol{\Pi} + \mathbf{E} \cdot \frac{\partial \mathbf{D}}{\partial t} + \mathbf{H} \cdot \frac{\partial \mathbf{B}}{\partial t} = -\mathbf{j}_{ext} \cdot \mathbf{E} \tag{108}$$

The right-hand side describes the energy exchange between the field and the current due to the external charges (this current can for example describe an external source which provides energy to the field). The left member contains different contributions: free energy density of the field, potential energy stored in the material and dielectric losses

CHAPTER 4

Electrodynamics of continuous media - II

1. Summary

We show that Maxwell equations are satisfied as soon as one defines response functions (conductivity, permittivity, susceptibility, permeability). The next chapter will show how these response functions can be calculated using microscopic models.

2. Introduction

We have introduced to subsidiary fields $\mathbf{D}$ and $\mathbf{H}$ from the Maxwell equations to describe the propagation of waves in media. From now on, we assume that there is no external charge $\rho_{ext} = 0$, so that $\mathbf{j} = \mathbf{j}_{free}$. To make progresses, we make the following assumptions: local response, non-magnetic materials, linear materials (don't shine a laser light !), isotropic systems, homogeneous materials.

(1) Locality: For a conductor where conductivity is the important parameter, linear response means that the current is proportional to the electrical field. Assuming an instantaneous (same t) response, this means

$$\mathbf{j}(\mathbf{r}, t) = \sigma \mathbf{E}(\mathbf{r}, t) \tag{109}$$

Locality means that the current at point $\mathbf{r}$ depends only on the electrical field at $\mathbf{r}$ (and not at a point far away or in the neighborhood). True ? There is always a relaxation time and a distance (mean free path) for things to relax to zero. Locality is generally OK is one work in a regime where

$$\text{Mean Free Path(s)} \ll \text{Typical Wavelength of } \mathbf{E} \tag{110}$$

(2) Linearity: In general, we assume for a dielectric

$$\mathbf{P} = \overleftrightarrow{\chi}_e \, \mathbf{E} \tag{111}$$

where $\overleftrightarrow{\chi}$ is a 3×3 matrix (a tensor). If the material becomes magnetic

$$\mathbf{M} = \overleftrightarrow{\chi}_m \, \mathbf{H} \tag{112}$$

From this, we have

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P} = \epsilon_0 \, \overleftrightarrow{\epsilon} \, \mathbf{E} \tag{113}$$

where $\overleftrightarrow{\epsilon}$ is the permittivity tensor.

We can also define the permeability tensor

$$\mathbf{B} = \overleftrightarrow{\mu}_m \, \mathbf{H} \tag{114}$$

We use matrices (i.e. tensors) for $\overleftrightarrow{\epsilon}$, $\overleftrightarrow{\mu}$, since linearity does not imply that things have the same direction ! There are, for example, crystalline orientation axes where $\mathbf{P}$ is not co-linear with $\mathbf{E}$.

(3) Isotropic materials: The tensors were introduced above on purpose., since crystalline symmetries are in general important. To makes things as simple as possible, say

$$\overleftrightarrow{\epsilon} = \epsilon \mathbb{I} \tag{115}$$

or

$$\mathbf{D} = \epsilon_0 \epsilon \mathbf{E} \qquad \mathbf{P} = \epsilon_0(\epsilon - 1)\mathbf{E} \tag{116}$$

3. Linear response and causality

The frequency dependence of the conductivity occurs because matter cannot responses instantaneously to an external perturbation.

Let us concentrate on a time-dependent conductivity function $\sigma(\tau)$. A time delay appears between the perturbation and the response, but the response must be causal. Linear response says

$$\mathbf{j}(\mathbf{r}, t) = \int_{-\infty}^{t} dt' \, \sigma(t - t')\mathbf{E}(\mathbf{r}, t') \tag{117}$$

where the current at time t depends on the electrical field at earlier time t' (causality). Obviously,

$$\sigma(\tau) \to 0 \quad \text{as} \quad \tau \to +\infty \tag{118}$$

For practical purposes, we define the response function $\sigma(\tau)$ such that

$$\sigma(\tau) = \quad \text{if} \quad \tau < 0 \tag{119}$$

and write

$$\mathbf{j}(\mathbf{r}, t) = \int_{-\infty}^{+\infty} dt' \, \sigma(t - t')\mathbf{E}(\mathbf{r}, t') \tag{120}$$

as a convolution integral. w As usual, we define the Fourier transform

$$\sigma(t) = \frac{1}{2\pi} \int d\omega e^{-i\omega t} \tilde{\sigma}(\omega) \quad \tilde{\sigma}(\omega) = \int dt \sigma(t) e^{i\omega t} \tag{121}$$

and use the convolution theorem

$$\tilde{\mathbf{j}}(\mathbf{r}, \omega) = \tilde{\sigma}(\omega)\tilde{\mathbf{E}}(\mathbf{r}, \omega) \tag{122}$$

An important property of $\tilde{\sigma}(\omega) = \tilde{\sigma}'(\omega) + i\tilde{\sigma}''(\omega)$ follows from the fact that both $\mathbf{j}(\mathbf{r}, t)$ and $\mathbf{E}(\mathbf{r}, t)$ are real. This means

$$\tilde{\sigma}(\omega) = \tilde{\sigma}^\star(-\omega) \tag{123}$$

or

$$\tilde{\sigma}'(\omega) = \tilde{\sigma}'(-\omega) \quad \text{and} \quad \tilde{\sigma}''(\omega) = -\tilde{\sigma}''(-\omega) \tag{124}$$

To conclude, all these properties apply to the complex permittivity $\tilde{\epsilon}(\omega)$. We will see in the next paragraph that the complex permittivity and the complex conductivity which are both response functions are not independent from each other. A priori, $\tilde{\epsilon}'(\omega)$ can be positive or negative, but $\tilde{\sigma}'(\omega)$ is certainly positive.

EXERCICE 3.1. *As said before, we have*

$$\epsilon(\omega) = \epsilon^*(-\omega) \tag{125}$$

Assume a real field $\mathbf{E}$ *at frequency* ω

$$\mathbf{E} = \mathbf{E}_0 e^{i\omega t} + \mathbf{E}_0^* e^{-i\omega t} \tag{126}$$

Show (superposition principle) that if $\mathbf{E}$ *is real, then* $\mathbf{D}(\omega) = \epsilon_0 \tilde{\epsilon}(\omega)\mathbf{E}$ *is real if (125) holds*[4].

4. The complex permittivity and the complex conductivity

We assume that both $\mathbf{E}(\mathbf{r},t)$ and $\mathbf{B}(\mathbf{r},t)$ are real fields varying as

$$\mathbf{E}_0 e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} + \mathbf{E}_0^* e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)} \tag{127}$$

and we give the relation under which the wave propagate (the relation between k and ω). To do this, we will concentrate on transverse waves where both $\mathbf{E}(\mathbf{r},t)$ and $\mathbf{B}(\mathbf{r},t)$ are $\perp$ to $\mathbf{k}$.

Consider one of the Maxwell equation

$$\boldsymbol{\nabla}\times\mathbf{H} = \mathbf{j} + \frac{\partial \mathbf{D}}{dt} \tag{128}$$

where the fields $\mathbf{H}$ and $\mathbf{D}$ are both real quantities.

Using (127) in (128) gives

$$\boldsymbol{\nabla}\times\tilde{\mathbf{H}}(\omega) = \tilde{\mathbf{j}} - i\omega\tilde{\mathbf{D}}(\omega) \tag{129}$$

Assume

$$\tilde{\mathbf{j}}(\omega) = \tilde{\sigma}'(\omega)\tilde{\mathbf{E}}(\omega) \quad \text{and} \quad \tilde{\mathbf{D}}(\omega) = \epsilon_0\tilde{\epsilon}'(\omega)\tilde{\mathbf{E}}(\omega) \tag{130}$$

where $\tilde{\epsilon}'(\omega)$ and $\tilde{\sigma}'(\omega)$ are both real numbers for $\tilde{\mathbf{j}}(\omega)$ to be real. Eq. (128) can now be written as:

$$\mathbf{k}\wedge\mathbf{H} = -\omega\epsilon_0\left[\tilde{\epsilon}'(\omega) + \frac{i}{\epsilon_0\omega}\tilde{\sigma}'(\omega)\right]\tilde{\mathbf{E}}(\omega) \tag{131}$$

In vacuum, the same equation is written

$$\mathbf{k}\wedge\mathbf{H} = -\omega\tilde{\epsilon}_0\mathbf{E} \tag{132}$$

Comparing these two equations, one defines the complex permittivity from $\tilde{\epsilon}'(\omega)$ and $\tilde{\sigma}'(\omega)$

$$\tilde{\epsilon}(\omega) = \tilde{\epsilon}'(\omega) + \frac{i}{\epsilon_0\omega}\tilde{\sigma}'(\omega) \tag{133}$$

As a result, this equation in a dispersive medium is

$$\mathbf{k}\wedge\mathbf{H} = -\omega\tilde{\epsilon}_0\tilde{\epsilon}(\omega)\tilde{\mathbf{E}}(\omega) \tag{134}$$

and this equations looks like the same equation in the vacuum but with the complex permittivity $\tilde{\epsilon}(\omega)$

In the same way, we define the complex conductivity by $\tilde{\sigma}(\omega) = \tilde{\sigma}'(\omega) + i\tilde{\sigma}''(\omega)$. Using this definition, write (131) as

$$\begin{aligned}\mathbf{k}\wedge\mathbf{H} &= -\omega\epsilon_0\left[1 + \frac{i}{\omega}\tilde{\sigma}(\omega)\right]\mathbf{E}\\ &= -\omega\epsilon_0\left[1 + \frac{i}{\epsilon_0\omega}\tilde{\sigma}'(\omega) - \frac{1}{\epsilon_0\omega}\tilde{\sigma}''(\omega)\right]\mathbf{E}\end{aligned} \tag{135}$$

For definitions (131) and (135) to be coherent

$$\tilde{\epsilon}'(\omega) = 1 - \frac{\sigma''(\omega)}{\epsilon_0\omega} \tag{136}$$

In summary, the relation between the complex permittivity and complex conductivity is:

$$\tilde{\epsilon}(\omega) = 1 + \frac{i}{\epsilon_0\omega}\tilde{\sigma}(\omega) \tag{137}$$

When considering a specific type of material (metal, insulator, ionic solid, superconductor) it is sometimes better to work out the conductivity and other times better to derive the dielectric function. Equation (137) allows one to translate back and forth between them.

Exercice 4.1. *Show that in CGS Gaussian units*

$$\tilde{\epsilon}(\omega) = 1 + \frac{4\pi i}{\omega}\tilde{\sigma}(\omega) \tag{138}$$

REMARK 4. *This way to write the Maxwell equation predicts that the low frequency limit of the dielectric function has the form*

$$\epsilon \approx \epsilon_s + \frac{i}{\epsilon_0 \omega}\tilde{\sigma} \tag{139}$$

where σ and ϵ_s are the static conductivity and dielectric constant.

5. The complex refractive index

To get the relation between the wave number k and the frequency ω - this means the dispersion relation - , we start from the Maxwell equation

$$\boldsymbol{\nabla} \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \tag{140}$$

And assuming again (127) for a monochromatic wave

$$i\mathbf{k} \wedge \tilde{\mathbf{E}}(\omega) = i\omega \tilde{\mathbf{B}}(\omega) \tag{141}$$

Using the identity

$$\mathbf{k} \wedge (\mathbf{k} \wedge \mathbf{H}) = (\mathbf{k} \cdot \mathbf{H})\mathbf{H} - k^2 \mathbf{H} \tag{142}$$

in (134), we get a relation between k and ω

$$k^2 = \frac{\omega^2}{c^2}\tilde{\epsilon}(\omega) \tag{143}$$

where $\tilde{\epsilon}(\omega)$ is the complex dielectric constant.

Let us define the complex refractive index N, though $N^2 = \tilde{\epsilon}(\omega)$ with

$$N = n + i\kappa \quad \text{with} \quad \kappa > 0 \tag{144}$$

The coefficient n is the refractive index, and κ is the extinction coefficient.

