

Electromagnetic field in lossy media

Rocco Martinazzo

E-mail: rocco.martinazzo@unimi.it

Contents

1	Introduction	2
2	Electromagnetic waves in dielectrics	4
3	Electromagnetic waves in conductors	6
4	Boundary conditions	9
5	Simple models	14
6	Dielectric polarization	16
7	Conduction	23
8	Appendix A: Averages of microscopic densities and fields	38
9	Appendix B: Analytic properties of response functions	40
10	Appendix C: Autocorrelation functions	44
11	Appendix D: General linear response theory	49
12	Appendix E: Charge and current density in quantum mechanics	58

1 Introduction

These notes summarize the basic equations needed to understand the interaction of the electromagnetic field with matter. We start with the *microscopic* Maxwell equations for the electric (\mathbf{E}) and magnetic (\mathbf{B}) fields, here written in gaussian units:

$$\nabla \mathbf{E} = 4\pi \rho \quad (1)$$

$$\nabla \mathbf{B} = 0 \quad (2)$$

$$\nabla \wedge \mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} = \mathbf{0} \quad (3)$$

$$\nabla \wedge \mathbf{B} - \frac{1}{c} \frac{\partial \mathbf{E}}{\partial t} = \frac{4\pi}{c} \mathbf{J} \quad (4)$$

Here ρ and \mathbf{J} are the *total* charge and the current density, respectively, which obey a conservation equation which follows from Eq.s 1 and 4

$$\frac{4\pi}{c} \nabla \mathbf{J} = -\frac{1}{c} \frac{\partial}{\partial t} \nabla \mathbf{E} = -\frac{4\pi}{c} \frac{\partial \rho}{\partial t}$$

namely

$$\frac{\partial \rho}{\partial t} + \nabla \mathbf{J} = 0$$

The above equations determine the *field dynamics* for given sources ρ and \mathbf{J} , and must be supplemented with an equation describing the *charge dynamics*, *i. e.* the Lorentz force (in a classical setting)

$$\mathbf{F}_i = q_i \left(\mathbf{E}(\mathbf{r}_i, t) + \frac{\mathbf{v}_i}{c} \wedge \mathbf{B}(\mathbf{r}_i, t) \right)$$

for each charge q_i located at \mathbf{r}_i with speed \mathbf{v}_i .

The *macroscopic* Maxwell equations are obtained by performing suitable averages over microscopically large but macroscopically small volumes of space to obtain fields which are experimentally measurable (see Appendix A for a sketch of the derivation). In doing this, care has to be taken to include “higher orders” of the microscopic density in order to define the observed fields. For instance, the macroscopic density in a neutral system vanishes (as it is the average over volumes containing neutral molecules) but the field is not necessarily zero (as the molecule may have a dipole and this might not average to zero). The result is the set of equations

$$\nabla \mathbf{D} = 4\pi \rho \quad (5)$$

$$\nabla \mathbf{B} = 0 \quad (6)$$

$$\nabla \wedge \mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} = \mathbf{0} \quad (7)$$

$$\nabla \wedge \mathbf{H} - \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t} = \frac{4\pi}{c} \mathbf{J} \quad (8)$$

where the *auxiliary* fields \mathbf{D} and \mathbf{H} (known as electric and magnetic *displacements*) contain the effects of the higher order moments of the densities, and ρ and \mathbf{J} are now the *macroscopic* charge and current densities¹. Note that \mathbf{H} is also called magnetic *field* ($\mathbf{H} = \mathbf{B}$ in vacuum) and then \mathbf{B} is the magnetic *induction*. These auxiliary fields are, to first order, given by

$$\mathbf{D} \cong \mathbf{E} + 4\pi\mathbf{P}$$

$$\mathbf{H} \cong \mathbf{B} - 4\pi\mathbf{M}$$

where \mathbf{P} and \mathbf{M} are the mean number of electric and magnetic dipoles per unit volume. The equations are closed by the *constitutive* relations

$$\mathbf{D} = \mathbf{D}[\mathbf{E}, \mathbf{B}] \quad \mathbf{H} = \mathbf{H}[\mathbf{E}, \mathbf{B}] \quad \mathbf{J} = \mathbf{J}[\mathbf{E}, \mathbf{B}]$$

which are material specific and not necessarily simple.

In the simplest case, *i. e.* for static fields,

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

$$\mathbf{H} = \mu^{-1}\mathbf{B}$$

are first order expressions involving the *dielectric tensor* ϵ and the *magnetic permeability tensor* μ . In general the relations are neither local in time nor in space, *e. g.*,

$$D_\alpha(\mathbf{r}, t) = \sum_\beta \int d^3\mathbf{r}' dt' \epsilon_{\alpha\beta}(\mathbf{r} - \mathbf{r}', t - t') \mathbf{E}_\beta(\mathbf{r}', t')$$

where we have still assumed space and time translational invariance (homogeneous system in thermal equilibrium).

Neglecting spatial non-locality, however, we can still write

$$\tilde{\mathbf{D}}(\mathbf{r}, \omega) = \tilde{\epsilon}(\mathbf{r}, \omega) \tilde{\mathbf{E}}(\mathbf{r}, \omega)$$

for the Fourier-transforms

$$\tilde{\mathbf{E}}(\mathbf{r}, \omega) = \int_{-\infty}^{+\infty} \mathbf{E}(\mathbf{r}, t) e^{i\omega t} dt, \quad \tilde{\mathbf{D}}(\mathbf{r}, \omega) = \int_{-\infty}^{+\infty} \mathbf{D}(\mathbf{r}, t) e^{i\omega t} dt$$

and

$$\tilde{\epsilon}(\mathbf{r}, \omega) = \int_{-\infty}^{+\infty} \epsilon(\mathbf{r}, t) e^{i\omega t} dt$$

The static result is a special case ($\omega \rightarrow 0$) of the above equations.

¹As in the previous, microscopic case they are related to each other by the continuity equation, $\partial\rho/\partial t + \nabla\mathbf{J} = 0$.

$\epsilon_{\alpha\beta}(\mathbf{r}, t)$ is a *response function* and must satisfy the *causality* condition, namely $\epsilon_{\alpha\beta}(\mathbf{r}, t) \equiv 0$ for $t < 0$, which guarantees that the system responds only to the field in the past. This general requirement has important consequence on the analytic properties of the Fourier transform $\tilde{\epsilon}(\mathbf{r}, \omega)$, see Appendix B for an account.

2 Electromagnetic waves in dielectrics

Without external sources, in neutral dielectrics we can put $\rho = 0$ and $\mathbf{J} = 0$ and obtain

$$\begin{aligned}\nabla D &= 0 \\ \nabla \wedge \mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} &= \mathbf{0} \\ \nabla \wedge \mathbf{H} - \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t} &= \mathbf{0} \\ \nabla \mathbf{B} &= 0\end{aligned}$$

Upon Fourier transforming in time, and noticing that

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

we obtain

$$\begin{aligned}\nabla \tilde{D} &= 0 \\ \nabla \wedge \tilde{\mathbf{E}} - \frac{i\omega}{c} \tilde{\mathbf{B}} &= \mathbf{0} \\ \nabla \wedge \tilde{\mathbf{H}} + \frac{i\omega}{c} \tilde{\mathbf{D}} &= \mathbf{0} \\ \nabla \tilde{\mathbf{B}} &= 0\end{aligned}$$

where we can now introduce $\tilde{\mathbf{D}} = \tilde{\epsilon} \tilde{\mathbf{E}}$ and $\tilde{\mathbf{H}} = \tilde{\mu}^{-1} \tilde{\mathbf{B}}$ to write

$$\begin{aligned}\nabla \wedge \tilde{\mathbf{B}} + \frac{i\omega}{c} \tilde{\mu} \tilde{\epsilon} \tilde{\mathbf{E}} &= \mathbf{0} \\ \nabla \wedge \tilde{\mathbf{E}} - \frac{i\omega}{c} \tilde{\mathbf{B}} &= \mathbf{0}\end{aligned}$$

Multiplying the above expressions for $\nabla \wedge$ and assuming that $\tilde{\mu}$ and $\tilde{\epsilon}$ are uniform in space, we finally arrive at²

²Remember that

$$\nabla \wedge (\nabla \wedge F) = \nabla(\nabla F) - \nabla^2 F$$

holds. Indeed, with the implicit sum convention on repeated indexes, $(\nabla \wedge (\nabla \wedge F))_i = e_{ijk} \partial_j (\nabla \wedge F)_k = e_{ijk} \partial_j e_{klm} \partial_l F_m = e_{ijk} e_{klm} \partial_j \partial_l F_m = (\delta_{il} \delta_{jm} - \delta_{im} \delta_{jl}) \partial_j \partial_l F_m = \partial_i (\partial_j F_j) - \partial_j \partial_j F_i$.

$$\nabla^2 \tilde{\mathbf{B}} + \frac{\omega^2}{c^2} \tilde{\mu} \tilde{\epsilon} \tilde{\mathbf{B}} = 0 \quad (9)$$

$$\nabla^2 \tilde{\mathbf{E}} + \frac{\omega^2}{c^2} \tilde{\mu} \tilde{\epsilon} \tilde{\mathbf{E}} = 0 \quad (10)$$

These equations can be further simplified if $\tilde{\epsilon}$ and $\tilde{\mu}$ are simple scalars, as we assume is the case in the following by writing $\tilde{\epsilon}$ and $\tilde{\mu}$ in their place.

Thus, each component of the electric and magnetic field satisfies a wave equation of the form

$$\nabla^2 u(\mathbf{r}, \omega) + \frac{\omega^2}{c^2} \tilde{\mu} \tilde{\epsilon} u(\mathbf{r}, \omega) = 0$$

with $\tilde{\mu}$ and $\tilde{\epsilon}$ possibly ω -dependent. For each ω this is a standard eigenvalue problem

$$-\nabla^2 u(\mathbf{r}, \omega) = \lambda(\omega) u(\mathbf{r}, \omega)$$

which has solutions

$$u(\mathbf{r}, \omega) \propto e^{i\mathbf{k}\mathbf{r}} \text{ where } k^2 = \lambda(\omega) = \frac{\omega^2}{c^2} \tilde{\mu} \tilde{\epsilon} = \frac{\omega^2}{v^2}$$

In the last term on the r.h.s. we have introduced $v = v(\omega)$ (or $v = v(k)$) which is the ω -dependent speed of light in the medium, as we shall see below. We also introduce the generalized refraction index η as

$$\eta^2 = \tilde{\mu} \tilde{\epsilon}$$

in such a way

$$k = \frac{\omega}{c} \eta$$

The general solution of the above wave-equation then reads as

$$u(\mathbf{r}, t) = \int \frac{d\omega}{2\pi} u(\mathbf{r}, \omega) e^{-i\omega t} = \int \frac{d\omega}{2\pi} \left[\int \frac{d^3\mathbf{k}}{(2\pi)^3} u(k, \omega) e^{i\mathbf{k}\mathbf{r}} \delta(k - \frac{\omega}{c} \eta) \right] e^{-i\omega t}$$

i.e., introducing $\hat{\mathbf{k}} = \mathbf{k}/k$,

$$u(\mathbf{r}, t) = \int d\hat{\mathbf{k}} \int d\omega f(\hat{\mathbf{k}}, \omega) e^{i\omega(\frac{\eta}{c} \hat{\mathbf{k}}\mathbf{r} - t)}$$

where it appears as a superposition of elementary waves

$$u_{\mathbf{k}, \omega}(\mathbf{r}, t) = e^{i\omega(\frac{\eta}{c} \hat{\mathbf{k}}\mathbf{r} - t)}$$

traveling at a speed $v = \frac{c}{\eta}$ in direction $\hat{\mathbf{k}}$.

The same applies when the refraction index has an imaginary component (which can be the case, since $\eta^2 = \tilde{\mu} \tilde{\epsilon}$ and $\tilde{\mu}, \tilde{\epsilon}$ can be complex, being the Fourier transform of μ, ϵ). Writing $\eta = \eta' + i\eta''$, with η' and η'' real numbers,

$$u_{\mathbf{k}, \omega}(\mathbf{r}, t) = e^{i\omega \frac{\eta''}{c} \hat{\mathbf{k}}\mathbf{r}} e^{i\omega(\frac{\eta'}{c} \hat{\mathbf{k}}\mathbf{r} - t)}$$

Hence

$$\eta' = \text{Re}\sqrt{\tilde{\mu}\tilde{\epsilon}}$$

is the frequency-dependent “traditional” refraction index $n(\omega)$ determining the phase velocity of the waves in the medium ($v \equiv c/n(\omega)$) and

$$\eta'' = \text{Im}\sqrt{\tilde{\mu}\tilde{\epsilon}}$$

relates to the *absorption coefficient* $\kappa(\omega)$ of the medium³. Indeed, the “intensity” of the wave in the medium decays in the $\hat{\mathbf{k}}$ direction as

$$|u_{\hat{\mathbf{k}},\omega}(\mathbf{r}, t)|^2 = e^{-2\omega \frac{\eta'}{c} \hat{\mathbf{k}}\mathbf{r}} = e^{-\kappa \hat{\mathbf{k}}\mathbf{r}}$$

i. e.

$$\kappa = \frac{2\omega}{c}\eta''$$

In most media $\tilde{\mu} \approx 1$ and thus $\eta^2 \approx \tilde{\epsilon}$. The relation between η and $\tilde{\epsilon}$ is given schematically in Fig. 1 for two representative cases.

Notice also

$$\epsilon' = \eta'^2 - \eta''^2$$

$$\epsilon'' = 2\eta'\eta''$$

and for normal dispersion ($\eta'' \ll \eta'$), $\epsilon' \approx \eta'^2 > 0$ and $\eta'' \approx \frac{\epsilon''}{2\sqrt{\epsilon'}}$ i. e.

$$\kappa \approx \frac{\omega\epsilon''}{c\sqrt{\epsilon'}}$$

3 Electromagnetic waves in conductors

Conductors differ from dielectrics by the possibility of sustaining a current when an electric field is applied. The latter is almost always accurately described by Ohm’s law, which takes the form

$$\mathbf{J}_\alpha(\mathbf{r}, t) = \sum_\beta \int d^3\mathbf{r}' \int dt' \sigma_{\alpha\beta}(\mathbf{r} - \mathbf{r}', t - t') \mathbf{E}_\beta(\mathbf{r}', t')$$

if we include retardation effects and spatial non-locality. In the following, for simplicity, we neglect spatial non-locality, consider isotropic media only ($\sigma_{ij} = \delta_{ij}\sigma$), and write the Fourier transform as

$$\tilde{\mathbf{J}}(\mathbf{r}, \omega) = \tilde{\sigma}(\omega) \tilde{\mathbf{E}}(\mathbf{r}, \omega)$$

³For notational convenience, here and in the following, we abandon the traditional use of α for the absorption coefficient. The inverse κ^{-1} is also called *attenuation length*.

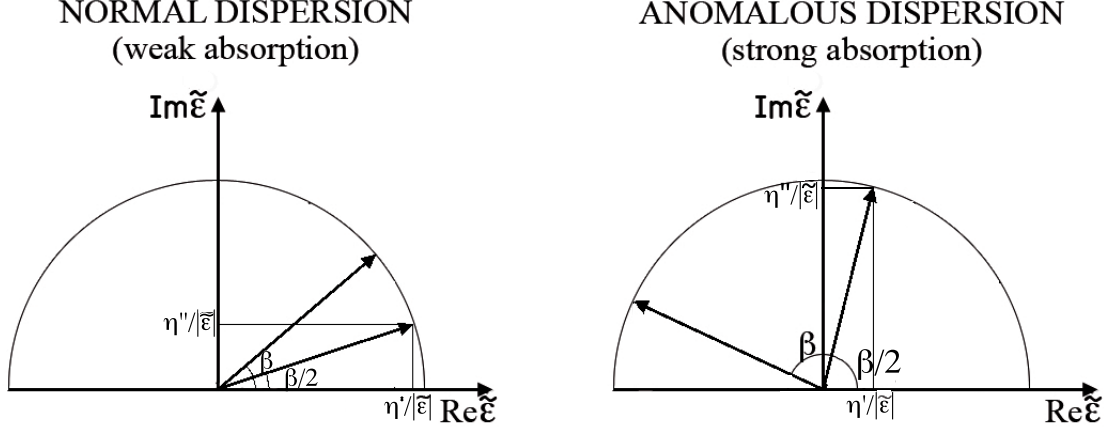


Figure 1: Relation between η and $\tilde{\epsilon}$ for weak (left panel) and strong (right) absorption

where $\tilde{\sigma}(\omega)$ is the *frequency-dependent conductivity*. The traditional conductivity, *i. e.* for static fields, is recovered for $\omega \rightarrow 0$

$$\lim_{\omega \rightarrow 0} \tilde{\sigma}(\omega) = \sigma_0 = \int_{-\infty}^{+\infty} \sigma(t) dt \equiv \int_0^{\infty} \sigma(t) dt$$

Note that for high frequencies there is no real distinction between dielectrics and conductors as \mathbf{J} describes in any case an oscillatory motion of the charges. This becomes more evident from the Maxwell equations themselves, that read in this case as

$$\begin{aligned} \nabla \tilde{D} &= 4\pi \tilde{\rho} \\ \nabla \wedge \tilde{\mathbf{E}} - \frac{i\omega}{c} \tilde{\mathbf{B}} &= 0 \\ \nabla \wedge \tilde{\mathbf{H}} + \frac{i\omega}{c} \tilde{\mathbf{D}} &= \frac{4\pi}{c} \tilde{\mathbf{J}} \\ \nabla \tilde{\mathbf{B}} &= 0 \end{aligned}$$

where the frequency-dependent charge and current density have been introduced. Using Ohm's law, the third equation above can be re-arranged as (after introducing $\tilde{\mathbf{D}} = \tilde{\epsilon} \tilde{\mathbf{E}}$ and $\tilde{\mathbf{B}} = \tilde{\mu} \tilde{\mathbf{H}}$)

$$\nabla \wedge \tilde{\mathbf{B}} + \frac{i\omega}{c} \tilde{\mu} \left(\tilde{\epsilon} + \frac{i4\pi}{\omega} \tilde{\sigma} \right) \tilde{\mathbf{E}} = 0$$

which is identical to that found above for dielectrics

$$\nabla \wedge \tilde{\mathbf{B}} + \frac{i\omega}{c} \tilde{\mu} \tilde{\epsilon} \tilde{\mathbf{E}} = 0 \quad (11)$$

provided we identify the *total dielectric function* as

$$\tilde{\epsilon}_{tot}(\omega) = \tilde{\epsilon}(\omega) + \frac{i4\pi}{\omega}\tilde{\sigma}(\omega)$$

Since $\tilde{\epsilon}$ is associated with “bound-charges” (it characterizes the polarization of these charges) the extra term on the r.h.s. is the contribution of the “free charges”, which is singular for $\omega \rightarrow 0$ because in that limit polarization of these charges becomes *current generation*. Apart from this singular behavior, however, there is no real distinction for $\omega \neq 0$ between dielectrics and conductors. Only the total dielectric function is relevant and the only difference between dielectrics and conductors is the behavior for $\omega \rightarrow 0$ in that function: for conductors $\tilde{\epsilon}_{tot}$ is singular at $\omega = 0$ and the singularity is related to the “direct-current” (DC) conductivity σ_0 .

Notice that Eq.(11), upon applying $\nabla \wedge$, reduces to a wave equation

$$\nabla^2 \tilde{\mathbf{B}} + \frac{\omega^2}{c^2} \tilde{\mu} \tilde{\epsilon}_{tot} \tilde{\mathbf{B}} = 0$$

thanks to the condition $\nabla \tilde{\mathbf{B}} = 0$, whereas the same manipulation on the second Maxwell equation (after the introduction of $\tilde{\mathbf{D}} = \tilde{\epsilon} \tilde{\mathbf{E}}$ and $\tilde{\mathbf{B}} = \tilde{\mu} \tilde{\mathbf{H}}$) gives

$$\nabla^2 \tilde{\mathbf{E}}(\omega) + \frac{\omega^2}{c^2} \tilde{\mu} \tilde{\epsilon}_{tot} \tilde{\mathbf{E}} = 4\pi \frac{\nabla \tilde{\rho}}{\tilde{\epsilon}}$$

However, continuity equation in the form

$$-i\omega \tilde{\rho}(\omega) + \nabla \tilde{\mathbf{J}}(\omega) = 0$$

along with Ohm’s law gives⁴

$$\left(\tilde{\epsilon}(\omega) + \frac{i4\pi}{\omega} \tilde{\sigma}(\omega) \right) \tilde{\rho}(\omega) \equiv \tilde{\epsilon}_{tot}(\omega) \tilde{\rho}(\omega) = 0$$

Thus, unless $\tilde{\epsilon}_{tot}(\omega) = 0$ (and this happens at the so-called *plasmon frequency*, see below) the above equation becomes similar to the one given above, and wave propagation depends on the properties of $\eta(\omega) = \sqrt{\tilde{\mu} \tilde{\epsilon}_{tot}}$.

Stated differently, for any frequency but the plasmon one no *charge density oscillation* is supported in the system. This does not mean that charges are static, rather that the current density has to satisfy $\nabla \mathbf{J} = 0$. Such currents are called *transverse* for reasons made clear in Appendix E. For homogeneous and isotropic systems the same has to hold for the electric field \mathbf{E} if the Ohm’s law $\mathbf{J} = \sigma \mathbf{E}$ applies. In other words, with the exception above, we can put $\tilde{\rho} = 0$ in the Maxwell equations and keep only the current term.

⁴This just means that the only *Fourier transformable* solution of the continuity equation in Ohmic systems is $\rho \equiv 0$.

4 Boundary conditions

In the previous Sections we have considered wave propagation *within* either a dielectric or a conductor without caring about how the electromagnetic field traverses the *surface* sample from *e.g.* the vacuum to its bulk. To this end we consider here wave propagation across a flat surface⁵ separating two media 1 and 2 with refractive index $\eta_i = \sqrt{\epsilon_i \mu_i}$ and $\eta_t = \sqrt{\epsilon_t \mu_t}$, respectively, and call \mathbf{n} the surface normal from medium 1 to medium 2.

Clearly, an incident wave with wavenumber \mathbf{k}_i will in general be splitted into a transmitted (or refracted) wave with vector \mathbf{k}_t and a reflected wave with vector \mathbf{k}_r . Since scattering is elastic (*i.e.* $k_r = k_i$ and $k_t/\eta_t = k_i/\eta_i = k_0 \equiv \omega/c$) and parallel momentum is conserved ($k_i^\parallel = k_r^\parallel = k_t^\parallel$) the following relations exist between the incident $\theta_i = \cos^{-1}(\mathbf{n}\hat{\mathbf{k}}_i)$, the reflection $\theta_r = \cos^{-1}(-\mathbf{n}\hat{\mathbf{k}}_r)$ and the refraction angle $\theta_t = \cos^{-1}(\mathbf{n}\hat{\mathbf{k}}_t)$ (*Snell's law*)⁶

$$\theta_r = \theta_i \quad \eta_t \sin(\theta_t) = \eta_i \sin(\theta_i)$$

To determine the intensity of the reflected and transmitted waves we need the relations between the values of the vector fields right below the surface and those right above it. In other words, if a local reference frame is chosen such as its z axis is aligned with the surface normal and the surface is at $z = 0$, we would need the limiting vectors $\lim_{z \rightarrow 0^\pm} \mathbf{F} = \mathbf{F}^\pm$ for $\mathbf{F} = \mathbf{E}, \mathbf{D}, \mathbf{B}, \mathbf{H}$. In general, if $\nabla \mathbf{F}$ is known to be continuous so is $\partial F_z / \partial z$ and hence necessarily $F_z^- \equiv F_z^+$ or equivalently $F_n^- \equiv F_n^+$ for the component $F_n = \mathbf{F}\mathbf{n}$ along the surface normal. With the same token, if $(\nabla \wedge \mathbf{F})_{x,y}$ are known to be continuous so are $\partial F_y / \partial z$ and $\partial F_x / \partial z$, hence $\mathbf{F}_t^- = \mathbf{F}_t^+$, where \mathbf{F}_t is the component of \mathbf{F} parallel (tangent) to the surface. This argument can be applied to the magnetic field \mathbf{B} only which satisfies $\nabla \mathbf{B} \equiv 0$ and gives

$$(\mathbf{B}^+ - \mathbf{B}^-)\mathbf{n} = 0$$

For the other fields and/or different components we use Gauss (Stokes) integral theorem (which only requires integrability of $\nabla \mathbf{F}$ ($\nabla \wedge \mathbf{F}$)) to a small volume (surface) element which crosses the boundary between medium 1 and medium 2 (see Fig. 2), and consider the limit where the transverse dimension δz vanishes. Then, equation (5) gives in general

$$(\mathbf{D}^+ - \mathbf{D}^-)\mathbf{n} = 4\pi\sigma$$

⁵We assume that a macroscopic description holds and macroscopic averages can be taken on scales much larger than the atomic one (this requires $\lambda \gg a_0$ where λ is the wavelength of radiation and a_0 is the Bohr radius). Hence the surface can be considered flat at least on the atomic scale.

⁶These equations hold for arbitrary (complex) refractive indexes, hence *complex* angles. A complex angle arises in lossy media and its physical meaning is not as immediate as a real angle. Thus, in lossy media, these equations are best replaced by those for the (complex) components of the \mathbf{k} vectors, $\mathbf{k} = k_x \mathbf{e}_x + k_y \mathbf{e}_y + k_z \mathbf{e}_z$, using the standard scalar product of a *real* vector space (*e.g.* putting $k^2 = (k_x \mathbf{e}_x + k_y \mathbf{e}_y + k_z \mathbf{e}_z)^2 = k_x^2 + k_y^2 + k_z^2 \in \mathbb{C}$). It thus follows, for instance, $(\mathbf{k}_t)_z = \sqrt{(\epsilon_t \mu_t - \epsilon_i \mu_i)k_0^2 + (\mathbf{k}_i)_z^2}$ for the components along the interface normal (z), or more simply $(\mathbf{k}_t)_z = k_0 \sqrt{\epsilon_t \mu_t - \epsilon_i \mu_i \sin^2(\theta_i)}$, where θ_i is the incidence angle, provided medium 1 is transparent. Notice that the “real” angle $\bar{\theta}$ that the propagating wave makes with the normal is determined by $\bar{\mathbf{k}} = \Re(k_x)\mathbf{e}_x + \Re(k_y)\mathbf{e}_y + \Re(k_z)\mathbf{e}_z$, *e.g.* it holds $\cos(\bar{\theta}) = \Re(\mathbf{k})_z / \bar{k}$ where $\bar{k}^2 = \bar{\mathbf{k}}\bar{\mathbf{k}}$.

