

# Classical microscopic theory of dispersion, emission and absorption of light in dielectrics

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## Abstract

This paper is a continuation of a recent one in which, apparently for the first time, the existence of polaritons in ionic crystals was proven in a microscopic electrodynamic theory. This was obtained through an explicit computation of the dispersion curves. Here the main further contribution consists in studying electric susceptibility, from which the spectrum can be inferred. We show how susceptibility is obtained by the Green–Kubo methods of Hamiltonian statistical mechanics, and give for it a concrete expression in terms of time–correlation functions. As in the previous paper, here too we work in a completely classical framework, in which the electrodynamic forces acting on the charges are all taken into account, both the retarded forces and the radiation reaction ones. So, in order to apply the methods of statistical mechanics, the system has to be previously reduced to a Hamiltonian one. This is made possible in virtue of two global properties of classical electrodynamics, namely, the Wheeler–Feynman identity and the Ewald resummation properties, the proofs of which were already given for ordered system. The second contribution consists in formulating the theory in a completely general way, so that in principle it applies also to disordered systems such as glasses, or liquids or gases, provided the two general properties mentioned above continue to hold.

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A first step in this direction is made here by providing a completely general proof of the Wheeler–Feynman identity, which is shown to be the counterpart of a general causality property of classical electrodynamics. Finally it is shown how a line spectrum can appear at all in classical systems, as a counterpart of suitable stability properties of the motions, with a broadening due to a coexistence of chaoticity. The relevance of some recent results of the theory of dynamical systems in this connection is also pointed out.

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## 1 Introduction

This paper complements and generalizes the results obtained in [1] on the microscopic foundations of the optics of materials. The main new result of that paper was a proof of the existence of polaritons in ionic crystals, that was obtained by calculating the normal modes and exhibiting the explicit form of the dispersion curves. Apparently, the existence of polaritons, whose qualitative importance is evident since it explains why crystals are transparent to visible light, was previously understood only at a phenomenological level, in terms of a macroscopic polarization field (see for example [2], page 239).

An interesting point is that the microscopic proof was obtained in [1] in a completely classical framework, on the basis of the system of Newton’s equations for each charge, in which the full electrodynamic forces are taken into account, both the mutual retarded ones and the individual radiation reaction forces. For example it is just retardation that makes it possible that the new polaritonic branches occur, and Born and Huang [3] couldn’t get this result just because they didn’t fully take the role of retardation into account.

The result was obtained in [1] by previously reducing the original electrodynamic model to a Hamiltonian conservative one. This in turn was made possible by exploiting two global properties of the original microscopic electrodynamic system, namely, the Wheeler-Feynman identity [4] and the Ewald–Oseen resummation of the far fields (see [5][6] and [7], page 101), which, jointly used, provide both a cancellation of the radiation reaction

force acting on each charge, and an elimination of the problems related to delay. Both properties were proven in [1] (following [8] and [9]), for the case of ionic crystals.

It is then natural to ask whether such a result concerning the dispersion curves may be complemented by providing a microscopic expression for the electric susceptibility of the system, which would allow one to determine the expected absorption and emission spectra. Moreover one might also look for an extension of the methods, formulating the theory in such a general frame that it can apply to disordered dielectric systems such as glasses, or even liquids or gases.

In the present paper we show how a microscopic expression for susceptibility is obtained for ordered systems, and how the result can be extended, at least partly, to cover the case of disordered systems.

Indeed we will show how, if the two mentioned global properties hold (so that the system can be reduced to a conservative Hamiltonian one), then the statistical mechanical methods of Green–Kubo type [10][11] can be used to provide a microscopic expression for macroscopic polarization, and so for susceptibility. In particular, it will be explicitly exhibited that the phenomena of absorption and emission are not related, at least in a any direct way, to the radiation reaction force, and can in fact be understood as symmetrical features of a time reversible dynamics. In order to obtain such results, we have to overcome a difficulty which arises if one tries to imitate in a strict way the Green–Kubo type methods generally used in the quantum case. Indeed, the available procedure makes use, in an apparently essential way, of the Gibbs measure in phase space, whereas Gibbs’ measure does not even exist in the classical case, due to the divergence induced by the attractive Coulomb potentials. We however show how susceptibility can actually be proven to exist, obtaining for it an expression in terms of time correlations. Then we study its properties, and in particular deduce the  $f$ -sum rule, the essentially classical character of which was already pointed out by Van Vleck and Huber [12].

The existence of susceptibility and its general expression are completely independent of the qualitative nature of the motions of the system. It is instead the form of the spectrum that depends on the stability properties of the motions. We show how a pure line spectrum occurs for stable (almost periodic) motions of the system, while a broadening of the lines or even a continuous spectrum occur when chaoticity sets in. We also discuss the relevance that in this connection have some quite recent results on the theory

of dynamical systems, in particular the results that made possible to extend to systems of interest for statistical mechanics the methods of perturbation theory [13][14][15] which allow one to estimate when a transition from ordered to chaotic motions should occur (see the numerical works [16][17]).

For what concerns the extension to disordered systems, all depends on proving the two mentioned global electrodynamic properties. For the Wheeler-Feynman identity, we do here more than required, because we give a proof which applies to completely general systems, and not just to dielectrics. In fact, the identity is shown to be equivalent to a general form of causality of electrodynamics, which is reminiscent of a general property assumed in quantum electrodynamics. The properties related to the Ewald resummation methods are instead assumed to hold for dielectrics, just by analogy with the case of ordered systems.

In section 2 it is recalled how a first step in passing from microscopic to macroscopic electromagnetism consists in performing a local space-average. Our treatment is standard, apart from a minor point. In section 3 the second step is performed, which involves a phase space (or ensemble) average, and leads to a Green-Kubo type formula for macroscopic susceptibility, in a completely symmetrical way for absorption and emission. The proof is obtained without using the Gibbs measure. Preliminarily, it is recalled how the reduction to a conservative Hamiltonian system is obtained through the Ewald resummation methods, making use of the Wheeler-Feynman identity. In section 4 the analyticity properties of susceptibility are recalled, and the  $f$ -sum rule is proven. In section 5 it is shown how under quite general conditions susceptibility is expressed in terms of equilibrium time-correlation functions between positions and velocities of the charges. In section 6 it is discussed how the spectrum depends on the qualitative stability properties of the motions of the system, and in particular how a pure spectrum arises in the presence of suitable stability properties (almost periodicity) of the orbits. Instead, a broadening of the lines, or even a continuous spectrum are expected to occur as chaoticity sets in. In section 7 this is illustrated by studying the particular case of ionic crystals. Some final comments are added in Section 8. An Appendix is devoted to a proof of the Wheeler-Feynman identity (and of the consequent cancellation of the radiation reaction forces), which applies in a completely general situation, irrespective of the ordered or disordered structure of the system.

## 2 From microscopic to macroscopic electromagnetism. First step: local space–averages and the microscopic polarization field

As we know, [18][19][20][21][22][23] macroscopic electromagnetism is characterized by four fields: the electric field  $\mathcal{E}$ , the magnetic induction field  $\mathcal{B}$ , the electric induction field  $\mathcal{D}$  and the magnetic field  $\mathcal{H}$ . Since the times of Lorentz, the first two are thought of as local space–averages of corresponding microscopic fields  $\mathbf{E}$ ,  $\mathbf{B}$ , while the latter ones are defined as  $\mathcal{D} = \mathcal{E} + 4\pi\mathcal{P}$  and  $\mathcal{H} = \mathcal{B} - 4\pi\mathcal{M}$ , where the polarization vector  $\mathcal{P}$  and the magnetization vector  $\mathcal{M}$  are the response of a material body to the presence of an external electric or magnetic field. In the macroscopic treatments one assumes that there hold the constitutive relations  $\mathcal{D} = \varepsilon\mathcal{E}$  and  $\mathcal{H} = \mu\mathcal{B}$ , or rather that analogous relations hold frequency by frequency, i.e., that one has

$$\hat{\mathcal{D}}(\mathbf{x}, \omega) = \varepsilon(\omega)\hat{\mathcal{E}}(\mathbf{x}, \omega) , \quad \hat{\mathcal{H}}(\mathbf{x}, \omega) = \mu(\omega)\hat{\mathcal{B}}(\mathbf{x}, \omega) ,$$

where  $\hat{\mathcal{E}}$ ,  $\hat{\mathcal{D}}$ ,  $\hat{\mathcal{B}}$  and  $\hat{\mathcal{H}}$ , are the time Fourier transforms of the corresponding fields. In this section we recall how, in order to obtain a macroscopic expression for polarization, a first step is accomplished through a local space–averaging procedure. This is a completely standard passage, and only a minor modification to the familiar procedure will be introduced.

Consider a dielectric body, thought of as microscopically constituted of a certain number  $N$  of neutral molecules or atoms, each containing a stable aggregate of point charges. In such a case the microscopic Maxwell equations read

$$\begin{aligned} \operatorname{div} \mathbf{E} &= 4\pi \sum_{k=1}^N \sum_{j=0}^{n_k} e_j \delta(\mathbf{x} - \mathbf{x}_{j,k}) \\ \operatorname{curl} \mathbf{E} &= -\frac{1}{c} \partial_t \mathbf{B} \\ \operatorname{div} \mathbf{B} &= 0 \\ \operatorname{curl} \mathbf{B} &= \frac{4\pi}{c} \sum_{k=1}^N \sum_{j=0}^{n_k} e_j \dot{\mathbf{x}}_{j,k} \delta(\mathbf{x} - \mathbf{x}_{j,k}) + \frac{1}{c} \partial_t \mathbf{E} , \end{aligned}$$

where  $\mathbf{x}_{j,k}$  is the position of the  $j$ -th particle (of charge  $e_j$ ) in the  $k$ -th molecule or atom.

## The local space–averaging procedure. Space–averaged fields and sources

Now, following Lorentz, the macroscopic fields  $\mathcal{E}$  and  $\mathcal{B}$  are defined as local space–averages of the values the microscopic fields take in what is sometime called a “physically infinitesimal domain” [22], or a “physically small volume element” [24], of volume  $\Delta V$  located about the considered point  $\mathbf{x}$ . Think for example of a cubic volume element with side 100 Åmstrong, which, in a solid or in a liquid, in ordinary conditions contains about one million molecules.

Due to the linearity of the Maxwell equations, the space–averaged fields are expected to be solutions of those same equations, having as sources the averaged charge and current densities. This becomes a rather simple theorem if the space–averaging procedure at  $\mathbf{x}$  is mathematically implemented through a convolution with a suitable smooth ( $C^\infty$  class) function  $N(\cdot)$  centered at  $\mathbf{x}$ , which essentially vanishes outside the chosen volume element, while having inside it essentially a constant normalizing value, namely,  $1/\Delta V$ . The macroscopic fields are thus defined as

$$\begin{aligned}\mathcal{E}(\mathbf{x}, t) &= N * \mathbf{E}(\mathbf{x}, t) \stackrel{\text{def}}{=} \int_{\mathbb{R}^3} d\mathbf{y} N(\mathbf{x} - \mathbf{y}) \mathbf{E}(\mathbf{y}, t) \\ \mathcal{B}(\mathbf{x}, t) &= N * \mathbf{B}(\mathbf{x}, t) \stackrel{\text{def}}{=} \int_{\mathbb{R}^3} d\mathbf{y} N(\mathbf{x} - \mathbf{y}) \mathbf{B}(\mathbf{y}, t) .\end{aligned}$$

As the microscopic fields are distributions (because  $\delta$  functions occur in the sources), it turns out that the differential operators commute with the convolution, i.e., one has

$$\begin{aligned}\text{div } \mathcal{E} &= N * \text{div } \mathbf{E} , & \text{curl } \mathcal{E} &= N * \text{curl } \mathbf{E} \\ \text{div } \mathcal{B} &= N * \text{div } \mathbf{B} , & \text{curl } \mathcal{B} &= N * \text{curl } \mathbf{B} ,\end{aligned}$$

exactly as it would occur if the fields were smooth. Thus, multiplying the Maxwell equations by  $N(\mathbf{x} - \mathbf{y})$  and integrating, due to the linearity of the equations the macroscopic fields are found, as expected, to satisfy the Maxwell equations with charge density  $\rho$  and current density  $\mathbf{j}(\mathbf{x}, t)$  which now are smooth fields rather than distributions, and are obtained by averag-

ing with the same procedure. So the macroscopic fields satisfy the equations

$$\begin{aligned}\operatorname{div} \boldsymbol{\mathcal{E}} &= 4\pi\rho \\ \operatorname{curl} \boldsymbol{\mathcal{E}} &= -\frac{1}{c}\partial_t\boldsymbol{\mathcal{B}} \\ \operatorname{div} \boldsymbol{\mathcal{B}} &= 0 \\ \operatorname{curl} \boldsymbol{\mathcal{B}} &= \frac{4\pi}{c}\mathbf{j} + \frac{1}{c}\partial_t\boldsymbol{\mathcal{E}} .\end{aligned}$$

which involve the space-averaged sources

$$\rho(\mathbf{x}, t) \stackrel{\text{def}}{=} \sum_{k=1}^N \sum_{j=0}^{n_k} e_j N(\mathbf{x} - \mathbf{x}_{j,k}) \quad (1)$$

$$\mathbf{j}(\mathbf{x}, t) \stackrel{\text{def}}{=} \sum_{k=1}^N \sum_{j=0}^{n_k} e_j \dot{\mathbf{x}}_{j,k} N(\mathbf{x} - \mathbf{x}_{j,k}) . \quad (2)$$

## The microscopic polarization field

We now show how the space-averaged charge density  $\rho$  can be written as the divergence of a field, which should be interpreted as a still microscopic form of the polarization field. This is obtained by expanding the positions of the charges entering the function  $N(\cdot)$ , about the centers of mass of their molecules or atoms. This makes the single microscopic dipoles come in.