To make this definition more meaningfull, recall that if we remove all directions $H = (cq/\omega)E$. Since $q = \omega N/c$, we have

$$H = NE = \sqrt{\epsilon} E \tag{145}$$

6. Traveling waves in matter

Combining two of the Maxwell equations in the absence of external stimuli, we have

$$\begin{aligned} \boldsymbol{\nabla} \times \boldsymbol{\nabla} \times \mathbf{E} &= -\mu_0 \frac{\partial^2 \mathbf{D}}{\partial t^2} \\ \mathbf{k}(\mathbf{k} \cdot \mathbf{E}) - k^2 \mathbf{E} &= -\epsilon(\mathbf{k}, \omega)\frac{\omega^2}{c^2}\mathbf{E} \end{aligned} \tag{146}$$

Two cases must be distinguished, depending on the polarization direction of the electric field vector:

(1) For TRANSVERSE waves with $\mathbf{k} \cdot \mathbf{E} = 0$, we have the generic dispersion relation:

$$k^2 = \epsilon(\mathbf{k}, \omega)\frac{\omega^2}{c^2} \tag{147}$$

(2) For LONGITUDODINAL waves with $\mathbf{k} \parallel$ to $\mathbf{E}$, we have

$$\epsilon(\mathbf{k}, \omega) = 0 \tag{148}$$

signifying that longitudinal collective oscillations can only occur at frequencies corresponding to zeros of $\epsilon(\mathbf{k}, \omega)$. These waves cannot exist in the vacuum but can exist in matter (see bulk plasmons).

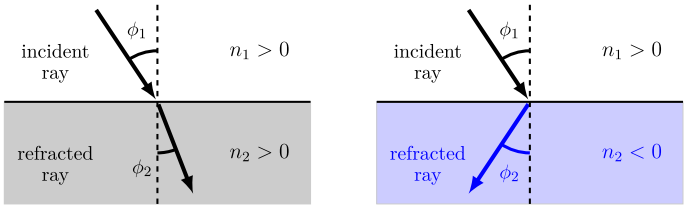

FIGURE 1. Snell law for positive and negative index materials.

REMARK 5. *The notion of negative index of refraction has been theoretically introduced 50 years ago by Veselago. J.B. Prendy is credited to to have shown that such materials can actually be made*[7]. *For refraction at interface, we have*

$$n_1 \sin\phi_1 = n_2 \sin\phi_2 \tag{149}$$

Consequently, if the refractive index of the two materials have opposite sign, then the refraction angle have also opposite sign.

For these nanophotonic artificial materials (actually meta materials), both ϵ and μ are negative in a limited frequency range. In such a material the triplet $(\mathbf{k}, \mathbf{E}, \mathbf{H})$ is left-handed.

EXERCICE 6.1. *Work out an exercice with*

$$\mathbf{E} = \mathbf{E}_0 e^{i(nx\omega/c-\omega t)} e^{-\kappa\omega x/c} \tag{150}$$

EXERCICE 6.2. *We consider the case of a light incident normally on an interface between two semi-infinite media, one with complex dielectric function ϵ_a (for the incoming and reflected field) and the other by ϵ_b (for the transmitted field). Let r and t be the reflexion and transmission coefficients. If the incoming wave is*

$$\mathbf{E}_i = E_0 e^{i(kx-\omega t)}\hat{\mathbf{u}}_y \qquad \mathbf{H}_i = N_a E_0 e^{i(kx-\omega t)}\hat{\mathbf{u}}_z \tag{151}$$

the reflected wave is of the form

$$\mathbf{E}_r = rE_0 e^{i(\pm kx-\omega t)}\hat{\mathbf{u}}_y \qquad \mathbf{H}_i = \pm N_a E_0 e^{i(\pm kx-\omega t)}\hat{\mathbf{u}}_z \tag{152}$$

(1) Choose the correct signs in the equation above;

(2) The transmitted fields $\mathbf{E}_t$ and $\mathbf{H}_t$ are

$$\mathbf{E}_t = tE_0 e^{i(kx-\omega t)}\hat{\mathbf{u}}_y \qquad \mathbf{H}_i = N_b t E_0 e^{i(kx-\omega t)}\hat{\mathbf{u}}_z \tag{153}$$

(3) Assume that both $\mathbf{E}$ and $\mathbf{H}$ are continuous at the interface. Conclude

$$r = \frac{N_a - N_b}{N_a + N_b} \tag{154}$$

(4) Assume that the incident wave is traveling in the vacuum. In experiments, one measures the intensity. Show that the reflectance intensity is given by

$$\mathcal{R} = \frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2} \tag{155}$$

Usual values for n range as $1.1 < n < 1.9$ (visible) and absorption is in general rather weak.

CHAPTER 5

Semi-classical theory for ϵ and σ

1. Drude absorption for free carriers in metals and semiconductors

This model predates quantum mechanics and igores Fermi-Dirac statistics as well as Bloch theorem. The model assumes:

(1) A density n of mobile charges (charge $-e$);
(2) That the carriers are free, there is no restoring forces, no interaction;
(3) A relaxation mechanism. If we set the system in motion, the system will relax towards equilibrium due to a damping (due to electron-electron collisions).

1.1. The conductivity. Let $\mathbf{E}_{ext}$ the applied field (and not the local field). For simplicity, assume that the $\mathbf{k} = k\hat{\mathbf{u}}_x$ is along the $x-$coordinate, so that

$$\mathbf{E} = E_0 e^{i(kx-\omega t)}\hat{\mathbf{u}}_y \tag{156}$$

with the equation of motion for the displacement y

$$m\ddot{y} = -eE_{ext} - \gamma\dot{y} \tag{157}$$

where γ is the damping coefficient. To find the solution, write

$$\dot{y} = V_0 e^{i(qx-\omega t)} \tag{158}$$

One finds:

$$V_0 = -\frac{e}{m(1/\tau - i\omega)} \tag{159}$$

where $\tau = m/\gamma$ is a characteristic time: τ is the mean time between collision (or, if you want, $1/\tau$ is the rate at which collisions occur). The electrical current is simply $j = -ne\dot{y}$, so that

$$\tilde{\sigma} = \frac{ne^2}{m(1/\tau - i\omega)} \tag{160}$$

Two limit cases are of interest:

(1) $\omega \to 0$, the velocity is in phase with the external electrical field $\mathbf{E}$;
(2) $\omega \gg 1/\tau$, the velocity is out of phase and decreases as $1/\omega$.

The dc conductivity

$$\sigma_{dc} = \frac{ne^2\tau}{m} \tag{161}$$

has the same expression in CGS and in SI. Typical numbers for Silver are as follows: $n = 5.910^{22} cm^{-3}$; $\rho = 1.610^{-6}\Omega.cm$ so that $1/\tau = 2.610^{13} s^{-1}$. The typical frequency range is of the order of $410^{14} Hz$.

Working out the real and imaginary part of the conductivity, one finds

$$\sigma'(\omega) = \frac{\sigma_{dc}}{1+\omega^2\tau^2} \quad \text{and} \quad \sigma''(\omega) = \frac{\omega\tau}{1+\omega^2\tau^2}\sigma_{dc} \tag{162}$$

1.2. The permittivity. To obtain the complex dielectric function, recall (163)

$$\tilde{\epsilon}(\omega) = \epsilon_c + \frac{i}{\epsilon_0 \omega}\tilde{\sigma}(\omega) \tag{163}$$

where we have substituted 1 by ϵ_c to take into account for the polarizibility of the ion cores. One finds

$$\tilde{\epsilon}(\omega) = \epsilon'(\omega) + i\tilde{\epsilon}''(\omega) \tag{164}$$

with

$$\tilde{\epsilon}'(\omega) = \epsilon_c - \frac{ne^2}{m\epsilon_0}\frac{\tau^2}{1+\omega^2\tau^2} \quad \text{and} \quad \tilde{\epsilon}''(\omega) = \frac{1}{\omega\tau}\frac{ne^2}{m\epsilon_0}\frac{\tau^2}{1+\omega^2\tau^2} \tag{165}$$

Then, it is interesting to define

$$\omega_p^2 = \frac{ne^2}{m\epsilon_0} \tag{166}$$

as the plasma frequency.

EXERCICE 1.1. *Do this calculation in CGS and show that the overall expression for the permittivity is the same with the plasma frequency*

$$\omega_p^2 = \frac{4\pi ne^2}{m} \tag{167}$$

1.3. The refractive index $\sqrt{\epsilon}$. Assume $\omega\tau \gg 1$ to make calculus as simple as possible. Then $\tilde{\epsilon}(\omega)$ is real

$$\tilde{\epsilon}(\omega) = \epsilon_c - \frac{\omega_p^2}{\omega^2} \tag{168}$$

and negative for $\omega < \omega_p/\sqrt{\epsilon_c}$. The refractive index is purely imaginary: E.M. wave cannot propagate in this range. At normal incidence, the total reflectance is unity. For $\omega > \omega_p/\sqrt{\epsilon_c}$, propagation is possible. The material becomes transparent. For most metals, ω_p is in the ultraviolet regime (5 eV- 15 eV).

The dispersion relation can be determined from $k^2 = |\mathbf{k}|^2 = \tilde{\epsilon}(\omega)\omega/c$

$$\omega(k) = \sqrt{\omega_p^2 + k^2/c^2} \tag{169}$$

If there is no propagation below the plasma frequency $\omega < \omega_p$, for $\omega > \omega_p$ waves propagate withe a group velocity $d\omega/dk < c$.

The physical origin of this behavior lies in the source of transmitted and reflected waves. For $\omega < \omega_p$, the medium radiates two waves: A backward propagating wave (reflected) and a forward-propagating wave which interferes destructively with the incident wave. For $\omega > \omega_p$, the polarization is no more in phase and the destructive interference between the two waves is lost. This phase change is reminiscent of an harmonic oscillator driven below and above its natural frequency.

1.4. Physical interpretation. To understand the physical interpretation of ω_p , consider the longitudinal oscillations of a conduction electron gas in a fixed background of positive charges. A slab displacement u with respect to the background leads to an effective charge density $\sigma = \pm neu$ where n is the density of $\pm$ charges.

To calculate the electric field, we realize that the problem is equivalent to a plate capacitor, so that the displacement u leads to an electric field

$$E = \frac{neu}{\epsilon_0} \tag{170}$$

The equation of motion reads as:

$$nm\ddot{u} = -\frac{n^2e^2u}{\epsilon_0} \quad \text{or} \quad \ddot{u} + \omega_p^2 u = 0 \tag{171}$$

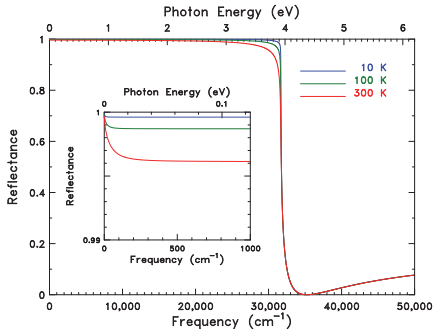

Fig. 14. Normal incidence reflectance of a Drude metal.

FIGURE 1. Normal incidence reflectance of a usual metal[9].

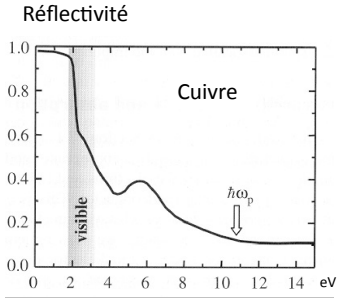

FIGURE 2. Reflectivity for cooper. Note that the reflectivity drops below the plasma frequency dur to interband transition in the visible range.

Note that interpretation assumes longitudinal modes where the displacement is parallel to $\mathbf{E}$. This type of plasmon (volume plasmon) cannot be excited by TEM where $\mathbf{E}$ is $\perp$ to the direction of propagation. They can only be excited by particle impacts.

REMARK 6. *But not all metals are mirrors. Some metals are colored (in reflection copper is red, gold is yellow) which reflects other mechanisms of absorption of radiation. Contrary to the case of aluminum, these metals have a reflectivity that drops well before ω_p. This drop in reflectivity is explained by the fact that in these metals inter-band transitions are possible at energies corresponding to the visible wavelengths.*

2. The Lorentz model

The Lorentz model applies to situation where electrons are bound by some force to an atom or to an ion. Assume that the molecule acquires a polarization $\mathbf{p} = \alpha_e \mathbf{E}_{local}$ where $\mathbf{E}_{local}$ is the local field at the molecule position (which differs a priori from the external field).

2.1. The dilute limit. The molecule having a dipole moment, it generates in turn a field at distance $\mathbf{r}$

$$\mathbf{E}_{dipole} = \frac{3(\mathbf{p}\cdot\mathbf{r})\hat{\mathbf{u}}_r - \mathbf{p}}{r^3} \tag{172}$$

For a molecule surrounded by its neighbors, the electrical field at the molecule position is the sum of the applied field, $\mathbf{E}_{applied}$ with the dipolar field generated by the neighbors, say $\mathbf{E}_n$

$$\mathbf{E}_{local} = \mathbf{E}_{applied} + \mathbf{E}_n \tag{173}$$

In the dilute limit we start with, we neglect the field generated by the neighbors, so that

$$\mathbf{E}_{local} = \mathbf{E}_{applied} \tag{174}$$

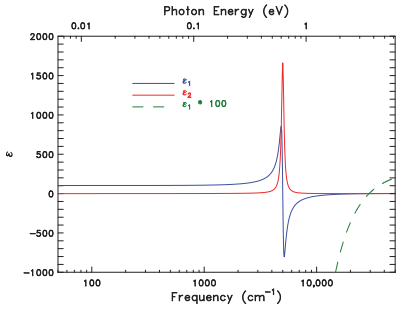

FIGURE 3. Real and imaginary parts of the permittivity of a typical Lorentz oscillator[9].

