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# Validity of Lorentz–Lorenz equation in porosimetry studies

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ABSTRACT

Ellipsometric porosimetry is a valuable tool to determine gas loading of porous materials. Usually the Lorentz–Lorenz effective medium theory is used, instead of the more accurate Bruggeman theory. In contrast to Lorentz–Lorenz, the Bruggeman model requires detailed knowledge on the constituents of the porous material. A first order perturbation of both effective medium approximations is used to analyze the difference between these models. Similar results are only found for materials with 70% porosity. Below 50% porosity, the gas load is underestimated with the Lorentz–Lorenz model. For porous silica and alumina with 50% porosity, the use of Lorentz–Lorenz leads to a systematic error of 18% of the load capacity.



## 1. Introduction

In ellipsometric porosimetry the loading of a porous host material with a guest material (a gas or liquid) is studied, for example the $CO_2$ sorption of a silica membrane [1]. In this technique the change of the dielectric function upon loading is measured. From this change, the amount of guest molecules in the host material or the material's porosity can be calculated. To do these calculations, the effect of the relative presence of the host and guest material dielectric function has to be evaluated from an effective medium approximation (EMA).

Usually a Lorentz–Lorenz (also referred to as Clausius–Mossotti) approach is used, instead of a generally more accurate Bruggeman approach [2–4]. The reason for this lies in the often unknown dielectric properties of the constituents of the porous material. For example, porous silica can often not be represented as a mixture of silicon oxide and voids due to the presence of many hydrogen bonds. The SiOH material leads to a higher dielectric function than quartz [1].

If the guest material has a small dielectric constant, which is usually the case for a dilute gas, the loading of the host material will result in a small change in the total dielectric function. This means that it's expected to be possible to describe the change by a first order perturbation. This linearization is done for both effective medium theories in this article and the result is compared. A significant deviation between the two is found for low porous materials.

## 2. Effective medium approaches

### 2.1. Lorentz–Lorenz

The Lorentz–Lorenz equation is derived from the Clausius–Mossotti relation, which relates the dielectric constant of spherical particles with their density $N$ and their polarizability $\alpha$ [8,9]. In SI units it is:

$$\frac{\langle\varepsilon\rangle-1}{\langle\varepsilon\rangle+2}=\frac{N\alpha}{3\varepsilon_0} \tag{1}$$

For a mixture of several materials with polarizability $\alpha_i$ and density $N_i$, the contributions of the individual components are counted up to give the effective dielectric function $\langle\varepsilon\rangle$ of the mixture. This approach was originally derived by Lorentz and Lorenz to describe the optical properties of a gas, a case in which the single molecules are well separated, and do not interact.

$$\frac{\langle\varepsilon\rangle-1}{\langle\varepsilon\rangle+2}=\frac{1}{3\varepsilon_0}\sum_i N_i\alpha_i \tag{2}$$

A linearization for a dilute gas ($\varepsilon_g\approx 1$) simplifies the expression to [8]:

$$\varepsilon_g=1+\frac{N_g\alpha_g}{\varepsilon_0} \tag{3}$$

For a porous material with dielectric function $\varepsilon_m$ and porosity $f$, the Lorentz–Lorenz is often used to describe the change in dielectric constant through the insertion of a gas with polarizability $\alpha_g$ into the pores. The gas is assumed to fill all pore volume homogeneously, and its density $N_g$ is increased upon loading. Eq. (2) can be adapted for the two components, the solid material, and the added gas to give the Lorentz–Lorenz equation [5–7]:

$$\frac{\langle\varepsilon\rangle-1}{\langle\varepsilon\rangle+2}=(1-f)\frac{\varepsilon_m-1}{\varepsilon_m+2}+f\frac{\varepsilon_g-1}{\varepsilon_g+2} \tag{4}$$

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Since the density in this system can be much higher than for a gas, the assumption of well separated and non-interacting molecules is not fulfilled in this approach, stretching the validity of the equation.

Eq. (4) can be rearranged to give the total dielectric function $\langle\varepsilon\rangle$:

$$\langle\varepsilon\rangle = \frac{2f\varepsilon_g + \varepsilon_g\varepsilon_m - 2f\varepsilon_m + 2\varepsilon_m}{\varepsilon_g + f\left(\varepsilon_m - \varepsilon_g\right) + 2} \tag{5}$$

### 2.2. Bruggeman effective medium approximation

Bruggeman calculated in his famous article [2] the dielectric constants for mixed media of different dimensionality and topology. Usually his result for media made up of spheres of two materials is called the Bruggeman approach and is probably the most common EMA used in ellipsometry. By integrating the Rayleigh mixing formula for two components Bruggeman calculated the expression for the dielectric constant $\langle\varepsilon\rangle$.

Adapted for the case of a host material with spherical pores which are filled with guest molecules of density $N_g$, the effective dielectric constant $\langle\varepsilon\rangle$ is given by:

$$0 = (1-f)\frac{\varepsilon_m - \langle\varepsilon\rangle}{\varepsilon_m + 2\langle\varepsilon\rangle} + f\frac{\varepsilon_g - \langle\varepsilon\rangle}{\varepsilon_g + 2\langle\varepsilon\rangle} \tag{6}$$

Fig. 1 shows the solutions for a material with dielectric constant $\varepsilon_m = 2.1$ and different porosities as a function of guest permittivity $\varepsilon_g$ for the Lorentz-Lorenz and Bruggeman equation. Especially for guests with a small $\varepsilon_g$, i.e. a very dilute gas, and a porosity of 10% to 60% both approaches differ. This signifies that the choice between Lorentz–Lorenz and Bruggeman in ellipsometric porosimetry is in this region significant for the obtained result. Because the Bruggeman approach is regarded to be the more accurate one, the use of the Lorentz–Lorenz approach leads to a systematic error.

