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Insight of molecular simulation to better assess deformation and failure of clay-rich rocks in compression and extension

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Abstract

Clay minerals constituent an essential component of clayey rocks. Macroscopic mechanical behaviors of those rocks can be significantly driven by local deformation and failure processes of clay minerals. In this study, the mechanical behavior of Montmorillonite (MMT) crystal at the atomistic scale is investigated by using molecular dynamics (MD) simulations. In consistency with macroscopic laboratory tests, both triaxial compression and extension with constant mean stress are considered. A series of MD simulations are performed for these two loading paths with different values of mean stress and respectively applied in the parallel and perpendicular directions to crystal layers. It is found that the mechanical behavior of MMT crystal exhibits a clear dissymmetry between compression and tension, a strong anisotropy along two loading orientations and an important dependency on mean stress. The inter-layer space collapse and atomic sheet bending are two failure mechanisms of crystal structure. The results issued from MD simulations provide a microscopic insight on macroscopic deformation and failure of clay-rich rocks.

Keywords: Clay-rich rocks, Montmorillonite, Anisotropy, Failure, Loading path, Molecular simulation

1 1. Introduction

Clay-rich rocks have been widely investigated in geological issues and engineering prac tices. For instance, shale rocks constitute the main reservoir or cap layers in unconventional

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hydrocarbon exploration. Hard claystone and swelling clay are used as geological and en-4 gineered barriers for the underground storage of radioactive wastes (Armand et al., 2013). 5 Clavey rocks are characterized by complex mineralogical compositions and multi-scale struc-6 tures (Robinet et al., 2012; Bennett et al., 2015; Abedi et al., 2016). At the atomistic scale, 7 clay sheets are organized in layered crystals (particles) (Carrier et al., 2014). Clay particles 8 are further structured in clay aggregates with inter-particles voids (Robinet et al., 2012) at 9 nanometer scale. At micrometer scale, clay aggregates constituent a porous clay matrix. 10 Mineral and organic grains, such as quartz, carbonate and kerogen, are embedded inside the 11 clayey matrix. 12

Macroscopic mechanical behaviors of clayey rocks are controlled by the local mechanical 13 properties of constituents and their interactions at the different scales. In particular, clay 14 particles play a dominant role on macroscopic deformation and failure process of clay-rich 15 rocks. For instance, macroscopic plastic deformation is mainly driven by the local deforma-16 tion mechanisms of clay particles and aggregates at the nanometer and micrometer scales 17 (Bornert et al., 2010; Wang et al., 2015). It is assumed that macroscopic time-dependent de-18 formation of clay-rich rocks is also related to the local motion of clay particles (Armand et al., 19 2017; Liu et al., 2018). Further, as the mechanical behavior of clay particles at the atomistic 20 and microscopic scales depends on water content in inter-layer space and inter-particle voids, 21 the macroscopic mechanical behavior of clay-rich rocks is also strongly sensitive to water sat-22 uration degree (Chiarelli et al., 2003; Vales et al., 2004; Liu and Shao, 2016; Zhang et al., 23 2012; Zeng et al., 2019). The molecular dynamic motion is also influenced by temperature 24 leading to the thermal effect on macroscopic mechanical properties (Zhang, 2018; Liu et al., 25 2019a). Moreover, the layered structure of clay crystals at the nanometer scale can be one 26 of origins for strongly anisotropic mechanical behaviors of clay-rich rocks (Niandou et al., 27 1997; Liu et al., 2015; Armand et al., 2017; Zhang et al., 2019). Therefore, the characteri-28 zation of mechanical behaviors of clayey rocks should be based on multi-scale approaches in 29 order to properly take into account influences of mineralogical compositions and multi-scale 30 heterogeneity. Understanding of deformation and failure mechanisms of clay particles at the 31 atomistic scale is an essential task. However, it is very difficult to perform direct experimen-32

tal measurement at such small scales in view of identifying those mechanisms. Appropriate
numerical calculations provide alternative solutions. In this context, molecular dynamics
simulations (MD) have been rapidly developed and widely used in modeling the clay-rich
materials at different scale.

MD simulations were first applied to studying hydration related swelling behavior, struc-37 ture distribution, diffusion of water molecules or cation ions between layers (Boek et al., 38 1995b; Shroll and Smith, 1999; Yeh and Hummer, 2004; Underwood and Bourg, 2020). Af-39 terward, works on the mechanical property of clay minerals with MD have been reported in 40 stages. At the very beginning, most of the studies have focused on the elastic property of 41 clay particles under different conditions, such as different values of stress and temperature 42 (Ebrahimi et al., 2012; Brochard et al., 2017), extent of hydration (Mazo et al., 2008b,a; 43 Suter et al., 2007), types of inter-layer cation (Carrier et al., 2014), stress orientations (Mazo 44 et al., 2008b,a; Suter et al., 2007), different contents of CO_2 and $H_2O(Zhang et al., 2015)$. 45 Nowadays, the failure property and mechanism become important topics. For instance in 46 (Zartman et al., 2010), the authors have suggested roughly that sliding of layers, in-plane 47 kinks, and cation intrusion into layers can be the potential failure mechanisms of clay. In 48 (Duque-Redondo et al., 2014) it has been shown that the failure was mainly due to deco-49 hesion of inter-layer space under uniaxial tension perpendicular to layers and to stick-slip 50 between clay layers under shear loading. In the work reported in (Hantal et al., 2014), the 51 authors have proved that the mechanical performance of clay hybrid material under uniaxial 52 tension perpendicular to layers and shear along layers was dependent only on the cohesion 53 between layers, while the layers themselves do not participate in the failure mechanism. The 54 Coulombic force was more significant when a tensile strain was applied, while the hydrogen 55 bonding became relevant under shear loading. In (Faisal et al., 2020), it has been stated 56 that the hierarchical structure of Na-Mt clay mineral was composed of four relevant levels: 57 unit clay mineral layer, tactoid, aggregate, multiple aggregate. The mechanical response of 58 Na-Mt tactoid was evaluated under compression, tension and shear. All the previous studies 59 mentioned above have shown that the mechanical behavior of clay exhibited an anisotropic 60 behavior because of the internal structure and the failure process was influenced by the 61