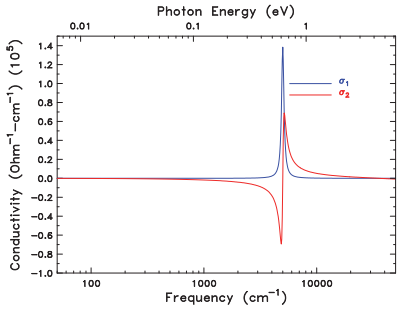

FIGURE 4. Real and imaginary parts of of the conductivity of a typical Lorentz oscillator[9].

For an electron bound by an harmonic force, the equation of motion is

$$m\ddot{x} = -m\omega_0^2 x - m\gamma\dot{x} - eE_0 e^{-i\omega t} \tag{175}$$

where γ is a damping term. Formally, this is identical to the Drude model, but the underlying physics is different. Drude model assumes that $e^- - e^-$ collisions give rise to γ. Here, impurities and phonons etc. give this damping. If

$$x = x_0 e^{i\omega t} \tag{176}$$

we have

$$x_0 = -\frac{e/m}{\omega_0^2 - \omega^2 - i\gamma\omega} \tag{177}$$

Since the dipole moment for one molecule is $p = -ex$, the electronic polarizability per molecule is

$$\alpha_e = \frac{e^2/m}{\omega_0^2 - \omega^2 - i\gamma\omega} \tag{178}$$

If n is the density of molecules, the total dipole moment P is np. Since, the susceptibility, a response function, is $\mathbf{P} = \chi_e \mathbf{E}$, we have

$$\chi_e = \frac{ne^2/m}{\omega_0^2 - \omega^2 - i\gamma\omega} \tag{179}$$

From

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P} = \epsilon_0 \epsilon \mathbf{E}$$

one finds

$$\chi_e = \epsilon_0(\epsilon - 1)$$

and

$$\epsilon(\omega) = 1 + \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\gamma\omega} \tag{180}$$

In the low frequencies limit, we can approximate this expression as

$$\epsilon(\omega) = 1 + \frac{\omega_p^2}{\omega_0^2} \tag{181}$$

so that, unlike metals, see (168), $\tilde{\epsilon}(\omega) > 0$ in the $\omega \to 0$ limit.

2.2. The depolarizing field. In this section, we don't assume anymore the dilute limit. We still have $\mathbf{p} = \alpha_e \mathbf{E}_{local}$, but the local field $\mathbf{E}_{local}$ is the sum of the applied field and the field generated by the surrounding. We split the later into two contribution. The immediate surrounding (immediate neighbors) and the medium

$$\mathbf{E}_{local} = \mathbf{E}_{ext} + \mathbf{E}_{neigh} + \mathbf{E}_{medium} \tag{182}$$

(1) The field $\mathbf{E}_{neigh}$ is the finite sum of the fields due to the neighboring molecules. For cubic symmetry, each term appears with its symmetric, but with a minus sign, so that this (finite) sum is zero;
(2) To calculate $\mathbf{E}_{medium}$, we carve a spherical cavity inside a uniformly polarized medium. The uniform polarization $\mathbf{P}$ outside the cavity leads to a surface charge density $\sigma = \mathbf{P} \cdot \mathbf{n}$. This charge density varies as $\cos(\theta)$, and leads to a uniform field in the cavity, see Exercice.

$$\mathbf{E}_{medium} = \frac{\mathbf{P}}{3\epsilon_0} \tag{183}$$

The polarization $\mathbf{P}$ is, therefore:

$$\mathbf{P} = n\alpha_e \left[\mathbf{E}_{ext} + \frac{\mathbf{P}}{3\epsilon_0} \right] \tag{184}$$

which is self-consistent for $\mathbf{P}$. Since $\alpha_e(\omega)$ is known from (178), we have

$$\mathbf{P} = \frac{n\alpha_e(\omega)}{1 - n\alpha_e(\omega)/(3\epsilon_0)} \mathbf{E}_{ext} \tag{185}$$

From $\chi = \epsilon_0(\epsilon - 1)$, one finds the Clausius-Maussotti formula

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{n\alpha}{3\epsilon_0} \tag{186}$$

which reads as

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi n\alpha}{3} \tag{187}$$

when using CGS units.

EXERCICE 2.1. *In CGS units*

$$\mathbf{P} = \frac{n\alpha_e(\omega)}{1 - 4\pi n\alpha_e(\omega)/3} \mathbf{E}_{ext} \tag{188}$$

Using ((178)), we find

$$\tilde{\epsilon}(\omega) = 1 + \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\omega\gamma - 1/3\omega_p^2} \tag{189}$$

which amounts to a reduction of the bare resonant frequency

$$\omega_e = \left(\omega_0^2 - \frac{1}{3}\omega_p^2 \right)^{1/2} \tag{190}$$

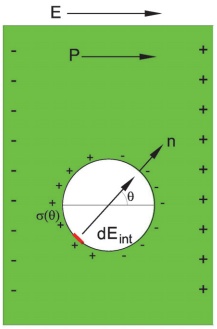

FIGURE 5. A sphere is carved out from a uniformly polarized material. There is a surface charge density on the surface of the spherical cavity that is the source of a uniform depolarizing field in the cavity.

EXERCICE 2.2. *There is a general method to solve Laplace equation with boundary conditions. We apply this method to the Lorentz cavity of radius R. The problem can be stated as follows. Find the solution of the Laplace equation* [1]

$$\Delta V = 0 \text{ for } r > R \text{ and } r < R \tag{192}$$

with the appropriate boundary conditions.

(1) The potential $V(r,\theta)$ is continuous at $r = R$;
(2) The normal component of the electrical field obeys

$$-\frac{\partial V_{out}}{\partial r} + \frac{\partial V_{in}}{\partial r} = \frac{\sigma(\theta)}{\epsilon_0} = \frac{1}{\epsilon_0}\mathbf{P}\cdot\mathbf{n} = \frac{1}{\epsilon_0}P\cos(\theta) \tag{193}$$

The general solution of (192) is found using the basis of the Legendre polynomials $P_l(x)$

$$V(r,\theta) = \sum_{l\geq 0}(A_l r^l + \frac{B_l}{r^{l+1}})P_l(\cos(\theta)) \tag{194}$$

where the A_l and B_l's are the coefficients to be determined using the boundary conditions. This means that if you plug (194) in (192), you find $\Delta V = 0$. The first two Legendre polynomials are easy to remember

$$P_0(x) = 1 \qquad P_1(x) = x \tag{195}$$

(1) Check that (194) is indeed a solution of the Laplace equation when we keep only the $l = 1$ term in the expansion.
(2) What are the A_l's for $r > R$?
(3) What are the B_l's for $r < R$?
(4) Take $l = 1$ in (194). Work out the boundary conditions to find A_1 and B_1. Since the boundary conditions can be satisfied, and since the solution is unique, $l = 1$ is enough;
(5) Compute the electrical field inside the Lorentz cavity. Remember

$$\mathbf{E} = -\boldsymbol{\nabla}V = -\frac{\partial V}{\partial r}\mathbf{u}_r - \frac{1}{r}\frac{\partial V}{\partial \theta}\mathbf{u}_\theta - \frac{1}{r\sin\theta}\frac{\partial V}{\partial \phi}\mathbf{u}_\phi \tag{196}$$

---

[1] $$\Delta V = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial V}{\partial r}\right] + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial V}{\partial\theta}\right] + \frac{1}{r^2\sin^2\theta}\frac{\partial^2 V}{\partial\phi^2} \tag{191}$$

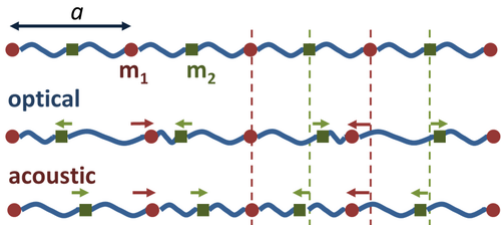

FIGURE 6. Optical and acoustic modes (phonons) of a diatomic linear chain.

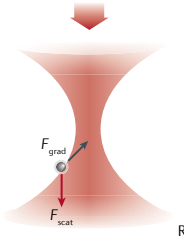

FIGURE 7. Principles of optical tweezers. Forces acting on a dielectric sphere interacting with light, with the incident light beam focused by a high-numerical aperture (NA) lens. a | A Rayleigh particle smaller than the wavelength of light experiences a scattering force (F_{scat}, red arrow) that pushes the particle along the direction of propagation of the light and a gradient force (F_{grad}, black arrow) that attracts it towards the focus.

3. Semiconductors

4. Polar Crystals

The collective vibrational modes of the atoms in the crystal lattice are responsible for the absorption and dispersion. Explain optical modes.

5. Optical tweezers

Optical tweezers are a method to exert forces or torques on individual molecules and/or to directly measure the forces or torques generated in the course of their biochemical reactions. In 1970, Arthur Ashkin exploited the fact that photons carry momentum to entrain and transport micron-sized latex spheres suspended in water using laser beams[1].

Because the bead is very small, it can be considered to be an induced dipole in an approximately uniform electric field due to the laser. The problem of a dielectric sphere located in a uniform electric field is solved in many books on electromagnetic theory. The induced dipole moment of the dielectric sphere (radius a) can be written as

$$\mathbf{P} = \frac{K-1}{K+2} a^3 \mathbf{E} \qquad K = \epsilon/\epsilon_m \tag{197}$$

where ϵ_m is the permittivity of the medium (generally water) and ϵ the permittivity of the dielectric. The electric potential energy of the induced dipole can then be written as

$$U = -\mathbf{P} \cdot \mathbf{E} \tag{198}$$

which means that the sphere is trapped in the region where the field is maximum.

EXERCICE 5.1. *From Ref.[8]. Metal nanoparticles are known to exhibit distinctive opti-Metal nanoparticles are known to exhibit distinctive optical cal characteristics, such as surface-enhanced Raman scat- characteristics, such as surface-enhanced Raman scattering tering (SERS) and second harmonic generation, relative to (SERS) and second harmonic generation, relative*

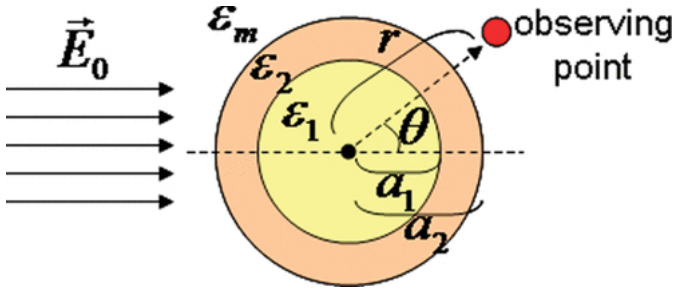

FIGURE 8. Schematic view of a nanoshell nanoparticle (dielectric core + metallic shell). In this problem, we consider only metallic nanoparticles without dielectric core.

to the bulk the bulk form of metals. Representatives of the use of metal form of metals. Representatives of the use of metal nano- particles are biomolecular manipulation, labeling, and detection with SERS [2].

One of the most important factors for all of those applications is the enhancement of the electromagnetic field intensities around subwave length-size metal particles due to the coupling between the incident photons and collective oscillation of free electrons at the metal surface. Here we compute this factor.

Consider first a homogenous, isotropic sphere placed in a medium of radius a in which there exists a static uniform electric field $\mathbf{E} = E_0\hat{\mathbf{u}}_z$. *The electric fields inside and outside the sphere,* $\mathbf{E}_1$ *and* $\mathbf{E}_2$, *are the gradients of the scalar potential* $\Phi_{1,2}(r,\theta)$ *as*

$$\mathbf{E}_{1,m} = -\boldsymbol{\nabla}\Phi_{1,m} \tag{199}$$

where

$$\nabla^2\Phi_{1,m} = 0 \text{ for } r < a \text{ and } r > a \tag{200}$$

Because of the symmetry of the problem, the potentials are independent of the azimuthal angle Φ.