Denote by  $\mathbf{x}_k^0$  the position of the center of mass of the  $k$ -th molecule or atom,<sup>1</sup> and by  $\mathbf{q}_{j,k} \stackrel{\text{def}}{=} \mathbf{x}_{j,k} - \mathbf{x}_k^0$  the corresponding displacements (which are assumed to be bounded) of the charges. We have now to find which expression does the space averaged charge density  $\rho$  take, as a function of the displacements  $\mathbf{q}_{j,k}$ . Here the familiar procedure consists in introducing a multipole expansion and a truncation, through which  $\rho$  is shown to be the divergence of a vector field.

We obtain this result, perhaps in a simpler and more rigorous way, by making use of the finite-increment Lagrange formula, according to which for a smooth function  $f$  one has

$$f(\mathbf{x} + \mathbf{h}) - f(\mathbf{x}) = \int_0^1 d\zeta \frac{d}{d\zeta} f(\mathbf{x} + \zeta\mathbf{h}) .$$

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<sup>1</sup>In the case of crystals the formulas are simplified if one even thinks of  $\mathbf{x}_k^0$  as a fixed position of a cell, for example a given corner.

Indeed one then has

$$\begin{aligned}
N(\mathbf{x} - \mathbf{x}_{j,k}) &= N(\mathbf{x} - \mathbf{x}_k^0) + \int_0^1 d\zeta \frac{d}{d\zeta} N(\mathbf{x} - \mathbf{x}_k^0 - \zeta \mathbf{q}_{j,k}) \\
&= N(\mathbf{x} - \mathbf{x}_k^0) - \int_0^1 d\zeta \mathbf{q}_{j,k} \cdot \nabla N(\mathbf{x} - \mathbf{x}_k^0 - \zeta \mathbf{q}_{j,k}) \\
&= N(\mathbf{x} - \mathbf{x}_k^0) - \operatorname{div} \left( \mathbf{q}_{j,k} \int_0^1 d\zeta N(\mathbf{x} - \mathbf{x}_k^0 - \zeta \mathbf{q}_{j,k}) \right) .
\end{aligned}$$

Thus, substituting this formula in the expression (1) for the space-averaged charge density  $\rho$ , and recalling that the molecules are neutral so that

$$\sum_{j=0}^{n_k} e_j N(\mathbf{x} - \mathbf{x}_k^0) = 0 ,$$

one finds

$$\rho = -4\pi \operatorname{div} \mathbf{P} , \tag{3}$$

where the field  $\mathbf{P}$  is given by

$$\mathbf{P}(\mathbf{x}) \stackrel{\text{def}}{=} \sum_{k=1}^N \sum_{j=0}^{n_k} e_j \left( \mathbf{q}_{j,k} \int_0^1 d\zeta N(\mathbf{x} - \mathbf{x}_k^0 - \zeta \mathbf{q}_{j,k}) \right) . \tag{4}$$

Without much error this can be written in the simplified form

$$\mathbf{P}(\mathbf{x}) = \frac{1}{\Delta V} \sum_{\mathbf{x}_k^0 \in \Delta V} \sum_{j=0}^{n_k} e_j \mathbf{q}_{j,k} , \tag{5}$$

i.e., as the sum of the dipole moments of the single molecules or atoms with respect to their centers of mass, as one might have expected.

On the other hand we know that, in a dielectric, the macroscopic charge density is expressed as the divergence of polarization. So one might be tempted to altogether identify  $\mathbf{P}$  with the macroscopic polarization  $\mathcal{P}$  itself. This however is not correct. The reason is that the field  $\mathbf{P}(\mathbf{x})$  still is a dynamical variable, by which we mean a function defined on the global “mechanical phase space” of the charges, a point of which, call it  $z$ , is identified through the positions and the momenta of all charges. Now,  $\mathbf{P}(\mathbf{x})$  evidently depends on the phase point, and thus may be called the *microscopic polarization field*.



The microscopic magnetization field could be given along similar lines. However we don't need it for our aims, because with good approximation in dielectrics one can put  $\mu = 1$ , unless one is just interested in magneto-optical phenomena.

## Need for an ensemble average

As usual in statistical mechanics, a macroscopic quantity is defined as the average over phase space of a microscopic quantity (a function of  $z$ ), with respect to a given measure. Denoting such an averaging in the mechanical phase space by  $\langle \cdot \rangle$ , the macroscopic polarization field will then be defined by

$$\mathcal{P}(\mathbf{x}) = \langle \mathbf{P}(\mathbf{x}) \rangle ,$$

i.e., by

$$\mathcal{P}(\mathbf{x}) = \frac{1}{\Delta V} \left\langle \sum_{\mathbf{x}_k^0 \in \Delta V} \sum_{j=0}^{n_k} e_j \mathbf{q}_{j,k} \right\rangle .$$

Now, the microscopic polarization, being itself a space-mean over many molecules, should already satisfy some central limit theorem and so should not fluctuate very much as the phase space point  $z$  is varied. In such a case the ensemble average just provides a “typical value”, so that the use of a further ensemble average may appear to be redundant. This is not so, because it is just by performing ensemble averages that analytical manipulations can be performed which lead to significant results. One such result, as we will see, is the existence itself of electric susceptibility, namely, the fact that polarization responds linearly to an external perturbation even if the unperturbed system presents highly nonlinear motions. This is obtained by Green-Kubo methods in phase space, just because of the linearity of the equation of motion for the probability density. A further result is the proof of the  $f$ -sum rule.

However, it is not at all obvious how phase space methods can be used in a microscopic model which involves both retarded forces and dissipative ones. How to do this, and how to use Hamiltonian techniques in phase space will be shown in the next section.

### 3 Ensemble average and Green–Kubo theorem for polarization. Role of the Wheeler–Feynman identity and of the Ewald resummation methods

#### Reduction to the mechanical phase space (Wheeler–Feynman and Ewald–Oseen)

The reduction of the original electrodynamic problem to a purely mechanical one in the mechanical phase space is quite hard a task. First of all, the original problem is different from those usually studied in statistical mechanics because, due to the finite propagation speed of the electromagnetic interactions among the charges, the equations of motion for the displacements  $\mathbf{q}_{j,k}$  of the charges turn out to be differential equations with delay. Notice that the delay cannot be neglected, as it produces qualitatively essential features. For example, in the case of ionic crystals it is just retardation that produces the two new branches of the dispersion relation which correspond to polaritons (see formula (15) of ([1]), thus explaining why visible light can propagate inside them. Thus, in the original electrodynamic problem, having to deal with equations with delay we know nothing about the properties of the corresponding dynamical system, not even how to correctly frame a Cauchy problem. Neither do we know which is the phase space suited to the system, nor can we know which measure should be used to define the averages. Finally, the system is not a conservative one, at least not in any obvious way, inasmuch as the charges should radiate energy away during their necessarily accelerated motions.

From a heuristic point of view such problems can be overcome in the following way. Due to the long range character of the field produced by any single charge (a range much longer than the purely Coulomb one), in order to determine the force acting on any charge and produced by all the other ones, one necessarily has to perform a “resummation” of the forces. This can be done in an exact way in the case of crystals (through the so called Ewald method, as implemented for example in [1]) by suitably splitting the field into two contributions. The first one essentially comes from the near (in a microscopic sense) charges, and can thus be considered to all effects as being instantaneous, while the second one is essentially due to the far charges.

In turn, the contribution of the far charges too can be divided into two parts. One of them exactly cancels the radiation reaction force (which necessarily is nonvanishing, because of the accelerated motions of the charges). This indeed is the so called Wheeler–Feynman identity, which was postulated by those authors in their paper of the year 1945 and was proven, in the case of ionic crystals, in [1], following [8] and [9]. The second part of the contribution of the far charges enters in the same way as an external electromagnetic field, which propagates inside matter with a suitable refractive index (see the first term in the force entering formula (15) of ([1]), notwithstanding the fact that the microscopic far fields entering the original problem do propagate with the speed of light in vacuum (this is the so-called Ewald–Oseen cancellation property). So we have to deal both with the Wheeler–Feynman property (or identity) and with the Ewald–Oseen resummation properties.

In the case of ionic crystals both properties were proved to hold, so that the original electrodynamic equations of motion for the charges could be consistently dealt with as a system of non dissipative differential equations (possibly depending on time), of the form

$$m_j \ddot{\mathbf{q}}_{j,k} = \sum_{\mathbf{x}_{k'}^0 \in U} \sum_{j'} \mathbf{F}_{j,j'}(\mathbf{q}_{j,k} - \mathbf{q}_{j',k'}) + e_j \mathcal{E}^c(\mathbf{x}_k^0, t)$$

where  $U$  is a microscopic (namely, much smaller than  $\Delta V$ ) neighborhood of  $\mathbf{x}_k^0$ , while the field  $\mathcal{E}^c$  is what Ewald calls the “exciting” electric field (“*erregende Feld*” in his words, see [5], page 7). This is the field produced by the far charges that actually enters the equations of motion as if it were an external field, propagating with a macroscopic refractive index.

Analogous proofs should be provided here for the disordered case of interest for dielectrics. For what concerns the Wheeler–Feynman identity, we here do more than required, because we give in an Appendix a proof which holds in any situation, and actually shows the deep significance of the identity, as corresponding to some general form of causality.

Instead, the Ewald–Oseen property is not proven here for the case of disordered systems, and its validity is assumed to hold by analogy with the case of crystals. We are confident that a proof may be provided on another occasion.

## The macroscopic polarization through a Green–Kubo type theorem. General expression of the response function for an absorption process

So our phase space can be taken to be the usual one of statistical mechanics, namely, the space having as coordinates the positions  $\mathbf{q}_{j,k}$  and the momenta  $\mathbf{p}_{j,k} \stackrel{\text{def}}{=} m_j \dot{\mathbf{q}}_{j,k}$  of all the charges of the system, and our aim is now to obtain an expression for the electric susceptibility following the standard methods of Green–Kubo type of quantum statistical mechanics. Here however a difficulty arises. Indeed the analogous methods transported to the classical case amount to studying the Liouville equation for the probability density in phase space, looking for its time evolution under the action of a perturbation. However, in the quantum case it is first of all assumed that an unperturbed (or equilibrium) solution exists, given exactly by the Gibbs ensemble. Now, if one looks at the procedures used in the proofs, one might have the impression that the role of the Gibbs density is essential, and that the proof couldn't be obtained without using it. On the other hand we have to deal with Coulomb attractive interactions, which have the effect that the Gibbs measure does not even exist, in the classical case. We show here how any reference to the equilibrium Gibbs measure can be avoided, and even in a rather simple way.