62 loading path.

However, in most previous studies, MD simulations were performed on crystal samples 63 subjected to very simple loading paths, for instance, uniaxial compression or tension, triaxial 64 compression with constant confining stress. However, most geological materials can be 65 subjected to other types of loading paths. From a practical point of view, for example in 66 the case of underground cavity excavation, two loading paths are particularly relevant (Liu 67 et al., 2019a). In the first path here called triaxial decompression, starting from initial in-situ 68 stress state, one principal stress is increased in compression while two others are decreased 69 so that the mean stress remains constant. In the second path called triaxial extension, 70 one compressive principal stress is relaxed and two other ones are increased by keeping 71 the mean stress at a constant value. The comparison between these loading paths allow 72 studying the effect of third stress invariant (or Lode's angle) on mechanical behavior. Indeed, 73 it has been found that mechanical behaviors of most geological materials were generally 74 different along these two loading paths (Liu et al., 2019b). On the other hand, the influence 75 of loading path should also be coupled with loading orientation for anisotropic materials 76 such as clay-rich rocks. Therefore, the effects of loading path and orientation should be 77 investigated together. To the best of our knowledge, these important features have so far 78 not been investigated on atomistic modeling of mechanical behavior of MMT particles. In 79 this study, we shall perform MD simulations on a typical Na-montmorillonite (NaMMT) 80 crystal structure by considering the triaxial compression and extension with different values 81 of mean stress. Further, the compression and extension will be applied respectively to the 82 parallel and perpendicular directions with respect to crystal layers. The main objective here 83 is to identify the basic mechanisms of deformation and failure at the atomistic scale and 84 then to establish some links between microscopic (single NaMMT crystals) and macroscopic 85 (clayey rocks) behaviors. However, there is no pretension in this study to develop a multi-86 scale modeling of macroscopic mechanical properties of clayey rocks, which are influenced 87 by complex heterogeneity (voids, mineral phases) at different scale. It is only focused at 88 studying deformation and failure properties of one of principal constituent (clay minerals) of 89 clayey rocks at the atomistic scale. The results obtained from MD simulations can be used 90

for the first step of multi-scale bottom-up modeling of clayey rocks. Further, among various factors influencing mechanical behaviors of NaMMT particles such as stress state, hydration and temperature, the emphasis of the present work is put on the effects of loading path and orientation as well as mean stress. Effects of hydration and temperature on deformation and failure properties of NaMMT are investigated in other studies.

96 2. Computational method

Molecular dynamics (MD) is adopted here as computational method. Like most previous studies on MD simulations, atoms are considered as basic particles. The atomistic movement is described by Newton equations of motion, and the forces acting on the atoms are driven by inter-atomic potentials (force fields) which contains bonded and non-bonded interactions. In this section, the different steps of MD simulations performed in this study are first presented.

102 2.1. Crystal structure

¹⁰³ The crystal structure considered here is based on the natural Wyoming MMT (Boek ¹⁰⁴ et al., 1995b,a; Chang et al., 1995). The unit cell formula is as follows:

$$Na_{0.75}nH_2O[Si_{7.75}Al_{0.25}][Al_{3.5}Mg_{0.5}]O_{20}(OH)_4.$$
(1)

The space group of unit cell is C2/M, monoclinic system, with a=5.23A, b=9.06A, c=9.6A, 105 $\alpha = \gamma = 90^{\circ}$ and $\beta = 99^{\circ}$. It is characterized by sheets of silica tetrahedra and alumina octahedra 106 that coordinate to form a TOT (tetrahedron-octahedron-tetrahedron) layer. The layer is 107 negatively charged by the aliovalent substitution of Mg^{2+} for Al^{3+} in the octahedral sheet 108 and of Al^{3+} for Si^{4+} in the tetrahedron sheet. Specifically, one of thirty-two Si^{4+} is replaced 109 by Al^{3+} and one of eight Al^{3+} is replaced by an Mg^{2+} . This process is called the isomorphous 110 substitution. The negative charge is balanced by the incorporation of Na cations in the 111 inter-layer space. The model used in this study is an 8^{4} super-cell. The failed crystal 112 structure is shown in Figure 1. 113



Figure 1: Crystal structure of MMT and definition of compression and extension loading along z-axis



Figure 2: Crystal structure of MMT and definition of compression and extension loading along x-axis

