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Short Communication

Simulating multifaceted interactions between kaolinite platelets

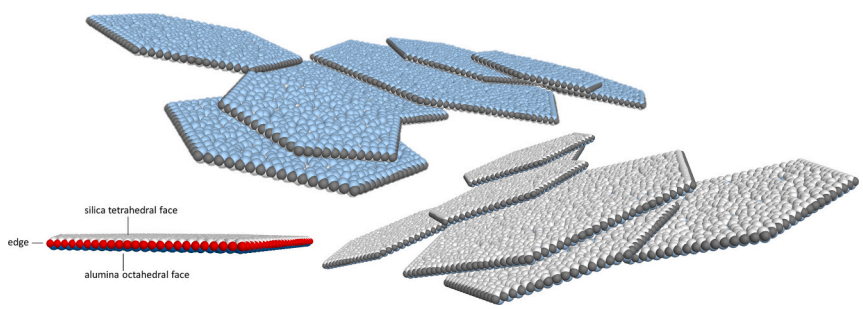
John de Bono *, Glenn McDowell

Nottingham Centre for Geomechanics, University of Nottingham, Nottingham, UK

HIGHLIGHTS

- Using Discrete Element Method to model kaolinite platelets.
- Each platelet has 3 distinct surfaces: silica face, alumina face, edge.
- Different interactions used between different surfaces.
- Using multifaceted interactions controls ability to aggregate/flocculate.

GRAPHICAL ABSTRACT



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ABSTRACT

It is well known that kaolinite platelets readily aggregate into 'stacks', having face-to-face contact. The traditional view of kaolin has been that the platelet faces are negatively charged and the edges are positively charged in an acidic environment, but that some attraction between faces may exist at some close range of approach. Particle-scale simulations in this paper show that this is insufficient to explain aggregation during sedimentation. Recently it has been established that the silica and alumina faces of kaolinite platelets have opposite charges in acidic conditions, and taking these findings into account, discrete element simulations are presented which replicate and explain the face-to-face aggregation that occurs during sedimentation. The results demonstrate the importance of correctly modelling the interactions between the various surfaces of individual platelets in any particle-based model.

1. Introduction

Particle-scale numerical modelling is a useful tool for simulating and investigating the behaviour of particulate materials. This is especially true for coarse-grained materials such as sand, where the discrete element method (DEM) has been used to explain several well-known macroscopic phenomena. For finer-grained materials, such as clays, particle-scale simulations are more problematic—clay minerals typically possess shapes which are inefficient to model (i.e. platelets, as opposed to quasi-spherical sand grains), and exhibit complex interactions, which continue to be a topic of research.

Despite these difficulties, there have been several noteworthy attempts to simulate clays at the particle scale, using either DEM or molecular dynamics (both of these approaches focus on computing the motion of a large number of interacting particles, although they differ slightly in terminology). As will be discussed however, these previous numerical models simulating kaolinite [1–9] have used simplified and potentially inaccurate particle interactions. Several of these past

* Corresponding author.
E-mail address: john.debono@nottingham.ac.uk (J. de Bono).

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attempts have compared well with specific experimental data, however none of them took into account the different interactions between the various surfaces of individual clay platelets. Nonetheless, these studies provide a solid foundation for the development of more advanced particle-scale simulations of clay. It is the aim of this paper to demonstrate appropriate interactions required in any model to capture the correct platelet behaviour when compared with available evidence.

1.1. Kaolinite

This study focusses on and simulates interactions between kaolinite platelets. Kaolinite is a 1:1 layered mineral, consisting of alternating layers of silica tetrahedral and alumina octahedral sheets [10,11]. Kaolinite exists in the form of flat platelets, typically <1 μm wide and < 0.05 μm thick [10,11]. Thus a single kaolinite particle has 3 surfaces: a silica (tetrahedral) face, an alumina (octahedral) face, and an edge surface. The interactions between kaolinite particles at this scale are determined by the surface chemistry and environmental conditions, rather than by purely mechanical forces. This typically has required specialised interaction laws to be implemented to any numerical model, and involves a significant deal of uncertainty.

