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Dispersion forces in cement suspensions

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Abstract

Dispersion forces, often also referred to as van der Waals forces, are the main cause for agglomeration of cement particles in concrete and of the poor resulting flow properties. To counter these forces and improve flow, dispersants are added. The balance of attractive and repulsive forces between cement particles has a profound impact on the flow of concrete.

This paper only addresses the attractive force which requires an evaluation of the Hamaker constant of cement phases. It presents an approximation that allows to estimate the magnitude of this force despite the lacking experimental data on the dielectric properties of cement phases.

Keywords: Dispersion; Rheology; Workability

1. Introduction

Concrete flow ability is enhanced by the addition of polymeric dispersants commonly referred to as superplasticizers in the cement literature [1,2]. The main effect of these chemical admixtures is to disperse the agglomerated cement particles [3–7]. Depending on the molecular architecture of the polymer, this dispersion can be expected to be predominantly due to steric hindrance or a combination of steric hindrance and electrostatic repulsion [5,6,8]. Based on the calculation of interparticle forces, it has been suggested that depletion interactions might also be important [5]. Other calculations, using a more complete examination of the frequencies of contact between particles of different sizes, together with a force balance between shear and interparticle interaction conclude that steric hindrance is sufficient [9]. Such approaches rely on interparticle force calculations that are dependent on the quality of the models and hypothesis implied. One of these involves an estimation of the Hamaker constant used in the calculation of the dispersion force. These can be found to vary between 4.55×10^{-20} J [4] and 1.68×10^{-21} J [6].

In addition to modifying interparticle forces, superplasticizers also affect the ongoing chemical reactions in the cement suspension [2,10]. This can also influence flow properties, and there is a debate about the relative importance of both mechanisms. This is particularly true for cases where specific combinations of cements and superplasticizers exhibit exceptionally poor rheological behavior. For the purpose of eliminating these incompatibilities or at least avoiding them, it is important to quantify the relative importance of both chemical reactions and dispersion, as well as the nature of the dispersion mechanism involved.

In this context, it is essential to evaluate the magnitude of the attractive interparticle force that causes cement particles to agglomerate in the first place. Even by simplifying the geometry of cement particles to spheres, it is currently impossible to carry out this calculation rigorously. The reason is that the dielectric properties of cement or even of the pure phases found in cement have not been characterized experimentally. As a result, investigators that have attempted to evaluate interparticle interactions in cement suspensions have always resorted to arbitrarily using the data of some other mineral.

In this paper, the rigorous continuum theory to calculate the dispersion force of a set of minerals with well-characterized dielectric properties is used. These minerals have been selected for suspected similar properties to the main phases of cement. It is shown that the nonretarded Hamaker constants of these minerals scale with their density in a way that is suggested by approximations made to the less elaborate microscopic theory. Furthermore, it is shown that normalized retardation is essentially the same

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for all these minerals. Consequently, it is possible to present what is believed to be a reliable approximation to the calculation of dispersion forces between cement particles. Further approximations that serve for calculating forces at close separations are also discussed in the light of obtaining simplified expressions for the maximum of the attractive force.

2. Background

Dispersion forces, also called van der Waals forces, "arise because local fluctuations in the polarization within one particle induce, via propagation of electromagnetic waves, a correlated response in the other" [11]. For two particles made of the same isotropic matter, this interaction is always attractive. The terminology "of dispersion forces" can therefore be somewhat confusing. In fact, it arises from the fact that the equations used to describe the phenomena are similar to those which describe light scattering (light dispersion). Between particles of different composition or different faces of anisotropic particles, these forces can become repulsive. Such situations might occur in cementitious systems but are beyond the scope of this paper.

The range of interparticle dispersion forces is much larger than that of the individual dipoles. This is because in condensed media, the fluctuations of dipoles are correlated. Mathematically, one can express the interaction by the summation of the interactions between all dipoles of the intervening particles. The way this summation has been performed has changed over the years, both as a result of a better physical description of the phenomena and of an increased ability to deal numerically with more complete formulations of the interaction.

In what follows, the essence of both the microscopic and continuum theory is presented so that the approach that leads to our approximation for the dispersion force between cement particles may be understandable by most readers. For a more detailed treatment of either of these theories, the reader is referred to the comprehensive treatment [11].

2.1. Microscopic theory

The microscopic theory was the first to lead to a description of the dispersion force between particles. It is based on a pairwise summation of interacting dipoles. The interaction reduces to the product of two terms: the Hamaker constant A and a geometric factor H. The Hamaker constant depends on the optical properties of the materials constituting both the particles and the intervening medium. The geometric factor accounts for the dependence on morphology, orientation, and separation of the interacting particles. In what follows, the description given is limited to the case of spherical particles with different radii. The interaction potential, Φ, of two spherical particles (i.e., the energy involved in bringing the surfaces of two particles of radius a_k and a_l from an infinite separation to a finite separation distance h) is given by:

$$\Phi = -AH_{(a_k,a_l,h)} \tag{1}$$

where:

$$H_{(a_k,a_l,h)} = \frac{1}{6}\left(\frac{2a_ka_l}{2(a_k+a_l)h+h^2} + \frac{2a_ka_l}{4a_ka_l+2(a_k+a_l)h+h^2} + \ln\left(\frac{2(a_k+a_l)h+h^2}{4a_ka_l+2(a_k+a_l)h+h^2}\right)\right) \tag{2}$$

