A replacement of the Lorentz law for the shape of the spectral lines in the infrared region

A. Carati        A.M. Maiocchi

November 18, 2015

Abstract

We propose a new phenomenological law for the shape of the spectral lines in the infrared, which accounts for the exponential decay of the extinction coefficient in the high frequency region, observed in many spectra. We apply this law to the measured infrared spectra of LiF, NaCl and MgF$_2$, finding a good agreement, over a wide range of frequencies.

1 Introduction

At a phenomenological level, the experimental data for the complex susceptibility $\chi(\omega)$ are fitted by taking for each line a contribution of the form

$$\hat{\chi}(\omega) = \frac{\omega_0 A}{\omega^2 - \omega_0^2 + 2i\gamma\omega},$$

(1)

where $\omega_0$ is the line frequency, $\gamma$ is related to its width and $A$ to its intensity. This formula was originally obtained by thinking of each line as corresponding to a “physical” microscopic dipole oscillating with frequency $\omega_0$ and with a damping characterized by the constant $\gamma$. In the literature this is often referred to as the “Lorentz model”. However, some difficulties arise in connection with the imaginary part of the complex susceptibility, which, in the transparency region of dielectrics, dictates the behavior of the extinction coefficient $\kappa$.

In fact, it is known since the seventies that for dielectrics, in the region of high transparency, the Lorentz formula (1) provides for the

\[\text{Re} \chi = n^2 - \kappa^2 - 1 \quad \text{and} \quad 4\pi \text{Im} \chi = 2n\kappa.\]

As is well known, the susceptibility $\chi$ is related to the extinction coefficient $\kappa$ and the refractive index $n$ by $4\pi \text{Re} \chi = n^2 - \kappa^2 - 1$ and $4\pi \text{Im} \chi = 2n\kappa$. So, in the region in which the dielectric is transparent, i.e., where $n$ is approximately constant, the behavior of $\text{Im} \chi$ determines the behavior of $\kappa$. 

1
extinction coefficient not only a too large value (by orders of magnitude), but also a qualitatively incorrect behavior.

Indeed, relation (1) gives, for the imaginary part,

$$\text{Im } \hat{\chi}(\omega) = \frac{2\gamma_0 \omega A}{(\omega^2 - \omega_0^2)^2 + 4\gamma^2 \omega^2},$$

which reduces to the well known Lorentz formula

$$\text{Im } \hat{\chi}(\omega) \simeq \frac{\gamma A / 2}{(\omega - \omega_0)^2 + \gamma^2},$$

for frequencies near the absorption peak, \(\omega \simeq \omega_0\). So, formula (2) predicts that the extinction coefficient decreases as \(\omega^{-3}\) for large \(\omega\), whereas, in the transparency region, i.e., for \(\omega \neq \omega_0\), the measured values of the extinction coefficient (see [1, 2]) exhibit a decay which is exponential rather than as an inverse power of \(\omega\). In the literature (see [3, 4]) one finds involved ab initio computations which reproduce quite well the experimental findings, but a simple general reason for the observed behavior is lacking.

In this paper we propose an explanation of the observed exponential decay of the extinction coefficient, as due to the fact that the time auto-correlation of polarization should be an analytic function of time. We also propose a simple phenomenological formula which should be substituted for the Lorentz one, in order to describe the exponential decay of the experimental data. Such a formula involves the asymptotic (in time) behavior of the time auto-correlation of polarization, as described below.

In Section 2 the theoretical argument is presented and the corresponding proposed formula is given. In Section 3 a quantitative check of the proposed formula is performed, by fitting the experimental data for three dielectrics (LiF, NaCl, MgF\(_2\)) over a very large interval of frequencies in the infrared region. In the last Section 4 some comments are added, in particular concerning the relaxation of the correlations of polarization.