(1) *The dielectric constants of the sphere and of the surrounding medium are* ϵ_1 *and* ϵ_2, *respectively. What are the two boundary conditions that* Φ *and its derivative must obey at* $r = a$ *?*

(2) *It is required that the electric field is the unperturbed applied electric field at large distance*

$$\Phi_m(r,\theta) - E_0 r\cos\theta = -E_0 z \text{ for } r \gg a \tag{201}$$

Show

$$\Phi_1(r,\theta) = a_1 r\cos\theta \quad \Phi_m(r,\theta) = a_m r\cos\theta + b_m\frac{\cos\theta}{r^2} \tag{202}$$

is solution of the problem for some values of the contants a_1, a_m, b_m. *These solutions for the potentials could be also derived rigorously using Legendre polynomials;*

(3) *Give* $\mathbf{E}_{1,2}(r,\theta)$ *and* $|\mathbf{E}_{1,2}(r,\theta)|^2$;

(4) *What are the angles* θ *for which the field is maximum at a given distance* r *?*

(5) *For these two values of* θ, *give the value of the enhancement factor as a function of* r;

$$\eta = \frac{|\mathbf{E}_2|^2}{|\mathbf{E}_0|^2} \tag{203}$$

(6) *For what value of* r *is this factor maximum ?*

[2]Other optoelectronic fields inspired by metal nanoparticles are also emerging, such as multiphoton absorption and fluorescence excitation for microscopy, microfabrication and optical data storage, all-optical nanoscale network, and surface plasmon enhanced light absorption for photovoltaic materials.

(7) *Express your result in terms of the factor*

$$\alpha = 4\pi a^3 \frac{\epsilon_1 - \epsilon_m}{\epsilon 1 + 2\epsilon_m} \tag{204}$$

Consider $r = a$. If the nanoparticle is the air, what is the value of ϵ_m ? If the nanoparticle is in water, what is the value of ϵ_m ?

(8) *Can we have a maximum for α if the core is made of a dielectric ?*

(9) *For a metallic nanoparticle with plasma frequency ω_p, give the frequency at which the enhancement factor is maximum.*

CHAPTER 6

Electromagnetic waves at interfaces: Plasmonics

1. Summary

Many optical biosensors are based on the phenomenon of surface plasmon resonance (SPR) techniques. This utilises a property of and other materials; specifically that a thin layer of gold on a high refractive index glass surface can absorb laser light, producing electron waves (surface plasmons) on the gold surface. This occurs only at a specific angle and wavelength of incident light and is highly dependent on the surface of the gold, such that binding of a target analyte to a receptor on the gold surface produces a measurable signal (Wikipedia). This is modern technology. The optical properties of metal nanostructures have been used by artists long before (see Lycurgus cup or the color windows at St. Stephan Church by M. Chagall).

In this chapter we study how electromagnetic waves propagate at the interface between a metal and dielectric material. For this, we have first to derive the boundary conditions for E.M. fields at interfaces.

2. Boundary conditions for E.M. fields

We consider two homogeneous media, says medium 1 and 2 separated by a surface S. Let $\hat{\mathbf{n}}$ be the normal to S. $\mathcal{C}$ is a rectangular contour containing the normal $\hat{\mathbf{n}}$. Its orientation is given by a vector $\hat{\mathbf{t}}$ perpendicular to $\hat{\mathbf{n}}$ and tangent to surface S. Σ is a small cylinder with axis normal to S.

From the divergence theorem

$$\iint_\Sigma d^2r\, \mathbf{S}\cdot\hat{\mathbf{n}} = \int_V d^3r\, \rho_{ext} \quad \text{and} \quad \iint_\Sigma d^2r\, \mathbf{B}\cdot\hat{\mathbf{n}} = 0 \tag{205}$$

The cylinder having radial symmetry

$$\iint_\Sigma d^2r\, \mathbf{S}\cdot\hat{\mathbf{n}} = \iint_{Top\,in\,1} d^2r\, \mathbf{S}\cdot\hat{\mathbf{n}} + \iint_{Bottom\,in\,2} d^2r\, \mathbf{S}\cdot\hat{\mathbf{n}} \tag{206}$$

Le σ_S be the charge density at the interface (free charges).

$$(\mathbf{D}_1-\mathbf{D}_2)\cdot\hat{\mathbf{n}}\Delta\Sigma = \sigma_S\Delta\Sigma \quad \text{and} \quad (\mathbf{B}_1-\mathbf{B}_2)\cdot\hat{\mathbf{n}}\Delta\Sigma = 0 \tag{207}$$

We also have the Stokes theorem (for the surface $\int$ enclosed by the contour $\mathcal{C}$)

$$\oint_{\mathcal{C}} \mathbf{H}\cdot d\mathbf{l} = \iint_\int d^2\int \left(\mathbf{j}_S + \frac{\partial D}{\partial t}\right)\cdot\hat{\mathbf{t}} \quad \text{and} \quad \oint \mathbf{E}\cdot d\mathbf{l} = -\iint_\int \hat{\mathbf{t}}\cdot\frac{\partial \mathbf{B}}{\partial t} \tag{208}$$

From the Fig.

$$(\hat{\mathbf{t}}\wedge\hat{\mathbf{n}})\cdot(\mathbf{E}_1-\mathbf{E}_2)\,\Delta l = 0 \quad \text{and} \quad (\hat{\mathbf{t}}\wedge\hat{\mathbf{n}})\cdot(\mathbf{H}_1-\mathbf{H}_2)\,\Delta l = \mathbf{j}_S\cdot\hat{\mathbf{t}}\Delta t \tag{209}$$

The first equation gives that the parallel components $\mathbf{E}_\parallel$ are continuous

$$\mathbf{E}_{\parallel,1} = \mathbf{E}_{\parallel,2} \tag{210}$$

The charge density σ_s and the surface current density $\mathbf{j}_S$ are both mathematical singular objects. In real conductors, they are usually taken to zero, so that

$$\mathbf{H}_{\parallel,1} = \mathbf{H}_{\parallel,2} \quad \mathbf{D}_{\perp,1} = \mathbf{D}_{\perp,2} \quad \mathbf{B}_{\perp,1} = \mathbf{B}_{\perp,2} \tag{211}$$

3. Surface Plasmons

Consider the following situation:

(1) For $z > 0$: Dielectric with complex permittivity ϵ_1;
(2) For $z < 0$: Metal with complex permittivity ϵ_2.

with boundary conditions

$$\begin{aligned} D_{1,z} = D_{2,z} \qquad B_{1,z} = B_{2,z} \qquad i = 1,2 \\ E_{1,x,y} = E_{2,x,y} \qquad H_{1,x,y} = H_{2,x,y} \qquad i = 1,2 \end{aligned} \tag{212}$$

EXERCICE 3.1. *(1) We start with the Ansatz of a transverse magnetic mode (for a transverse magnetic mode, there is no magnetic field in the direction of propagation)*

$$\begin{aligned} \mathbf{E}_i = (E_{i,x}, 0, E_{i,z}) e^{i(\mathbf{k}_i \cdot \mathbf{r} - \omega t)} \qquad \mathbf{D}_i = \epsilon_0 \epsilon_i \mathbf{E}_i \\ \mathbf{H}_i = (0, H_{i,y}, 0) e^{i(\mathbf{k}_i \cdot \mathbf{r} - \omega t)} \qquad \mathbf{H}_i = \mu_0 \mathbf{B}_i \end{aligned} \tag{213}$$

where $\mathbf{k}_i = (\beta, 0, k_{i,z})$, with $k_{i,x}$ indicating the direction of propagation along x. We assume that there no charge and no current at the interface. This wave is a surface plasmon (actually a surface polariton). Since $\mathbf{E}$ is perpendicular to the direction of propagation, a surface plasmon is a transverse mode. What is the difference with a bulk plasmon (that we have seen in the preceding chapter) ?

(2) From

$$\omega \mathbf{B} = \mathbf{k} \wedge \mathbf{E} \tag{214}$$

and from the equation of continuity for $\mathbf{D}_i$ along the normal z-direction, show:

$$\begin{aligned} E_{1,x} = E_{2,x} \\ \epsilon_1 E_{1,z} = \epsilon_2 E_{2,z} \end{aligned} \tag{215}$$

(3) Use $\boldsymbol{\nabla} \cdot \mathbf{D} = 0$ and show

$$\beta E_{i,x} / E_{i,z} = -k_{i,z} \qquad i = 1,2 \tag{216}$$

(4) Deduce

$$\frac{k_{1,z}}{\epsilon_1} = \frac{k_{2,z}}{\epsilon_2} \tag{217}$$

(5) We are looking for modes bound to the interface where the fields decay exponentially normal to the interface. What are the conditions for the $k_{i,z}$'s ?
(6) We write

$$k_{i,z} = j\kappa_i \qquad j^2 = -1 \tag{218}$$

The normal being oriented either upwards or downwards, what are the signs of $\kappa_1 < 0$ κ_2 ?
(7) What is the condition on the signs of ϵ_1 and ϵ_2 for (218) to hold ? Can surface plasmon be excited at the interface between two metals or two dielectrics ?
(8) What is the dispersion relation in the metallic part ?
(9) What is the dispersion relation in the dielectric part ?
(10) Show

$$\beta = \frac{\omega}{c} \sqrt{\frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2}} \tag{219}$$

(11) For a dielectric, ϵ_1 is constant. But, for $\omega < \omega_p$, $\epsilon_2 = 1 - \omega_p^2/\omega^2$. Plot ω/ω_p in the vacuum and for a surface plasmon as a function of $\beta c/\omega_p$. Show that the surface plasmon resides below the light cone.
(12) Can a surface plasmon be directly excited by light ?

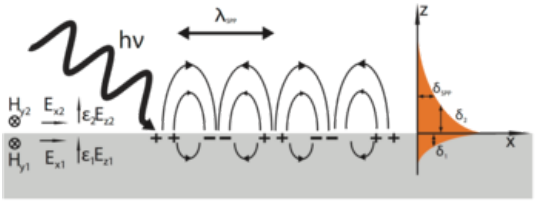

FIGURE 1

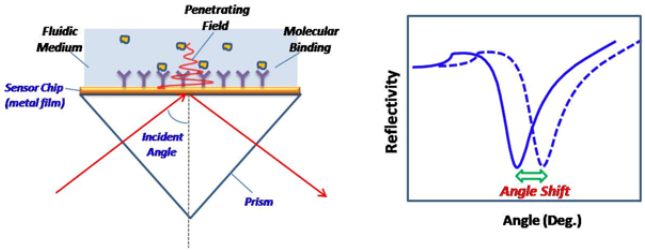

FIGURE 2. Prism coupling: The Kretschmann configuration. From https://biosensingusa.com/technical-notes/technical-note-102-spr-sensitivity-detection-limit/

(13) *A typical experiment in schematized in the Fig. 2. A metal film is evaporated on top of a glass prism. To excite the surface plasmon, a second layer of dielectric is deposited between the prism and the metallic layer. In this two layers geometry, one can, excite a SPP.*

CHAPTER 7

The consequences of causality: The Kramer-Krönig relations

1. An example

Consider a filter which is opaque to only one wavelength but transparent to all other. This means that the transmittance is 1 at all wavelengths but 0 at, say, $\omega = \omega_0$.

Consider a wavepacket of the Fig. This is an amplitude versus trace for an incident wave packet at a fixed point in the medium. Let $t = 0$ be the first appearance of this wave packet at this observation point.

This wave packet contains many frequencies. If $f(t)$ is the signal, the spectrum $\tilde{f}(\omega)$ is simply the Fourier transform

$$f(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \tilde{f}(\omega)\, d\omega \tag{220}$$

Let the pulse be incident on the filter. What does the filter is to remove one frequency ω_0. So, if the amplitude of this component is A_{ω_0}, the frequency spectrum BEHIND the filter is

$$\tilde{g}(\omega) = \tilde{f}(\omega) - A_{\omega_0}\delta(\omega - \omega_0) \tag{221}$$

Fourier transforming back gives the signal after the fiter

$$g(t) = f(t) - A_{\omega_0} \cos(\omega_0 t + \phi_0) \tag{222}$$

There is an obvious problem: $A_{\omega_0} \cos(\omega_0 t + \phi_0)$ is finite at all time. The effect of the filter is to produce a signal at the detector long before the pulse arrived at the filter ! This breaks causality.

The medium must, therefore, introduce some kind of phase shift in all other frequencies to produce destructive interferences so that causality is not broken. We have seen that absorption is related to $\tilde{\epsilon}''(\omega)$. Te phase shift is due to the real part $\tilde{\epsilon}'(\omega)$. Therefore, $\epsilon'(\omega)$, cannot be independent of $\tilde{\epsilon}''(\omega)$ os, the neigborhood of ω_0.