Traditionally, it was accepted that the faces of kaolinite platelets possessed a permanent negative surface charge, whilst the edges possessed a pH-dependent surface charge, which could either be positive (low pH) or negative (high pH). This view led to the notion that acidic conditions contribute to a loose, flocculated arrangement of platelets, and alkaline conditions contribute to a dense, layered arrangement of platelets [10–12]. Considering the sedimentation of kaolinite in water for instance, as simplified in Fig. 1, if all platelet surfaces exhibit negative surface charges, and electrostatic repulsion prevents any coagulation, the suspended platelets are able to easily slide over one another and form a dense, layered sediment. If electrostatic attraction occurs between edges and faces, the platelets readily flocculate and form a very loose, open structure. This belief is consistent with experimental measurements of sediment volumes and settling rates of kaolinite suspensions, measured at varying pHs [12–15].

Despite the above simplified notion of behaviour, a well-known phenomenon for kaolinite is the face-to-face 'stacking' or aggregation of platelets [e.g. 11,16,17]. An example SEM image showing aggregation in a kaolinite slurry is given in Fig. 2, further images including showing aggregation in suspensions and sediments can be found in [16–18]. Given the traditional view that the face surfaces of kaolinite platelets possess negative surface charges, which ordinarily would lead to face-to-face repulsion, any aggregation (i.e. face-to-face attraction) has generally been attributed to van der Waals forces [10], or alternatively ion-correlation (where positively charged counter-ions act as 'glue') [11,19]. Thus, it has usually been assumed that the interaction between two parallel, like-charged platelets is repulsive at large separations with an attractive region at close range, as shown in Fig. 3 [10,11]. This figure shows increasing repulsion as two particles approach one another from distance, with a small region of attraction at close-range. Beyond this, at closer separation, very stiff repulsion prevents any physical penetration.

Experimental findings in the last few years however have since clarified that the two basal surfaces of kaolinite platelets possess separate and opposite charges [20,21]. It has been shown that the alumina face possesses a positive surface charge at low pH (< 7) and a negative surface charge at higher pH; while the silica face as well as the edge surface both possess negative charges across all pH values of interest (> 4). It is worth noting that in these experiments, for repulsive long-range interactions, no significant attraction was observed at close-range [20,21].

This newer understanding provides a better explanation as to why kaolinite platelets aggregate so readily, and is entirely consistent with previous observations, as well as SEM images of kaolinite sediments and suspensions [7–9], in which platelet aggregation is easily visible despite the platelets not being subjected to any significant perturbation (e.g. compression).

1.2. Numerical modelling of platelet interactions

In the geotechnical numerical modelling community, previous attempts to simulate particle-scale behaviour of kaolinite have typically used the outdated understanding of platelet interactions (where all faces are considered to possess identical (negative) surface charges, and only the edges might be considered to have a variable charge). Of those past attempts [1–8], the majority considered different surface charges on the edges and faces, however none distinguished between the two distinct faces of the platelets. In those studies which could simulate any face-to-face aggregation, this was typically done by implementing an

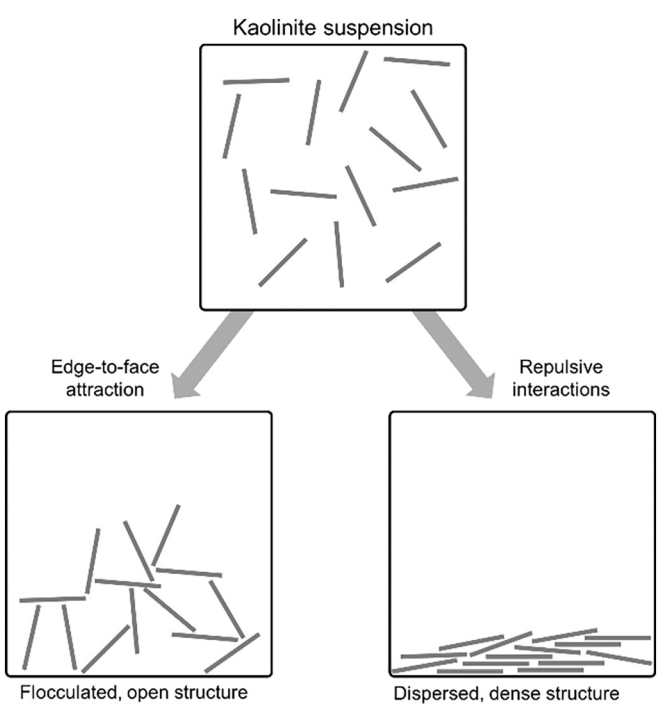

Fig. 1. Schematic showing the assumed settling mode for kaolinite platelets with and without edge-to-face attraction.

