

Coarse-grained molecular dynamics simulations of clay compression

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Abstract

This paper outlines a framework for using molecular dynamics to simulate compression of kaolinite saturated at alkaline pH (=8) in a low (1 mM) concentration solution. The particles are modelled as flat (3D) ellipsoids and their interactions are described by a modified form of the Gay-Berne potential, calibrated against DLVO theory. The LAMMPS software was used to generate monodisperse and slightly polydisperse samples, and to simulate isotropic compression to 100 kPa. The influences of sample size and strain rate on the void ratio and the arrangement of particles within the samples were investigated via parametric studies. It is useful to consider the extent to which the system temperature (a measure of the average kinetic energy) is controlled when assessing whether the applied strain rate is appropriate. It is found that the number of particles that can be considered a representative element volume is orders of magnitude larger than the number simulated in earlier studies and that larger number of particles are required in polydisperse samples than in the monodisperse case. A comparison between the results obtained and those of published experimental studies show that the methodology proposed can deliver sensible results for the material considered.

Keywords: Clay; Molecular Dynamics; DLVO theory; Discrete Element Method; Micro-Macro; Gay-Berne potential

List of Symbols

Greek symbols

γ : global shift of the potential minimum

γ_{sb} : pair-wise shift of the potential minimum

δ : thickness of the ellipsoidal particles

δ_1, δ_2 : thickness of interacting particles

Δt_{bm} : benchmark time-step used as comparison with Δt_1 and Δt_2

Δt_{crit} : critical time-step

Δt_{simul} : time-step used to integrate equations of motions in MD simulations

$\Delta t_1, \Delta t_2$: time-step value obtained by multiplying θ_1, θ_2 and Δt_{crit}

$\dot{\epsilon}_f$: compression rate computed at the end of each NPT simulation

$\epsilon_{ia}, \epsilon_{ib}, \epsilon_{ic}$: relative well-depths for particle i

$\epsilon_{ja}, \epsilon_{jb}, \epsilon_{jc}$: relative well-depths for particle j

ϵ_r : relative permittivity

ϵ_0 : permittivity of free space

ϵ : energy scale

κ : thickness of the double layer

ψ_1, ψ_2 : surface potential of interacting particles

ρ_s : salt concentration of solution considered

σ : atomic interaction radius

θ_1, θ_2 : reduction factors used to compute the time-step

Roman Symbols

A_H : Hamaker constant

C_c : compressibility index (for 1D simulations)

D : diameter of the ellipsoidal particles

e : sample void ratio

$e_{100\text{ kPa}}$: void ratio at 100 kPa

E_{Edl} : pair-wise double layer electrostatic energy per unit area

$E_{MD,Tot}$: total energy of the system from MD

E_T : pair-wise total energy per unit area

E_{vdW} : pair-wise van der Waals energy per unit area

F_{Edl} : pair-wise double layer electrostatic force

F_{vdW} : pair-wise van der Waals attractive force

h : separation distance between particle surfaces

h_{eb} : separation distance between particle surfaces corresponding to the energy barrier

h_{12} : closest distance between particle surfaces

k : stiffness of the pair-wise interaction

k_{max} : maximum stiffness associated with particle interaction

$K_{MD,Tot}$: total kinetic energy of the system from MD

l_0 : periodic box dimension at the beginning of compression

l_f : periodic box dimension at the end of each NPT simulation

m : particle mass

m_{min} : minimum particle mass in the system

N : total number of particles

P : pressure applied to the system

t_f : total time length of the j th NPT simulation

T : thermodynamics temperature

T_{DOF} : oscillation period of a simple DOF system

U_{GB} : pair-wise Gay-Berne potential energy

$U_{GB,Repulsive}$: repulsive component of the pair-wise Gay-Berne potential energy

$U_{GB,Repulsive}^{sb}$: repulsive component of the pair-wise Gay-Berne potential energy computed using γ_{sb}

$U_{MD,Tot}$: total potential energy of the system from MD

V : volume of the system

1. Introduction

Clay minerals are ubiquitous in soil deposits everywhere. Predicting clay behaviour is non-trivial; its response to applied loads is non-linear, rate- and time-dependent, and measurably influenced by the clay chemistry, mineralogy and particle morphology, the stress history of the deposit, the pore water chemistry and temperature (e.g., Anandarajah, 2000a; Lambe and Whitman, 1969; Leroueil and Hight, 2003; Mitchell and Soga, 2005; Santamarina et al., 2001b). A comprehensive understanding of clay behaviour is important to deliver engineering solutions to key infrastructure challenges (e.g., tunnelling in stiff clays, road embankments on soft clays, barriers for nuclear waste disposal, etc.). Current understanding of clay behaviour is based on in-situ observation and sophisticated laboratory testing (e.g., Burland, 1990; Leroueil and Hight, 2003; Leroueil and Vaughan, 1991); while these have enabled frameworks for prediction, explanations of the fundamental mechanisms involve significant conjecture.

Particle-scale models are generally accepted in geomechanics as a research tool to advance the understanding of sand behaviour (e.g., Cheng et al., 2004; O'Sullivan, 2011; Thornton, 2000). However, relatively few studies have documented particle-scale simulations of clay because the characterisation of both the elementary units and the interparticle forces between them is significantly more complicated (Delage, 2010). Such simulations are the only way to quantitatively link particle-scale mechanisms to the complex features of behaviour that are routinely encountered in engineering practice. Given the increased availability of particle-scale simulation tools, namely open-source discrete element methods (DEM) and molecular dynamics (MD) codes that can in principle exploit large distributed-memory high performance computers, it is timely to consider how these simulations can be delivered.

This contribution considers how best to use currently available resources to study the mechanical behaviour of clay by considering the compressive behaviour of kaolinite, an

inactive clay. The key decisions required to develop a particle-scale model of clay are critically analysed to lay out a coherent framework for using [Coarse-grained Molecular Dynamics \(CGMD\)](#) to simulate a soil mechanics element test. [In the context of the current study, the term “coarse-grained” means that the simulated particles are the clay particles, rather than their constituent atoms.](#) Firstly, the literature on clay particle interactions is reviewed to justify the interparticle forces adopted here. The choices of modelling approach and particle geometry are based on consideration of previous studies. Then, the potential function adopted and its calibration are explained before considering the steps required to simulate a mechanical element test. Data from parametric studies are used to discuss important issues, namely the appropriate number of particles to consider and the selection of the compression rate.

2. Quantifying clay particle interactions

Any particle-based model requires an analytical description of the variation in force or energy with particle [surface](#) separation (h) and relative orientation. The force-separation relationship for clay particles with given relative orientation is relatively complex as both contact and non-contact forces must be considered (in the physics and chemistry communities these forces are also referred to as short- and long-range interactions, respectively). For contacting particles, the mechanical short-range forces are modelled by the Born repulsion (e.g., Lu et al., 2008; Sjoblom, 2016; Yao, 2001), which dominates the interaction only when particles come into very close proximity (generally less than 1 nm) (Anandarajah and Yao, 2005; Lu et al., 2008; Yao, 2001). The non-contact forces are usually described by DLVO theory (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948), developed in the 1940s to explain colloidal stability in solutions. DLVO theory describes both van der Waals attractive force (F_{vdW}) and the electrostatic diffuse double layer contribution (F_{Edl}). Given the small particle sizes and large specific surface areas in clays, non-contact forces are understood to strongly influence key aspects of the overall behaviour including response to applied loads, volume change

characteristics and strength (Anandarajah, 2000a; Bolt, 1956; Lambe and Whitman, 1969; Lu et al., 2008). Non-contact forces also influence the evolution of clay fabric during deposition as they can determine whether an open or closed material fabric forms (Lambe and Whitman, 1969). Clays exhibit a chemical-mechanical coupling due to the sensitivity of these forces to the pore-fluid chemistry (Santamarina et al., 2001b).

DLVO equations are often expressed as energies per unit area; forces are defined as the negative slope of the energy-separation distance profiles. Within the DLVO framework, the total interaction energy between two charged colloidal particles, E_T [J/m^2], is the sum of the van der Waals (E_{vdw}) and electrostatic (E_{Edl}) contributions:

$$E_T = E_{Edl} + E_{vdw} \quad \text{Eq. (1)}$$

The total energy is defined relative to the energy at infinite separation; therefore, **negative** slopes indicate repulsion, while **positive** slopes indicate attraction.

E_{vdw} [J/m^2] is a weak short-range attractive energy originating from the correlated motions of electrons in adjacent colloidal particles (Mitchell and Soga, 2005). Its dependence on the clay mineralogy is quantified through the Hamaker constant (A_H [J]) parameter, which is challenging to measure and depends, amongst other factors, on the dielectric permittivity of the pore fluid (Israelachvili, 2011). Generally, a value of the order of 1×10^{-20} J is suggested in the literature for colloidal particles interacting through water (Israelachvili, 2011). Here, A_H values measured on kaolinite surfaces with the atomic force microscopy (AFM) by Gupta (2011) are used. There is general agreement in the literature on the mathematical expression for E_{vdw} for two **charged, parallel and infinite planar surfaces** (Israelachvili, 2011; Mitchell and Soga, 2005). This study used the form employed by Gupta (2011):

$$E_{vdw} = -\frac{A_H}{12\pi} [h^{-2} + (h + \delta_1 + \delta_2)^{-2} - (h + \delta_1)^{-2} - (h + \delta_2)^{-2}] \quad \text{Eq. (2)}$$

where A_H [J] is the Hamaker constant, h [m] is the separation distance between the particle surfaces, and δ_1 [m] and δ_2 [m] are the thicknesses of the two interacting plates.

E_{Edl} is the Coulombic interaction between charged surfaces screened by ions in solution which partially neutralise them (Masiliyah and Bhattacharjee, 2006). E_{Edl} can be either repulsive or attractive depending on the signs of the charges of the interacting surfaces (Bandera et al., 2019; Gupta, 2011; Gupta and Miller, 2010; Kumar et al., 2017; Liu, 2015): surfaces whose charges have the same sign repel and those with oppositely signed charges attract. While there are several expressions that relate E_{Edl} to the separation of the two charged surfaces, an exact analytical solution does not exist. The linearised solution proposed by Hogg et al. (1966) is accepted to be valid when the surface potential is low (a suggested upper limit is usually 25mV where the electrolyte is monovalent and the temperature is 300K). While non-linear formulations exist in the literature (Honig and Mul, 1971), their implementation is non-trivial. Referring to data presented in Hogg et al. (1966) and Masiliyah and Bhattacharjee (2006) the current study follows Gupta et al. (2011) and adopts the linearised E_{Edl} -separation distance relationship predicted by the DLVO equation defined for infinitely long planar surfaces. While we adopt this assumption here, it is only where a constant and low surface electrical potential is assumed that the linearisation is reasonably accurate.

$$E_{Edl} = \varepsilon_r \varepsilon_0 \kappa \left[\frac{2\psi_1 \psi_2 \exp(\kappa h) - \psi_1^2 - \psi_2^2}{\exp(2\kappa h) - 1} \right] \quad \text{Eq. (3)}$$

where ψ_1 [V] and ψ_2 [V] are the surface potentials (pH-dependent) of the interacting particles, ε_r [–] is the relative permittivity, ε_0 [F/m] is the permittivity of free space and κ [m^{-1}] is the reciprocal thickness of the double layer (reciprocal Debye length), which depends on the ion

concentration of the solution. Eq. (3) was developed assuming a constant surface electrical potential.

Recent studies have applied linearised DLVO expressions to AFM data to determine the surface potential along each of the three kaolinite particle surfaces, i.e. the alumina face, the silica face, and the edge. (Gupta, 2011; Kumar et al., 2017; Liu, 2015). The solution pH influences the particles' surface chemistries and charge densities and so the pH determines whether the interactions are attractive or repulsive. Pedrotti and Tarantino (2018) analysed SEM images and mercury intrusion porosimetry (MIP) data for kaolinite samples saturated with water at different pH. They observed a variation in fabric with pH; they attributed this to the activation or deactivation of some interaction mechanisms as a consequence of the variation in the surface chemistry of the edges.

DLVO theory has been qualitatively invoked to explain observations in experimental studies (e.g. Gupta, 2011; Mitchell and Soga, 2005; Pedrotti and Tarantino, 2018; Wang and Siu, 2006a). However, it is broadly acknowledged that this theory over-simplifies the interactions. Discrepancies have been observed between predictions using DLVO theory and the behaviour of many clays (Mitchell and Soga, 2005). DLVO theory implicitly incorporates many assumptions and can be highly inaccurate when used outside its conditions of validity. The Gouy-Chapman theory of the electric double-layer, which is incorporated in the DLVO model, (Bharat and Sridharan, 2015; Güven, 1992; Masiliyah and Bhattacharjee, 2006; Mitchell and Soga, 2005; van Olphen, 1977) neglects the ion sizes by considering them as point charges (Sridharan and Prakash, 1999); additionally, the theory is valid only for low to moderate surface potentials and low salt concentrations (Güven, 1992; Masiliyah and Bhattacharjee, 2006). Furthermore, the measurement of the surface properties (surface potential) required to use this theory in quantitative predictions is challenging (Mitchell and Soga, 2005). Ebrahimi et al. (2014) and Carrier (2014) argued that DLVO theory cannot accurately capture the

interaction at short distances (less than 1 nm), which, as will be shown later, is irrelevant for many of the large scale properties considered.

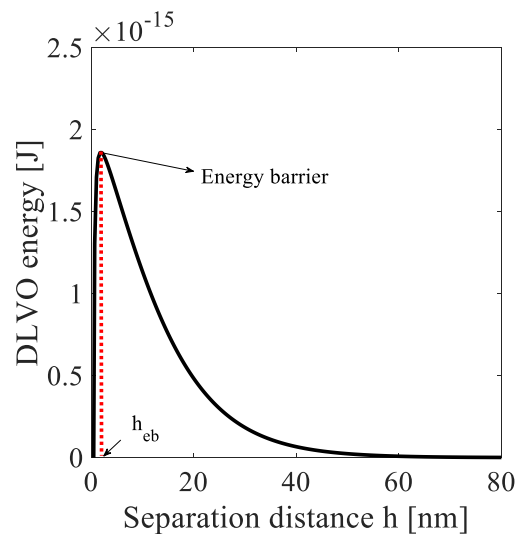


Figure 1. Schematic of the energy-separation distance plot for two interacting clay particles illustrating the energy barrier; h_{eb} is the separation distance at which the energy barrier (global maximum) is attained

Figure 1 presents a schematic of the energy- surface separation distance plot for two interacting particles. As particle separation increases from the fully contacting case, there is a sharp rise in the DLVO energy up to a local maximum termed energy barrier (Israelachvili, 2011), as shown in Figure 1; before this maximum, interactions are dominated by an attractive force. A reduction in the surface potential reduces the energy barrier, leading to flocculation (Israelachvili, 2011). Subsequent increases in separation result in a monotonic reduction in the energy and a repulsive force.

Arguably the value of DLVO is limited to providing a conceptual framework within which to understand how clay's qualitative behaviour arises from microscopic interactions and the net balance of interparticle forces (Güven, 1992). However, it is important to acknowledge that while DLVO cannot capture the *fine* detail of clay-clay interactions especially at very short distances, it still contains a description of the dominant physical forces, which should lead at least to a correct description of trends. More generally, as previously argued in other fields

(Angioletti-Uberti, 2017), the fine details of the energy-separation distance relation might not be too relevant for a correct description of meso-scale or integrated properties, as long as the important features, e.g., the presence of minima, or barriers, and their relative position, are correctly captured.