114 2.2. Force filed

The interactions in crystal systems are described by forces fields which are 115 derived from energy potential functions. In the present study, the CLAYFF force field 116 developed by (Cygan et al., 2004) is adopted. This force field is mainly based on an non-117 bonded description of interatomic interactions consisting solely of electrostatic and Lennard-118 Jones terms except for the O-H bond, which is constrained by a harmonic bond stretch 119 potential. In the last few decades, the CLAYFF force field has been shown to be highly 120 effective in modeling the crystal structure of a number of different clays (Suter et al., 2007; 121 Porion et al., 2007; Wang et al., 2005; Leng and Cummings, 2006; Cygan et al., 2004), 122 mobility of interlayer water (Suter et al., 2007; Porion et al., 2007; Wang et al., 2005; Leng 123 and Cummings, 2006; Kalinichev et al., 2007) because of the huge advantage of providing 124

atoms with complete translational freedom. Recently, it has also widely used to study the 125 mechanical behavior of clay and contributed to the understanding of the basic mechanical 126 mechanisms from atomic level (Manevitch and Rutledge, 2004; Cygan et al., 2004; Ebrahimi 127 et al., 2012; Mazo et al., 2008b,a; Suter et al., 2007; Ebrahimi et al., 2012; Carrier et al., 128 2014; Zhang et al., 2015). Besides, the effectiveness of CLAYFF force field in the study of 129 mechanical properties of clay minerals was evaluated through the comparison of simulation 130 and experimental results by some researchers (Teich-McGoldrick et al., 2012). The total 131 potential energy (E_{total}) is composed of the Coulombic interactions (E_{Coul}) , the van der Waals 132 interactions (E_{VDW}) and the bonded interactions. The bonded terms include the bond stretch 133 energy $(E_{bond \ strech})$ and the angle bend energy $(E_{angle \ bend})$ that is used in water and metal 134 with hydroxyl. One gets: 135

(

$$E_{total} = E_{Coul} + E_{VDW} + E_{bond-strech} + E_{angle-bend}$$

$$E_{Coul} = (e^2/4)\pi\epsilon_0 \sum_{i\neq j} q_i q_j / r_{ij}$$

$$E_{VDW} = \sum_{i\neq j} D_{0,ij} [(R_{0,ij}/r_{ij})^{12} - 2(R_{0,ij}/r_{ij})^6]$$

$$E_{bond-strech} = k_1 (r_{ij} - r_0)^2$$

$$E_{angle-bend} = k_2 (\theta_{ijk} - \theta_0)^2$$
(2)

 r_{ij} is the distance between the atoms i and j. In the Coulombic energy, e is the charge of an electron, ϵ_0 is the dielectric permittivity of a vacuum $(8.85419 \times 10^{12} F/m)$ and q_i and q_j are the atomic partial charges, which can be derived from quantum mechanics calculations. In the Van der Waals energy, the terms $D_{0,ij}$ and $R_{0,ij}$ are calculated by:

$$\begin{cases}
R_{0,ij} = 1/2(R_{0,i} + R_{0,j}) \\
D_{0,ij} = (D_{0,i} + D_{0,j})1/2
\end{cases}$$
(3)

About the (O - H) bond stretch energy, k_1 defines a force constant and r_0 represents the equilibrium bond length. Finally for the angle bend energy, k_2 is a force constant, θ_{ijk} denotes the bond angle for the mental-oxygen-hydrogen and θ_0 is the equilibrium bond angle. The values of parameters involved in the different forces are given in Tables 1, 2 and 3 respectively.

species	symbol	charge (e)	$\mathrm{D}_0(\mathrm{kcal/mol})$	$R_0(\text{\AA})$
tetrahedral silicon	st	2.1000	1.8405×10^{-6}	3.7064
bridging oxygen	ob	-1.055	0.1554	3.5532
bridging oxygen with octahedral substitution	obos	-1.1808	0.1554	3.5532
octahedral aluminum	ao	1.5750	1.3298×10^{-6}	4.7943
hydroxyl oxygen	oh	-0.9500	0.1554	3.5532
hydroxyl hydrogen	ho	0.4250		
hydroxyl oxygen with substitution	ohs	-1.0808	0.1554	3.5532
octahedral magnesium	mgo	1.3600	9.0298×10^{-7}	5.9090
aqueous sodium ion	Na	1.0000	0.1301×10^{-6}	2.6378
bridging oxygen with tetrahedral substitution	obts	-1.1688	0.1554	3.5532
tetrahedral aluminum	at	1.5750	1.8405×10^{-6}	3.7064

Table 1: Non-bond energy parameters for the CLAYFF force field

species i	species j	$k_1(\text{kcal/mol} \text{ Å}^2)$	$r_0(\text{\AA})$
oh	ho	554.1349	1.000
ohs	ho	554.1349	1.000

Table 2: Bond stretch energy parameters for the CLAYFF force field

Table 3: Angle bend energy parameters for the CLAYFF force field

species i	species j	species k	$k_2(\text{kcal/mol rad}^2)$	$\theta_0(\mathrm{deg})$
Metal	oh	ho	30.0	109.47
Metak	ohs	ho	30.0	109.47