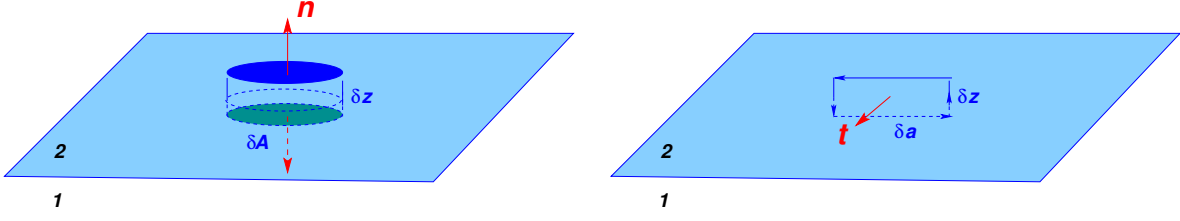


Figure 2: The small volume and surface elements (left and right panel, respectively) used to determine the boundary conditions for the normal and the parallel components of the fields, respectively. In the left panel \mathbf{n} is the outward normal of the elemental volume in medium 2 and is also the surface normal defined in the main text. In the right panel \mathbf{t} is normal to the elemental surface and thus parallel to the boundary.

where σ is the surface charge density (if any) which makes ρ discontinuous at the surface. Specifically, if $\delta Q = \lim_{\delta z \rightarrow 0} Q$ is the charge contained in the volume *when its height shrinks to zero*, we have $\sigma = \lim_{\delta A \rightarrow 0} \delta Q / \delta A$ where δA is the surface element parallel to the boundary⁷. With the same token, since $\partial \mathbf{B} / \partial t$ and $\partial \mathbf{D} / \partial t$ are always finite, from Eqs (7,8) we obtain

$$(\mathbf{E}^+ - \mathbf{E}^-) \wedge \mathbf{n} = \mathbf{0}$$

and

$$(\mathbf{H}^+ - \mathbf{H}^-) \wedge \mathbf{n} = \frac{4\pi}{c} \mathbf{K}$$

respectively, where \mathbf{K} is the surface charge current (if any) which makes \mathbf{J} discontinuous at the surface. Similarly to above, if $\hat{\mathbf{j}}$ is the unit vector along $\mathbf{J}_t = \mathbf{J} - (\mathbf{J} \cdot \mathbf{n})\mathbf{n} \equiv \mathbf{n} \wedge (\mathbf{J} \wedge \mathbf{n})$ and $\delta I = \lim_{\delta z \rightarrow 0} I$ is the current through the infinitesimal surface element $\delta a \delta z \hat{\mathbf{j}}$ *when its height shrinks to zero*, we have $\mathbf{K} = \lim_{\delta a \rightarrow 0} \delta I / \delta a \hat{\mathbf{j}}$ ⁸.

To summarize, at the boundary we have

$$\begin{aligned} (\mathbf{D}^+ - \mathbf{D}^-) \cdot \mathbf{n} &= 4\pi\sigma & (\mathbf{B}^+ - \mathbf{B}^-) \cdot \mathbf{n} &= 0 \\ (\mathbf{E}^+ - \mathbf{E}^-) \wedge \mathbf{n} &= \mathbf{0} & (\mathbf{H}^+ - \mathbf{H}^-) \wedge \mathbf{n} &= \frac{4\pi}{c} \mathbf{K} \end{aligned}$$

where \mathbf{n} is the surface normal and σ, \mathbf{K} are surface densities defined by

$$\sigma(\mathbf{x}) = \lim_{\epsilon \rightarrow 0} \int_{-\epsilon}^{\epsilon} \rho(\mathbf{x} + z\mathbf{n}) dz, \quad \mathbf{K}(\mathbf{x}) = \lim_{\epsilon \rightarrow 0} \int_{-\epsilon}^{\epsilon} \mathbf{J}_t(\mathbf{x} + z\mathbf{n}) dz$$

for any \mathbf{x} on the boundary.

In the most typical situation no surface density term appears⁹ and the \mathbf{D} and \mathbf{B} fields preserve their

⁷Such a term only appears if ρ takes locally the form $\rho(\mathbf{x}) \approx \sigma(x, y)\delta(z)$, with the above choice of coordinates, for \mathbf{x} close to the boundary.

⁸Similarly to above, such a term only appears if the intensity of the current density parallel to the boundary is of the form $J_t(\mathbf{x}) \approx K(x, y)\delta(z)$.

⁹Notable exceptions are dielectric-conductor interfaces with a *static* distribution of charges. In such cases the electric field must vanish in the conductor, and thus σ necessarily builds up to make non-vanishing the field outside the conductor.

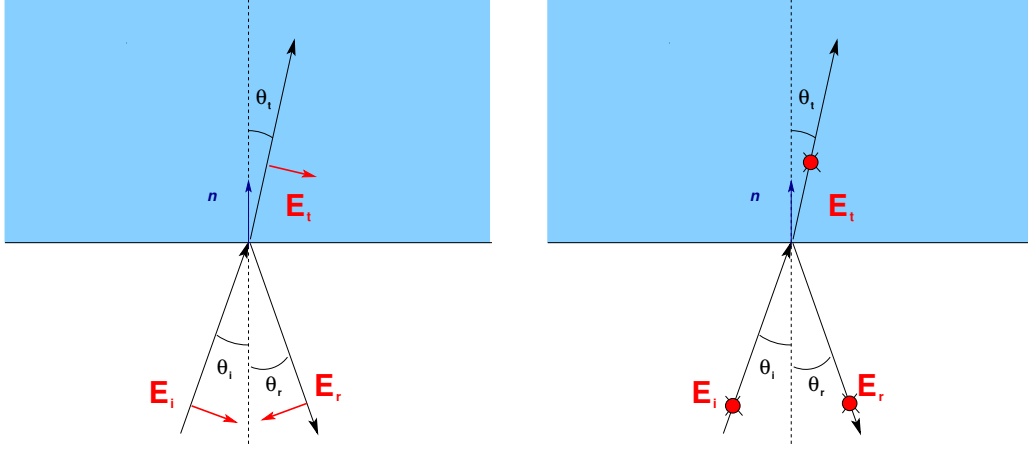


Figure 3: The scattering plane, with the indicated electric fields $\mathbf{E}_i, \mathbf{E}_r$ and \mathbf{E}_t , for the P - and the S -polarization cases (left and right panel, respectively). Also indicated the surface normal \mathbf{n} and the incident (θ_i), the reflection (θ_r) and the refraction angles (θ_t).

normal component while \mathbf{E} and \mathbf{H} preserve their parallel component. These are the relations we were looking for to determine the intensity of the reflected and transmitted waves. To this end, let $\tilde{\mathbf{E}}, \tilde{\mathbf{D}}, \dots$ be the components at frequency ω of an electromagnetic wave $\mathbf{E}, \mathbf{D}, \dots$ and consider isotropic media. In either medium the fields of a uniform plane wave traveling in direction $\hat{\mathbf{k}}$ would satisfy

$$\mu\omega\tilde{\mathbf{H}} = c\hat{\mathbf{k}} \wedge \tilde{\mathbf{E}} \quad \omega\tilde{\epsilon}_{tot}\tilde{\mathbf{E}} = -c\hat{\mathbf{k}} \wedge \tilde{\mathbf{H}}$$

where $\mathbf{k} = \frac{\omega}{c}\eta\hat{\mathbf{k}}$ and $\tilde{\epsilon}_{tot}$ is the total dielectric function introduced above¹⁰, or, equivalently,

$$\mu\tilde{\mathbf{H}} = \eta\hat{\mathbf{k}} \wedge \tilde{\mathbf{E}} \quad \eta\tilde{\mathbf{E}} = -\mu\hat{\mathbf{k}} \wedge \tilde{\mathbf{H}}$$

Because of the presence of the interface, though, both “right-” and “left-” moving components along z appears for each field F

$$F(z) = F_+(z) + F_-(z) = F_+^0 e^{ik_z z} + F_-^0 e^{-ik_z z}$$

where k_z is the z component of the \mathbf{k} vector. These two components are useful to describe *propagation* within each medium ($F_{\pm}(z + \Delta z) = F_{\pm}(z)e^{\pm ik_z \Delta z}$) but are inconvenient to *match* the fields across the boundary. Hence, we need to seek two independent variables f_1, f_2 that replace F_{\pm} and are *continuous* across the separation surface. For a generic incident wave with vector \mathbf{k}_i we distinguish two cases,

¹⁰These are nothing that that the “rotor equations” in k -space. There is no need to consider the “divergence equations” here since they are both contained in the above expressions, namely $\mathbf{k}\tilde{\mathbf{H}} = 0$ and $\mathbf{k}\tilde{\mathbf{E}} = 0$. Stated differently (see Appendix E), an electromagnetic *wave* has only *transverse* components, $\mathbf{E} = \mathbf{E}_{\perp}$ and $\mathbf{B} = \mathbf{B}_{\perp}$ (Notice that trasverse and parallel components below have nothing to do with the boundary, only with the \mathbf{k} vector). In general, $\mathbf{B} \equiv \mathbf{B}_{\perp}$ while $\mathbf{E} = \mathbf{E}_{\perp} + \mathbf{E}_{\parallel}$, where the *parallel* component of the electric field is the only one that results from a charge density, *i.e.* according to $c\mathbf{k}\mathbf{E}_{\parallel} = -i\rho(k)$ for a uniform medium in k -space. Notice that the charge density relates to the *parallel* component of the current density, $-i\partial\rho/\partial t + \mathbf{k}\mathbf{J}_{\parallel} = 0$. The transverse component \mathbf{J}_{\perp} , by definition, is solenoidal, *i.e.* its flux vanishes for any closed surface and thus \mathbf{J}_{\perp} cannot describe any change of the total charge contained in its interior.

according to whether the electric field $\tilde{\mathbf{E}}_i$ is on the scattering plane (*P polarization*, from “parallel”) or perpendicular to it (*S polarization*, from “senkrecht”, the German word for perpendicular), see Fig. 3, left and right panel respectively. They are also called *transverse magnetic* (TM) and *transverse electric* (TE), respectively, depending on which field is perpendicular to the surface normal. We consider first the TE (or *S*) case, and write $\mathbf{E} \equiv E\hat{\mathbf{x}}$ assuming that the scattering plane is *yz*. Since \mathbf{E} is parallel to the surface, E is continuous across the boundary, $E_1 = E_2$, and we choose E as the first component of the “matching” vector, $e_1 = E$. A second independent variable follows from the continuity of the parallel component of \mathbf{H} , which can be readily computed from the Maxwell’s equations,

$$\mu\mathbf{H} = -i\frac{c}{\omega}\left(\frac{\partial E}{\partial z}\hat{\mathbf{y}} - \frac{\partial E}{\partial y}\hat{\mathbf{z}}\right), \quad \mathbf{H}_{\parallel} = -i\frac{c}{\omega\mu}\frac{\partial E}{\partial z}\hat{\mathbf{y}}$$

and is conveniently chosen as $e_2 = E'/\mu$ where E' is understood to be the z derivative of the electric field. Hence the vector $\mathbf{e}^t = (E, E'/\mu)$ is continuous across the surface and relates to the right- and left-moving components through

$$\mathbf{e} = \begin{bmatrix} 1 & 1 \\ i\mu^{-1}k_z & -i\mu^{-1}k_z \end{bmatrix} \begin{bmatrix} E_+ \\ E_- \end{bmatrix} \quad \text{and viceversa} \quad \begin{bmatrix} E_+ \\ E_- \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 1 & -i\frac{\mu}{k_z} \\ 1 & +i\frac{\mu}{k_z} \end{bmatrix} \mathbf{e}$$

Now, for the configuration of Fig. 3 with $\hat{\mathbf{z}} \equiv \mathbf{n}$, the transmitted field in medium 2 is purely right moving (*i.e.* moving along the positive z direction), $\mathbf{E}_t = E_t\hat{\mathbf{x}} \equiv E_{+,2}\hat{\mathbf{x}}$ and at the boundary it holds

$$\begin{bmatrix} E_+ \\ E_- \end{bmatrix}_1 = \frac{1}{2} \begin{bmatrix} 1 & -i\frac{\mu_1}{k_{z,1}} \\ 1 & +i\frac{\mu_1}{k_{z,1}} \end{bmatrix} \mathbf{e}_1 = \frac{1}{2} \begin{bmatrix} 1 & -i\frac{\mu_1}{k_{z,1}} \\ 1 & +i\frac{\mu_1}{k_{z,1}} \end{bmatrix} \mathbf{e}_2 \equiv \frac{1}{2} \begin{bmatrix} 1 + \frac{\mu_1}{\mu_2}\frac{k_{z,2}}{k_{z,1}} \\ 1 - \frac{\mu_1}{\mu_2}\frac{k_{z,2}}{k_{z,1}} \end{bmatrix} E_t$$

It follows that the field amplitudes of the trasmitted and reflected waves are related to that of the incident wave by

$$\frac{E_t}{E_i} = \frac{2\mu_2 k_{z,1}}{\mu_2 k_{z,1} + \mu_1 k_{z,2}} \equiv \frac{2\mu_t \eta_i \cos(\theta_i)}{\mu_i \eta_t \cos(\theta_i) + \mu_t \eta_i \cos(\theta_t)}$$

$$\frac{E_r}{E_i} = \frac{\mu_2 k_{z,1} - \mu_1 k_{z,2}}{\mu_2 k_{z,1} + \mu_1 k_{z,2}} \equiv \frac{\mu_t \eta_i \cos(\theta_i) - \mu_i \eta_t \cos(\theta_i)}{\mu_i \eta_t \cos(\theta_i) + \mu_t \eta_i \cos(\theta_t)}$$

which can also be written in terms of the incident angle only with the help of Snell’s law

$$\eta_t \cos(\theta_t) = \sqrt{\eta_t^2 - \eta_i^2 \sin^2(\theta_i)}$$

Similarly for the TM (or *P*) case, where $\mathbf{H} \equiv H\hat{\mathbf{x}}$ and $\mathbf{E}_{\parallel} = i\frac{c}{\omega\epsilon}H'\hat{\mathbf{y}}$, H' being the z derivative of the magnetic field. In this case $\mathbf{h}^t = (H, \epsilon^{-1}H')$ is the appropriate “matching” vector,

$$\mathbf{h} = \begin{bmatrix} 1 & 1 \\ i\epsilon^{-1}k_z & -i\epsilon^{-1}k_z \end{bmatrix} \begin{bmatrix} H_+ \\ H_- \end{bmatrix} \quad \text{and viceversa} \quad \begin{bmatrix} H_+ \\ H_- \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 1 & -i\frac{\epsilon}{k_z} \\ 1 & +i\frac{\epsilon}{k_z} \end{bmatrix} \mathbf{h}$$

relate h_1, h_2 to the right- and left- moving components H_{\pm} of the magnetic field, and

$$\frac{H_t}{H_i} = \frac{2\epsilon_2 k_{z,1}}{\epsilon_2 k_{z,1} + \epsilon_1 k_{z,2}} \equiv \frac{2\mu_t^{-1} \eta_t \cos(\theta_i)}{\mu_t^{-1} \eta_t \cos(\theta_i) + \mu_i^{-1} \eta_i \cos(\theta_t)}$$

$$\frac{H_r}{H_i} = \frac{\epsilon_2 k_{z,1} - \epsilon_1 k_{z,2}}{\epsilon_2 k_{z,1} + \epsilon_1 k_{z,2}} \equiv \frac{\mu_t^{-1} \eta_t \cos(\theta_i) - \mu_i^{-1} \eta_i \cos(\theta_t)}{\mu_t^{-1} \eta_t \cos(\theta_i) + \mu_i^{-1} \eta_i \cos(\theta_t)}$$

are the appropriate transmission and reflection amplitude coefficients. The electric field amplitudes then read as $E_i = \mu_i \eta_i^{-1} H_i$, $E_r = \mu_i \eta_i^{-1} H_r$ and $E_t = \mu_t \eta_t^{-1} H_t$, as it follows from $\mathbf{E} = \mu \eta^{-1} \hat{\mathbf{k}} \wedge \mathbf{H}$ which hold separately for each component.

The above expressions allow us to write down the (power) *transmission* (T) and *reflection* (R) *coefficients* which are defined by¹¹

$$T = \text{Re} \left(\frac{\mu_i \eta_t \cos \theta_t}{\mu_t \eta_i \cos \theta_i} \right) \frac{|E_t|^2}{|E_i|^2} \quad R = \frac{|E_r|^2}{|E_i|^2}$$

and satisfy $R + T = 1$. In particular, at normal incidence we have

$$T = 4 \frac{n_t n_i + \kappa_t \kappa_i}{(n_t + n_i)^2 + (\kappa_t + \kappa_i)^2} \quad R = \frac{(n_t - n_i)^2 + (\kappa_t - \kappa_i)^2}{(n_t + n_i)^2 + (\kappa_t + \kappa_i)^2}$$

in terms of the real and imaginary parts of the refractive indexes, here written as $\eta_i = n_i + i\kappa_i$ and $\eta_t = n_t + i\kappa_t$.

The above expressions are rather general, provided we remember that they apply right at the boundary between medium 1 and medium 2; if one of the two is absorbing (*i.e.* either κ_i or κ_r is not vanishing) the measured intensity ratios differ from the ones predicted by the above expression because absorption occurs in traveling from the boundary to the detector and/or from the source to the boundary. In the simplest case, medium 1 is transparent with $n_i \equiv 1$ (*e.g.* air) and the reflection coefficient reads

$$R = \frac{(1 - n)^2 + \kappa^2}{(1 + n)^2 + \kappa^2} \quad (12)$$

where now n, κ are the real and imaginary parts of the medium 2 under study. Furthermore, if medium 2 is only weakly absorbing ($\kappa \approx 0$ and $n \approx 1$) radiation can be collected after passing through a second interface between medium 1 and 2; under such circumstances reflections at both interfaces is negligible, and the overall transmission coefficient just account for absorption in medium 2. More generally, one has to take into account both interfaces, and possibly sum over all contributing paths with multiple reflections; in such case, however, the result depends on whether such paths interfere with each other (when the coherence length is larger than the sample dimension), or the probabilities just add up

¹¹The ratio $\mu_i \eta_i \cos \theta_t / \mu_t \eta_i \cos \theta_i$ appearing in the trasmission coefficient is a flux-related term that accounts for the different speed that the wave has in the two media and for the fact that the flux has to be projected onto the normal of the boundary surface.

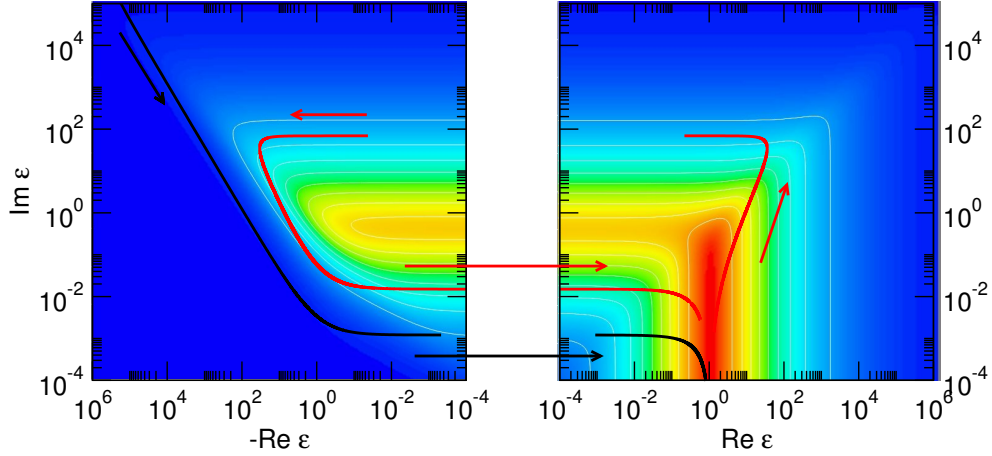


Figure 4: Contour map of the reflection coefficient at normal incidence (Eq. 12) on the complex ϵ -plane given in a log-scale (colours change linearly from red to blue for R going from zero to one). Also shown two typical paths undertaken by the dielectric function $\epsilon(\omega)$ when increasing ω as indicated by the arrows direction. Red curve is for a dielectric (just close to a resonance peak) and black curve for a conductor. Parameters are the same as in the next Figs 5,6.

classically (when the coherence length is much smaller than the sample dimension)¹².

The above expressions show how, *e.g.*, reflection from a surface depends on the *frequency-dependent* refractive index or total dielectric function $\tilde{\epsilon}_{tot}$, thereby determining how solid substances look like. The dependence of $\tilde{\epsilon}_{tot}$ on the frequency is clearly crucial for that, and Sections below give some general properties for dielectrics and conductors. Here, we just exploit the consequences of such analysis and report in Fig. 4, on a log-log scale, the behaviour of R at normal incidence on the complex ϵ -plane, along with two typical “paths” of the functions $\epsilon(\omega)$ when changing ω , one for a dielectric and one for a conductor. As you can see from Fig. 4 the dielectric is mostly transparent, even close to a resonance (absorption) peak, whereas a conductor reflects the vast majority of the radiation incident on it unless the frequency takes a very large value (larger than the plasmon frequency mentioned in the previous Section, which typically lies in the ultra-violet region).

5 Simple models

The main features of the dielectric function are easily understood in terms of a simple model of matter, the *Lorentz* model, where a number of charges q_i are harmonically bounded to some center (of opposite charge if the matter has to be neutral) and forced by an external electric field. The equation for one

¹²In this respect, transmission through *thin films* can be safely handled as a coherent process and the above described “propagation” and “matching” steps can be easily combined to describe the optical properties of arbitrarily layered structures.

such charge reads as (in one dimension)

$$m\ddot{x}(t) + m\gamma\dot{x}(t) + m\omega_0^2 x(t) = \zeta(t) + eE(t) \quad (13)$$

where m is the mass, ω_0 the frequency and e the charge. In this equation we have introduced a *damping* coefficient γ which describes system relaxation to the equilibrium state, and a *fluctuating* force $\zeta(t)$ which describes the environmental-induced fluctuations.

Since we are interested in the average behavior (of an ensemble of identical systems) Eq. 13 can be rewritten in terms of $\langle x \rangle$ (note that $\langle \zeta(t) \rangle = 0$):

$$m \langle \ddot{x} \rangle + m\gamma \langle \dot{x} \rangle + m\omega_0^2 \langle x \rangle = eE$$

Upon Fourier transforming¹³

$$-m\omega^2 \langle \tilde{x}(\omega) \rangle - i\omega m\gamma \langle \tilde{x}(\omega) \rangle + m\omega_0^2 \langle \tilde{x}(\omega) \rangle = eE$$

$$\langle \tilde{x}(\omega) \rangle = \frac{1}{\omega_0^2 - \omega^2 - i\omega\gamma} \frac{eE}{m}$$

and the average polarization vector is obtained by introducing the number of dipoles per unit volume, N , *i. e.* the number density of molecules

$$\tilde{P}(\omega) = Ne \langle \tilde{x}(\omega) \rangle = \frac{Ne^2}{m} \frac{\tilde{E}(\omega)}{\omega_0^2 - \omega^2 - i\omega\gamma}$$

If each molecules has Z electrons, and each oscillates with a characteristic frequency ω_i and relaxation γ_i

$$\tilde{P}(\omega) = \frac{Ne^2}{m_e} \sum_i^Z \frac{f_i \tilde{E}(\omega)}{\omega_i^2 - \omega^2 - i\omega\gamma_i}$$

where f_i is the number of electrons¹⁴ (*oscillator strength*) with the given set of ω_i , γ_i parameters, and $\sum_i f_i = Z$. These relations define the *electric susceptibility*

$$\chi_e(\omega) = \frac{Ne^2}{m_e} \sum_i^Z \frac{f_i}{\omega_i^2 - \omega^2 - i\omega\gamma_i}$$

as N times the molecular polarizability

$$\tilde{\alpha}_{mol}(\omega) = \frac{e^2}{m_e} \sum_i^Z \frac{f_i}{\omega_i^2 - \omega^2 - i\omega\gamma_i}$$

¹³This amounts to focus on the “stationary” solution only, *i.e.* the one prevailing after the transient (which does depend on the detailed initial conditions) has decayed.

¹⁴This is not necessarily an integer.

It relates to $\tilde{\epsilon}$ through

$$\tilde{\epsilon}(\omega) = 1 + 4\pi\chi_e(\omega)$$

In deriving these equations we have implicitly assumed that the *local* fields are also the *macroscopic* ones, *i.e.* we neglected the fields generated by the (induced) molecular dipoles on the one under observation. This is reasonable in *low density* media, in condensed matter $\chi_e(\omega) = N\tilde{\alpha}_{mol}(\omega)$ has to be revised to account for the local fields generated by the polarized medium.

For conductors, one of the frequencies is zero and we exhibit separately this term to write

$$\tilde{\epsilon}_{tot}(\omega) = 1 + 4\pi \frac{Ne^2}{m_e} \sum_{i \neq 0}^Z \frac{f_i}{\omega_i^2 - \omega^2 - i\omega\gamma_i} + i \frac{4\pi}{\omega} \frac{\gamma_0}{\gamma_0 - i\omega} \sigma_0$$

where

$$\sigma_0 = \frac{Ne^2}{m_e} \frac{f_0}{\gamma_0}$$

is the *Drude's DC conductivity* for a metal with Nf_0 electrons per unit volume, with an average relaxation time $\tau = \gamma_0^{-1}$, and

$$\tilde{\sigma}(\omega) = \frac{\gamma_0 \sigma_0}{\gamma_0 - i\omega}$$

is the Drude's frequency-dependent conductivity.

Note that γ_i 's enter the above equations as a broadening factor, and this may be of secondary importance for $\omega_i > 0$ (since the main interest in that case is in the *position* of the resonance) but is of fundamental importance for $\omega_i = 0$ (since it determines the DC conductivity).

6 Dielectric polarization

Let us now focus on dielectrics ($\sigma_0 = 0$). For $\omega \rightarrow 0$, $\tilde{\epsilon}_{tot}(\omega) \rightarrow \tilde{\epsilon}(0) = \tilde{\epsilon}'(0) = 1 + 4\pi N\tilde{\alpha}_{mol}(0)$, *i. e.* $\tilde{\epsilon}$ becomes real at low frequencies and $\tilde{\epsilon} \approx 1$ to a good approximation in low-density media ($\tilde{\alpha}_{mol}(0)$ is the static polarizability which is of the order of molecular volume, *i. e.* much smaller than the volume available to each molecule, N^{-1}); for $\omega \gg 0$, $\tilde{\epsilon}(\omega)$ differs from $\tilde{\epsilon}(0)$ only close to the resonant frequencies and, in any case, for $\omega \rightarrow \infty$

$$\tilde{\epsilon}_{tot}(\omega) = 1 - \frac{\omega_P^2}{\omega^2}$$

where ω_P is given by

$$\omega_P^2 = 4\pi \frac{NZe^2}{m_e}$$

and is known as *plasmon frequency*. At such high frequency, the behaviour of any system no longer depends on its detailed structure, and the charges (either bound or free) behave in a universal way as the matter were fully ionized.