A number of authors (Güven, 1992; Israelachvili, 2011; Mitchell and Soga, 2005) have argued that the most rigorous approach to study clay particle interactions is to adopt atomistic molecular dynamics (MD) simulations. However, atomistic simulations are too computationally expensive to be used to study most properties of clay. Some researchers have recently used atomistic MD to develop coarse-grained potential functions to describe clay particle interactions (Carrier, 2014; Ebrahimi et al., 2012; Honorio et al., 2018, 2017), but no data are available for kaolinite.

Table 1. DLVO parameters (Gupta, 2011) used to compute face-face and edge-edge interactions under the assumption of constant surface potential. Af-Af, Sf-Sf and Af-Sf indicate Alumina face – Alumina face, Silica face – Silica face and Alumina face – Silica face interactions, respectively. E-E indicates the Edge – Edge interaction

DLVO parameter	Af – Af	Sf – Sf	Af – Sf	E – E
A_H [J]	3.9×10^{-20}	1.11×10^{-20}	2.08×10^{-20}	2.37×10^{-20}
ψ_1 [V]	-55.27×10^{-3}	-67.05×10^{-3}	-55.27×10^{-3}	-125.29×10^{-3}
ψ_2 [V]			-67.05×10^{-3}	
ε_r [–]	78			
ϵ_0 [F/m]	8.854×10^{-12}			
κ [1/m]	9.6×10^{-9}			
δ_1 (and δ_2) [m]	Particles diameter (as in Table 2)			Particles thickness (as in Table 2)

This study explores how we can implement DLVO in a particle-based model so that its relevance to clay behaviour can be critically analysed. The DLVO equations provided in the literature cannot be directly used in a DEM / MD code where the platelets have a finite size

and interact at arbitrary relative orientations in three-dimensional space. Instead, the DLVO energy-separation relationships must be used to develop and calibrate specific potential functions or contact constitutive models for use in a MD or DEM code, respectively. Kaolinite saturated in an electrolyte solution with a KCl (Potassium Chloride) salt concentration $\rho_s = 1mM$ at pH=8 is considered. Under these conditions, all the interactions are repulsive. The surface potential values were estimated from surface force measurements obtained using the AFM (Gupta, 2011; Gupta and Miller, 2010) (Table 1). For the alkaline conditions considered here, the Alumina face – Alumina face (Af-Af), Alumina face – Silica face (Af-Sf) and Silica face -Silica face (Sf-Sf) interactions are comparable as these surfaces all have a similar potential. This is not the case when low pH conditions are considered and so the modelling approach proposed cannot be directly applied for all pH values.

3. Choice of modelling framework and particle type

3.1. Overview of available modelling frameworks

Prior attempts to simulate the mechanical behaviour of a system of clay particles (e.g., Anandarajah, 2000a; Ebrahimi, 2014; Pagano et al., 2020) have used either DEM (Cundall and Strack, 1979) or MD (Alder and Wainwright, 1959; Smith and Frenkel, 2002). These two techniques are algorithmically similar; both consider the equilibrium of a system of discrete rigid bodies at discrete time intervals and use a simple, explicit time integrator to simulate the evolution of the system. There are, however, some key differences. In DEM, the frictional contacts between particles are modelled by means of orthogonal springs and force-displacement relationships describe the interactions between grains. In MD interactions are modelled by considering the variation of the potential energy with respect to distance (and orientation, for rigid bodies like in our case). Friction between particles does not have to be explicitly implemented as it arises from the potential used, as well as from the coarse-graining procedure followed. Whether DEM or MD was used, fully saturated samples of clay were

considered; the systems were assumed to be fully drained so that excess pore water pressures did not develop. The pore water chemistry was accounted for via the choice of interaction model and model parameters.

Configurations obtained using MD are consistent with various probability distributions, called “ensembles” (Ercolessi, 1997), which generate a different distribution of particles, positions and momenta and ensure the correct equilibrium properties are obtained. Following a convention in the physics and chemistry communities, these “ensembles” are labelled with a three-letter sequence, e.g., NVE, NVT and NPT, where N denotes the number of particles, E denotes the total energy (kinetic + potential), and V, T and P denote volume, temperature and pressure, respectively. Temperature and pressure, which, in reality, are imposed by a material’s environment, must be imposed by artificial computational devices known as “thermostats” and “barostats”, respectively. The MD “ensembles” define specific conditions on a group of particles. These conditions are automatically associated with the equations of motion used to simulate the dynamics of the system, which by construction can be shown to keep the quantities indicated by the letters V, E, P and T at controllable target values (Allen and Tildesley, 1987). For our simulations this means that in the case of NVE, once the initial positions and velocities of the particles are given, the energy is determined and is constant throughout the simulation. In the case of NVT, volume is constant, and a computational device known as a thermostat replicates the constant temperature of the simulated system. Here the NPT ensemble was used to compress the sample; in this case a thermostat replicates constant T conditions; a barostat was used to control the pressure, which in our simulations was increased linearly. In all of these “ensembles” the number N of particles is constant. The way these ensembles are used here is summarised in Figure 2 and further detailed below.

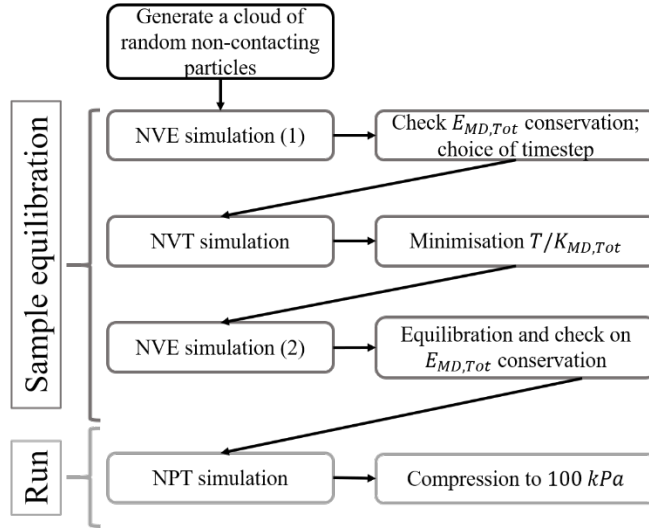


Figure 2. Work-flow employed to perform molecular dynamics simulations of kaolinite considering alkaline pH conditions. T is the temperature of the system and $E_{MD,Tot}$ and $K_{MD,Tot}$ are the total energy and the kinetic energy of the system from CGMD simulations, respectively

3.2. Modelling options to represent clay particle morphology

When developing a particle-based model, it is important to choose a particle shape which can realistically represent the material modelled. Clay particles are phyllosilicate platelets, they are primarily hydrous aluminium silicates sheet structures. Kaolinite is a 1:1 clay so that an octahedral sheet comprising aluminium cations alternates with a tetrahedral silica sheet (Mitchell and Soga, 2005). A kaolinite particle has a diameter (D) between $0.1\mu m$ and $4\mu m$ and a thickness (δ) of about $0.05\mu m - 2\mu m$ (Lambe & Whitman, 1969; Mitchell & Soga, 2005; Santamarina et al., 2001). The particle shape is often observed (from Scanning Electron Microscopy (SEM) images) to be pseudo-hexagonal.

Anandarajah and his colleagues have explored the use of DEM to simulate one-dimensional compression of kaolinite. Initially they considered 2D rectangular particles (Anandarajah, 2000a, 2000b, 1994); their subsequent 3D work used cuboids (Anandarajah and Yao, 2005; Yao, 2001). They included F_{vdW} and F_{Edl} in their interaction model, but they neglected the negative electrostatic force that arises from the different surface potentials on opposite sides of

the particles. A typical simulation considered 400 randomly oriented particles enclosed by rigid planar boundaries. Pagano et al. (2020) also employed DEM to simulate one-dimensional compression of kaolinite using 2D rod-like particles made of disk-clusters. They developed a simple tri-linear contact model based on qualitative experimental observations (Pedrotti and Tarantino, 2018). The open-source software MercuryDPM (Weinhart et al., 2020) was used to simulate 300 randomly oriented particles enclosed within rigid wall boundaries, which, however, introduce artefacts in the particle arrangement (Allen and Tildesley, 1987; Anandarajah, 2000b; Huang et al., 2014). These two-dimensional models are, effectively, simple conceptual models as they cannot capture the real material's 3D geometric complexity. In fact, it is well-established that there are both quantitative and qualitative distinctions between 2D and 3D models (Visscher and Bolsterli, 1972).

Liu (2015) performed coarse-grained MD simulations using the LAMMPS software (Plimpton, 1995) to capture cluster formation in suspensions of kaolinite under different pH conditions. Each hexagonal particle was represented by a clump of spheres on a hexagonal lattice. Particle interactions were computed using a combination of the DLVO model and a shifted and truncated Lennard-Jones (LJ) potential (Liu et al., 2014). They considered about 1,000 composite particles and used periodic boundary conditions to prevent boundary effects. A similar modelling approach was used to simulate kaolinite in one-dimensional compression (Sjoblom, 2016) and triaxial compression (Aminpour and Sjoblom, 2019). In both cases, composite particles with a diameter-to-thickness ratio ≈ 12 were modelled as rigid hexagons using two types of smaller sub-particles to differentiate the responses of the particle faces and edges. Interparticle forces were captured using the DLVO theory with the addition of Stern and Born short-range repulsion forces, modelled by means of orthogonal springs. LAMMPS was used with periodic boundary conditions and a typical cubic sample contained 4,700 (Sjoblom, 2016) or 1,000 (Aminpour and Sjoblom, 2019) particles. The sphere clumps used in prior

studies comprised 122 and >160 sub-spheres (Liu, 2015; Sjoblom, 2016, respectively) so that up to $\approx 15,000$ sub-sphere interactions must be calculated for a single face-face interaction between two particles. This has implications for computational cost and may inhibit achieving a representative element volume (REV) in MD/DEM simulations, as we will argue later.

Ebrahimi (2014) used LAMMPS in his simulations of Na-montmorillonite to quantify its effective macro-scale stiffness. He modelled montmorillonite particles using prolate ellipsoids (spheroids) (Ebrahimi et al., 2016, 2014) and the interparticle interactions were described by the Gay-Berne (GB) potential (Everaers and Ejtehadi, 2003; Gay and Berne, 1981). The GB potential is a modified form of the Lennard-Jones potential. It is widely used in molecular dynamics simulations of colloidal systems to simulate non-spherical particles, and, like the LJ potential, is characterised by a repulsive and attractive component. While it has been criticised for its empirical nature (Everaers and Ejtehadi, 2003), the Gay-Berne potential is used here as it allows simulations of three-dimensional systems containing ellipsoids of various aspect ratios interacting at different orientations and it is already implemented in LAMMPS (Brown et al., 2009; Everaers and Ejtehadi, 2003; Plimpton, 1995). Ebrahimi (2014) showed that by an appropriate choice of the principal radii, a circular disc can be described as a flat ellipsoid and used to model clay grains. Ebrahimi's simulations considered 1,000 randomly oriented particles under periodic boundary conditions.

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Table 2. Sample ID, diameter, thickness and aspect ratios information of samples considered

	Sample ID	ID Particle Type	Diameter D (nm)	Thickness δ (nm)	Aspect ratio (D/ δ)
Monodisperse	Mono_1	1	2000	200	10
Polydisperse	Poly_1	3	1300	130	10
		2	1650	165	10
		1	2000	200	10

265

266 3.3. Strategy adopted here

267 In this contribution, MD is used to simulate kaolinite particles as oblate spheroids (i.e.,
268 ellipsoids with equal major and intermediate semi-axis lengths); the system is assumed to be
269 fully saturated and fully drained and the influence of pore water chemistry on interactions is
270 accounted for via the potential function. Figure 3(a) presents a schematic showing plane and
271 side views of the particles used to model kaolinite in this study. Pair-wise interactions are
272 described by the GB potential. Two sample types were considered here as detailed in Table 2.
273 Sample *Mono_1* contains monodisperse ellipsoidal particles with an aspect ratio AR (ratio
274 between diameter and thickness) of 10 and $D = 2000 \text{ nm}$. The polydisperse sample contained
275 a 1:1:1 (approximate) mixture of three particle types. The average diameter is the mean value
276 in the range suggested by Santamarina et al. (2001); the two additional diameter values were
277 taken as 20% above and 20 % below the average. *Poly_1* contains particles with different
278 dimensions but all having AR=10.

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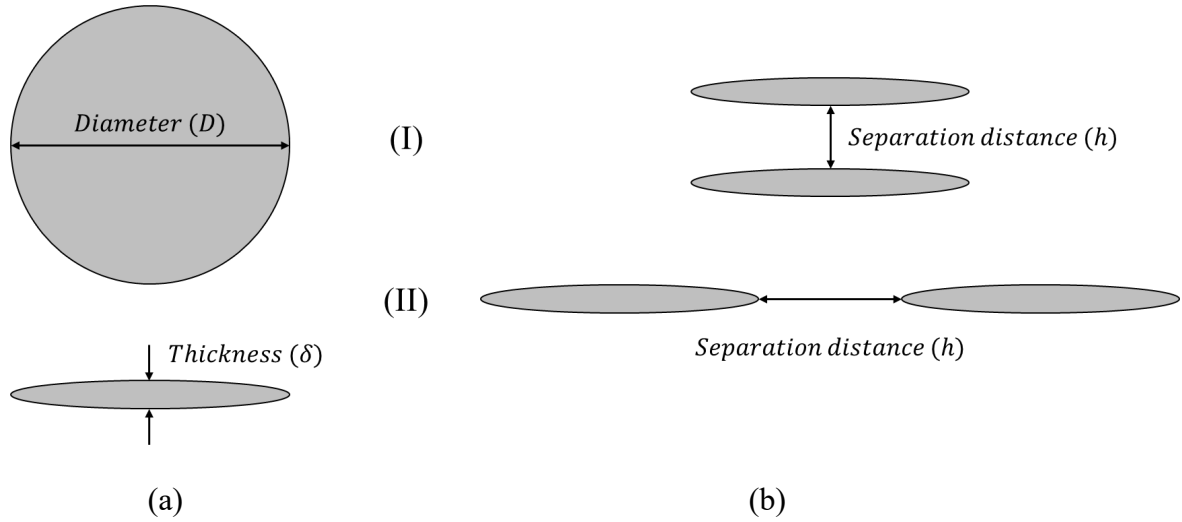


Figure 3. (a) Plane and side view of ellipsoidal kaolinite particles; (b) Face-face (I) and edge-edge (II) reference configurations