144 2.3. MD simulation procedure

A parallel molecular dynamics code Lammps (Plimpton, 1993) is used to perform simu-145 lations on the crystal structure of Na-Montmorillonite defined above. The samples are first 146 relaxed at the desired temperature using an NVT (conserving the number of atoms, volume, 147 and temperature) ensemble for 200 ps followed by an independent relaxation in three direc-148 tions using an NPT (conserving the number of atoms, pressure, and temperature to mimic 149 bulk behavior) ensemble for another 200 ps with zero pressure in all the directions. These 150 relaxation steps are performed to uniformly distribute the excess free energy through the 151 whole system. 152

Mechanical loads are then applied to the samples and their deformations are calculated. As mentioned above, mechanical responses of clayey rocks clearly depend on loading paths. Two representative loading paths are here considered: triaxial compression and extension, as shown in Figure 1. For both loading paths, a hydrostatic compressive mean stress is first applied in three principal directions of the crystal sample. Then, after the stabilization of

strains under the mean stress, in the compression loading, one of three principal stresses is 158 further increased (called the axial stress and denoted as $\sigma_a > 0$) while the other others are 159 decreased (called the radial stress and denoted as $\sigma_r < 0$) so that the value of mean stress 160 remains unchanged $(\Delta \sigma_a + 2\Delta \sigma_r) = 0$. For the extension loading, the axial principal stress 161 is relaxed ($\sigma_a < 0$) from the initial value while the radial stress is increased ($\sigma_r > 0$) so 162 that the mean stress is kept constant $(\Delta \sigma_a + 2\Delta \sigma_r) = 0$. In this study, four different values 163 of mean stress are considered, namely $\sigma_m=5$, 10, 15, 20GPa. The increase or decrease of 164 the axial stress is proceeded at the rate 10MPa/fs while that of the radial stress at the rate 165 5MPa/fs according to the Parrinello-Rahman method under the given temperature which is 166 controlled by the Nose-Hoover thermostat. All simulations are run until failure of sample. 167 All simulations are carried out using an MD time step of 0.01 fs. A periodic boundary 168 condition is adopted in all directions. It is worth noticing that the values of mean stress 169 used here are much higher as those usually considered in macroscopic tests on clayey rocks. 170 Indeed, due to its strong order and very small inter-layer pore, the single NaMMT crystal is 171 much stiffer than macroscopic samples. Therefore, in order to facilitate the investigation of 172 deformation and failure of such a single crystal, high values of stresses are generally adopted 173 in most MD simulations, for instance on NaMMT particles (Schmidt et al., 2005; Thapa 174 et al., 2020). Similar values are adopted in this study for mean stress. As a consequence, 175 results obtained from MD simulations on NaMMT crystal are mainly used to investigate 176 atomistic physical origins of some macroscopic properties and to identify links between 177 microscopic and macroscopic behaviors. 178

¹⁷⁹ Moreover, in order to investigate the anisotropic responses of MMT crystal, both the ¹⁸⁰ compression and extension paths are applied respectively the parallel (x-axis) and perpen-¹⁸¹ dicular (z-axis) directions to the crystal layers. The detailed description of loading paths ¹⁸² are presented in the supplementary file. Finally, all MD simulations presented in this study ¹⁸³ are performed with a constant temperature of T = 300K.

184 3. Basic mechanical behavior and discussions

In this section, the basic mechanical behavior of NaMMT crystal samples is first pre-185 sented through the results obtained from MD simulations. We shall then investigate effects 186 of loading path, crystal structure anisotropy, mean stress on overall stress-strain responses. 187 It is worth noticing that different types of phenomenological and micro-mechanical constitu-188 tive models have been proposed for the description of elastic-plastic and damage behaviors 189 of clayey rocks the effects mentioned here, for instance (Shao et al., 2006; Hoxha et al., 190 2007; Shen et al., 2013; Shen and Shao, 2015). However, all those models are inspired or 191 calibrated from macroscopic experimental results. As basic differences with these models, 192 MD simulations are entirely based on the motion of crystal systems. Mechanical behaviors 193 are predicted by solving fundamental motion equations without any a priori assumptions. 194 On the other hand, contrary to classical constitutive models, MD modeling is at this stage 195 devoted to engineering structure calculations but to analyze different physical mechanisms 196 of deformation and failure at small scales. 197

198 3.1. Basic stress-strain response

As example, the stress-strain curves for a mean stress of $\sigma_m = 20GPa$ are selected and shown in Figures 3, when the axial stress is along x-axis and z-axis respectively. By using conventional rock mechanics notation, axial (ϵ_a) and radial (ϵ_r) strains are plotted versus differential stress $q = \sigma_a - \sigma_r$.