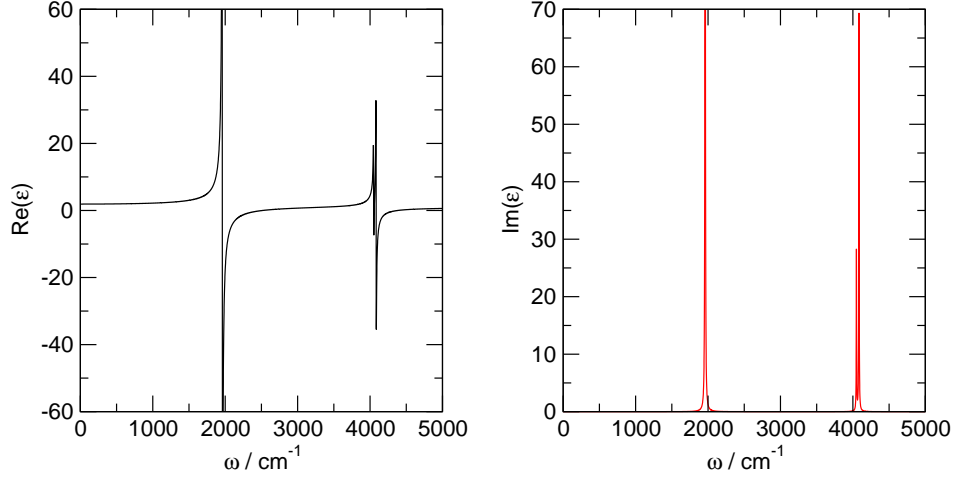


Figure 5: Typical behaviour of the real (left panel) and imaginary (right) parts of the dielectric function. Data are for a model system resembling water vapour at a density $n = 10^{-2} \text{ g cm}^{-3}$ with three resonant frequencies in the infrared region, $\omega_i = 1960, 4049, 4048 \text{ cm}^{-1}$ with a common relaxation time $\gamma^{-1} = 1 \text{ ps}$ and oscillator strengths $f_i = 0.1, 0.02, 0.05$, respectively.

At intermediate frequencies the general behavior can be easily guessed from

$$\tilde{\epsilon}'(\omega) = 1 + 4\pi \frac{Ne^2}{m_e} \sum_i^Z \frac{f_i(\omega_i^2 - \omega^2)}{(\omega_i^2 - \omega^2)^2 + \omega^2 \gamma_i^2}$$

$$\tilde{\epsilon}''(\omega) = 4\pi \frac{Ne^2}{m_e} \sum_i^Z \frac{f_i \omega \gamma_i}{(\omega_i^2 - \omega^2)^2 + \omega^2 \gamma_i^2}$$

and is illustrated in Fig.5. Notice that for “normal dispersion” (which occurs unless $\tilde{\epsilon}''$ is very high or $\tilde{\epsilon}'$ becomes negative) the absorption coefficient can be written as

$$\kappa(\omega) \approx \frac{1}{n(\omega)} \frac{\omega}{c} \epsilon''(\omega) \approx \frac{1}{n(\omega)} \frac{4\pi\omega}{c} N \tilde{\alpha}_{mol}''(\omega)$$

(where $n(\omega) \approx \sqrt{\epsilon'}$ is the refractive index) and becomes proportional to N , in agreement with *Lambert-Beer* law. In this context, then, one also defines the *molecular photoabsorption cross-section*

$$\sigma_{ph}(\omega) \equiv \kappa(\omega)/N$$

which reads in the non-dispersive limit ($n(\omega) \approx 1$) as

$$\sigma_{ph}(\omega) = \frac{4\pi\omega}{c} \tilde{\alpha}_{mol}''(\omega) \quad (14)$$

Notice that in the limit¹⁵ $\gamma_i \approx 0$

$$\kappa(\omega) \approx 4\pi \frac{Ne^2}{m_e} \frac{\omega}{c} \sum_i \pi \delta(\omega_i^2 - \omega^2) f_i = \frac{2\pi^2 Ne^2}{m_e c} \sum_i f_i \delta(\omega - \omega_i)$$

and thus

$$\sigma_{ph}(\omega) = \frac{2\pi^2 e^2}{m_e c} \sum_i^Z f_i \delta(\omega - \omega_i)$$

and

$$\tilde{\alpha}_{mol}''(\omega) = \frac{\pi e^2}{2m_e \omega} \sum_i^Z f_i \delta(\omega - \omega_i) \quad (15)$$

The above equations, though referring to a rather crude model of the matter, offer a number of alternative possibilities to compute the optical properties of dielectrics.

In the low-density limit, for instance, each individual molecule contributes independently of the others and one can directly follow the dipole moment μ of a single molecule in time and compute the frequency dependent polarizability by Fourier transforming

$$\mu(t) - \mu_0 = \int_{-\infty}^{\infty} \alpha_{mol}(t - t') E(t') dt'$$

Here, an arbitrary *classical* field¹⁶ is used (*e.g.* a kick $E(t) = I_0 \delta(t)$ –where $-I_0/|e|$ is the impulse given to each electron– directly gives $\alpha_{mol}(t) = \Delta\mu(t)/I_0$) and the molecular (electron) dynamics is followed to extract $\mu(t)$, *i.e.* the time-dependent Schrödinger equation for the molecule in the external field

$$i\hbar \frac{d|\Psi\rangle}{dt} = (H_{mol} + H_{int}(t)) |\Psi\rangle$$

is solved to compute $\mu(t) = \langle \Psi(t) | \mu | \Psi(t) \rangle$ for a reasonably long time interval. Notice that the integral above actually runs for $t' \leq t$ since $\alpha_{mol}(t)$ obeys causality, and μ_0 is the dipole at any time before the field has been switched on¹⁷. This approach is rather general, and goes well beyond the linear-response regime used above to define α_{mol} in terms of E .

Linear-response, when holds, provides simpler (“more practical”) approaches to the problem. For instance, for a (closed) system initially in its ground-state, the problem (in the limit $\gamma \rightarrow 0$) is equivalently handled in ordinary perturbation theory to give

$$\alpha_{mol}(t) = \Theta(t) \frac{2}{\hbar} \sum_n |\langle \phi_n | \mu | \phi_0 \rangle|^2 \sin(\omega_{n0} t) \quad (16)$$

where μ is the dipole operator and $\omega_{n0} = (E_n - E_0)/\hbar$ are the transition frequencies. To show this,

¹⁵We use $\omega\gamma_i/((\omega_i^2 - \omega^2)^2 + \omega^2\gamma_i^2) \approx \pi\delta(\omega_i^2 - \omega^2)$.

¹⁶This is *semiclassical* theory of the interaction between matter and radiation. Quantization of the electromagnetic field is necessary for describing spontaneous emission processes.

¹⁷We assume that the system was initially in an equilibrium state, typically the ground-state (this is fine for the electronic contribution which is the main contribution in the visible range).

consider the system initially in its ground state, $|\Psi(t)\rangle = |\Psi_0(t)\rangle = e^{-iE_0t/\hbar} |\Phi_0\rangle$ for $t < 0$, and a kick $H_{int} = -\mu I_0 \delta(t)$ at time $t = 0$. The field $E(t) = I_0 \delta(t)$ is treated here in the dipole approximation, which means that it is considered to be *uniform* over the molecular volume. It is clear that before and after the kick the systems evolves under the unperturbed Hamiltonian H_{mol} , thus the problem reduces to determining the state for $t \rightarrow 0^+$. This can be solved by writing the integral form of the Schrödinger equation

$$i\hbar |\Psi(t)\rangle = i\hbar |\Psi(0^-)\rangle + \int_{0^-}^t H |\Psi(t')\rangle dt'$$

and taking the limit $t \rightarrow 0^+$ after replacing $\Psi(t)$ with the unperturbed solution $\Psi_0(t)$

$$i\hbar |\Psi(0^+)\rangle = i\hbar |\Phi_0\rangle - \mu I_0 |\Phi_0\rangle$$

Hence, $|\Psi(t)\rangle = |\Phi_0\rangle e^{-iE_0t/\hbar} + iI_0/\hbar \sum_n |\Phi_n\rangle \langle \Phi_n | \mu | \Phi_0 \rangle e^{-iE_n t/\hbar}$ can be used to compute $\Delta\mu$ (to first order in I_0) at any time $t > 0$, and α_{mol} follows as given in Eq.(16). On taking the Fourier transform of the latter equation^{18,19},

$$\tilde{\alpha}_{mol}(\omega) = \frac{1}{\hbar} \sum_n |\langle \Phi_n | \mu | \Phi_0 \rangle|^2 \lim_{\epsilon \rightarrow 0} \left(\frac{1}{\omega + \omega_{n0} + i\epsilon} - \frac{1}{\omega - \omega_{n0} + i\epsilon} \right) \quad (17)$$

and for $\omega > 0$

$$\tilde{\alpha}_{mol}''(\omega) = \frac{\pi}{\hbar} \sum_n |\langle \Phi_n | \mu | \Phi_0 \rangle|^2 \delta(\omega - \omega_n)$$

On comparing with Eq.(15) we get the quantum-mechanical definition of the oscillator strength²⁰

$$f_n = \frac{2m_e \omega_{n0}}{e^2 \hbar} |\langle \Phi_n | \mu | \Phi_0 \rangle|^2 \quad (18)$$

Thus, one can solve the time-independent Schrödinger equation for the isolated molecule

$$H_{mol} |\Phi_n\rangle = E_n |\Phi_n\rangle$$

and obtain the necessary transition frequencies ω_{n0} and transition moments $\mu_{n0} = \langle \Phi_n | \mu | \Phi_0 \rangle$.

Eq. (16) analogously follows from the frequency-dependent polarizability obtained previously within the classical model,

$$\alpha_{mol}(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \left[\frac{e^2}{m_e} \sum_i \frac{f_i}{\omega_i^2 - \omega^2 - i\omega\gamma_i} \right] e^{-i\omega t} d\omega$$

¹⁸The ϵ converging factor plays here the role of a damping coefficient which is present in real systems but seldom considered in calculations.

¹⁹It also follows $\alpha_{mol}(t) = \frac{1}{\hbar} \text{Im} (e^{iE_0t/\hbar} \langle \chi_0 | \chi_t \rangle)$ where $|\chi_0\rangle = \mu |\Phi_0\rangle$ and $|\chi_t\rangle = e^{-iHt/\hbar} |\chi_0\rangle$.

²⁰It can be shown that, analogously to the classical case, the *sum rule* $\sum_n f_n = Z$ holds.

Here, each term in the sum, as a function of a *complex* ω , has poles in the lower half plane²¹

$$\omega_{i,\pm} = -i\frac{\gamma_i}{2} \pm \Omega_i \text{ where } \Omega_i = \sqrt{\omega_i^2 - \frac{\gamma_i^2}{4}}$$

and for $t > 0$ ($t < 0$) the integral can be evaluated by contour integration by closing the contour with a large semicircle in the lower (upper) half plane. The result is

$$\alpha(t) = \Theta(t) \frac{e^2}{m_e} \sum_i \frac{f_i}{\Omega_i} \sin(\Omega_i t) e^{-\frac{\gamma_i}{2} t}$$

which reduces to Eq.(16) in the limit $\gamma_i \rightarrow 0$, provided Eq.(18) is used.

More generally, Eq.(17) represents a sort of equilibrium *dipole-dipole correlation function*, here evaluated for a non-degenerate ground-state at $T = 0$ K. This general result is best appreciated at the classical level by going back to the original Langevin equation, Eq.(13). Indeed, it is clear that the *average response* of the system to the *external* field is also the *pointwise response* to the *fluctuating* force in the field-free situation, *i.e.*²²

$$\tilde{\mu}(\omega) = \frac{1}{\omega_0^2 - \omega^2 - i\omega\gamma} \frac{|e|}{m_e} \xi(\omega)$$

This relates to the equilibrium spontaneous fluctuations of the dipole in the system, as can be seen upon remembering that, according to the Wiener-Khinchine theorem, the square modules of above expression relates to the Fourier transform of some autocorrelation function²³, *i.e.*

$$\tilde{C}_\mu(\omega) = \left| \frac{1}{\omega_0^2 - \omega^2 - i\omega\gamma} \right|^2 \frac{e^2}{m_e^2} \tilde{C}_\xi(\omega)$$

where $C_\mu(t) = \langle \mu(t)\mu(0) \rangle$, $C_\xi(t) = \langle \xi(t)\xi(0) \rangle$ and \tilde{C} 's are their Fourier transforms. Here the environmental fluctuations relate to the dissipative kernel²⁴ through $\tilde{C}_\xi(\omega) = 2m_e k_B T \gamma'$ and thus we obtain

$$\frac{\omega \tilde{C}_\mu(\omega)}{2} = \frac{e^2 k_B T}{m_e} \text{Im} \left(\frac{1}{\omega_0^2 - \omega^2 - i\omega\gamma} \right)$$

²¹We work in the *underdamped* limit, $\gamma_i/2 < \omega_i$. This also excludes conductors, which have a pole for $\omega = 0$.

²²General (frequency-dependent) memory kernels can be accommodated as well.

²³For a (real) *stationary* process $\xi(t)$ a proper Fourier transform can be defined through $\xi_T(\omega) = \int_{-T}^{+T} \xi(t) e^{i\omega t} dt$ where $[-T, +T]$ is a large but finite interval. Accordingly,

$$\langle |\xi_T(\omega)|^2 \rangle = \int_{-T}^{+T} \int_{-T}^{+T} \langle \xi(t') \xi(t'') \rangle e^{i\omega(t' - t'')} dt' dt'' \approx \int_{-T}^{+T} dt \int_{-\infty}^{+\infty} d\tau \langle \xi(\tau) \xi(0) \rangle e^{i\omega\tau} = 2T \tilde{C}_\xi(\omega)$$

since $C_\xi(\tau) = \langle \xi(\tau)\xi(0) \rangle \equiv \langle \xi(\tau+t)\xi(t) \rangle$ holds thanks to the stationarity condition. In deriving this equation we have used $(t', t'') \rightarrow (t, \tau) = ((t' + t'')/2, t' - t'')$ and assumed that C_ξ decays on a short time interval compared to T .

²⁴This follows from the fact that, at equilibrium, fluctuating forces are balanced by dissipative ones (Fluctuation-Dissipation theorem of the second kind). In practice, $C_\mu(0) = e^2 \langle x^2 \rangle$ has to be consistent with the equilibrium condition, $m_e \omega_0^2 \langle x^2 \rangle = k_B T$ (equipartition law).

For a number of (uncorrelated) oscillators, each with its own ω_i and γ_i , we obtain

$$\frac{\omega \tilde{C}_\mu(\omega)}{2} = \frac{e^2 k_B T}{m_e} \sum_i \text{Im} \left(\frac{1}{\omega_i^2 - \omega^2 - i\omega\gamma_i} \right) = k_B T \tilde{\alpha}_{mol}''(\omega) \quad (19)$$

for the autocorrelation function of the total dipole defined as $\mu = \sum_i ex_i$. Upon rearranging we obtain the imaginary (dissipative) part of the frequency dependent polarizability as

$$\tilde{\alpha}_{mol}''(\omega) = \frac{\omega \tilde{C}_\mu(\omega)}{2k_B T} = \frac{\omega}{2k_B T} \int_{-\infty}^{\infty} \langle \mu(t) \mu(0) \rangle e^{i\omega t} dt \equiv \frac{\omega}{k_B T} \int_0^{\infty} \langle \mu(t) \mu(0) \rangle \cos(\omega t) dt$$

which allows us to write $\tilde{\alpha}_{mol}(z)$ for any complex frequency z in the upper half plane as (see Appendix B)

$$\tilde{\alpha}_{mol}(z) = \frac{1}{\pi} \int \frac{\tilde{\alpha}_{mol}''(\omega')}{\omega' - z} d\omega'$$

Notice that for $\omega \rightarrow 0$ we have

$$\tilde{\alpha}_{mol}(0) = \tilde{\alpha}_{mol}'(0) = \frac{1}{2\pi k_B T} \int_{-\infty}^{+\infty} \tilde{C}_\mu(\omega') d\omega' \equiv \frac{\langle \mu(0)^2 \rangle}{k_B T}$$

consistently with equipartition, $\langle \mu^2 \rangle = e^2 \sum_i \langle x_i^2 \rangle = e^2 / m_e \sum_i \omega_i^{-2} k_B T$.

Thus, we can write the absorption coefficient as²⁵

$$\kappa(\omega) \approx \frac{\omega \epsilon''(\omega)}{cn(\omega)} = \frac{2\pi\omega^2 N}{3n(\omega)c} \frac{1}{k_B T} \int_{-\infty}^{\infty} \langle \mu(t) \mu(0) \rangle e^{i\omega t} dt$$

This formula can be used, in conjunction with classical, canonical molecular dynamics calculations, to extract the “classical” contributions to the absorption coefficient, for instance those due to rotations of permanent dipoles and low-frequency vibrations which can be treated at a classical level²⁶.

To see that Eq.(17) represents indeed a sort of dipole autocorrelation function we notice that the *retarded* “Green’s function” defined by

$$C^>(t) = \frac{i}{\hbar} \Theta(t) \langle [\mu(t), \mu(0)] \rangle = -\frac{2}{\hbar} \Theta(t) \text{Im} \langle \mu(t) \mu(0) \rangle$$

is exactly the polarizability response

$$C^>(t) = -\frac{2}{\hbar} \Theta(t) \text{Im} \langle \phi_0 | e^{iHt/\hbar} \mu e^{-iHt/\hbar} | \phi_0 \rangle = -\frac{2}{\hbar} \Theta(t) \text{Im} \sum_n e^{i(E_0 - E_n)t/\hbar} \langle \phi_0 | \mu | \phi_n \rangle \langle \phi_n | \mu | \phi_0 \rangle$$

²⁵The factor 3 in this expression arise from the replacement of the one-dimensional dipole μ with the dipole vector $\boldsymbol{\mu}$.

²⁶Notice that the temperature enters here just because of the equilibrium condition, which in the Langevin model can only be enforced by a relation between the dissipative and the fluctuating forces. From this perspective, Eq.(19) is best written as

$$\frac{\omega \tilde{C}_\mu(\omega)}{2} = \frac{\langle \mu(0)^2 \rangle}{\tilde{\alpha}_{mol}(0)} \tilde{\alpha}_{mol}''(\omega)$$

$$= \frac{2}{\hbar} \Theta(t) \sum_n \sin(\omega_{n0}t) |\langle \phi_n | \mu | \phi_0 \rangle|^2 \equiv \alpha_{mol}(t)$$

and the important imaginary part of its Fourier transform reads as

$$\tilde{\alpha}_{mol}''(\omega) = -\frac{2}{\hbar} \int_0^\infty \text{Im} \langle \mu(t) \mu(0) \rangle \sin(\omega t) dt \equiv \frac{i}{\hbar} \int_{-\infty}^{+\infty} \text{Im} \langle \mu(t) \mu(0) \rangle e^{i\omega t} dt$$

Here, the complex-conjugation symmetry of the correlation function $C_{\mu\mu}(t) = \langle \mu(t) \mu(0) \rangle$,

$$C_{\mu\mu}(t)^* = \langle \mu(0) \mu(t) \rangle = \langle \mu(-t) \mu(0) \rangle \equiv C_{\mu\mu}(-t)$$

translates into symmetry properties of its the real and imaginary parts

$$\text{Re}C_{\mu\mu}(-t) = \text{Re}C_{\mu\mu}(t) \quad \text{Im}C_{\mu\mu}(-t) = -\text{Im}C_{\mu\mu}(t)$$

and of their Fourier transforms

$$\tilde{C}_{\mu\mu}(\omega) = \tilde{C}_{\mu\mu}^*(\omega) = \mathcal{S}(\omega) + \mathcal{A}(\omega)$$

where

$$\mathcal{S}(\omega) = \frac{\tilde{C}_{\mu\mu}(\omega) + \tilde{C}_{\mu\mu}(-\omega)}{2} \equiv \int_{-\infty}^{+\infty} \text{Re}C_{\mu\mu}(t) e^{i\omega t} dt \equiv 2 \int_0^\infty \text{Re}C_{\mu\mu}(t) \cos(\omega t) dt$$

and

$$\mathcal{A}(\omega) = \frac{\tilde{C}_{\mu\mu}(\omega) - \tilde{C}_{\mu\mu}(-\omega)}{2} \equiv i \int_{-\infty}^{+\infty} \text{Im}C_{\mu\mu}(t) e^{i\omega t} dt \equiv -2 \int_0^\infty \text{Im}C_{\mu\mu}(t) \sin(\omega t) dt$$

Hence, the general result

$$\tilde{\alpha}_{mol}''(\omega) = \frac{\mathcal{A}(\omega)}{\hbar} \tag{20}$$

expresses the dissipative part of the polarizability response in terms of the antisymmetric part of the so-called *spectral density* (of the fluctuations) of the stochastic process²⁷ $\mu(t)$.

The connection with the previous result, Eq.(19), obtained for the classical, damped Harmonic oscillator model, can be established with the help of the *Kubo-Martin-Schwinger* detailed-balance condition on the *canonical* correlation function (see Appendix C), namely, for $\beta^{-1} = k_B T$,

$$\tilde{C}_{\mu\mu}(-\omega) = \tilde{C}_{\mu\mu}(\omega) e^{-\beta \hbar \omega}$$

²⁷The origin of the name becomes clear upon noticing that $\langle \mu^2 \rangle = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \tilde{C}_{\mu\mu}(\omega) d\omega$, see also Footnote 23.

or, equivalently²⁸,

$$\mathcal{S}(\omega) = \coth\left(\frac{\beta\hbar\omega}{2}\right) \mathcal{A}(\omega) \quad (21)$$

Therefore, Eq.(20) can be written in terms of $\mathcal{S}(\omega)$

$$\tilde{\alpha}_{mol}''(\omega) = \frac{1}{\hbar} th\left(\frac{\beta\hbar\omega}{2}\right) \mathcal{S}(\omega)$$

and in the classical limit ($\beta\hbar\omega \ll 1$) $\hbar^{-1}th\left(\frac{\beta\hbar\omega}{2}\right) \approx \beta\omega/2$ we obtain Eq.(19)

$$\tilde{\alpha}_{mol}''(\omega) = \frac{\omega \mathcal{S}(\omega)}{2k_B T}$$

upon noticing that $\mathcal{S}(\omega) \rightarrow \tilde{C}_{cl}(\omega)$.

7 Conduction

As already mentioned in the previous section, conductors differ from dielectrics by the behaviour of those charge carriers at $\omega = 0$ that are free to move and hence able to sustain a current. In the Ohmic limit, $\tilde{J}(\omega) = \tilde{\sigma}(\omega)\tilde{E}(\omega)$ holds, and the continuity equation can be “closed” with the help of the first Maxwell equation to give

$$\left(\tilde{\epsilon}(\omega) + \frac{i4\pi}{\omega}\tilde{\sigma}(\omega)\right)\tilde{\rho}(\omega) = 0$$

where $\tilde{\epsilon}(\omega)$ accounts for the polarizabilities of the ion cores, and the second term is just the free carrier contribution to the total dielectric constant. Thus, unless $\tilde{\epsilon}_{tot}(\omega) = 0$, the only admissible solution which is Fourier transformable is $\rho(t) \equiv 0$, as we have already seen above.

Solutions for given initial state densities²⁹ $\rho(0)$ decay exponentially in time, as is shown in the following

²⁸This can be proved with a direct calculation in the case of a collection of (uncorrelated) harmonic oscillators of coordinates $\{x_k\}$ and the “dipole” $\mu(t) = \sum_k q_k x_k(t)$. Indeed, with the help of the solution of the Heisenberg equation of motion for the phonon annihilation operator of the k -th oscillator, $a_k(t) = a_k(0)\exp(-i\omega_k t)$, we can write

$$\langle \mu(t)\mu(0) \rangle = \sum_{k,l} q_k q_l \Delta x_k \Delta x_l \langle (a_k(t) + a_k(t)^\dagger)(a_l(0) + a_l(0)^\dagger) \rangle = \sum_k q_k^2 \Delta x_k^2 \left[(\langle a_k^\dagger a_k \rangle + 1)e^{-i\omega_k t} + \langle a_k^\dagger a_k \rangle e^{i\omega_k t} \right]$$

(here $\Delta x_k^2 = 1/2m_k\omega_k$) or, equivalently,

$$C_{\mu\mu}(t) = \hbar \sum_k \frac{q_k^2}{2m_k\omega_k} \{(\bar{n}_k + 1)e^{-i\omega_k t} + \bar{n}_k e^{i\omega_k t}\}$$

where $\bar{n}_k = \langle a_k^\dagger a_k \rangle = (e^{\beta\hbar\omega_k} - 1)^{-1}$ is the mean number of phonons in the k -th oscillator in thermal equilibrium. Hence

$$A(\omega) = \hbar \frac{\pi}{2} \sum_k \frac{q_k^2}{m_k\omega_k} [\delta(\omega - \omega_k) - \delta(\omega + \omega_k)]$$

and

$$S(\omega) = \hbar \frac{\pi}{2} \sum_k \frac{q_k^2}{m_k\omega_k} \coth\left(\frac{\beta\hbar\omega_k}{2}\right) [\delta(\omega - \omega_k) + \delta(\omega + \omega_k)] \equiv \coth\left(\frac{\beta\hbar\omega}{2}\right) A(\omega)$$

²⁹These have an accompanying electric field $E(t)$ which solves the first Maxwell equation $\nabla E(t) = 4\pi\rho(t)$, see below.

where, for simplicity, we focus on the case $\tilde{\epsilon} \equiv 1$ (unpolarizable ion cores). We replace $\rho(t)$ with the function $\rho_L(t)$ such that $\rho_L(t) = 0$ for $t < 0$ and $\rho_L(0^+) = \rho(0)$, and denote with $\tilde{\rho}_L$ its Fourier transform. The continuity equation in the Ohmic medium then reads as

$$\frac{\partial \rho_L}{\partial t}(t) + 4\pi \int_{-\infty}^{+\infty} \sigma(t-t') \rho_L(t') dt' = 0$$

where the integral over times actually runs for $t' \in [0, t]$, consistently with an initial state problem and with causality of the conductivity kernel. Upon noticing that

$$\int_{-\infty}^{+\infty} e^{i\omega t} \frac{\partial \rho_L}{\partial t}(t) dt = e^{i\omega t} \rho_L(t) \Big|_0^{+\infty} - i\omega \int_{-\infty}^{+\infty} \rho_L(t) e^{i\omega t} dt \equiv -\rho(0) - i\omega \tilde{\rho}_L(\omega)$$

we can take the Fourier transform of the above equation to obtain

$$-\rho(0) - i\omega \tilde{\rho}_L(\omega) + 4\pi \tilde{\sigma}(\omega) \tilde{\rho}_L(\omega) = 0$$

and

$$\tilde{\rho}_L(\omega) = \frac{i\rho(0)}{\omega + i4\pi\tilde{\sigma}(\omega)}$$

It follows

$$\rho_L(t) = \frac{\rho(0)}{2\pi} \int_{-\infty}^{+\infty} \frac{i}{\omega + i4\pi\tilde{\sigma}(\omega)} e^{-i\omega t} d\omega$$

which provides the solution $\rho_L(t)$. Note that for $t < 0$ the integral vanishes (as it should do) since the denominator is analytic and does not vanish in the upper half plane, thereby guaranteeing that no pole of the integrand appears when using contour integration in the upper half plane³⁰.