2. Principal part

In general, there are many cases where for an arbitrary function $g(x)$, with $g(a) \neq 0$, the integral

$$\int_{-\infty}^{+\infty} dx\, \frac{g(x)}{x - a} \tag{223}$$

makes no sense. For some problems, it is useful to define the limit

$$\lim_{\epsilon \to 0} \left[\int_{-\infty}^{a-\epsilon} dx\, \frac{g(x)}{x - a} + \int_{a+\epsilon}^{+\infty} dx\, \frac{g(x)}{x - a} \right] \tag{224}$$

In general, (223) and (224) are different. Why ? (223) has a meaning iff the following limit exists

$$lim_{\epsilon_1 \to 0} lim_{\epsilon_2 \to 0} \left[\int_{-\infty}^{a-\epsilon_1} dx\, \frac{g(x)}{x - a} + \int_{a+\epsilon_2}^{+\infty} dx\, \frac{g(x)}{x - a} \right] \tag{225}$$

where ϵ_1 and ϵ_2 both go to zero but independently. For this reason, (224) can makes sense even if (223) does not make sense. To differentiate the two integrals, we use the notation (PP =

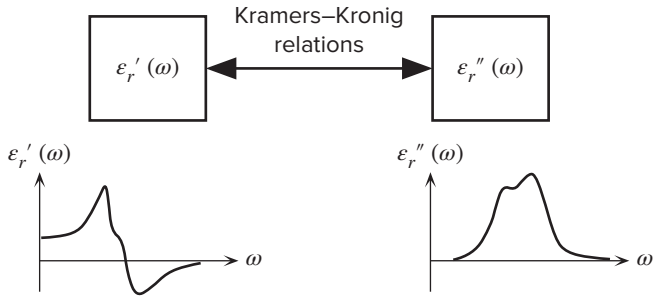

FIGURE 1. Kramer-Krönig relations give that the real and imaginary parts of a response function are related to each other. The material has to be linear

Principal Part)

$$PP\int_{-\infty}^{+\infty} dx\,\frac{g(x)}{x-a} = \lim_{\epsilon\to 0}\left[\int_{-\infty}^{a-\epsilon} dx\,\frac{g(x)}{x-a} + \int_{a+\epsilon}^{+\infty} dx\,\frac{g(x)}{x-a}\right] \tag{226}$$

In particular

$$PP\int_{-\infty}^{+\infty} dx\,\frac{1}{x^2} = 0 \tag{227}$$

3. Time domain response and causality

Let us consider the dipolar moment $\mathbf{P}$ and the electric field $\mathbf{E}$. In general

$$\mathbf{P}(\mathbf{r},t) = \int d^3\mathbf{r}' \int_{-\infty}^{t} dt' \chi(\mathbf{r},\mathbf{r}',t,t')\mathbf{E}(\mathbf{r}',t') \tag{228}$$

If we look for local responses

$$\chi(\mathbf{r},\mathbf{r}',t,t') = \delta^{(3)}(\mathbf{r}-\mathbf{r}')\chi(t-t') \tag{229}$$

where we also have assumed time translational invariance. This means

$$\begin{aligned}\mathbf{P}(\mathbf{r},t) &= \int_{-\infty}^{t} dt' \chi(t-t')\mathbf{E}(\mathbf{r},t') \\ &= \int_{0}^{+\infty} d\tau\,\chi(\tau)\mathbf{E}(\mathbf{r},t-\tau)\end{aligned} \tag{230}$$

Define the Fourier transform as usual

$$\tilde{\chi}(\omega) = \int_{-\infty}^{+\infty} dt \chi(t) e^{i\omega t} = \int_{0}^{+\infty} dt \chi(t) e^{i\omega t} \tag{231}$$

Since $\mathbf{P}$ and $\mathbf{E}$ are both real numbers, $\chi(t)$ is also a real number. But $\tilde{\chi}(\omega)$ is a $\mathbb{C}$-number. We have

$$\tilde{P}(\omega) = \int_{-\infty}^{+\infty} dt'\,\mathbf{E}(t')\left[\int_{-\infty} +\infty e^{i\omega t}e^{-i\omega t'}\right] e^{i\omega t'} \quad = \tilde{\chi}(\omega)\tilde{\mathbf{E}}(\omega) \tag{232}$$

4. The Kramer-Krönig relation

For all response functions the real and imaginary parts are not independent of each other

$$\begin{aligned}\tilde{\chi}'(\omega) &= \frac{1}{\pi} PP\int_{-\infty}^{+\infty} d\omega' \frac{\tilde{\chi}''(\omega')}{\omega'-\omega} \\ \tilde{\chi}''(\omega) &= -\frac{1}{\pi} PP\int_{-\infty}^{+\infty} d\omega' \frac{\tilde{\chi}'(\omega')}{\omega'-\omega}\end{aligned} \tag{233}$$

EXERCICE 4.1. *Consider a harmonic oscillator with damping coefficient γ. The equation of motion is*

$$m\ddot{x}(t) + \gamma\dot{x}(t) + kx(t) = F(t) = mf(t) \tag{234}$$

The response function is defined by the displacement-force relation

$$x(t) = \int_{-\infty}^{t} dt' \chi(t-t')F(t') \tag{235}$$

(1) It is interesting to consider the response to an ac field

$$F(t) = F_0 e^{-i\omega t} \qquad x(t) = \tilde{\chi}(\omega)F_0 e^{-i\omega t} \tag{236}$$

Show

$$\tilde{\chi}(\omega) = \tilde{\chi'}(\omega) + i\tilde{\chi''}(\omega) = \int_0^{\infty} dt\, \chi(t)e^{i\omega t} \tag{237}$$

so that $\tilde{\chi}(\omega)$ is a complex function.

(2) Since the actual applied field is real, only the real part $F_0\cos(\omega t)$ is meant. The response is, therefore, the real part of the response to the complex field. Show

$$x(t) = \tilde{\chi'}(\omega)F_0\cos(\omega t) + \tilde{\chi''}(\omega)F_0\sin(\omega t) \tag{238}$$

(3) Find the real and imaginary part of $\tilde{\chi}(\omega)$ (recall $\chi(\tau) = 0$ for $\tau < 0$)

(4) Show that

$$\chi(\omega) = -\frac{1/m}{(\omega-\omega_1)(\omega-\omega_2)} \text{ with } \omega_{1,2} = -i/(2\tau) \pm \tilde{\omega} \text{ and } \tilde{\omega} = \sqrt{\omega_0^2 - 1/4\tau^2} \tag{239}$$

As a result, the poles of $\tilde{\chi}(\omega)$ are in lower part of the complex plane. This property is generic and are of constant use in more complicated theory.

(5) Show $\tilde{\chi}(\omega) = \tilde{\chi}^{\star}(-\omega)$.Conclude that $\tilde{\chi}'(\omega)$ is even and that $\tilde{\chi}''(\omega)$ is odd.

EXERCICE 4.2. *We can demonstrate the Kraemer-Krönig relations if we accept the two following prerequisites*

(1) The convolution theorem:

$$\int_{-\infty}^{+\infty} dt e^{i\omega t} f(t)g(t) = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} f(\omega-\omega')g(\omega') \tag{240}$$

(2) The Fourier transform of the $\theta(t)$ function:

$$\int_{-\infty}^{+\infty} dt\theta(t)e^{i\omega t} = \lim_{\epsilon\to 0+} \int_{-\infty}^{+\infty} dt\theta(t)e^{i(\omega+i\epsilon)t} = \frac{i}{\omega+i\epsilon} \tag{241}$$

where

$$\forall f(\omega): \quad \lim_{\epsilon\to 0+} \int_{-\infty}^{+\infty} d\omega \frac{if(\omega)}{\omega+i\epsilon} = PP\int \frac{if(\omega)}{\omega} + \pi f(0) \tag{242}$$

The last equation is proved using the residu theorem.

Because of causality, the response function must be of the form

$$\chi(t) = \theta(t)y(t) \tag{243}$$

where $y(t) = \chi(t)$ for $t > 0$. We are, however, free to choose $y(t)$ for $t > 0$ as we want because of (243).

(1) Choose $y(-|t|) = y(|t|)$. Is $\tilde{y}(\omega)$ a pure real function ? Use the convolution of (243) to demonstrate one of the Kraemer-Krönig equation;

(2) Choose $y(-|t|) = -y(|t|)$. Then prove the second relation.

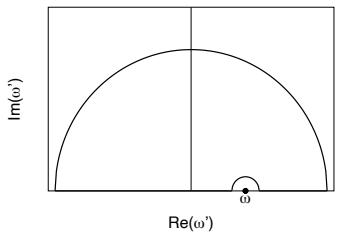

FIGURE 2. Contour used to demonstrate the Kramer-Krönig relations.

5. The Kramer-Krönig relation as a a consequence of the Cauchy relation

Here, we demonstrate the Kramer-Krönig equations (233) using complex analysis. First we show that causality implies that $\tilde{\chi}(\omega)$ is analytic in the upper half of the complex z plane, when considered as a function of the complex frequency z (whose real part is the physical frequency ω). Writing $z = x + iy$, where $x = \omega$

$$\begin{aligned} \tilde{\chi}'(\omega) &= \int_0^\infty \chi(t)\cos(\omega t)e^{-yt} \\ \tilde{\chi}''(\omega) &= \int_0^\infty \chi(t)\sin(\omega t)e^{-yt} \end{aligned} \tag{244}$$

The Cauchy relations are necessary and sufficient conditions for a function to be analytic

$$\begin{aligned} \frac{d\tilde{\chi}'(\omega)}{dx} &= \frac{d\tilde{\chi}''(\omega)}{dy} \\ \frac{d\tilde{\chi}''(\omega)}{dx} &= -\frac{d\tilde{\chi}'(\omega)}{dy} \end{aligned} \tag{245}$$

It suffices to interchange the operations of differentiation and integration. This is possible, because of the exponential factor which is always negative. If the $\chi(t)$ have not been causal, the integral had run from $-\infty$ to $+\infty$ and going to the upper half plane would not have been possible.

Cauchy's theorem gives the identity

$$\oint_C dz \frac{\tilde{\chi}(\omega)}{z-\omega} = 0 \tag{246}$$

for any contour C confined to a region where $\tilde{\chi}(\omega)$ is analytic and not containing the point $z = \omega$. Use the contour of Fig. 2.

The integral over the small arc of circle is parametrized as $z = \omega + \epsilon e^{i\phi}$ with $dz = i\epsilon e^{i\phi} d\phi$ and the large C contour vanishes as z goes to infinity. All together

$$0 = PP\int_{-\infty}^{+\infty} d\omega' \frac{\tilde{\chi}(\omega')}{\omega'-\omega} + \lim_{\epsilon\to 0}\int_\pi^0 \frac{i\epsilon e^{i\phi}d\phi}{\epsilon e^{i\phi}}\chi(\omega+\epsilon e^{i\phi}) \tag{247}$$

This becomes the general relation

$$\tilde{\chi}(\omega) = \frac{1}{i\pi} PP\int_{-\infty}^{+\infty} d\omega' \frac{\tilde{\chi}(\omega')}{\omega'-\omega} \tag{248}$$

which is equivalent to (233) after separating the real and imaginary part.

CHAPTER 8

Scattering and structure factor

We have neutron, X-Ray or light scattering. What are we talking about ? Here we are concerned with phenomena where adsorption is negligible. We distinguish:

(1) Elastic scattering: When radiation is emitted by the illuminated sample without change in frequency and in all directions of space. Typical examples are Rayleigh scattering for light scattering and Thomson scattering for X-rays. Elastic scattering probe physical properties of heterogeneities. It gives geometrical structural informations. A typical example is the diffusion of the light of the headlights of a car at night and in fog (Rayleigh diffusion).

(2) Inelastic scattering: We have a change in frequency when the radiation is reemitted by the sample. Typical example are florescence spectroscopy or Brilloin and Raman spectroscopy. Inelastic scattering requires the resonance of an atomic or molecular oscillator. It is of prime importance in chemistry.

1. Elementary theory: Bragg's law

We consider elastic scattering with the scattering from parallel planes with separation distance d. The incident wave has vector $\mathbf{k}$ and the scattered wave has $\mathbf{k}'$. If λ is the wavelength $k = 2\pi/\lambda$.

The condition for constructive interferences is given by

$$2d\sin\theta = n\lambda \qquad n = 1, 2, \dots \tag{249}$$

where 2θ is the angle between the incident and scattered particles. Scattering at angle θ gives, therefore, information on periodicity $\lambda/2\sin\theta$. In short, scattering at angle 2θ gives information about fluctuations of inhomogeneities at length scale $\lambda/(2\sin\theta)$.

In a more advanced approach valid for weak scattering (meaning that only one scattering event is considered, multiscattering is disregarded), the transition from state $|\mathbf{k}\rangle$ to state $|\mathbf{k}'\rangle$ is given by the matrix element (Fermi's golden rule)

$$M_{k,k'} = \langle \mathbf{k}'| U |\mathbf{k}\rangle = \int d^d r\, e^{-i\mathbf{k}\cdot\mathbf{r}} U(r) e^{i\mathbf{k}'\cdot\mathbf{r}} \tag{250}$$

where $U(r)$ is the scattering potential (and where we use unnormalized wave function $e^{i\mathbf{k}\cdot\mathbf{x}}$)).