In the microscopic description, the Hamaker constant is independent of separation distance and is determined as follows [11]:

$$A = \frac{3}{8}k_BT\sum_{m=0}^{\infty}{}'[N\alpha(i\xi_m) - \bar{N}\bar{\alpha}(i\xi_m)]^2 \tag{3}$$

where m is an integer between zero and infinity, the $'$ sign indicates that the zero frequency term has a prefactor of 1/2, N, $\bar{N}$, $\alpha(i\xi_m)$ and $\bar{\alpha}(i\xi_m)$ are the number density of molecules and their polarizability in the solid and the intervening fluid at the set of discrete imaginary frequencies for which:

$$\xi_m = m\frac{4\pi^2k_BT}{h}$$

where h is Planck's constant, k_B is Boltzman's constant, T is the absolute temperature.

The dispersion force is equal to the derivative with respect to separation distance of interaction potential.

$$F = -\frac{\partial\Phi}{\partial h} = A\frac{\partial H_{(a_k,a_l,h)}}{\partial h} \tag{4}$$

2.2. Continuum theory

2.2.1. Formulation

The continuum theory takes the microscopic theory a step further in describing dispersion forces. Instead of treating the interaction as a summation of individual dipole interactions, the continuum theory considers the fluctuating electromagnetic fields, which exist in each particle. These fields extend beyond their boundaries in the form of travelling waves and standing waves. Since the original treatment of the continuum theory by Lifshitz [12], it has been realized that standing waves alone suffice to quantify dispersion forces [13]. Another important step in simplifying the treatment of the continuum theory was made by Mahanty and Ninham Ref. [14, section 2.7] who showed that these interactions could be described by a discrete series of equally spaced imaginary frequencies instead of having to evaluate the interaction over the whole electromagnetic spectrum. This leaves the description of the interaction potential as a function of the normal modes associated with a particular geometry and of the specific dielectric properties of the materials (particles and intervening medium).

2.2.2. Geometry

The interaction between flat plates leads to an analytical solution, which can be expressed in a similar way as the result from the microscopic theory. However, in this case, the Hamaker constant is an effective Hamaker constant A_h, which depends also on the separation distance h. This distance dependence accounts for the fact that although correlation of the fluctuating dipoles takes place at the speed of light, it requires a finite time. With increasing separation, this time becomes comparable to the time scale of the fluctuations, leading to a lower correlation and a decrease in the effective Hamaker constant A_h. This effect is termed retardation.

For spheres, retardation is much more complex. Its adequate numerical description by Langbein [15] is renowned for its extremely slow convergence. Pailthorpe and Russel [16] have proposed an algorithm giving good precision for much less numerical effort. They express the dispersion potential in a similar way as for the microscopic theory, the product between the geometrical factor for spheres and an effective Hamaker constant. This effective Hamaker constant is calculated as follows:

$$A_h = \frac{3}{2} k_B T \sum_{m=1}^{\infty} \left(\frac{\xi_m}{\xi_C}\right)^2 \int_1^{\infty} dp\ p\ Ln \left[\left(1 - \left(\frac{S_1\varepsilon_0 - p\varepsilon_1}{S_1\varepsilon_0 + p\varepsilon_1}\right)^2 \exp\left(-\frac{\xi_m}{\xi_C}p\right)\right) \times \left(1 - \left(\frac{S_1 - p}{S_1 + p}\right)^2 \exp\left(-\frac{\xi_m}{\xi_C}p\right)\right)\right] \quad (5)$$

where $\xi_C = c/2h\sqrt{\varepsilon_0}$, ${S_1}^2 = p^2 - 1 + \varepsilon_1/\varepsilon_0$, $\varepsilon_j = \varepsilon_j(i\xi_m)$ is the dielectric response function of material j (0 for intervening fluid and 1 for particle matte), c is the speed of light, and h is the distance of closest contact between the spheres. Note that the dielectric permitivity ε of the material, introduced by the continuum theory, which is the analogue to the polarizability α of the molecule in the microscopic theory.

They tested this approach for equal spheres and found a good correlation with the full calculations using Langbein's [15] formulation. In what follows, the use of this approach is extended to the case of unequal spheres.

$$F = -\frac{\partial \Phi}{\partial h} = A_h \frac{\partial H_{(a_k, a_l, h)}}{\partial h} + H_{(a_k, a_l, h)} \frac{\partial A_h}{\partial h} \quad (6)$$

It should be pointed out that the dispersion interaction comprises a static term ($m = 0$) that is nonretarded (does not decrease with separation) and therefore is correctly calculated by simpler approaches. Furthermore, the static term is the only one effected by electrolytes and is completely screened beyond 1 debye length κ^{-1} given by:

$$\kappa^{-1} = \sqrt{\frac{\varepsilon\varepsilon_0 k_B T}{\sum_k e^2 z_k^2 n_k^b}} \quad (7)$$

where ε is the relative dielectric constant for water, n_k^b is the concentration of species k in the bulk, z_k is the charge of the species k, and e is the electronic charge.

