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A priori calculation of the refractive index of some simple gas hydrates of structures I and II

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Abstract

This work aims at providing theoretical values of the refractive index of some gas hydrates using up-to-date physical data. Indices of refraction have been computed with a modified Lorenz–Lorentz model for a pressure between 2 and 15 MPa, a temperature between 0 and 12 °C and wavelengths in the extended visible domain. Given the prohibitive time required to perform the calculations with the standard procedure (up to 20 min for one P–T–λ set), we considered separately the crystalline structure and the molecules that occupy its sites. Thus, we obtain a series of tensors, characterising the sole structure, that we can easily use to get the refractive indices within less than 1 s. In this paper, all data are given to calculate the absolute or relative refractive index of any gas hydrate, provided the host gas polarisability is known. The numerical results are in agreement with experimental data.

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1. Introduction

Literature is abundant on gas hydrates, which give rise to a growing attention. The novice can safely refer to Sloan's book [1] for a detailed presentation of these crystals. Among the industrial contexts where they appear, we shall cite: hydrate plugs obstructing oil- or gas-pipelines, energy resources in form of methane hydrates trapped in permafrost or submarine sediments, natural gas transport in form of a slurry or gas separation by fractionated crystallisation.

The intelligent exploitation of hydrates in these contexts require a considerable amount of scientific data and the research efforts of many nations (United States, Russia, France, Germany, Great Britain, Japan and China, to cite the most active ones) greatly contribute to this goal. From this perspective, it seems to us that the knowledge of hydrates dielectric properties is a valuable tool, in particular for those who wish to measure the particle size distribution of hydrates in suspension via diffusion methods. Here, we need to cite the works of Melnikov et al. [2] and, previously, of Bylov and Rasmussen [3].

The structure of this document is following. We first develop the calculation method. The index of refraction is the convergence point of a macroscopic approach in terms of field and of a microscopic approach in terms of crystalline structure. We then present the experimental data we used to perform the calculations and, eventually the numerical results (absolute and relative refractive indices). Finally, we study the sensibility of the results and compare with experimental data available in the literature.

2. Calculation method

We will successively use two approaches to express the polarisation $\boldsymbol{P}$ as a function of the field $\boldsymbol{E}$. The first approach is macroscopic and utilizes the dielectric permittivity $[\epsilon]$ whereas the second one is microscopic. It utilizes the crystal molecular structure and superposition principle. This method is presented in numerous reference books (see, for instance, Durand [4] or Ashcroft and Mermin [5]) and was first

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applied to hydrates by Herri and Gruy [6]. The comparison of the two relationships that we will get provides a mean to express the dielectric permittivity as a function of the crystal structure.

2.1. Macroscopic approach

When we apply an electric field $\boldsymbol{E}_{\mathrm{A}}$ to a dielectric medium, this field creates a polarisation $\boldsymbol{P}$ which, in turn, produces a depolarising field $\boldsymbol{E}_{\mathrm{dep}}$ opposed to the applied field $\boldsymbol{E}_{\mathrm{A}}$. The total field $\boldsymbol{E}$ in the dielectric medium is the sum of the two fields:

$$\boldsymbol{E} = \boldsymbol{E}_{\mathrm{A}} + \boldsymbol{E}_{\mathrm{dep}} \tag{1}$$

The dielectric permittivity (or dielectric constant) may be defined by the following relationship between polarisation and electric field:

$$\boldsymbol{P} = \frac{[\epsilon] - I}{4\pi}\boldsymbol{E} \tag{2}$$

2.2. Microscopic approach

2.2.1. Expression of the local field

At a given time, the macroscopic field $\boldsymbol{E}$ at position $\boldsymbol{r}$ is the spatial average of $\boldsymbol{E}_{\boldsymbol{r}}^{\mathrm{micro}}$ on a sphere of radius r_0, centered around $\boldsymbol{r}$, and such that r_0 is small compared to the macroscopic length scale and big compared to characteristic atomic dimensions (intermolecular distances). The local field $\boldsymbol{E}_{\boldsymbol{r}}^{\mathrm{loc}}$ at $\boldsymbol{r}$ is the existing field at $\boldsymbol{r}$ if we remove the atom at this place. To calculate it, we decompose the space into two zones: one sphere B of radius r_1 centered at $\boldsymbol{r}$ and the rest of the space $\overline{B}$. We could have taken a cube but the subsequent calculations would have been more complicated. The radius r_1 is small compared to the crystal size and big compared to r_0. With this decomposition, we get:

$$\boldsymbol{E}^{\mathrm{loc}} = \boldsymbol{E}_{\overline{B}}^{\mathrm{loc}} + \boldsymbol{E}_{B}^{\mathrm{loc}} \tag{3}$$

