Numerical integration of van der Waals force between clay plates

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ABSTRACT

Van der Waals interaction is one of the most important interactions between clay particles. Some complicated behavior of clay can be explained from the van der Waals interaction point of view. However, due to the complexity in the mathematical formulation, it is very difficult to analytically integrate the function. This study provides a method to numerically integrate the van der Waals force function. The numerical integration implementation and validation are introduced. The effects of geometric configuration of two clay plates on the van der Waals interaction are quantitatively discussed. The geometry variables include clay plate size, plate separation, plate inclination and the offset of two plates.

Keywords: clay, van der Waals force, numerical integration, geometric configuration

1 INTRODUCTION

Clay are composed of plate-like particles. The complicated physical and mechanical behavior of clay originates from the physico-chemo-mechanical interactions between clay plates. The double-layer repulsive force and the van der Waals force are two major responsible physico-chemical forces. This paper focuses on study of the van der Waals force between clay plates.

London (1930) first developed an equation to calculate the inter-molecule energy associated with van der Waals force. Later, according to the work by Hamaker (1937) and de Boer (1936), the van der Waals force between two macrobodies can be obtained by integrating London’s equation over the volume of the two macrobodies.

London’s equation is valid only for rarefied bodies, such as gas. The retardation of the dispersion energy at large separation distance was considered by modifying the London’s equation (Schenkel and Kitchener, 1960; Anandarajah and Chen, 1995). Later, Anandarajah and Chen (1997) derived an analytical solution to the van der Waals force between a finite thin plate and an infinitely large thin plate with a prescribed thickness; this solution was used as an approximation of the van der Waals force between two thin plates of finite size by assuming that one of the two thin plates is infinitely large but the thickness remains unchanged. However, the error in this approximation has not been discussed.

Although the van der Waals force has long been studied, a solution valid for arbitrarily aligned clay plates of finite size are still not available. This study tries to provide some solutions obtained using numerical integration and provides discussions on the integration implementation and the implication of the integration results.

2 NUMERICAL INTEGRATION OF VAN DER WAALS FORCE

2.1 Van der Waals force calculation

The energy associated with the van der Waals force between two atoms/molecules was developed by London (1930):

\[ u(r) = -\frac{B}{r^{6}} \]

where \( B \) is referred as London constant and \( r \) is the distance between two atoms/molecules.

According to Anandarajah and Chen (1995), the London’s equation was modified to consider the retardation effects:
where \( c = 49.363 \text{ nm} \).

According to Hamaker (1937) and de Boer (1936), integration can be performed to obtain the energy associated with the van der Waals force between two microbodies:

\[
U = \int_{V_1} \int_{V_2} \rho_1 \rho_2 u d\Omega_1 d\Omega_2
\]

where \( V_1 \) and \( V_2 \) are volumes of two microbodies (clay plates in our study), and \( \rho_1 \) and \( \rho_2 \) are molecular densities of the two macrobodies.

The force can be obtained by integrating the van der Waals force between two atoms/molecules as

\[
F = \int_{V_1} \int_{V_2} \frac{\partial u}{\partial r} d\Omega_1 d\Omega_2
\]

### 2.2 Van der Waals force calculation

As a preliminary study, we assume that clay particles are planar rectangle (with no thickness). The integration thus obtained can be readily extended to real case where clay particles are thin plates with finite thickness. Fig. 1 presents the geometric configuration of the two clay particles. The geometry parameters are listed in Table 1.

![Geometric configuration of two clay particles](image)

Fig. 1. Geometric configuration of two clay particles.

### Table 1. Geometry parameters.

| Symbol | Geometrical meaning                          |
|--------|----------------------------------------------|
| \( L \) | Length of clay plates (in the x-axis direction) |
| \( D_1 \) | Width of the upper clay plate (in the y-axis direction) |
| \( D_2 \) | Width of the lower clay plate (in the y-axis direction) |
| \( d \)  | Half of the distance of the two plates at the origin |
| \( \alpha \) | Half of the angle made by the two plates |
| \( E \)  | Lateral offset of the lower plate in the x-axis direction |
| \( F \)  | Lateral offset of the lower plate in the y-axis direction |

In order to numerically integrate Eq. (4), the clay plates in Fig. 1 are divided into small squares with a length = \( a \). The van der Waals force between a square from the upper plate and a square form the lower plate can be approximated as

\[
F = Bc \rho_1 \rho_2 \frac{1}{2} \left( \frac{6}{r^7} \left( r + c \right)^3 \right) + \frac{1}{2} \left( \frac{6}{r^7} \left( r + c \right)^3 \right)
\]

All pairs of squares from the lower and upper plates are traversed and the pair-wise van der Waals force are summed up to yield the total van der Waals force between the lower and the upper clay plates.