This means that the only frequency that is unaffected by separation (static term) has no effect in this system because the presence of electrolytes completely screens its effect down to separations inferior to 1 nm. Consequently, the Hamaker constant evolution can be estimated without worrying about the static term. This is precisely what Eq. (5) does and makes it therefore particularly relevant to cement suspensions in which electrolyte concentrations are very high. For zero separation the Hamaker constant (non retarded) is most efficiently calculated (with or without screening) by the following below [16] than by Eq. (5):

$$A_{(0)} = \frac{3}{8} k_B T {\sum_{m=0}^{\infty}}' \sum_{s=1}^{\infty} \frac{\Delta^{2s}}{s^3} \quad (8)$$

where:

$$\Delta = \frac{\varepsilon(i\xi_m) - \bar{\varepsilon}(i\xi_m)}{\varepsilon(i\xi_m) + \bar{\varepsilon}(i\xi_m)} \quad (9)$$

2.3. Dielectric properties

One important part of the evaluation of the dispersion interaction is to obtain a valid description of the dielectric properties of the particles and of the intervening fluid. Roth and Lenhoff [18] recently questioned the validity of the generally accepted representation for the dielectric properties of water developed by Parsegian and Weiss [19]. They presented a presumably more accurate description based on a damped oscillator model. Using that model, Bergström [16] found, for Hamaker constant of many inorganic minerals, discrepancies of up to 40% with respect to previously published values. More recently, Dagastine et al. [20], using additional recent experimental data, computed what appears to be so far the best description of dielectric properties of water.[1] It has been used in this paper, though only minor discrepancies were found with respect to previously published results [5] using the model by from Roth and Lenhof [17]. Papers concerned with Hamaker constants in cementitious materials either use data for other minerals or provide obscure estimations predating the publication of reliable dielectric data of water.

More problematic than the accurateness of the description of the dielectric properties of water is the total absence

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[1] Data can be downloaded at http://www.cheme.cmu.edu/jcis/.

Table 1
Spectral characteristics of selected minerals [16] and their density

	Structure	C_{UV}	$\omega_{UV} \times 10^{16}$ (rad/s)	C_{IR}	$\omega_{IR} \times 10^{14}$ (rad/s)	Density (g/cm^3)
$CaCO_3$ (calcite)	Average[a]	1.516	1.897	5.7	2.691	2.71
α-Al_2O_3	Hexagonal	2.072	2.00	7.03	1	3.97
MgO	Cubic	1.946	1.71	6.85	1.0	3.60
SiO_2 (quartz)	Trigonal	1.359	2.032	1.93	2.093	2.65
SiO_2 (silica)	Amorphous	1.098	2.034	0.829	0.867	2.20
$MgAl_2O_4$	Cubic	1.887	1.87	5.41	1.0	3.55
Mica (muscovite)	Monoclinic	1.508	1.963	0.723	1.541	2.83

[a] Average of the different orientations for this mineral that is anisotropic.

of such data for the phases that constitute cement particles. In order to bypass this problem, one must at first resort to examining a set of minerals for which that data is available and which in addition can be expected to have some similarities (mainly based on atomic compositions) to the major pure cement phases found in cement. The minerals chosen for this purpose are amorphous silica, quartz, mica, spinel ($MgO{\cdot}Al_2O_3$), MgO, calcite and α-alumina. They were selected from a list of inorganic compounds of which Bergström [16] has discussed the behavior of dispersion forces. The spectral features of these minerals have less elaborate description than water and are well represented by:

$$\varepsilon(i\xi_m) = 1 + \frac{C_{IR}}{1+\left(\frac{\xi}{\omega_{IR}}\right)^2} + \frac{C_{UV}}{1+\left(\frac{\xi}{\omega_{UV}}\right)^2} \tag{10}$$

where $i\xi_m$ is the set of discrete imaginary frequencies given by $\xi_m = m((4\pi^2 k_B T)/h)$ (m being an integer), C_{IR} and C_{UV} are the absorption strengths (IR or UV), while ω_{IR} and ω_{UV} are the characteristic absorption frequencies (IR or UV). Values for the minerals considered are given in Table 1.

3. Results and discussion

3.1. Nonretarded Hamaker constants

Using either Eq. (5) or (8) together with Eq. (9), the nonretarded Hamaker constants (equivalent to zero separation) were calculated for the previously mentioned set of minerals (amorphous silica, quartz, mica, spinel ($MgO{\cdot}Al_2O_3$), MgO, and calcite). Their spectral data was taken from Table 1, while data for water was that of Dagastine et al. [20]. Results both for screened and unscreened Hamaker constants are plotted against the square of the density difference between the material and water. This choice is dictated by an approximation to the microscopic theory described below.