For multiparticle systems, the scattering potential $U(x)$ is the sum of all atomic potentials

$$U(\mathbf{r}) = \sum_\alpha U_\alpha(\mathbf{r} - \mathbf{r}_\alpha) \tag{251}$$

and the matrix element becomes

$$M_{k,k'} = \langle \mathbf{k}'| U |\mathbf{k}\rangle = \sum_\alpha \int d^d r\, e^{-i\mathbf{k}'\cdot\mathbf{r}} U_\alpha(\mathbf{r} - \mathbf{r}_\alpha) e^{i\mathbf{k}\cdot\mathbf{r}} \tag{252}$$

The differential section per unit angle is given by

$$\frac{d^2\sigma}{d\Omega} = \frac{2\pi}{\hbar}|M_{k,k'}|^2 \tag{253}$$

where $d\Omega = sin\theta d\theta d\phi$ is the solid angle .

2. The structure factor

Take $\mathbf{R}_\alpha = \mathbf{r} - \mathbf{x}_\alpha$

$$\begin{aligned} \langle \mathbf{k}' | \, U \, | \mathbf{k} \rangle &= \sum_\alpha \int d^d R_\alpha \, e^{-i\mathbf{k}'\cdot(\mathbf{x}_\alpha + \mathbf{R}_\alpha)} U_\alpha(\mathbf{R}_\alpha) e^{i\mathbf{k}'\cdot(\mathbf{x}_\alpha+\mathbf{R}_\alpha)} \\ &= \sum_\alpha \left[\int d^d R_\alpha e^{-i\mathbf{q}\cdot\mathbf{R}_\alpha} U_\alpha(\mathbf{R}_\alpha) \right] e^{-i\mathbf{q}\cdot\mathbf{x}_\alpha} \\ &= \sum \tilde{U}_\alpha(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{x}_\alpha} \end{aligned} \tag{254}$$

where $\mathbf{q} = \mathbf{k}' - \mathbf{k}$ is the the scattering wave vector and where $\tilde{U}_\alpha((q)$ is the atomic form factor (the Fourier transform of the atomic potential).

We have

$$|\langle \mathbf{k}' | \, U \, | \mathbf{k} \rangle|^2 = \sum_{\alpha,\alpha'} \tilde{U}_\alpha(\mathbf{q}) \tilde{U}^\star_\alpha(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{x}_\alpha + i\mathbf{q}\cdot\mathbf{x}_{\alpha'}} \tag{255}$$

For identical atoms, $\tilde{U}_\alpha$ is independent of α and the differential cross-section reads as

$$\frac{d^2\sigma}{d\Omega} = \left| \tilde{U}(\mathbf{q}) \right|^2 I(\mathbf{q}) \tag{256}$$

where the structure function is the double sum

$$I(\mathbf{q}) = < \sum_{\alpha,\alpha'} e^{-i\mathbf{q}\cdot(\mathbf{x}_\alpha - \mathbf{x}_{\alpha'})} > \tag{257}$$

In this equation, <> means that we have taken the thermal average over the positions $\mathbf{x}_\alpha$. In solids, $I(q)$ is proportional to N^2, where N is the total number of atoms. To define extensive quantities

$$S(\mathbf{q}) = \frac{1}{N} I(\mathbf{q}) \tag{258}$$

All these formula are valid for a) plane waves, b) single scattering events.

We can generalize for inhomogeneous materials:
Let us assume some fluctuations in the concentration field:

$$n(\mathbf{x}, t) = n_0 + \delta n(\mathbf{x}, t) \tag{259}$$

where the fluctuations $\delta n(\mathbf{r}, t)$ can be expanded as a sum of Fourier modes

$$\delta n(\mathbf{x}, t) = \frac{1}{V} \sum_k \tilde{\delta n}(\mathbf{k}, t) e^{i\mathbf{k}\cdot\mathbf{x}} \tag{260}$$

The quantity measured in elastic scattering experiments is the structure factor

$$S(\mathbf{q}) = < \left| \tilde{\delta n}(\mathbf{q}, t) \right|^2 > = \int d\mathbf{x} d\mathbf{x}' \, < \delta n(\mathbf{x}, t) \delta n(\mathbf{x}', t) > \tag{261}$$

In this equation, <> means thermal average. If the Fourier expansion of of $\delta n(\mathbf{x}, t)$ contains one dominant wave vector (meaning that the fluctuations have a characteristic length scale $1/q_{max}$), then the structure factor will have to shape of the figure.

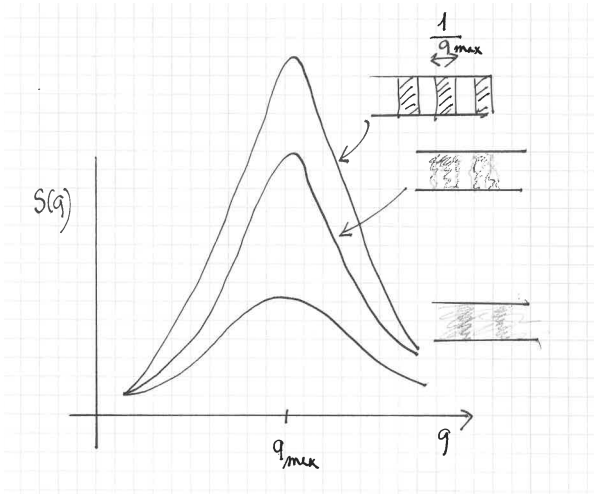

FIGURE 1. Structure factor when a density fluctuation at characteristic wave number q_{max} growths with time.

3. Photons, neutrons and electrons

From Bragg's law, $2d\sin\theta = n\lambda$ and λ must be less than $2d$. Atomic interspacing is generally on the Angström scale, so we must consider typical energies for the incident radiation.

- Visible light with energy around 1 eV ($0.4\,\mu m < \lambda < 0.7\mu m$). As we have seen, visible light probe structures at the μm (variations in the dielectric constant);
- Probing structures at the Å scale need s, therefore, $10^4 eV$: This means X-rays !
- Electrons have a dispersion relation

$$\frac{\hbar^2 k^2}{2m} = \frac{h^2}{2m\lambda^2} \tag{262}$$

so $\lambda \approx 1$ Å corresponds to $100eV$. But electrons scatter from electrostatic potentials which are often large and we are no more in the weak scattering limit. For bulk materials, this is often large ans electron scattering is mainly use for surface phenomena to avoid multiple scattering events ;

- Neutrons have a similar relationship but with a much larger mass. A wavelength of 1 Å corresponds to $0.1eV$ (ie thermal neutrons, since $\approx 400K$). This means that neutrons have the correct energy (and are of used to probe phonon spectrum for example).

4. Intermezzo: What is a correlation function ?

A material in thermal equilibrium may be macroscopically homogeneous and static, but it fluctuates on the micro scale because of thermal fluctuations. We measure how systems fluctuate and evolve in space and time using correlation functions.

Consider for example the density (at position $\mathbf{x}$) $n(\mathbf{x}, t)$. Because of thermal fluctuations, $n(\mathbf{x}, t)$ at a given position $\mathbf{x}$ fluctuates randomly in time. If the mean is n_0, a measure of cross-correlation for the fluctuations at two points distant of $\mathbf{r}$ is

$$C(\mathbf{r}, \tau) =< (n(\mathbf{x}, t) - n_0)(n(\mathbf{x} + \mathbf{r}, t + \tau) - n_0) > \tag{263}$$

where we have averaged the product and not taken the product of the averages. When $\mathbf{r} = \mathbf{0}$ and $\tau = 0$, the correlation function is simply the variance of the fluctuations. However, when $\mathbf{r}$ or τ is large, what happens at $\mathbf{x}$ is statistically independent of what happens at $\mathbf{x} + \mathbf{r}$ (same thing when τ is large). In this case, averaging the product amounts of taking the products of the averages. In one of these limits

$$C(\mathbf{r}, \tau) \to 0 \quad \text{if } \mathbf{r} \to +\infty \text{ or } \tau \to +\infty \tag{264}$$

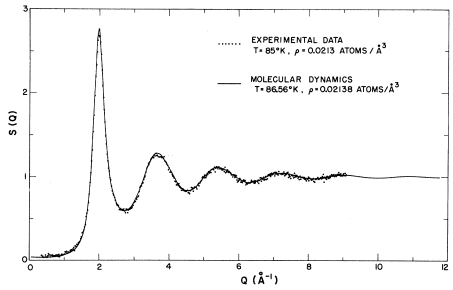

FIGURE 2. Experimental structure factor $S(q)$ for liquid Ar at 85 K[10] compared with molecular dynamic simulations.

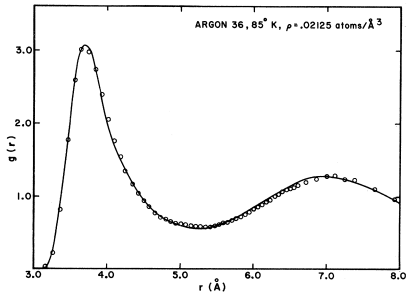

FIGURE 3. Experimental density-density correlation function for Ar compared with Monte Carlo simulations.[10]

An important application of correlation functions is their interpretation in terms of probability. If one rescales the density $n(\mathbf{x}, t)$ by the mean, $n(\mathbf{x}, t)$ is simply the probability to find a particle at $\mathbf{x}$ and time t. Eq. (264) can now be interpreted as a conditional probability. Given that a particle is at $\mathbf{x}$ at time t, what is the probability to find an other particle at position $\mathbf{x} + \mathbf{r}$ at a time τ later.

5. Density operator and correlation functions

In this section we derive an important result. The structure factor is the Fourier transform of the correlation for the density of particles (at equal time). In other words, the structure factor $S(\mathbf{q})$ mesure the correlation between fluctuations. To get extensive quantities, define (V = volume) the Fourier transform of the correlation function

$$\tilde{C}(\mathbf{q}) = \frac{1}{V} \int d^d\mathbf{x}_1 \int d^d\mathbf{x}_2 e^{-i\mathbf{q}\cdot(\mathbf{x}_1 - \mathbf{x}_2)} < (n(\mathbf{x}_1, t) - n_0)(n(\mathbf{x}_2, t) - n_0) > \tag{265}$$

Expending the product inside the integral

$$I(\mathbf{q}) = \left| \int d^d x e^{-i\mathbf{q}\cdot\mathbf{x}} < n(\mathbf{x}) > \right|^2 + V\tilde{C}(\mathbf{q}) \tag{266}$$

In liquids

$$\int d^d x e^{-i\mathbf{q}\cdot\mathbf{x}} < n(\mathbf{x}) >= V < n > \delta_{\mathbf{q},\mathbf{0}} \tag{267}$$

with the definition of delta function

$$V\delta_{\mathbf{q},\mathbf{0}} = (2\pi)^3 \delta(\mathbf{q}) \tag{268}$$

In general, the pic at $q = 0$ is not seen.

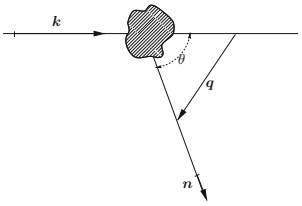

FIGURE 4. Schematic diagram of a scattering experiment. The incident radiation is a plane wave propagating in the direction of the wave vector **k**. The irradiated sample emits scattered radiation in all directions in space. A particular direction of observation, the one in which a detector is placed, for example, is represented by the unit vector **n** which forms an angle θ with the incident direction.

6. Small Angle Scattering - Introduction

Small angle scattering[6] is produced by heterogeneities that are a priori non-periodic (so it is different from Bragg diffraction which assumes periodic materials) and, moreover, often fluctuating due to the inevitable thermal agitation present in any sample. For the study of condensed matter, small angle scattering is essentially practiced with electromagnetic radiation (visible light, X-rays) and, of course, neutrons. In its broad outline, the phenomenon of scattering is largely independent of the nature of the radiation used.

A good way to represent, semi-quantitatively, the phenomenon of elastic scattering is as follows: because it has been "conditioned" (by the monochromator, collimation devices, etc.), the incident radiation passing through the sample can be seen, within the heterogeneities of the sample, as a plane wave

$$\psi(\mathbf{x}, t) = \psi_0 \exp\{i(\mathbf{k} \cdot \mathbf{x} - \omega t)\} \tag{269}$$

where ψ depends on the nature of the radiation. For EM waves (i.e. visible, X-Rays), ψ is the amplitude of the electric field (magnetic field) with $\omega = ck$, $n = 1$. For neutrons, ψ is the wave function with

$$\hbar\omega = \frac{\hbar k^2}{2M} \tag{270}$$

where M is the mass of the neutron.