Indeed in this section the existence of susceptibility is proven, and a quite general expression for it is provided, essentially without introducing any requirement at all on the equilibrium measure. Then in section 5 it will be shown how susceptibility is expressed in terms of time–correlation functions, if an assumption of a quite general character for the measure is introduced (validity of the large deviation principle for momenta).

So we only assume that an equilibrium probability density exists, which will be denoted by  $\rho_0$  (no confusion with the space–averaged charge density should occur), and its form will not need be specified. In other terms,  $\rho_0$  is only assumed to be invariant under the flow determined by the equations of motion, i.e., to be a stationary solution of the continuity equation

$$\partial_t \rho + \mathbf{v} \cdot \nabla \rho = 0 ,$$

where  $\mathbf{v}$  is the vector field defined by the equations of motion in phase space for the isolated system.<sup>2</sup>

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<sup>2</sup>For the sake of simplicity we are admitting that the vector field  $\mathbf{v}$  has vanishing

Consider now the case in which there is an external electromagnetic field  $\mathbf{E}^{in}$  (for example a monochromatic wave of frequency  $\omega$ ) which incides on the body, with an intensity that starts increasing slowly and then reaches a stationary value (the so called case of an adiabatically switched on perturbation). Then a change, say  $\delta\mathcal{E}^c(\mathbf{x}, t)$ , will be induced on the Ewald exciting field, which is the one actually entering the equations of motion for the charges. The change is due both to the presence itself of the incoming external field, and to the fact that the far charges which are responsible for that field are now moving in a modified way.

For the sake of consistency, the relation between  $\delta\mathcal{E}^c$  and the incoming external field  $\mathbf{E}^{in}$  should be determined, and to this end the validity of the Lorentz–Lorenz relation should be established. This is in any case a necessary step, if macroscopic optics should be deduced at all. This problem will not be dealt with in the present paper.

Under the perturbation induced by the external field, the density  $\rho$  will evolve according to the equation

$$\partial_t \rho + \mathbf{v} \cdot \nabla \rho + \sum_{k,j} e_j \delta\mathcal{E}^c(\mathbf{x}_k^0, t) \frac{\partial \rho}{\partial \mathbf{p}_{j,k}} = 0 , \quad (6)$$

inasmuch as the equation of motion for  $\mathbf{q}_{j,k}$  contains the further force term  $e_j \delta\mathcal{E}^c(\mathbf{x}_k^0, t)$ . As  $\delta\mathcal{E}^c$  is assumed to be a small perturbation, one can look for the solution as a series expansion

$$\rho = \rho_0 + \rho_1 + \dots ,$$

and the first order term  $\rho_1$  is immediately seen to satisfy the equation

$$\partial_t \rho_1 = -\mathbf{v} \cdot \nabla \rho_1 - \sum_{k,j} e_j \delta\mathcal{E}^c(\mathbf{x}_k^0, t) \frac{\partial \rho_0}{\partial \mathbf{p}_{j,k}} . \quad (7)$$

Clearly the suited “initial” condition is the asymptotic one

$$\rho_1 \rightarrow 0 \quad \text{for} \quad t \rightarrow -\infty , \quad (8)$$

and the corresponding well known solution is then

$$\rho_1(z, t) = - \int_{-\infty}^t ds \sum_{k,j} e_j \delta\mathcal{E}^c(\mathbf{x}_k^0, s) \frac{\partial \rho_0}{\partial \mathbf{p}_{j,k}} \left( \Phi^{s-t} z \right) , \quad (9)$$

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divergence. Nothing should change in the general case.

where  $\Phi^t z$  is the flow relative to the *unperturbed* equations of motion,

The macroscopic polarization  $\mathcal{P}(\mathbf{x}, t)$  can now be computed to first order, as the average of the microscopic polarization  $\mathbf{P}(\mathbf{x}, t)$  with respect to the density  $\rho_0 + \rho_1$ . Assuming that  $\mathcal{P}$  vanishes at equilibrium (absence of ferroelectricity), one remains with the contribution of  $\rho_1$  only, which gives

$$\mathcal{P}(\mathbf{x}, t) = - \int dz \mathbf{P}(\mathbf{x}, t) \int_{-\infty}^t ds \sum_{k,j} e_j \delta \mathcal{E}^c(\mathbf{x}_k^0, s) \frac{\partial \rho_0}{\partial \mathbf{p}_{j,k}} (\Phi^{s-t} z). \quad (10)$$

One has now to insert the expression (5) for the microscopic polarization  $\mathbf{P}(\mathbf{x}, t)$ . Then, first of all one performs two elementary transformations (namely, interchange of the integration orders of  $s$  and  $z$ , an change of variable  $z \rightarrow \Phi^{t-s} z$  – taking into account that the modulus of the jacobian determinant of  $\Phi^t z$  is unitary<sup>3</sup>). Moreover, one uses the fact that  $\delta \mathcal{E}^c(\mathbf{x}_k^0, s)$ , being a macroscopic field, takes on essentially the same value  $\delta \mathcal{E}^c(\mathbf{x}, s)$  at all points of the volume element  $\Delta V$ . This eventually produces the result that macroscopic polarization depends linearly on the exciting field. So the macroscopic polarization can be written in the familiar form of linear response theory, namely as

$$\mathcal{P}(\mathbf{x}, t) = \int_{-\infty}^t ds \delta \mathcal{E}^c(\mathbf{x}, s) \tilde{\chi}(t-s), \quad (11)$$

in terms of a dielectric response function  $\tilde{\chi}(t)$ , which is given by

$$\tilde{\chi}(t) \stackrel{\text{def}}{=} -\frac{1}{\Delta V} \int dz \sum_{\mathbf{x}_k^0, \mathbf{x}_{k'}^0 \in \Delta V} \sum_{j,j'=0}^{n_k} e_j e_{j'} \mathbf{q}_{j',k'}(t) \frac{\partial \rho_0}{\partial \mathbf{p}_{j,k}}. \quad (12)$$

Actually, in this expression for the response function we have introduced one more simplification. This consists in the fact that, when the expression (5) for the microscopic polarization  $\mathbf{P}$  is introduced into formula (10), one has two sums over  $k$  and  $k'$ , corresponding to two volume elements, whereas now the first sum was restricted to just the molecules that belong to the volume element entering the second sum. This amounts to presuming that

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<sup>3</sup>Because the unperturbed vector field has vanishing divergence.

the microscopic dynamics in two different macroscopic volume elements be totally uncorrelated. This point will be discussed later.

We add now some comments.

The first one concerns the fact that in the deduction of the formula for the dielectric response function no reference at all was made to nonconservative forces. Indeed, it was explicitly assumed that in the equation of motion for each charge the radiation reaction force be canceled by a part of the retarded forces due to the “far” charges of the dielectric body.<sup>4</sup> The first scientist who realized the occurring of this cancellation (already in the year 1916) is the Swedish physicist Oseen [25]. However, his result was ignored, having even been qualified as wrong (*“irrig”* (see [26], page 266), as also was essentially ignored the work of Wheeler and Feynman, in which the same property was conjectured to hold quite in general. So we are dealing with a time-reversible dynamical system. An asymmetry in the proof was however introduced above through the choice of the incoming external field  $\mathbf{E}^{in}$  (which was adiabatically switched on), and through the corresponding choice (8) for the “initial” (or rather, asymptotic in the past) condition needed to solve the continuity equation for the probability density (vanishing of  $\rho_1$  as  $t \rightarrow -\infty$ ). Clearly, these are the choices which are responsible for the fact that the formula just found corresponds to an absorption process. How an emission process can be analogously described in the present time-reversible frame, will be shown in the next subsection.

The second remark is that the proof shows how the existence of a linear response to the external field is quite independent of the nature of the unperturbed motions, which may have either an ordered or a disordered character. The linearity of the response is inherited from that of the Liouville equation, under the only assumption that the higher order corrections (beyond the first one) to the equilibrium solution be negligible. This fact is characteristic of linear response theory, and so also occurs in its present classical formulation in phase space. The situation was quite different with the older approaches. In the oldest one, typically described in Drude’s book [18] but still somehow surviving in the Born–Wolf book [7], to each observed spectral line was associated the motion of a material oscillator, which was supposed to perform linear oscillations, forced by the incident field. For example, in the words of

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<sup>4</sup>Curiously enough, the radiation reaction force is still taken into consideration in the paper of Callen and Welton [29] which is usually considered to be the first modern work on the fluctuation–dissipation theorem.

Kronig [27], in that approach one is dealing with “*an electric charge, elastically bound to an equilibrium position, having – as he even adds – a damping proportional to its velocity*”. A different attitude was taken by Van Vleck [28] who, working in the spirit of Bohr’s approach, thought it appropriate to formulated a theory of susceptibility by assuming that the unperturbed system performs quasi periodic motions. Here, instead, essentially no property is required for the unperturbed motions.

## Emission process

The proof of the existence of a linear response was given above in a way suited to describe an absorption process. However, the proof was formulated in the general frame of a time-reversible dynamics, in such a way that different types of nonequilibrium processes can be looked upon as determined by an asymmetry of the asymptotic conditions. So an emission process should be described by the same equations previously considered, just choosing a suitable asymptotic condition, and external field (see [30]).

The suitable asymptotic condition can be inferred in the following way. Recall how the absorption process was described. For  $t \rightarrow -\infty$  we have a stationary state described by an equilibrium probability density  $\rho_0$ , in the presence of a well defined exciting field  $\mathcal{E}^c$ . A perturbation is then introduced through a “free” field  $\mathbf{E}^{in}$ , incoming from infinity. During the process, one has a density  $\rho_0 + \rho_1$  and a corresponding exciting field  $\mathcal{E}^c + \delta\mathcal{E}^c$ , and one presumes that eventually, for  $t \rightarrow +\infty$ , one will have a new equilibrium (at a higher energy), with a density  $\rho'_0 = \lim (\rho_0 + \rho_1)$ , together with a new exciting field  $\mathcal{E}^{c'}$  and a new free field  $\mathbf{E}^{out}$ . Moreover, one should have  $\mathbf{E}^{out} \simeq 0$ , as the whole incoming field is supposed to have been absorbed.

Let us now consider the inverse process, namely, the one which is obtained with the interchanges  $t \rightarrow -t$  and  $\mathbf{p}_{j,k} \rightarrow -\mathbf{p}_{j,k}$  (the Hamiltonian being assumed to be even in the momenta). So one starts up with a density  $\rho'_0$  at  $t = -\infty$ , and asymptotically when  $t \rightarrow +\infty$  one gets a density  $\rho_0$ , whereas the electric field is now the sum of the exciting field  $\mathcal{E}^c$  and of the free field  $\mathbf{E}^{in}$ . This means that the field  $\mathbf{E}^{in}$  was emitted from the body, in passing from the state  $\rho'_0$  to the state  $\rho_0$ .

Mathematically, the process is still described through the perturbed continuity equation (6), provided the asymptotic condition

$$\rho \rightarrow \rho_0 \quad \text{for} \quad t \rightarrow +\infty ,$$



be assumed. If, as in the case of the absorption process, we look for the solution in the form of a series, the first correction  $\rho_1$  has to satisfy the same equation (7) as before, but now with the “final” condition

$$\rho_1 \rightarrow 0 \quad \text{for } t \rightarrow +\infty \quad (13)$$

So the solution now has the form

$$\rho_1(\mathbf{x}, t) = \int_t^{+\infty} ds \sum_{k,j} e_j \delta \mathcal{E}^c(\mathbf{x}_k^0, s) \frac{\partial \rho_0}{\partial \mathbf{p}_{j,k}} \left( \Phi^{s-t} z \right), \quad (14)$$

and thus, in the same hypotheses as before, the final polarization can be written as

$$\mathcal{P}(\mathbf{x}, t) = \int_t^{+\infty} ds \delta \mathcal{E}^c(\mathbf{x}, s) \tilde{\chi}(t-s), \quad (15)$$

with  $\tilde{\chi}$  given exactly by the expression (12) that occurs in the absorption process.