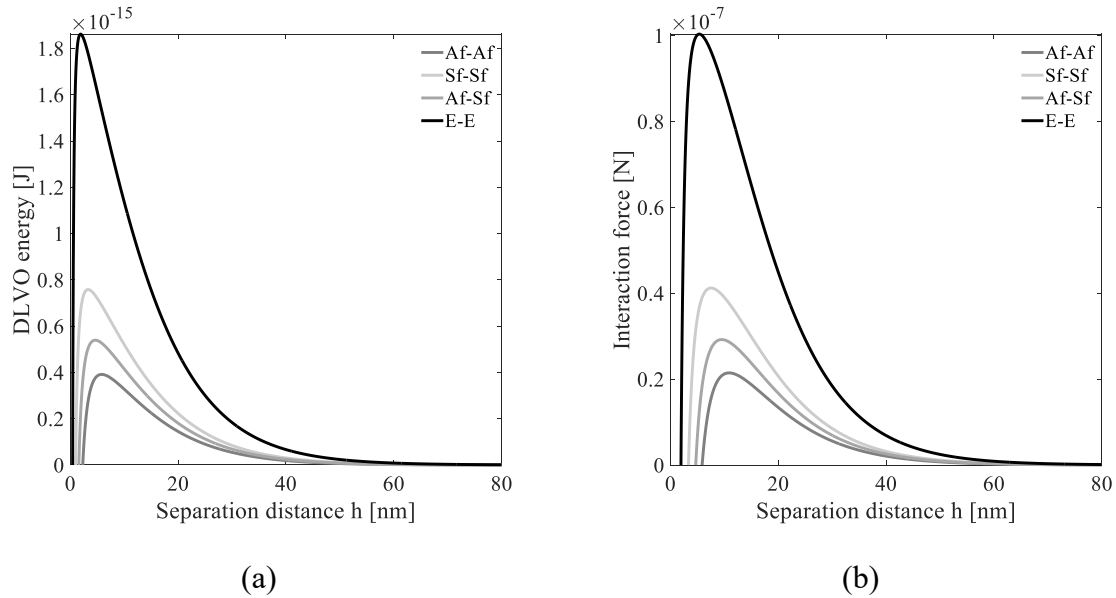
4. Development and Calibration of a modified Gay-Berne Potential

The GB potential, as implemented in LAMMPS, is given by the following functional form (Berardi et al., 1995; Brown et al., 2009; Everaers and Ejtehadi, 2003):

$$U_{GB} = 4\epsilon \left[\left(\frac{\sigma}{h_{12} + \gamma\sigma} \right)^{12} - \left(\frac{\sigma}{h_{12} + \gamma\sigma} \right)^6 \right] \times \eta \times \chi \quad \text{Eq. (4)}$$

where ϵ [J] is the energy scale, σ [nm] is the atomic interaction radius, γ [–] is the shift of the potential minimum, and h_{12} [nm] is the closest distance between particle surfaces (this distance equals the surface separation distance h in Eq. (2) and Eq. (3) only when particles are in the reference configurations as in Figure 3(b) so that when $h_{12} \sim 0$, particles are almost touching). The quantity h_{12} is determined by the particle sizes and orientations. The dimensionless quantities η and χ (the shape and energy anisotropies, respectively) depend on the particle dimensions, their orientation and on the relative well-depth values, ϵ_{ia} , ϵ_{ib} , ϵ_{ic} , ϵ_{ja} , ϵ_{jb} , ϵ_{jc} , which are defined for face-face, side-side (which is equivalent to the face-face here), and edge-edge interactions. The letters i and j refer to the interacting particles, while a , b and c indicate the semi-axes directions these quantities refer to. For the ellipsoids used here $\epsilon_{ia} =$

295 ε_{ib} and $\varepsilon_{ja} = \varepsilon_{jb}$. The first term of U_{GB} [J] is related to repulsion, while $\left(-\frac{\sigma}{h_{12}+\gamma\sigma}\right)^6$ is the
 296 attractive component of the potential. The GB potential parameters do not have a direct
 297 physical meaning and cannot easily be linked to clay surface chemistry and pore fluid
 298 chemistry. The GB potential is defined such that, if faces and edges are characterised by a
 299 surface potential with the same sign (i.e., negative in the case examined), a unique set of
 300 parameters can reproduce the energy-separation distance relationship observed considering the
 301 face-face and edge-edge reference configurations (Figure 3(b)).



302 *Figure 4. Interactions for particles in sample Mono_1 (kaolinite saturated in an electrolyte solution with a KCl*
 303 *$\rho_s = 1\text{mM}$ at $\text{pH}=8$); Af, Sf and E denote Alumina face, Silica face and Edge respectively. (a) DLVO energy-*
 304 *separation distance relationships and (b) DLVO force-separation distance relationships*

305 Figure 4(a) and Figure 5 present energy-separation data for *Mono_1* and *Poly_1* generated
 306 using the DLVO expressions (Eq. (2) and Eq. (3)) for the two reference configurations and
 307 using the surface potential values given in Gupta (2011) (Table 1). Eq. (3) was also applied in
 308 the edge-edge configuration, for which we determined the energy density using the expressions
 309 for infinite parallel surfaces, i.e., using Eq. (3). The energy computed for this configuration
 310 may be overestimated as we fail to account for edge effects and, in principle, the Derjaguin

assumption for curved surfaces could be applied (Israelachvili, 2011). Eq. (2) and Eq. (3) provide data in terms of energy/unit area. Energy – separation distance profiles were obtained multiplying Eq. (2) and Eq. (3) by the interacting areas in the two reference configurations. For simplicity, the interacting areas were determined based on geometrical considerations and defined as $A_{faces} = \pi \times \left(\frac{D}{2}\right)^2$ and $A_{edges} = \pi \times \left(\frac{D}{2}\right) \times \delta$, which is half the area of the edges. For the pore fluid conditions considered, the data show a purely repulsive response at distances h exceeding h_{eb} , the height of the energy barrier in the system (see Figure 1 for reference). Equivalent force data obtained via numerical differentiation are illustrated in Figure 4(b) and Figure 6, for *Mono_1* and *Poly_1* samples, respectively; these data are within the range of force values reported in the literature (Israelachvili, 2011; Yao, 2001). The data on Figure 4(a) and Figure 5 were used to calibrate the GB potential parameters. It is assumed that the interactions at intermediate orientations are correctly predicted by the GB model once the face-to-face and edge-to-edge interactions are correctly calibrated (Ebrahimi et al., 2014; Gay and Berne, 1981). Due to its mathematical form, the GB potential cannot reproduce the attraction at short distances predicted by DLVO equations, arising when $h < h_{eb}$ (Bandera et al., 2019). This does not present a problem during initial loading; rather, it must be solved to simulate unloading, and this is beyond the scope of the current study. The calibration process focussed on separation distances greater than h_{eb} and so can describe the variation of the interparticle forces with pore fluid chemistry (e.g., pH, salt concentration). Once calibrated, the GB potential represents a good analytical framework that can capture both the energy-separation distance relationship predicted by DLVO and simulate particle rotation.

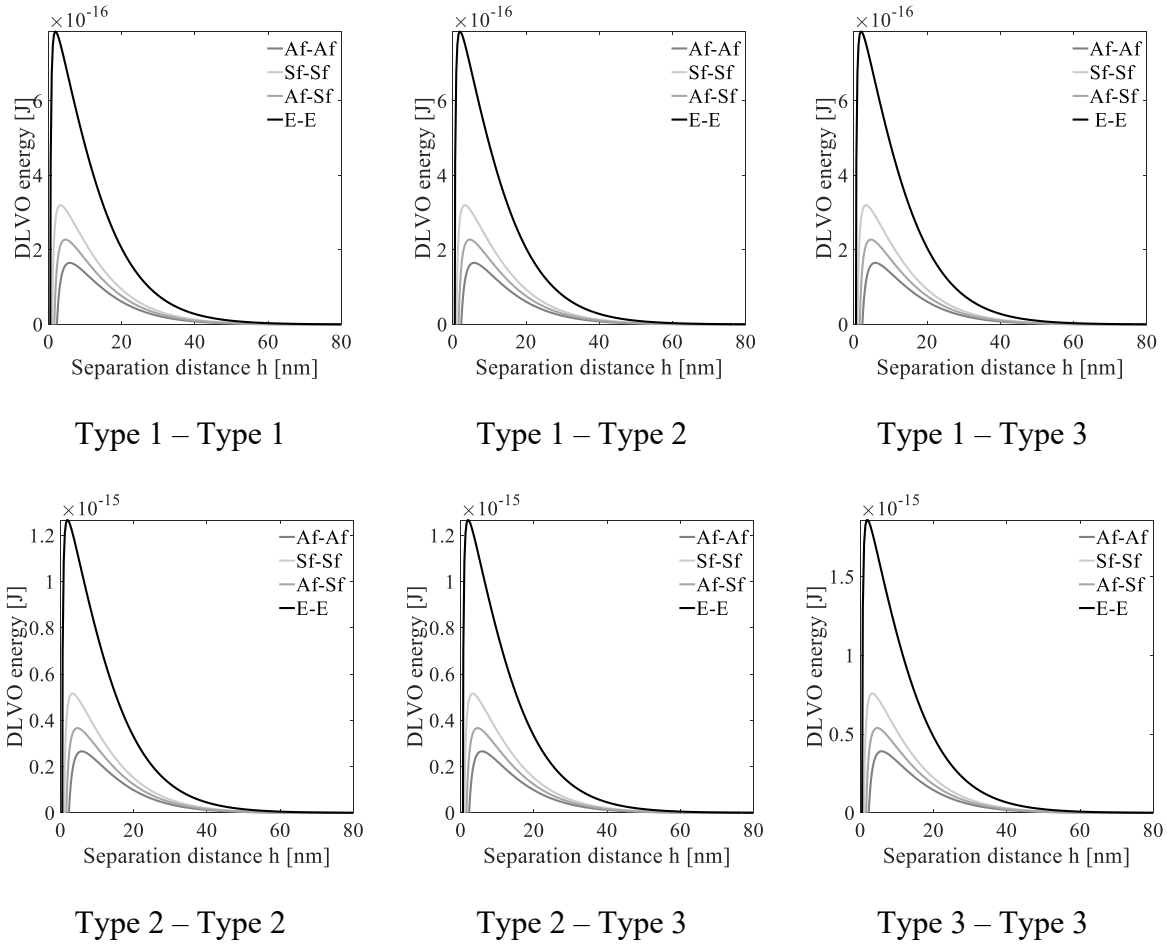


Figure 5. DLVO energy-separation distance relationships for particles in sample Poly_1 (kaolinite saturated in an electrolyte solution with a KCl $\rho_s = 1\text{mM}$ at $\text{pH}=8$); Af, Sf and E denote Alumina face, Silica face and Edge respectively. All six possible interactions are considered (Plots consider different scales on the vertical axes)

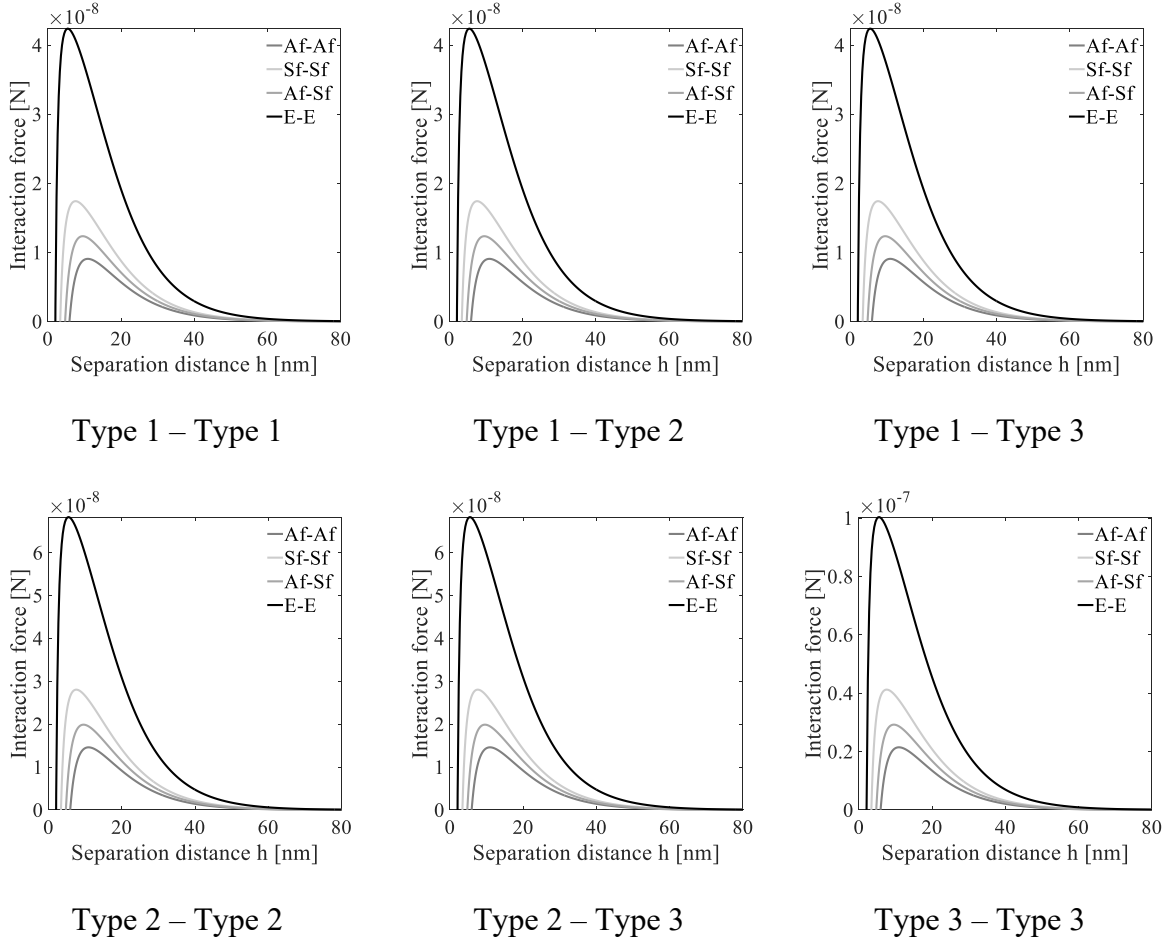


Figure 6. DLVO force-separation distance relationships for particles in sample Poly_1 (kaolinite saturated in an electrolyte solution with a KCl $\rho_s = 1\text{mM}$ at $\text{pH}=8$); Af, Sf and E denote Alumina face, Silica face and Edge respectively. All six possible interactions are considered (Plots consider different scales on the vertical axes)

In the general case, **nine** GB potential parameters (γ , ε , σ , ε_{ia} , ε_{ib} , ε_{ic} , ε_{ja} , ε_{jb} , ε_{jc}) must be calibrated to reproduce the energy-separation distance relationship predicted by the DLVO model. However, for monodisperse samples with spheroidal particles there are only **five** independent parameters as $\varepsilon_{ia} = \varepsilon_{ja} = \varepsilon_{ib} = \varepsilon_{jb}$ and $\varepsilon_{ic} = \varepsilon_{jc}$.