## 2 The susceptibility according to linear response theory

In modern terms, the Lorentz law (1) can be justified through linear response theory as follows. The susceptibility is nothing but the Fourier transform of
the time correlation of polarization. In formulæ, one has

\[ \hat{\chi}(\omega) = \frac{V}{4\pi k_B T} \int_0^{+\infty} e^{-i\omega t} \langle P(0) \dot{P}(t) \rangle \, dt, \quad (4) \]

where \( P(t) \) is the system polarization and the brackets denote a suitable average (for example the canonical one). Now, the classical formula (1) is obtained simply by integration if one supposes that the correlation decays exponentially for \( t \to +\infty \) as a damped sinusoid, i.e., as proportional to

\[ \langle P(0) \dot{P}(t) \rangle \propto -\sin \omega_0 t e^{-\gamma t}. \]

However, if at first sight such expression for the correlation can appear physically sound, one has to recall that the correlation \( \langle P(0) \dot{P}(t) \rangle \) is an odd function of time (because it is the derivative of the correlation \( \langle P(0) P(t) \rangle \), which has to be even). Thus the correct expression should rather be

\[ \langle P(0) \dot{P}(t) \rangle \propto -\sin \omega_0 t e^{-\gamma |t|}, \quad (5) \]

which is not an analytic function of time, due to the presence of \(|t|\) in the argument of the exponential.

This rather abstract remark immediately implies that the imaginary part of susceptibility, and thus the extinction coefficient, cannot decay exponentially if the correlation has the form (5). In fact, from (4) one has

\[ \text{Im} \hat{\chi}(\omega) = -\frac{1}{2} \frac{V}{4\pi k_B T} \int_{\mathbb{R}} \sin \omega t \langle P(0) \dot{P}(t) \rangle \, dt, \]

which shows that the extinction coefficient decays exponentially if and only if \( \langle P(0) \dot{P}(t) \rangle \) is analytic as a function of time.

On the other hand, there is no reason for the appearance of a singularity at \( t = 0 \) in the expression of the correlation, and it seems instead natural to suppose that \( \langle P(0) \dot{P}(t) \rangle \) should be taken as an analytic function. So the problem is now reduced to finding a simple analytic function which is odd and decays exponentially. One should however take into account the fact that \( \langle P(0) \dot{P}(t) \rangle \) is a correlation, in particular the derivative of the time auto–correlation \( \langle P(0) P(t) \rangle \), which is a positive–definite function (in the sense of Bochner, see [3], p. 17). This apparently abstract mathematical requirement in particular implies that the extinction coefficient be positive at all frequencies\(^3\); a very sound physical constraint indeed.

\(^2\)We are here considering isotropic systems, otherwise a susceptibility tensor should be considered, and the formulæ should be changed accordingly.

\(^3\)In fact, since \( \langle P(0) P(t) \rangle \) is positive–definite, one has

\[ \langle P(0) P(t) \rangle = \int_{\mathbb{R}} d\omega \alpha(\omega) \cos(\omega t), \]
Figure 1: Real part of the Laplace transform of the function at the r.h.s. of (6) computed numerically (circles), together with the real part of the Lorentz expression for $\hat{\chi}$ as given in (9), solid line. Here the relevant parameters are $\omega_0 = 0.0818$, $\gamma = 8.01 \cdot 10^{-4}$, $\Omega = 0.082$, $\Gamma = 4.58 \cdot 10^{-4}$.

The simplest choice, in our opinion, is to take

$$\langle P(0) \dot{P}(t) \rangle \propto -\frac{\sin \omega_0 t}{\cosh \gamma t} ,$$

which satisfies all the requirements. It is then an easy task to compute the imaginary part of $\hat{\chi}(\omega)$ through the residue theorem, and one finds

$$\text{Im} \hat{\chi}(\omega) \propto \frac{1}{\gamma} \left( \text{sech} \left( \frac{\pi (\omega - \omega_0)}{2\gamma} \right) - \text{sech} \left( \frac{\pi (\omega + \omega_0)}{2\gamma} \right) \right) ,$$

As can be easily checked, this expression gives an exponential decay at high frequencies, while reducing to a Lorentzian for $\omega$ near $\omega_0$.  

with $\alpha(\omega) \geq 0$, $\forall \omega \in \mathbb{R}$, in virtue of Bochner theorem. Then,

$$\langle P(0) \dot{P}(t) \rangle = -\int_\mathbb{R} d\omega \omega \alpha(\omega) \sin(\omega t) ,$$

so that $\text{Im} \hat{\chi}(\omega) = A \omega \alpha(\omega)$ with a suitable constant $A > 0$, and so $\text{Im} \hat{\chi}$ is positive for...
Figure 2: Real (left) and imaginary (right) parts of susceptibility versus frequency for a LiF crystal. Circles are experimental data taken from [7]. Solid lines represent real and imaginary parts of the fitting function (10), with constants chosen as in Table 1 and $\chi_\infty = 7.64 \cdot 10^{-2}$, as given by [8].