### 2.3 Precision and validation of numerical integration implementation

The choice of division size i.e., the square size \( a \), is discussed first. Fig. 2 presents the influence of division size on integration results.

With the decrease of \( a \), the clay particles are divided finer and the obtained van der Waals force increases asymptotically and becomes almost stable when \( a \) is smaller than \( a \) threshold. After a large number of trials and errors, it is concluded that when \( a \cos \alpha / L \) is no greater than 1/50 and \( a / d \) is no greater than 1/8, the error in numerical integration is less than 2%.

The analytical solution of van der Waals force between two equally-sized parallel infinite clay plates can be derived based on Eq. (2) as

\[
\frac{F}{L^2} = \frac{\pi Bc \rho_1 \rho_2}{16 (c + 2d) d^2}
\]

The same case is numerically integrated by setting \( D_1 = D_2 = L \), \( E = F = 0 \), \( \alpha = 0 \) and \( d = 5 \text{ nm} \). When \( L \) is large enough, the numerically integrated case is close to the infinite clay plate case in the analytical solution. Fig. 3 shows that, by increasing \( L \), the numerically integrated normalized force asymptotically approaches the analytical solution. It is confirmed that the numerical integration is correctly implemented.
3 PARAMETRIC STUDY

A parametric study is carried out to explore the effects of geometric configuration of two clay plates on their van der Waals interaction. The basic set of parameters are: \( L = 120 \, \text{nm}, D_1 = D_2 = 600 \, \text{nm}, d = 50 \, \text{nm}, \alpha = 30^\circ, E = 0 \, \text{nm}, F = 0 \, \text{nm} \). When the effects of one parameter are discussed, this parameter is changed while other parameters use the values in the basic set.

3.1 Effects of clay plate size \((L)\)

Fig. 4 presents the variations of normalized van der Waals force with parameter \( L \). Fig. 4 shows that the interaction is along the z-axis direction with \( F_{N,x} \) and \( F_{N,y} \) close to zero. As the clay plate size increases, the van der Waals force increases nonlinearly with a decaying rate. When \( L \) exceeds 150 nm, the force only changes slightly with increasing \( L \). The increased areas of the two plates due to increased \( L \) is too far apart in the z-axis direction when \( L \) is already large enough (say greater than 150 nm). The interaction of van der Waals force decays with the inverse seventh power as implied in Eq. (2). Therefore, if clay particles are very large, for example in the order of microns, the van der Waals force would be a local interaction around the area where two particles are close enough.

3.2 Effects of clay plate separation \((d)\)

Fig. 5 presents the variations of normalized van der Waals force with plate separation \( d \). Fig. 5 shows that the van der Waals force is very sensitive to the plate separation, which is a result of the inverse seventh power in Eq. (2). When the separation is greater than 17 nm, the van der Waals force interaction can be ignored. It implies that when a clay sample is very loose, the attractive van der Waals interaction is limited.

3.3 Effects of plate inclination \((\alpha)\)

Fig. 6 presents the variations of normalized van der Waals force with plate inclination \( \alpha \). Fig. 6 shows that the van der Waals force decreases with the increase of \( \alpha \). When the inclination \( \alpha \) is greater than 70°, the van der Waals force interaction can be ignored. The observation in Fig. 6 implies that van der Waals interaction in a face-to-face system would be statistically greater than that in the card-house and edge-to-edge systems.

3.4 Effects of lateral offset \((F)\)

Fig. 7 presents the variations of normalized van der Waals force with lateral offset of the lower clay plate in the y-axis direction, corresponding to the parameter \( F \). Fig. 7 shows that both \( F_{N,y} \) and \( F_{N,z} \) are significant. When the lateral offset exceeds 800 nm (about 7 times of the clay plate size \( L \)), the van der Waals force vanishes. The significance of \( F_{N,y} \) here indicates that a
reliable evaluation of van der Waals force is required in future DEM simulations.

![](image)

Fig. 7. Effects of lateral offset in the y-axis direction (parameter $F$) on van der Waals interaction.

4 CONCLUSIONS

The van der Waals interaction between two clay plates is quantitatively studied by numerical integration. The following conclusions can be reached.

1. Van der Waals force heavily depends on the geometric configuration of clay plates. The force is very sensitive to clay plate separation and inclination.
2. Van der Waals force can be significant in all three directions, not just in the vertical direction as assumed in previous study.
3. It is possible that the macroscopically measurable quantities in soil mechanics can be correlated with the clay particle system’s van der Waals interaction, which deserves further research.

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