In the microscopic theory, the nonretarded Hamaker constant is obtained by summing the differences between the dielectric responses of the particle of the fluid according to Eq. (3) throughout the entire spectrum of frequencies. This interaction can be related to both of the number density of molecules N and their polarizability α as in Eq. (3).

For materials considered, it turns out that one may use the following analogy to that equation using:

$$A\alpha(\rho_{solid} - \rho_{liquid})^2 \tag{11}$$

Quite surprisingly in fact, this very simple scaling with the density difference shows a good correlation as indicated in Fig. 1. Thus, without attempting an explanation for why this scaling works so well for these materials, one can make use of it to estimate the Hamaker constants of cement phases.

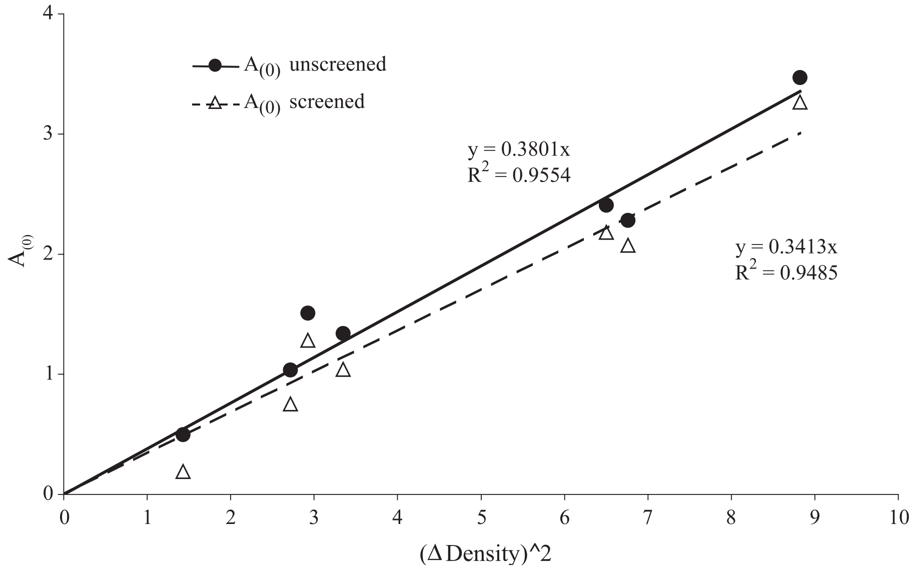


Fig. 1. Density-based estimation of nonretarded Hamaker constants for cementitious materials.

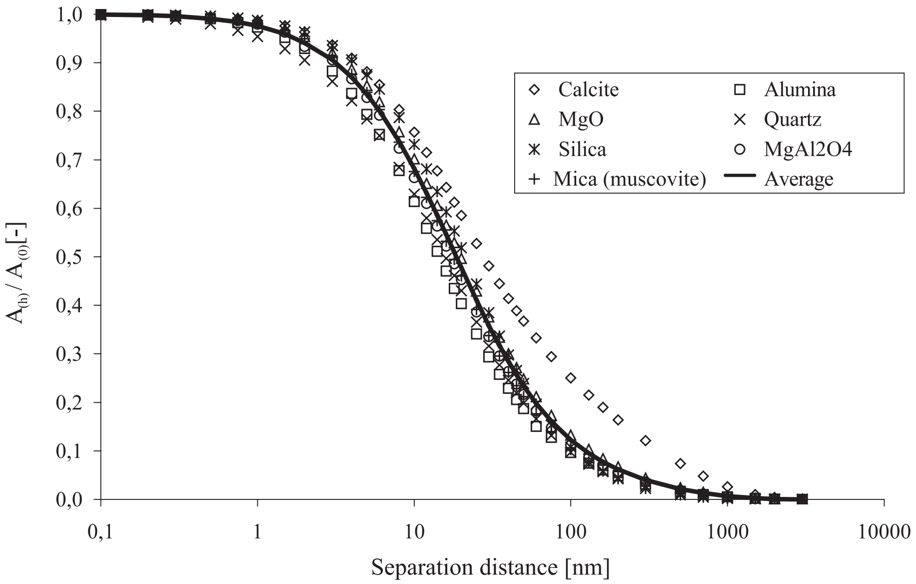


Fig. 2. Retardation of the screened Hamaker constants of the minerals used to estimate the behavior of cement.

For cement with a density of 3.15 g/cm^3, neglecting the static term (screened case) because of the high electrolyte concentration, the nonretarded Hamaker constant A (or zero separation Hamker constant, A_0) estimated from the regression parameters given in Fig. 1 would be about 1.6×10^{-20} J. The hydrated particles in the cement paste have a lower density of about 2.13 g/cm^3, the screened Hamaker constant would be estimated to be about 0.44×10^{-20} J.