## 4 Susceptibilities for absorption and for emission. Analyticity properties, and the $f$ -sum rule

### Susceptibilities

Susceptibilities are defined as responses to forcings of given frequencies, and thus are obtained from the formulas (11) and (15) if the latter are expressed in the form of convolutions, namely, with integrals over the whole real axis  $\mathbb{R}$ . Thus we introduce the functions

$$\chi^{abs}(t) \stackrel{\text{def}}{=} \begin{cases} \tilde{\chi}(t) & \text{for } t > 0, \\ 0 & \text{for } t \leq 0 \end{cases} \quad (16)$$

$$\chi^{em}(t) \stackrel{\text{def}}{=} \begin{cases} 0 & \text{se } t > 0 \\ -\tilde{\chi}(t) & \text{se } t \leq 0 \end{cases} \quad (17)$$

so that through the change of variables  $s \rightarrow t-s$  formulas (11) and (15) for the polarizations in an absorption or an emission process take the form

$$\mathcal{P}(\mathbf{x}, t) = \int_{\mathbb{R}} ds \delta \mathcal{E}^c(\mathbf{x}, t-s) \chi^{abs}(s),$$

$$\mathcal{P}(\mathbf{x}, t) = \int_{\mathbb{R}} ds \delta\mathcal{E}^c(\mathbf{x}, t - s) \chi^{em}(s) ,$$

namely, of convolutions between the change of exciting field and the function  $\chi^{abs}(t)$  or  $\chi^{em}(t)$  respectively.

Now, as the Fourier transform of a convolution is the product of the Fourier transforms (which we denote by a hat), the relations between polarization and exciting field can be written in the familiar form

$$\begin{aligned} \hat{\mathcal{P}}(\mathbf{x}, \omega) &= \hat{\chi}^{abs}(\omega) \delta\hat{\mathcal{E}}^c(\mathbf{x}, \omega) \\ \hat{\mathcal{P}}(\mathbf{x}, \omega) &= \hat{\chi}^{em}(\omega) \delta\hat{\mathcal{E}}^c(\mathbf{x}, \omega) \end{aligned} \quad (18)$$

where

$$\begin{aligned} \hat{\chi}^{abs}(\omega) &= - \int_{-\infty}^0 dt \tilde{\chi}(t) e^{i\omega t} \\ \hat{\chi}^{em}(\omega) &= \int_0^{+\infty} dt \tilde{\chi}(t) e^{i\omega t} . \end{aligned} \quad (19)$$

As  $\tilde{\chi}$  is odd (see below), by the change of variable  $t \rightarrow -t$  in the second integral one gets that  $\hat{\chi}^{em}$  is the complex conjugate of  $\hat{\chi}^{abs}$ . So the emission and the absorption spectra coincide.

To show that  $\tilde{\chi}(t)$  is an odd function, we notice that, from the definition, one has

$$\tilde{\chi}(-t) = \int dz \frac{1}{\Delta V} \sum_{\mathbf{x}_k^0, \mathbf{x}_{k'}^0 \in \Delta V} \sum_{j, j'} e_j e_{j'} \mathbf{q}_{j', k'}(-t) \frac{\partial \rho_0}{\partial \mathbf{p}_{j, k}} ,$$

so that, performing into the integral the substitution  $\mathbf{p}_{j, k} \rightarrow -\mathbf{p}_{j, k}$ , one finds

$$\tilde{\chi}(-t) = - \int dz \frac{1}{\Delta V} \sum_{\mathbf{x}_k^0, \mathbf{x}_{k'}^0 \in \Delta V} \sum_{j, j'} e_j e_{j'} \mathbf{q}_{j', k'}(t) \frac{\partial \rho_0}{\partial \mathbf{p}_{j, k}} = -\tilde{\chi}(t)$$

(indeed, as  $\rho_0$  is even, its derivatives are odd, whereas, by changing sign to the momenta,  $\mathbf{q}_{j', k'}(-t)$  goes into  $\mathbf{q}_{j', k'}(t)$ ).

## Analyticity properties. The Kramers–Kronig relations

It is well known that, as the function  $\chi^{abs}(t)$  vanishes for  $t < 0$ , then its Fourier transform enjoys two relevant properties:

- It is analytic in the half plane  $\text{Im } \omega > 0$ ;
- The Kramers–Kronig relations hold

$$\begin{aligned}\text{Re } \hat{\chi}^{abs}(\omega) &= \frac{1}{\pi} \int_{\mathbb{R}} d\Omega \frac{\text{Im } \hat{\chi}^{abs}(\Omega)}{\Omega - \omega} \\ \text{Im } \hat{\chi}^{abs}(\omega) &= -\frac{1}{\pi} \int_{\mathbb{R}} d\Omega \frac{\text{Re } \hat{\chi}^{abs}(\Omega)}{\Omega - \omega} .\end{aligned}\tag{20}$$

From a conceptual point of view the Kramers–Kronig relations are often interpreted as expressing the causality principle, the latter being meant in the sense that the affect (here, polarization) cannot precede the cause (the exciting field). On the other hand, analogous relations obviously hold also for the function  $\hat{\chi}^{em}(\omega)$ , which clearly is not causal in that sense, as  $\chi^{em}(t)$  vanishes after the field is applied.

A second remark concerns the poles of the two susceptibilities. Since the original work of Kramers, the emission was attributed to the presence of the radiation reaction force (proportional to the time derivative of acceleration) in the equations of motion. In such a way, however, in the expression for the susceptibility, calculated by considering a single damped and forced oscillator, there appeared a pole in the wrong half–plane, and Kramers himself had to patch the expression in some suitable way. Instead, with the full electrodynamic treatment considered here, in virtue of the Wheeler–Feynman cancellation the radiation reaction forces entering the original equations of motion eventually disappears, and the expressions of the susceptibilities have poles in the correct half–plane.

## The $f$ –sum rule

We finally come to the  $f$ –sum rule. The reason of the name will be recalled in the next section.

For the sake of concreteness we here concentrate on the case of the absorption susceptibility, because the formulas for the case of emission are simply obtained by passing to the conjugate complex. In order to have simpler notations, we also omit the superscript *abs*, i.e., we let  $\hat{\chi}^{abs} \equiv \hat{\chi}$ .

The  $f$ –sum rule states that

$$\int_{\mathbb{R}} \omega \text{Im } \hat{\chi}(\omega) d\omega = \frac{\pi}{\Delta V} \sum_{\mathbf{x}_k^0 \in \Delta V} \sum_j \frac{e_j^2}{m_j} ,\tag{21}$$

so that it essentially relates the total absorption to the electron charge density. Indeed one should take into account that for nuclei the ratio  $e_j^2/m_j$  is negligible with respect to that of the electrons, so that the sum at the right hand side can be restricted to the electrons present in the considered volume. Thus, denoting by  $e$  and  $m$  the charge and the mass of the electron, the r.h.s. just reduces to  $\pi e^2/m$  times the electron density (number of electrons per unit volume).

The next part of this section is devoted to a proof of the  $f$ -sum rule (21). We start noting that for a smooth functions  $f(t)$  one has

$$\int_{\mathbb{R}} -i\omega \hat{f}(\omega) d\omega = 2\pi \dot{f}(0) .$$

Indeed, on the one hand the Fourier transform of  $\dot{f}(t)$  is given by  $-i\omega \hat{f}(\omega)$ , as one immediately checks by an integration by parts. On the other hand the inversion theorem for the Fourier transform gives

$$\int_{\mathbb{R}} -i\omega \hat{f}(\omega) e^{-i\omega t} d\omega = 2\pi \dot{f}(t) .$$

So the thesis should follow by simply taking  $t = 0$ . However, in our case  $\dot{\chi}(t)$  presents a discontinuity of first type at  $t = 0$ , as it vanishes for  $t > 0$ , while being equal to  $\dot{\tilde{\chi}}(t)$  for  $t < 0$ . Now, the inversion theorem tells us that at a discontinuity points the integral equals the semi sum of the right and the left limits, so that eventually one has

$$\int_{\mathbb{R}} -i\omega \hat{\chi}(\omega) d\omega = \pi \dot{\tilde{\chi}}(0) .$$

However, as is easily checked,<sup>5</sup>  $\text{Re } \hat{\chi}(\omega)$  is an even function of  $\omega$ , so that one has

$$\int_{\mathbb{R}} -i\omega \hat{\chi}(\omega) d\omega = \int_{\mathbb{R}} \omega \text{Im } \hat{\chi}(\omega) d\omega = \pi \dot{\tilde{\chi}}(0) .$$

Now it turns out that  $\dot{\tilde{\chi}}(0)$  can be evaluated exactly and, as will be seen in a moment, one has

$$\dot{\tilde{\chi}}(0) = \frac{1}{\Delta V} \sum_{\mathbf{x}_k^0 \in \Delta V} \sum_j \frac{e_j^2}{m_j} ,$$

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<sup>5</sup>Indeed, one has

$$\text{Re } \hat{\chi}(\omega) = \int_{-\infty}^0 \tilde{\chi}(t) \cos(\omega t) dt$$

so that, changing  $\omega$  into  $-\omega$ , the value of the integral does not change.

which indeed proves the  $f$ -sum rule (21).

In order to show the latter relation, we differentiate the expression (12) for  $\tilde{\chi}(t)$ . Exchanging derivative and integral one gets

$$\begin{aligned}\dot{\tilde{\chi}}(0) &= - \int dz \frac{1}{\Delta V} \sum_{\mathbf{x}_k^0, \mathbf{x}_{k'}^0 \in \Delta V} \sum_{j,j'} e_j e_{j'} \dot{\mathbf{q}}_{j',k'}(0) \frac{\partial \rho_0}{\partial \mathbf{p}_{j,k}} = \\ &= - \int dz \frac{1}{\Delta V} \sum_{\mathbf{x}_k^0, \mathbf{x}_{k'}^0 \in \Delta V} \sum_{j,j'} \frac{e_j e_{j'}}{m_{j'}} \mathbf{p}_{j',k'}(t) \frac{\partial \rho_0}{\partial \mathbf{p}_{j,k}},\end{aligned}$$

where in the second line use was made of  $\dot{\mathbf{q}}_{j',k'}(0) = \mathbf{p}_{j',k'}/m_{j'}$ . Now there just remains to integrate by parts. The boundary term vanishes (due to the vanishing of the probability for a particle to have an infinite momentum), so that

$$\begin{aligned}\dot{\tilde{\chi}}(0) &= \int dz \frac{1}{\Delta V} \sum_{\mathbf{x}_k^0, \mathbf{x}_{k'}^0 \in \Delta V} \sum_{j,j'=0} \frac{e_j e_{j'}}{m_{j'}} \frac{\partial \mathbf{p}_{j',k'}}{\partial \mathbf{p}_{j,k}} \rho_0 = \\ &= \int dz \frac{1}{\Delta V} \sum_{\mathbf{x}_k^0 \in \Delta V} \sum_j \frac{e_j^2}{m_j} \rho_0 = \frac{1}{\Delta V} \sum_{\mathbf{x}_k^0 \in \Delta V} \sum_j \frac{e_j^2}{m_j},\end{aligned}$$

inasmuch as  $\frac{\partial \mathbf{p}_{j',k'}}{\partial \mathbf{p}_{j,k}} = \delta_{k,k'} \delta_{j,j'}$ , whereas the density  $\rho_0$  is assumed to be normalized to 1.