From these Figures, one can see that the basic mechanical behavior of MMT in both com-203 pression and extension is characterized by strongly nonlinear stress-strain curves. There is a 204 short linear phase at the beginning of loading. This phase can represent the elastic behavior 205 of MMT. The linear phase is followed by a nonlinear one with increasing axial and radial 206 strain until the peak differential stress is reached. This nonlinear phase corresponds to plas-207 tic deformation of crystal sample. The peak differential stress characterizes the maximum 208 mechanical strength for a given loading condition. Starting from the stress value around the 209 peak strength, the internal crystal bonds are progressively damaged, leading to the reduction 210 of their mechanical strength. As a consequence, one gets the material softening behavior in 211

the post-peak regime. Moreover, the plastic deformation is inherently coupled with the dam-212 age of crystal bonds. When the strain becomes large enough, a residual strength of material 213 can be obtained and it is due to the forces in the remaining crystal bonds. It is interesting to 214 notice that the basic mechanical behaviors obtained at the atomistic scale are qualitatively 215 very similar to those observed on various clayey rocks (Chiarelli et al., 2003; Vales et al., 216 2004; Zhang et al., 2012; Liu and Shao, 2016; Armand et al., 2017; Zeng et al., 2019), for 217 instance elastic and plastic deformation as well as induced damage. However, as mentioned 218 above, the order of magnitude of stresses is much higher, while that it strain is lower, at the 219 atomistic scale than that at the macroscopic scale. Therefore, the objective here is to inves-220 tigate relationships between microscopic mechanisms and macroscopic properties, but not to 221 make quantitative comparisons. Indeed, for a same loading path, the macroscopic strength 222 of clayey rocks is generally significantly lower than that of MMT crystal at the atomistic 223 scale. This difference can be basically explained by strong multi-scale heterogeneity effects. 224 Clayev rocks are heterogeneous composites containing voids and mineral phases at different 225 scales. In particular, inter-particular voids and interfaces should play a strong weakening 226 effect in macroscopic strength properties. The local responses of clay minerals affect only 227 partially the overall behaviors of clayey rocks. 228



(a) Differential stress - axial strain (b) Differential stress - radial strain

Figure 3: Typical stress-strain curves in compression and extension (T=300K, σ_m =20GPa)

229 3.2. Effect of loading path

For a quantitative comparison between compression and extension, the peak values of axial stress (σ_a), radial stress (σ_r) and differential stress obtained in compression and extension under 300k are given in Table 4. It is worth noticing that the basic difference between these two loading paths lies on the value of Lode angle defined on the octahedral plane for a given value of mean stress or equivalently the third stress invariant. Indeed, the Lode angle is equal to $\theta_{\sigma} = -30$ for compression and $\theta_{\sigma} = 30$ for extension.

From the date obtained, a number of significant remarks can be drawn. When the 236 axial stress is applied along z-axis (perpendicular to crystal layers), the absolute values 237 of peak differential stress are systematically higher in compression than in extension for 238 all selected values of mean stress σ_m . However, the difference between compression and 239 extension becomes smaller when the mean stress is higher. This means that dissymmetry of 240 peak strength between these two loading paths is progressively attenuated by the increase 241 of mean stress. In the three-dimensional stress space, the strength surface in the octahedral 242 plane approaches a circular lotus when the mean stress is high enough. This kind of result 243 agrees well with macroscopic experimental results obtained on most rocks as mentioned 244 above. When the axial stress is parallel to x-axis, the absolute value of peak stress in 245 compression is also higher than that in extension for three low values of mean stress. But 246 the difference between compression and extension is significantly reduced from $\sigma_3=5$ GPa to 247 $\sigma_3=15$ GPa. For the case of $\sigma_3=20$ GPa, the peak strength in extension even becomes higher 248 than that in compression. This particular result will be further discussed later in relation 249 with the failure process of MMT crystal structure. In a general way, it is worth noticing 250 that the dependency of failure strength on loading path observed at the atomistic scale is 251 qualitatively consistent with few macroscopic results obtained on clayey rocks samples (Liu 252 et al., 2019a). Therefore, it seems that in spite of many other factors affecting macroscopic 253 behaviors of clayey rocks, the stress-path dependency of their macroscopic strength have 254 some origins at the atomistic scale. 255

		Compression					_	Extension					
σ_m	x-axis			z-axis		_	x-axis			z-axis			
	σ_{a}	σ_r	q	σ_{a}	σ_r	q		σ_r	σ_{a}	q	σ_r	σ_{a}	q
5	22.22	-2.52	24.74	28.05	-6.41	34.46		13.26	-11.32	-24.59	10.98	-1.09	-12.06
10	29.42	0.35	29.06	34.27	-2.03	36.30		19.03	-7.74	-26.77	20.07	-0.50	-20.58
15	34.69	5.11	29.57	40.33	2.32	38.00		24.94	-4.64	-29.58	28.11	-0.05	-28.16
20	39.55	10.14	29.41	45.42	7.23	38.19		30.42	-0.60	-31.03	31.91	-1.77	-33.69

Table 4: Peak values of axial stress, radial stress and differential stress in compression and extension and along x-axis and z-axis (T=300K)

256 3.3. Effect of loading orientation

²⁵⁷ Based on the peak values of stresses given in Table 4 and the overall stress-strain responses ²⁵⁸ obtained from performed calculations, the effect of loading orientation with respect to the ²⁵⁹ crustal layers is here further discussed. For this purpose, we compare here the stress-strain ²⁶⁰ curves between compression and extension for two values of mean stress ($\sigma_m = 20GPa$, ²⁶¹ $\sigma_m = 10GPa$), as shown in Figure 4 and 5.

