

# Van der Waals interactions in systems involving gas hydrates

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## Abstract

The goal of this work is to quantify the Van der Waals interactions in systems involving gas hydrates. Gas hydrates are crystalline compounds that are often encountered in oil and gas industry, where they pose problems (pipeline plugging, etc.) and represent opportunities (energy resources, gas transport, etc.). We focus on methane hydrate, which is the most common one, and calculate its Hamaker constant. Two methods are used and lead to results in good agreement. The Hamaker, microscopic, approach gives a first estimate of the Hamaker constant of  $4.59 \times 10^{-21}$  J for the hydrate–water–hydrate system. The Lifshitz, macroscopic, method used in combination with the Kramers–Kronig relationship gives a value of  $8.25 \times 10^{-21}$  J. The Hamaker constant is also computed for three phases systems (gas hydrate clathrate and liquid water with ice, dodecane, quartz, sapphire, Teflon, metals). The interaction potential in different geometrical configurations is then calculated by a hybrid method and various cases of practical interest are studied.

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## 1. Introduction

### 1.1. Context

Gas hydrate clathrates are crystalline compounds composed of host gas molecules trapped in a lattice of water molecules. In industrial contexts, the host gas is commonly methane, ethane or carbon dioxide but clathrates may form with other gases like light alkanes (up to C<sub>4</sub>), hydrogen sulfide, dioxygen, dinitrogen and some rare gases (argon, neon, krypton, etc.). Literature is abundant on gas hydrates and 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 the Hamaker constant of systems involving gas hydrates is a key point, in particular, for those who wish to predict the agglomeration behaviour of these systems. Since we do not expect the Hamaker constant to depend too much from the host gas nature, we restrict our study to methane hydrates.

### 1.2. Interactions between molecules

As a short reminder, when electrostatic interactions are absent or negligible, molecular interactions are of two natures: the short range, repulsive interactions due to the non-overlapping electronic clouds and the long range, attractive interactions. Three of them are known and they all have a potential that varies as the inverse sixth power of the intermolecular distance. The orientation (or Keesom) interaction tends to correlate the relative orientation of two polar molecules. The induction (or Debye) interaction is observed between an apolar molecule and a polar molecule. The latter creates an electric field that induces a dipole moment on the apolar but polarisable molecule. Eventually, the dispersion (or London) interaction is observed between two apolar molecules and was first explained by Eissenschitz

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Table 1  
Contributions to the induction, orientation and dispersion interactions  
( $\times 10^{-79}$  J m<sup>6</sup>)

	$C_{\text{ind}}$	$C_{\text{orient}}$	$C_{\text{disp}}$	$C_{\text{total}}$
H <sub>2</sub> O–H <sub>2</sub> O	10	96	33	139
CH <sub>4</sub> –CH <sub>4</sub>	0	0	102	102
H <sub>2</sub> O–CH <sub>4</sub>	9	0	58	67

and London [2]. The time fluctuations of the electronic cloud density, produce a transient dipole moment, which average is zero. At every moment, however, this dipole moment generates an electric field that acts on the second molecule and induces a dipole moment.

### 1.3. Retardation effect

We should note the existence of a retardation effect of the dispersion interaction. When two apolar molecules are separated by a relatively long distance, the time required for the electric field to travel ( $t = 2L/c$ ) can become comparable to the fluctuation period of the dipole itself.<sup>1</sup> In this case, the field that comes back on the first molecule finds that the instantaneous dipole direction changed and produces a smaller attraction. Casimir and Polder [3] showed that the retardation effect is negligible for distances below  $\approx 10$  nm and that, for distances above  $\approx 100$  nm, this effect creates a dependence in  $-1/r^7$  instead of  $-1/r^6$ .

### 1.4. Van der Waals interaction potential

The Van der Waals interaction(s) is the generic name for the three attractive interactions. Its potential is the sum of the corresponding potentials

$$u(r) = -\frac{C}{r^6} \quad (1)$$

where  $C$  is the Van der Waals constant, positive and equal to the sum of the three contributions

$$C = \frac{1}{(4\pi\epsilon_0)^2} \left[ \frac{\mu_1^2 \mu_2^2}{3kT} + \alpha_1 \mu_2^2 + \alpha_2 \mu_1^2 + \frac{3\alpha_1 \alpha_2 h \nu_1 \nu_2}{2(\nu_1 + \nu_2)} \right] \quad (2)$$

Table 1 gives these constants for different pairs of molecules. Data are from Israelachvili [4].

## 2. Hamaker approach: theory

This Hamaker approach to calculate the interactions between macroscopic bodies is also known as the microscopic approach since it focuses at the molecular structure scale.

<sup>1</sup> The revolution time of the electron of the Bohr atom is equal to the inverse of the first ionisation frequency which is about  $3 \times 10^{15}$  s<sup>-1</sup>.

### 2.1. Hypothesis

In 1937, Hamaker [5] proposed a method to calculate the interaction force between two macroscopic bodies (1 and 2). He made two assumptions.

- The retardation effect of the dispersion interaction is neglected, whatever the distances are.
- The interaction potential between two molecules keeps the same form even if other molecules surround them. This is often called *additivity assumption*.

Hamaker used a potential in  $1/r^6$  to describe the Van der Waals interaction forces between two molecules and the expression (2) to calculate the Van der Waals constant  $C$ . Then, he summed up the pair-potentials between molecules in body (1) and molecules in body (2).

### 2.2. Interaction potential

The Hamaker method leads to expressions in form of a product of two functions  $A$  and  $f$ . The function  $f$  depends only on the shape of the bodies and on the separation distance  $d \geq 0$ . Table 2 gives this function for different geometries and for different separation distances (the plate width is noted  $e$ ). The function  $A$  is the Hamaker constant. Since we use the Hamaker method, we write “H” as superscript. We can estimate the interaction potential  $U$  by the expression

$$U_{(d)}^H = -A^H f_{(d,\text{geometry})} \quad (3)$$

Tadmor [7] proposes an expression for  $f$  in the case of two spherical shells, one spherical shell and a sphere as well as one spherical shell and a half-space. These expressions may be of interest, for example, in the case of water droplets undergoing crystallisation into hydrate.

For a sphere in a cylindrical pore, the work of Bhattacharjee and Sharma [8] reviews the existing calculation methods. Zeman and Wales [9] as well as Papadopoulos and Kuo [10] proposed numerical methods to solve this question. However, they require prohibitive computing time. Bhattacharjee and Sharma use the two Hamaker assumptions to simplify these expressions. They study the limiting case of a particle near the revolution axis and near the pore wall. This study is of major interest to evaluate the interaction potential between a particle and the wall of a porous medium. In the particular case of an infinite cylindrical pore containing a spherical particle near the wall, we have the following approximation

$$f_{(d,\text{geometry})} = \frac{\lambda^3}{3[(1 - \eta(1 - \lambda))^2 - \lambda^2] \sqrt{(1 - \eta(1 - \lambda))^2(1 + \eta(1 - \lambda)) - \lambda^2}}$$

where  $\lambda = \frac{R_{\text{pore}}}{R_{\text{particle}}}$  and  $\eta = \frac{r}{R_{\text{pore}} - R_{\text{particle}}}$  with  $R_{\text{pore}}$ ,  $R_{\text{particle}}$  and  $r$  representing, respectively, the pore radius, the particle

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