## 5 Response functions and susceptibilities in terms of correlation functions

After the detour on the analyticity properties of the dielectric response functions and susceptibilities, which were based on the general expression (12), we show here how more transparent expressions are obtained if a further property of a quite general character is introduced for the equilibrium density  $\rho_0$ . The point is that formula (12) involves sums of integrals of the type

$$\mathcal{I}_{k,j,k',j'} = \int dz \mathbf{q}_{j',k'}(t-s) \frac{\partial \rho_0}{\partial \mathbf{p}_{j,k}}, \quad (22)$$

the computation of which requires to have available a definite expression for the derivative of  $\rho_0$  with respect to  $\mathbf{p}_{j,k}$ . Now, if we were allowed to

take for  $\rho_0$  the Gibbs form, the above quantity would be proportional to  $\mathbf{p}_{j,k} \rho_0$ . On the other hand, essentially the same result is guaranteed under much milder conditions, essentially under conditions which allow for a large deviation principle to hold with respect to the momenta only, irrespective of the positions (which, through the attractive Coulomb potential, introduce divergences in the classical form of Gibbs' measure). Indeed this allows one to get

$$\frac{\partial \rho_0}{\partial \mathbf{p}_{j,k}} = -\frac{1}{m_{j'} \sigma_p^2} \mathbf{p}_{j,k} \rho_0 , \quad (23)$$

where the constant  $\sigma_p^2$  is nothing but the mean square deviation of momentum, which would just reduce to temperature if the density were the Gibbs one. For the large deviation argument one can see the classical book of Khinchin [31]. So we have

$$\begin{aligned} \mathcal{I}_{k,j,k',j'} &= \frac{-1}{m_{j'} \sigma_p^2} \int dz \mathbf{q}_{j',k'}(t-s) \mathbf{p}_{j,k} \rho_0(z) \\ &= \frac{-1}{m_{j'} \sigma_p^2} \langle \mathbf{q}_{j',k'}(t-s) \mathbf{p}_{j,k}(0) \rangle , \end{aligned}$$

namely, the integrals (22) are just equilibrium time–correlations between position and momentum of each charge.

This fact, by the way, makes reasonable a property that was assumed in the last part of section 3, when passing from (10) to (15). Namely, the property that the integrals (22) should present a fast decay with respect to spatial separation of the charges, i.e., that one should have

$$\mathcal{I}_{k,j,k',j'} = 0$$

if the molecules  $\mathbf{x}_k^0$  e  $\mathbf{x}_{k'}^0$  belong to different volume elements.

In conclusion, the expression (12) for the dielectric response function can be rewritten in the form

$$\tilde{\chi}(t) = \frac{1}{\sigma_p^2} \sum_{\mathbf{x}_k^0, \mathbf{x}_{k'}^0 \in \Delta V} \sum_{j,j'} \frac{e_j e_{j'}}{m_j} \langle \mathbf{q}_{j',k'}(t) \mathbf{p}_{j,k}(0) \rangle , \quad (24)$$

which involves equilibrium time–correlations of momenta and positions of the charges.

Now there remains the problem that we have to compute phase averages with respect to the equilibrium probability density  $\rho_0$ , the form of which

is still essentially undetermined. A great step forward is accomplished by making use of a general principle of statistical mechanics according to which, under extremely mild conditions, the phase space equilibrium averages can be computed as corresponding time averages (see for example [31], page 63).

So we estimate the required phase space integral as time averages, i.e. as

$$\begin{aligned} \langle \mathbf{q}_{j',k'}(t) \mathbf{p}_{j,k}(0) \rangle &= \\ &= \lim_{T \rightarrow +\infty} \frac{1}{2T} \int_{-T}^T \mathbf{q}_{j',k'}(t+s) \cdot \mathbf{p}_{j,k}(s) ds . \end{aligned} \quad (25)$$

## 6 Line spectrum and the “virtual orchestra”

Here we show how it can at all happen that a conservative Hamiltonian system (to which our original electrodynamic system has been reduced) presents a line spectrum. This depends of the qualitative properties of the dynamical orbits (or motions) of the system, because it turns out that a discrete spectrum occurs if the motion of the representative point in phase space is, informally speaking, “non chaotic”. Indeed in dynamical systems theory the property of presenting a continuous spectrum is sometimes even assumed to be the characteristic property for an orbit to be chaotic. More precisely, one certainly has a pure line spectrum if the motion is assumed to be “almost periodic” in the sense introduced in the year 1924 by Harald Bohr, the brother of Niels Bohr. <sup>6</sup>

### Pure line spectrum for almost periodic motions

Almost periodicity can be defined in several equivalent ways. However, the following characteristic property (which thus can be taken as a definition), is more significant for our purposes: if an orbit, say the motion  $\mathbf{q}_{j,k}(t)$  of a particle, is almost periodic, then it can be represented by a generalized Fourier expansion

$$\mathbf{q}_{j,k}(t) = \sum_n [\mathbf{c}_{j,k}^n \cos(\omega_n t) + \mathbf{d}_{j,k}^n \sin(\omega_n t)] \quad (26)$$

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<sup>6</sup>For an introduction to almost periodic functions see for example [32], Part II, Chapter 5, where in particular the relations between almost periodicity and Liapunov stability of an orbit are discussed.

where the sequence  $\{\omega_n\}$  of *positive* frequencies is determined in the following way. Having defined the functions<sup>7</sup>  $\mathbf{c}_{j,k}(\omega)$  and  $\mathbf{d}_{j,k}(\omega)$  by

$$\mathbf{c}_{j,k}(\omega) = \lim_{t \rightarrow +\infty} \frac{1}{2t} \int_{-t}^t \mathbf{q}_{j,k}(s) \cos(\omega s) ds ,$$

$$\mathbf{d}_{j,k}(\omega) = \lim_{t \rightarrow +\infty} \frac{1}{2t} \int_{-t}^t \mathbf{q}_{j,k}(s) \sin(\omega s) ds ,$$

then these functions turn out to vanish for all frequencies but for a discrete set of frequencies  $\{\omega_n\}$ . This determines the frequencies. Then, the coefficients of the expansion simply are the values of the expansion simply are the values of the the above functions at  $\omega_n$ , i.e., one has

$$\mathbf{c}_{j,k}^n = \mathbf{c}_{j,k}(\omega_n) , \quad \mathbf{d}_{j,k}^n = \mathbf{d}_{j,k}(\omega_n) .$$

Corresponding to the expansion (26) for the position as a function of time, one also has an analogous expansion for the momenta, namely,

$$\mathbf{p}_{j,k}(t) = m_j \sum_n -\omega_n \mathbf{c}_{j,k}^n \sin(\omega_n t) + \omega_n \mathbf{d}_{j,k}^n \cos(\omega_n t) , \quad (27)$$

which is obviously obtained by differentiating with respect to time the expansion for  $\mathbf{q}_{j,k}(t)$ .

One thus obtains

$$\begin{aligned} \langle \mathbf{q}_{j',k'}(t) \mathbf{p}_{j,k}(0) \rangle &= \\ &= \sum_n \omega_n \left[ \frac{\mathbf{c}_{j,k}^n \cdot \mathbf{c}_{j',k'}^n + \mathbf{d}_{j,k}^n \cdot \mathbf{d}_{j',k'}^n}{2} \sin \omega_n t \right. \\ &\quad \left. + \frac{\mathbf{c}_{j,k}^n \cdot \mathbf{d}_{j',k'}^n - \mathbf{d}_{j,k}^n \cdot \mathbf{c}_{j',k'}^n}{2} \cos \omega_n t \right] . \end{aligned} \quad (28)$$

This relation is obtained by evaluating the integrals through the familiar prosthaphaeresis formulas, recalling that the time average of any non constant trigonometric function vanishes. The result is the following one.

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<sup>7</sup>For almost periodic functions these limits are proven to exist. See for example the classical text [33].



Defining

$$\begin{aligned}
I_{sc} &\stackrel{\text{def}}{=} \lim_{T \rightarrow +\infty} \frac{1}{2T} \int_{-T}^T \sin \omega s \cos \omega'(t+s) ds \\
I_{ss} &\stackrel{\text{def}}{=} \lim_{T \rightarrow +\infty} \frac{1}{2T} \int_{-T}^T \sin \omega s \sin \omega'(t+s) ds \\
I_{cc} &\stackrel{\text{def}}{=} \lim_{T \rightarrow +\infty} \frac{1}{2T} \int_{-T}^T \cos \omega s \cos \omega'(t+s) ds \\
I_{cs} &\stackrel{\text{def}}{=} \lim_{T \rightarrow +\infty} \frac{1}{2T} \int_{-T}^T \cos \omega s \sin \omega'(t+s) ds ,
\end{aligned}$$

one finds that all the  $I$ 's vanish for  $\omega \neq \omega'$ , whereas for  $\omega = \omega'$  one has

$$I_{sc} = I_{cs} = -\frac{1}{2} \sin \omega t , \quad I_{ss} = I_{cc} = -\frac{1}{2} \cos \omega t .$$

## Form of susceptibility for almost periodic motions

Now, substitute into formula (24) the expression (28) just found for the correlations. Remarking that, due to the antisymmetry with respect to the interchange  $k, j \leftrightarrow k', j'$  of the terms occurring in the sum. one has

$$\sum_{\mathbf{x}_k^0, \mathbf{x}_{k'}^0 \in \Delta V} \sum_{j, j'} \frac{e_j e_{j'} \mathbf{c}_{j,k}^n \cdot \mathbf{d}_{j',k'}^n - \mathbf{d}_{j,k}^n \cdot \mathbf{c}_{j',k'}^n}{m_j} = 0 ,$$

one obtains

$$\begin{aligned}
\tilde{\chi}(t) &= \frac{1}{\sigma_p^2} \sum_n \omega_n \sin \omega_n t \cdot \\
&\cdot \sum_{\mathbf{x}_k^0, \mathbf{x}_{k'}^0 \in \Delta V} \sum_{j, j'} \frac{e_j e_{j'} \mathbf{c}_{j,k}^n \cdot \mathbf{c}_{j',k'}^n + \mathbf{d}_{j,k}^n \cdot \mathbf{d}_{j',k'}^n}{m_j} ,
\end{aligned}$$

In order to find the susceptibility there just remains to compute the Fourier transform of  $\tilde{\chi}(t)$ . A not difficult computation shows that one has

$$\int_{-\infty}^0 \sin \omega_n t e^{i\omega t} dt = \frac{-\omega_n}{\omega_n^2 - \omega^2} + i\pi \left( \delta(\omega - \omega_n) + \delta(\omega + \omega_n) \right) .$$

Thus, defining

$$f_n \stackrel{\text{def}}{=} \omega_n^2 \left[ \sum_{\mathbf{x}_k^0, \mathbf{x}_{k'}^0 \in \Delta V} \sum_{j, j'} \frac{e_j e_{j'} \mathbf{c}_{j,k}^n \cdot \mathbf{c}_{j',k'}^n + \mathbf{d}_{j,k}^n \cdot \mathbf{d}_{j',k'}^n}{m_j} \right], \quad (29)$$

for the real and the imaginary parts of susceptibility one finds the expressions

$$\begin{aligned} \text{Re } \chi(\omega) &= \sum \frac{f_n}{\omega_n^2 - \omega^2} \\ \text{Im } \chi(\omega) &= \pi \sum \frac{f_n}{2\omega_n} \left( \delta(\omega - \omega_n) + \delta(\omega + \omega_n) \right). \end{aligned} \quad (30)$$

## The “virtual orchestra” of Bohr, Kramers and Slater

Due to the delta functions appearing in the imaginary part of susceptibility, formula (30) shows that the spectrum of a macroscopic dielectric body performing almost periodic motions presents infinitely tight absorption lines, in correspondence of the frequencies  $\omega_n$ . This is the way in which, in the spectrum of a macroscopic dielectric body, “lines” show up without necessarily having to make reference to energy levels of the single molecule or atom.

This result is exactly the property of a spectrum which, before the advent of quantum mechanics, (starting from Lorentz [19] and Drude up to Kronig [27] and even Born and Wolf [7]), was interpreted in microscopic terms by thinking that each line should be attributed to the motion of a material harmonic “resonator”, of exactly that frequency. Analogously the molecules were thought of as constituted of charges with mutual elastic bonds. So there would exist corresponding normal modes, which could be equivalently described as harmonic oscillators with characteristic frequencies  $\omega_n$  (which were introduced from outside, in correspondence with the observed ones).

However, as the lines are infinite in number, one was meeting with the absurd situation that any atom or molecule had to be composed of an infinite number of oscillating charges. For this reason such oscillators were denoted as “virtual” i.e., as somehow non physical (see [34]), and each of them was weighted with a suitable weight (usually called “force”)  $f_n$ . In the year 1925 the “ $f$ -sum rule” was empirically discovered, according to which the “forces” of the virtual oscillators were not arbitrary, but had to satisfy the rule

$$\sum_n f_n = \frac{1}{\Delta V} \sum_{\mathbf{x}_k^0 \in \Delta V} \sum_j \frac{e_j^2}{m_j}. \quad (31)$$

Namely, the sum of the “forces” of the oscillators just equals the number of electrons per atom or per molecule, times the factor  $e^2/m_e$  (indeed, as already explained, the contribution of the nuclei is negligible).