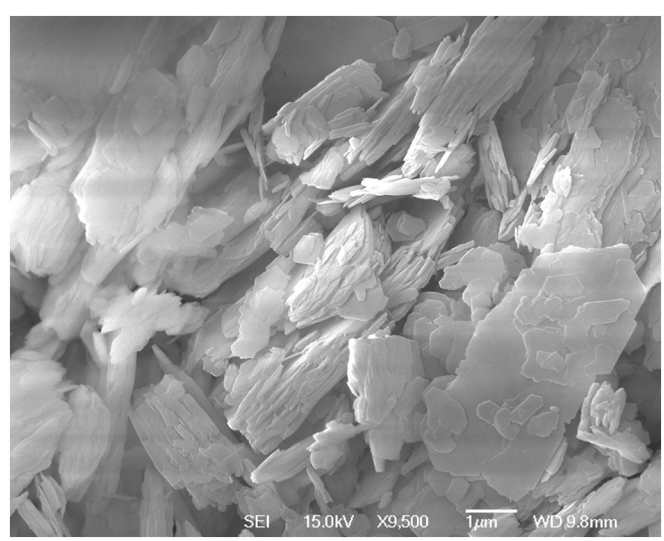

Fig. 2. SEM image of a kaolinite slurry, prepared at a moisture content of 125%.

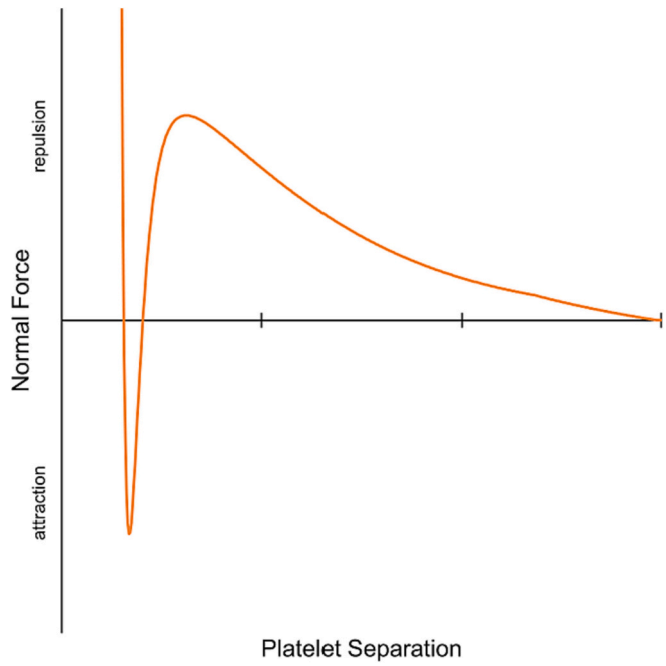

Fig. 3. Idealised force versus separation interaction curve between two parallel kaolinite platelets.

interaction law between platelets of the form shown in Fig. 3, i.e. long-range repulsion combined with close-range attraction. This was either applied to all types of platelet interactions, or used in conjunction with a separate edge-to-face attraction.

It should also be noted that even in those past simulations which did not allow for any aggregation [3,9]—i.e. the interactions between the faces of platelets were purely repulsive—after subjecting these numerical samples to external load, the forced rearrangement and packing of the platelets still gives the appearance of aggregation. To demonstrate the actual effects of implementing the correct, multifaceted interactions that exist between real kaolinite platelets, some brief sedimentation simulations will be demonstrated in this paper. These will show how the platelet interactions affect the abilities of the platelets to naturally flocculate and/or aggregate, without subjecting the sample to any external loading.