## 3. Linearization of the EMA

If the dielectric constant of the guest material is small, the loading is expected to result in a small change of the dielectric constant. This guest material could be for example a dilute gas. To estimate the change of the dielectric constant it is therefore sufficient to describe it by a first order perturbation. According to Eq. (3) the change is expected to depend on the polarizability $\alpha_g$ and the guest density $N_g$. If the dielectric constant of the empty host material is $\langle\varepsilon\rangle_0$, the change upon gas loading is expressed by a term $\delta\varepsilon$:

$$\langle\varepsilon\rangle = \langle\varepsilon\rangle_0 + \delta\varepsilon = \langle\varepsilon\rangle_0 + C\frac{fN_g\alpha_g}{\varepsilon_0} \tag{7}$$

Where the product $fN_g$ is the guest molecule density inside the pores. The linearization coefficient $C$ depends on the effective medium approach employed. For the Bruggeman and Lorentz–Lorenz approach the coefficients $C_B$ and $C_L$ are respectively (see Appendix for derivation):

$$C_B = \frac{1}{f}\frac{(3f-1)\langle\varepsilon\rangle_0 + \varepsilon_m}{2\langle\varepsilon\rangle_0 + \frac{\varepsilon_m}{\langle\varepsilon\rangle}} \tag{8}$$

$$C_L = \frac{(\langle\varepsilon\rangle_0 + 2)^2}{9} \tag{9}$$

Note that for the Bruggeman approach both the porosity $f$ and the host material dielectric constant $\varepsilon_m$ are needed, quantities which are usually not known. On the other hand for the Lorentz–Lorenz approach, only the effective dielectric function of the empty, porous material is needed, which can be easily measured.

### 3.1. Validity of the linearizations

To test the validity of the linearizations, they were compared with the exact results for the parameters of a porous silica material ($\varepsilon_m = 2$, $f = 0.5$) loaded with a dilute gas ($\varepsilon_g = 1.001$), a dense gas ($\varepsilon_g = 1.1$) and a liquid ($\varepsilon_g = 1.8$).

The effective dielectric function is calculated as a function of the relative concentration $N_g/N_{full}$, which corresponds to an increasing guest density inside the pores.

Fig. 2 shows the comparison between the exact solution for the Lorentz-Lorenz approach and its linearization calculated with Eq. (9). While the linearization provides a good representation for the insertion of a dilute gas, the insertion of a denser gas or even of a liquid results in a substantial deviation between the linearized and the exact evaluation.

In Fig. 3 the exact and linearized results for the Bruggeman approach are presented, using the same parameters as in Fig. 2. The results show that the linearization gives a very good representation of the exact solution. Even for a very dense guest material ($\varepsilon_g = 1.8$) the linearization is still acceptable up to 50% relative concentration. Therefore, the loading of a porous material can be well described by the linearized version of Bruggeman's equation.

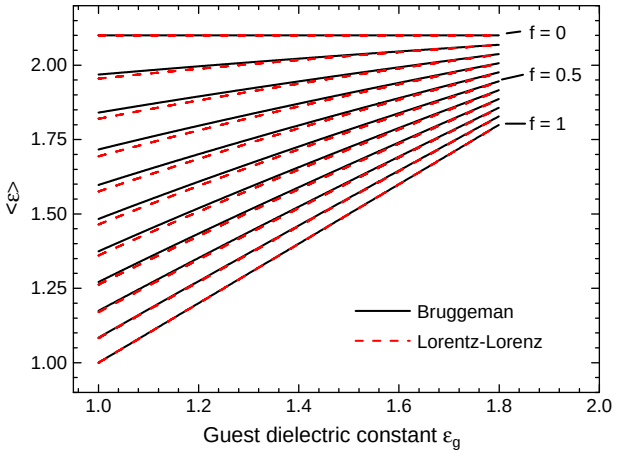


**Fig. 1.** Solution for the effective dielectric constant $\varepsilon$ as a function of $\varepsilon_g$ and for porosity f from 0 to 1 (line separation 0.1) for the Lorentz-Lorenz (dash) and Bruggeman (solid) equation. The host material has $\varepsilon_m = 2.1$.

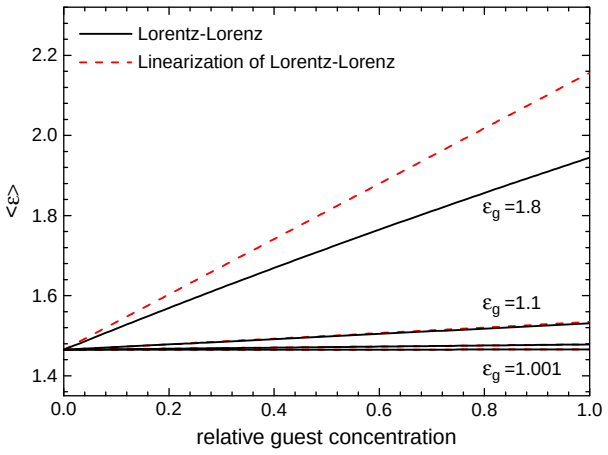


**Fig. 2.** Comparison of the exact and linearized solution for the Lorentz-Lorenz approach. Three different guest materials with $\varepsilon_g = 1.8$ (liquid), 1.1 and 1.001 (gas) are used.