From these results, it is found that during the short linear stage at the beginning of 262 differential stress loading for both compression and extension paths, the mechanical behav-263 ior of MMT crystal is almost identical in the two loading orientations. It seems that the 264 elastic properties of MMT crystal are quasi isotropic. However, one can observe important 265 differences of mechanical responses during the plastic phase and in the -peak regime. For 266 compression loading, the plastic deformation is smaller but the peak strength is higher in 267 z-axis than in x-axis. Further, the mechanical behavior in z-axis is more brittle than in x-268 axis in the post-peak regime by showing a faster decrease of differential stress. However, the 269

asymptotic residual strength is almost the same for the two loading orientation. In contrary, 270 for the extension loading, the plastic deformation is clearly more important in z-axis than in 271 x-axis. At the same time, the MMT shows a more ductile behavior in the post-peak regime 272 in z-axis than in x-axis. The difference of peak differential stress between the two loading 273 orientations depends on the values of mean stress. It seems that the peak strength in z-axis 274 is higher than in x-axis for different values of mean stress ($\sigma_m = 10GPa$, $\sigma_m = 20GPa$). 275 It is worth noticing that z-axis is perpendicular to crystal layers while x-axis is parallel to 276 them. Therefore, the difference of mechanical behavior between the two loading orientations 277 is inherently related to different deformation and damage processes at the atomistic scale. 278 More detailed discussions are presented in Section 4. It is interesting to point out that the 279 strength anisotropy obtained at the atomistic scale is consistent with the macroscopic one 280 observed in clayey rocks (Niandou et al., 1997; Liu et al., 2015; Armand et al., 2017; Zhang 281 et al., 2019). It seems that the macroscopic strength anisotropy of clayey rocks is partially 282 due to the layered structures of clay particles. However, it is noticed that the microscopic 283 anisotropy is stronger than the macroscopic one. Such a difference can be explained by the 284 fact that clayey rocks are multi-scale poly-crystalline materials. Random distribution of clay 285 particles and other mineral phases can attenuate the macroscopic anisotropy of materials. 286



Figure 4: Comparison of stress-strain curves in compression between two loading orientations



Figure 5: Comparison of stress-strain curves in extension between two loading orientations

287 3.4. Effect of mean stress

The mechanical behavior of geological materials is generally dependent on mean stress. 288 This basic property is here verified at the atomistic scale on the MMT crystal. For this 289 purpose, four values of mean stress are selected, ranging from 5 MPa to 20 MPa. The stress-290 strain curves obtained from compression and extension and in both loading orientations 291 are here compared and presented in Figures 6 and 7. In a general way, little difference is 292 observed on the initial slopes of stress-strain curves for almost all cases. That indicates 293 that the elastic properties of the MMT crystal are almost independent on mean stress. But 294 mean stress strongly affect plastic deformation and failure strength. For compression in 295 x-axis, larger plastic deformation is developed and the peak strength is lower when mean 296 stress is smaller. But the mean stress dependency of peak strength is clearly nonlinear. 297 Indeed, the dependence of peak strength on mean stress is significantly attenuated when 298 mean stress is higher than 10 MPa. The post-peak behavior is more brittle and the residual 299 strength is lower when mean stress is smaller. The mechanical behavior during extension 300 in x-axis shows a much more regular dependency on mean stress than in compression. The 301 plastic deformation increases and the peak and residual strengths decrease when mean stress 302 becomes smaller. The influence of mean stress on the mechanical response in compression 303

along z-axis is qualitatively similar to that in x-axis. Among all cases, the most important 304 effect of mean stress is found on the mechanical responses in extension along z-axis. The 305 peak strength shows a very important increase when mean stress varies from 5 GPa to 20 306 GPa. Further, for the three low values of mean stress (5, 10, 15GPa), very large axial plastic 307 strains are obtained and one observes a typical ductile behavior. At the same time, the 308 radial strains remain significantly smaller than axial ones. For the case of high mean stress 309 (20 GPa), the post-peak behavior is characterized by three different phases: a first phase of 310 slow decrease of differential stress, a second phase with rapid decrease of differential stress, 311 and a third phase marking the residual strength. This atomistic effect of mean stress is 312 quite different with classical brittle-ductile transition of rocks with increasing mean stress 313 at the macroscopic scale. It seems that mean stress can play an essential role on plastic 314 deformation and failure process of clay crystals at the atomistic scale. Again, the dependence 315 of mechanical behavior on mean stress of the NaMMT crystal, in particular the increase of 316 failure strength with mean stress, is also very consistent with macroscopic results obtained 317 on various clayev rocks (Chiarelli et al., 2003; Armand et al., 2017; Liu et al., 2019a; Zhang 318 et al., 2019). Again, there is a clear link between the microscopic and macroscopic behaviors 319 in terms of mean stress effects. 320

On the other hand, in Figures 6 and 7, the variations of volumetric strain are also pre-321 sented. It is interesting to see that in a general way, there is a clear transition from volumetric 322 compaction to dilation when the differential stress is increased. The volumetric dilatancy 323 increases very quickly in the post-peak regime. There is thus a clear correlation between 324 volumetric dilatancy and crystal structure damage. For compression in x-axis (parallel to 325 crystal layers), the volumetric dilatancy is higher when the mean stress is lower because the 326 expansion of inter-layer space is prevented by compressive mean stress. For extension in 327 x-axis, the volumetric dilatancy is smaller when the mean stress is lower but its effect is less 328 significant. For these two cases, the volumetric strain remains very small before the peak 329 strength is reached. This is due to the fact that the deformation before the peak strength 330 is essentially elastic and the mean stress is kept constant. For compression in z-axis (per-331 pendicular to crystal layers), the volumetric strain is clearly compressive before the peak 332