The brief simulations presented here all use 500 platelets, with diameters of 0.75, 1.0 and 1.5 μm in equal proportions. The platelets have thicknesses of 0.055 μm, and consist of a rigid arrangements of spheres (shown in Fig. 4). This is the same approach used by many others to simulate platelets, and is explained and justified more fully in [6,22]. In

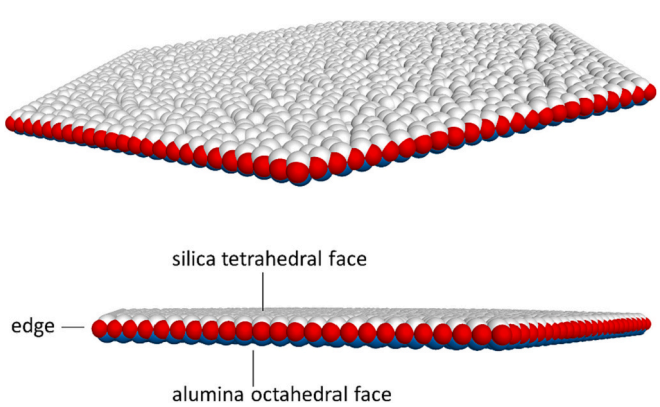

Fig. 4. Numerical kaolinite platelet used in this study. Platelet shown has a diameter of 1.5 μm and a thickness of 0.055 μm.

summary, this approach of constructing platelets from spheres allows categorically different interactions to occur between different parts of the platelets, and inherently accounts for arbitrary orientations between platelets. To implement separate interactions between the various surfaces (including the two distinct faces), the platelets are constructed from two layers of spheres, with an additional set of spheres around the edges (different coloured spheres in Fig. 4). These allow for separate interactions to be implemented between any pair of spheres from amongst these three groups. Thus, the net interaction between two platelets is the cumulative sum of all interactions between constituent spheres.

To achieve the desired platelet interactions, custom interactions laws between the spheres were implemented. These interaction laws calculate the normal force acting between a pair of spheres as a function of separation, and dictate the shape of the force-separation curves. In these simulations, interactions laws of the form $F \sim r^{-\alpha} - r^{-\beta}$ are used (F is force, r is separation, α, β are constants). Further details can be found in [6], however, any interaction law may be used which achieves the desired force-separation curve, for example see [2,23].

Results from four simulations will now be shown, each using a different interaction regime. For further information on the platelets, and how the interactions outlined below are calibrated, see [22]. Each simulation starts with the platelets randomly created in an enclosed 10 × 10 μm cylinder. They are then allowed to settle under gravity, assuming a particle density of 2700 kg/m^3.

The interaction regimes compared are summarised in Fig. 5. Each subplot in this corresponds to a single simulation, and shows the normal interactions between the different platelet surfaces. The tangential platelet interactions are not varied across the simulations, and in all cases a linear tangential stiffness with a coefficient of friction of 0.05 is used. Due to the (even greater) uncertainty over tangential platelet behaviour, this coefficient was chosen somewhat arbitrarily bearing in mind the smooth nature of the platelets (however, in the absence of significant external forces, varying the friction coefficient has no effect on the settling behaviour).

Simulation I corresponds to the conventional approach commonly used in particle-scale simulations: the platelets exhibit face-to-face repulsion, and edge-to-face attraction, shown in Fig. 5(a). To allow the possibility of aggregation, face-to-face interactions include close-range attraction (which has often been attributed to van der Waals forces). Allowing the platelets to settle freely with minimal damping results in the very loose, open structure shown in Fig. 6(a). At the final steady state, all 'contacts' are edge-to-face, with no face-to-face aggregation. The magnitude of the interactions shown in Fig. 5 are chosen arbitrarily, however, regardless of the forces, so long as there is long-range edge-to-face attraction, and long-range face-to-face repulsion, the resulting sediment structure is the same. Simulating Brownian motion, by giving the platelets random velocities and rotations also leads to the same result.