345

Table 3. Calibrated GB parameters for sample Mono_1

GB parameter	Value
$\gamma_{sb} [-]$	0.37
$\epsilon [J]$	2.36×10^{-24}
$\sigma [nm]$	230
$\epsilon_{1a} = \epsilon_{2a} [-]$	850
$\epsilon_{1b} = \epsilon_{2b} [-]$	850
$\epsilon_{1c} = \epsilon_{2c} [-]$	250

346

347

Table 4. Calibrated GB parameters for sample Poly_1

GB parameter	Type 1 – Type 1	Type 1 – Type 2	Type 1 – Type 3	Type 2 – Type 2	Type 2 – Type 3	Type 3 – Type 3
$\gamma_{sb} [-]$	0.35	0.32	0.32	0.305	0.305	0.39
$\epsilon [J]$	1.4×10^{-25}	6.95×10^{-26}	6.95×10^{-26}	6.95×10^{-26}	6.95×10^{-26}	1.74×10^{-24}
$\sigma [nm]$	370	370	390	340	350	350
$\epsilon_{1a} [-]$	1100	1100	1100	1050	1050	1050
$\epsilon_{1b} [-]$	1100	1100	1100	1050	1050	1050
$\epsilon_{1c} [-]$	600	600	600	470	470	300
$\epsilon_{2a} [-]$	1100	1050	1050	1050	1050	1050
$\epsilon_{2b} [-]$	1100	1050	1050	1050	1050	1050
$\epsilon_{2c} [-]$	600	470	300	470	300	300

348

349 For the scenario considered here, DLVO predicts a purely repulsive interaction and so a
 350 modified GB potential expression which considers only the repulsive term was implemented
 351 in the LAMMPS source code to avoid spurious, non-physical interactions:

$$U_{GB,Repulsive} = 4\epsilon \left[\left(\frac{\sigma}{h_{12} + \gamma\sigma} \right)^{12} \right] \times \eta \times \chi \quad \text{Eq. (5)}$$

352 The new implementation was cross-checked by comparison with data generated by MATLAB
 353 for a single interaction. In the monodisperse case both the interaction energy and forces
 354 predicted by MATLAB matched those obtained in LAMMPS. In the polydisperse case, a
 355 discrepancy arose because LAMMPS inhibits the use of different γ values for different
 356 interacting pairs, as γ is set as a global parameter. The issue was resolved by further modifying

the code of the GB potential at source by introducing a new, pair-dependent, γ parameter, γ_{sb} .

The repulsive energy then becomes:

$$U_{GB,Repulsive}^{sb} = 4\epsilon \left[\left(\frac{\sigma}{h_{12} + \gamma_{sb}\sigma} \right)^{12} \right] \times \eta \times \chi \quad \text{Eq. (6)}$$

The trial and error calibration process used was informed by a parametric study. Table 3 and Table 4 summarise the calibrated parameters for the two samples considered here. Figure 7 and Figure 8 compare the calibrated GB potential with the DLVO prediction by considering the energy-separation distance relationships (for $h > h_{eb}$) for the *Mono_1* and *Poly_1* cases, respectively. As can be seen in Figure 7 and Figure 8, the GB potential calibration focuses on low potential values. This represents the most likely scenario in the case of virgin compression from a cloud of non-contacting particles. We did not seek to accurately describe the initial part of the DLVO curve for two reasons. Firstly, the DLVO theory provides an unphysical description at very small distances, where effectively the potential should become repulsive because particles cannot physically overlap (Anandarajah, 2003, 2000a). The second reason is that when interacting particles enter this short distance region, the material fabric does not change significantly with a further increase in pressure (Hanley et al., 2015) and it becomes less sensitive to the exact details of the potential.

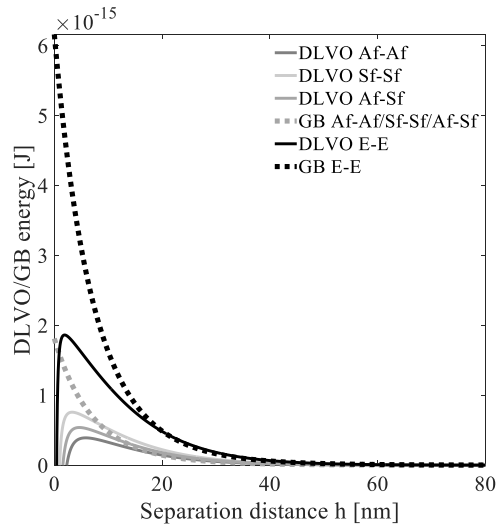


Figure 7. GB potential calibrated against DLVO energy-separation distance profiles for Mono_1 sample. DLVO denotes DLVO prediction, GB denotes the calibrated GB potential; Af, Sf and E denote Alumina face, Silica face and Edge respectively

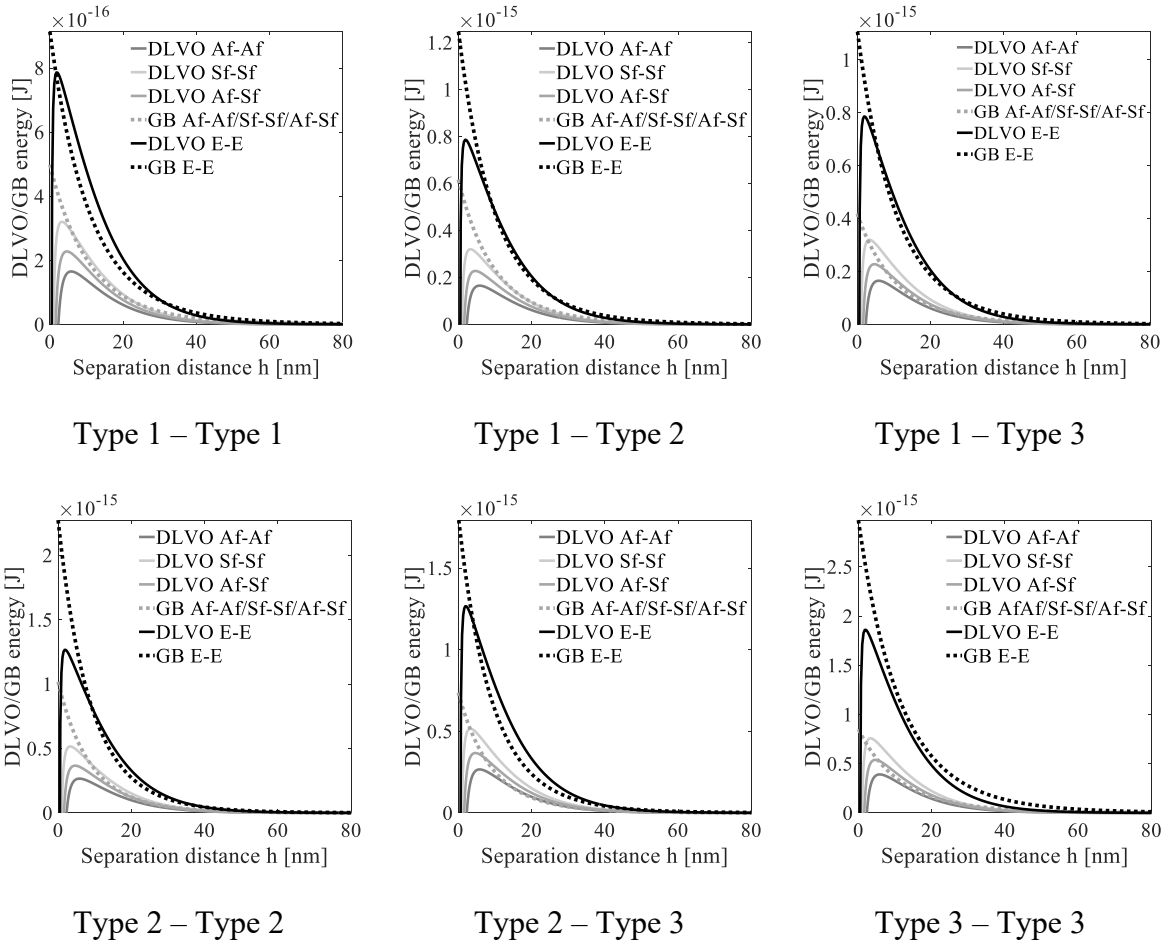


Figure 8. GB potential calibrated against DLVO energy-separation distance profiles Poly_1 sample. DLVO denotes DLVO prediction, GB denotes the calibrated GB potential; Af, Sf and E denote Alumina face, Silica face and Edge respectively

5. Simulation of Compression

5.1. Sample Generation and initial equilibration

Figure 2 summarises the simulation work-flow we converged to for the CGMD simulations described here. Initial sample configurations were created by placing the centroids of the ellipsoids at positions defined by a simple cubic lattice so that the centre-to-centre spacing between them was larger than the particle diameter to avoid overlap. Random orientations were assigned to each particle and particles were also given initial random velocities at a specified kinetic temperature $T = 300 K$. Periodic boundaries conditions were used in all three directions, x, y, and z. Sample generation inevitably involves a decision on the size of the

system to be simulated. The large computational resources required limit discrete numerical simulations to consider an incredibly small number of particles compared to the number of particles contained in samples used for laboratory element tests. In principle, use of periodic boundaries enables very large assemblies of particles to be simulated; conceptually only a subdomain of the entire system is considered and then replicated infinitely in three-dimensional space. However, it is still necessary to achieve a representative element volume (REV). An REV is the minimum volume of material for which the macroscopic parameters of interest are not influenced by the size of the sample and it can be identified via parametric studies where the sample size is systematically varied (Barreto, 2009).

The smallest sample size considered here (1,000 particles) is in line with prior published studies (Table 5). The parametric study included additional specimens with 10,000 and 100,000 particles so that the influence of sample size on the simulated material behaviour could be examined. These virtual samples were visualised using the open-source software OVITO (Open Visualisation Tool) (Stukowski, 2010). Figure 9 (a) and (b) present representative images of 1,000-particle samples of *Mono_1* and *Poly_1* to show the particle arrangements immediately after specimen generation. At this stage, the specimens were gas-like, that is, had very low density, were characterised by a very high percentage of voids and had little interaction amongst particles.

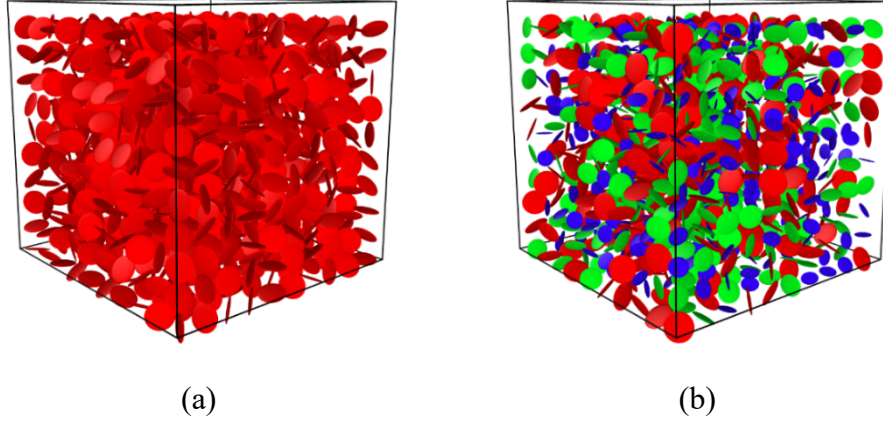
For each sample, following generation, a NVE simulation, in which particles move and interact with each other while meeting the constant energy constraint ($E_{MD,Tot}$) was performed. Because the initial configuration is very far from equilibrium, large forces develop between particles at the beginning of the NVE simulation. This causes the energy of the system to oscillate over a few time-steps before the equations of motion can be correctly integrated (Allen and Tildesley, 1987; Tuckerman, 2010). During this NVE simulation, the temperature (T) calculated from the average of the particles kinetic energies increased to a high value,

indicating the system had not yet reached equilibrium. The sample in the non-equilibrated stage was then subjected to a NVT simulation in which its temperature was reduced to room temperature by applying a Nose'-Hoover (Shinoda et al., 2004) thermostat; the system was left equilibrating until the temperature had stabilised. Before compression, an additional NVE analysis was performed on the systems at room temperature to assess the suitability of the time-step chosen for the explicit integration of the equations of motion for the system. Figure 9 (c) and (d) shows *Mono_1* and *Poly_1* samples at the end of the equilibration stage.

Table 5. Number of particles used in previous numerical studies of clay

Authors	Material modelled	Number of particles used
Anandarajah and Yao (2003)	Kaolinite (2D/3D)	400
Ebrahimi (2014)	Montmorillonite (3D)	1000
Liu (2015)	Kaolinite (3D)	1000
Sjoblom (2016)	Kaolinite (3D)	4700
Aminpour and Sjoblom (2019)	Kaolinite (3D)	1000
Pagano et al. (2020)	Kaolinite (2D)	300

Particle arrangement after sample generation



Particles arrangement before compression

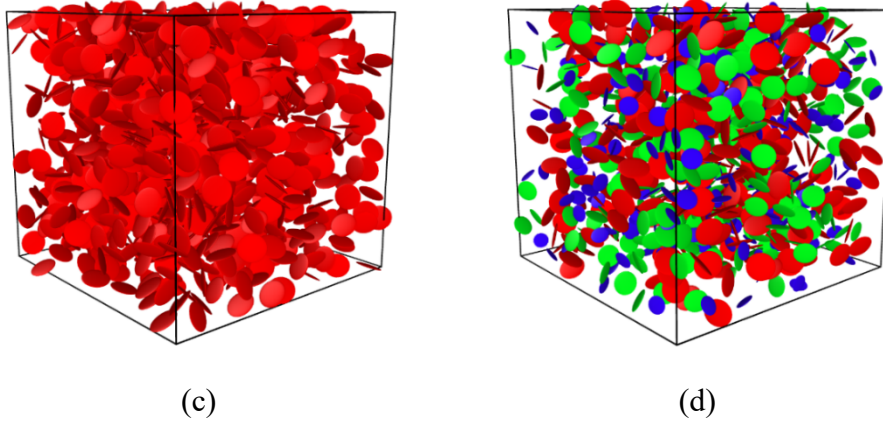


Figure 9. Illustration of small (1,000 particle) samples: (a) Mono_1 post-generation (b) Poly_1 post-generation (c) Mono_1 just prior compression (d) Poly_1 just prior compression. In (b) and (d) images are color-coded according to their types (see Table 2): Type 1 particles are red, Type 2 are green and Type 3 are blue

5.2. Selecting simulation time-step

The second-order Verlet integration scheme is used to integrate the equations of motion in MD/DEM in LAMMPS (Otsubo et al., 2017). The Verlet algorithm is explicit, conditionally stable and to ensure numerical stability, the time-step Δt_{simul} must be smaller than Δt_{crit} (critical timestep) (O’Sullivan and Bray, 2004; Otsubo et al., 2017). The non-linearity of the interaction model used here significantly complicates the calculation of Δt_{crit} . Following prior published numerical simulations of clay (e.g., Yao, 2001), a simplified method, which