3.2. Retarded Hamaker constants

In the continuum calculation, the Hamaker constant decreases with increasing separation distance. This has been calculated using by integrating Eq. (5) using an adaptive Romberg method. The same set of minerals was used and their spectral properties as well as those of water were the same as previously mentioned. Values normalized by the value at zero separation (A_0 or nonretarded Hamaker constant A) are plotted in Fig. 2. Apart from calcite, all curves exhibit an extremely similar behavior. Because of this, using the average of all these curves seems a reasonable way of estimating retardation between cement particles. In Fig. 3, the average data points, as well as a fitted function, are plotted. This function has no physical basis. It is a high-quality fit, which allows to reduce substantially the computational effort for obtaining retarded Hamaker constant as a function of separation distance. It is given by:

$$\frac{A_h}{A_0} = (m_1 h^2 + m_2 h + m_3)\exp(-m_4 h) + m_5 \exp(-m_6 h) \tag{12}$$

where m_{1-6} are fitting parameters given in Fig. 3.

In the continuum theory, the dispersion force acting is given by Eq. (6). In fact, it turns out that for spheres up to very large separations, the first term is much more important than the second. So the force can be written as:

$$F \cong A_h \frac{\partial H_{(a_k,a_l,h)}}{\partial h} \tag{13}$$

So that Eq. (4) is almost recovered, apart from the fact that the value of the Hamaker constant now depends on the particle–particle separation.

In cement suspensions, there is a monotonic increase in attraction force up to close contact. The maximum attractive force, which is relevant to yield stress calculations, therefore occurs at very small separations. Though the minimal separation can be increased by the presence of adsorbed polymers, values remain small. For small separations this gives:

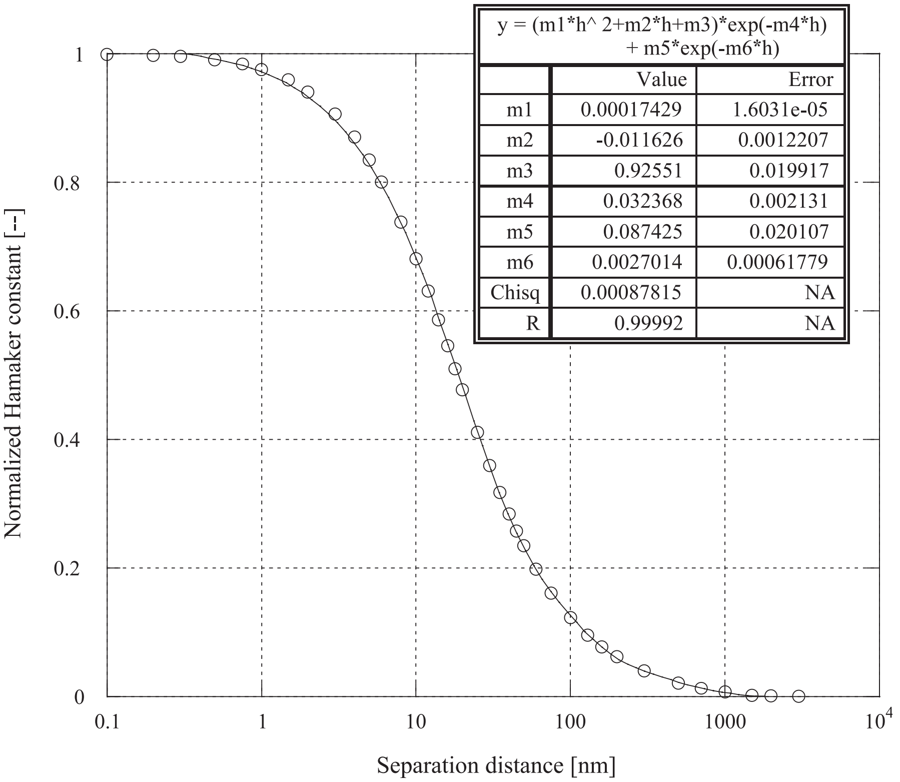
$$\frac{\partial H_{(a_k,a_l,h)}}{\partial h} \cong \frac{1}{6}\left(\frac{\bar{a}}{2h^2} + \frac{1}{2\bar{a}} - \frac{1}{h}\right) \tag{14}$$

where $\bar{a} = (2a_k a_l)/(a_k + a_l)$ is the harmonic average radius of the two interacting particles.

To evaluate the quality of this approximation, the separation distance below which Eq. (14) leads to a relative error inferior to 20% in a cement suspension where particle sizes would typically range from 0.4 to 100 μm in diameter is calculated. Results in Fig. 4 indicate that 20% accuracy is guarantied for separations below 70 nm.

At yet shorter separations, one obtains:

$$\frac{\partial H_{(a_k,a_l,h)}}{\partial h} \cong \frac{\bar{a}}{12h^2} \tag{15}$$



y = (m1*h^ 2+m2*h+m3)*exp(-m4*h)
+ m5*exp(-m6*h)

	Value	Error
m1	0.00017429	1.6031e-05
m2	-0.011626	0.0012207
m3	0.92551	0.019917
m4	0.032368	0.002131
m5	0.087425	0.020107
m6	0.0027014	0.00061779
Chisq	0.00087815	NA
R	0.99992	NA

Fig. 3. Average of normalized retardation and fitted curve.