Each point of heterogeneity in the sample takes a part of the energy brought by the incident radiation to give back the totality of this energy in the form of a divergent spherical wave, at the same frequency as that of the incident wave - the scattering is elastic. Finally, the scattered radiation is made of the superposition, and thus the interference in coherent scattering, of all these spherical wavelets.

$$\psi(\mathbf{R}, t) = \frac{\psi_0}{R} \exp\{i(\mathbf{k} \cdot \mathbf{R} - \omega t)\} \tag{271}$$

All the heterogeneities do not take energy from the incident wave with the same efficiency. As a result, all the wavelets that interfere do not have the same amplitude. The scattered radiation therefore also contains some information about the efficiency of the plane wave $\rightarrow$ spherical wave conversion, related to the contrast of the sample

The characteristic scale at which the sample heterogeneity is probed by the radiation is defined by the modulus q of the scattering wave vector and is typically $1/q$. Since $\mathbf{q} = k\mathbf{n} - \mathbf{k}$ with the notations in Fig. 4, it follows

$$q = 2k \sin\frac{\theta}{2} = \frac{4\pi}{\lambda_0} \sin\frac{\theta}{2} \tag{272}$$

Therefore, small q's correspond to small angles θ. Typical numbers are as follows:

(1) Light: $q \in [210^{-3}, 210^{-2}]$ nm^{-1};
(2) X Rays $q \in [10^{-1}, 210^{2}]$ nm^{-1};

(3) Neutrons $q \in [410^{-2}, 210^{+1}]$ nm^{-1};

7. Small Angle Scattering - Colloidal dispersion

Consider now a solute and a solvent. The volume fraction of the solute is ϕ (we assume that the solvent and the solute have the same molecular volume, so the volume fraction and the density are the same). We also assume that both species are incompressible. Thus local variations in the concentrations of solute lead to light (x-rays ou neutron) scattering. Here we replace local variations in density by local variations in volume fraction.

$$\phi(x,t) = \phi_0 + \delta\phi(\mathbf{x},t) \tag{273}$$

So

$$I(q) \propto < \left| \int_V d^3x e^{-i\mathbf{q}\cdot\mathbf{x}} \delta\phi(\mathbf{x},t) \right|^2 > \tag{274}$$

where, as before, the proportionality constant accounts for

(1) The intensity of the incoming wave;
(2) There is a factor $1/R^2$, because the scattered wave is a spherical wave;
(3) The contrast between the solvent and the solute.

It is interesting to consider the limits $ql_c \gg 1$ and $ql_c \ll 1$.

8. Porod's law

Let l_c be the structural characteristic length (dimension). This law is valid in the limit $ql_c \gg 1$ (ex. micelles, oil dispersion ...)

$$I(q) \propto \frac{1}{q^4} \tag{275}$$

A notable exception to Porod's law are polymers where $I(\mathbf{q}) \propto 1/q^2$ at large q.

9. Small q limit

In the other limit $ql_c \ll 1$. For a binary fluid

$$I(\mathbf{q} \to 0) \propto k_B T \phi \frac{\left[\frac{\partial \Pi}{\partial \phi}\right]^{-1}}{1 + q^2\xi^2} \tag{276}$$

where

$$\Pi = \phi \partial f \partial \phi - f \tag{277}$$

is the osmotic pressure. In the last equation, f is the free energy of the system per unit volume. Near the critical point for continuous phase transitions, both Π and ξ go to infinity. The last equation is generally used to explain the phenomenon of critical opalescence.

EXERCICE 9.1. *Consider the free energy (from the pure entropy of mixing)*

$$f = k_B T \left[\phi \ln(\phi) + (1-\phi)\ln(1-\phi)\right] \tag{278}$$

and compute $I(\mathbf{q})$.

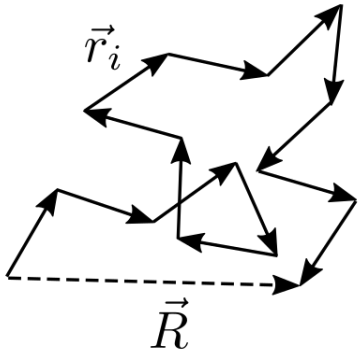

FIGURE 5. The end-to-end distance $\mathbf{R}$ is the sum of elementary vectors.

10. The structure factor of an ideal polymer

An ideal chain (or freely jointed chain) is the simplest model to describe polymers, such as nucleic acids and proteins. It only assumes a polymer as a random walk and neglects any kind of interactions among monomers. Although it is simple, its generality gives insight about the physics of polymers.

We can think of the chain as the trace made by a random walk. All steps $\mathbf{r}_i$ have equal length but they vary in direction. The $\mathbf{r}_i$'s are independent stochastic variables with

$$< \mathbf{r}_i >= 0 \quad < \mathbf{r}_i \cdot \mathbf{r}_j >= a^2 \delta_{i,j} \tag{279}$$

where a is the step size.

We will be interested in the end-to end distance $\mathbf{R}$. By definition, $\mathbf{R}$ is a vector and the sum of all the $\mathbf{r}_i$ gives $\mathbf{R}$, see Fig. 5:

$$\mathbf{R} = \sum_{i=1,N} \mathbf{r}_i \tag{280}$$

and the norm of $\mathbf{R}$ should not be confused with the total length of the polymer which is Nl. The end-to-end distance is the sum of $3N$ random variables (each vector has three components in a three-dimensional space) and the x component of $\mathbf{R}$ follows from (280) as

$$R_x = \sum_{i=1,N} r_{i,x} \tag{281}$$

with (by the democracy rule which tells us that all directions are equivalent)

$$r_{i,x}^2 = r_{i,y}^2 = r_{i,z}^2 = a^2/3 \tag{282}$$

We can apply the central limit theorem to find the distribution of $\mathbf{R}$ over different realizations of the random walks. We know that the distribution of the vector $\mathbf{R}$ is Gaussian in the large N limit

$$P(\mathbf{R}) = P(R_x, R_y, R_z) = \left[\frac{3}{2\pi N a^2}\right]^{3/2} \exp\left\{\left[-\frac{3\mathbf{R}^2}{2Na^2}\right]\right\} \tag{283}$$

with for the norm

$$|\mathbf{R}| = a\sqrt{N} \tag{284}$$

Eq. (284) is known as the radius of gyration. The factor 3 in (283) arises because the walker took $N/3$ steps on average in each direction.

EXERCICE 10.1. *Compute the probability distribution for the norm* $|\mathbf{R}|$ *of the vector* $\mathbf{R}$.

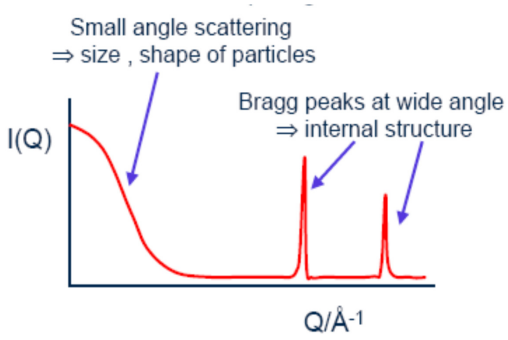

FIGURE 6. Sketch of typical scattering intensity as a a function of the wave vector $\mathbf{q}$ for "particules" (atoms, molecules, polymers, proteins etc.) with a periodic motif. The small angle scattering (small $\mathbf{q}$) gives informations on the size or shape of the particles. The high $\mathbf{q}$ limit gives the Bragg peaks characteristic of a periodic structure corresponding to atomic positions.

11. Summary: Form factor, structure factor

A typical intensity plot of the the scattering intensity is presented in Fig. 6. Everything is in the wave vector $\mathbf{q}$ (or the angle θ). Large structures scatter at small angles. For techniques using small angles, we probe material properties rather than atomic properties. In general the scattered intensity for a solution of "particles" is of the form

$$I(\mathbf{q}) = N_p V_p^2 (\rho_p - \rho_s)^2 |F(q)|^2 S(q) + B \tag{285}$$

where

- N_p = number of particles;
- V_p = volume of the particle;
- ρ a contrast parameter to distinguish the solvent from the solute;
- B = Background;
- $F(q)$ = Scattering from within the particle (depends on particle shape);
- $S(q)$ = Scattering from different particles. For dilute solution $S(q) = 1$.

EXERCICE 11.1. *We have seen that the structure factor is related to the pair correlation function. One of the must useful illustration of this property is given by polymers. Under some circonstances, you have seen that a polymer can be seen as a random walk of N steps of length a.*

Let $\mathbf{R}$ be the average vector for the position the position of the first monomer to the last:

$$\mathbf{R} = \mathbf{r}_N - \mathbf{r}_1 \tag{286}$$

Since the the step directions are completely uncorrelated

$$< \mathbf{R} >= 0 \tag{287}$$

but the averaged square scales with the number of steps

$$< \mathbf{R}^2 >= Na^2 \tag{288}$$

The average radius of gyration determines the characteristic size of the polymer is simply equal to the the root mean square separation of the end points. That is

$$R_G = \left[< \mathbf{R}^2 >\right]^{1/2} \propto N^{1/2} \tag{289}$$

For polymers, the number of steps is called the index of polymerization. The previous result which relates the radius R_g to N is of central importance. We remark that this result does not depend on the dimension. We have the same law for $d = 1, 2, 3$ or 4.

For polymers, the structure factor is a measurable quantity using neutron scattering, see Fig. 7 for two canonical examples (at and above the theta point). In this problem, we would like to determine this structure factor analytically.

(A) (B)

FIGURE 7. (A) $S(q)^{-1}$ for polymers in theta solvent where ideal chain statistics apply. (B) $S(q)^{-1}$ in good solvent where excluded volume effects are important[3].

(1) In this part, we want to compute the structure factor using the radial distribution function $g_F(r)$. It will be useful to consider the dimension d of the space as a variable. We have

$$S(q) \propto \int g_F(r) e^{-i\mathbf{q}\cdot\mathbf{r}} d^d r \tag{290}$$

Consider first an ideal polymer in $d = 3$ dimension.

(2) We know that a segment of random walk is itself a random walk. This means that the structure is fractal and invariant under magnification. How many monomers $n(r)$ can we observe in a sphere of radius r given that there is one monomer at the origin ? (use (289)).

(3) We want to compute the radial distribution function $g_F(r)$. What is the volume of the shell between radius r and $r + dr$? What is the number of monomers within this shell ? Deduce the probability to find a monomer at a distance r and give $g_F(r)$.

(4) Give $g_F(r)$ for arbitrary d (leave unimportant factors aside and don't forget the remark following (289)).

(5) We consider $d = 3$. For polymer, what is the interesting limit for neutron scattering (i.e. $qR_G \gg 1$ or $qR_G \ll 1$) ?

(6) Again $d = 3$. How $S(q)$ scales with the wave vector q. Compare with the two cases of Fig. 7. In which case the polymer chain is more swollen and in which case the chain in more swollen ? Can you guess what happens in the system if we don't neglect anymore the interaction between the monomers ?

(7) Redo the previous calculation if (289) is changed as $\mathbf{R}^2 = a^2 N^{2\nu}$, with $\nu = 3/(d+2)$. Remark that d decreases as the dimensions d increases from 1 to 3. What happens for $d = 4$?

(8) We now want to calculate the structure factor directly without using the pair correlation function. The equivalent of (274) is given by

$$P(q) = \frac{1}{N^2} \sum_{i,j}^{N} < e^{-i\mathbf{q}\cdot\mathbf{r}_{ij}} > \tag{291}$$

where $\mathbf{r}_{ij}$ is the relative distance between monomers i and j. Give $< \mathbf{r}_{ij}^2 >$ as a function of $|i - j|$.

(9) Polymer coils in theta solvents follow Gaussian statistics whereby the inter-monomer distance is given by

$$P(r_{ij}) = \left(\frac{3}{2\pi < r_{ij}^2 >}\right)^{3/2} \exp\left\{\left[-\frac{3r_{ij}^2}{2 < r_{ij}^2 >}\right]\right\} \tag{292}$$

with $< r_{ij}^2 >= a^2|i-j|$. *Here we will average the structure factor of this probability (ensemble average over the conformations of the polymer chains). Give the single chain structure factor* $S(\mathbf{q})$.

(10) Use the following identity for Gaussian integrals

$$< e^{-iq_x x_{ij}} >= \exp\left\{\left[-\frac{q_x^2 < x_{ij}^2 >}{2}\right]\right\} \tag{293}$$

to show

$$S(\mathbf{q}) = \frac{1}{N^2} \sum_{i,j} e^{-\frac{q^2 a^2 |i-j|}{6}} \tag{294}$$

(11) For any function $F(x)$, *we have the following identity (which is easy to prove and do it)*

$$\sum_{i,j=1,N} F(|i-j|) = NF(0) + 2 \sum_{k=1,N} (n-k)F(k) \tag{295}$$

Show

$$S(q) = \frac{1}{N^2}\left[N + 2 \sum_{k=1,N} (N-k) e^{-\frac{q^2 a^2 k}{6}}\right] \tag{296}$$

(12) As usual, we can transform the discrete sum into an integral when N *is large. Using the definition of a Riemann integral*

$$\sum_{k=1,n} f(\frac{k}{n})\Delta\left[\frac{k}{n}\right] = \int_0^1 f(x)dx \tag{297}$$

show

$$S(q) = \frac{2}{q^4 R_g^4}\left[e^{-q^2 R_g^2} - 1 + q^2 R_g^2\right] \tag{298}$$

where we have defined R_g *as*

$$R_g = \left[Na^2/6\right]^{1/2} \tag{299}$$

Plot this function and recover the result obtained in the first part of this problem.