435 considers the oscillation period of a single degree of freedom (DOF) system with mass m and
 436 stiffness k , is used. The critical time-step Δt_{crit} [s] was computed as (Eq. (7))

$$\Delta t_{crit} = \frac{T_{DOF}}{\pi} \quad \text{Eq. (7)}$$

437 T_{DOF} [s] is the oscillation period of a single DOF system, defined as:

$$T_{DOF} = 2\pi \sqrt{\frac{m_{min}}{k_{max}}} \quad \text{Eq. (8)}$$

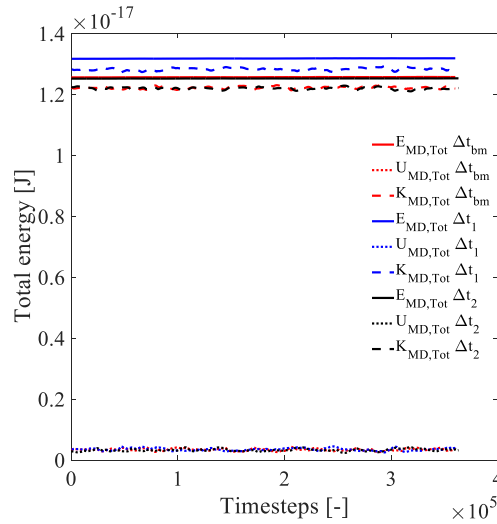
438 where m_{min} [kg] is the minimum mass in the system and k_{max} [N/m] is the maximum
 439 stiffness associated with particle-particle interactions. The stiffness, k , is computed [here](#)
 440 numerically as the second derivative of the pair energy with respect to the separation distance
 441 for the two reference configurations (Figure 3(b)). As the interaction is purely repulsive for
 442 pH=8, k_{max} is observed when [particles touch](#) at $h = 0$. To account for the existence of multiple
 443 contacts within the system (Otsubo et al., 2017), Δt_{crit} is multiplied by a reduction factor,
 444 $\vartheta[-]$, such that the time-step used to integrate the equations of motions in MD, Δt_{Simul} ,
 445 satisfies the following condition:

$$\Delta t_{Simul} \leq \vartheta \Delta t_{crit} \quad \text{Eq. (9)}$$

446

447 Different values for ϑ can be found in the literature (e.g. Anandarajah, 1994; O’Sullivan and
 448 Bray, 2004; Pagano et al., 2020; Yao, 2001). In this paper, two ϑ values, defining two different
 449 time-steps Δt_1 and Δt_2 , are considered: $\vartheta_1 = 0.17$ obtained by O’Sullivan and Bray (2004) for
 450 3D analyses of uniform spheres, and $\vartheta_2 = 0.02$, obtained from results in Pagano et al. (2020).
 451 An NVE simulation was carried out to assess which time-step value, Δt_1 or Δt_2 , ensured energy
 452 conservation and, hence, correct integration of the equations of motion. Results obtained from
 453 analyses carried out with Δt_1 and Δt_2 were compared with results of a simulation performed

454 with a very small time-step, used as a benchmark: $\Delta t_{bm} = 1 \times 10^{-11}$ s. Figure 10 plots
 455 potential ($U_{MD,Tot}$), kinetic ($K_{MD,Tot}$), and total ($E_{MD,Tot}$) energies obtained by performing
 456 simulations for *Mono_I* with 1,000 particles. In all the cases, $E_{MD,Tot}$ is conserved. However,
 457 when considering Δt_1 , higher $K_{MD,Tot}$ and $E_{MD,Tot}$ energies were observed compared to the
 458 benchmark case ($\Delta t_{simul} = \Delta t_{bm}$). Here $\Delta t_{simul} \approx \Delta t_2$ were employed:
 459 $\Delta t_{simul} = 1.1 \times 10^{-10}$ s for *Mono_I* and $\Delta t_{simul} = 2.26 \times 10^{-10}$ s for *Poly_I*, respectively.
 460 The Δt_{simul} values used in prior simulations of kaolinite (e.g., Pagano et al., 2020; Sjoblom,
 461 2016) are comparable with the Δt_{simul} used here.



462
 463 Figure 10. Energy profiles (total, $E_{MD,Tot}$, potential, $U_{MD,Tot}$ and kinetic, $K_{MD,Tot}$) considering 1,000-particle
 464 *Mono_I* sample analysis carried out with different time-step values

465 6. Isotropic compression

466 After the second NVE simulation (Figure 2), samples were subjected to isotropic compression
 467 by performing NPT simulations at a constant $T = 300K$, while a linear variation of pressure
 468 (P) up to 100 kPa was applied. [Selecting the compression rate is a key issue for these](#)
 469 [simulations](#). Compression tests on platy aspherical particles are computationally expensive.
 470 LAMMPS can run on distributed-memory high performance computers (HPCs). A single node
 471 with 48 CPUs was used to simulate the 10,000-particle specimen; 10 nodes and a total of 480

CPUs were employed to simulate the 100,000-particle specimen. For each sample size and type, four NPT simulations were performed at different compression rates to determine which value was appropriate to achieve reasonable results. These compression rates are significantly bigger than those used in experimental studies. The fastest compression rate at which the output is independent of the strain rate is the one that should be used as a trade-off between having a simulation that can be performed and that is meaningful when compared to experimental results. Table 6 summarises the length of the analyses considered. The compression rate values for *Mono_1* and *Poly_1* are slightly different, as the periodic box dimensions cannot be directly controlled during the NPT simulations; however, they are of the same order of magnitude and thus direct comparison is valid.

Table 6. Length of the isotropic compression tests performed on Mono_1 and Poly_1 samples

Simulation ID	Simulation length (s)
NPT1	5×10^{-5}
NPT2	5×10^{-4}
NPT3	5×10^{-3}
NPT4	1×10^{-2}

6.1. Effects of compression rate

6.1.1 Macroscopic effects

The effects of sample size and strain rate on the behaviour of virtual specimens cannot be completely decoupled and so we first consider all three sample sizes and then focus only on the samples with 100,000 particles.

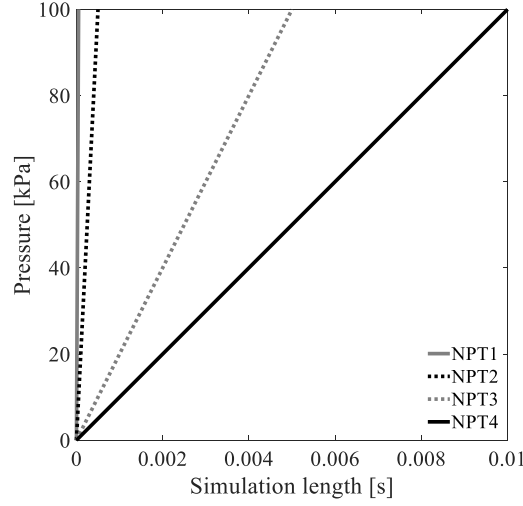


Figure 11. Pressure profiles used in isotropic compression simulations

The pressure profiles applied in the simulations are shown in Figure 11; *NPT1* had the fastest compression rate, while *NPT4* was the slowest. The void ratio $e = e_{100kPa}$ [-] at the end of each compression test (i.e. at 100 kPa) is plotted against the compression rate in Figure 12(a) and Figure 14(a) for *Mono_1* and *Poly_1*, respectively. The compression rate at the end of each *NPT* simulation, $\dot{\epsilon}_f$ [1/s], was computed using Eq. (10):

$$\dot{\epsilon}_f = \frac{\frac{l_0 - l_f}{l_0}}{t_f} \quad \text{Eq. (10)}$$

where l_0 [m] is the periodic box dimension at the beginning of the compression, l_f [m] is the box dimension in either direction at the end of each *NPT* simulation and t_f [s] is the total time length of the analysis.

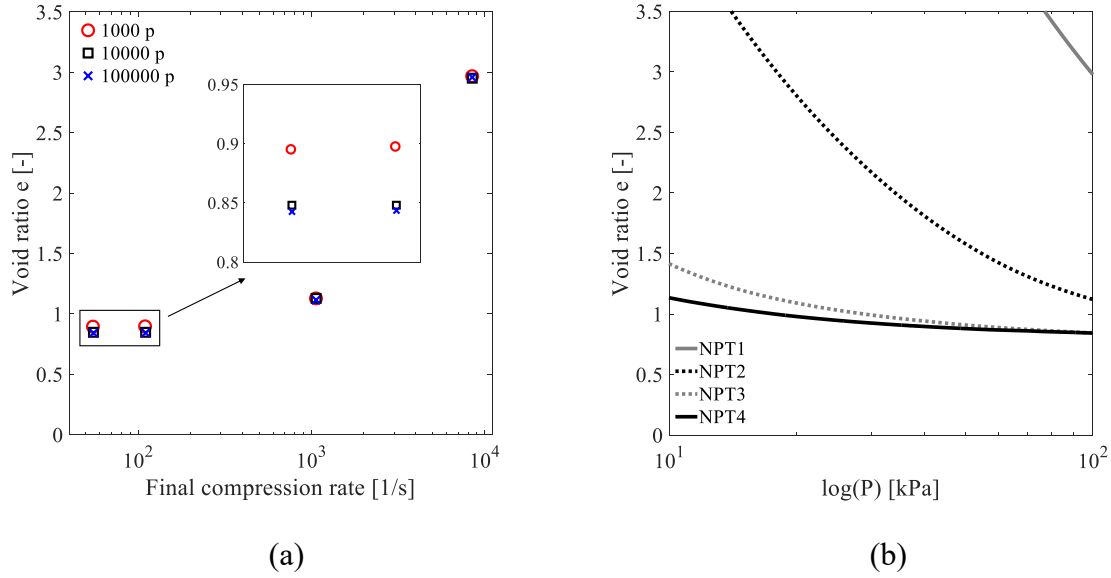
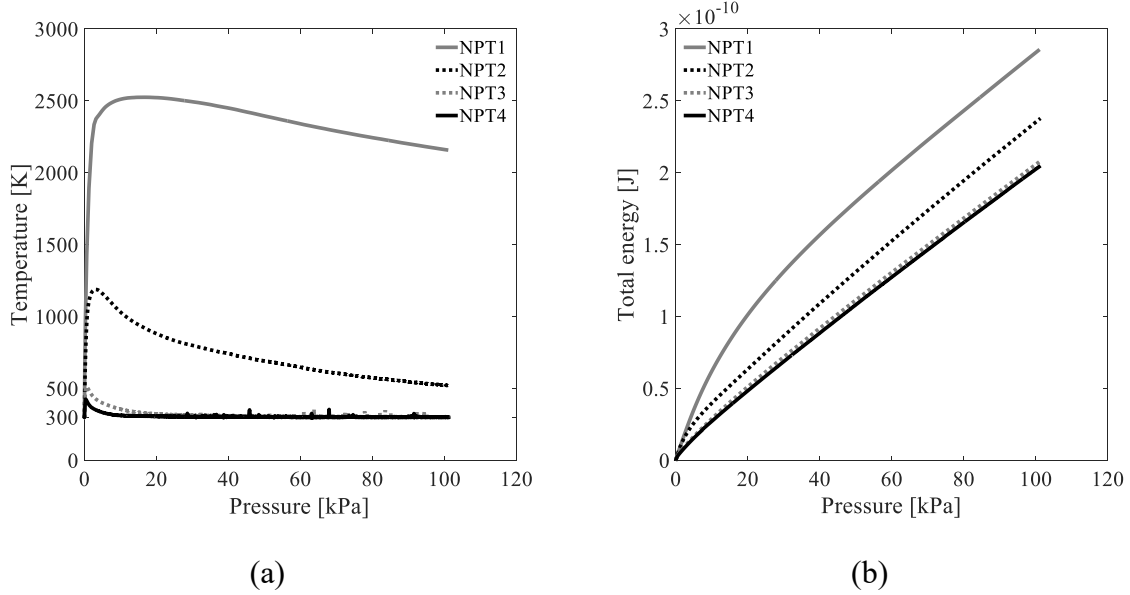


Figure 12. Sensitivity of response to sample size and strain rate for *Mono_I* samples: (a) Variation in void ratio at 100 kPa with compression rate and sample size (b) Variation in void ratio - pressure relationship with strain rate for 100,000-particle sample

The data for the *Mono_I* samples in Figure 12(a) show that for the three sample sizes considered, e_{100kPa} is clearly influenced by the compression rate. There is a significant decrease in e_{100kPa} comparing *NPT2* with *NPT1*. For the two slowest compression rates (i.e., *NPT3* and *NPT4*), the void ratio reached a stable value, indicating a quasi-static compression had been achieved.

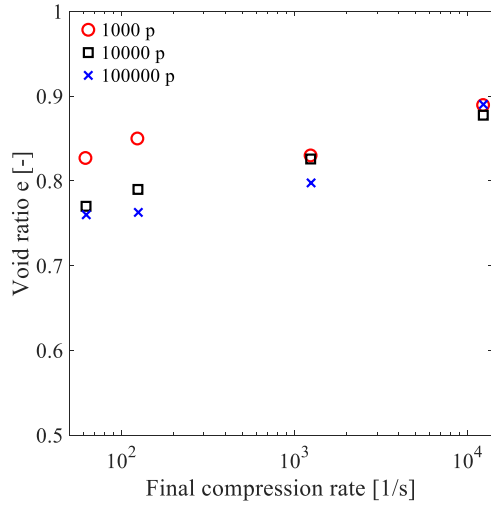
Figure 12(b) plots the variation of e with pressure for the 100,000-particle sample and shows that the compression rate also influences the slopes of the compression curves. The differences between the curves decrease with decreasing compression rate and they have a similar slope at pressures > 50 kPa. Two additional quantities were monitored during the compression phase; T and the total energy $E_{MD,Tot}$, to further confirm quasi-static conditions were being achieved. The temperature variation in the system with pressure for the different strain rates considered is shown in Figure 13(a). *NPT3* and *NPT4* had the lowest T values which oscillated around the room temperature value, i.e., $T \sim 300$ K. Figure 13(b) considers how $E_{MD,Tot}$ varies with

516 pressure: quasi-static simulations are associated with the lowest value of the total energy in the
 517 system.

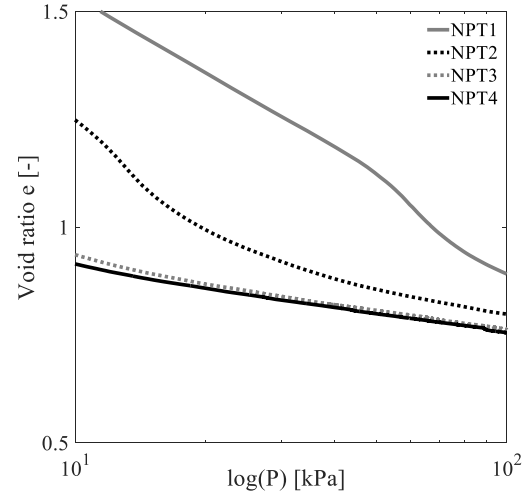


518 *Figure 13. Data for energy variation during compression at different strain rates for Mono_1 100,000-particle*
 519 *sample: (a) Variation in temperature with pressure (b) Variation in total energy with pressure*

520 The variation in e_{100kPa} with $\dot{\epsilon}_f$ for the *Poly_1* samples is shown in Figure 14(a). In comparison
 521 with the *Mono_1* samples, the *Poly_1* sample e_{100kPa} values are much closer to each other. The
 522 smallest samples with 1,000 particles show no clear sensitivity to $\dot{\epsilon}_f$; e_{100kPa} for NPT3 is higher
 523 than e_{100kPa} for NPT2. The influence of compression rate becomes clear for the large samples;
 524 this indicates that the 1,000-particle *Poly_1* sample is far from being a REV. Figure 14(b) plots
 525 how the compression curves defined for the biggest *Poly_1* sample change when considering
 526 different compression rates. Just as in *Mono_1*, e_{100kPa} decreases with reducing compression
 527 rate. However, the slope of the e -log(p) curve (i.e., compressibility) varies markedly less than
 528 in the *Mono_1* samples. Both T and $E_{MD,Tot}$ were monitored throughout the compression phase
 529 and results are displayed in Figure 15(a) and Figure 15(b). Similar to *Mono_1*, at the slowest
 530 compression rate, the system is characterised by the lowest total energy and T is close to 300K
 531 throughout.