Simulation II features long-range repulsion between all particle surfaces (Fig. 5(b)). As shown in Fig. 6(b), this regime results in a dense, layered sediment with much smaller volume. Simulations I and II together correspond very well to the simplified regimes depicted in Fig. 1.

Simulation III distinguishes between the two faces of each platelet (the silica and alumina faces), therefore requiring additional types of interactions to be implemented. The interactions are shown in Fig. 5(c), and feature attraction between *different* faces (with opposite charges), and repulsion between like faces. The platelet edges exhibit attraction with the alumina faces and repulsion with the silica faces. In this case, no close-range attraction is included in the interactions between like-charged surfaces. The edges and the silica faces are assumed to have the same surface charge density, so the interactions are identical when normalised by surface area in contact in Fig. 5(c). The resulting sediment is shown in Fig. 6(c), which demonstrates a similar open and disordered flocculated structure to that shown in Simulation I.

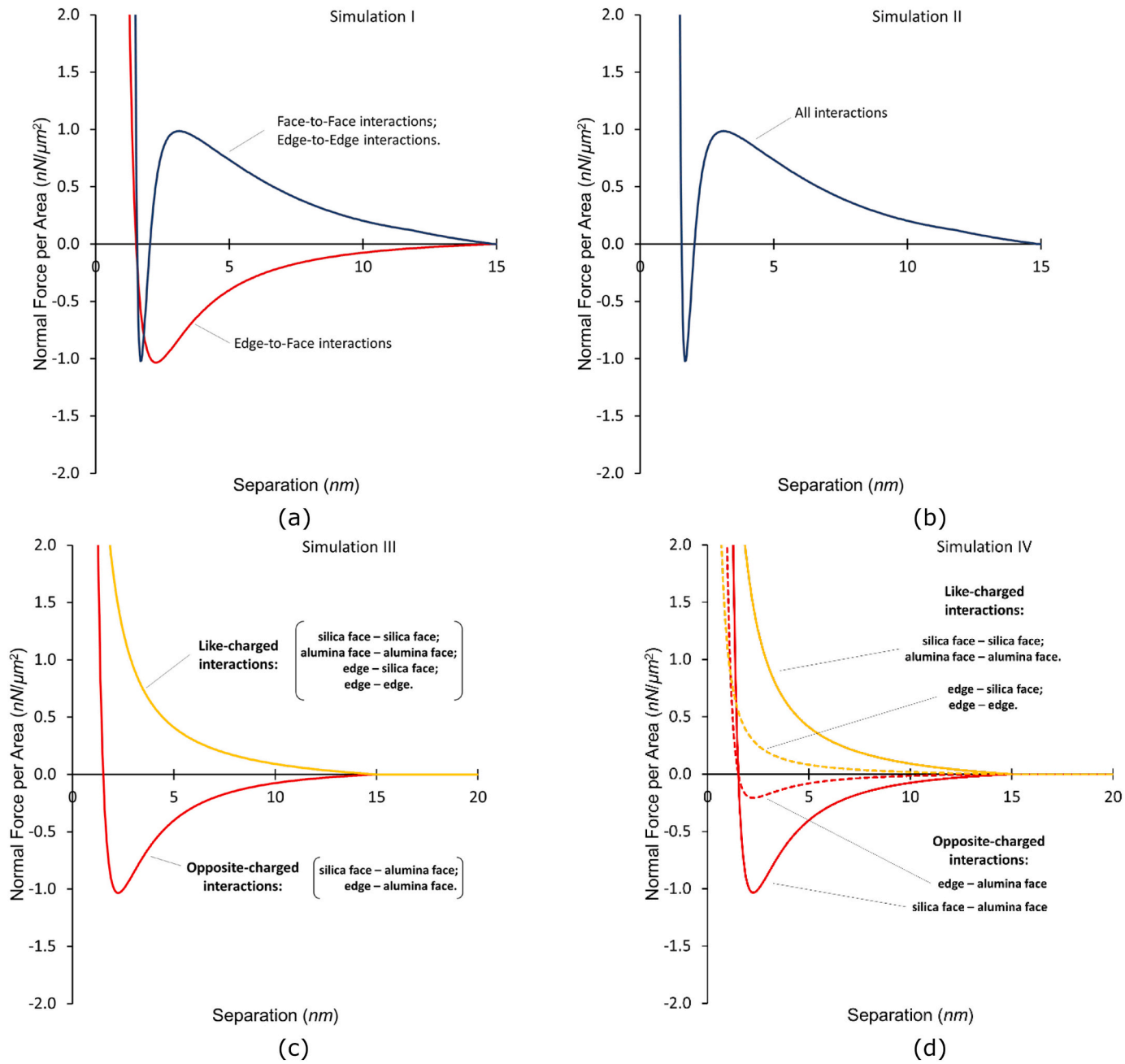

Fig. 5. Four different interactions regimes simulated.

Lastly, Simulation IV uses a similar regime but assumes a weaker surface charge density on the edges, shown in Fig. 5(d). Given that the edges themselves consist of alternating layers of silica and alumina sheets, it follows that the net surface charge would be smaller than that of the negative silica face, and therefore the interaction forces would be smaller. The resulting sediment is shown in Fig. 6(d), which displays unique behaviour compared to the other cases, with a higher prevalence of large, flake-like