It is instead impossible to find a close expression for the real part of $\hat{\chi}(\omega)$. However some approximating expansions can be found, starting from the expansions (see [6], p. 191) for the Laplace transform of the hyperbolic secant

$$\mathcal{L}(s) \overset{\text{def}}{=} \int_0^{+\infty} \frac{e^{-st}}{\cosh t} \, dt = 2 \sum_{k=0}^{\infty} \frac{(-1)^k}{s + 2k + 1} = \frac{1}{s + \frac{1}{s + \frac{4}{s + \frac{9}{\ldots}}}}. \quad (8)$$

The first expansion at the r.h.s. should be used for small $s$, i.e., near the peak, while for larger values of $s$ the continued fraction expansion should be $\omega \geq 0$.

One has to recall that $\text{sech} x \overset{\text{def}}{=} \frac{1}{\cosh x} \simeq (1 + x^2/2)^{-1}$ for $x \simeq 0$. Obviously we are in the case in which the line width is much smaller than the frequency of the peak, so that at most one of the terms is non-negligible in expression (7).
used. On the other hand one can check by inspecting Figure I that a good approximation for the real part of susceptibility is given by

$$\text{Re} \hat{\chi}(\omega) \simeq \Omega A' \frac{\Omega^2 - \omega^2}{(\Omega^2 - \omega^2)^2 + 4\Gamma^2\omega^2}$$  \hspace{1cm} (9)$$

with suitably chosen constants $A'$, $\Omega$ and $\Gamma$. In particular $\Omega$ is very close to $\omega_0$, while $\Gamma$ turns out to be smaller than $\gamma$.

So we propose that formula (7) should be used in place of (2) in fitting the experimental data for the imaginary part of $\hat{\chi}$, which are those actually obtained from the experimental values of $n$ and $\kappa$. As an example, we have selected three relevant cases of ionic crystals, and show below that good fits are obtained. Moreover, the parameters entering the fit provide a good approximation also for the real part of susceptibility, as expected.
Table 1: Fitting constants for the function (10), for the three selected substances.

| Substance | \( A_k \) | \( \omega_k \) | \( \gamma_k \) |
|-----------|------------|----------------|-------------|
| LiF       |            |                |             |
| NaCl      |            |                |             |
| MgF\(_2\) |            |                |             |

3 Fit of the susceptibilities of selected crystals

We present here, for three selected elements, the fits of the real and the imaginary parts of susceptibility for three much studied ionic crystals, i.e., LiF, NaCl and MgF\(_2\). As, in general, several lines could be present, we choose to fit the data with the following function

\[
\hat{\chi}(\omega) = \hat{\chi}_\infty + \sum_{k=1}^{N} A_k \left[ \mathcal{L} \left( i \frac{\omega + \omega_k}{\gamma_k} \right) - \mathcal{L} \left( i \frac{\omega - \omega_k}{\gamma_k} \right) \right],
\]

(10)

where \( i \) is the imaginary unit, \( N \) is the number of terms that should be chosen in order to match the experimental data, \( \mathcal{L}(\cdot) \) is the function defined in (8), while \( \hat{\chi}_\infty \) is the electronic contribution to susceptibility which, in the infrared region, just reduces to a real constant. The values of the parameters we found are summarized in Table 1, while in Figures 2–4 we plot both the experimental data and the curves found.

For what concerns the experimental data, we recall that only the values of \( n \) and \( \kappa \), and not those of the complex susceptibility \( \hat{\chi} \), are usually reported in the literature (see [7] and the references therein). Thus, the complex susceptibility has to be recovered from the tabulated values of \( n \) and \( \kappa \): this is simple if, for a given frequency, the values of both \( n \) and \( \kappa \) are tabulated.
Figure 4: Real (left) and imaginary (right) parts of susceptibility versus frequency for the ordinary ray in a MgF$_2$ crystal. Circles are experimental data taken from [7]. Solid lines represent real and imaginary parts of the fitting function (10), with constants chosen as in Table 1 and $\tilde{\chi}_\infty = 7.08 \cdot 10^{-2}$.

(see footnote 1). As this is not always the case in the region where $n$ is almost constant, we estimated the refractive index $n$ by linear interpolation when needed.