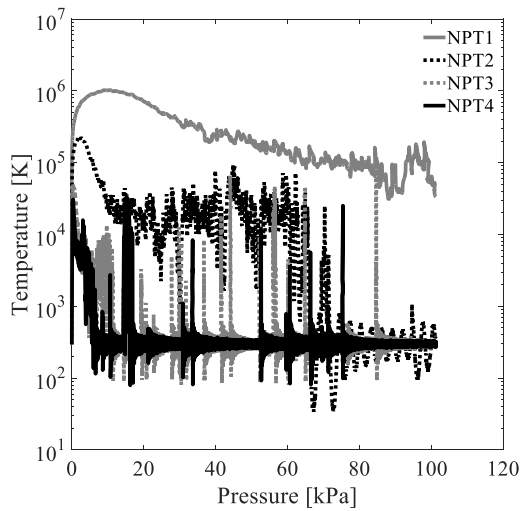


(a)

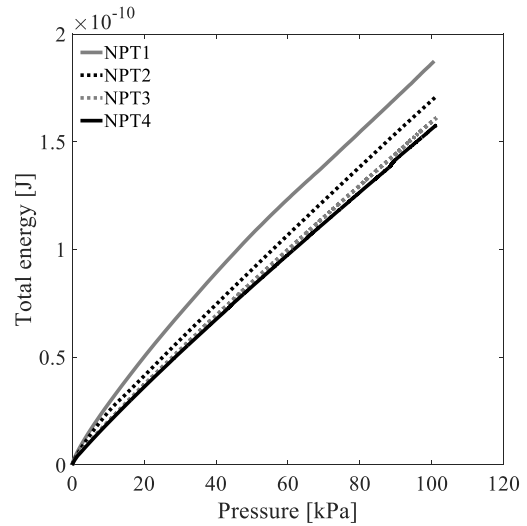


(b)

Figure 14. Sensitivity of response to sample size and strain rate for Poly_1 samples: (a) Variation in void ratio at 100 kPa with compression rate and sample size (b) Variation in void ratio - pressure relationship with strain rate for 100,000-particle sample



(a)



(b)

Figure 15. Data for energy variation during compression at different strain rates for Poly_1 100,000-particle sample: (a) Variation in temperature with pressure (b) Variation in total energy with pressure

Figure 16 compares the isotropic compression curves for the 100,000-particle *Mono_1* and *Poly_1* samples with results of 1D compression tests carried out by Pedrotti and Tarantino

(2018) on kaolinite samples at alkaline pH. At pressures less than 50 kPa, the *Mono_I* compression curve exhibits a behaviour similar to that observed in the laboratory when samples are consolidated from a slurry (Delage, 2010; Leroueil and Vaughan, 1991). Then, between 50 and 100 kPa, the $e - \log(p)$ curve obtained in the laboratory and those associated with both *Mono_I* and *Poly_I* sample are parallel, having the same slope ≈ 0.20 . Data provided in Lambe and Whitman (1969) suggest that C_c values vary from 0.19 to 0.26 for kaolinite. Differences between numerical and experimental void ratios may be explained by differences in the kaolinite and pore fluid conditions used in AFM experiments by Gupta (2011) and those used by Pedrotti and Tarantino (2018). Differences may also arise due to the assumptions that are adopted in this simulation approach. Specifically, using the DLVO model assumes the validity of the Gouy-Chapman double layer theory. By using Eq. (3) we are assuming it is acceptable to use a linearised version of the solution to the Poisson-Boltzmann equation and that a constant surface potential can be adopted. The parameters employed when adopting Eq. (3) rely on the accuracy of the AFM measurements on kaolinite surfaces in Gupta (2011). Furthermore, the CGMD simulations depend on the ability of the GB potential to reproduce the DLVO interaction energy for configurations other than the face-face and edge-edge.

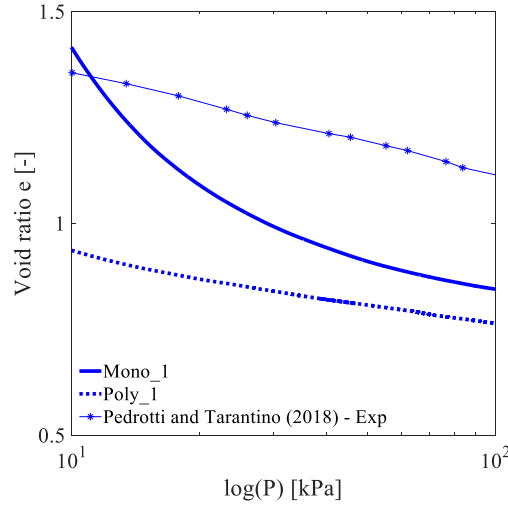


Figure 16. Comparison between $e - \log(p)$ profiles for *Mono_1* and *Poly_1* virtual samples containing 100,000 particles and 1D compression results obtained by Pedrotti and Tarantino (2018) on kaolinite saturated at alkaline pH.

6.1.2 Fabric

Figure 17 presents snapshots and polar histograms of the particle orientations following isotropic compression for the 100,000-particle *Mono_1* samples. The polar histograms are all approximately semi-circular indicating the expected isotropic fabric after isotropic compression was attained (Hattab and Fleureau, 2010; Hicher et al., 2000). In fact, based on our understanding of the behaviour of this material, crystalline structures are not likely to emerge in kaolinite samples following isotropic compression.

The ability of particles to rearrange during compression is influenced by $\dot{\epsilon}_f$. The fabric for the *NPT1* simulations is relatively open with little evidence of cluster formation. A likely explanation is that there is insufficient time for the particles to move freely and rearrange. The formation of clusters becomes then clearer as the strain rate decreases (Figure 17(a)-(d)). Since the values of e_{100kPa} are indistinguishable, and the polar histograms are similar, further microscale analyses are needed to ultimately reveal differences in fabric for the *NPT3* and *NPT4* simulations.

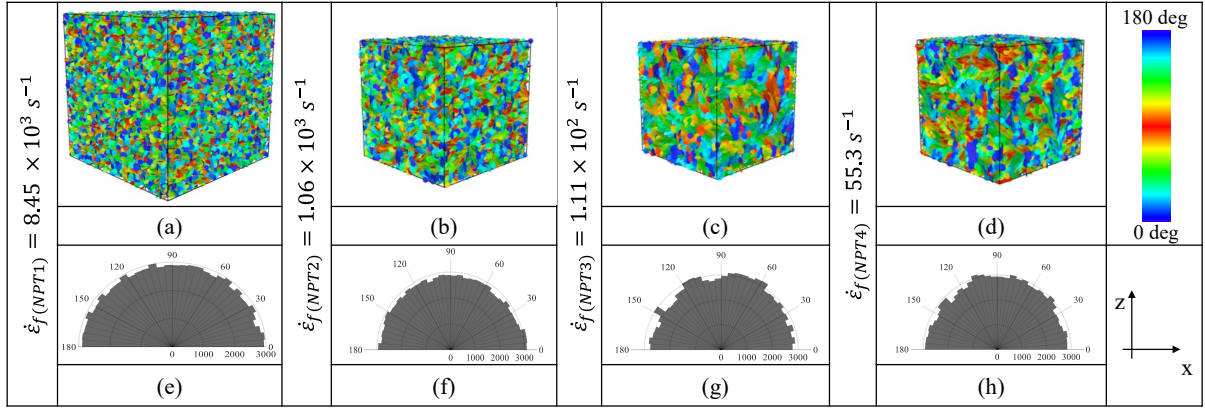


Figure 17. Variation of particles arrangements with compression rate at 100 kPa (100,000-particle *Mono_1* sample). Particles in snapshots (a-d) are colour-coded according to their orientation in the x-z plane. Polar histograms (e-h) indicate particles orientation in the x-z plane

Figure 18 considers similar data for the 100,000-particle *Poly_1* simulation. The material fabric as observed in the snapshot images does not exhibit a strong rate-dependence; in contrast to the *Mono_1* case, here the cluster formation is evident even for *NPT1*. For the lowest strain rates different clusters and void spaces can be identified. In contrast to *Mono_1*, the polar histograms are not relatively smooth semi-circles particularly for the *NPT3* and *NPT4* simulations, indicating, that in this case, a REV might not be obtained, as discussed further below.

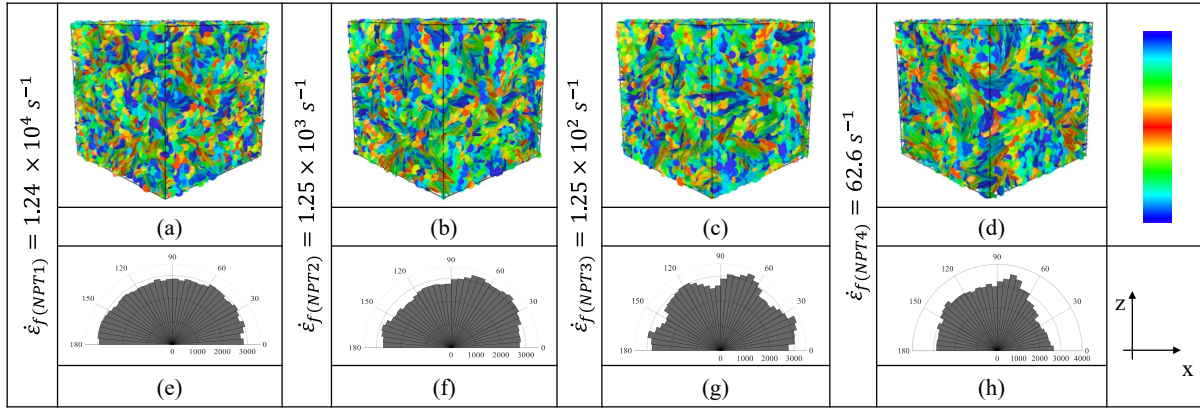


Figure 18. Variation of particles arrangements with compression rate at 100 kPa (100,000-particle *Poly_1* sample). Particles in snapshots (a-d) are colour-coded according to their orientation in the x-z plane. Polar histograms (e-h) indicate particles orientation in the x-z plane

6.2. Effect of sample size

6.2.1 Macroscopic effects

The effect of sample size is assessed by comparing the simulations of specimens with 1,000, 10,000 and 100,000 particles. Figure 12(a) and Figure 14(a) show that for both *Mono_1* and *Poly_1* samples, the influence of sample size on the void ratio values is negligible at high compression rates (i.e. *NPT1* and *NPT2*), which were shown to provide unreliable results in section 6. However, sample size becomes relevant when considering quasi-static simulations (i.e. *NPT3* and *NPT4*). The void ratio difference can also be seen in Figure 19(a) and Figure 19(b), where compression curves obtained at the *NPT4* strain rate are shown. A noticeable variation in the void ratio is observed when moving from 1,000 to 10,000 particles, while compression curves overlap when simulating either 10,000 or 100,000 particles. This indicates that the 1,000-particle samples are too small to be considered an REV for kaolinite. Figure 19 also shows that, while the final void ratio is sample size dependent, the slope of the compression curves between 50 and 100 kPa is not influenced by sample size.

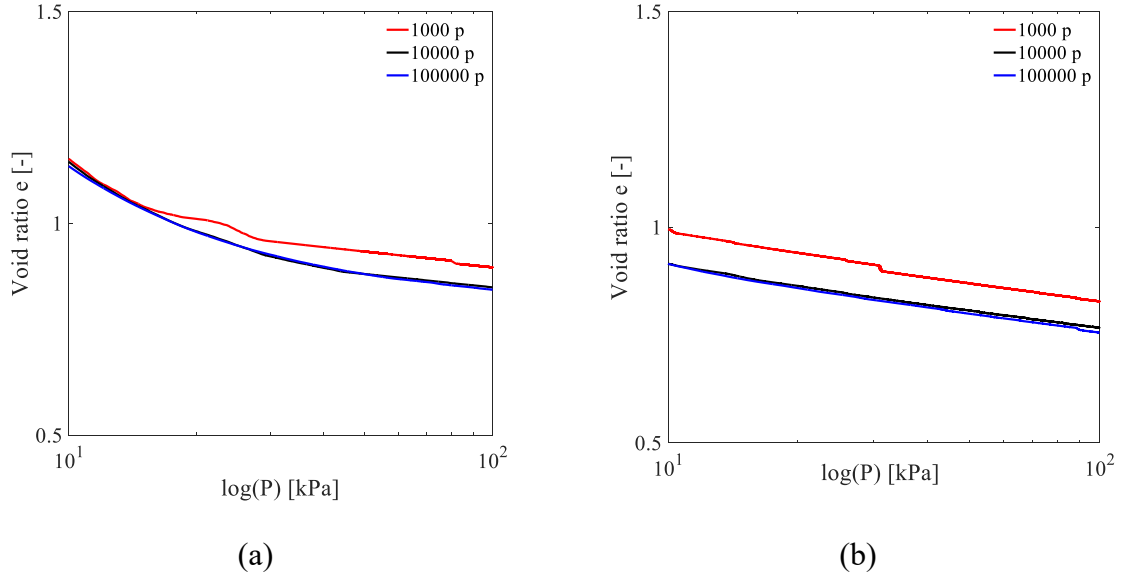


Figure 19. Isotropic compression profiles for (a) *Mono_1* and (b) *Poly_1* samples with 1,000, 10,000 and 100,000 particles obtained considering *NPT4*

6.2.1 Fabric

Fabric evaluation is a key driver for particle-scale analysis and so it is important to establish the sensitivity of the fabric data to the simulation variables, including sample size. Figure 20 presents polar histograms for the *Mono_1* samples at the slowest strain rate, *NPT4*, after the equilibration stage (Figure 20(a-c)) and at the end of compression (Figure 20(d-f)). The 1,000-particle (Figure 20(a) and (d)) sample shows an irregular polar histogram. With increasing sample size, the polar histogram approaches the relatively smooth semi-circular shape expected for an isotropic sample, indicating that 100,000 particles are a more appropriate REV for this type of sample (Figure 20(c) and (f)). This was also proven by some simple statistical analyses which compared the distribution of particle orientations in the 1,000-particle sample with data from a series of random 1,000-particle sub-samples taken from the 100,000-particle one. The standard deviation of the number of particles in each bin was much larger in the 1,000-particle sample than in any of the 1,000-particle sub-samples.

The evolution of particle arrangements with size is shown in Figure 21, where particles are colour-coded according to their orientation in the x-z plane. The prototype sample (Figure 21(a)) shows a limited number of clusters whose size is large relative to the sample, while in the biggest sample (Figure 21(c)) more complex aggregate shapes form involving more particles and having a smaller size relative to the sample size. These data suggest that in the case of *Mono_1*, a sample containing 100,000 particles is required for any meaningful fabric analysis.