One of the big triumphs of quantum mechanics was to “explain” the  $f$ -sum rule in terms of the quantum commutation rules. On the other hand, such a rule holds in the classical case too. Indeed an explicit computation gives

$$\int_{\mathbb{R}} \omega \operatorname{Im} \chi(\omega) d\omega = \pi \sum f_n ,$$

which, using the general formula (21), actually gives the  $f$ -sum rule (31).

## 7 Broadening and chaoticity: the case of ionic crystals

So, a pure line spectrum occurs for stable (almost periodic) motions, whereas a broadening of the lines and even a continuous spectrum are expected to occur when chaoticity of the motions sets in. This connection between optical properties of the system and qualitative properties (order or chaos, or their coexistence) of the corresponding orbits can be illustrated in a particularly clear way in the case of ionic crystals.

If one is interested in the infrared spectrum, in the expression (24) for the dielectric response function it is sufficient to limit oneself to the motions of the ions only. In such a case it is convenient to choose as a reference point  $\mathbf{x}_k^0$  (with respect to which the displacements  $\mathbf{q}_{j,k}$  are computed), an arbitrary fixed point inside each cell of the lattice. In such a way the index  $k$  is now labeling also the cells. Following [1] one can pass to the normal modes of the lattice, which we here denote by  $A_{\xi,l}(t)$  and are defined by

$$\mathbf{q}_{j,k}(t) = \sum_l \int_{\mathcal{B}} \mathbf{u}_l(j, \boldsymbol{\xi}) A_{\xi,l}(t) e^{i\boldsymbol{\xi} \cdot (\mathbf{x}_k^0 + \boldsymbol{\tau}_j)} d\boldsymbol{\xi} .$$

Here, the integration is performed over the Brillouin zone  $\mathcal{B}$ , the vectors  $\mathbf{u}_l(j, \boldsymbol{\xi})$  are the eigenvectors of the dynamical matrix of the crystal, while the vector  $\boldsymbol{\tau}_j$  specifies the equilibrium position of the  $j$ -th atom inside the cell  $k$ . The index  $l$  is now a label for the different branches of the dispersion

relation.<sup>8</sup> So, one gets the relation

$$\sum_{\mathbf{x}_k^0 \in \Delta V} \mathbf{q}_{j,k}(t) \simeq (2\pi)^3 \sum_l \mathbf{u}_l(j, 0) A_{0,l}(t) ,$$

because, in summing over a volume element, one has

$$\sum_{\mathbf{x}_k^0 \in \Delta V} e^{i\boldsymbol{\xi} \cdot \mathbf{x}_k^0} \simeq (2\pi)^3 \delta(\boldsymbol{\xi}) .$$

Thus, in the case of a ionic crystal the dielectric response function for the ions can be written as

$$\begin{aligned} \tilde{\chi}(t) = & \frac{1}{\sigma_p^2} \sum_{l,l'} \left( \sum_{j,j'} e_j e_{j'} \mathbf{u}_l(j, 0) \cdot \mathbf{u}_l(j', 0) \right) \\ & \langle A_{0,l}(t)(t) \dot{A}_{0,l'}(0) \rangle , \end{aligned}$$

so that the relevant quantities now are the time correlations of the modes  $A_{0,l}(t)$ .

If the harmonic approximation, each mode performs a periodic motion with frequency  $\omega_l$ , so that one has

$$\langle A_{0,l}(t)(t) \dot{A}_{0,l'}(0) \rangle = C_l \delta_{ll'} \sin(\omega_l t) ,$$

being  $\delta_{ll'}$  the Kronecker's delta, and one ends up with a formula of the type (30), now however with only a finite number of terms, each corresponding to a branch of the dispersion relation (omitting the ‘‘acoustic’’ branches , for which it is  $A_{0,l} = 0$ ).

On the other hand, if the nonlinear terms are taken into account the motion is no more integrable, and the previous analysis has to be changed. In the case of a ‘‘small’’ nonlinearity, the behavior of the correlations over some (large) time–scale does not change with respect to the unperturbed (i.e., linear) case, whereas over a larger time scale the correlations are expected to decay to zero, so that one should have

$$\langle A_{0,l}(t)(t) \dot{A}_{0,l}(0) \rangle = C_l e^{-\sigma_l t} \sin(\omega_l t) ,$$

---

<sup>8</sup>We recall that, while in the purely mechanical case the number of branches is  $3N$  ( $N$  being the number of ions in the fundamental cell), instead, when the interaction with the field of the far ions is taken into account, the number of branches can vary, and polaritonic branches can appear.

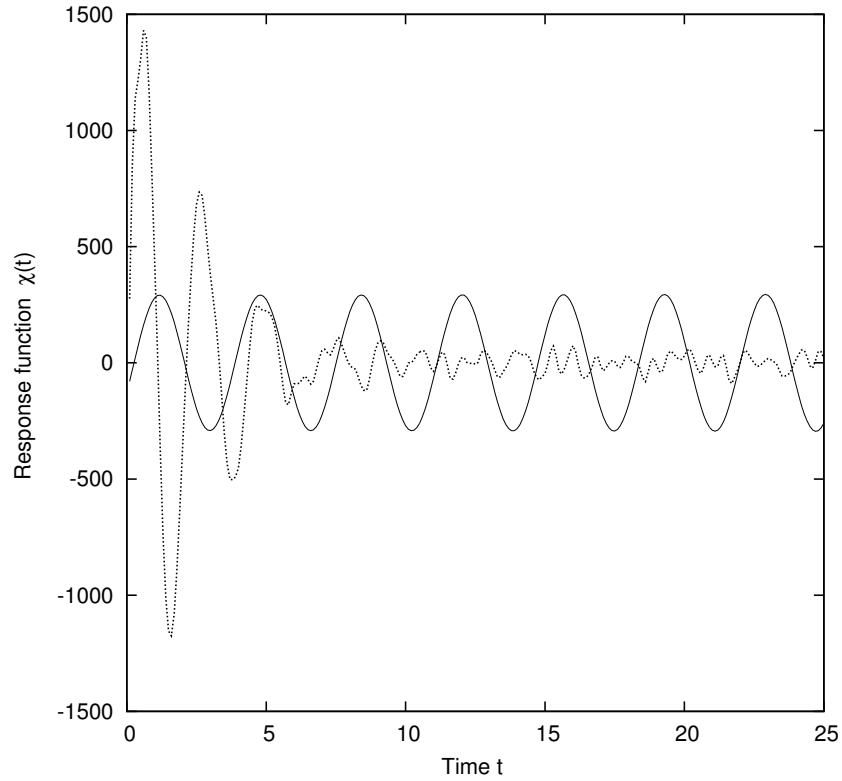


Figure 1: The response function  $\chi$  versus time. Solid line refers to the system at low temperature, while broken line refers to the system at high temperature.

In conclusion, passing to the Fourier transform, one can presume that in the case of a small nonlinearity one should get

$$\int_0^{+\infty} e^{i\omega t} \langle A_{0,l}(t) \dot{A}_{0,l}(0) \rangle = \frac{f_l}{(\omega^2 - \omega_l^2 + \sigma_l^2) + 2i\sigma_l\omega} ,$$

i.e., the classical expression of Lorentz and Drude [19][18], that such authors interpreted in terms of motions of material damped “resonators”. Thus the line broadening corresponds to a decay of the time correlations which is induced by the nonlinearity and the presumably associated chaoticity (or rather partial chaoticity) of the motions. Here no damping is active, neither the linear one which was heuristically introduced by Lorentz and Drude, nor

that of the radiation reaction, which was always taken into consideration by Van Vleck, Planck and many others. Indeed the radiation reaction, although being actually present in the original full electrodynamic model, turns out to be eliminated by the electrodynamic action of the far charges, through the Wheeler–Feynman mechanism.

So much for the case of a small nonlinearity, i.e., for the case of what may be called the “perturbation regime” (with respect to the linear one). Instead, in the case of a large nonlinearity the motion is expected to be completely chaotic, displaying time correlations completely different from those of the linear case. In particular the spectrum should be now a continuous one, with no peaks anymore.

On the other hand, when in statistical mechanics one makes reference to the qualitative properties of the motions with respect to order (stability) or chaoticity type, it is usually presumed that in the thermodynamic limit the motions should always be chaotic. This has the consequence that, in our case, which is concerned with macroscopic dielectric systems dealt with in a classical frame, one would always meet with a continuous spectrum. Now, in the domain of the theory of classical dynamical systems, particularly in connection with the so called Fermi–Pasta–Ulam problem, a long debate is going on about this point, and the results of numerical computations appeared to be not yet conclusive. However, rather recently it was analytically proven [13] that in the perturbation regimes significant stability properties do persist in the thermodynamic limit, and indeed in a form suited for applications to statistical mechanics. In particular, in the works [15] and [14] it was proven that in the FPU and in related models the normal mode energies remain correlated for long times also in the thermodynamic limit (see also the numerical work [16], or the work [17] concerning plasmas). Thus one can conclude that the conjecture that macroscopic systems should perform chaotic motions is, at least, not always appropriate, and should be checked in any particular case.

Just in order to give an example which should exhibit in a qualitative way the features described above, we report here the results of a numerical computation performed on the classical one–dimensional alternating masses model (with 1024 particles), introduced already in the year 1912 by Born and von Kármán. Through a numerical simulation of the dynamics we computed the response function  $\chi(t)$ , defined by (24) with the sum extended over all particles of the crystal, and then the corresponding spectrum. We considered two cases relative to a low temperature and to a larger one. The response

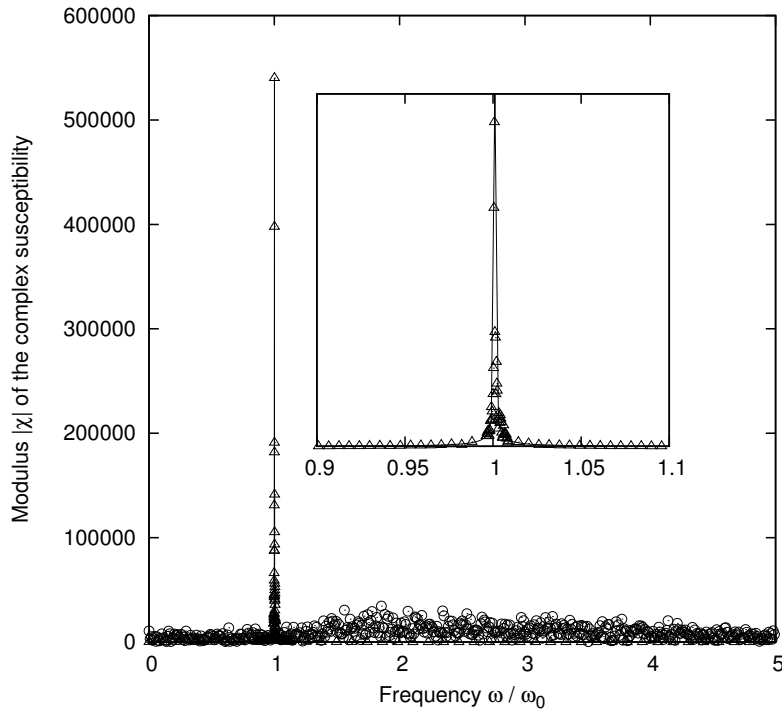


Figure 2: Plot of  $|\chi(\omega)|$  versus  $\omega$  for two different temperatures. Circles refer to the system at a high temperature (no peak), while the triangles, which exhibit a peak for  $\omega \simeq \omega_0$ , refer to the system at a low temperature. In the inset, which concerns the system at low temperature, the plot of  $|\chi(\omega)|$  is reported for  $\omega$  near  $\omega_0$ , together with the best-fit Lorentzian curve (solid line). Here,  $\omega_0$  is the frequency of the optical branch.

functions for the two temperatures are reported in Fig. 1, whereas the corresponding spectra (computed as the discrete Fourier transforms) are reported in Fig. 2. In the case of low temperature the response function presents a well distinct profile, apparently not very dissimilar from a periodic one. However a decay occurs at much longer times, as witnessed by the broadened form of the spectrum (shown in the inset of Fig. 2). Further results not reported here show that with increasing temperature the broadening, and a shift too, become larger and larger. Finally, at some high temperature, the results reported in the figures show that the response function presents a decay at a short time, and the corresponding spectrum is essentially a continuum.