For $t > 0$ we specifically study the Lorentz-model expression of the conductivity

$$\tilde{\sigma}(z) = \frac{\gamma_0 \sigma_0}{\gamma_0 - iz}$$

to get a realistic representation of $\rho(t)$. The integral then reads as

$$\rho_L(t) = \frac{\rho(0)}{2\pi} \oint \frac{-\gamma_0 + iz}{(z - z_+)(z - z_-)} e^{-izt} dz$$

where

$$z_{\pm} = -i\frac{\gamma_0}{2} \pm \Omega, \quad \Omega^2 = 4\pi\sigma_0\gamma_0 - \frac{\gamma_0^2}{4} = \omega_P^2 - \frac{\gamma_0^2}{4}$$

and we consider only the case³¹ $\Omega^2 > 0$ or, equivalently, $\omega_P > \gamma_0/2$. Contour integration in the lower

³⁰ $\tilde{\sigma}(z)$ is analytic in the uhp and satisfies $\text{Re}\tilde{\sigma}(z) > 0$. It follows $\text{Im}(\omega + i4\pi\tilde{\sigma}(\omega)) = \text{Im}\omega + 4\pi\text{Re}\tilde{\sigma}(\omega) > 0$.

³¹Notice that even for $\Omega^2 < 0$ the poles z_{\pm} are confined to the lhp.

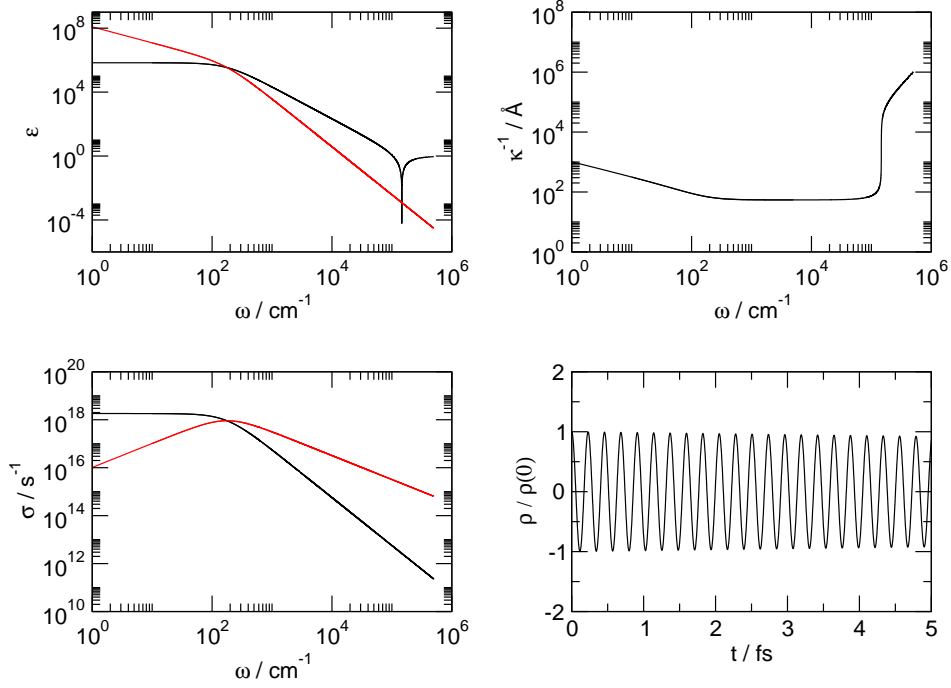


Figure 6: Typical behaviour of the real and imaginary parts of the dielectric function (absolute values are given in the black and red curves of the upper left panel) and of the conductivity (lower left panel, same color coding), along with the corresponding attenuation length (upper right), for a model conductor. Data are given for a model system with a Wigner-Seitz radius $r_s = 1.0 \text{ \AA}$ and relaxation time $\gamma^{-1} = 0.03 \text{ ps}$. The corresponding plasma resonant frequency is in the ultraviolet, $\lambda_P \approx 70 \text{ nm}$ and the Drude's conductivity is $\sigma_0 \approx 2 \cdot 10^{18} \text{ s}^{-1}$. The lower right panel shows the behaviour of $\rho(t)/\rho(0)$ for the chosen set of parameters.

half plane then gives for $t > 0$

$$\rho_L(t) = \rho(0) \frac{e^{-\frac{\gamma_0}{2}t}}{\Omega} [\gamma_0 \sin(\Omega t) + \Omega \cos(\Omega t)] \quad (22)$$

which shows that the initial density decays in time with a relaxation time $2\gamma_0^{-1}$ while oscillating at a frequency $\Omega \approx \omega_P$.

As is evident from the above discussion, the plasma frequency ω_P plays a central role in studying the optical properties of a conductor, which we now detail a bit more by focusing on the simple Lorentz-Drude-model, namely on

$$\tilde{\epsilon}_{tot}(\omega) = 1 + \frac{i4\pi\tilde{\sigma}(\omega)}{\omega} = 1 + \frac{i}{\omega} \frac{\omega_P^2}{\gamma_0 - i\omega} \equiv 1 - \frac{\omega_P^2}{\gamma_0^2 + \omega^2} + i \frac{\gamma_0}{\omega} \frac{\omega_P^2}{\gamma_0^2 + \omega^2}$$

where $\omega_P^2 = 4\pi\sigma_0\gamma_0$ has been used. The general behaviour of the relevant response functions is shown in Fig.6 and the optical properties can be directly read off from the rightmost term of the last expression.

It is evident that for any frequency but the smallest (in other words, for $\omega \gtrsim \gamma_0$) we have, to a good approximation,

$$\tilde{\epsilon}_{tot}(\omega) \approx 1 - \frac{\omega_P^2}{\omega^2}$$

This means that $\tilde{\epsilon}_{tot}(\omega)$ is approximately real and $\tilde{\epsilon}_{tot}(\omega) < 0$ ($\tilde{\epsilon}_{tot}(\omega) > 0$) holds for $\omega < \omega_P$ ($\omega > \omega_P$). Thus, a quick look at the wave equations Eq.s (9,10) reveals that wave propagation is only allowed for $\omega > \omega_P$: for $\tilde{\epsilon}_{tot}(\omega) < 0$ the solutions decay exponentially within the conductor on a short length scale, which increases when approaching ω_P (see Fig.6). Specifically, we have

$$\kappa \approx \frac{2}{c} \text{Re} \sqrt{\omega_P^2 - \omega^2} = 2 \sqrt{k_P^2 - k^2} \quad \text{for } \gamma_0 \ll \omega \leq \omega_P$$

where $k = 2\pi/\lambda$ and $k_P = 2\pi/\lambda_P$ have been introduced, with λ_P typically in the ultra-violet region, $\lambda_P \sim 100 \text{ nm}$. The behaviour of the system at the onset of propagation, *i.e.* exactly at the plasma frequency, follows from Eq.(22) upon noticing that for $\gamma_0 \ll \omega_P$ (a condition which is well satisfied in ordinary situations) this equation simplifies to

$$\rho_L(t) \approx \rho(0) \cos(\omega_P t)$$

This means that for a charge (“plasma”) oscillation to exist the accompanying electric field (*i.e.* that solving $\nabla E = 4\pi\rho$) has to oscillate at the plasma frequency.

Microscopic models and exact results parallel those introduced above for dielectrics. The Lorentz model of harmonically bound charges reduces -in the limit of vanishing frequency of the harmonic oscillator- to the free-electron model by Drude, *i.e.*

$$m_e \dot{v}(t) + m_e \gamma_e v(t) = -|e|E(t) + \zeta(t) \quad (23)$$

where $v = \dot{x}$ is the electron velocity, γ_e is the relaxation rate and E a uniform, possibly time-dependent electric field. Neglecting a transient which decays on a microscopic time scale $\tau_e \sim \gamma_e^{-1}$, the stationary solution for the ensemble average

$$\langle \tilde{v}(\omega) \rangle = -\frac{1}{m_e} \frac{|e|}{\gamma_e - i\omega} \tilde{E}(\omega)$$

provides the Drude’s expression for the *admittance*

$$\tilde{A}(\omega) = \frac{1}{m_e} \frac{|e|^2}{\gamma_e - i\omega}$$

(and the electron *mobility* $\mu_0 = \lim_{\omega \rightarrow 0} \tilde{A}(\omega) = |e|^2 \tau_e / m_e$) which allows one to express the frequency-

dependent conductivity as

$$\tilde{\sigma}(\omega) = n_e \tilde{A}(\omega) = \frac{n_e}{m_e} \frac{|e|^2}{\gamma_e - i\omega} = \frac{\gamma_e \sigma_0}{\gamma_e - i\omega}$$

where n_e is the number density of free electrons and $\sigma_0 = n_e e^2 \tau_e / m_e$ is the Drude's DC conductivity. The limitations of the Drude's model are well-known, and can be traced back to the intrinsic quantum behaviour of electrons³². Also, the nature of the scattering processes turned out to be very different from those originally envisaged by Drude, who identified in the collision with the ion cores the source of momentum relaxation. In fact, ion cores -if periodically arranged- become transparent to propagation of electron *waves* for all but few energy intervals: scattering only occurs because of *disorder*, *e.g.* lattice vibrations, impurities and defects. Even at very low temperatures, conduction is limited by *impurities* which can never be removed from real samples. However, the Drude model does capture some important features of the electron dynamics which remain unaltered in the more sophisticated approaches, what makes it still interesting nowadays.

In a static field and in samples much larger than the *mean free path* $l_e = v \tau_e$, (where v is a typical electron velocity), electrons undergo many collisions before being “probed” and, on average, acquire a *drift velocity*³³, $v_{drift} = -|e|E\tau_e/m_e$. This is much smaller than the typical magnitude of the electron velocity, but oriented with the field, and drives the electrons against the “thermal” random motion in the direction of the field. The motion is *drift-diffusion* and the regime is called *diffusive*. This has to be distinguished from the *ballistic motion* observed on time scales $\lesssim \tau_e$ where electrons are accelerated by the field.

The specific connection with diffusion is best appreciated at the classical level by noticing that, according to Eq.(23), and similarly to the previous discussion on dipoles, the average response to the field $-|e|E(t)$ is also the pointwise response to the fluctuating force $\zeta(t)$ which is responsible for diffusion and for thermal equilibrium,

$$\tilde{v}(\omega) = \frac{1}{m_e} \frac{\tilde{\zeta}(\omega)}{\gamma_e - i\omega}$$

On taking the square modulus of this expression and using the Wiener-Kinchine theorem, we obtain

$$\tilde{C}_v(\omega) = \frac{1}{m_e^2} \frac{1}{|\gamma_e - i\omega|^2} \tilde{C}_\zeta(\omega)$$

where $\tilde{C}_A(\omega)$ is the Fourier transform of the autocorrelation function $C_A(t) = \langle A(t)A \rangle$. Here, as usual,

³²For instance, if the electron gas were classical one would have a contribution $\frac{3}{2}k_B$ per electron to the heat capacity, which is not observed.

³³A collision-limited velocity $\tilde{v}(\omega)$ is attained for any frequency $\omega \lesssim \gamma_e$, which signals that dissipative processes are on.

$\tilde{C}_\zeta(\omega) = 2m_e\gamma_e k_B T$ ensures the correct equilibrium condition, *i.e.* $m_e C_v(0) = k_B T$, and thus³⁴

$$\tilde{C}_v(\omega) = \frac{2k_B T}{m_e} \frac{\gamma_e}{|\gamma_e - i\omega|^2} = \frac{2k_B T}{e^2} \text{Re}\tilde{A}(\omega)$$

or, equivalently³⁵,

$$\tilde{A}(\omega) = \frac{e^2}{k_B T} \int_0^\infty C_v(t) e^{i\omega t} dt$$

In the limit $\omega \rightarrow 0$,

$$\mu_0 = \frac{e^2}{k_B T} \int_0^\infty C_v(t) dt \equiv \frac{e^2}{k_B T} D$$

where D is the *diffusion coefficient*,

$$D = \lim_{t \rightarrow \infty} \frac{\langle (\mathbf{x}(t) - \mathbf{x}(0))^2 \rangle}{2dt} \equiv \frac{1}{d} \int_0^\infty \langle \mathbf{v}(t) \mathbf{v}(0) \rangle dt$$

here written in general for d spatial dimensions in terms of the d -dimensional position and velocity vectors, $\mathbf{x}(t)$ and $\mathbf{v}(t)$, respectively.

The above discussion, being based on classical statistics, fails in describing the *quantum* electron “gas” but provides some hints on how to correct such classical picture. In this perspective, the Drude’s conductivity reads as

$$\sigma_0 = e^2 \frac{n_e}{k_B T} D$$

where $\rho_e = n_e/k_B T$ is the *number of states per unit volume per unit energy* available for diffusion. This is the quantity suffering most of quantum restrictions, provided the diffusion coefficient is interpreted quantum mechanically. Thus, we may heuristically replace this term with the appropriate *density of states*.

The following simple argument, which has its roots in the *semiclassical* theory of electron dynamics, provides the route to the exact result. For fields which vary on a length scale much larger than the typical interatomic spacing, the band-structure picture holds locally on microscopically large but macroscopically small volumes, and we can thus introduce a *local electrochemical potential*³⁶

$$\mu(\mathbf{x}) = \mu_e(\mathbf{x}) - |e|\phi(\mathbf{x})$$

where $\mu_e(\mathbf{x})$ is the chemical potential of the unperturbed band structure (*i.e.* referenced to the field-free situation) and $-|e|\phi(\mathbf{x})$ is the energy shift of each electron level due to the presence of the external field. This quantity describes the driving force for restoring equilibrium when non-equilibrium

³⁴Analogous result holds in the non-Markovian case, $\gamma = \gamma(\omega)$, provided the correct fluctuation-dissipation relation of the second kind is used, $\tilde{C}_\zeta(\omega) = 2m_e k_B T \text{Re}\tilde{\gamma}(\omega)$.

³⁵Remembering that $A(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \tilde{A}(\omega) e^{-i\omega t} dt$ is real and satisfies causality, it is not hard to check that $A(t) = \frac{e^2}{k_B T} \Theta(t) C_v(t)$.

³⁶From a thermodynamic point of view, this is just the chemical potential describing the local equilibrium in the presence of the field.

conditions prevail, through the flux (in linear regime)

$$\mathbf{J}_e = -C \nabla \mu$$

Here C is a constant which can be determined by noticing that formally, when $\phi(\mathbf{x}) \equiv 0$, \mathbf{J} can only be due to a concentration gradient,

$$\mathbf{J}_e(\mathbf{E} = 0) = -C \nabla \mu_e = -D \nabla n_e$$

Hence,

$$C = D \left(\frac{\partial n_e}{\partial \mu} \right)_{\mathbf{E}=0}$$

where $\partial n_e / \partial \mu$ is the appropriate density of states for the diffusion process. For a degenerate electron gas (the rather *standard* case!) at $T = 0 \text{ K}$

$$\left(\frac{\partial n_e}{\partial \mu} \right)_{eq} \equiv \rho_e(\epsilon_F)$$

where $\rho_e(\epsilon_F)$ is the usual density of states at the Fermi level $\epsilon_F = \mu$. This is the main effect of the Fermi statistics, which allows one to “probe” the electron levels when progressively increasing the electron density at $T = 0 \text{ K}$. Then, in general, the charge current density reads as

$$\mathbf{J} = +|e| D \nabla n + e^2 D \rho_e \mathbf{E}$$

and the conductivity of a degenerate electron gas follows as

$$\sigma_0 = e^2 D \rho_e(\epsilon_F) \tag{24}$$

where D is the diffusion coefficient of the electrons at the Fermi level³⁷,

$$D = \frac{v_F^2}{d\gamma_e} = \frac{v_F^2 \tau_e}{d}$$

$v_F^2 = \langle \mathbf{v}^2 \rangle$ being the root-mean-square (group) velocity of the electrons at the Fermi level. Eq.(24) is also commonly re-written in terms of the *mean-free-path* $l_e = v_F \tau$

$$\sigma_0 = e^2 \rho_e(\epsilon_F) \frac{v_F l_e}{d}$$

³⁷In the Markov approximation the equilibrium velocity autocorrelation function decays exponentially, $\langle \mathbf{v}(t) \mathbf{v}(0) \rangle = \langle \mathbf{v}(t) \mathbf{v}(0) \rangle e^{-\gamma_e t}$. Notice that the subscript e in γ_e and τ_e stand also for *elastic* scattering, which is the main scattering mechanism limiting conduction.

Here, in weakly disordered samples, l_e is inversely proportional to the defect concentration n_i

$$\frac{1}{l_e} = n_i \sigma_e$$

the constant of proportionality σ_e being essentially the (elastic) scattering cross *section* (*length* for $d = 2$). Under such conditions, one can replace the density of states of the disordered sample with that of the *unperturbed* system, and find for an isotropic system

$$\rho_e(\epsilon_F) v_F = \frac{\partial n}{\partial \epsilon_F} \frac{1}{h} \frac{\partial \epsilon_F}{\partial k_F} = \frac{1}{h} \frac{\partial n}{\partial k_F}$$

where

$$n_e = \frac{g_v g_s}{V} \sum_{\mathbf{k}}^{k \leq k_F} 1 = \frac{g_v g_s}{V \Delta k} \int_{k \leq k_F} d^d k = \begin{cases} \frac{g_s g_v}{(2\pi)^2} \pi k_F^2 & \text{for } d = 2 \\ \frac{g_s g_v}{(2\pi)^3} \frac{4}{3} \pi k_F^3 & \text{for } d = 3 \end{cases}$$

Here, $g_s (\equiv 2)$ and g_v are the *spin* and *valley* degeneracies, and $\Delta k = (2\pi)^d/V$ is the volume (area) occupied by each k point upon application of the appropriate Born - von Karman boundary conditions on the sample volume (area) V . For instance,

$$\sigma_0 = g_v \frac{e^2}{h} k_F l_e$$

is “universal” in $2D$ electron gas systems, *i.e.* it holds irrespective of the dispersion relation (provided is isotropic).

Eq.(24) can also be written in a form which fully displays its quantum character (within the assumed one-electron approximation). To this end, we explicitly introduce the quantum expression of the relevant diffusion coefficient³⁸

$$D = \lim_{t \rightarrow \infty} \frac{\langle (\mathbf{x}(t) - \mathbf{x}(0))^2 \rangle_F}{2td}$$

where the average has to be taken on the *microcanonical* ensemble at the Fermi level

$$\langle (\mathbf{x}(t) - \mathbf{x}(0))^2 \rangle_F = \frac{\text{tr} \{ \delta(\epsilon_F - H) (\mathbf{x}(t) - \mathbf{x}(0))^2 \}}{\text{tr} \{ \delta(\epsilon_F - H) \}}$$

and notice that³⁹

$$\text{tr} \{ \delta(\epsilon_F - H) \} = V \rho_e(\epsilon_F)$$

³⁸As above, operators with a time dependence are meant to be in the Heisenberg picture.

³⁹ $\text{tr} \{ \delta(\epsilon_F - H) \} = \frac{\partial}{\partial \epsilon_F} \text{tr} \{ \Theta(\epsilon_F - H) \} = (dN/d\epsilon)_F$ where $N(\epsilon)$ is the total number of states at energy $\leq \epsilon$.

to arrive at⁴⁰

$$\sigma(\epsilon_F) = \frac{e^2}{2Vd} \lim_{t \rightarrow \infty} \frac{\text{tr} \{ \delta(\epsilon_F - H) (\mathbf{x}(t) - \mathbf{x}(0))^2 \}}{t} \quad (25)$$

This is transformed into the appropriate velocity autocorrelation function in the standard way, *i.e.* re-writing the numerator above, upon using $\mathbf{x}(t) - \mathbf{x}(0) = \int_0^t \mathbf{v}(t') dt'$, in the form

$$\langle (\mathbf{x}(t) - \mathbf{x}(0))^2 \rangle = \int_0^t dt_1 \int_0^t dt_2 \langle \mathbf{v}(t_1) \mathbf{v}(t_2) \rangle \approx \int_0^t dT \int_{-\infty}^{+\infty} d\tau \langle \mathbf{v}(T + \frac{\tau}{2}) \mathbf{v}(T - \frac{\tau}{2}) \rangle \equiv t \int_{-\infty}^{+\infty} \langle \mathbf{v}(\tau) \mathbf{v}(0) \rangle d\tau$$

where

$$\int_{-\infty}^{+\infty} \langle \mathbf{v}(\tau) \mathbf{v}(0) \rangle d\tau = \int_0^{\infty} \langle \mathbf{v}(\tau) \mathbf{v}(0) \rangle d\tau + \int_0^{\infty} \langle \mathbf{v}(-\tau) \mathbf{v}(0) \rangle d\tau = 2\text{Re} \int_0^{\infty} \langle \mathbf{v}(\tau) \mathbf{v}(0) \rangle d\tau$$

follows from $C_v(t) = C_v(-t)^*$. It follows,

$$\sigma(\epsilon_F) = \frac{e^2}{Vd} \int_0^{\infty} dt \text{tr} \left\{ \delta(\epsilon_F - H) \frac{[\mathbf{v}(t), \mathbf{v}(0)]_+}{2} \right\} = \frac{e^2}{Vd} \int_0^{\infty} dt \text{tr} \{ \delta(\epsilon_F - H) \text{Re}(\mathbf{v}(t), \mathbf{v}(0)) \}$$

and since

$$\text{tr} \{ \delta(\epsilon_F - H) \mathbf{v}(t) \mathbf{v}(0) \} = \text{tr} \left\{ \delta(\epsilon_F - H) e^{+\frac{i}{\hbar} H t} \mathbf{v} e^{-\frac{i}{\hbar} H t} \mathbf{v} \right\} = \text{tr} \left\{ \delta(\epsilon_F - H) \mathbf{v} e^{+\frac{i}{\hbar} (\epsilon_F - H) t} \mathbf{v} \right\}$$

$$\text{tr} \{ \delta(\epsilon_F - H) \mathbf{v}(0) \mathbf{v}(t) \} = \text{tr} \left\{ \delta(\epsilon_F - H) \mathbf{v} e^{+\frac{i}{\hbar} H t} \mathbf{v} e^{-\frac{i}{\hbar} H t} \right\} = \text{tr} \left\{ \delta(\epsilon_F - H) \mathbf{v} e^{-\frac{i}{\hbar} (\epsilon_F - H) t} \mathbf{v} \right\}$$

hold, after introducing the proper regularization (see also Appendix B)

$$\int_0^{+\infty} dt e^{\pm \frac{i}{\hbar} (\epsilon_F - H) t} = \pm i \hbar G^{\pm}(\epsilon), \quad i (G^+(\epsilon) - G^-(\epsilon)) = 2\pi \delta(\epsilon - H)$$

we finally arrive at

$$\sigma(\epsilon_F) = \frac{\pi \hbar e^2}{Vd} \text{tr} \{ \delta(\epsilon_F - H) \mathbf{v} \delta(\epsilon_F - H) \mathbf{v} \} \quad (26)$$

in terms of the velocity operator in the Schrödinger picture. Also,

$$\sigma(\epsilon_F) = \frac{\pi e^2}{Vd} \sum_{i,f} \langle \epsilon_F f | \mathbf{v} | \epsilon_F i \rangle \langle \epsilon_F i | \mathbf{v} | \epsilon_F f \rangle = \frac{\pi e^2}{Vd} \sum_{i,f} | \langle \epsilon_F f | \mathbf{v} | \epsilon_F i \rangle |^2$$

expresses the (zero-frequency) conductivity in terms of the eigenvectors of the (disordered) Hamiltonian

⁴⁰At finite temperatures $\delta(\epsilon_F - H)$ has to be replaced with $-\partial f(H)/\partial \epsilon$ where $f_\beta(\epsilon)$ is the Fermi-Dirac function at temperature $T = (k_B \beta)^{-1}$. This also gives

$$\sigma_\beta = \int d\epsilon \left(-\frac{\partial f_\beta}{\partial \epsilon} \right) (\epsilon) \sigma_{T=0}(\epsilon)$$

where $\sigma_{T=0}(\epsilon)$ is the $T = 0K$ conductivity of the system when the Fermi level is adjusted at the energy ϵ (provided scattering mechanisms can be considered temperature- independent).

at energy ϵ_F . Notice that if these eigenvectors represent bound states, *i.e.* if they *localize* within the sample volume, the “on-shell” matrix elements of the velocity operator vanish, being $\mathbf{v} = \frac{i}{\hbar}[H, \mathbf{x}]$: in this case the conductivity vanishes even if the states form a continuum, and one speaks about a *localization* regime⁴¹.

The exact expression for the frequency-dependent conductivity tensor, in linear regime, can be obtained with the help of the general linear response theory. The theory is outlined in Appendix D (see also Appendix E for the definitions of charge and current density operators), and gives, for a perturbation of the form $H_{int} = -a(t)A$, an expression for the response

$$\langle \delta B(t) \rangle = \int_{-\infty}^{+\infty} a(t') \chi_{BA}(t-t') dt'$$

in the form

$$\chi_{BA}(t) = \Theta(t) \frac{i}{\hbar} \langle [B(t), A] \rangle = \Theta(t) \beta C_{BA}^K(t)$$

where the second equality, involving the *Kubo correlation function* $C_{BA}^K(t)$, holds in *canonical* equilibrium. Of interest here is the special case $B = \dot{A}$,

$$\langle \dot{A}(t) \rangle = \int_{-\infty}^{+\infty} a(t') \chi_{\dot{A}A}(t-t') dt', \quad \chi_{\dot{A}A}(t) = \frac{d}{dt} \chi_{AA}(t) \equiv \Theta(t) \frac{i}{\hbar} [\dot{A}(t), A] = \Theta(t) \beta C_{\dot{A}A}^K(t)$$

for the perturbation describing an electric field^{42,43}

$$\hat{H}_{int} = \int d\mathbf{r}' \phi^{ext}(\mathbf{r}', t) \hat{n}(\mathbf{r}')$$

here written in terms of the charge density operator. Linear response then gives

$$-\langle \frac{\partial \hat{n}}{\partial t}(\mathbf{r}, t) \rangle = \int d\mathbf{r}' \int_{-\infty}^{+\infty} \chi_{\delta n \delta n}(\mathbf{r}, \mathbf{r}' | t-t') \phi^{ext}(\mathbf{r}', t)$$

where (in canonical equilibrium)

$$\chi_{\delta n \delta n}(\mathbf{r}, \mathbf{r}' | t-t') = \Theta(t) \int_0^\beta \langle \frac{\partial \hat{n}}{\partial t}(\mathbf{r}', -i\hbar\tau) \frac{\partial \hat{n}}{\partial t}(\mathbf{r}, t) \rangle d\tau$$

⁴¹This is the celebrated *absence of quantum diffusion* in strongly disordered media, and arises because of the destructive interference which dominates a multiple collision process when the scatterers are randomly arranged.