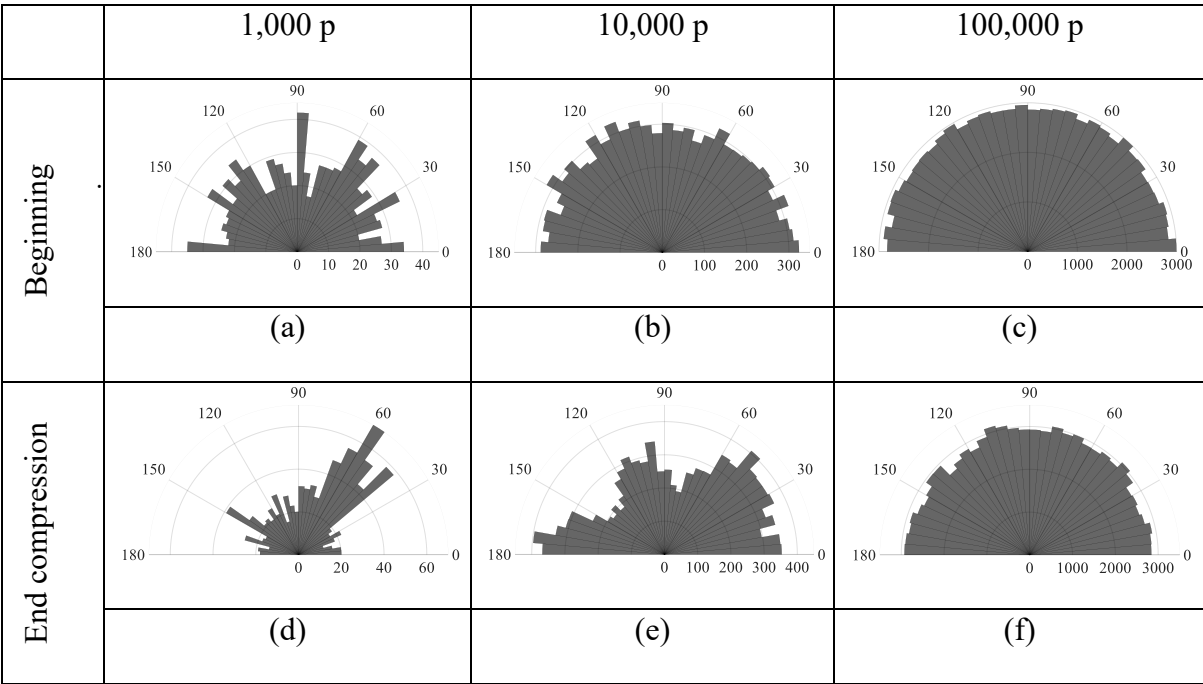


Figure 20. Polar histograms to quantify particle orientations at the beginning (a-c) and at the end (d-f) of isotropic compression for *Mono_1* samples with 1,000, 10,000 and 100,000 particles

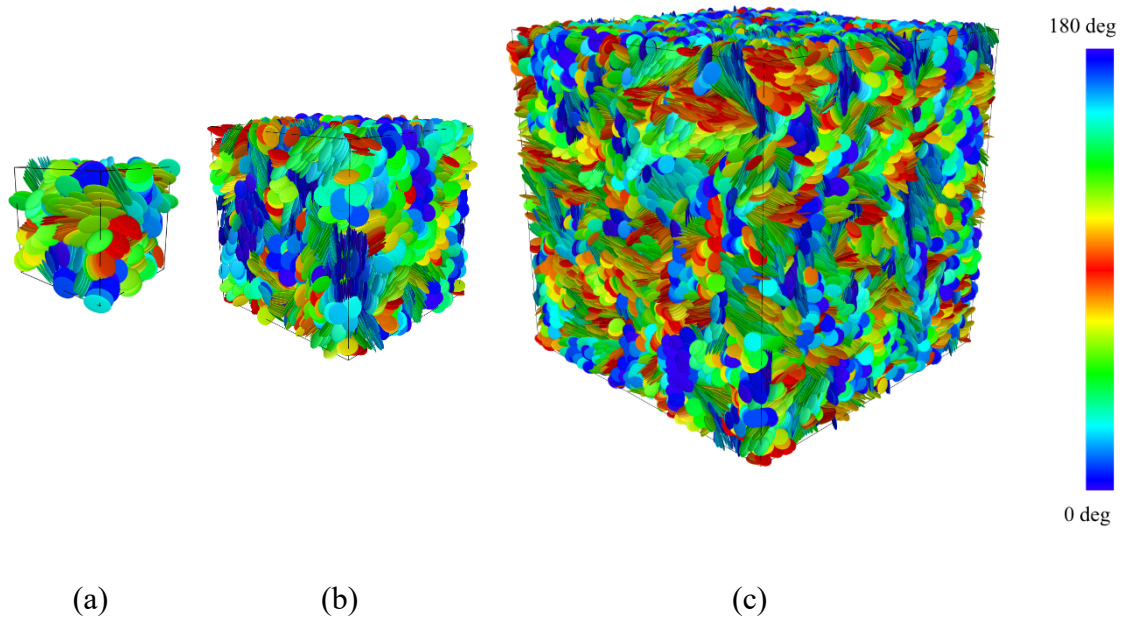


Figure 21. Particle arrangements colour-coded according to particle orientations in the x-z plane for *Mono_I* samples with (a) 1,000 particles, (b) 10,000 particles and (c) 100,000 particles (boxes dimensions are not in scale)

In contrast to the *Mono_I* samples, Figure 22 shows that for *Poly_I*, an irregular polar histogram was obtained for all samples, including the 100,000-particle sample (Figure 22(f)). The orientation of particles within the sample is not isotropic even at this lowest strain rate considered, suggesting that the sample may be too small to be an REV. Computational limitations compromised our ability to explore this further in the current study.

Figure 23 shows that, as in the *Mono_I* case, the size and the shape of the clusters evolve with sample size. Both Figures 21 and 23 highlight the complex topology of the system in three dimensions; supporting the view that only limited insight can be obtained from 2D analyses.

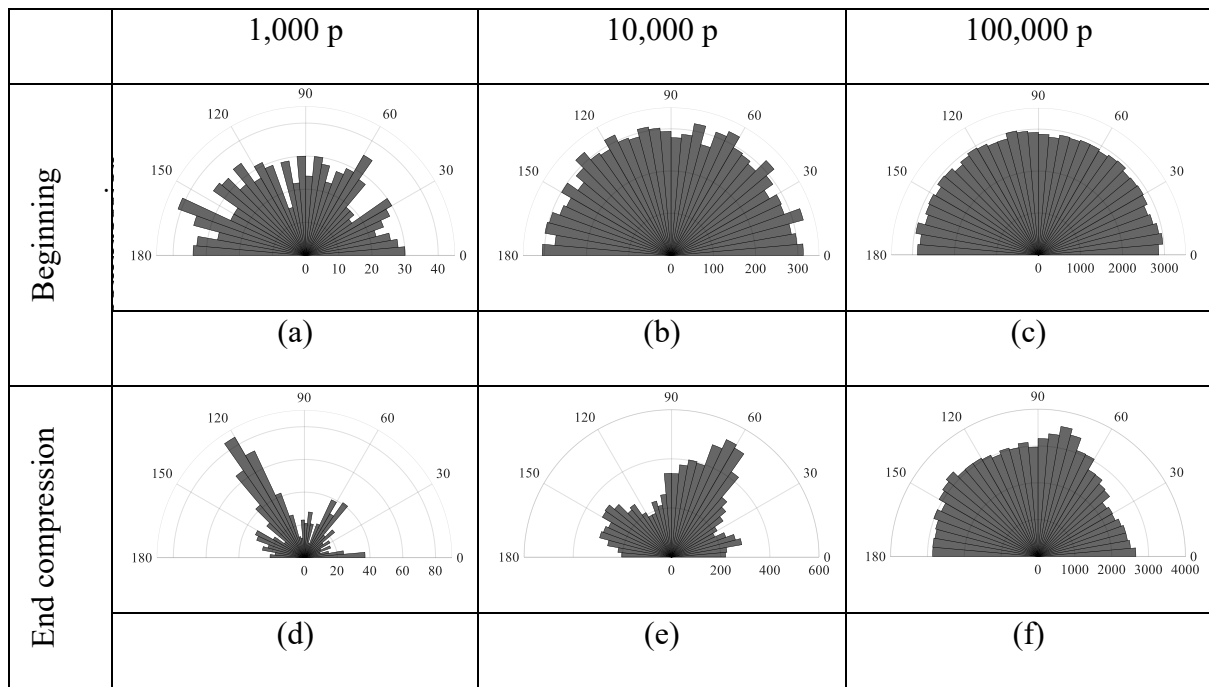


Figure 22. Polar histograms to quantify particle orientations at the beginning (a-c) and at the end (d-f) of isotropic compression for Poly_1 with 1,000, 10,000 and 100,000 particles

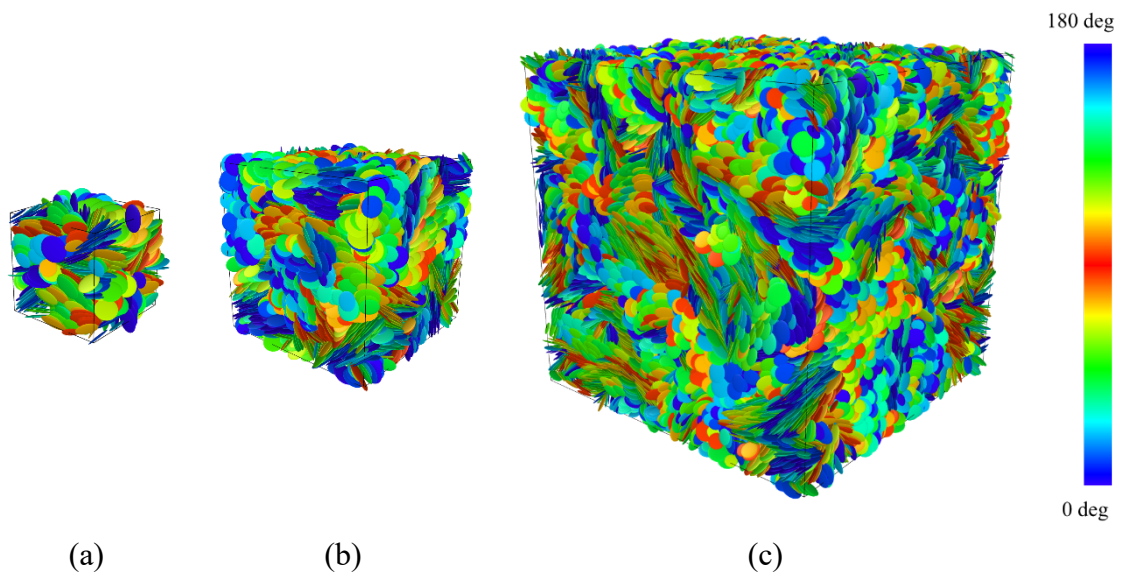


Figure 23. Particles arrangement colour-coded according to particles orientation in the x-z plane for Poly_1 samples with (a) 1,000 particles, (b) 10,000 particles and (c) 100,000 particles (boxes dimensions are not in scale)

7. Conclusions

This paper has presented a particle-based framework to effectively simulate the compressive behaviour of a non-active clay (kaolinite) by performing molecular dynamics simulations. Given its general acceptance in the geotechnical literature, the DLVO model was used to quantify kaolinite particles interactions. Following Ebrahimi (2014), clay particles were modelled as flat ellipsoids (oblate spheroids) and DLVO theory was used to calibrate a modified Gay-Berne potential. Monodisperse and slightly polydisperse samples were simulated. A work-flow for using MD to simulate isotropic compression of clay was outlined. Comparison of the overall macroscale response with relevant experimental data indicates that, for both monodisperse and polydisperse cases, the methodology outlined can deliver reasonable results when considering a non-active clay saturated at alkaline pH.

The following main conclusions can be drawn from the simulation data presented:

- The current study used DLVO theory to predict the energy-separation relationship while also recognising the limitations of DLVO theory. Currently this is the [most accessible](#) approach to calibrate the potential expressions for use in particle-scale (coarse-grained) MD simulations to model assemblies of clay particles. [There is a need for research that uses atomistic MD simulations to develop more accurate and realistic](#) interaction models.
- The Gay-Berne potential is an attractive potential form to use for simulating clay behaviour; it is significantly less computationally expensive than using a cluster/agglomerate of spheres to model a clay particle. However, to model kaolinite under the pore-fluid conditions considered here, it cannot be used without modification. Additionally, the GB potential calibration against DLVO energy-separation distance is possible only for separation distances that exceed the separation at which the energy

barrier is reached, i.e. $h > h_{eb}$, which is only adequate when performing virgin compression.

- Comparison between results obtained considering the biggest samples (i.e., 100,000 particles) compressed at the lowest strain rate (i.e., $NPT4$) and published experimental results on kaolinite show agreement on the value of the slope of the compression curves. Differences in the final void ratio may be due to differences in the type of kaolinite and pore fluid conditions used to perform AFM measurements and in laboratory tests and on the assumptions introduced in the approach used and in the CGMD simulations performed.
- Sample size influences the void ratio reached at the end of compression. Results of a parametric study indicate that the prototype sample containing 1,000 particles is too small to be considered representative (i.e. an REV) for the material examined, while samples with 10,000 and 100,000 particles exhibit overlapping $e - \log(p)$ curves, meaning they can both be used to infer macroscopic information on the material behaviour. Prior particle-based simulations documented in the literature were about two orders of magnitude smaller than those performed here.
- The strain rate was found to affect the void ratio at the end of the isotropic compression and the slope of the compression curves to different extents for monodisperse and polydisperse samples. This strain-rate dependency is non-linear and plateaus with reducing strain rate if the strain rate is sufficiently low. Monitoring the temperature (T) and the total energy ($E_{MD,Tot}$) within the system at different strain rates is proven to be useful to inform selection of an appropriate compression rate. Stable simulations are characterised by temperature profiles oscillating around the temperature specified (~ 300 K). The parametric study also showed that the total energy-pressure profiles converge as the rate decreases to the stable case.

- Analysis of particle orientations before and after compression, provides additional insight into the extent to which an REV is attained. For both *Mono_I* and *Poly_I*, samples containing 10,000 particles exhibit a jagged polar histogram, which appears to indicate an anisotropic fabric following isotropic compression indicating that these simulations cannot be used to draw conclusions about the material fabric. The smooth, isotropic, distribution of orientations in the 100,000-particle sample supports the conclusion that this size is sufficient to attain an REV for the monodisperse case. However, when polydispersity is introduced, an isotropic distribution of orientation of particles at the end of compression is not seen even for the 100,000-particle system, suggesting that an even larger sample is needed if polydispersity is included in the model.
- Snapshots portraying the 100,000-particle sample were useful to observe the evolution of particle arrangement (fabric) with strain rate. These snapshots provided supplementary information to assess which strain rate was appropriate to use for inferring microscale information.
- The time-step used in MD simulations (Δt_{simul}) was computed by considering the period of a simple one-DOF system reduced by a factor ϑ , to account for multiple interactions. The conservation of the total energy $E_{MD,Tot}$ in the sample is used as means to assess whether Δt_{simul} is appropriate.