For an analogous phenomenon occurring in a model of interest for plasma confinement, in which a transition from an ordered to a chaotic motion is witnessed by the form of the spectrum, see [17].

We leave for a future work the numerical study of the spectrum for a realistic three-dimensional model of a ionic crystal involving the microscopic electrodynamic forces, already considered in [1] in connection with the dispersion curves.

## 8 Final comments

So we have complemented the result obtained in [1], by showing how electric susceptibility can be consistently proven to exist for a dielectric macroscopic body, in a classical microscopic theory in which the full electrodynamic interactions among the charges are taken into account. Preliminarily we had to make essential use of two global properties of the electrodynamic interactions, i.e., the Wheeler–Feynman identity and the Ewald–Oseen resummation properties. The former was proved here for a general system in the thermodynamic limit, whereas the latter were proven in [1] for crystals, their proof for a general system being still lacking. Thus our result is at the moment proven only for crystals, although we are firmly convinced that it can be extended to cover the case of a generic dielectric body.

On the basis of such global electrodynamic properties, the dynamical system can be dealt with as if it were a Hamiltonian one, and in particular the radiation reaction forces are completely eliminated, so that absorption and emission appear as completely symmetrical phenomena of a time-reversal invariant system. Susceptibility turns out to be expressed in terms of the time correlation functions of positions and velocities of the charges, calculated for motions of the system at equilibrium, i.e., in the absence of an external field. Notice however that the system still contains a trace of the electrodynamic interactions, because the equations of motion of the charges, that have to be solved in order that the time correlation functions may be computed, still contain the force of the “exciting field”, namely, the field originated by the far charges, that propagates in the body as an external field, having however the correct refractive index.

Having reduced the original electrodynamic system to a Hamiltonian one, susceptibility was proven to exist through methods of Green–Kubo type. However, this required to overcome the difficulties of working in the absence



of a Gibbs measure, which does not exist for systems with attractive Coulomb interactions,

For what concerns the spectrum, which is the same for absorption and for emission, we have illustrated how it reflects the stability properties of the unperturbed equilibrium motions of the system. For stable (almost periodic) motions, as occurs with a crystal in the linear approximation, one has a purely line spectrum. So, the susceptibility presents the standard form that, since the first work of Lorentz of the year 1872, was explained by thinking of the system as if it were composed of single linear material oscillators with proper frequencies equal to the observed ones (see the booklet [36] of Pauli).

When chaoticity sets in, as occurs in a crystal in the presence of nonlinearities, one might conjecture that the motions be completely chaotic, so that the lines completely disappear, and a continuous spectrum occurs. We have however pointed out that the most recent analytical result appear to support the conjecture that, at least in the case of crystals, partially ordered motions persist in the thermodynamic limit (i.e., for a macroscopic system). Thus the time correlations in general should decay only after a sufficiently long time, with the consequence that the lines are in general broadened. In such a case the spectrum has the form that would occur if the system were composed of single linear material oscillators with the observed frequencies, having in addition suitable linear dissipative forces. However, no physical dissipative force is actually present in our system, because, in virtue of the Wheeler–Feynman identity, the radiation reaction forces are canceled by the electrodynamic forces due to the far charges. So, the decay of correlations occurs in the familiar dynamical way which characterizes autonomous Hamiltonian systems that are (at least partially) chaotic, and has nothing to do with the radiation reaction force, to which for example Planck, Van Vleck and many others were thinking. Correspondingly, the poles of susceptibility in the complex frequency plane quite naturally do lie in the correct half plane.

In any case, while in the theory of dynamical systems the presence of a continuous or partly continuous spectrum is sometimes used as a tool to qualify the ordered or chaotic character of motions, here the situation is reversed, and it is the spectrum itself, in its original physical optical connotation, that is a pure line spectrum in the case of ordered motions, while presenting broadened lines or a fully continuous aspect in the case of partly or fully chaotic motions.

## 9 Appendix. Proof of the Wheeler–Feynman identity

### Proof of the identity

The Wheeler–Feynman identity deals with the classical problem of the solutions of the inhomogeneous wave equation

$$\square_2 A^\nu = j^\nu(t, \mathbf{x}) ,$$

for the four–potential  $A^\nu$ , with a given four–current  $j^\nu(t, \mathbf{x})$ , and states that, possibly under suitable conditions, the advanced potential coincides with the retarded one, or more precisely, in terms of their difference which is a regular function, that one has

$$A_{ret}^\nu - A_{adv}^\nu = 0 .$$

Clearly this is not true for an arbitrary current, and the authors, on the basis of four arguments, advanced the conjecture that the identity should hold if the problem is considered as a global one involving, as they said, all charges “of the universe”. A much more innocuous setting in which the problem can be framed, is the standard one of statistical mechanics, where reference is made to the “thermodynamic limit”. So we consider the microscopic current inside a domain of volume  $V$  (i.e., the “truncated” function  $j_V$  which coincides with  $j$  inside the domain and vanishes outside), and take the limit in which both the volume and the number of elementary charges constituting the current tend to infinity, in such a way that the charge density (number of charges per unit volume) remains constant.

Such a framing of the problem is immediately reflected in a deep mathematical property of the current, because for the current density one clearly has to give up any property of decrease at infinity, and one should assume for example only the property  $j^\nu \in L^\infty(\mathbb{R}^3)$ , i.e., that the density  $j^\nu(t, \mathbf{x})$  be only locally integrable. As a possible substitute for the global integrability condition there is one that quite naturally comes to one’s mind for its physical significance. Moreover, it is somehow analogous to what is sometimes called the locality condition of quantum field theory, although it rather appears to express a kind of causality condition. Precisely, we start up defining the autocorrelation of the current density  $j^\nu$  by

$$\mathcal{C}_{j^\nu}(s, t, \mathbf{x}) \stackrel{\text{def}}{=} \lim_{V \rightarrow \mathbb{R}^3} \frac{1}{V} \int_V j^\nu(s, \mathbf{y}) j^\nu(s + t, \mathbf{y} - \mathbf{x}) d\mathbf{y} , \quad (32)$$

where the symbol  $V$  denotes both the space region of integration and its (Lebesgue) measure. It is implicitly assumed that the average of  $j^\nu(t, \mathbf{x})$  over the whole space–time vanishes.

Now our global hypothesis reads as follows.

**Definition 1 (Causality Condition)** *A source  $j(t, \mathbf{x})$  satisfies the Causality Condition, iff 1)  $j \in L^\infty(\mathbb{R}^3)$ , 2) the correlation  $\mathcal{C}_j(s, t, \mathbf{x})$  exists for all  $s, t, \mathbf{x}$ , and 3) for all  $s$  one has*

$$\mathcal{C}_j(s, t, \mathbf{x}) = 0 \quad \text{for} \quad c^2 t^2 - \mathbf{x} \cdot \mathbf{x} \leq 0 . \quad (33)$$

In other terms we are assuming that there exists no correlation between space–separated points of space–time. This requirement is natural from the physical point of view, because one should assume that the interactions cannot propagate faster than light, so that it seems natural to assume that space separated events be independent.<sup>9</sup>

We now show that the above “causality condition” is sufficient to guarantee the validity of the identity. Indeed the following Theorem 1 holds:

**Theorem 1** *Consider the wave equation*

$$\square_2 A = j(t, \mathbf{x}) , \quad (34)$$

*having as source a current  $j(t, \mathbf{x})$  satisfying the Causality Condition 1. Let  $A_{ret}$  and  $A_{adv}$  be the retarded and the advanced solutions respectively. Then for all  $t$  one has*

$$\lim_{V \rightarrow \infty} \frac{1}{V} \int_V \left( A_{ret}(t, \mathbf{x}) - A_{adv}(t, \mathbf{x}) \right)^2 d\mathbf{x} = 0 . \quad (35)$$

This theorem states that for causal currents the retarded and advanced fields are almost equal, i.e., they differ at most on a set having zero relative measure.

To prove the theorem, let us start defining by  $j_V(t, \mathbf{x})$ , the “truncated” current, i.e. the function coinciding with  $j(t, \mathbf{x})$  inside  $V$ , and vanishing outside it. The wave equation (34) can be written in Fourier space (with respect to the spatial coordinates) as

$$\ddot{A}_{\mathbf{k}} + \omega_k^2 A_{\mathbf{k}} = \hat{j}_V(t, \mathbf{k}) ,$$

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<sup>9</sup>We do not discuss here whether this is active or passive locality in the sense of Nelson [35].

where  $\omega_k = c|\mathbf{k}|$ , whereas  $\hat{j}_V(t, \mathbf{k})$  is the space Fourier transform of the truncated current. The retarded and advanced solutions are then given by

$$\begin{aligned} A_{\mathbf{k}}^{ret} &= \int_{-\infty}^t \frac{\sin \omega_k(t-s)}{\omega_k} \hat{j}_V(t, \mathbf{k}) ds \\ A_{\mathbf{k}}^{adv} &= - \int_t^{\infty} \frac{\sin \omega_k(t-s)}{\omega_k} \hat{j}_V(t, \mathbf{k}) ds , \end{aligned}$$

so that one gets

$$A_{\mathbf{k}}^{ret} - A_{\mathbf{k}}^{adv} = \frac{1}{2i\omega_k} \left( e^{i\omega_k t} \hat{j}_V(-\omega_k, \mathbf{k}) - e^{-i\omega_k t} \hat{j}_V(\omega_k, \mathbf{k}) \right) ,$$

where  $\hat{j}_V(\omega, \mathbf{k})$  is the Fourier transform, with respect to time, of  $\hat{j}_V(t, \mathbf{k})$ . Now one uses the Plancherel theorem, which states

$$\int_{\mathbb{R}^3} \left| A^{ret}(t, \mathbf{x}) - A^{adv}(t, \mathbf{x}) \right|^2 d\mathbf{x} = \int_{\mathbb{R}^3} \left| A_{\mathbf{k}}^{ret} - A_{\mathbf{k}}^{adv} \right|^2 d\mathbf{k} , \quad (36)$$

to get (use  $2|\mathbf{a} \cdot \mathbf{b}| \leq a^2 + b^2$ )

$$\begin{aligned} & \int_{\mathbb{R}^3} \left| A^{ret}(t, \mathbf{x}) - A^{adv}(t, \mathbf{x}) \right|^2 d\mathbf{x} \\ & \leq \int_{\mathbb{R}^3} \frac{1}{2\omega_k^2} \left( |j_V(-\omega_k, \mathbf{k})|^2 + |j_V(\omega_k, \mathbf{k})|^2 \right) d\mathbf{k} \\ & = \frac{1}{2c^2} \int \left( |j_V(-ck, \mathbf{k})|^2 + |j_V(ck, \mathbf{k})|^2 \right) dk d\Omega , \end{aligned} \quad (37)$$

where  $d\Omega$  is the surface element on the unit sphere in the  $\mathbf{k}$  space. We now use the causal property of the current. In fact one has the following theorem, which will be proven below:

**Theorem 2** *If  $j(t, \mathbf{x})$  is a causal current in the sense of Definition 1, then one has*

$$\lim_{V \rightarrow +\infty} \frac{1}{V} \int_{\mathcal{C}} |\hat{j}_V(\omega, \mathbf{k})|^2 d\Omega dR = 0 , \quad (38)$$

on each circular cone  $\mathcal{C} \stackrel{\text{def}}{=} \{|\omega| = \alpha|\mathbf{k}|, \alpha \geq c\}$ , where  $d\Omega$  is the surface element on the unit sphere in the  $\mathbf{k}$  space, while  $dR$  runs along the cone generatrix.