Two remarks are in order: the first one is that our procedure to determine the parameters, which involves only the imaginary part of susceptibility given by expression (7), was just that of trial and error. In other terms, we find by hands some values of the parameters which, in our opinion, give acceptable fits for the experimental data over a large range of values of $\tilde{\chi}$ (nine orders of magnitude). No procedure of error minimization, nor any statistical test, are used to check the quality of the fit. This in particular implies that also the number of terms $N$ in the sum is taken in a sense in an arbitrary way. This point will be discussed below. The data of the real part of susceptibility, which do not enter the fit, are then used for determining the constant $\tilde{\chi}_\infty$.

The second remark is that most of the “experimental data” in the region of the “peaks”, are not experimental at all, because in such a region neither the extinction coefficient nor the refractive index can be actually measured. They
are actually inferred from other measured quantities (such as the reflectivity) assuming that susceptibility can be described in a fairly good way by the Lorentz model. This is particularly evident in Figure 2 in which two sets of data are present in the region between 800 cm$^{-1}$ and 1000 cm$^{-1}$. The set of values which presents an exponential decay corresponds to the directly measured values of $\kappa$, while the other one contains the values which are inferred from reflectivity measurements.

In view of these two remarks, we expect that the overall accuracy of the fits would be improved if a reprocessing were performed of the experimental data, in the spectral region where the extinction coefficient and the refractive index are not directly measurable.

4 A final Comment

We discuss here the problem of the number $N$ of terms to be used in the expression (10) for the fit of the imaginary part of susceptibility. Naively, one might expect $N$ to be equal to the number of most “evident” lines, but actually a larger number of terms is needed: in particular (as shown by Table 1) five terms are needed to match the data for LiF, six for NaCl and seven for MgF$_2$. For example, in order to have a good global fit three different terms have to be associated to the LiF line at 307 cm$^{-1}$, all with the same frequency, but with three well different damping constants. Something analogous occurs for the NaCl line at about 160 cm$^{-1}$ and for the MgF$_2$ line at about 245 cm$^{-1}$, for which several terms of very near frequencies are needed, with however different values of $\gamma$.

This can be interpreted by saying that several time–scales are involved in the decay of the relevant correlations, so that the relaxation of the correlations is a much more complicated process than just a simple exponential decay.

This is a well known fact in other fields, for example in glasses (see [9]), or in relaxation spectroscopy (see for example [10]), which involve the behavior of susceptibility at low frequencies (in the micro-waves region), where continuous distributions of relaxation times are actually used. So our result could be read as a hint that, also in the infrared region, the process of the decay of correlations is a complicated one. And indeed, the numerical evidence in some cases seems to support this view. We refer to computations performed by us in the case of a one component model of plasma, see [11], and of a model of LiF crystal, see [12].

5 In any case, more work is needed to
Acknowledgments. We thank prof. L. Galgani for thorough discussions and for his invaluable help in correcting the manuscript.

References

[1] G. Rupprecht, Phys. Rev. Lett. 12, 580 (1964).
[2] T.F. Deutsch, J. Phys. Chem. Solids 34, 2091 (1973).
[3] M. Sparks, L.J. Sham, Phys Rev. B 9, 827 (1974).
[4] M. Sparks, L.J. Sham, Phys Rev. B 8, 3037 (1973).
[5] W. Rudin, Fourier Analysis on groups, Wiley–Interscience, New Jersey, 1990.
[6] S. Khrushchev, Orthogonal Polynomials and Continued Fractions, Encyclopedia of Mathematics and Its Application 122, Cambridge University Press, Cambridge, 2008.
[7] E. Palik, Handbook of optical constants of solids (Academic Press, Amsterdam, 1998).
[8] A. Kachare, G. Andermann, L.R. Brantley, J. Phys. Chem. Solids 33, 467 (1972).
[9] M.D. Ediger, C.A. Angell, S.R. Nagel, J. Phys. Chem. 100, 13200 (1996).
[10] L. A. Dissado, R. M. Hill, Proc. Roy. Soc. A 390, 131 (1983).
[11] A. Carati, F. Benfenati, A. Maiocchi, L. Galgani, Chaos 24, 013118 (2014).
[12] F. Gangemi, A. Carati, L. Galgani, R. Gangemi, A. Maiocchi, Eur. Phys. Lett. 110, 47003 (2015).

---

of time, but an example of such a plot can be found at the following URL: http://fangemi.unibs.it/LiF_results/avg-corr_na4096-T300_10sim.png