⁴²We work in a gauge where $\mathbf{E}(r, t) = -\nabla \phi^{ext}(r, t)$. We are actually focusing on the *parallel* components of the electric field and current density, and extract $\sigma(\omega)$ from these components. This is easier since \mathbf{E} and \mathbf{B} are linked to each other through their *transverse* components only, and is legitimate as long as Ohm's law $\tilde{\mathbf{J}}(\omega) = \sigma(\omega) \tilde{\mathbf{E}}(\omega)$ holds for the overall (parallel plus transverse) vector fields. The above choice amounts to consider a purely transverse vector potential, *i.e.* $\nabla \cdot \mathbf{A} = 0$ (Coulomb gauge), and identifies in ϕ and \mathbf{A} the potentials responsible for the parallel and perpendicular components of the field, respectively.

⁴³In the following, to avoid confusion, we identify operators with a hat, see Appendix E.

Using the continuity equation $\partial\hat{n}/\partial t + \nabla\hat{\mathbf{J}} = 0$ we obtain⁴⁴

$$-\nabla_\beta \langle \hat{\mathbf{J}}_\beta(\mathbf{r}, t) \rangle = \int d\mathbf{r}' \int_{-\infty}^{+\infty} \phi^{ext}(\mathbf{r}', t') \Theta(t - t') \nabla_\beta \nabla'_\alpha \int_0^\beta \langle \hat{\mathbf{J}}_\alpha(\mathbf{r}', -i\hbar\tau) \hat{\mathbf{J}}_\beta(\mathbf{r}, t - t') \rangle d\tau$$

where the manipulation

$$\phi^{ext}(\mathbf{r}, t) \nabla_\alpha \hat{\mathbf{J}}_\alpha(\mathbf{r}, t) = \nabla_\alpha (\phi^{ext} \hat{\mathbf{J}}_\alpha)(\mathbf{r}, t) - \hat{\mathbf{J}}_\alpha \nabla_\alpha \phi^{ext}(\mathbf{r}, t) = \nabla_\alpha (\phi^{ext} \hat{\mathbf{J}}_\alpha)(\mathbf{r}, t) + \hat{\mathbf{J}}_\alpha \mathbf{E}_\alpha(\mathbf{r}, t)$$

makes the electric field explicit,

$$\nabla_\beta \langle \hat{\mathbf{J}}_\beta(\mathbf{r}, t) \rangle = \nabla_\beta \int d\mathbf{r}' \int_{-\infty}^{+\infty} dt' \Theta(t - t') \left(\int_0^\beta \langle \hat{\mathbf{J}}_\alpha(\mathbf{r}', -i\hbar\tau) \hat{\mathbf{J}}_\beta(\mathbf{r}, t - t') \rangle d\tau \right) \mathbf{E}_\alpha^{ext}(\mathbf{r}', t')$$

In writing this expression a surface integral has been neglected since it accounts for the charges leaving the sample at its boundaries⁴⁵ and thus the conductivity tensor follows as⁴⁶

$$\sigma_{\beta\alpha}(\mathbf{r}, \mathbf{r}' | t) = \Theta(t) \int_0^\beta \langle \hat{\mathbf{J}}_\alpha(\mathbf{r}', -i\hbar\tau) \hat{\mathbf{J}}_\beta(\mathbf{r}, t) \rangle d\tau \quad (27)$$

This is known as *Kubo-Nakano* formula of conductivity and is best written in the energy representation, on noticing that

$$\langle \hat{\mathbf{J}}_\alpha(\mathbf{r}', -i\hbar\tau) \hat{\mathbf{J}}_\beta(\mathbf{r}, t) \rangle \equiv \sum_{nm} \rho_n \langle \Psi_n | \hat{\mathbf{J}}_\alpha(\mathbf{r}') | \Psi_m \rangle \langle \Psi_m | \hat{\mathbf{J}}_\beta(\mathbf{r}) | \Psi_n \rangle e^{\tau(E_n - E_m)} e^{-\frac{i}{\hbar}(E_n - E_m)t}$$

where $|\Psi_n\rangle$ are N -electron eigenstates with energies E_n and $\rho_n = e^{-\beta E_n}/Z$ are the corresponding thermal populations.

In the *monoelectronic approximation*⁴⁷ $|\Psi_n\rangle$'s are determinants and $\langle \Psi_n | \hat{\mathbf{J}}_\alpha(\mathbf{r}') | \Psi_m \rangle$ is non-vanishing only if $|\Psi_n\rangle$ differs from $|\Psi_m\rangle$ by at most one single-particle state. Thus, if $n_0 = \{i_1 i_2 \dots i_{N-1}\}$ is a collection of $N - 1$ indexes and $i, f \notin n_0$

$$\langle \Psi_{n_0 i} | \hat{\mathbf{J}}_\alpha | \Psi_{n_0 f} \rangle = \langle \phi_i | \hat{\mathbf{J}}_\alpha | \phi_f \rangle$$

⁴⁴The sum is implicit on repeated greek indexes.

⁴⁵In the static limit it reads as

$$-\sum_i \phi_i \int_{\partial V_i} d\mathbf{S}' \int_{-\infty}^t dt' \left(\int_0^\beta \langle \hat{\mathbf{J}}_\alpha(\mathbf{r}', -i\hbar\tau) \frac{\partial \hat{n}}{\partial t}(\mathbf{r}, t - t') \rangle d\tau \right)$$

where ϕ_i are the potentials of the conductors to which the sample is contacted, and the integrals run over the contact surfaces.

⁴⁶Of course, the equality should hold to within a term of the form, $\nabla \wedge \mathbf{F}$, but the homogeneous condition, $J \rightarrow 0$ when $E \rightarrow 0$, sets this term to zero.

⁴⁷We keep on using the standard (first quantization) version of quantum mechanics. Second quantization simplify things considerably.

where $|\phi_i\rangle$ are single-particle states and $\hat{\mathbf{j}}_\alpha$ is the mono-electronic current operator

$$\hat{\mathbf{j}}_\alpha(\mathbf{r}) = -\frac{|e|\hbar}{2m}[\hat{\mathbf{v}}_\alpha, \delta(\mathbf{r} - \hat{\mathbf{r}})]_+$$

On account of the permutation symmetry restrictions, the sum over states transforms according to

$$\sum_{n_0} \sum_{i \notin n_0} \sum_{f \notin n_0} \rho_{n_0 i} \{ \dots \} \equiv \sum_{i, f} f(\epsilon_i) (1 - f(\epsilon_f)) \{ \dots \}$$

where

$$f(\epsilon) = \frac{1}{e^{\beta(\epsilon - \mu)} + 1}$$

is the Fermi distribution function. Thus,

$$\langle \hat{\mathbf{J}}_\alpha(\mathbf{r}', -i\hbar\tau) \hat{\mathbf{J}}_\beta(\mathbf{r}, t) \rangle = \sum_{i, f} f(\epsilon_i) (1 - f(\epsilon_f)) \langle \phi_i | \hat{\mathbf{j}}_\alpha(\mathbf{r}') | \phi_f \rangle \langle \phi_f | \hat{\mathbf{j}}_\beta(\mathbf{r}) | \phi_i \rangle e^{\tau(\epsilon_i - \epsilon_f)} e^{-i\omega_{if}t}$$

where ω_{if} are the transition frequencies. On integrating over τ and noticing that

$$f(\epsilon_i) (1 - f(\epsilon_f)) (e^{\beta(\epsilon_i - \epsilon_f)} - 1) \equiv f(\epsilon_f) - f(\epsilon_i)$$

we can Fourier transform in time using

$$\lim_{\epsilon \rightarrow 0^+} \int_0^\infty e^{-\epsilon t} e^{i\omega t} e^{-i\omega_{if}t} dt = i\mathcal{P} \left(\frac{1}{\omega - \omega_{if}} \right) + \pi\delta(\omega - \omega_{if})$$

to arrive at (upon swapping i for f)

$$\tilde{\sigma}_{\beta\alpha}(\mathbf{r}, \mathbf{r}' | \omega) = \sum_{if} \left(-\frac{\Delta f}{\Delta \epsilon} \right)_{fi} \langle \phi_i | \hat{\mathbf{j}}_\beta(\mathbf{r}) | \phi_f \rangle \langle \phi_f | \hat{\mathbf{j}}_\alpha(\mathbf{r}') | \phi_i \rangle \left\{ i\mathcal{P} \left(\frac{1}{\omega - \omega_{fi}} \right) + \pi\delta(\omega - \omega_{fi}) \right\}$$

where

$$\left(\frac{\Delta f}{\Delta \epsilon} \right)_{fi} := \frac{f(\epsilon_f) - f(\epsilon_i)}{\epsilon_f - \epsilon_i} = \left(\frac{\Delta f}{\Delta \epsilon} \right)_{if}$$

In homogeneous systems $\tilde{\sigma}_{\beta\alpha}(\mathbf{r}, \mathbf{r}' | \omega)$ is actually a function of $\mathbf{r} - \mathbf{r}'$, which we write simply as $\bar{\sigma}_{\beta\alpha}(\mathbf{r} - \mathbf{r}' | \omega)$. Its spatial Fourier transform,

$$\bar{\sigma}_{\beta\alpha}(\mathbf{q} | \omega) = \int d\mathbf{r} \bar{\sigma}_{\beta\alpha}(\mathbf{r} | \omega) e^{-i\mathbf{q}\mathbf{r}}$$

enters the linear response result

$$\langle \tilde{J}_\beta(\mathbf{q}, \omega) \rangle = \bar{\sigma}_{\beta\alpha}(\mathbf{q} | \omega) \tilde{E}_\alpha(\mathbf{q}, \omega)$$

and is related to $\tilde{\sigma}_{\beta\alpha}(\mathbf{r}, \mathbf{r}'|\omega)$ by a double spatial transform

$$\bar{\sigma}_{\beta\alpha}(\mathbf{q}|\omega) \approx \frac{1}{V} \int d\mathbf{r}_1 \int d\mathbf{r}_2 e^{-i\mathbf{q}(\mathbf{r}_1 - \mathbf{r}_2)} \tilde{\sigma}_{\beta\alpha}(\mathbf{r}_1, \mathbf{r}_2|\omega)$$

Here the dependence on $\mathbf{r}_1, \mathbf{r}_2$ only occurs in the current density

$$\int d\mathbf{r} \hat{j}_\alpha(\mathbf{r}) e^{-i\mathbf{q}\mathbf{r}} \equiv -\frac{|e|}{2} [\hat{v}_\alpha, e^{-i\mathbf{q}\hat{\mathbf{r}}}]_+$$

therefore, in the long-wavelength limit (*i.e.* for spatially uniform fields), $\hat{j}_\alpha(\mathbf{q}) \rightarrow -|e|\hat{v}_\alpha$ and

$$\bar{\sigma}_{\beta\alpha}(\mathbf{0}|\omega) = \frac{e^2}{V} \sum_{if} \left(-\frac{\Delta f}{\Delta\epsilon} \right)_{fi} \langle \phi_i | \hat{\mathbf{v}}_\beta | \phi_f \rangle \langle \phi_f | \hat{\mathbf{v}}_\alpha | \phi_i \rangle \left\{ i\text{P} \left(\frac{1}{\omega - \omega_{fi}} \right) + \pi\delta(\omega - \omega_{fi}) \right\}$$

The randomly disordered system can be considered isotropic, $\bar{\sigma}_{\beta\alpha}(\mathbf{0}|\omega) = \delta_{\alpha\beta} \bar{\sigma}(\mathbf{0}|\omega)$, where

$$\bar{\sigma}(\mathbf{0}|\omega) = \frac{e^2}{Vd} \sum_{if} \left(-\frac{\Delta f}{\Delta\epsilon} \right)_{fi} |\langle \phi_i | \hat{\mathbf{v}}_\alpha | \phi_f \rangle|^2 \left\{ i\text{P} \left(\frac{1}{\omega - \omega_{fi}} \right) + \pi\delta(\omega - \omega_{fi}) \right\}$$

and, in particular,

$$\text{Re}\bar{\sigma}(\mathbf{0}|\omega) = \frac{\pi e^2}{Vd} \sum_{if} \left(-\frac{\Delta f}{\Delta\epsilon} \right)_{fi} |\langle \phi_i | \hat{\mathbf{v}} | \phi_f \rangle|^2 \delta(\omega - \omega_{fi}) \quad (28)$$

Thanks to causality, this expression is sufficient to reproduce the whole frequency dependent conductivity in the $\mathbf{q} = \mathbf{0}$ limit, and in the mono-electronic approximation, and is known as *Kubo-Greenwood* formula of conductivity. It can be converted to a previous expression, Eq.(26), by replacing the free sums over i, f with integrals over energies ϵ, ϵ' and sums over degeneracy indexes i, f ($\Delta\epsilon \equiv \epsilon' - \epsilon$)

$$\text{Re}\bar{\sigma}(\mathbf{0}|\omega) = \frac{\pi e^2}{Vd} \int d\epsilon \int d\epsilon' \left(-\frac{\Delta f}{\Delta\epsilon} \right) \sum_{if} |\langle \epsilon i | \hat{\mathbf{v}} | \epsilon' f \rangle|^2 \delta(\omega - \frac{\Delta\epsilon}{\hbar})$$

where

$$\sum_{if} |\langle \epsilon i | \hat{\mathbf{v}} | \epsilon' f \rangle|^2 \equiv \text{tr} \{ \hat{\mathbf{v}} \delta(\epsilon - H) \hat{\mathbf{v}} \delta(\epsilon' - H) \}$$

Thus, in the limit of vanishing frequency, we recover the previous result,

$$\text{Re}\bar{\sigma}(\mathbf{0}|0) = \frac{\pi \hbar e^2}{Vd} \int d\epsilon \left(-\frac{\partial f}{\partial \epsilon} \right) \text{tr} \{ \hat{\mathbf{v}} \delta(\epsilon - H) \hat{\mathbf{v}} \delta(\epsilon - H) \}$$

or, equivalently,

$$\text{Re}\bar{\sigma}(\mathbf{0}|0) = \int d\epsilon \left(-\frac{\partial f}{\partial \epsilon} \right) \sigma_{T=0K}(\epsilon)$$

where

$$\sigma_{T=0K}(\epsilon) = \frac{\pi \hbar e^2}{Vd} \text{tr} \{ \hat{\mathbf{v}} \delta(\epsilon - H) \hat{\mathbf{v}} \delta(\epsilon - H) \}$$

is the limiting conductivity at zero temperature when the Fermi level is set to ϵ , $\lim_{T \rightarrow 0} \text{Re} \bar{\sigma}(\mathbf{0}|0)$, since $\lim_{T \rightarrow 0} \left(-\frac{\partial f}{\partial \epsilon}\right) = \delta(\epsilon - \epsilon_F)$ holds with $\epsilon_F = \lim_{T \rightarrow 0} \mu$.

It is worth noticing at this point that Eq.(28) is very general, and describes the conductivity at both small and high frequencies (*i.e.* from the DC/AC “domain” up to the optical region and more), provided the appropriate Hamiltonian including disorder is considered. However, disorder is only relevant at low frequencies $\omega \lesssim \tau_e$, where τ_e is the disorder-related relaxation time. At high frequencies ($\omega \gg \tau_e$) relaxation processes are negligible on the time scale of the electron dynamics $\sim \omega^{-1}$, and thus the conductivity is best evaluated with the much simpler disorder-free Hamiltonian,

$$(\omega \gg \tau_e) \quad \bar{\sigma}_{\beta\alpha}(\mathbf{0}|\omega) \approx \bar{\sigma}_{\beta\alpha}^0(\mathbf{0}|\omega) = i \frac{2e^2}{(2\pi)^d} \sum_{if} \lim_{\eta \rightarrow 0^+} \int_{BZ} d^d \mathbf{k} \left(-\frac{\Delta f}{\Delta \epsilon} \right)_{fi} \frac{\langle \mathbf{k}i | \hat{v}_\beta | \mathbf{k}f \rangle \langle \mathbf{k}f | \hat{v}_\alpha | \mathbf{k}i \rangle}{\omega - \omega_{fi}(\mathbf{k}) + i\eta}$$

where the sum over initial and final states has been written explicitly in terms of Bloch vectors and band index, and the translational symmetry has been used to simplify matrix elements,

$$\langle \mathbf{k}i | \hat{v}_\beta | \mathbf{k}'f \rangle = \delta_{\mathbf{k}\mathbf{k}'} \langle \mathbf{k}i | \hat{v}_\beta | \mathbf{k}f \rangle$$

prior to the usual replacement $\sum_{\mathbf{k}} \rightarrow V/(2\pi)^d \int_{BZ} d^d \mathbf{k}$ which introduces the integral over the Brillouin zone (the factor of 2 comes from the fact that the original sum was also over the spin projections). Here it is worth exhibiting separately the diagonal term $i = f$

$$i \frac{2e^2}{(2\pi)^d} \sum_n \lim_{\eta \rightarrow 0^+} \frac{1}{\omega + i\eta} \int_{BZ} d^d \mathbf{k} \left(-\frac{\partial f}{\partial \epsilon}(\epsilon_n(\mathbf{k})) \right) \langle \mathbf{k}n | \hat{v}_\beta | \mathbf{k}n \rangle \langle \mathbf{k}n | \hat{v}_\alpha | \mathbf{k}n \rangle$$

which is non-vanishing for conductors only thanks to the term $-\partial f(\epsilon)/\partial \epsilon \approx \delta(\epsilon - \mu)$. In particular, the $T = 0$ K limit of the real part of this contribution reads as

$$\text{Re} \bar{\sigma}_{\beta\alpha}^D(\mathbf{0}|\omega) = \pi D_{\beta\alpha}^0 \delta(\omega) \quad (29)$$

where D^0 is termed *Drude weight* and is given by

$$D_{\beta\alpha}^0 = e^2 \rho(\epsilon_F) \langle v_\beta v_\alpha \rangle_{\epsilon_F}$$

with $\rho(\epsilon) = 2 \int_{BZ} d^d \mathbf{k} / (2\pi)^d \delta(\epsilon(\mathbf{k}) - \epsilon)$ the density of states per unit volume and $\langle \dots \rangle_{\epsilon_F}$ an average over the Fermi surface. Most often $D_{\alpha\beta}^0 = \delta_{\alpha\beta} D^0$ where

$$D^0 = \frac{e^2 \rho(\epsilon_F) v_F^2}{d}$$

On comparing with Eq.(24) $D^0 \equiv \sigma_0 \gamma_e$ as in the Drude model⁴⁸, and is a measure of the number density of electrons available at the Fermi level weighted by their average speed $v_F^2 := \langle \mathbf{v}^2 \rangle_{\epsilon_F}$; of

⁴⁸For $\sigma(\omega) = \sigma_0 \gamma_e / (\gamma_e - i\omega)$ and $D^0 = \sigma_0 \gamma_e \equiv Ne^2/m_e$ we have $\text{Re} \sigma(\omega) = \sigma_0 \gamma_e^2 / (\gamma_e^2 + \omega^2) \rightarrow \pi D^0 \delta(\omega)$ for $\gamma_e \rightarrow 0$.

course, the δ -peak appearing in Eq.(29) (in place of a Lorentzian of width $\sim \gamma_e$) arises from the use of a disorder-free Hamiltonian which cannot describe electron scattering.

We thus see that

$$\text{Re}\bar{\sigma}_{\beta\alpha}^0(\mathbf{0}|\omega) = \pi D_{\beta\alpha}^0 \delta(\omega) + \text{Re}\bar{\sigma}_{\beta\alpha}^{opt}(\mathbf{0}|\omega)$$

where

$$\text{Re}\bar{\sigma}_{\beta\alpha}^{opt}(\mathbf{0}|\omega) = \frac{e^2}{(2\pi)^{d-1}\omega} \sum_{i \neq f} \int_{BZ} d^d \mathbf{k} (f(\epsilon_i(\mathbf{k})) - f(\epsilon_f(\mathbf{k}))) \langle \mathbf{k}i | \hat{\mathbf{v}}_\beta | \mathbf{k}f \rangle \langle \mathbf{k}f | \hat{\mathbf{v}}_\alpha | \mathbf{k}i \rangle \delta(\omega - \omega_{fi}(\mathbf{k}))$$

is the genuine optical conductivity containing *inter-band* transitions only, and therefore

$$\text{Re}\bar{\sigma}_{\beta\alpha}(\mathbf{0}|\omega) \approx \frac{\sigma_{DC} \gamma_e^2}{\gamma_e^2 + \omega^2} + \text{Re}\bar{\sigma}_{\beta\alpha}^{opt}(\mathbf{0}|\omega)$$

with σ_{DC} and γ_e computed with the full Hamiltonian H including disorder,

$$(T = 0 \text{ K}) \quad \sigma_{DC} = \frac{\pi \hbar e^2}{Vd} \text{tr} \{ \hat{\mathbf{v}} \delta(\epsilon_F - H) \hat{\mathbf{v}} \delta(\epsilon_F - H) \}, \quad \gamma_e = \frac{D^0}{\sigma_{DC}}$$

at the expense of neglecting the possible effect of disorder on the low energy *inter-band* transitions, which is surely a good approximation if the onset of such transitions ω_0 is such that $\omega_0 \gtrsim \gamma_e$.

8 Appendix A: Averages of microscopic densities and fields

We sketch in this Appendix the derivation of the macroscopic Maxwell equations from the microscopic ones, focusing on the simplest case of Eq.1. We start introducing a suitable averaging function $f(\mathbf{r})$ peaked at the origin, which is small ranged on a macroscopic scale but extends (smoothly) on a microscopically large volume containing many molecules. The average of the microscopic quantity $F(\mathbf{r}, t)$ is then defined according to

$$F_{macro}(\mathbf{r}, t) = \langle F(\mathbf{r}, t) \rangle = \int d^3\mathbf{r}' f(\mathbf{r}') F(\mathbf{r} - \mathbf{r}', t) = \int d^3\mathbf{r}' f(\mathbf{r} - \mathbf{r}') F(\mathbf{r}', t)$$

provided f is normalized to 1. It follows $\partial F_{macro}/\partial x_i = \langle \partial F(\mathbf{r}, t)/\partial x_i \rangle$ and similarly $\partial F_{macro}/\partial t = \langle \partial F(\mathbf{r}, t)/\partial t \rangle$.

With this definition, averaging Eq.1 gives $\nabla \mathbf{E}_{macro} = 4\pi \rho_{macro}$ where $\rho_{macro}(\mathbf{r}, t)$ is the average of the molecular and the free charge density,

$$\rho_{micro}(\mathbf{r}, t) = \sum_i \rho_i^{mol}(\mathbf{r}, t) + \sum_i q_i \delta(\mathbf{r} - \mathbf{r}_i(t))$$

For the i -th molecule at position \mathbf{R}_i the contribution of its density to the average in \mathbf{r} can be obtained upon noticing that $\rho_i^{mol}(\mathbf{r}', t)$ is strongly peaked around $\mathbf{r}' = \mathbf{R}_i$

$$\langle \rho_i^{mol}(\mathbf{r}, t) \rangle = \int d^3\mathbf{r}' f(\mathbf{r} - \mathbf{r}') \rho_i^{mol}(\mathbf{r}', t) \approx \int d^3\mathbf{r}' f(\mathbf{r} - \mathbf{R}_i) \rho_i^{mol}(\mathbf{r}', t) - \int d^3\mathbf{r}' \nabla f(\mathbf{r} - \mathbf{R}_i) \rho_i^{mol}(\mathbf{r}', t) (\mathbf{r}' - \mathbf{R}_i)$$

i.e.,

$$\langle \rho_i^{mol}(\mathbf{r}, t) \rangle \approx f(\mathbf{r} - \mathbf{R}_i) q_i^{mol} - \nabla f(\mathbf{r} - \mathbf{R}_i) \mathbf{p}_i^{mol}$$

where

$$q_i^{mol} = \int d^3\mathbf{r}' \rho_i^{mol}(\mathbf{r}', t)$$

is the molecular charge (if any) and

$$\mathbf{p}_i^{mol} = \int d^3\mathbf{r}' \rho_i^{mol}(\mathbf{r}', t) (\mathbf{r}' - \mathbf{R}_i)$$

its dipole (with origin in \mathbf{R}_i). Thus, from a different perspective, the first term is the average of a point charge density $\rho_i^{point}(\mathbf{r}, t) = q_i^{mol} \delta(\mathbf{r} - \mathbf{R}_i(t))$ (similar to the contribution of the free-charges) and the second term is (minus) the gradient of the average of a dipole density

$$\mathbf{p}_i(\mathbf{r}, t) = \mathbf{p}_i^{mol}(t) \delta(\mathbf{r} - \mathbf{R}_i(t))$$

As a result

$$\rho_{macro}(\mathbf{r}, t) = \rho(\mathbf{r}, t) - \nabla \mathbf{P}(\mathbf{r}, t)$$

where now $\rho(\mathbf{r}, t)$ is the number density of molecular and free charges at \mathbf{r} , $\mathbf{P}(\mathbf{r}, t)$ is the number density of dipoles, and

$$\nabla (\mathbf{E}(\mathbf{r}, t) + 4\pi\mathbf{P}(\mathbf{r}, t)) = 4\pi\rho(\mathbf{r}, t)$$

Notice that $\rho(\mathbf{r}, t)$ is usually termed the “free” charge density, even though it contains both charges which are “free” to move (q_i above) and ion cores which are essentially fixed in space (*e.g.* in an alkali metal q_i ’s are the free-electron charges and q_i^{mol} ’s are alkaline ions which sit on the lattice positions). This result is rather general and can be specialized to the cases of interest: in a dielectric there are no free charges and $\rho(\mathbf{r}, t)$ describes the *external* charges deposited onto the molecules $\rho(\mathbf{r}, t) \equiv \rho_i^{point}(\mathbf{r}, t)$ whereas in a conductor, as mentioned above, it accounts for both the conduction electron density and the ion-core densities, $\rho(\mathbf{r}, t) = \rho^{cond}(\mathbf{r}, t) + \rho^{ion}(\mathbf{r}, t)$, where the latter is quasi-static, *i.e.* $\tilde{\rho}(\mathbf{r}, \omega) \approx \tilde{\rho}^{cond}(\mathbf{r}, \omega)$ for $\omega > 0$, though an ionic contribution $\tilde{\rho}^{ion}(\mathbf{r}, \omega)$ may appear at frequencies resonant with the lattice vibrations.