So, dividing relation (37) by  $V$ , using (38) with  $\alpha = c$  and taking the limit, one gets (35).

As a comment, one may add that from (36) it is rather easily seen that the validity almost everywhere of the Wheeler–Feynman identity implies the vanishing of the “spectrum of the current”, i.e. of the limit of  $|\hat{j}_V(\omega, \mathbf{k})|^2/V$ , on almost the whole light cone  $\omega^2 = c^2 \mathbf{k} \cdot \mathbf{k}$ .

So, the problem of proving the Wheeler–Feynman identity is reduced to proving formula (38) of theorem 2. To this end, we start defining the function

$$K_V(t, \mathbf{x}) \stackrel{\text{def}}{=} \int j_V(s, \mathbf{y}) j_V(s+t, \mathbf{y} + \mathbf{x}) ds d\mathbf{y} , \quad (39)$$

which, apart from the factor  $1/V$ , is nothing but the correlation of the truncated current, integrated over  $s$ , as one would naturally do in defining correlations for functions having domain in space–time. One then immediately sees that:

- one has

$$\lim_{V \rightarrow +\infty} \frac{1}{V} K_V(t, \mathbf{x}) = 0 , \quad \text{if } c^2 t^2 - \mathbf{x} \cdot \mathbf{x} \leq 0 \quad (40)$$

- the Fourier transform  $\hat{K}_V(\omega, \mathbf{k})$  of  $K_V(t, \mathbf{x})$  coincides with  $|\hat{j}_V(\omega, \mathbf{k})|^2$ .

Indeed the first property is just a translation of the fact that  $j_V(t, \mathbf{x})$  is causal, i.e., that (33) holds, whereas the second one is nothing but the “faltung” theorem on the Fourier transform of a convolution.

Now, considering the spherical mean of the spectrum  $|\hat{j}_V(\omega, \mathbf{k})|^2$ , one gets

$$\begin{aligned} \int_{S_2} |\hat{j}_V(\omega, \mathbf{k})|^2 d\Omega &= \frac{1}{\pi^2} \int dt d\mathbf{x} K_V(t, \mathbf{x}) \int_{S_2} e^{i(\omega t + \mathbf{k} \cdot \mathbf{x})} d\Omega \\ &= \frac{2}{\pi} \int dt d\mathbf{x} K_V(t, \mathbf{x}) \int_0^\pi e^{i(\omega t + kr \cos \vartheta)} \sin \vartheta d\vartheta \\ &= \frac{2}{\pi^2} \int dt dr r \frac{e^{i(\omega t + kr)} - e^{i(\omega t - kr)}}{ik} \int_{S_2} K_V(t, \mathbf{x}) d\Omega \\ &= \frac{2}{\pi} \int dt dr r \tilde{K}_V(t, r) \frac{e^{i(\omega t + kr)} - e^{i(\omega t - kr)}}{ik} , \end{aligned} \quad (41)$$

where  $\tilde{K}_V(t, r)$  is the spherical mean of  $K_V(t, \mathbf{x})$ . Now, if one makes use of the of parity property of the correlation  $K_V(t, \mathbf{x}) = K_V(-t, -\mathbf{x})$ , which

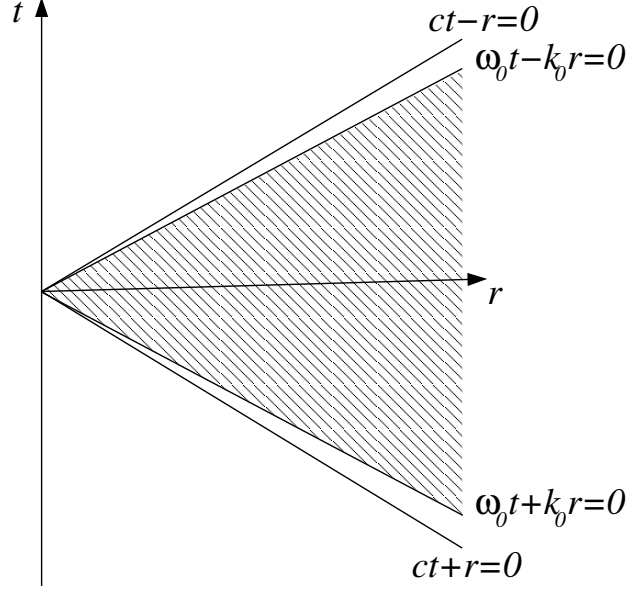


Figure 3: The domain  $\mathcal{D}$  of integration in formula (43).

easily follows from the very definition (39), one finds that the spherical mean  $\tilde{K}_V(t, r)$  is an even function of time, so that the imaginary part of the integral in the last line of (41) vanishes, and one gets

$$\int_{S_2} |\hat{j}_V(\omega, \mathbf{k})|^2 d\Omega = \frac{2}{\pi} \int dt dr r \tilde{K}_V(t, r) \left[ \frac{\sin(\omega t + kr)}{k} - \frac{\sin(\omega t - kr)}{k} \right]. \quad (42)$$

Consider now “a ray” in the momentum  $(\omega, \mathbf{k})$  space, i.e. all vectors of the form  $(R\omega_0, R\mathbf{k}_0)$ ,  $R > 0$ , and integrate relation (42) along this ray: one gets

$$\int_0^\infty dR \int_{S_2} |\hat{j}_V(R\omega_0, R\mathbf{k}_0)|^2 d\Omega = \frac{2}{\pi} \int dt dr r \tilde{K}_V(t, r) \frac{1}{k_0} \left[ \int_0^\infty dR \frac{\sin(R(\omega_0 t + k_0 r))}{R} - \int_0^\infty dR \frac{\sin(R(\omega_0 t - k_0 r))}{R} \right].$$

Now using the relation

$$\int_0^\infty dR \frac{\sin \alpha R}{R} = \begin{cases} \frac{\pi}{2} & \text{if } \alpha > 0 \\ 0 & \text{if } \alpha = 0 \\ -\frac{\pi}{2} & \text{if } \alpha < 0, \end{cases}$$

one gets

$$\int_0^\infty dR \int_{S_2} |\hat{j}_V(R\omega_0, R\mathbf{k}_0)|^2 d\Omega = 2 \int_{\mathcal{D}(\omega_0, k_0)} dt dr r \tilde{K}_V(t, r) \quad (43)$$

where the domain  $\mathcal{D}(\omega_0, k_0)$  (depicted in figure 3) is the domain in the half-plane  $r > 0$ , bounded by the two half-lines  $\omega_0 t \pm k_0 r = 0$ . Now, dividing by  $V$  and taking the limit, the integral is seen to vanish if  $\omega_0^2 - k_0^2 \geq 0$ . In fact, by the causality property (40), in that limit  $\tilde{K}_V(t, r)/V$  vanishes for all points inside the region bounded by the lines  $ct \pm r = 0$ , i.e., in particular, for all points of  $\mathcal{D}(\omega_0, k_0)$ . So (38) holds and Theorem 1 is proven.

## Use of the identity in canceling the radiation reaction forces

In their paper [4], Wheeler and Feynman showed how the condition

$$A_{ret}^\mu - A_{adv}^\mu = 0$$

implies the vanishing of the radiation reaction force (or self force) acting on each charge. One starts from the relativistic equation of motion for the charge

$$m\ddot{q}^\mu = f_{mec}^\mu + \tilde{F}_{ret}^{\mu\nu} \dot{q}_\nu + \frac{2e^2}{3c^3} \left( \ddot{q}^\mu + \dot{q}^\nu \dot{q}_\nu \dot{q}^\mu \right),$$

where  $m$  and  $e$  are the charge and the mass of the particle, dots represent derivatives with respect to proper time, repeated index means summation (Einstein convention),  $f_{mech}^\mu$  is a four-force of mechanical (non electromagnetic) type, while  $\tilde{F}_{ret}^{\mu\nu}$  is the retarded electromagnetic field due to all other

charges, evaluated at the four-position  $q^\mu$  of the considered charge, and finally the term  $\frac{2e^2}{3c^3}(\ddot{q}^\mu + \ddot{q}^\nu \ddot{q}_\nu \dot{q}^\mu)$  is the relativistic expression for the radiation reaction force.

The electromagnetic field  $\tilde{F}_{ret}^{\mu\nu}$ , or rather the field  $\tilde{F}_{ret,\mu\nu}$ , is defined as

$$\tilde{F}_{ret,\mu\nu} = \sum \left( \partial_\mu A_{ret,\nu}^k - \partial_\nu A_{ret,\mu}^k \right),$$

where  $A_{ret,\nu}^k$  is the retarded field produced by the  $k$ -th charge, and the summation is extended over all charges but the considered one. The field  $\tilde{F}_{ret,\mu,\nu}$  can be rewritten in a more useful form as

$$\begin{aligned} \tilde{F}_{ret,\mu\nu} &= \sum \left( \partial_\mu \frac{A_{ret,\nu}^k + A_{adv,\nu}^k}{2} - \partial_\nu \frac{A_{ret,\mu}^k + A_{adv,\mu}^k}{2} \right) \\ &+ \sum \left( \partial_\mu \frac{A_{ret,\nu}^k - A_{adv,\nu}^k}{2} - \partial_\nu \frac{A_{ret,\mu}^k - A_{adv,\mu}^k}{2} \right), \end{aligned}$$

because, as we will show below, the Wheeler–Feynman identity implies that

$$\begin{aligned} \sum \left( \partial_\mu \frac{A_{ret,\nu}^k - A_{adv,\nu}^k}{2} - \partial_\nu \frac{A_{ret,\mu}^k - A_{adv,\mu}^k}{2} \right) &= \\ - \frac{2e^2}{3c^3} \left( \ddot{q}^\mu - \ddot{q}^\nu \ddot{q}_\nu \dot{q}^\mu \right), & \end{aligned} \quad (44)$$

so that the equations of motion, at the end, can be written as

$$m\ddot{q}^\mu = f_{mec}^\mu + \frac{\tilde{F}_{ret}^{\mu\nu} + \tilde{F}_{adv}^{\mu\nu}}{2} \dot{q}_\nu$$

with

$$\begin{aligned} \frac{\tilde{F}_{ret,\mu\nu} + \tilde{F}_{adv,\mu\nu}}{2} &= \\ \sum \left( \partial_\mu \frac{A_{ret,\nu}^k + A_{adv,\nu}^k}{2} - \partial_\nu \frac{A_{ret,\mu}^k + A_{adv,\mu}^k}{2} \right). & \end{aligned}$$

The new form of the equations of motion clearly shows that they are indeed reversible and the radiation reaction has disappeared. So, such a force cannot be held responsible for the emission.

To show how relation (44) follows from the Wheeler–Feynman identity, one first has to notice that such an identity states that one has

$$A_{\mu,ret} - A_{\mu,adv} = \sum_{\text{all}} (A_{ret,\mu}^k - A_{adv,\mu}^k) = 0,$$



where the sum is extended to all charges. Thus, at all points  $x^\mu \neq q^\mu$  (i.e., at all points different from the four-position of the considered charge) one has

$$\sum_{\text{all}} \left( \partial_\mu \frac{A_{ret,\nu}^k - A_{adv,\nu}^k}{2} - \partial_\nu \frac{A_{ret,\mu}^k - A_{adv,\mu}^k}{2} \right) = 0, \quad (45)$$

because the vanishing of the potentials implies the vanishing of their derivatives. Now, it was shown by Dirac (see [30]) that for the field  $\frac{A_{ret,\mu}^j - A_{adv,\mu}^j}{2}$  created by the particle  $q^\mu$  itself one has

$$\lim_{x^\mu \rightarrow q^\mu} \left( \partial_\mu \frac{A_{ret,\nu}^j - A_{adv,\nu}^j}{2} - \partial_\nu \frac{A_{ret,\mu}^j - A_{adv,\mu}^j}{2} \right) \dot{q}^\mu = \frac{2e^2}{3c^3} \left( \ddot{q}^\mu + \ddot{q}^\nu \ddot{q}_\nu \dot{q}^\mu \right),$$

while on the other hand the remaining fields are regular at  $q^\mu$ . So taking the limit of the previous relation (45) for  $x^\mu \rightarrow q^\mu$ , one gets (44).

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