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CALCULATION OF HAMAKER CONSTANTS APPLIED TO THE DEPOSITION OF METALLIC OXIDE PARTICLES AT HIGH TEMPERATURE

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ABSTRACT

In pressurized water nuclear reactors, the deposition of particles is the cause of several technical problems as the fouling of the heat exchanger and the radioactive contamination of primary coolant circuit. The deposition of particles is due to several thermohydraulic or chemical processes. To model this phenomenon, the chemical interactions could be described by DLVO theory, where the total interaction between two surfaces is the sum of electrostatic forces and Van der Waals forces. In the fouling of pipes and heat exchanger, the intensity of Van der Waals forces depends on Hamaker constant of the system metal / water / metallic oxide. The calculation of an accurate value of this constant using the Lifshitz theory requires several parameters (UV-Vis-IR spectral data) whose published values are hardly documented at room temperature or high temperature. Several approximations to calculate the Hamaker constant with parameters more easily available in literature (refractive indexes, dielectric constants, Hamaker constants of individual materials, ...) have been evaluated, and the results have been compared with Lifshitz theory results at room temperature for several systems. A difference between a few percents to an order of magnitude has been found depending on the approximation. The influence of temperature has been also taken into account to propose a method to calculate an approximate value of Hamaker constant with materials and physical conditions found in pressurized water reactors.

INTRODUCTION

In pressurized water nuclear reactors, the deposition of particles is the cause of several technical problems such as the fouling of the heat exchanger and the radioactive contamination of primary coolant circuit. The deposition of particles is due to several thermohydraulic or chemical processes (Basset et al., 2000; Grandgeorge et al., 1998). To model this phenomenon, the chemical interactions could be described by DLVO theory, where the total interaction between two surfaces is the sum of electrostatic forces and Van der Waals forces (Israelachvili, 1992). In the fouling of pipes and heat exchanger, phenomena which are involved are the deposition of particles in suspension in water (metal oxides, carbonates,...) on the metal, or on the previously deposited particles (fouling layer). The electrostatic interactions have been studied in numerous works (Lefèvre et al., 2006; Lefèvre et al., 2008; Cerovic et al., 2009). The intensity of Van der Waals forces depends on Hamaker constant of the system metal / water / particles or deposited particles / water / particles, and on geometry of the system. For example, for sphere/plane interactions, the following formulas can be used for energy and force as a function of the distance between solids, d:

$$E_{VdW} = -\frac{A_{1W2}R}{6d} \tag{1a}$$

$$F_{VdW} = \frac{A_{1W2}R}{6d^2}$$
(1b)

where *R*, the radius of spherical particles, A_{1W2} , the Hamaker constant for the system solid 1/water/solid 2, *d*, the separation distance

The calculation of an accurate value of this constant using the Lifshitz theory requires several parameters whose published values are hardly documented at room temperature or high temperature (UV-Vis-IR spectral data). We have tested several approximations to calculate A_{1w3} with parameters more easily available in literature such as refractive indexes, dielectric constants, A_{ii} , The results have been compared with Lifshitz theory results at room temperature for several systems. The influence of temperature has been also taken into account to propose a method to calculate an approximate value of Hamaker constant.

RESULTS AND DISCUSSION

Calculations with Lifshitz theory

A rigorous approach to evaluate the Van der Waals interactions between materials through a medium was introduced by Lifshitz. It is based upon the fluctuations in the electromagnetic field between two macroscopic bodies, modified by the separating medium. The Hamaker constant was estimated from the frequency dependent dielectric properties of the components and can be expressed by the following equation (Israelachvili, 1992):

$$A_{132} = \frac{3}{2} kT \sum_{j=0}^{\infty} \left(\frac{\mathbf{e}_{1}(i\mathbf{n}_{j}) - \mathbf{e}_{3}(i\mathbf{n}_{j})}{\mathbf{e}_{1}(i\mathbf{n}_{j}) + \mathbf{e}_{3}(i\mathbf{n}_{j})} \right) \frac{\mathbf{e}_{2}(i\mathbf{n}_{j}) - \mathbf{e}_{1}(i\mathbf{n}_{j})}{\mathbf{e}_{2}(i\mathbf{n}_{j}) + \mathbf{e}_{1}(i\mathbf{n}_{j})} \right)$$
(2)

with $\mathbf{n}_{j} = j \frac{2\mathbf{p}kT}{\hbar}$ and the $\hat{}$ means that the j = 0 term is to

be multiplied by $\frac{1}{2}$. Several representations have been proposed for the function $e(in_j)$. From the knowledge of the refractive index and the absorption frequency of materials, the simplified expression (3) can be used (Israelachvili, 1992).