9 Appendix B: Analytic properties of response functions

Spectral representation of analytic functions in the uhp

Let $f(z)$ be an analytic function in the upper half plane such that $|f(z)| \rightarrow 0$ as $|z| \rightarrow \infty$. Cauchy's representation theorem reads as

$$f(z) = \frac{1}{2\pi i} \int_{-\infty}^{+\infty} \frac{f^+(x)}{x-z} dx \equiv \frac{1}{2\pi i} \int_{-\infty}^{+\infty} dx f^+(x) \left\{ \frac{1}{x-z} \pm \frac{1}{x-z^*} \right\}$$

where $f^+(x) = \lim_{\epsilon \rightarrow 0^+} f(x + i\epsilon)$ ($x \in \mathbb{R}$) and the second term on the rightmost hand side has been added since it is analytic in the uhp and thus does not affect the value of the integral. Hence

$$f(z) = \frac{1}{\pi i} \int_{-\infty}^{+\infty} f^+(x) \operatorname{Re} \left\{ \frac{1}{x-z} \right\} dx = \frac{1}{\pi} \int_{-\infty}^{+\infty} f^+(x) \operatorname{Im} \left\{ \frac{1}{x-z} \right\} dx$$

and, upon taking the real and imaginary parts of these expressions,

$$f(z) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\operatorname{Im} f^+(x)}{x-z} dx = \frac{1}{\pi i} \int_{-\infty}^{+\infty} \frac{\operatorname{Re} f^+(x)}{x-z} dx$$

We call these expressions the *spectral representations* of $f(z)$: they give f for any z in the uhp in terms of its limiting real or imaginary parts on the real axis. Notice that for $z = x + i\epsilon$ and $\epsilon \rightarrow 0^+$ the integral can be easily computed using the formal identity

$$\frac{1}{x' - z} \rightarrow \mathcal{P} \frac{1}{x' - x} + i\pi \delta(x - x')$$

(where \mathcal{P} denotes the Cauchy principal value of the integral) and gives

$$f^+(x) = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{+\infty} \frac{\operatorname{Im} f^+(x')}{x' - x} dx' + i \operatorname{Im} f^+(x) = \frac{1}{\pi i} \mathcal{P} \int_{-\infty}^{+\infty} \frac{\operatorname{Re} f^+(x')}{x' - x} dx' + \operatorname{Re} f^+(x)$$

i.e.

$$\operatorname{Re} f^+(x) = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{+\infty} \frac{\operatorname{Im} f^+(x')}{x' - x} dx' \text{ and } \operatorname{Im} f^+(x) = -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{+\infty} \frac{\operatorname{Re} f^+(x')}{x' - x} dx'$$

which are the celebrated *Kramers-Kronig relations*.

Spectral representation of response functions

We define a *response function* a function of the form

$$\chi(t) = \Theta(t)g(t)$$

where g is a real function, and Θ is the usual Heaviside function, $\Theta(t) = 1$ for $t \geq 0$ and $\Theta = 0$ otherwise. The Fourier transform

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

can be “analytically continued” in the upper half plane through⁴⁹

$$\tilde{\chi}_c(z) = \int_{-\infty}^{+\infty} \chi(t) e^{izt} dt$$

since the integrand is well-behaved for $t \rightarrow \infty$ for any z with $\text{Im} z > 0$. This also *defines* the Fourier transform for those functions that do not admit a proper transform. According to the previous results, the function admits the two spectral representations

$$\tilde{\chi}_c(z) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\text{Im} \tilde{\chi}(\omega)}{\omega - z} d\omega = \frac{1}{\pi i} \int_{-\infty}^{+\infty} \frac{\text{Re} \tilde{\chi}(\omega)}{\omega - z} d\omega$$

now in terms of the real and imaginary parts of Fourier transform above. Here the necessary real or imaginary parts are given by

$$\text{Re} \tilde{\chi}(\omega) = \int_0^{+\infty} g(t) \cos(\omega t) dt = \frac{1}{2} \int_{-\infty}^{+\infty} g_S(t) e^{i\omega t} dt = \frac{\tilde{g}_S(\omega)}{2}$$

$$\text{Im} \tilde{\chi}(\omega) = \int_0^{+\infty} g(t) \sin(\omega t) dt = -\frac{i}{2} \int_{-\infty}^{+\infty} g_A(t) e^{i\omega t} dt = -i \frac{\tilde{g}_A(\omega)}{2}$$

where g_S , g_A are the symmetric, antisymmetric extensions of g for negative times, *i.e.* for $t < 0$ $g_S(t) = g(-t)$ and $g_A(t) = -g(-t)$. It also follows⁵⁰

$$\text{Re} \tilde{\chi}(\omega) = \text{Re} \tilde{\chi}(-\omega)$$

$$\text{Im} \tilde{\chi}(\omega) = -\text{Im} \tilde{\chi}(-\omega)$$

which allow further simplifications in the above spectral representations, namely

$$\tilde{\chi}_c(z) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\text{Im} \tilde{\chi}(\omega)}{\omega - z} d\omega \equiv \frac{2}{\pi} \int_0^{\infty} \frac{\omega \text{Im} \tilde{\chi}(\omega)}{\omega^2 - z^2} d\omega$$

or

$$\tilde{\chi}_c(z) = \frac{1}{\pi i} \int_{-\infty}^{+\infty} \frac{\text{Re} \tilde{\chi}(\omega)}{\omega - z} d\omega \equiv \frac{2}{\pi i} \int_0^{\infty} \frac{z \text{Re} \tilde{\chi}(\omega)}{\omega^2 - z^2} d\omega$$

⁴⁹This is not a true analytic continuation since the Fourier transform is defined on the real axis only, *i.e.* it does not make sense to talk about analyticity in this case. However, the procedure is close to an analytic continuation, in the sense that $\tilde{\chi}_c(z)$ is analytic in the uhp and $\tilde{\chi}_c^+(\omega) = \lim_{\epsilon \rightarrow 0} \tilde{\chi}_c(\omega + i\epsilon) = \tilde{\chi}(\omega)$.

⁵⁰This is a consequence of the fact that χ is real.

Extensions

For a function $f(z)$ which is analytic in the uhp, the spectral representation given above is also well defined in the *lower* half plane. Thus, we are led to consider the function

$$f_e(z) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\text{Im}f^+(x)}{x - z} dx$$

which is analytic in the whole complex plane but the real axis. This can be considered an “extension” of the original $f(z)$. It is *not* an analytic continuation, since

$$\lim_{\epsilon \rightarrow 0^+} f_e(x \pm i\epsilon) = \frac{1}{\pi} \text{P} \int_{-\infty}^{+\infty} \frac{\text{Im}f^+(x')}{x' - x} dx' \pm i\text{Im}f^+(x)$$

i. e.

$$f_e^+(x) - f_e^-(x) = 2i\text{Im}f^+(x)$$

which show that the function is not even continuous when crossing the real axis, on the support of $\text{Im}f^+$. The real axis represents indeed a branch cut for this function, and the limiting value of $\text{Im}f$ (or $\text{Re}f$) on this cut (*e.g.* from above) is sufficient to reconstruct the function on the whole complex plane. Notice also that the above expression is the limiting case of the conjugation property

$$f_e(z^*) = f_e(z)^*$$

which can also be read directly from the definition of f_e .

All these results hold in particular for the response function defined above, and the extension reads as

$$\tilde{\chi}_e(z) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\text{Im}\tilde{\chi}(\omega)}{\omega - z} d\omega$$

Notice that $\tilde{\chi}_e(z)$ gives back the Fourier transform $\tilde{\chi}(\omega)$ when z approaches the real axis from *above*, whereas $\lim_{\epsilon \rightarrow 0^+} \tilde{\chi}_e(\omega - i\epsilon) = \tilde{\chi}_e^-(\omega) \equiv \tilde{\chi}(\omega)^*$.

Sum rules

As above, let $f(z)$ be an analytic function in the upper half plane such that $|f(z)| \rightarrow 0$ as $|z| \rightarrow \infty$. In particular, suppose that $f(z) \approx C_n/z^n$ as $|z| \rightarrow \infty$, where $n \geq 1$ is an integer and C_n is a constant. Applying Cauchy theorem on the real axis supplemented with a large semicircle in the uhp,

$$\oint f(z) dz = 0 = \int_{-\infty}^{+\infty} f^+(x) dx + \lim_{R \rightarrow \infty} \int_{\Gamma_R} \frac{C_n}{z^n} dz \equiv \int_{-\infty}^{+\infty} f^+(x) dx + \lim_{R \rightarrow \infty} \frac{iC_n}{R^{n-1}} f_n$$

where $f^+(x) = \lim_{\epsilon \rightarrow 0^+} f(x + i\epsilon)$, Γ_R is the semicircle $\{z|z = Re^{i\theta}, \theta \in [0, \pi]\}$ and $f_n = \delta_{n,1}\pi + i(1 - \delta_{n,1})\frac{1-(-)^{n-1}}{n-1}$. If $n > 1$ the second integral on the r.h.s vanishes and we obtain

$$\int_{-\infty}^{+\infty} dx f^+(x) = 0$$

The same holds for the functions $f_m(z) = z^m f(z)$ for $m = 1, 2, \dots, n-2$, *i.e.*

$$\int_{-\infty}^{+\infty} dx x^m f^+(x) = 0 \quad \text{for } m \leq n-2$$

On the other hand, for $m = n-1$, $f_{n-1}(z) \approx C_n/z$ at infinity and we get

$$\int_{-\infty}^{+\infty} dx x^{n-1} f^+(x) = -i\pi C_n$$

or, more generally,

$$\frac{i}{\pi} \int_{-\infty}^{+\infty} dx x^m f^+(x) = \begin{cases} 0 & m = 0, 1, \dots, n-2 \\ C_n & m = n-1 \end{cases}$$

This allows us to compute a number of “moments” of the limiting function $f^+(x)$ by just looking at the asymptotic behaviour of $f(z)$.

For instance, for the dielectric function given in the main text the high-frequency limit reads as $\tilde{\epsilon}(\omega) - 1 \approx -\omega_P^2/\omega^2$ (independently of the model), where ω_P is the plasmon frequency. Thus $n = 2$, $C_n = -\omega_P^2$ and the above relation reads as

$$\frac{i}{\pi} \int_{-\infty}^{+\infty} d\omega \omega [\tilde{\epsilon}(\omega) - 1] = -\omega_P^2$$

or equivalently

$$\frac{2}{\pi} \int_0^{+\infty} d\omega \omega \text{Im} [\tilde{\epsilon}(\omega) - 1] = \omega_P^2$$

In the low-density, non-dispersive limit, for the Lorentz model discussed in the main text we get

$$-i \int_{-\infty}^{+\infty} d\omega \omega \tilde{\alpha}_{mol}(\omega) \equiv \int_{-\infty}^{+\infty} d\omega \omega \tilde{\alpha}_{mol}''(\omega) = \frac{\pi Z e^2}{m_e}$$

i.e.

$$\int_0^{\infty} d\omega \sigma_{ph}(\omega) = \frac{2\pi^2 Z e^2}{m_e c}$$

10 Appendix C: Autocorrelation functions

Let us consider an *isolated* system and an observable A . The equilibrium *autocorrelation function* of the observable A is defined as

$$C_A(t) = \langle A(t)A(0) \rangle = \text{tr}(\rho A(t)A(0))$$

where ρ is the (equilibrium) system density operator, tr is the trace operation and $A(t)$ is the Heisenberg-picture operator corresponding to the observable A , namely $A(t) = e^{\frac{i}{\hbar}Ht}A_se^{-\frac{i}{\hbar}Ht}$ where A_s is the usual Schrödinger-picture operator and H is the system Hamiltonian. Notice that when the system is part of a larger systems, the very existence of a Heisenberg picture requires the correlation function above to be defined on the whole, isolated system for which a Hamiltonian can be introduced⁵¹.

In general, C_A above is not real, and its real and imaginary parts read as

$$\begin{aligned} \text{Re}C_A(t) &= \langle \text{Re}(A(t)A(0)) \rangle = \frac{\langle [A(t), A(0)]_+ \rangle}{2} \equiv \langle \text{Re}(A(0)A(t)) \rangle \\ \text{Im}C_A(t) &= \langle \text{Im}(A(t)A(0)) \rangle = \frac{\langle [A(t), A(0)] \rangle}{2i} \equiv -\langle \text{Im}(A(0)A(t)) \rangle \end{aligned}$$

As we shall see below, thanks to the equilibrium condition these properties translate into interesting symmetry properties of the corresponding Fourier transforms.

Symmetry properties

Since the system is assumed to be in equilibrium, $\rho \equiv \rho(H)$, $A(t)$ can be regarded as a *stationary* stochastic process. In practice,

$$C_A(t) \equiv \langle A(t+\tau)A(\tau) \rangle$$

holds for any τ , as can be directly proved using the definition above,

$$\begin{aligned} \text{tr}(\rho A(t+\tau)A(\tau)) &= \text{tr}\left(\rho e^{+\frac{i}{\hbar}H\tau}A(t)e^{-\frac{i}{\hbar}H\tau}e^{+\frac{i}{\hbar}H\tau}A(0)e^{-\frac{i}{\hbar}H\tau}\right) = \\ &= \text{tr}\left(e^{+\frac{i}{\hbar}H\tau}\rho A(t)e^{-\frac{i}{\hbar}H\tau}e^{+\frac{i}{\hbar}H\tau}A(0)e^{-\frac{i}{\hbar}H\tau}\right) \equiv \text{tr}(\rho A(t)A(0)) \end{aligned}$$

where use has been made of the equilibrium condition $[\rho, f(H)] = 0$ (for any function of H) and of the cyclic property of the trace. In particular, for $\tau = -t$ we have

$$C_A(t) \equiv \langle A(0)A(-t) \rangle$$

⁵¹The knowledge of the reduced density operator at any time t is *not* enough to compute the correlation function. In classical statistics, this would amount to know the probability density function at a single time t , $P_1(x, t)$, while the correlation above requires the *joint* probability density function $P_2(x_1, t_1; x_2, t_2)$.

and hence

$$\text{Re}C_A(t) = \text{Re}C_A(-t)$$

$$\text{Im}C_A(t) = -\text{Im}C_A(-t)$$

or equivalently,

$$C_A(t)^* = C_A(-t)$$

It follows that the Fourier transform

$$\tilde{C}_A(\omega) = \int_{-\infty}^{+\infty} C_A(t) e^{i\omega t} dt$$

is *real*

$$\tilde{C}_A^*(\omega) = \int_{-\infty}^{+\infty} C_A^*(t) e^{-i\omega t} dt = \int_{-\infty}^{+\infty} C_A(-t) e^{-i\omega t} dt \equiv \tilde{C}_A(\omega)$$

and the Fourier transforms of its real and imaginary parts are just the symmetric and antisymmetric parts of $\tilde{C}_A(\omega)$,

$$\tilde{C}_A(\omega) = \int_{-\infty}^{+\infty} (\text{Re}C_A(t) + i\text{Im}C_A(t)) e^{i\omega t} dt = \mathcal{S}(\omega) + \mathcal{A}(\omega)$$

where

$$\mathcal{S}(\omega) = \int_{-\infty}^{+\infty} \text{Re}C_A(t) e^{i\omega t} dt \equiv \int_{-\infty}^{+\infty} \text{Re}C_A(t) \cos(\omega t) dt = \mathcal{S}(-\omega)$$

$$\mathcal{A}(\omega) = i \int_{-\infty}^{+\infty} \text{Im}C_A(t) e^{i\omega t} dt \equiv - \int_{-\infty}^{+\infty} \text{Im}C_A(t) \sin(\omega t) dt = -\mathcal{A}(-\omega)$$

Detailed balance

The autocorrelation function of the observable A of a system in *canonical* equilibrium has an additional symmetry which is not evident from the previous results, but directly follows from the exponential form of the canonical statistical operator⁵²,

$$\begin{aligned} C_A(t) &= \frac{1}{Z} \text{tr} \left(e^{-\beta H} e^{\frac{i}{\hbar} H t} A e^{-\frac{i}{\hbar} H t} \right) = \frac{1}{Z} \text{tr} \left(A e^{-\beta H} e^{\frac{i}{\hbar} H t} A e^{-\frac{i}{\hbar} H t} e^{\beta H} e^{-\beta H} \right) \\ &= \frac{1}{Z} \text{tr} \left(A e^{\frac{i}{\hbar} H (t + i\hbar\beta)} A e^{-\frac{i}{\hbar} H (t + i\hbar\beta)} e^{-\beta H} \right) \equiv \langle A(0) A(t + i\hbar\beta) \rangle \end{aligned}$$

⁵²Apart from normalization, the canonical statistical operator is the evolution operator of the imaginary-time Schrödinger equation, *i.e.* the solution of $H\rho = i\hbar d\rho/dt$ for $t = -i\hbar\beta$ and initial condition $\rho(0) = 1$.

where $\beta = 1/k_B T$ and Z is the canonical partition function, $Z = \text{tr}(e^{-\beta H})$. Taking the complex conjugate, we get the *Kubo-Martin-Schwinger relation*,

$$C_A(t)^* = \langle A(t - i\hbar\beta)A(0) \rangle$$

which allows to write the (real!) Fourier transform $\tilde{C}_A(\omega)$ in the equivalent form

$$\tilde{C}_A(\omega) = \int_{-\infty}^{+\infty} C_A^*(t) e^{-i\omega t} dt = \int_{-\infty}^{+\infty} \langle A(t - i\hbar\beta)A(0) \rangle e^{-i\omega t} dt$$

to be compared with

$$\tilde{C}_A(-\omega) = \int_{-\infty}^{+\infty} \langle A(t)A(0) \rangle e^{-i\omega t} dt$$

This suggests to study the contour integral

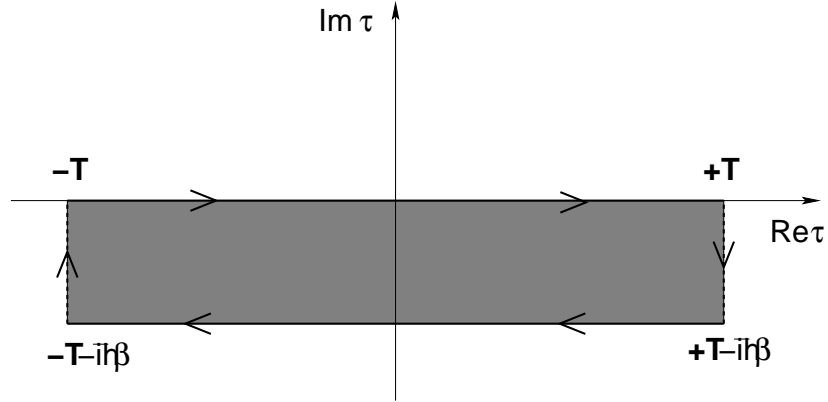


Figure 7: Contour path used to prove the detailed balance condition.

$$\oint \langle A(\tau)A(0) \rangle e^{-i\omega\tau} d\tau$$

where the path is the rectangle shown in figure 7. The function is analytic on its interior, since in the energy representation it reads as

$$\langle A(\tau)A(0) \rangle = \frac{1}{Z} \sum_{nm} |\langle \phi_n | A | \phi_m \rangle|^2 e^{-\beta E_n} e^{\frac{i}{\hbar} \tau (E_n - E_m)}$$

where for $\text{Im}\tau \leq 0$ diverging terms $E_n > E_m$ only appear for $\text{Im}\tau < -\hbar\beta$ (the exponent indeed goes as $\propto \exp \left\{ \frac{1}{\hbar} [-(\hbar\beta + \text{Im}\tau) E_n + \text{Im}\tau E_m] \right\}$). Thus, assuming that⁵³

$$\langle A(\pm T - ix)A(0) \rangle \rightarrow 0 \text{ for } T \rightarrow \infty, x \in (0, \hbar\beta)$$

⁵³This is usually *not* satisfied in finite systems. In some instances, however, the contributions of the paths $\pm T - i\tau$ cancel, see e.g. the case of the harmonic oscillator mentioned in the main text.

we obtain

$$\begin{aligned}\tilde{C}_A(-\omega) &= \int_{-\infty}^{+\infty} \langle A(t)A(0) \rangle e^{-i\omega t} dt = \int_{-\infty-i\hbar\beta}^{+\infty-i\hbar\beta} \langle A(\tau)A(0) \rangle e^{-i\omega\tau} d\tau \\ &= e^{-\hbar\beta\omega} \int_{-\infty}^{+\infty} \langle A(\tau)A(0) \rangle e^{-i\omega\tau} d\tau = e^{-\hbar\beta\omega} \tilde{C}_A(\omega)\end{aligned}$$

Accordingly,

$$\mathcal{S}(\omega) \equiv \frac{1 + e^{-\hbar\beta\omega}}{2} \tilde{C}_A(\omega), \quad \mathcal{A}(\omega) \equiv \frac{1 - e^{-\hbar\beta\omega}}{2} \tilde{C}_A(\omega)$$

and

$$\mathcal{S}(\omega) = \coth\left(\frac{\beta\hbar\omega}{2}\right) \mathcal{A}(\omega)$$

which shows that knowledge of $\mathcal{A}(\omega)$ is sufficient to reconstruct the Fourier transform of the correlation function, $\tilde{C}_A(\omega)$.

Fluctuations

The Fourier transform $\tilde{C}_A(\omega)$ is a sort of spectral weight of the fluctuations of the observable A at equilibrium, since

$$C(0) \equiv \langle A^2 \rangle = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \tilde{C}_A(\omega) d\omega$$

A closer connection can be established similarly to the classical case (Wiener-Kinchine theorem for stationary stochastic processes). To see this, let us consider the following operator

$$\tilde{A}(\omega) = \int_{-\infty}^{+\infty} A(t) e^{i\omega t} dt$$

(the Fourier transform of the “stationary process” $A(t)$) and the equilibrium average

$$\langle \tilde{A}(\omega) \tilde{A}^\dagger(\omega') \rangle = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \langle A(t_1) A(t_2) \rangle e^{i\omega t_1} e^{-i\omega' t_2} dt_1 dt_2$$

Here $\langle A(t_1) A(t_2) \rangle = C_A(t_1 - t_2)$ depends on the time difference only, and thus with the change of variables

$$\begin{pmatrix} t_1 \\ t_2 \end{pmatrix} \rightarrow \begin{pmatrix} t \\ \tau \end{pmatrix} = \begin{pmatrix} (t_1 + t_2)/2 \\ t_1 - t_2 \end{pmatrix}$$

we can write

$$\langle \tilde{A}(\omega) \tilde{A}^\dagger(\omega') \rangle = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} C_A(\tau) e^{i\omega(t+\tau/2)} e^{-i\omega'(t-\tau/2)} dt d\tau$$

$$= 2\pi\delta(\omega - \omega') \int_{-\infty}^{+\infty} C_A(\tau) e^{i(\omega+\omega')\tau/2} d\tau \equiv 2\pi\delta(\omega - \omega') \tilde{C}_A(\omega)$$

More precisely, the Fourier transform given above is in general ill-defined, and thus we introduce a long but finite time interval $[-T, +T]$ and put

$$\tilde{A}_T(\omega) = \int_{-T}^{+T} A(t) e^{i\omega t} dt \equiv \int_{-\infty}^{+\infty} A_T(t) e^{i\omega t} dt$$

where $A_T(t) = A(t)$ if $t \in [-T, +T]$ and $A_T(t) = 0$ otherwise. In this way the above relation holds to a good approximation

$$\langle \tilde{A}_T(\omega) \tilde{A}_T^\dagger(\omega') \rangle \approx 2 \frac{\sin((\omega - \omega')T)}{\omega - \omega'} \tilde{C}_A(\omega)$$

(provided the autocorrelation function $C_A(t)$ decays on a time-scale much shorter than T) and we can write down an explicit expression for $\omega = \omega'$

$$\langle \tilde{A}_T(\omega) \tilde{A}_T^\dagger(\omega) \rangle \approx 2T \tilde{C}_A(\omega)$$

When $\tilde{A}_T(\omega)$ is easily available (*e.g.* by Fourier analysis of the equation of motion) this expression provides an easy route to compute $\tilde{C}_A(\omega)$ and hence $C_A(t)$.

11 Appendix D: General linear response theory

We consider here the main results of linear response theory, which relates the response of a system in equilibrium to a (weak) external perturbation, by generalizing the approach given in the main text. We then suppose that an equilibrium ensemble has been isolated from its environment with minor disturbance, and that the system state can be represented by a density operator which is some function of the system Hamiltonian⁵⁴ H , $\rho^{eq} = f(H)$. External forces of the form $H_{int} = -a(t)A$ are then turned on at some time t_0 and we look at the system state at some time $t > t_0$. If the interaction is weak enough, it is reasonable to expect that, to leading order,

$$\delta\rho(t) = \rho(t) - \rho^{eq} \approx \int_{-\infty}^{+\infty} a(t')g_A(t-t')dt'$$

where g_A is some operator-valued function of the observable A , as well as of the time delay⁵⁵. Thus, we can focus on the “kick” $a(t) = \delta(t)$ and get direct access to $g_A(t)$ and to any average of interest. Starting from the Liouville-von Neumann equation

$$\frac{\partial\rho}{\partial t} = -\frac{i}{\hbar}[H, \rho] = -\frac{i}{\hbar}[H + H_{int}(t), \rho]$$

in integral form

$$\rho(t) = \rho^{eq} - \frac{i}{\hbar} \int_0^t [H + H_{int}(t'), \rho(t')]dt$$

we use first-order perturbation theory and replace ρ on the r.h.s. with its unperturbed value $\rho(t) \equiv \rho^{eq}$. In the limit $t \rightarrow 0^+$, we thus obtain

$$\rho(0^+) \approx \rho^{eq} - \frac{i}{\hbar} \int_0^{0^+} [H + H_{int}(t'), \rho^{eq}]dt = \rho^{eq} + \frac{i}{\hbar}[A, \rho^{eq}]$$

This provides the initial state right after the kick, which then propagates in time according to the free evolution propagator, *i.e.*

$$\rho(t) \approx \rho^{eq} + \frac{i}{\hbar} e^{-\frac{i}{\hbar} H t} [A, \rho^{eq}] e^{\frac{i}{\hbar} H t} = \rho^{eq} + \frac{i}{\hbar} [A(-t), \rho^{eq}]$$

where now $A(t)$ is the Heisenberg-picture A operator. Hence, for $t > 0$

$$\delta\rho(t) \approx +\frac{i}{\hbar} [A(-t), \rho^{eq}] \equiv g_A(t) \tag{30}$$

⁵⁴This is just to emphasize that the system needs to be isolated. For relaxation effects to be (implicitly) taken into account in the following analysis, H must actually include both the proper “system” and the “reservoir”.