The associated error is given in Fig. 5 as a function of the separation distance for the following cases:

- two particles of 0.4 μm diameter (typically the lower bound of cement particles)
- two of 10 μm diameter (mass average particle size)
- one 0.4 μm particle with one 10 μm particle.

For example, if a precision of 30% is required, the maximum interparticle force would have to occur at sepa-

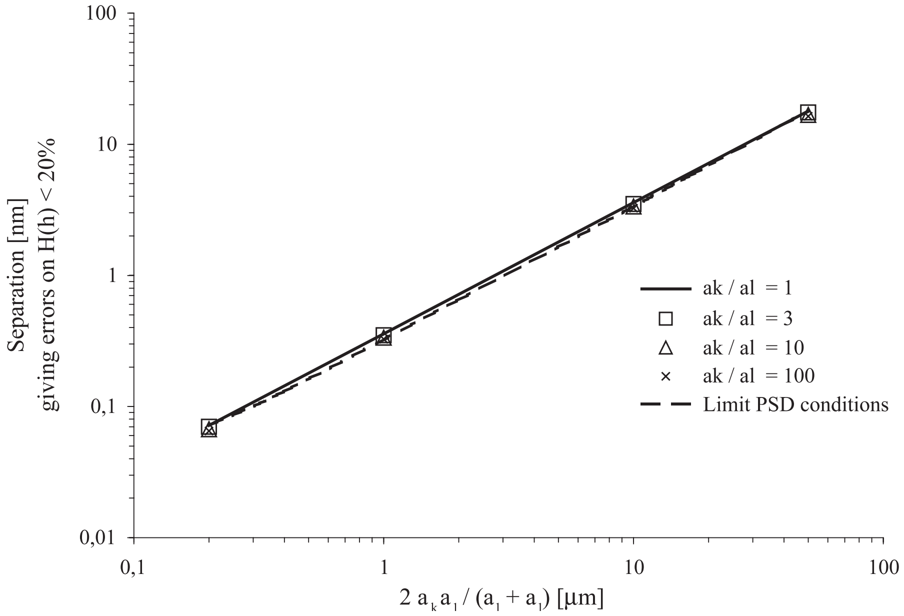


Fig. 4. Separation beyond which the approximation a_1, $a_2 >> h$ leads to errors larger than 20%. The various curves are for different ratios a_1/a_2. Note that errors are independent of the material considered.

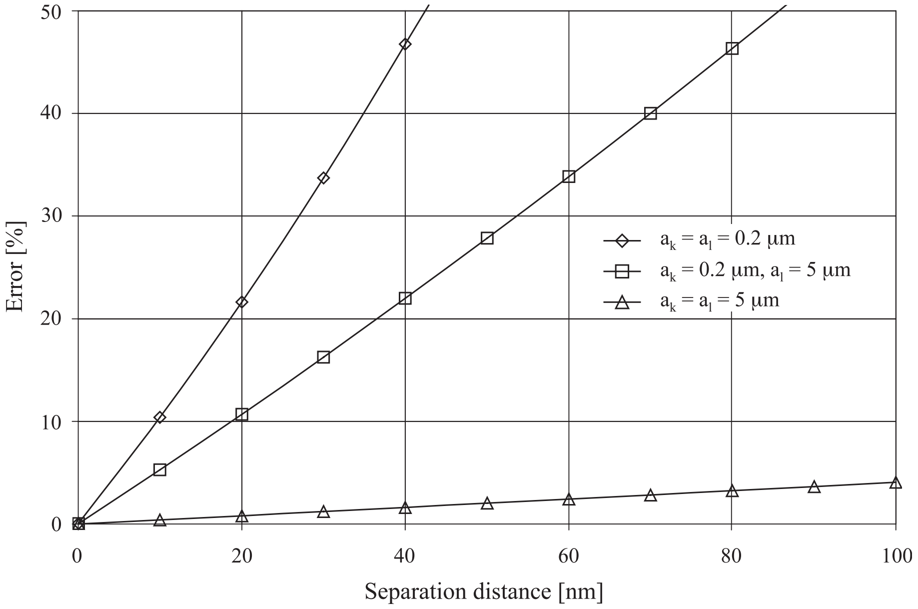


Fig. 5. Error induced by the approximation in Eq. (15).

rations smaller than 30 nm for the first case. It would correspond to the beginning of an interaction between two particles having an uncharged adsorbed polymer layer of 15-nm thickness. From the limited set of polymer studied by Sakai and Daimon [3], it appears that this is about the upper bound of dispersants considered for use in concrete. So Eq. (15) should provide a reliable estimation of the maximum dispersion force even between the smallest cement particles.

Using the separation distance of 30 nm, the importance of using the harmonic average radius, $\bar{a}$, rather than the arithmetic average radius, $\hat{a}=(a_k+a_l)/2$, of the interacting particles is evaluated. The ratio between the forces calculated in either case is independent of the Hamaker constant. Values are plotted in Fig. 6 for various size ratios between the intervening particles. It can be seen for example that for a size ratio of 10, calculating the dispersion force with the arithmetic average would give a result that would be off by a factor larger than 3.