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References

- Alder, B.J., Wainwright, T.E., 1959. Studies in Molecular Dynamics. I. General Method. *J. Chem. Phys.* 31, 459–466. <https://doi.org/https://aip.scitation.org/doi/10.1063/1.1730376>
- Allen, M.P., Tildesley, D.J., 1987. *Computer Simulation of Liquids*. Oxford Science Publications.
- Aminpour, P., Sjoblom, K.J., 2019. Multi-scale modelling of kaolinite triaxial behaviour. *Géotechnique Lett.* 9, 178–185. <https://doi.org/10.1680/jgele.18.00194>
- Anandarajah, A., 2003. Discrete Element Modelling of Leaching-Induced apparent Overconsolidation in Kaolinite. *Soils Found.* 43, 1–12.
- Anandarajah, A., 2000a. Numerical simulation of one-dimensional behaviour of a kaolinite. *Géotechnique* 50, 509–519. <https://doi.org/10.1680/geot.2000.50.5.509>
- Anandarajah, A., 2000b. On influence of fabric anisotropy on the stress-strain behavior of clays. *Comput. Geotech.* 27, 1–17. [https://doi.org/10.1016/S0266-352X\(00\)00005-7](https://doi.org/10.1016/S0266-352X(00)00005-7)
- Anandarajah, A., 1994. Discrete-Element Method for Simulating Behavior of Cohesive Soils. *J. Geotech. Eng.* 120, 1593–1613.
- Anandarajah, A., Yao, M., 2005. Discrete element methods, *The Finite Element Method Set*. <https://doi.org/10.1016/b978-075066431-8/50196-x>
- Angioletti-Uberti, S., 2017. Theory, simulations and the design of functionalized nanoparticles for biomedical applications: A Soft Matter Perspective. *npj Comput. Mater.* 3, 1–15. <https://doi.org/10.1038/s41524-017-0050-y>
- Bandera, S., O’Sullivan, C., Angioletti-Uberti, S., Tangney, P., 2019. An evaluation of contact models for particle-scale simulation of clay. *E3S Web Conf.* 92, 1–6.

747 <https://doi.org/10.1051/e3sconf/20199214001>

748 Barreto, D., 2009. Numerical and experimental investigation into the behaviour of granular
749 materials under generalised stress states. Univ. London 357.

750 Berardi, R., Fava, C., Zannoni, C., 1995. A generalized Gay-Berne intermolecular potential for
751 biaxial particles. Chem. Phys. Lett. 236, 462–468. [https://doi.org/10.1016/0009-](https://doi.org/10.1016/0009-2614(95)00212-M)
752 2614(95)00212-M

753 Bharat, T.V., Sridharan, A., 2015. Prediction of compressibility data for highly plastic clays
754 using diffuse double-layer theory. Clays Clay Miner. 63, 30–42.
755 <https://doi.org/10.1346/CCMN.2015.0630103>

756 Bolt, G.H., 1956. Physico-chemical analysis of the compressibility of pure clays. Geotechnique
757 6, 86–93. <https://doi.org/10.1680/geot.1956.6.2.86>

758 Brown, W.M., Petersen, M.K., Plimpton, S.J., Grest, G.S., 2009. Liquid crystal nanodroplets
759 in solution. J. Chem. Phys. 130. <https://doi.org/10.1063/1.3058435>

760 Burland, J.B., 1990. On the compressibility and shear strength of natural clays. Géotechnique
761 40, 329–378. <https://doi.org/10.1680/geot.1990.40.3.329>

762 Carrier, B., 2014. Influence of water on the short-term and long-term mechanical properties of
763 swelling clays: experiments on self-supporting films and molecular simulations.

764 Cheng, Y.P., Bolton, M.D., Nakata, Y., 2004. Crushing and plastic deformation of soils
765 simulated using DEM. Geotechnique 54, 131–141.
766 <https://doi.org/10.1680/geot.2004.54.2.131>

767 Cundall, P.A., Strack, O.D.L., 1979. A discrete numerical model for granular assemblies.
768 Géotechnique 29, 47–65. <https://doi.org/10.1680/geot.1980.30.3.331>

769 Delage, P., 2010. A microstructure approach to the sensitivity and compressibility of some
770 eastern Canada sensitive clays. *Géotechnique* 60, 353–368.
771 <https://doi.org/10.1680/geot.2010.60.5.353>

772 Derjaguin, B., Landau, L.D., 1941. Theory of the Stability of Strongly Charged Lyophobic Sols
773 and of the Adhesion of Strongly Charged Particles in Solution of Electrolytes. *Acta*
774 *Physicochim* 14.

775 Ebrahimi, D., 2014. Multiscale modeling of clay-water systems. Massachusetts Institute of
776 Technology.

777 Ebrahimi, D., Pellenq, R.J.M., Whittle, A.J., 2016. Mesoscale simulation of clay aggregate
778 formation and mechanical properties. *Granul. Matter* 18, 1–8.
779 <https://doi.org/10.1007/s10035-016-0655-8>

780 Ebrahimi, D., Pellenq, R.J.M., Whittle, A.J., 2012. Nanoscale elastic properties of
781 montmorillonite upon water adsorption. *Langmuir* 28, 16855–16863.
782 <https://doi.org/10.1021/la302997g>

783 Ebrahimi, D., Whittle, A.J., Pellenq, R.J.-M., 2014. Mesoscale properties of clay aggregates
784 from potential of mean force representation of interactions between nanoplatelets. *J.*
785 *Chem. Phys.* 140, 154309. <https://doi.org/10.1063/1.4870932>

786 Ercolessi, F., 1997. A molecular dynamics primer.

787 Everaers, R., Ejtehadi, M.R., 2003. Interaction potentials for soft and hard ellipsoids. *Phys.*
788 *Rev. E - Stat. Physics, Plasmas, Fluids, Relat. Interdiscip. Top.* 67, 8.
789 <https://doi.org/10.1103/PhysRevE.67.041710>

790 Gay, J.G., Berne, B.J., 1981. Modification of the overlap potential to mimic a linear site-site
791 potential. *J. Chem. Phys.* 74, 3316–3319. <https://doi.org/10.1063/1.441483>

792 Gupta, V., 2011. Surface Charge Features of Kaolinite Particles and Their Interactions. The
 793 University of Utah.

794 Gupta, V., Miller, J.D., 2010. Surface force measurements at the basal planes of ordered
 795 kaolinite particles. *J. Colloid Interface Sci.* 344, 362–371.
 796 <https://doi.org/10.1016/j.jcis.2010.01.012>

797 Güven, N., 1992. Molecular Aspects of Clay-Water Interactions, in: *Clay-Water Interface and*
 798 *Its Rheological Implications.* Clay Minerals Society, pp. 1–79.
 799 <https://doi.org/doi:10.1346/CMS-WLS-4.1>

800 Hanley, K.J., O’Sullivan, C., Huang, X., 2015. Particle-scale mechanics of sand crushing in
 801 compression and shearing using DEM. *Soils Found.* 55, 1100–1112.
 802 <https://doi.org/10.1016/j.sandf.2015.09.011>

803 Hattab, M., Fleureau, J.M., 2010. Experimental study of kaolin particle orientation mechanism.
 804 *Géotechnique* 60, 323–331. <https://doi.org/10.1680/geot.2010.60.5.323>

805 Hicher, P.Y., Wahyudi, H., Tessier, D., 2000. Microstructural analysis of inherent and induced
 806 anisotropy in clay. *Mech. Cohesive-Frictional Mater.* 5, 341–371.

807 Hogg, R., Healy, T.W., Fuerstenau, D.W., 1966. Mutual coagulation of colloidal dispersions.
 808 *Trans. Faraday Soc.* 62, 1638–1651. <https://doi.org/10.1039/tf9666201638>

809 Honig, E.P., Mul, P.M., 1971. Tables and equations of the diffuse double layer repulsion at
 810 constant potential and at constant charge. *J. Colloid Interface Sci.* 36, 258–272.
 811 [https://doi.org/10.1016/0021-9797\(71\)90171-8](https://doi.org/10.1016/0021-9797(71)90171-8)

812 Honorio, T., Brochard, L., Vandamme, M., 2018. Effective stresses and estimations of the
 813 apparent Biot coefficient in stacked clay layers. *Géotechnique Lett.* 8, 97–101.
 814 <https://doi.org/10.1680/jgele.17.00170>

815 Honorio, T., Brochard, L., Vandamme, M., 2017. Hydration Phase Diagram of Clay Particles
816 from Molecular Simulations. *Langmuir* 33, 12766–12776.
817 <https://doi.org/10.1021/acs.langmuir.7b03198>

818 Huang, X., Hanley, K.J., O’Sullivan, C., Kwok, F.C.Y., 2014. Effect of sample size on the
819 response of DEM samples with a realistic grading. *Particuology* 15, 107–115.
820 <https://doi.org/10.1016/j.partic.2013.07.006>

821 Israelachvili, J., 2011. Intermolecular and Surface Forces, Third. ed, Intermolecular and
822 Surface Forces. Academic Press. <https://doi.org/10.1016/C2009-0-21560-1>

823 Kumar, N., Andersson, M.P., Van Den Ende, D., Mugele, F., Siretanu, I., 2017. Probing the
824 Surface Charge on the Basal Planes of Kaolinite Particles with High-Resolution Atomic
825 Force Microscopy. *Langmuir* 33, 14226–14237.
826 <https://doi.org/10.1021/acs.langmuir.7b03153>

827 Lambe, T.W., Whitman, R. V., 1969. Soil Mechanics. John Wiley & Sons, Inc., New York.

828 Leroueil, S., Hight, D.W., 2003. Behaviour and properties of natural soils and soft rocks.
829 *Charact. Eng. Prop. Nat. Soils* 29–254.

830 Leroueil, S., Vaughan, P.R., 1991. The general and congruent effects of structure in natural
831 soils and weak rocks. *Géotechnique* 41, 281–284.
832 <https://doi.org/10.1680/geot.1991.41.2.281>

833 Liu, J., 2015. Surface properties of kaolinite particles - Their interactions and flotation
834 considerations. The University of Utah.

835 Liu, J., Sandaklie-Nikolova, L., Wang, X., Miller, J.D., 2014. Surface force measurements at
836 kaolinite edge surfaces using atomic force microscopy. *J. Colloid Interface Sci.* 420, 35–
837 40. <https://doi.org/10.1016/j.jcis.2013.12.053>

838 Lu, N., Anderson, M.T., Likos, W.J., Mustoe, G.W., 2008. A discrete element model for
 839 kaolinite aggregate formation during sedimentation. *Int. J. Numer. Anal. Methods*
 840 *Geomech.* 32, 965–980. <https://doi.org/10.1002/nag.656>

841 Masiliyah, J.H., Bhattacharjee, S., 2006. *Electrokinetic and Colloid Transport Phenomena*. John
 842 Wiley & Sons, Inc. <https://doi.org/doi:10.1002/0471799742>

843 Mitchell, J.K., Soga, K., 2005. *Fundamentals of Soil Behavior*, Third. ed. John Wiley & Sons,
 844 Inc., Hoboken, New Jersey.

845 O’Sullivan, C., 2011. *Particulate Discrete Element Modelling. A Geomechanics Perspective*.
 846 Routledge.

847 O’Sullivan, C., Bray, J.D., 2004. Selecting a suitable time step for discrete element simulations
 848 that use the central difference time integration scheme. *Eng. Comput.* (Swansea, Wales)
 849 21, 278–303. <https://doi.org/10.1108/02644400410519794>

850 Otsubo, M., O’Sullivan, C., Shire, T., 2017. Empirical assessment of the critical time increment
 851 in explicit particulate discrete element method simulations. *Comput. Geotech.* 86, 67–79.
 852 <https://doi.org/10.1016/j.compgeo.2016.12.022>

853 Pagano, A.G., Magnanimo, V., Weinhart, T., Tarantino, A., 2020. Exploring the
 854 micromechanics of non-active clays by way of virtual DEM experiments. *Géotechnique*
 855 70, 303–316. <https://doi.org/10.1680/jgeot.18.P.060>

856 Pedrotti, M., Tarantino, A., 2018. An experimental investigation into the micromechanics of
 857 non-active clays. *Géotechnique* 68, 666–683. <https://doi.org/10.1680/jgeot.16.P.245>

858 Plimpton, S.J., 1995. Short-Range Molecular Dynamics. *J. Comput. Phys.* 117, 1–19.
 859 <https://doi.org/10.1006/jcph.1995.1039>

860 Santamarina, J.C., Klein, K.A., F., M.A., 2001a. *Soils and Waves: Particulate Materials*

861 Behaviour, Characterisation and Process Monitoring. John Wiley & Sons, Inc.

862 Santamarina, J.C., Klein, K.A., Palomino, A.M., Guimaraes, M., 2001b. Micro-Scale Aspects
863 of Chemical-Mechanical Coupling: Interparticle Forces and Fabric, in: Chemo-
864 Mechanical Coupling in Clays: From Nano-Scale to Engineering Applications. Taylor and
865 Francis.

866 Shinoda, W., Shiga, M., Mikami, M., 2004. Rapid estimation of elastic constants by molecular
867 dynamics simulation under constant stress. *Phys. Rev. B - Condens. Matter Mater. Phys.*
868 69. <https://doi.org/10.1103/PhysRevB.69.134103>

869 Sjoblom, K.J., 2016. Coarse-grained molecular dynamics approach to simulating clay
870 behavior. *J. Geotech. Geoenvironmental Eng.* 142, 1–6.
871 [https://doi.org/10.1061/\(ASCE\)GT.1943-5606.0001394](https://doi.org/10.1061/(ASCE)GT.1943-5606.0001394)

872 Smith, B., Frenkel, D., 2002. *Understanding Molecular Simulations. From Algorithms to*
873 *Application.* Academic Press. [https://doi.org/https://doi.org/10.1016/B978-0-12-267351-](https://doi.org/10.1016/B978-0-12-267351-1.X5000-7)
874 [1.X5000-7](https://doi.org/10.1016/B978-0-12-267351-1.X5000-7)

875 Sridharan, A., Prakash, K., 1999. Mechanisms controlling the undrained shear strength
876 behaviour of clays. *Can. Geotech. J.* 36, 1030–1038.

877 Stukowski, A., 2010. Visualization and analysis of atomistic simulation data with OVITO-the
878 Open Visualization Tool. *Model. Simul. Mater. Sci. Eng.* 18.
879 <https://doi.org/10.1088/0965-0393/18/1/015012>

880 Thornton, C., 2000. Numerical simulations of deviatoric shear deformation of granular media.
881 *Geotechnique* 50, 43–53.

882 Tuckerman, M.E., 2010. *Statistical Mechanics: Theory and Molecular Simulation.* Oxford
883 University Press, 2010.

884 van Olphen, H., 1977. An Introduction to Clay Colloid Chemistry. John Wiley & Sons, Inc.

885 Verwey, E.J.W., Overbeek, J.T.G., 1948. Theory of the Stability of Lyophobic Colloids: The
886 Interaction of Sol Particles Having an Electric Double Layer. Elsevier Inc.

887 Visscher, W.M., Bolsterli, M., 1972. Random packing of equal and unequal spheres in two and
888 three dimensions. *Nature* 239, 504–507. <https://doi.org/10.1038/239504a0>

889 Wang, Y.H., Siu, W.K., 2006. Structure characteristics and mechanical properties of kaolinite
890 soils. I. Surface charges and structural characterizations. *Can. Geotech. J.* 43, 587–600.
891 <https://doi.org/10.1139/T06-026>

892 Weinhart, T., Orefice, L., Post, M., van Schroyen Lantman, M.P., Denissen, I.F.C.,
893 Tunuguntla, D.R., Tsang, J.M.F., Cheng, H., Shaheen, M.Y., Shi, H., Rapino, P.,
894 Grannonio, E., Losacco, N., Barbosa, J., Jing, L., Alvarez Naranjo, J.E., Roy, S., den
895 Otter, W.K., Thornton, A.R., 2020. Fast, flexible particle simulations — An introduction
896 to MercuryDPM. *Comput. Phys. Commun.* 249, 107129.
897 <https://doi.org/10.1016/j.cpc.2019.107129>

898 Yao, M., 2001. Three-Dimensional Discrete Element Method Analysis of Cohesive Sols. Johns
899 Hopkins University.

900