



# Particles interaction forces and their effects on soil aggregates breakdown



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## ABSTRACT

Soil aggregates profoundly influence soil fertility and environmental problems, and usually improving soil aggregation is the central issue in soil management. Compared with external forces, the internal forces of soil, i.e., surface hydration force, electrostatic force and van der Waals force, may play a crucial role in aggregate formation and stability. However, there are few quantitative investigations on those fundamental issues. In the present work we aim to calculate surface hydration force, electrostatic force and van der Waals force of soil/clay particles in aqueous solution, and then quantitatively evaluate the effects of the three forces on soil/clay aggregates breakdown. There was critical surface potential in particles interaction pressure and aggregates breakdown, and if the surface potential exceeded this critical point, a further increase of the surface potential could not significantly increase particles interaction pressure and aggregate breakdown. The critical surface potentials for particle interaction pressure were 207.0 and 179.7 mV for the soil and montmorillonite, respectively. Our study suggested two steps in aggregate breakdown when dried aggregates were re-wetted: (1) separating soil particles in aggregates to a distance of 1.2–1.4 nm between two adjacent particle surfaces by the surface hydration forces (swelling process); (2) breaking soil aggregates in a way of explosion or dispersion under strong or weak electric field conditions. Surface hydration force played a crucial role in aggregate swelling, and without this repulsive pressure, a dried aggregate could not be dispersed again after re-wetting.

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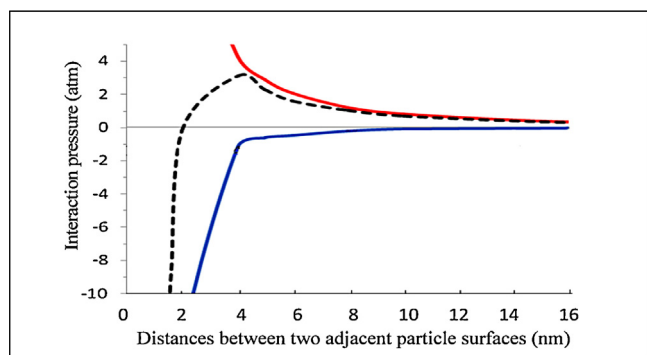
## 1. Introduction

Soil aggregates profoundly influence soil fertility and environmental problems, and usually improving soil aggregation is a major objective of management. When a rain drop falls on a “dried” clay aggregate, it has been reported that the rain drop impact force can directly break the aggregate (Yang, 2006; Boardman and Poesen, 2006). However, aggregate immersion in an aqueous solution without any impact force present can also rapidly disrupt aggregates. While rain drop impact pressure has been reported to reach from 1 to 3 atm (Nearing et al., 1987), the van der Waals attractive pressure among clay particles may be stronger than 1000 atm (Li et al., 2009, 2013). Thus rain drop impact force or other external forces may be less critical to aggregate breakdown than clay particle interactions within aggregates under aqueous condition.

The Derjaguin–Landau–Verwey–Overbeek (DLVO) theory posits two internal forces that dominate soil particles interaction in aqueous solution: the electrostatic repulsive force and the van der Waals attractive force (Zhang et al., 2012; Chinchalikar et al., 2012; Yu et al., 2012; Holthusen et al., 2010; McBride and Baveye, 2002). The DLVO theory has been widely used to explore the mechanism of particle interactions in soil and aqueous system (Adamczyk and Weroński, 1999; Itami and Fujitani, 2005; Liang et al., 2007; Wang et al., 2013). Generally, the electrostatic force is a repulsive force that resists soil particles aggregation whilst the van der Waals force is an attractive force that induces aggregation. Fig. 1 shows the typical distributions of the electrostatic force, van der Waals force and the net force between the two forces (Yu et al., 2012; Hou et al., 2009; Li et al., 2009). Fig. 1 clearly shows that, when the distance between two adjacent particle surfaces is less than 2 nm, the net force is strong attractive (black dashed line). Our calculation, based on the DLVO theory, indicated that at a distance of 0.1 nm between two adjacent particle surfaces the net attractive pressure would be as strong as  $2 \times 10^4$  atm. At this pressure aggregation will be an irreversible process that cannot be overcome by the electrostatic repulsive force. The electrostatic repulsive force is also referred to

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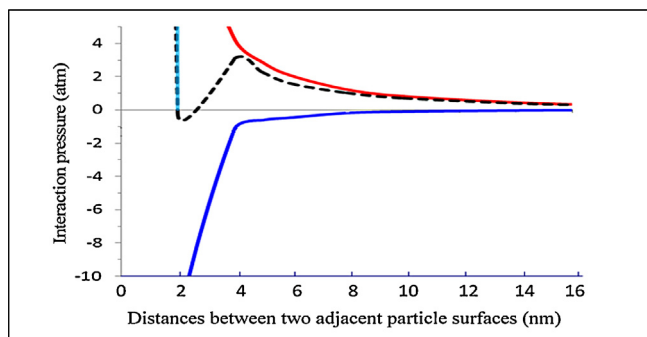


**Fig. 1.** Distributions of the electrostatic force (—), van der Waals force (—) and the net force (---) when the surface potential and Hamaker constant was  $-330$  mV and  $12 \times 10^{-20}$  J in a  $0.0001 \text{ mol L}^{-1}$  1:1 type electrolyte solution (Li et al., 2009).

as “electro-chemical dispersion force or osmotic force” of an overlapped double layer (Shainberg, 1992; Sumner, 1992), which is an important force for soil aggregates breakdown (Le Bissonnais, 1996). However, Fig. 1 shows that the electrostatic repulsive force cannot break soil aggregates, because the net DLVO force between van der Waals attractive and electrostatic repulsive forces (black dashed line) is attractive when the distance of two adjacent particle surfaces in a dried aggregate is less than 2 nm. Therefore, DLVO forces could explain the coagulation process of particles, but not the dispersion process of dried aggregates in aqueous condition.