structures, and visible aggregation. This displays a greater likeness to real images of kaolinite, despite the highly simplified platelets used in these simulations. Further reducing the interaction forces for edge-to-face interactions does not lead to any significant differences, suggesting the influence of edge-to-face interactions in previous numerical models may have been overestimated.

The difference between the sediments is also reflected in quantitative measurements. Given that each sphere represents a finite area of platelet surface, the 'contact' area between two interacting platelets can be assessed by summing the number of interacting spheres. Simulation IV exhibits the greatest 'contact area' (65 μm^2) between all platelets, due to the prevalence of face-to-face aggregation. Simulations I and III both demonstrate no aggregation, and the resulting contact area is much lower (both ~15 μm^2). Simulation II, despite forming the densest sediment, with platelets largely aligned with each other, has the smallest contact area (0.5 μm^2) due to the platelets only interacting or 'touching' minimally, at the fewest number of points due to the overall repulsion. It is also possible to estimate the voids ratios of the four sediments. This is done considering only the lowest parts of each sample, without considering the sediment height (which is not well-defined in most cases). The loose and flocculated sediments from Simulations I and III possess voids ratios of approximately 18–19. The dense sediment from Simulation II gives a voids ratio of 2.75, while Simulation IV gives a voids ratio of approximately 9. These compare to voids ratios measured experimentally of around 8–9 for acidic samples of kaolinite [12,15],