$$e(in) = 1 + \frac{n^2 - 1}{1 + \frac{n^2}{n_e^2}}$$
(3)

A more accurate representation using the numerical conversion of full spectra into forces was detailed by Parsegian (2006):

$$\boldsymbol{e}(\boldsymbol{i}\boldsymbol{n}) = 1 + \sum_{j} \frac{d_{j}}{1 + \boldsymbol{n}\boldsymbol{t}_{j}} + \sum_{j} \frac{f_{j}}{\boldsymbol{w}_{j} + \boldsymbol{g}_{j}\boldsymbol{n} + \boldsymbol{n}^{2}}$$
(4)

where d_j , t_j , f_j , w_j , and g_j are parameters illustrating the dielectric dispersion of the materials. In this work, this representation was used for water and copper with parameters listed in Parsegian (2006).

With the parameters listed in Table 1, the Hamaker constant was calculated by the sum for the 4000 first terms. 14 systems oxide 1 / water / oxide 2, whose the list of materials is detailed in Table 1, have been studied. This set was used to compare the accuracy of the two other simpler methods (Tabor-Winterton, and combining relations). These materials have mainly been chosen for the availability of the parameters used in calculations, and several ones can be found in industrial plants.

Table 1. Parameters for materials

Compound	n^{a}	n _e	ϵ_0^{a}	A ₁₁
		(10^{16} rad/s)		(10^{-20} J)
Silica ¹	1.448	2.03 ^a	3.82	6.5 ^{c,e}
Alumina ¹	1.753	2.00 ^a	10.1	15 ^{c,e}
BeO ²	1.708	2.11 ^a	7.18	14.5 ^b
CaCO ₃ ²	1.586	1.90 ^a	8.2	24 °
MgO ²	1.716	1.71 ^a	9.8	12.1 ^b
Quartz ²	1.536	2.03 ^a	4.29	8.5 °
$\operatorname{TiO_2}^2$	2.464	73.5 ^a	114	15 ^{c,e}
ZnO ²	1.91	89.5 ^a	11.8	9.2 ^{b,e}
$\operatorname{Fe_2O_3}^2$	3	53 ^f	25	25 ^g
Cu ²	_	-	10^{5}	40 ^h

References: ^a Bergström, 1997, ^b Rahaman, 2006, ^c Médout-Marère, 2000, ^e Rosenholm et al., 2008, ^f calculated from optical data by Kerker et al., 1979, ^g De Mesquita et al., 2003, ^h Israelachvili, 1992 (estimation). Subscripts (1 and 2) refer to Eq. (2).

Calculations using Tabor-Winterton assumption

The main drawback of the summation (2) is the availability of parameters used in the formula, mainly the absorption frequency. In absence of this value, the assumption that the absorption frequencies of the three media are the same leads to the Tabor-Winterton (TW) representation (Israelachvili, 1992) (Eq. (5)).

$$A_{132} \approx \frac{3}{4} kT \left(\frac{\boldsymbol{e}_{0,1} - \boldsymbol{e}_{0,3}}{\boldsymbol{e}_{0,1} + \boldsymbol{e}_{0,3}} \right) \left(\frac{\boldsymbol{e}_{0,2} - \boldsymbol{e}_{0,3}}{\boldsymbol{e}_{0,2} + \boldsymbol{e}_{0,3}} \right) + \frac{3h\boldsymbol{u}_{e}}{8\sqrt{2}} \frac{(n_{1}^{2} - n_{3}^{2})(n_{2}^{2} - n_{3}^{2})}{(n_{1}^{2} + n_{3}^{2})^{1/2} (n_{2}^{2} + n_{3}^{2})^{1/2} \left\{ (n_{1}^{2} + n_{3}^{2})^{1/2} + (n_{2}^{2} + n_{3}^{2})^{1/2} \right\}}$$
(5)

with $\mathbf{n}_{e} = 1.88 \times 10^{15}$ rad/s. The results of the calculations using formula (5) have been compared to the results of the Equation (2) (Fig. 1). Two series of data are present in the figure: half the values are very close to exact ones, since an overestimation is seen for another half. Thus, this method surprisingly fails for numerous systems. To understand the origin of the problem, it is useful to remember the main assumption of this method, i.e. the same absorption frequency for the three components. For the systems described here, the absorption frequency of each component is known, and the error between TW and exact formulas versus the difference between mean absorption frequency of components 1 and 2 and absorption frequency of water ($\mathbf{n}_{e,12}$) $-\mathbf{n}_{e,w}$). A correlation is clearly shown: the more erroneous is the initial assumption, the less accurate is the calculated value.