EXERCICE 11.2. *In this problem we ask the following question: What is the scattering from independent particles immersed in the solvent ? For simplicity, we assume that all particles are identical (the density inside the particle is* ρ_p *and the density of the solvent is* ρ_s. *We neglect correlations between the particles (so we work in the dilute limit) and we assume that the particles are spherical with radius* R.

The scattering intensity per unit volume is

$$I(q) = \frac{N}{V}\left(\rho_s - \rho_p\right)^2 V_p^2 < \frac{1}{V_p}\left|\int_{particle} e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}\right|^2 > \tag{300}$$

where

$$F(q) = \frac{1}{V_p}\left|\int_{particle} e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}\right| \tag{301}$$

is called the form factor.

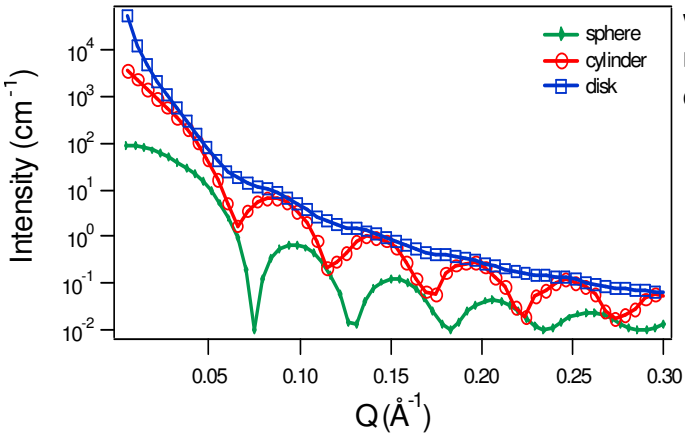

FIGURE 8. Shape of the intensity for different shapes of the particles in dilute solutions.

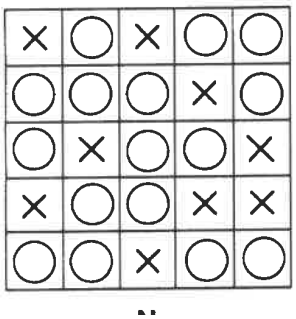

FIGURE 9. Lattice model to calculate the entropy of mixing.

(1) Since q is given by the experimental setup (you know where you put your detector), we can parametrize the system as we want. Take $\mathbf{q} = (0, 0, q_z)$. Show the two equations:

$$\begin{aligned} F(q) &= 2\pi \int_0^\pi \int_0^R \left(\cos(qr\cos\theta) + i\sin(qr\cos\theta)\right) r^2 dr \sin\theta d\theta \\ &= \frac{4\pi}{q} \int_0^R r\sin(qr) dr \end{aligned} \tag{302}$$

The last integral can be done by integrating by parts. Show ($V_p = 4\pi R^3/3!$):

$$F(q) = 3V_p \frac{\sin(qR) - qR\cos(qR)}{(qR)^3} \tag{303}$$

(2) How behaves $|F(qR)|^2$ in the limit $qR \ll 1$ (Guinier regime) ?
(3) How behaves $|F(qR)|^2$ in the limit $qR \gg 1$ (Porod regime) ?

The actual shape of the from factor depends on the shape of the particle (cylinders, disks, or spheres give distinct signals), see Fig. 8.

12. Mixing Entropy

We are concerned with the thermodynamics of self-assembly of molecules (polymers, surfactants, phospholipids and so on). We start by considering the mixing of two lipid species, or solute/solvant, on a flat 2D membrane which reflects the behavior of the miscibility of sucrose into water.

The simplest approach to calculate the entropy of mixing of N_A molecules A with N_B molecules B is to adopt a coarse-grained or lattice model. In that case, we divide the membrane

into $N = N_A + N_B$ compartments (little cells with ONE molecule, solvant or solute, per cell). Molecules interchanges positions by diffusion. The conformational probability of the last section is replaced by the probability to distribute molecules among the different compartments. This is the origin of the mixing entropy.

Let us distribute N_A of A molecules in N compartments. Since the A molecules are indistinguishable, there are

$$\frac{N!}{N_A!\,(N-N_A)!} \tag{304}$$

ways to do it. All that remains is to place the B molecules. Since the B molecules are also indistinguishable, there is only one way. Thus

$$\Omega = \frac{N!}{N_A!\,(N-N_A)!} = \frac{N!}{N_A!N_B!} \tag{305}$$

and for the total entropy (if one wants the entropy per volume, divide by N)

$$S = k_b \ln \Omega \tag{306}$$

This expression is exact, but working with factorial is clumsy. To go ahead, use the Stirling approximation

$$\ln(x!) \approx x\,(\ln x - 1) \quad x \gg 1 \tag{307}$$

and get for the entropy per volume

$$\begin{aligned} S/N &= -k\left[\frac{N_A}{N}\ln\frac{N_A}{N} + \frac{N_B}{N}\ln\frac{N_B}{N}\right] \\ &= -k\left[\phi_A \ln\phi_A + (1-\phi_A)\ln(1-\phi_A)\right] \end{aligned} \tag{308}$$

where $\phi_A = N_A/N$ is the fraction of surface occupied by the A molecules. We see that the mixing entropy depend sonly on the A molecule and, from now on, it is simpler to drop the A and to take $\phi_A = \phi$. To obtain the free energy per volume, recall

$$F/N = U/N - TS/N \tag{309}$$

where U is the internal energy. In this simple system, there is no interaction and no external field. Therefore, $U = 0$ and, for practical purpose, $F = -TS$.

13. Chemical potential

For a lattice model, it is much more convenient to work at fixed total number of compartments. This is equivalent to work at a given volume and the appropriate thermodynamic potential is the free energy

$$F = U - TS \tag{310}$$

The chemical potential per unit surface area is

$$\mu = \left(\frac{\partial F}{\partial \phi}\right)_T \tag{311}$$

For ideal solutions, there is no energy $U = 0$. The free energy is purely entropic. Taking the derivative of the ln, we get:

$$\mu = kT \ln\frac{\phi}{1-\phi} \tag{312}$$

Ideal solutions makes sense in the low density limit. In the hight density limit, molecules start interacting and the ideal solution concept is meaningless. For this reason, we take the small ϕ limit so that

$$\mu = +\mu_0 + kT\ln\phi \tag{313}$$

where μ_0 is the chemical potential of a reference state. For a 3D-problem, the surface fraction is replaced by the volume fraction and ϕ is usually replaced by the concentration c.

For any type of gas A^+B (real or perfect) the partial pressure of the gas A is defined as :

$$p_A = x_A p \tag{314}$$

where x_A is the mole fraction of A.

$$x_A = \frac{N_A}{N_A + N_B} \quad x_B = \frac{N_B}{N_A + N_B} \tag{315}$$

The total pressure is sum of the partial pressures

$$p_A + p_B = p \tag{316}$$

For a gas, the chemical potential is generally written in terms of the of the partial pressures

$$\begin{aligned} \mu^A &= \mu_0^A(T,P) + kT \ln p_A/p \\ \mu^B &= \mu_0^B(T,P) + kT \ln p_B/p \end{aligned} \tag{317}$$

where $\mu_0^A(T,P)$ is the chemical potential of the A or B component in the PURE phase.

Note that the chemical potential for a ideal gas is

$$\mu(p) = \mu_0 + kT \ln p \tag{318}$$

where μ_0 is the chemical potential of the reference state where $p = 1$ atm.

Exam Ray & Matter
Master Nanosciences
April 27, 2022

This exam is obviously much too long. This is on purpose. The rating scale for this exam is higher than 20, but your score will not exceed 20.

I Optical modes in Ionics crystals: We consider a crystal with a polarization density $\mathbf{P}$. Associated with this polarization, there is an electric field $\mathbf{E}$ and an electric displacement $\mathbf{D}$, related by (using c.g.s. units)

$$\mathbf{D} = \epsilon\mathbf{E} = \mathbf{E} + 4\pi\mathbf{P} \tag{319}$$

Assume $\mathbf{D}$, $\mathbf{E}$, $\mathbf{P}$ all parallel to each other with

$$\begin{pmatrix}\mathbf{D}\\ \mathbf{E}\\ \mathbf{P}\end{pmatrix} = \begin{pmatrix}\mathbf{D}_0\\ \mathbf{E}_0\\ \mathbf{P}_0\end{pmatrix} e^{i\mathbf{k}\cdot\mathbf{r}} \tag{320}$$

(a) If there is no free charge. What is $\boldsymbol{\nabla}\cdot\mathbf{D}$? From this deduce that either $\mathbf{D} = 0$ or give a condition on the direction of the vectors $\mathbf{D}$, $\mathbf{E}$, $\mathbf{P}$ with respect to $\mathbf{k}$.

(b) If $-1/c\partial\mathbf{B}/\partial t$ is negligible, what is $\boldsymbol{\nabla}\times\mathbf{E}$? By analogies with the preceding question, gives the two cases where this mays happen.

(c) Show that the two conditions are consistent with each other if and only if ϵ approaches in value two limit cases that you will identify.

II Displacement polarizability: We have seen in class that the polarizability of the atomic cloud depends on frequency ω as [1]

$$\alpha_{at}(\omega) = \frac{e^2}{m}\frac{1}{\omega_0^2 - \omega^2} \tag{321}$$

where ω_0 is a typical frequency for an electronic transition (some eV) and where all damping terms are discarded. Neglecting the contribution of the ions, this allowed us to calculate the dielectric constant $\epsilon(\omega)$. Here we study $\epsilon(\omega)$ for ionic materials where the ionic contribution cannot be neglected.

We consider an elementary cell with two charged atoms +e and -e respectively (masses M_+ and M_-) and displacements u_+ and u_-. The equations of motion are

$$\begin{aligned} M_+\ddot{u}_+ &= -k(u_+ - u_-) + eE\\ M_-\ddot{u}_- &= -k(u_- - u_+) - eE \end{aligned} \tag{322}$$

(a) Does E denote an averaged macroscopic field or a local field? (1 ligne)

(b) We will pose

$$\frac{1}{M} = \frac{1}{M_+} + \frac{1}{M_-} \text{ with } \bar{\omega}^2 = \frac{k}{M} \tag{323}$$

where $\bar{\omega}$ is a typical vibrational frequency (phonon).If the polarization is defined as $p_{ion}(\omega) = e(u_+ - u_-)$, give the polarizability $\alpha_{ion}(\omega)$.

(c) To take into account both the atomic polarizability, see Eq. (321), and the ionic contribution, we loosely define the total polarizability by summing all contribution

$$\alpha(\omega) = 2\alpha_{at}(\omega) + \alpha_{ion}(\omega) \tag{324}$$

Do you expect $\alpha_{at}(\omega)$ to be constant in the range of frequencies where $\alpha_{ion}(\omega)$ varies ? Why ?

[1] Reminder: The polarization $p(\omega)$ is defined as $p(\omega) = \alpha(\omega)E(\omega)$, where $E = E_0\,\mathrm{Re}\,(e^{iwt})$ is an a.c. field. Eq. (321) is correct when the damping coefficient is equal to 0. This will be the case here.

(d) The Clausius-Mossetti relation that we have seen during the lectures reads as

$$\frac{\epsilon(\omega)-1}{\epsilon(\omega)+2}=\frac{4\pi}{3}\alpha(\omega) \tag{325}$$

In the present context, high frequencies means much above vibrational frequencies but below atomic frequencies (which is usually the case for visible light). Define

(i) $\epsilon(\omega)=\epsilon_0$ for $\omega \ll \bar{\omega}$;
(ii) $\epsilon(\omega)=\epsilon_\infty$ for $\bar{\omega} \ll \omega \ll \omega_0$.

Give ϵ_0 and ϵ_∞ as a function of the givens of the problem.

(e) This question is optional. Show

$$\epsilon(\omega)=\epsilon_\infty+\frac{\epsilon_\infty-\epsilon_0}{(\omega/\omega_T)^2-1} \text{ with } \omega_T^2=\bar{\omega}^2\left(\frac{\epsilon_\infty+2}{\epsilon_0+2}\right) \tag{326}$$

(f) Plot $\epsilon(\omega)$ and indicate the frequencies corresponding to the two cases of the preceding problem.

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