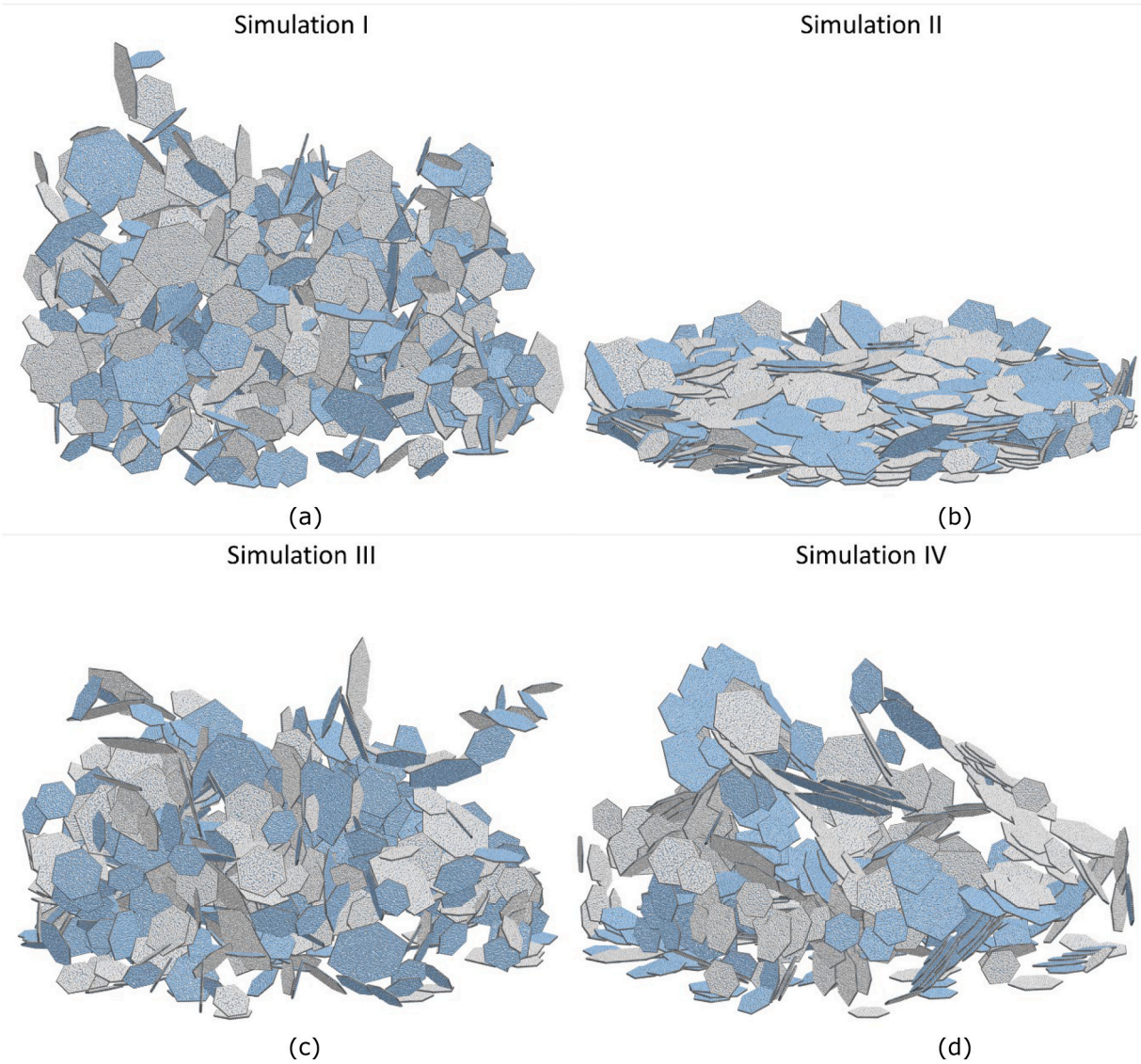

Fig. 6. Images of the four samples after settling.

which further supports the approach used in Simulation IV.

1.3. Concluding remarks

Following on from relatively recent experiment findings, these simple simulations have explored the effects of implementing multifaceted interactions between the various surfaces of kaolinite particles within the field of particle-scale modelling. Simple sedimentation simulations appear to show that not only is modelling long-range repulsion between all faces of kaolinite platelets incorrect, but that the role of edge-to-face interactions may have been overestimated. To achieve a sediment with a structure that corresponds satisfactorily to real kaolinite observed via SEM, it is important to model some form of attraction between oppositely charged faces of the platelets, and to moderate the influence of edge-to-face interactions.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

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References

[1] K.J. Sjoblom, Coarse-grained molecular dynamics approach to simulating clay behavior, J. Geotech. Geoenviron. ASCE. 142 (2015) 1–6, https://doi.org/10.1061/(ASCE)GT.1943-5606.0001394.
[2] P. Aminpour, K.J. Sjoblom, Multi-scale modelling of kaolinite triaxial behaviour, Géotechnique Lett. 9 (2019) 178–185, https://doi.org/10.1680/jgele.18.00194.
[3] A.G. Pagano, V. Magnanimo, T. Weinhart, A. Tarantino, Exploring the micromechanics of non-active clays by way of virtual DEM experiments, Géotechnique. 70 (2020) 303–316, https://doi.org/10.1680/jgeot.18.P.060.
[4] M. Yao, A. Anandarajah, Three–dimensional discrete element method of analysis of clays, {ASCE}, J. Eng. Mech. 129 (2003) 585–596.