3.3. Effect of hydration

In the proceeding sections, a correlation that allows to estimate the nonretarded Hamaker constant of cementitious materials interacting across water was first established.

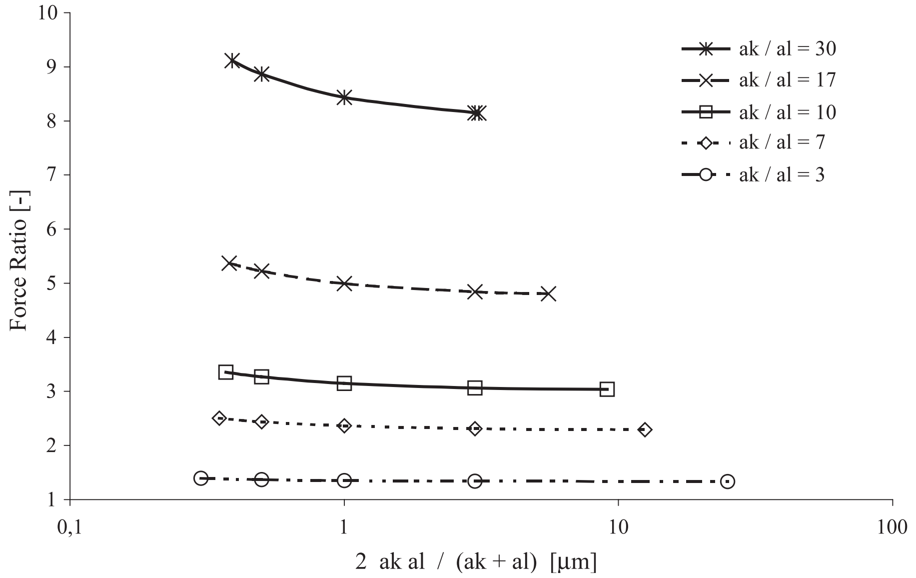


Fig. 6. Ratio between dispersion force evaluated with an arithmetic averaged radius $\hat{a}$ versus the force evaluated with the harmonic average radius $\bar{a}$. Limits are put for particles between 0.1 and 50 μm in radii.

Another function allows to determine the retardation (change with separation distance) of that constant. These calculations hold as well for unhydrated cement particles as for hydrates.

Approximations to the geometrical term were examined. They consider limits of the particle size distribution of most cements. For hydrate crystallites smaller than 0.4 μm, Eqs. (14) and (15) will only provide satisfactory approximations to Eq. (2) for smaller separation distances than discussed above, scaling approximately linearly with the ratio of the hydrate size to the smallest cement particle considered previously (0.4 μm).

The extent of hydration reached by cement during its workable period is low. Thus, it is not so much the volume of newly formed hydrated phase that might alter the initial interparticle forces rather than the location at which they form. The very first hydration reaction lead to the formation of a phase of ettringite-like composition, intermixed with calcium silicate hydrate at the surface of cement particles. The impact of this layer on the net dispersion interaction is now briefly examined.

The density of ettringite is about 1.4 g/cm^3, that of C-S-H with the nonstructural water is about 1.76 g cm^3, C-S-H crystallites are 2.43 g/cm^3, and C_3S is 3.15 g/cm^3. Thus, our approximation predicts that Hamaker constants for these phases are 0.055, 0.20, 0.70, and 1.6 J, respectively. There is a difference of a factor 30 between ettringite and C_3S. Thus, it is essential to identify which constant is most appropriate. Unfortunately, to the author's knowledge, there is only a rigorous solution for the interaction of layered materials in the case of flat plates [14].

Nevertheless, one may expect general trends to be similar. Russel and Prieve [21] have calculated the distance dependence of the interaction force between two flat semi-infinte bodies, one of which is coated by a thin layer of a material with dielectric properties intermediate between the bulk material and the intervening fluid. They show that at short separations, the interaction of the coated material is governed by the coating; while at large separation, it is the bulk material that dominates. In our case, a similar situation will arise. The two following situations may be distinguished:

1. Large separations made possible by the presence of an adsorbed chemical admixture. In this case, the Hamaker constant is that of the unhydrated material. However, the separation distance must account not only for the dispersant but also for the thickness of the early hydration layer.
2. Small separations due to agglomeration in absence of dispersant. The Hamaker constant can be expected to be that of the hydrate thus much lower. However, the separation distance relevant for calculation is between the exterior surface of both hydrate layers.

However, at those very small separation distances (~ 2 nm), other forces will become important such as ion correlation forces, which were recently demonstrated to account for the cohesion among C-S-H particles [22,23].

For spheres, a crude approximation is outlined in Appendix A. Results presented in Fig. 7, suggest that at separations larger than twice the hydrate layer thickness, the dispersion interaction is indeed well predicted by the sole interaction of the unhydrated particle core.