A repulsive hydration force has been observed when the distance between two adjacent particle surfaces was shorter than 1.5 or 2 nm (Pashley, 1981; Ducker and Pashley, 1992; Leng, 2012). Fig. 1 could be hence changed to Fig. 2 when this strong surface hydration force was considered (Li et al., 2013). The net force distribution shown in Fig. 2 clearly indicates that an aggregate could be dispersed by the combination of the electrostatic repulsive force and the hydration repulsive force; the latter one could play a crucial role in soil aggregate breakdown.

The objective of this study is to quantitatively evaluate the strength of the three interaction forces of soil/clay particles and their effects on soil/clay aggregate breakdown in the absence of the other three classical forces: rain drop impact, compression of entrapped air and differential swelling.



**Fig. 2.** Distributions of the electrostatic force (—), hydration force (—), van der Waals force (—) and the net force (---) when the surface potential and Hamaker constant was  $-330$  mV and  $12 \times 10^{-20}$  J in a  $0.0001 \text{ mol L}^{-1}$  1:1 type electrolyte solution (Li et al., 2009) and the consideration of surface hydration force from Pashley (1981).

## 2. Materials and methods

### 2.1. Materials

A clay (montmorillonite or Mont.) and the purple soil classified as Regosols in FAO Taxonomy or Entisols in USDA Taxonomy in Sichuan Basin, China were used in this study. The surface charge number and specific surface area were  $16.0 \text{ cmol}_c \text{ kg}^{-1}$  and  $48.0 \text{ m}^2 \text{ g}^{-1}$  for the soil, and  $84.8 \text{ cmol}_c \text{ kg}^{-1}$  and  $716 \text{ m}^2 \text{ g}^{-1}$  for the clay, respectively. Soils were loam with a clay, silt, and sand content of 37.9%, 47.9%, and 14.2%, respectively, with the main clay minerals being mica, montmorillonite, illite and vermiculite. Selected soil properties analyzed were: the bulk density was  $1.33 \text{ g cm}^{-3}$ ; organic matter content was  $12.3 \text{ g kg}^{-1}$ ; and pH (solution/soil ratio: 5:1) was 7.11.

### 2.2. Sample preparation

For quantitative evaluation of particle interaction forces, soil and clay particle surfaces were  $\text{K}^+$ -saturated. Air-dried samples (800 g) were washed by dispersion (agitation for 24 h at 200 rpm), centrifugation and decantation using three successive portions of 4 L  $0.5 \text{ mol L}^{-1}$  KCl solution. The KCl treatments were followed by dispersion in three successive portions of deionized water. Each  $\text{K}^+$ -saturated sample was dried at 333 K, crushed and passed through nested 5 and 1 mm sieves to collect aggregates of 1–5 mm for experiments.

### 2.3. Determination of the aggregates breakdown

The breakdown process of an aggregate was observed under a microscope  $50\times$  after we put a prepared  $\text{K}^+$ -saturated aggregate into  $10^{-5}$  and  $1 \text{ mol L}^{-1}$  KCl solution, respectively.

We adopted the measured quantities of small particles (primary clay particles and micro-aggregates) released after aggregate breakdown to reflect the degree of aggregates breakdown. Specifically, a given mass of  $\text{K}^+$ -saturated soil/clay aggregates (20 g) was weighed into cylinders (500 mL) containing  $10^{-5}$ ,  $10^{-3}$ ,  $10^{-2}$ ,  $5 \times 10^{-2}$ ,  $10^{-1}$  or  $1 \text{ mol L}^{-1}$  KCl solution, respectively. Solution temperature was 298 K. Released particles were distributed uniformly by turning the cylinders up and down slightly and carefully. Then, the mass percentage ( $M(<d)$  %) particles with diameters of 10, 5 and  $2 \mu\text{m}$  were measured using the pipette method.

In our experiments, KCl was adopted to adjust the electric field. The electrolyte concentrations of KCl were set as  $10^{-5}$ ,  $10^{-3}$ ,  $10^{-2}$ ,  $5 \times 10^{-2}$ ,  $10^{-1}$  and  $1 \text{ mol L}^{-1}$ , respectively. Thus the calculated (Hou et al., 2009; Li et al., 2009) surface potential of the soil/clay particles are shown in Table 1.

### 2.4. Calculations of particle interaction forces

#### 2.4.1. The electrostatic repulsive force

The electrostatic repulsive pressure that comes from the repulsive force can be calculated by Eq. (1) (Hou et al., 2009; Li et al., 2009, 2013):

**Table 1**

The surface potentials of purple soil and montmorillonite particle at different electrolyte concentrations.

Electrolyte concentration ( $\text{mol L}^{-1}$ )	Surface potential (mV)					
	$10^{-5}$	$10^{-3}$	$10^{-2}$	$5 \times 10^{-2}$	$10^{-1}$	1
Purple soil	-384	-265	-206	-165	-147	-88.1
Montmorillonite	-331	-212	-153	-112	-94	-34.9

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