strength is reached and then turns into dilating in the post-peak region. This is clearly a 333 consequence of compaction of inter-layer space along the z-axis. For extension in z-axis, 334 nearly no volumetric compaction is obtained even before the peak strength. The volumetric 335 dilatancy is significantly enhanced by low values of mean stress, and it is clearly correlated 336 with the expansion of inter-layer space. Therefore, the evolution of volumetric strain of clay 337 particle is significantly influenced by loading path and orientation as well as mean stress. 338 These atomistic results on NaMMT particle are in good consistency with macroscopic re-339 sponses of most clayey rocks, in particular under low values of mean stress (Chiarelli et al., 340 2003; Armand et al., 2017; Liu et al., 2019a; Zhang et al., 2019). However, the macroscopic 341 volumetric deformation of clayey rocks is not only influenced by clay particles, but also by 342 many other factors such compaction or expansion of multi-scale voids, opening or closure of 343 interfaces between mineral inclusions and clay matrix. As a consequence, it is noticed that 344 the macroscopic volumetric dilatancy is less pronounced than that of NaMMT crystals. 345



(c) Compressionin x-axis - volumetic strain

(d) Extension in x-axis - volumetric strain

Figure 6: Comparisons of stress-strain curves in x-axis between different values of mean stress



(c) Compression in z-axis - volumetrci strain (d) Extension in z-axis - volumetric strain

Figure 7: Comparisons of stress-strain curves in z-axis between different values of mean stress

346 3.5. Effect of crystal model size

Molecular dynamics studies provide a deep understanding of the properties of materials from the nanometer scale but also are limited by the system size. Previous studies have shown that some properties of materials are affected by the system size while some properties are size-independent in molecular dynamics simulations. For example, in (Yeh and Hummer, 2004), the authors have studied the system-size dependence of translational diffusion coefficients and viscosities of water and the Lennard-Jones fluid in molecular dynamics

simulations under periodic boundary conditions and concluded the diffusion coefficients in-353 creased strongly as the system size was larger while the shear viscosities showed no significant 354 system-size dependence. In (Sellan et al., 2010), the size effect of thermal conductivity has 355 been studied for Lennard-Jones argon and Stillinger-Weber silicon and found that there was 356 no discernible size dependence for the simulation systems containing $4^{*}4^{*}4$ to $8^{*}8^{*}8$ con-357 ventional unit cells under periodic boundary conditions. There are also some studies on 358 the mechanical properties of materials that have shown that the mechanical properties of 359 the materials could depend on the size of the simulation system (Koh and Lee, 2006; Heino 360 et al., 1998). The results of these previous works have shown that the mechanical param-36: eters, such as Young's modulus, turned out to be independent of the system size or close 362 to the theoretical bulk values for relatively large systems. However, to our best knowledge, 363 there is still no detailed report about the size selection of clay mineral models in the molecu-364 lar dynamics study of mechanical properties. In general, the super-cell of clay minerals used 365 in MD simulations is from $4^{*}2^{*}2$ to $16^{*}8^{*}8$ in the previously reported studies (Manevitch 366 and Rutledge, 2004; Cygan et al., 2004; Ebrahimi et al., 2012; Mazo et al., 2008b,a; Suter 367 et al., 2007; Ebrahimi et al., 2012; Carrier et al., 2014; Yang et al., 2019). In order to observe 368 the structural changes during the system failure process more clearly, we prefer to choose a 369 relatively small system in this study. However, it is our concern that small model may lead 370 to errors in our quantitative results. In order to better determine the size of the system, 371 we compare here two systems of different size of Na-MMT supercells to capture the system 372 size effect on the stress-strain behavior. The small system is the supercell of $8^{*}4^{*}4$ contain-373 ing 5216 atoms and the big one is a supercell of 16*8*8 containing 41728 atoms, which is 374 considered as big enough to ignore the size effect. The overall stress-strain curves of two 375 systems in the z-axis under a mean stress of 15GPa during compression and extension are 376 selected as example and shown in Fig. 8(a) and 8(b). It is obvious to observe that the 377 basic mechanical behavior is almost the same except a tiny difference of residual strength 378 for the two different systems. Thus, the Na-MMT supercell of $8^{*}4^{*}4$ chosen in the previous 379 simulations is considered as reasonable for the present study. 380



Figure 8: Stress-strain curves in z-axis for two systems of different size

381 4. Further discussion on deformation and failure properties

382 4.1. Analysis of failure stresses at atomistic scale

The peak values of differential stress obtained from MD simulations on the MMT crystal 383 are summarized and discussed here. In Figure 9, the peak differential stress is plotted as 384 mean stress for the compression and extension paths respectively in x-axis and z-axis. As a 385 first approximation, the peak differential stress can be expressed as a linear function of mean 386 stress. This corresponds to linear macroscopic failure criteria widely used at macroscopic 387 scale for geological materials. It is observed that for both loading orientations, the slopes of 388 failure stress lines in extension are higher than in compression. That means that the failure 389 stress in extension is more sensitive to mean stress than in compression. As the slopes of 390 failure stress lines are generally related to internal friction coefficient. It seems that the 391 internal friction in extension is higher than that in compression. This result suggests that 392 the failure surface (or criterion) of MMT crystal is a function of Lode's angle. 393



Figure 9: Compression and extension of failure stress in the $\sigma_m - q$ plane in x (blue lines) and z (red lines) axes

394 4.2. Deformation and failure process at atomistic scale

The deformed crystal structures at different levels of loading are shown in Figures 10 to 13 for the compression and extension respectively along two axes. $q_{(p)}$ denotes the peak differential stress and the $q_{(f)}$ is the differential stress at the first point of residual strength phase.