Fig. 1. (A) Comparison between values of Hamaker constants for several oxide / water /oxide calculated using summation (2) and TW representation (Eq. (5)). (B) Effect of $\mathbf{n}_{e,12} - \mathbf{n}_{e,w}$ on the difference found in calculations with the two equations.

Combining relations method

Another simple method was proposed to calculate A_{123} based upon the mean of individual contribution A_{jj} , using the following combining relation (CR) (Israelachvili, 1992):

$$A_{132} \approx (\sqrt{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{22}} - \sqrt{A_{33}})$$
(6)

The values of A_{ii} are available in literature for numerous solids (Table 1), and moreover the following relation allows calculating its value from the surface energy, **g**:

$$A_{jj} = \boldsymbol{g}_j \times 24 \boldsymbol{p} D_0^2 \approx 2.1 \times 10^{-21} \boldsymbol{g}_j \tag{7}$$

For water, A_{ww} is equaled to 3.7×10^{-20} J (Israelachvili, 1992). Israelachvili (1992) emphasized that "combining relations are applicable only when dispersion forces dominate (...), but break down when applied to media with high dielectric constants such as water". However, the formula (6) was used in several works on hydrous metal oxides systems (Sasaki et coll., 1994). Due to the simplicity of this calculation, it is interesting to evaluate the error, when comparing to the exact solution. The results obtained for several systems are illustrated in Fig. 2. Surprisingly, the values obtained for both methods are close, the formula (6)generally leading to lower values. It appears that such a method could be used for systems involving water, despite the warning of Israelachvili (1992). In fact, in the systems we have studied, the dispersion forces dominate, despite the presence of water. It is due to the high values of dielectric constants of metal oxides, whose difference with water is related to the intensity of non-dispersive forces (see Tabor-Winterton model), and dielectric constants far from water value. The error between values obtained with the CR formula and the summation formula was plotted versus a factor characterizing the relative intensity of non-dispersive forces, f_{nd} , expressed as the ratio between the difference of dielectric constants of water and materials and the difference of refractive indexes of water and materials:

$$f_{nd} = \frac{\left| \boldsymbol{e}_{0,12} - \boldsymbol{e}_{0,3} \right|}{\left| n_{12}^2 - n_3^2 \right|}$$
(8)

A correlation is clearly observed, all the more that the value calculated for the hexane/water/hexane system has been added (value corresponding to the highest f_{nd} in the Fig. 2B). In fact, this latter system is more usual in the field where such calculations were performed, which explains Israelachvili's recommendation.



Fig 2. (A) Comparison between values of Hamaker constants for several oxide / water /oxide calculated using summation (2) and combining relation (Eq. (6)). (B) Effect of relative intensity of non-dispersive forces on the difference found in calculations with the two equations.

Hamaker constants for the system metallic oxide / water / copper

Steam generators are built in metal (copper, inconel, titanium,...) and the first step of fouling can consist in deposition of metallic oxide or carbonate on this surface. For the approach using Van der Waals forces, metals have a peculiar behavior. Their dielectric constant is very large, or infinite, and the Eq. (3) does not apply, and can be replaced by:

$$\boldsymbol{e}(\boldsymbol{i}\boldsymbol{n}) = 1 + \frac{\boldsymbol{n}_e^2}{\boldsymbol{n}} \tag{9}$$

but the problem of available data for n_e remains. However, the Hamaker constant has been estimated for two metals

interacting across vacuum with this relation and a high value (about 40×10^{-20} J) comparing to non-conducting materials was obtained (Israelachvili, 1992). It would be interesting to know if the Van der Waals forces between a metal and a metallic oxide across water would be high too. To obtain a good estimation, the more accurate relation (4) was used for copper, since the parametric data have been published by Parsegian (2006). The calculation has been performed with the materials listed in Table 1, and the results are listed in Table 2. The values are higher than those obtained with only non-conductive materials (cf Fig. 2A), but by a small amount. For the copper / water / copper system, the value obtained with the numerical conversion of full spectra (Eq. 4) is lower than the roughly estimated value.

Table 2. Results of calculations for copper/water interfaces using summation (2).