4. Conclusion

The minerals that were selected for expected similarities, mainly based on atomic composition, to the pure phases of cement exhibit a very clear scaling of their nonretarded Hamaker constant with the square of the difference between their specific density and that of water. This is very useful because it provides a less arbitrary way of estimating Hamaker constants for cement than has been done up to now.

Furthermore, the retardation of all these minerals turns out to be quite similar, though calcite is somewhat of an outlier, having a somewhat slower decay of dispersion force with increasing separation distance. Nevertheless, once again this selection of minerals allows us to make a better

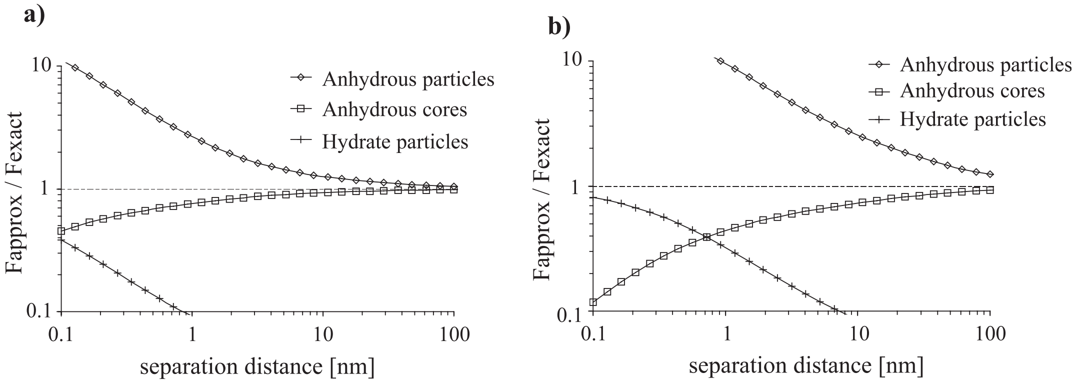


Fig. 7. Ratio of single-term approximation of interaction between spheres with hydration layer over best estimate of total interaction. (a) thickness layer 1 nm, (b) thickness layer 5 nm. The sphere radius is 200 nm.

evaluation of interaction forces between cement particles or phases. A fit to an average normalized retardation was presented. It must be emphasized that this equation has no pretension to any physical meaning.

Approximations to the force between particles in the size range encountered in cement suspensions have also been evaluated. A very convenient approximation that makes the interaction proportional to the harmonic average radius and to the inverse of the square of separation distance. For the smallest cement particles, errors would be larger than 30% beyond 30 nm separation. However, since the ultimate concern of this work is rheology, the relevant force is the maximum attractive force; and in cement suspensions, it occurs at close separation, typically on the order of twice the thickness of adsorbed layers. Measurements by Sakai and Daimon [3] suggest that 15 nm might be the upper bound of the thickness of polymers considered for use in controlling concrete rheology. Consequently, Eq. (15) can be reliably used to estimate the maximum attractive force in most cases.

Another important point is that the harmonic average radius $\bar{a}$ between intervening particles must be used rather than the arithmetic average $\hat{a}$. Considering the wide distribution of sizes in cement, it appears that this had important consequences on the estimation of rheological properties and on their modification by dispersants.

The role that a hydration layer may play in modifying the magnitude of the expected dispersion interaction has also been evaluated. It was found that provided the hydration layer remains on the order of some nanometers, the dispersion interaction may be calculated by the sole interaction of the unhydrated core of the particles, provided that the separation distance is larger than twice the hydration layer thickness. This situation is likely to occur when dispersants are used. This implies that the approximations presented in this paper are most appropriate for evaluating the interparticle forces of dispersed cement suspensions.

Finally, it must be noted that despite the improvements provided by this treatment, quantitative evaluation of interparticle forces in cement suspensions is intrinsically limited by the complexity of such systems. The most obvious features of this being the irregular shape of the particles, the multimineral nature of cement particles, and their reactivity in water. Thus, though the work presented should allow better estimation of rheological properties based on interparticle forces, these limitations must not be overlooked.

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Appendix A. Approximation for dispersion interaction of coated spheres

It must be emphasized that this treatment is only approximate and the complete treatment is not possible owing to the lack of correct description of the dielectric properties of cementitious materials.

Let us consider the interaction between two spheres of radius a at a surface to surface distance each h and having each a coating of thickness δ can be described as the sum of the dispersion interactions of the following:

1. Two unhydrated particles of radius $a-\delta$ with a separation distance $h+2\delta$.
2. Two hydrated shells of thickness δ with a separation distance of h.
3. One hydrated shell of thickness δ and one unhydrated particle of radius $a-\delta$ at a separation distance of $h+\delta$. This later interaction must be taken twice.

The interactions involving hydrated shells are estimated by taking the difference between the interaction of a hydrated sphere of radius a and a hydrated sphere of radius $a-\delta$. The separation distance in the second case is incremented by 2δ for Case 2 and by δ for Case 1.

The results in Fig. 7 suggest that the interaction may be well approximated by the interaction of the unhydrated spheres of radius $a-\delta$ at a separation 2, provided the separation distance h is larger than about 2δ.

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