⁵⁵Because of the equilibrium condition, g_A can only depend on the time difference. Of course, in addition, it satisfies causality.

and, more generally,

$$\delta\rho(t) \approx \frac{i}{\hbar} \int_{-\infty}^t a(t') [A(t' - t), \rho^{eq}] dt'$$

Therefore, we can write for a generic observable B

$$\delta B(t) = \langle B \delta\rho(t) \rangle = \frac{i}{\hbar} \int_{-\infty}^t a(t') \text{tr} (B[A(t' - t), \rho^{eq}]) dt'$$

where, on cycling under the trace operation and using the invariance under time translations,

$$\begin{aligned} \text{tr} (B[A(\tau), \rho^{eq}]) &= \text{tr} (BA(\tau)\rho^{eq} - B\rho^{eq}A(\tau)) = \text{tr} (\rho^{eq}(BA(\tau) - A(\tau)B)) \\ &= \text{tr} (\rho^{eq}[B, A(\tau)]) = \text{tr} (\rho^{eq}[B(-\tau), A]) \end{aligned}$$

i.e.

$$\delta B(t) = \int_{-\infty}^{+\infty} a(t') \chi_{BA}(t - t') dt'$$

with

$$\chi_{BA}(t) := \Theta(t) \frac{i}{\hbar} \langle [B(t), A] \rangle \quad (31)$$

Here, the averaged commutator entering the *response function* above can be further re-written in term of the *correlation function* $C_{BA}(t) = \langle B(t)A \rangle$ as

$$\langle [B(t), A] \rangle = \langle B(t)A \rangle - \langle (B(t)A)^\dagger \rangle = 2i\text{Im} \langle B(t)A \rangle = 2i\text{Im} C_{BA}(t)$$

hence

$$\chi_{BA}(t) := -\Theta(t) \frac{2}{\hbar} \text{Im} C_{BA}(t)$$

is explicitly real. We have already considered in the main text the case $B = A$, where the symmetries of the *autocorrelation functions* help simplifying things. In the general case, simplifications are possible only under special conditions.

Time reversal

We suppose here the system is invariant under time-reversal, *i.e.* that $[T, H] = 0$ holds for the *antiunitary* time-reversal operator T . We further assume that both A and B have well defined signatures, $T^\dagger AT = \tau_A A$ and similarly for B , with $\tau_{A,B} = \pm 1$. Let then be $\{|\Phi_n\rangle\}_n$ a system energy eigenbasis; since $[T, H] = 0$, the time-reversed basis $T|\Phi_n\rangle = |\Phi_n^T\rangle$ is an equivalent energy eigenbasis, and thus

$$C_{BA}(t) \equiv \sum_n \rho_n \langle T\Phi_n | B(t)A | T\Phi_n \rangle = \sum_n \rho_n \langle \Phi_n | T^\dagger B(t)AT | \Phi_n \rangle^* =$$

$$\sum_n \rho_n \langle \Phi_n | T^\dagger B(t) T T^\dagger A T | \Phi_n \rangle^* = \tau_A \tau_B \sum_n \rho_n \langle \Phi_n | B(-t) A | \Phi_n \rangle^* \equiv \tau_A \tau_B C_{BA}(-t)^*$$

where ρ_n are the eigenvalues (natural populations) of the equilibrium density operator⁵⁶⁵⁷. We distinguish two cases according to whether $\tau_A \tau_B = \tau = \pm 1$, since

$$\text{Re} C_{BA}(t) = \tau \text{Re} C_{BA}(-t) \quad \text{Im} C_{BA}(t) = -\tau \text{Im} C_{BA}(-t)$$

For the Fourier transform of the correlation function, $\tilde{C}_{BA}(\omega)$, we have

$$\tilde{C}_{BA}(\omega)^* = \tau \int_{-\infty}^{+\infty} C_{BA}(-t) e^{-i\omega t} dt \equiv \tau \tilde{C}_{BA}(\omega)$$

which shows that $\tilde{C}_{BA}(\omega)$ is pure real (imaginary) for $\tau = 1$ ($\tau = -1$).

Similarly, we consider the response function $\chi_{BA}(t)$ and its Fourier transform $\tilde{\chi}_{BA}(\omega)$ focusing on its real or imaginary part, as convenient. For $\tau = 1$

$$\text{Im} \tilde{\chi}_{BA}(\omega) = -\frac{2}{\hbar} \int_0^\infty \text{Im} C_{BA}(t) \sin(\omega t) dt = \frac{i}{\hbar} \int_{-\infty}^{+\infty} \text{Im} C_{BA}(t) e^{i\omega t} dt = \frac{\mathcal{A}(\omega)}{\hbar}$$

where $\mathcal{A}(\omega)$ is the antisymmetric part of $\tilde{C}_{BA}(\omega)$,

$$\mathcal{A}(\omega) = \frac{\tilde{C}_{BA}(\omega) - \tilde{C}_{BA}(-\omega)}{2}$$

Conversely, for $\tau = -1$,

$$\text{Re} \tilde{\chi}_{BA}(\omega) = -\frac{2}{\hbar} \int_0^\infty \text{Im} C_{BA}(t) \cos(\omega t) dt = -\frac{1}{\hbar} \int_{-\infty}^{+\infty} \text{Im} C_{BA}(t) e^{i\omega t} dt = \frac{i\mathcal{S}(\omega)}{\hbar}$$

where $\mathcal{S}(\omega)$ is the symmetric part of $\tilde{C}_{BA}(\omega)$,

$$\mathcal{S}(\omega) = \frac{\tilde{C}_{BA}(\omega) + \tilde{C}_{BA}(-\omega)}{2}$$

Thus,

$$\text{Im} \left(i^{(1-\tau)/2} \tilde{\chi}_{BA}(\omega) \right) = \frac{i^{(1-\tau)/2}}{\hbar} \frac{\tilde{C}_{BA}(\omega) + (-)^\tau \tilde{C}_{BA}(-\omega)}{2}$$

⁵⁶Care is needed in handling the trace operation with the antiunitary operator. For instance, $TA|\phi\rangle = T(\sum_n |\Phi_n\rangle \langle \Phi_n| A |\phi\rangle) = \sum_n \langle \Phi_n | A |\phi\rangle^* T |\Phi_n\rangle$ shows that, in general, $\text{tr}(TA) \neq \text{tr}(AT)$.

⁵⁷For $B = A$ we re-obtain the previous result $C_A(t) = C_A(-t)^*$, which holds irrespective of the time-reversal symmetry.

Canonical equilibrium

As already seen for the autocorrelation functions, the case of canonical equilibrium deserves special attention. Suppose that $\rho^{eq} \equiv e^{-\beta H}/Z(\beta)$ and consider the *real* function

$$\xi(t) = \frac{i}{\hbar} \langle [B(t), A] \rangle$$

Noticing that $\text{tr}(e^{-\beta H}[B(t), A]) \equiv \text{tr}([A, e^{-\beta H}]B(t))$ and defining $F(\beta) = [A, e^{-\beta H}]$ we can write a differential equation for $F(\beta)$

$$\frac{dF}{d\beta} = -[A, H e^{-\beta H}] = -[A, H]e^{-\beta H} - H F(\beta)$$

which can be solved for the initial condition $F(0) = 0$ in the form

$$F(\beta) = e^{-\beta H} \int_0^\beta e^{\tau H} [H, A] e^{-\tau H} d\tau$$

where $[H, A] \equiv -i\hbar \dot{A}$ and

$$e^{\tau H} \dot{A} e^{-\tau H} \equiv \dot{A}(-i\hbar\tau)$$

Thus

$$\xi(t) = \frac{i}{\hbar Z(\beta)} \text{tr} \left(e^{-\beta H} \int_0^\beta -i\hbar \dot{A}(-i\hbar\tau) B(t) d\tau \right) \equiv \int_0^\beta \langle \dot{A}(-i\hbar\tau) B(t) \rangle d\tau$$

and finally

$$\chi_{BA}(t) = \Theta(t) \int_0^\beta \langle \dot{A}(-i\hbar\tau) B(t) \rangle d\tau$$

or, equivalently,

$$\chi_{BA}(t) = \Theta(t) \int_0^\beta \langle \dot{A}B(t + i\hbar\tau) \rangle d\tau = \Theta(t) \int_0^\beta \langle \dot{A}(-t - i\hbar\tau) B \rangle dt$$

In the above expressions the quantity

$$C_{B\dot{A}}^K(t) = \frac{1}{\beta} \int_0^\beta \langle \dot{A}(-i\hbar\tau) B(t) \rangle d\tau = \frac{1}{\beta} \int_0^\beta \langle e^{\tau H} \dot{A} e^{-\tau H} B(t) \rangle d\tau$$

is also known as *Kubo canonical correlation function* of the observables \dot{A} and B , and with this definition

$$\text{Im} C_{BA}(t) = -\frac{\hbar\beta}{2} C_{B\dot{A}}^K(t) \equiv \frac{\hbar\beta}{2} \frac{d}{dt} C_{BA}^K(t) \quad (32)$$

and

$$\chi_{BA}(t) \equiv \Theta(t) \beta C_{B\dot{A}}^K(t) = -\Theta(t) \beta \frac{d}{dt} C_{BA}^K(t) \quad (33)$$

Hence,

$$\tilde{\chi}_{BA}(\omega) = \beta \int_0^\infty C_{BA}^K(t) e^{i\omega t} dt = -\beta \int_0^\infty \frac{dC_{BA}^K}{dt}(t) e^{i\omega t} dt$$

In general, the *real* function $C_{BA}^K(t)$ relates to the symmetric part of $C_{BA}(t)$, *i.e.* to $C_{BA}^S(t) = \text{Re}C_{BA}(t)$, as can be easily seen in the energy representation, since

$$C_{BA}^K(t) = \frac{1}{\beta} \sum_{nm} (\rho_m - \rho_n) A_{nm} B_{mn} \frac{e^{i\omega_{mn}t}}{\hbar\omega_{mn}}$$

and

$$C_{BA}^S(t) = \frac{1}{2} \sum_{nm} (\rho_m + \rho_n) A_{nm} B_{mn} e^{i\omega_{mn}t}$$

where $\rho_n = e^{-\beta E_n}/Z$ are the thermal occupation probabilities and $\omega_{mn} = (E_m - E_n)/\hbar$ are the transition frequencies. On Fourier transforming and using

$$\rho_n - \rho_m = \frac{\rho_n - \rho_m}{\rho_n + \rho_m} (\rho_n + \rho_m) = th \left(\frac{\hbar\beta\omega_{mn}}{2} \right) (\rho_n + \rho_m)$$

we arrive at

$$\tilde{C}_{BA}^S(\omega) = \frac{\beta\hbar\omega}{2} \coth \left(\frac{\beta\hbar\omega}{2} \right) \tilde{C}_{BA}^K(\omega)$$

With the same token, introducing the antisymmetric part of $C_{BA}(t)$, namely $C_{BA}^A(t) = i\text{Im}C_{BA}(t)$, and using Eq.(32) we obtain

$$\tilde{C}_{BA}^A(\omega) = \frac{\beta\hbar\omega}{2} \tilde{C}_{BA}^K(\omega)$$

and thus

$$\tilde{C}_{BA}^A(\omega) = th \left(\frac{\beta\hbar\omega}{2} \right) \tilde{C}_{BA}^S(\omega)$$

Usually, one writes the correlation functions in terms of the function

$$J_{BA}(\omega) = \frac{1}{\hbar} \tilde{C}_{BA}^A(\omega)$$

which is also known as *spectral density*, namely

$$\tilde{C}_{BA}^K(\omega) = \frac{2}{\beta\omega} J_{BA}(\omega)$$

$$\tilde{C}_{BA}^S(\omega) = \hbar \coth \left(\frac{\beta\hbar\omega}{2} \right) J_{BA}(\omega)$$

$$\tilde{C}_{BA}(\omega) = \hbar \left[\coth \left(\frac{\beta\hbar\omega}{2} \right) + 1 \right] J_{BA}(\omega) = \frac{2\hbar}{1 - e^{-\beta\hbar\omega}} J_{BA}(\omega)$$

Notice that in the classical limit ($\beta \rightarrow 0$) $\tilde{C}_{BA}^{\mathcal{S}}(\omega) \approx \tilde{C}_{BA}^K(\omega)$ and $\tilde{C}_{BA}^A(\omega) \approx 0$ or, in other words, $C_{BA}^K(t) \approx C_{BA}^{\mathcal{S}}(t) \approx C_{BA}(t)$ as it also follows from a direct calculation,

$$\lim_{\beta \rightarrow 0} C_{BA}^K(t) = \langle A(0)B(t) \rangle$$

In the above expressions $C_{BA}^{\mathcal{S}}(t)$ and $C_{BA}^A(t)$ refer to the symmetry with respect to the exchange of operators and, in general, should not be confused with the inverse Fourier transforms of $\mathcal{S}(\omega)$ and $\mathcal{A}(\omega)$ introduced above. However, in the presence of time-inversion symmetry, if A and B have definite signatures, for $\tau = 1$ $C_{BA}^{\mathcal{S}}(t) = \text{Re}C_{BA}(t)$ and $C_{BA}^A(t) = i\text{Im}C_{BA}(t)$ are also symmetric and antisymmetric under time inversion⁵⁸, respectively, and thus

$$(\tau = 1) \quad \tilde{C}_{BA}^{\mathcal{S}}(\omega) = S(\omega), \quad \tilde{C}_{BA}^A(\omega) = \mathcal{A}(\omega)$$

Conversely,

$$(\tau = -1) \quad \tilde{C}_{BA}^A(\omega) = S(\omega), \quad \tilde{C}_{BA}^{\mathcal{S}}(\omega) = \mathcal{A}(\omega)$$

Fluctuation-dissipation

The relations between response and correlation functions shown above provide similar links between the corresponding Fourier transforms, which enable one to express the susceptibility in terms of the spectral properties of the *fluctuations*. Since the imaginary part of the susceptibility is related to *dissipation*, this establishes a link between two physical phenomena: the fluctuation-dissipation theorem.

To derive it, we first need an expression for the average energy gain/loss of the system subjected to the external perturbation $H_{int} = -a(t)A$, *i.e.*

$$\frac{dH}{dt} = \frac{i}{\hbar}[H - aA, H] \equiv \frac{i}{\hbar}[H - aA, aA] \equiv a(t)\frac{dA}{dt}$$

(where the Heisenberg derivative is based on the Hisenberg picture of the total system) from which the *instantaneous power* absorbed by the system follows as

$$\frac{dW}{dt} = a(t) \left\langle \frac{dA}{dt} \right\rangle$$

For instance, for a harmonic field $a(t) = a\cos(\omega t)$ in linear regime we have

$$\langle A(t) \rangle - \langle A \rangle_{eq} = a \int_{-\infty}^{+\infty} \text{Re}(e^{i\omega t'} \chi_{AA}(t - t')) dt' \equiv a \text{Re} \{ e^{-i\omega t} \tilde{\chi}_{AA}(\omega) \}$$

⁵⁸In the case $B = A$ the relations $\text{Re}C_{AA}(t) = \text{Re}C_{AA}(-t)$ and $\text{Im}C_{AA}(t) = -\text{Im}C_{AA}(-t)$ hold irrespective of time-reversal symmetry. They follow directly from the stationarity condition.

and the power averaged over a period reads as

$$\frac{dW}{dt} \equiv a^2 \text{Re} \left\{ -i\omega \tilde{\chi}_{AA}(\omega) e^{-i\omega t} \overline{\cos(\omega t)} \right\} \equiv \frac{1}{2} a^2 \omega \text{Im} \tilde{\chi}_{AA}(\omega)$$

where we have used $\overline{\cos^2(\omega t)} = 1/2$ and $\overline{\sin(\omega t) \cos(\omega t)} = 0$. More generally, the total power absorbed by the system is given by

$$W = \int_{-\infty}^{+\infty} a(t) \frac{d\langle A \rangle}{dt} = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \tilde{a}(\omega)^* (-i\omega) \langle \tilde{A}(\omega) \rangle d\omega$$

where

$$\langle \tilde{A}(\omega) \rangle = \tilde{a}(\omega) \tilde{\chi}_{AA}(\omega)$$

and thus

$$W = \frac{1}{2\pi} \int_{-\infty}^{+\infty} |\tilde{a}(\omega)|^2 (-i\omega) \tilde{\chi}_{AA}(\omega) d\omega \equiv \frac{1}{2\pi} \int_{-\infty}^{+\infty} |\tilde{a}(\omega)|^2 \omega \text{Im} \tilde{\chi}_{AA}(\omega) d\omega$$

In the last equality, we have used the fact that only the antisymmetric component of $\tilde{\chi}_{AA}(\omega)$ gives a non-vanishing contribution to the integral, since $|\tilde{a}(\omega)|^2 \equiv a(\omega)a(-\omega)$ is an even function of ω . Thus, we see in general that the imaginary part of $\tilde{\chi}_{AA}(\omega)$ is responsible for dissipation. Thermodynamic arguments⁵⁹ also suggest that

$$\omega \text{Im} \tilde{\chi}_{AA}(\omega) \geq 0$$

We have already looked at this dissipative part of the susceptibility,

$$\text{Im} \tilde{\chi}_{AA}(\omega) = \frac{\mathcal{A}(\omega)}{\hbar} \equiv J_{AA}(\omega)$$

where $\mathcal{A}(\omega)$ is the antisymmetric component of $\tilde{\chi}_{AA}(\omega)$, which reduces to $C_{AA}^A(\omega)$ irrespective of time-reversal symmetry. For systems in canonical equilibrium, we can equivalently write

$$\text{Im} \tilde{\chi}_{AA}(\omega) = \frac{\beta\omega}{2} \tilde{C}_{AA}^K(\omega) = \frac{1}{\hbar} \left(\frac{\beta\hbar\omega}{2} \right) \tilde{C}_{AA}^S(\omega) \quad (34)$$

an expression now explicitly involving “ordinary” correlation functions. In the classical limit $\beta \rightarrow 0$,

$$\text{Im} \tilde{\chi}_{AA}(\omega) = \frac{\omega}{2k_B T} \int_{-\infty}^{\infty} \langle A(t)A(0) \rangle e^{i\omega t} dt = \frac{\omega}{k_B T} \int_0^{\infty} \langle A(t)A(0) \rangle \cos(\omega t) dt$$

Notice also that, in general,

$$\tilde{\chi}_{BA}(\omega) = -\beta \int_0^{\infty} e^{i\omega t} \frac{d}{dt} C_{BA}^K(t) dt = -\beta C_{BA}^K(0) - i\beta\omega \int_0^{\infty} e^{i\omega t} C_{BA}^K(t) dt$$

⁵⁹For infinite (*i.e.* dissipative) systems, the same equilibrium conditions prevail for $t \rightarrow \pm\infty$, where $a(t) \rightarrow 0$. Thus, energy can only be absorbed by the system, for arbitrary choices of $a(t)$.

and thus

$$\tilde{\chi}_{BA}(0) = -\beta C_{BA}^K(0)$$

is purely real provided, for $\omega \rightarrow 0$, $\tilde{C}_{BA}^K(\omega)$ converges to a finite value.

Finally, we derive an alternative expression of the above fluctuation-dissipation relation which may be useful in some circumstances. To this end, we notice that

$$\frac{d\langle A \rangle}{dt}(t) = \langle \dot{A}(t) \rangle = \int_{-\infty}^{+\infty} a(t') \frac{d\chi_{AA}}{dt}(t-t') dt'$$

where

$$\chi_{\dot{A}\dot{A}}(t) = \frac{d\chi_{AA}}{dt} = \delta(t)\beta C_{\dot{A}\dot{A}}^K(t) + \Theta(t)\beta C_{\dot{A}\dot{A}}^K(t) \equiv \Theta(t)\beta C_{\dot{A}\dot{A}}^K(t)$$

since $\beta C_{\dot{A}\dot{A}}^K(0) = -\frac{2}{\hbar} \text{Im} C_{AA}(0) \equiv 0$. Hence, on Fourier transforming,

$$-i\omega \tilde{\chi}_{\dot{A}\dot{A}}(\omega) = \beta \int_0^{\infty} C_{\dot{A}\dot{A}}^K(t) e^{i\omega t} dt$$

and, in particular,

$$\text{Re} \tilde{\chi}_{\dot{A}\dot{A}}(\omega) = \omega \text{Im} \tilde{\chi}_{\dot{A}\dot{A}}(\omega) = \beta \int_0^{\infty} C_{\dot{A}\dot{A}}^K(t) \cos(\omega t) dt$$

In the classical limit $C_{\dot{A}\dot{A}}^K(t) \rightarrow \langle \dot{A}(t) \dot{A}(0) \rangle$, and these equations read as

$$-i\omega \tilde{\chi}_{\dot{A}\dot{A}}(\omega) = \beta \int_0^{\infty} \langle \dot{A}(t) \dot{A}(0) \rangle e^{i\omega t} dt$$

$$\text{Re} \tilde{\chi}_{\dot{A}\dot{A}}(\omega) = \beta \int_0^{\infty} \langle \dot{A}(t) \dot{A}(0) \rangle \cos(\omega t) dt$$

For instance, for $H_{int} = -xF(t)$, where $F(t)$ is a (uniform) external force and x the position operator, $A \equiv x$, $\dot{A} = v$ and

$$\langle \tilde{v}(\omega) \rangle = F(\omega) \mu(\omega)$$

where $\mu(\omega) \equiv \tilde{\chi}_{vx}(\omega)$ is the *admittance*,

$$\mu(\omega) = \beta \int_0^{\infty} C_{vv}^K(t) e^{i\omega t} dt$$

For $\omega \rightarrow 0$ $\mu(0) = \text{Re} \mu(0) = \mu_0$ is the *mobility*⁶⁰,

$$\mu_0 = \beta \int_0^{\infty} C_{vv}^K(t) dt = \beta D$$

In the classical limit, the coefficient D reduces to the diffusion coefficient, $D = \int_0^{\infty} \langle v(t)v(0) \rangle dt$.

⁶⁰Note that for $\mu_0 = -i \lim_{\omega \rightarrow 0} \omega \tilde{\chi}_{xx}(\omega)$ to be non-vanishing $\tilde{C}_{xx}^K(\omega)$ has to diverge in the limit $\omega \rightarrow 0$.

	conjugation	Fourier Transform	conjugation of FT	response, $\chi_{AB}(t) =$
$C_{BA}^K(t) = \frac{1}{\beta} \int_0^\beta \langle A(-i\hbar\tau)B(t) \rangle d\tau$	$C_{BA}^K(t)$	$\frac{2}{\beta\omega} J_{BA}(\omega)$	$\tilde{C}_{BA}^K(-\omega)$	$\Theta(t)\beta C_{BA}^K(t) = -\Theta(t)\beta \frac{d}{dt} C_{BA}^K(t)$
$C_{BA}^S(t) = \text{Re} \langle B(t)A(0) \rangle$	$C_{BA}^S(t)$	$\hbar \coth\left(\frac{\beta\hbar\omega}{2}\right) J_{BA}(\omega)$	$\tilde{C}_{BA}^S(-\omega)$	$\frac{i}{\pi\hbar} \Theta(t) \int_{-\infty}^{+\infty} t h\left(\frac{\beta\hbar\omega}{2}\right) \tilde{C}_{BA}^S(\omega) e^{-i\omega t} d\omega$
$C_{BA}^A(t) = i\text{Im} \langle B(t)A(0) \rangle$	$-C_{BA}^A(t)$	$\hbar J_{BA}(\omega)$	$-\tilde{C}_{BA}^A(-\omega)$	$\frac{2i}{\hbar} \Theta(t) C_{BA}^A(t)$
$C_{BA}(t) = C_{BA}^S(t) + C_{BA}^A(t) = \langle B(t)A(0) \rangle$	$C_{BA}^S(t) - C_{BA}^A(t)$	$\frac{2\hbar}{1-e^{-\beta\hbar\omega}} J_{BA}(\omega)$	$\tilde{C}_{BA}^S(-\omega) - \tilde{C}_{BA}^A(-\omega)$	$\Theta(t) \int_{-\infty}^{+\infty} \frac{i(1-e^{-\beta\hbar\omega})}{2\pi\hbar} \tilde{C}_{BA}(\omega) e^{-i\omega t} d\omega$

Table 1: Main properties of the canonical correlation functions introduced in the text. The spectral density $J_{BA}(\omega)$ is defined to be $\tilde{C}_{BA}^A(\omega)/\hbar$. In the presence of time-reversal symmetry, if A, B have compound signature $\tau = 1$, the spectral density is real and odd ($J_{BA}(\omega) = J_{BA}(\omega)^* = -J_{BA}(-\omega)$) and $\text{Im}\tilde{\chi}_{BA}(\omega) = J_{BA}(\omega)$. For $\tau = -1$, it is pure imaginary and even ($J_{BA}(\omega) = -J_{BA}(\omega)^* = J_{BA}(-\omega)$) and $\text{Re}\tilde{\chi}_{BA}(\omega) = iJ_{BA}(\omega)$. The case $B = A$ is the same as $\tau = 1$, irrespective of time reversal.

12 Appendix E: Charge and current density in quantum mechanics

We focus here on the definition and the main properties of charge and current densities as appropriate in the standard (“first quantization”) framework of quantum mechanics. In this Section only, to avoid confusion, we explicitly identify operators with the help of a hat⁶¹.

Charge density

Given a system of charges q_i we define the *charge density operator* at \mathbf{r} as

$$\hat{n}(\mathbf{r}) = \sum_i q_i \delta(\mathbf{r} - \hat{\mathbf{r}}_i)$$

where $\hat{\mathbf{r}}_i$ is the position operator of the i -th charge. By definition, this operator is diagonal in any particle position operator, and its average value gives the usual charge density in terms of diagonal matrix elements of 1-particle density matrices,

$$\begin{aligned} \langle \hat{n}(\mathbf{r}) \rangle &= \sum_i q_i \text{tr}(\hat{\rho} \delta(\mathbf{r} - \hat{\mathbf{r}}_i)) = \sum_i q_i \int \Pi_j d\mathbf{r}_j \langle \mathbf{r}_1 \dots \mathbf{r}_i \dots \mathbf{r}_N | \hat{\rho} \delta(\mathbf{r} - \mathbf{r}_i) | \mathbf{r}_1 \dots \mathbf{r}_i \dots \mathbf{r}_N \rangle \\ &= \sum_i q_i \int \Pi_{j \neq i} d\mathbf{r}_j \langle \mathbf{r}_1 \dots \mathbf{r}_i \dots \mathbf{r}_N | \hat{\rho} | \mathbf{r}_1 \dots \mathbf{r}_i \dots \mathbf{r}_N \rangle = \sum_i q_i \langle \mathbf{r} | \hat{\rho}^{(i)} | \mathbf{r} \rangle \end{aligned}$$

where $\hat{\rho}^{(i)}$ is the i -th 1-particle reduced density operator

$$\hat{\rho}^{(i)} = \text{tr}^{j \neq i} \hat{\rho}$$

the trace being taken over all degrees of freedom but the i -th. The *characteristic* charge density operator (function) is defined as

$$\hat{G}(\mathbf{k}) = \int e^{i\mathbf{k}\mathbf{r}} \hat{n}(\mathbf{r}) d\mathbf{r}$$

and allows us to introduce the *charge moment operators* $\hat{\mu}_m$ as the coefficients of the power series expansion

$$\hat{G}(\mathbf{k}) = \sum_{m=0} \frac{(i\mathbf{k})^m}{m!} \hat{\mu}_m$$

i.e.

$$\hat{\mu}_m = \int \mathbf{r}^m \hat{n}(\mathbf{r}) d\mathbf{r}$$

⁶¹Functions of operators do not necessitate of such symbol if their argument(s) are correctly identified.