Compound 1	$A_{1wCu} (10^{-20} J)$		
Silica	1.7		
Alumina	6.3		
BeO	6.0		
CaCO ₃	3.6		
MgO	4.9		
Quartz	3.1		
TiO ₂	6.5		
ZnO	3.3		
Fe ₂ O ₃	6.7		
Cu	11		

Effect of temperature on Hamaker constant

Steam generators are working at different temperatures generally higher than room temperature. In the calculations performed above, and for most of the results found in literature, the temperature is nevertheless close to 298 K. It is interesting to know the effect of the increasing of temperature on the value of Hamaker constant. The first step is to define the calculation method which can be used in this purpose. The exact summation and the CR formula need parameters whose values are not known as a function of temperature. Thus, the TW formula looks the better choice, since refractive indexes and dielectric constants of water and materials can be found in literature. The system MgO/water/alumina was used as an example, because the value obtained at room temperature is in good agreement with the exact solution. In TW representation (Eq. (5)), the temperature is explicitly included in the non-dispersive term, which would increase linearly with temperature. Implicitly, the Hamaker constant depends on temperature due to its influence on dielectric constants, refractive indexes and absorption frequency. The evolution of the dielectric constant and refractive index of water has been calculated following the International Association for the Properties of Water and Steam standard formulations (IAPWS, 1997a and 1997b, Holmgren, 2007). For solids, few data are available, but it appears that the increase of temperature from 25°C to 350°C has a low influence on

these parameters. Thus, studies on Ta₂O₅ have shown an increase of less than 0.1 for refractive index, and less than 3 for dielectric constant (Chandra et al., 2008). The effect of the temperature on absorption frequency is another ill-documented parameter and, as a first approximation, it has been considered as constant. It is worth noticing that, in absence of water, the Hamaker constant for alumina across vacuum was calculated from 300 to 1925 K and went from 14.5 J to 15.2 J at 800 K, then down to 12.5 J (Parsegian, 2006), confirming the weak effect of temperature on Van der Waals forces of solid materials. The calculation of Hamaker constant between 25°C and 350°C (highest temperature in PWR circuit) has been performed with only $e_{0.3}$ and n₃ depending on temperature (Table 3).

Table 3. Results of calculations for MgO/water/alumina system using TW representation.

T (°C)	e _{0,3}	n ₃	$A_{1w2} (10^{-20} J)$
25	78.47	1.333	4.0
100	55.57	1.319	4.3
200	34.77	1.286	5.0
300	20.15	1.234	6.1
350	13.05	1.187	7.3

An increase by a factor 2 was observed, mainly resulting from the decrease of refractive index. The non-dispersive term remains negligible, which eliminates the direct effect of temperature on the value of the Hamaker constant.

CONCLUSIONS

- 1. The calculation of Hamaker constants is needed when considering the deposition of particles onto the surfaces of heat exchangers using DLVO theory. Its accurate determination by the summation of frequency dependent dielectric properties of the components requires the knowledge of numerous parameters. This limitation could be avoided by the use of simplified approaches, as Tabor-Winterton or combining relations methods. With a set of systems of metallic oxides in water, Hamaker constants have been calculated using these three approaches, in order to evaluate the accuracy of the simplified method and to determine the limitation of their use. Moreover, application with heat exchangers, the in calculations of Hamaker constants have been made for several copper/water/metallic oxides systems using summation method, and the influence of temperature has been evaluated using TW method.
- 2. An overestimation of results obtained by calculations using TW approximation have been found, compared to the summation method, by an error up to 200%. It was shown that the error is due to the assumption that absorption frequency is the same for solids and water, which is wrong in several cases. The same comparison has been made

for the CR method, where lower values were found, up to an error of -35%. The error has been correlated with a factor characterizing the relative intensity of non-dispersive forces. The calculations using copper/water/metallic oxides systems have led to higher values than those found for nonconductive materials. Using some assumptions on the non-dependence of temperature on properties of solids, the Hamaker constant of the MgO/water/alumina has been calculated between 25 and 350°C, showing an increase by a factor around 2.

NOMENCLATURE

- A Hamaker constant, J
- D₀ Intermolecular distance
- h Planck constant
- k Bolzman constant
- n Refractive index
- T Temperature, K
- e_0 Dielectric constant
- *g* Surface energy (J/m^2)
- \mathbf{n}_{e} Absorption frequency in UV domain (rad/s)

Subscript

- 1 Component 1
- 2 Component 2
- 12 Mean value for components 1 and 2
- Cu Copper
- w Water

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