[5] Y. Guo, X. Bill Yu, A holistic computational model for prediction of clay suspension structure, Int. J. Sediment Res. 34 (2019) 345–354, https://doi.org/10.1016/j.ijsrc.2018.12.002.
[6] J.P. de Bono, G.R. McDowell, Discrete element modelling of normal compression of clay, J. Mech. Phys. Solids. 162 (2022), 104847, https://doi.org/10.1016/j.jmps.2022.104847.
[7] K.A. Jaradat, S.L. Abdelaziz, On the use of discrete element method for multi-scale assessment of clay behavior, Comput. Geotech. 112 (2019) 329–341, https://doi.org/10.1016/j.compgeo.2019.05.001.
[8] M. Khabazian, A.A. Mirghasemi, H. Bayesteh, Compressibility of montmorillonite/kaolinite mixtures in consolidation testing using discrete element method, Comput. Geotech. 104 (2018) 271–280, https://doi.org/10.1016/j.compgeo.2018.09.005.
[9] S. Bandera, C. O'Sullivan, P. Tangney, S. Angioletti-Uberti, Coarse-grained molecular dynamics simulations of clay compression, Comput. Geotech. 138 (2021), 104333, https://doi.org/10.1016/j.compgeo.2021.104333.
[10] H. van Olphen, An Introduction to Clay Colloid Chemistry, John Wiley and Sons, New York, 1963.
[11] J.K. Mitchell, K. Soga, Fundamentals of Soil Behavior, 3rd ed., John Wiley and Sons, Hoboken, New Jersey, 2005.
[12] Y.-H. Wang, W.-K. Siu, Structure characteristics and mechanical properties of kaolinite soils. I. Surface charges and structural characterizations, Can. Geotech. J. 43 (2006) 587–600, https://doi.org/10.1139/t06-026.
[13] B. Rand, I.E. Melton, Particle interactions in aqueous kaolinite suspensions I, J. Colloid Interface Sci. 60 (1977) 331–336, https://doi.org/10.1016/0021-9797(77)90292-2.
[14] I.E. Melton, B. Rand, Particle interactions in aqueous kaolinite suspensions. III. Sedimentation volumes, J. Colloid Interface Sci. 60 (1977) 331–336, https://doi.org/10.1016/0021-9797(77)90292-2.
[15] M. Pedrotti, A. Tarantino, An experimental investigation into the micromechanics of non-active clays, Géotechnique (2017) 1–18, https://doi.org/10.1680/jgeot.16.P.245.
[16] K. Ma, A.C. Pierre, Clay sediment-structure formation in aqueous kaolinite suspensions, Clay Clay Miner. 47 (1999) 522–526, https://doi.org/10.1346/CCMN.1999.0470415.
[17] N.R. O'Brien, Fabric of kaolinite and Illite floccules, Clay Clay Miner. 19 (1971) 353–359, https://doi.org/10.1346/CCMN.1971.0190603.
[18] M.S. Zbik, R.S.C. Smart, G.E. Morris, Kaolinite flocculation structure, J. Colloid Interface Sci. 328 (2008) 73–80, https://doi.org/10.1016/j.jcis.2008.08.063.
[19] R. Kjellander, Ion-ion correlations and effective charges in electrolyte and macroion systems, Berichte Der Bunsengesellschaft Für Phys Chemie. 100 (1996) 894–904, https://doi.org/10.1002/bbpc.19961000635.
[20] V. Gupta, J.D. Miller, Surface force measurements at the basal planes of ordered kaolinite particles, J. Colloid Interface Sci. 344 (2010) 362–371, https://doi.org/10.1016/j.jcis.2010.01.012.
[21] J. Liu, L. Sandaklie-Nikolova, X. Wang, J.D. Miller, Surface force measurements at kaolinite edge surfaces using atomic force microscopy, J. Colloid Interface Sci. 420 (2014) 35–40, https://doi.org/10.1016/j.jcis.2013.12.053.
[22] J.P. de Bono, G.R. McDowell, Some important aspects of modelling clay platelet interactions using DEM, Powder Technol. 398 (2022), 117056, https://doi.org/10.1016/j.powtec.2021.117056.
[23] A. Anandarajah, Numerical simulation of one-dimensional behaviour of a kaolinite, Geotechnique. 50 (2000) 509–519, https://doi.org/10.1680/geot.2000.50.5.509.