Explicitly, the 0 – th moment is the unit operator times the total charge of the system,

$$\hat{\boldsymbol{\mu}}_0 = \int \hat{n}(\mathbf{r}) d\mathbf{r} \equiv \hat{1} \sum_i q_i$$

the first moment is the usual dipole moment

$$\hat{\boldsymbol{\mu}}_1 = \int \mathbf{r} \hat{n}(\mathbf{r}) d\mathbf{r}$$

and so on.

The charge density operator allows us to express in a very simple way the interaction energy of the system with any electric potential $\phi(\mathbf{r}, t)$ since

$$\hat{V} = \sum_i q_i \phi(\hat{\mathbf{r}}_i, t) = \sum_i q_i \int d\mathbf{r} \delta(\mathbf{r} - \hat{\mathbf{r}}_i) \phi(\mathbf{r}, t) \equiv \int d\mathbf{r} \hat{n}(\mathbf{r}) \phi(\mathbf{r}, t)$$

In this form $\hat{n}(\mathbf{r})$ becomes the system operator conjugate to the electric potential at \mathbf{r} .

Current density

To define the *current density operator* $\hat{\mathbf{J}}(\mathbf{r}, t)$ we look at the dynamics of the above system of charges under the action of the generic electromagnetic Hamiltonian

$$\hat{H} = \sum_i \frac{\left(\hat{\mathbf{p}}_i - \frac{q_i}{c} \mathbf{A}(\hat{\mathbf{r}}_i, t) \right)^2}{2m_i} + \sum_i q_i \phi(\hat{\mathbf{r}}_i, t)$$

Here $\mathbf{A}(\mathbf{r}, t)$ and $\phi(\mathbf{r}, t)$ are, respectively, the vector and scalar potentials of the electromagnetic field,

$$\mathbf{B} = \nabla \wedge \mathbf{A} \quad \mathbf{E} = -\nabla \phi - \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t}$$

and the i – th term between brackets represents the velocity of the i – th particle⁶²,

$$\begin{aligned} \hat{v}_{i,\alpha} &= \frac{i}{\hbar} [\hat{H}, \hat{x}_{i,\alpha}] \equiv \frac{i}{2m_i \hbar} \left[\left(\hat{\mathbf{p}}_i - \frac{q_i}{c} \mathbf{A}(\hat{\mathbf{r}}_i, t) \right)^2, \hat{x}_{i,\alpha} \right] = \\ &= \frac{i}{2m_i \hbar} \left\{ \left(\hat{\mathbf{p}}_i - \frac{q_i}{c} \mathbf{A}(\hat{\mathbf{r}}_i, t) \right) [\hat{\mathbf{p}}_i, \hat{x}_{i,\alpha}] + [\hat{\mathbf{p}}_i, \hat{x}_{i,\alpha}] \left(\hat{\mathbf{p}}_i - \frac{q_i}{c} \mathbf{A}(\hat{\mathbf{r}}_i, t) \right) \right\} \\ &= \frac{1}{m_i} \left(\hat{\mathbf{p}}_i - \frac{q_i}{c} \mathbf{A}(\hat{\mathbf{r}}_i, t) \right)_\alpha = \frac{1}{m_i} \hat{\Pi}_{i,\alpha} \end{aligned}$$

where $[\hat{\mathbf{p}}_i, \hat{x}_{i,\alpha}] = -i\hbar \mathbf{e}_\alpha$ has been used, \mathbf{e}_α being the unit vector along the α cartesian axis.

This Hamiltonian gives back the quantum-mechanical expression of the Lorentz force, as can be seen

⁶²Greek indexes α, β, \dots are used to denote cartesian components, which are named as the corresponding vectors appearing in bold. An exception is the position vector \mathbf{r} , whose cartesian components are x_α .

by computing the “force” felt by the $i - th$ particle,

$$\frac{d(m_i \hat{v}_{i,\alpha})}{dt} = \frac{d\hat{\Pi}_{i,\alpha}}{dt} = -\frac{q_i}{c} \frac{\partial A_\alpha}{\partial t}(\hat{\mathbf{r}}_i, t) + \frac{i}{\hbar} \left\{ \frac{1}{2m_i} [\hat{\mathbf{\Pi}}_i, [\hat{\mathbf{\Pi}}_i, \hat{\Pi}_{i,\alpha}]] \right\}_+ + q_i [\phi(\hat{\mathbf{r}}_i, t), \hat{\Pi}_{i,\alpha}]$$

where

$$[\phi(\hat{\mathbf{r}}_i, t), \hat{\Pi}_{i,\alpha}] = [\phi(\hat{\mathbf{r}}_i, t), \hat{p}_{i,\alpha}] = i\hbar \frac{\partial \phi}{\partial x_{i,\alpha}}(\hat{\mathbf{r}}_i, t)$$

and

$$[\hat{\Pi}_{i,\beta}, \hat{\Pi}_{i,\alpha}] = -\frac{q_i}{c} ([A_\beta(\hat{\mathbf{r}}_i, t), \hat{p}_{i,\alpha}] + [\hat{p}_{i,\beta}, A_\alpha(\hat{\mathbf{r}}_i, t)]) = -i\hbar \frac{q_i}{c} \left(\frac{\partial A_\beta}{\partial x_\alpha}(\hat{\mathbf{r}}_i, t) - \frac{\partial A_\alpha}{\partial x_\beta}(\hat{\mathbf{r}}_i, t) \right)$$

In the last expression⁶³,

$$\left(\frac{\partial A_\beta}{\partial x_\alpha}(\mathbf{r}, t) - \frac{\partial A_\alpha}{\partial x_\beta}(\mathbf{r}, t) \right) = e_{\alpha\beta\gamma} B_\gamma(\mathbf{r}, t)$$

and thus it follows

$$\frac{d\hat{\Pi}_{i,\alpha}}{dt} = q_i \left(\frac{\partial \phi}{\partial x_{i,\alpha}}(\hat{\mathbf{r}}_i, t) - \frac{1}{c} \frac{\partial A_\alpha}{\partial t}(\hat{\mathbf{r}}_i, t) \right) + \frac{q_i}{c} e_{\alpha\beta\gamma} \frac{[\hat{v}_{i,\beta}, B_\gamma(\hat{\mathbf{r}}_i, t)]_+}{2}$$

i. e.

$$\frac{d\hat{\mathbf{\Pi}}_\alpha}{dt} = q_i \mathbf{E}(\hat{\mathbf{r}}_i, t) + \frac{q_i}{c} \hat{\mathbf{v}}_i \wedge \mathbf{B}(\hat{\mathbf{r}}_i, t)$$

provided the vector product is defined on a symmetrized product of operators, $A_\alpha \circ B_\beta = \frac{1}{2}[A_\alpha, B_\beta]_+$. To define the current density operator we compute the (Heisenberg) time-derivative of the charge density operator, here written as partial derivative on account of the spatial dependence of such operator,

$$\frac{\partial \hat{n}}{\partial t}(\mathbf{r}) = \frac{i}{\hbar} \sum_i \frac{m_i}{2} [\hat{\mathbf{v}}_i^2, \hat{n}(\mathbf{r})] \equiv \frac{i}{2\hbar} \sum_i (\hat{\mathbf{v}}_i [\hat{\mathbf{p}}_i, \hat{n}] + [\hat{\mathbf{p}}_i, \hat{n}] \hat{\mathbf{v}}_i)$$

where $m_i [\hat{\mathbf{v}}_i, \hat{n}] = [\hat{\mathbf{p}}_i, \hat{n}]$ has been used, and

$$[\hat{\mathbf{p}}_i, \hat{n}] = -i\hbar \nabla_i \hat{n}(\mathbf{r}) \equiv +i\hbar q_i \nabla \delta(\mathbf{r} - \hat{\mathbf{r}}_i)$$

Hence

$$\frac{\partial \hat{n}}{\partial t}(\mathbf{r}) = -\frac{1}{2} \nabla \sum_i q_i (\hat{\mathbf{v}}_i \delta(\mathbf{r} - \hat{\mathbf{r}}_i) + \delta(\mathbf{r} - \hat{\mathbf{r}}_i) \hat{\mathbf{v}}_i)$$

⁶³We use the implicit sum convention on repeated indexes, and introduce the Ricci-Levi-Civita tensor, $e_{\alpha\beta\gamma} = -e_{\beta\alpha\gamma} = -e_{\alpha\gamma\beta} = e_{\beta\gamma\alpha} = \dots$, $e_{123} = 1$.

suggests the correct definition of current density operator⁶⁴

$$\hat{\mathbf{J}}(\mathbf{r}) = \frac{1}{2} \sum_i q_i [\hat{\mathbf{v}}_i, \delta(\mathbf{r} - \hat{\mathbf{r}}_i)]_+$$

satisfying the continuity equation

$$\frac{\partial \hat{n}}{\partial t} + \nabla \cdot \hat{\mathbf{J}} = 0$$

Notice that

$$\hat{\mathbf{J}}(\mathbf{r}) \equiv \frac{1}{2} \sum_i \frac{q_i}{m_i} [\hat{\mathbf{p}}_i, \delta(\mathbf{r} - \hat{\mathbf{r}}_i)]_+ - \sum_i \frac{q_i^2}{m_i c} \delta(\mathbf{r} - \hat{\mathbf{r}}_i) \mathbf{A}(\hat{\mathbf{r}}_i, t)$$

where

$$\hat{\mathbf{J}}_p(\mathbf{r}) = \frac{1}{2} \sum_i \frac{q_i}{m_i} [\hat{\mathbf{p}}_i, \delta(\mathbf{r} - \hat{\mathbf{r}}_i)]_+$$

is known as *paramagnetic* current density and

$$\hat{\mathbf{J}}_d(\mathbf{r}) = - \sum_i \frac{q_i^2}{m_i c} \delta(\mathbf{r} - \hat{\mathbf{r}}_i) \mathbf{A}(\hat{\mathbf{r}}_i, t)$$

as *diamagnetic* current density⁶⁵.

Density form of the electromagnetic Hamiltonian

With the help of the above definitions we can re-write the electromagnetic Hamiltonian in a form involving explicitly the charge and current densities. To this end we notice that upon squaring the velocity terms

$$\hat{H} = \sum_i \frac{\hat{\mathbf{p}}_i^2}{2m_i} - \sum_i \frac{q_i}{2m_i c} \left(\hat{\mathbf{p}}_i \cdot \hat{\mathbf{A}}_i + \hat{\mathbf{p}}_i \cdot \hat{\mathbf{A}}_i \right) + \sum_i \frac{q_i^2}{2m_i c^2} \hat{\mathbf{A}}_i^2 + \int d\mathbf{r} \hat{n}(\mathbf{r}) \phi(\mathbf{r}, t)$$

where we have introduced for short $\hat{\mathbf{A}}_i = \mathbf{A}(\hat{\mathbf{r}}_i, t)$, and used the previous result on the electric potential.

Here, on introducing

$$\hat{\mathbf{A}}_i = \int d\mathbf{r} \delta(\mathbf{r} - \hat{\mathbf{r}}_i) \mathbf{A}(\mathbf{r}, t)$$

in the second sum we get

$$\sum_i \frac{q_i}{2m_i c} [\hat{\mathbf{p}}_i, \hat{\mathbf{A}}_i]_+ = \int d\mathbf{r} \sum_i \frac{q_i}{2m_i c} [\hat{\mathbf{p}}_i, \delta(\mathbf{r} - \hat{\mathbf{r}}_i)]_+ \mathbf{A}(\mathbf{r}, t) \equiv \frac{1}{c} \int d\mathbf{r} \hat{\mathbf{J}}_p(\mathbf{r}, t) \mathbf{A}(\mathbf{r}, t) + \sum_i \frac{q_i^2}{m_i c^2} \hat{\mathbf{A}}_i^2$$

⁶⁴Notice that we could arrive at the same result if the chain rule of derivatives were applied in its symmetrized form on the Heisenberg derivative,

$$\frac{\partial \hat{n}}{\partial t}(\mathbf{r}, t) = \sum_i q_i \frac{\partial \delta(\mathbf{r} - \hat{\mathbf{r}}_i)}{\partial t} = \frac{1}{2} \sum_i q_i \left[\frac{d\hat{\mathbf{r}}_i}{dt}, \delta(\mathbf{r} - \hat{\mathbf{r}}_i) \right]_+$$

⁶⁵For equal charges $q_i = q$ and $m_i = m$, this term also reads as $\hat{\mathbf{J}}_d(\mathbf{r}) = -\frac{q}{mc} \hat{n}(\mathbf{r}) \mathbf{A}(\mathbf{r}, t)$.

where

$$\sum_i \frac{q_i^2}{m_i c^2} \hat{\mathbf{A}}_i^2 = -\frac{1}{c} \int d\mathbf{r} \hat{\mathbf{J}}_d(\mathbf{r}) \mathbf{A}(\mathbf{r}, t)$$

hence

$$\hat{H} = \sum_i \frac{\hat{\mathbf{p}}_i^2}{2m_i} - \frac{1}{c} \int d\mathbf{r} \hat{\mathbf{J}}_p(\mathbf{r}, t) \mathbf{A}(\mathbf{r}, t) + \frac{1}{2c} \int d\mathbf{r} \hat{\mathbf{J}}_d(\mathbf{r}) \mathbf{A}(\mathbf{r}, t) + \int d\mathbf{r} \hat{n}(\mathbf{r}) \phi(\mathbf{r}, t)$$

To connect with the results given in the main text, we notice that in the presence of an external electric potential only ($\mathbf{A}(\mathbf{r}, t) \equiv 0$ and $\phi(\mathbf{r}, t) = \phi_0(\mathbf{r}, t) + \phi^{ext}(\mathbf{r}, t)$) the previous Hamiltonian reduces to

$$\hat{H} = \hat{H}_0 + \int d\mathbf{r} \hat{n}(\mathbf{r}) \phi^{ext}(\mathbf{r}, t)$$

and

$$\langle \delta \hat{n}(\mathbf{r}, t) \rangle = \int d\mathbf{r}' dt' \chi_{nn}(\mathbf{r}, \mathbf{r}' | t - t') \phi^{ext}(\mathbf{r}', t')$$

where

$$\chi_{nn}(\mathbf{r}, \mathbf{r}' | t) = -\Theta(t) \frac{i}{\hbar} \langle [\hat{n}(\mathbf{r}, t), \hat{n}(\mathbf{r}')] \rangle$$

is the appropriate response function. For the dipole

$$\langle \delta \hat{\boldsymbol{\mu}}(t) \rangle = \int d\mathbf{r} \mathbf{r} \langle \delta \hat{n}(\mathbf{r}, t) \rangle = \int d\mathbf{r} \int d\mathbf{r}' dt' \mathbf{r} \chi_{nn}(\mathbf{r}, \mathbf{r}' | t - t') \phi^{ext}(\mathbf{r}', t')$$

and in the *dipole approximation*, $\phi^{ext}(\mathbf{r}, t) = -\mathbf{r} \cdot \mathbf{E}(t)$, we obtain

$$\begin{aligned} \alpha_{\alpha\beta}(t) &= - \int d\mathbf{r} \int d\mathbf{r}' \chi_{nn}(\mathbf{r}, \mathbf{r}' | t) x_\alpha x'_\beta = \Theta(t) \frac{i}{\hbar} \int d\mathbf{r} \int d\mathbf{r}' \langle [\hat{n}(\mathbf{r}, t), \hat{n}(\mathbf{r}')] \rangle x_\alpha x'_\beta \\ &= \Theta(t) \frac{i}{\hbar} \langle [\hat{\mu}_\alpha(t), \hat{\mu}_\beta(0)] \rangle \end{aligned}$$

Gauge invariance

The Hamiltonian formulation used above requires the introduction of the electromagnetic potentials from which the physical fields can be derived according to

$$\mathbf{B} = \nabla \wedge \mathbf{A} \quad \mathbf{E} = -\nabla \phi - \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t}$$

It is not hard to check that the *gauge* transformation

$$T_f \begin{pmatrix} \mathbf{A} \\ \phi \end{pmatrix} = \begin{pmatrix} \mathbf{A}' \\ \phi' \end{pmatrix} := \begin{pmatrix} \mathbf{A} + \nabla f \\ \phi - \frac{1}{c} \frac{\partial f}{\partial t} \end{pmatrix}$$

for an arbitrary function $f(\mathbf{r}, t)$, leaves the fields invariant, and thus the question arises of how this affects the system Hamiltonian and wavefunctions.

To this end, we focus on a single charge system and work, for simplicity, in the Schrödinger representation, assuming that $\psi(\mathbf{x}, t)$ is a solution of the evolution equation

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi$$

for some initial condition $\psi(\mathbf{x}, 0) = \psi_0(\mathbf{x})$, where

$$\hat{H} = \frac{(\hat{\mathbf{p}} - \frac{q}{c} \mathbf{A}(\hat{\mathbf{r}}, t))^2}{2m} + q\phi(\hat{\mathbf{r}}, t)$$

We then introduce

$$\psi'(\mathbf{x}, t) = e^{\frac{i}{\hbar} \chi(\mathbf{x}, t)} \psi(\mathbf{x}, t)$$

and notice that, on the one hand,

$$\left(i\hbar \frac{\partial}{\partial t} + \frac{\partial \chi}{\partial t} \right) \psi'(\mathbf{x}, t) = e^{\frac{i}{\hbar} \chi(\mathbf{x}, t)} i\hbar \frac{\partial \psi(\mathbf{x}, t)}{\partial t}$$

and, on the other hand,

$$\left(\hat{\mathbf{p}} - \frac{q_i}{c} \mathbf{A}(\hat{\mathbf{r}}, t) - \nabla \chi \right) \psi'(\mathbf{x}, t) = e^{\frac{i}{\hbar} \chi(\mathbf{x}, t)} \left(\hat{\mathbf{p}} - \frac{q_i}{c} \mathbf{A}(\hat{\mathbf{r}}, t) \right) \psi(\mathbf{x}, t)$$

$$\left(\hat{\mathbf{p}} - \frac{q_i}{c} \mathbf{A}(\hat{\mathbf{r}}, t) - \nabla \chi \right)^2 \psi'(\mathbf{x}, t) = e^{\frac{i}{\hbar} \chi(\mathbf{x}, t)} \left(\hat{\mathbf{p}} - \frac{q_i}{c} \mathbf{A}(\hat{\mathbf{r}}, t) \right)^2 \psi(\mathbf{x}, t)$$

Then, multiplying the Schrödinger equation above by $e^{\frac{i}{\hbar} \chi(\mathbf{x}, t)}$, we obtain

$$i\hbar \frac{\partial \psi'(\mathbf{x}, t)}{\partial t} = \left\{ \frac{(\hat{\mathbf{p}} - \frac{q}{c} \mathbf{A}(\hat{\mathbf{r}}, t) - \nabla \chi(\hat{\mathbf{r}}, t))^2}{2m} + q\phi(\hat{\mathbf{r}}, t) - \frac{\partial \chi}{\partial t}(\hat{\mathbf{r}}, t) \right\} \psi'(\mathbf{x}, t)$$

and with the choice $\chi = qf/c$ we can write the Schrödinger equation in the new gauge

$$i\hbar \frac{\partial \psi'(\mathbf{x}, t)}{\partial t} = \left\{ \frac{(\hat{\mathbf{p}} - \frac{q}{c} \mathbf{A}'(\hat{\mathbf{r}}, t))^2}{2m} + q\phi'(\hat{\mathbf{r}}, t) \right\} \psi'(\mathbf{x}, t)$$

This shows that there exists a unitary transformation of the state vectors accompanying the gauge transformation of the electromagnetic potential, namely

$$\hat{T}_f = \int d\mathbf{x} |\mathbf{x}\rangle e^{\frac{i}{\hbar} \frac{q}{c} f(\mathbf{x}, t)} \langle \mathbf{x}|$$

More generally, for a number of charges

$$\hat{T}_f = \int d\mathbf{x}_1 d\mathbf{x}_2 \dots d\mathbf{x}_N |\mathbf{x}_1 \mathbf{x}_2 \dots \mathbf{x}_N\rangle e^{\frac{i}{\hbar} \sum_i \frac{q_i}{c} f(\mathbf{x}_i, t)} \langle \mathbf{x}_1 \mathbf{x}_2 \dots \mathbf{x}_N |$$

or, equivalently,

$$\hat{T}_f = e^{\frac{i}{\hbar c} \int d\mathbf{r} \hat{n}(\mathbf{r}) f(\mathbf{r}, t)}$$

Unique potentials

The previous discussion concerning the electromagnetic potentials can be considerably simplified if the electromagnetic field is considered in the light of the *Helmholtz decomposition* of vector fields. To this end, we notice that for an arbitrary (smooth) vector field $\mathbf{F}(\mathbf{r})$ (the temporal dependence is here irrelevant) a unique decomposition

$$\mathbf{F}(\mathbf{r}) = \mathbf{F}_\perp(\mathbf{r}) + \mathbf{F}_\parallel(\mathbf{r})$$

is possible such that $\nabla \mathbf{F}_\perp = 0$ and $\nabla \wedge \mathbf{F}_\parallel = 0$. The components $\mathbf{F}_\parallel(\mathbf{r})$, $\mathbf{F}_\perp(\mathbf{r})$ are called *parallel* and *transverse* components for reasons which become clear when Fourier transforming the field

$$\tilde{\mathbf{F}}(\mathbf{k}) = \int d\mathbf{r} e^{-i\mathbf{k}\mathbf{r}} \mathbf{F}(\mathbf{r})$$

and *defining*

$$\mathbf{F}_\parallel(\mathbf{r}) = \int d\mathbf{k} e^{i\mathbf{k}\mathbf{r}} \hat{\mathbf{k}} \hat{\mathbf{k}}^t \tilde{\mathbf{F}}(\mathbf{k}), \quad \mathbf{F}_\perp(\mathbf{r}) = \int d\mathbf{k} e^{i\mathbf{k}\mathbf{r}} \left(1 - \hat{\mathbf{k}} \hat{\mathbf{k}}^t\right) \tilde{\mathbf{F}}(\mathbf{k})$$

where $\hat{\mathbf{k}}$ is the unit vector in direction \mathbf{k} . With these definitions, it is easy to check that the differential properties above are indeed satisfied and thus

$$\mathbf{F}_\parallel(\mathbf{r}) = \nabla \psi, \quad \mathbf{F}_\perp(\mathbf{r}) = \nabla \wedge \Psi(\mathbf{r})$$

for some appropriate *potentials* $\psi(\mathbf{r})$, $\Psi(\mathbf{r})$.

In this perspective, it is worth re-considering Maxwell's equations, Eq.s(1-4), in terms of the (spatially) Fourier transformed fields,

$$\mathbf{k} \tilde{\mathbf{E}}_\parallel = 4\pi \tilde{\rho} \quad \mathbf{k} \wedge \tilde{\mathbf{E}}_\perp + \frac{1}{c} \frac{\partial \tilde{\mathbf{B}}_\perp}{\partial t} = \mathbf{0}$$

$$\mathbf{k} \tilde{\mathbf{B}}_\parallel = 0 \quad \mathbf{k} \wedge \tilde{\mathbf{B}}_\perp - \frac{1}{c} \frac{\partial \tilde{\mathbf{E}}_\perp}{\partial t} = \frac{4\pi}{c} \tilde{\mathbf{J}}_\perp$$

A further equation can be obtained for the parallel component of the density current,

$$-\frac{1}{c} \frac{\partial \tilde{\mathbf{E}}_\parallel}{\partial t} = \frac{4\pi}{c} \tilde{\mathbf{J}}_\parallel$$

which is nothing that a form of continuity equation, once is noticed that $\tilde{\mathbf{E}}_{\parallel}$ is determined by $\tilde{\rho}$,

$$\frac{\partial \tilde{\rho}}{\partial t} + \mathbf{k} \tilde{\mathbf{J}}_{\parallel} = 0$$

We thus see that Maxwell's equations are of two kinds. The equations for the parallel components are simplest and define a unique scalar potential according to

$$\mathbf{E}_{\parallel} = -\nabla \phi \quad (35)$$

which can be determined by solving the Poisson equation

$$\nabla \mathbf{E} \equiv \nabla \mathbf{E}_{\parallel} = -\nabla^2 \phi = 4\pi \rho \quad (36)$$

The equations for the transverse components represent a single equation for a *transverse* vector potential \mathbf{A}_{\perp} defined as

$$\mathbf{B}_{\perp} = \nabla \wedge \mathbf{A}_{\perp} \quad (37)$$

since the first

$$\mathbf{k} \wedge \left(\tilde{\mathbf{E}}_{\perp} + \frac{1}{c} \frac{\partial \tilde{\mathbf{A}}_{\perp}}{\partial t} \right) = \mathbf{0}$$

implies

$$\mathbf{E}_{\perp} = -\frac{1}{c} \frac{\partial \mathbf{A}_{\perp}}{\partial t} \quad (38)$$

and the second reduces to

$$-\nabla^2 \mathbf{A}_{\perp} + \frac{1}{c^2} \frac{\partial^2 \mathbf{A}_{\perp}}{\partial t^2} = \frac{4\pi}{c} \mathbf{J}_{\perp} \quad (39)$$

Eq.s (36,39) *uniquely* define the potentials ϕ , \mathbf{A}_{\perp} in terms of the given (independent) sources ρ and \mathbf{J}_{\perp} , and the fields are given by Eq.s (38,35,37), along with, of course, $\mathbf{B}_{\parallel} = \mathbf{0}$.

In this perspective, the gauge transformation introduced in the previous paragraph uses just the degree of freedom which is left in the parallel component of the ordinary vector potential \mathbf{A} , $\mathbf{A}_{\parallel} \rightarrow \mathbf{A}_{\parallel} + \nabla f$, and which must be counterbalanced with an additional scalar potential, $\phi \rightarrow \phi - \frac{1}{c} \frac{\partial f}{\partial t}$, if

$$\mathbf{E}_{\parallel} = -\frac{1}{c} \frac{\partial \mathbf{A}_{\parallel}}{\partial t} - \nabla \phi$$

has to hold.

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