Since r_1 is big compared to r_0, $\boldsymbol{E}_{\overline{B}}^{\mathrm{loc}}$ may be approximated by the average of the microscopic electric field existing out of the sphere B, i.e., by the macroscopic field $\boldsymbol{E}_{\overline{B}}^{\mathrm{macro}}$. Moreover, the macroscopic field $\boldsymbol{E}$ may be decomposed in:

$$\boldsymbol{E} = \boldsymbol{E}_{B}^{\mathrm{macro}} + \boldsymbol{E}_{\overline{B}}^{\mathrm{macro}}$$

where $\boldsymbol{E}_{B}^{\mathrm{macro}}$ is the macroscopic field that would exist if there were only the charges in B (included the atom at $\boldsymbol{r}$). Thus, Eq. (3) becomes:

$$\boldsymbol{E}^{\mathrm{loc}} = (\boldsymbol{E} - \boldsymbol{E}_{B}^{\mathrm{macro}}) + \boldsymbol{E}_{B}^{\mathrm{loc}}$$

Given the previous decomposition of the macroscopic field $\boldsymbol{E}$, we finally get:

$$\boldsymbol{E}^{\mathrm{loc}} = \boldsymbol{E}_{\mathrm{A}} + \boldsymbol{E}_{\mathrm{dep}} - \boldsymbol{E}_{B}^{\mathrm{macro}} + \boldsymbol{E}_{B}^{\mathrm{loc}}$$

2.2.2. Geometrical simplifications

The hydrate particle is spherical, as well as the cavity that we have diged around the point. This is for sure an advantage since the field in a uniformly polarised sphere does not depend on its diameter and equals the Lorentz field. We can deduce that:

$$\boldsymbol{E}_{B}^{\mathrm{macro}} = \boldsymbol{E}_{\mathrm{dep}} = \frac{-4\pi}{3}\boldsymbol{P} \tag{4}$$

Thanks to this relationship, the equation of the local field can be simplified in:

$$\boldsymbol{E}^{\mathrm{loc}} = \boldsymbol{E}_{\mathrm{A}} + \boldsymbol{E}_{B}^{\mathrm{loc}} \tag{5}$$

2.2.3. Calculation of the field $\boldsymbol{E}_{B}^{\mathrm{loc}}$

The methane hydrate structure is such that water molecules are located on three types of crystallographic sites and gas molecules on two types of crystallographic sites. We now study the case where the center of the sphere B is a site of type k. For clear understanding, we replace the notation $\boldsymbol{E}_{B}^{\mathrm{loc}}$ by $\boldsymbol{E}_{B_k}^{\mathrm{loc}}$. The field $\boldsymbol{E}_{B_k}^{\mathrm{loc}}$ is the electric field created by the presence of water and gas molecules in the sphere B. We group together the contributions of molecules placed on a same type of site i:

$$\boldsymbol{E}_{B_k}^{\mathrm{loc}} = \sum_{i=1}^{5}\boldsymbol{Z}_i = \sum_{i=1}^{5}\sum_{j\in B}\boldsymbol{E}_{k,j(i)}$$

where $\boldsymbol{Z}_i$ is the sum of the fields $\boldsymbol{E}_{k,j(i)}$ created by the molecules $j(i)$ located on a site of type i. The electric field created on a site k by a dipole-molecule j located on a site i is:[1]

$$\boldsymbol{E}_{k,j(i)} = \frac{3(\boldsymbol{p}_i\boldsymbol{r}_{kj})\boldsymbol{r}_{kj} - \|\boldsymbol{r}_{kj}\|^2\boldsymbol{p}_i}{\|\boldsymbol{r}_{kj}\|^5}$$

with $\boldsymbol{r}_{kj} = \overrightarrow{\mathrm{KJ}} = \overrightarrow{\mathrm{OJ}} - \overrightarrow{\mathrm{OK}}$. To go further, we express the dipole moment of a molecule j located on a site of type i with its total polarisability α_i and the local field $\boldsymbol{E}_i^{\mathrm{loc}}$ that acts on it: $\boldsymbol{p}_i = \alpha_i \cdot \boldsymbol{E}_i^{\mathrm{loc}}$. Consequently, we get:

$$\boldsymbol{E}_{B_k}^{\mathrm{loc}} = \sum_{i=1}^{5}\sum_{j\in B}\alpha_i\frac{3(\boldsymbol{E}_i^{\mathrm{loc}}\boldsymbol{r}_{kj})\boldsymbol{r}_{kj} - \|\boldsymbol{r}_{kj}\|^2\boldsymbol{E}_i^{\mathrm{loc}}}{\|\boldsymbol{r}_{kj}\|^5}$$

Coming back to Eq. (5), we have $\boldsymbol{E}_k^{\mathrm{loc}} = \boldsymbol{E}_{\mathrm{A}} + \boldsymbol{E}_{B_k}^{\mathrm{loc}}$. In form of matrices, we have:

$$\boldsymbol{E}_k^{\mathrm{loc}} = \boldsymbol{E}_{\mathrm{A}} + \sum_{i=1}^{5}\alpha_i[W_{ki}]\boldsymbol{E}_i^{\mathrm{loc}} \tag{6}$$

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[1] Rigorously, we should utilize the index $j(i)$ instead of i when we write $\boldsymbol{p}_i$ and α_i, because the dipole moment and the polarisability do not depend on the site i but on the molecule j that occupies it. However, in hydrate, each site is occupied by only one type of molecule and, to keep it easy to read, we will use the compact writing.

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