More precisely, in Figure 10, one shows the progressive deformation process during com-399 pression in z-axis. In this case, as the compressive axial stress is applied in the perpendic-400 ular direction to the crystal layers, the principal deformation process is the compaction of 401 inter-layer space. The cohesion between layers is mainly contributed by the non-bonding 402 interaction, namely the Coulombic and Van der Waals forces coming from the cation-layer 403 and layer-layer interactions. The change of layer space will weaken the cohesion between 404 layers, as characterized in terms of energy in (Hantal et al., 2014; Duque-Redondo et al., 405 2014). When the peak stress is reached, the MMT-crystal still keeps a layered structure 406 in spite of large reduction of inter-layer space. When the residual state is finally obtained, 407

there is a complete collapse of layered crystal structure. The deformation process during 408 extension along z-axis is shown in Figure 11. Due to the fact that a tensile stress is applied 409 in the perpendicular direction to crystal layers, the inter-layer spacing is gradually increased 410 during both the elastic and plastic stages until 80% of peak strength. The atoms vibrate 411 around the equilibrium position and structural damage is observed. When the differential 412 stress approaches its peak value, there is bending of sheets and some atoms start moving 413 towards the inter-layer space. The phenomenon of sheet bending, caused by the progres-414 sively increasing lateral stress, is the principal damage mechanism of crystal structure in the 415 extension loading with a constant mean stress. 416

When the compressive stress is applied in the parallel direction to crystal layers (x-axis), as shown in Figure 12, one gets a progressive dilation of inter-layer space without structural damage until 80% of peak strength. The failure of crystal structure is essentially related to bending of sheets. For the case of extension along x-axis shown in Fig. 13, the reduction of inter-layer space is the principal deformation process and the structural failure is caused by the collapse of inter-layer space. But the inter-layer space is not totaly closed even at the final residual stage.

From these results, it can be concluded that the failure mechanisms of the MMT crystal 424 structure is not only influenced by loading paths (compression or extension) but also by 425 the loading orientation with respect to crystal layers. In summary, the failure is caused 426 by the collapse of inter-layer space for compression perpendicular to layers of for extension 427 parallel to layers. However, the sheet bending becomes the principal failure mechanism for 428 compression parallel to layer and extension perpendicular to layers. Finally, it is worth 429 noticing that the positions where the isomorphous substitution happens (green atoms) have 430 the tendency to form cracks. 431



Figure 10: Deformed MMT crystal structures at different loading stages during compression in z-axis



Figure 11: Deformed MMT crystal structures at different loading stages during extension in z-axis



Figure 12: Deformed MMT crystal structures at different loading stages during compression in x-axis



Figure 13: Deformed MMT crystal structures at different loading stages during extension in x-axis

432 5. Conclusions

A series of molecular dynamics simulations have been performed on the NaMMT crystal structure in order to investigate the mechanical behavior of clay particles at the atomistic scale. Two representative loading paths including compression and extension under constant mean stress were applied respectively in the parallel and perpendicular directions to crystal layers. Based on the results obtained, a number of concluding remarks can be formulated.

The basic stress-strain relationship at the atomistic scale is similar to that of most clayey rocks at the macroscopic scale. It is generally characterized by a short linear elastic phase followed by a large nonlinear plastic phase until the peak strength (represented by the absolute value of differential stress) is reached. A sharp or smooth material softening phase
is observed in the post-peak regime due to damage of crystal bonds until the residual strength
is reached.

The mechanical behavior of NoMMT crystal is strongly influenced by the loading path 444 and orientation. In the perpendicular direction, the failure strength in compression is sys-445 tematically higher than that in extension. But the difference is significantly reduced when 446 the mean stress is high. In the parallel direction, the failure strength in compression is 447 slightly higher than in extension under low mean stress but becomes slightly lower than 448 extension under high mean stress. In general, the failure strength in compression in the per-440 pendicular direction is higher than that the parallel direction. On the contrary, the strength 450 in extension in the perpendicular direction can become lower than that the parallel direction 451 under low mean stress. Therefore, the general failure criterion of NoMMT crystal depends 452 on Lode's angle, mean stress as well as loading orientation. On the other hand, the post-peak 453 stress-strain responses are also affected by these same factors, producing brittle or ductile 454 behavior. 455

The mechanical behavior of NoMMT crystal is further influenced by mean stress, but in a quite different manner in two loading orientations. In the parallel direction, the mean stress mainly affects the peak strength. But in the perpendicular direction, the mean stress affects not only the peak strength but also the post-peak stress-strain relationship by producing either a brittle or ductile behavior according to the value of mean stress. In a general way, the influence of mean stress is stronger in extension than in compression.

The deformation mechanism of crystal structure until around 80% of peak strength is 462 mainly driven by the compaction or dilation of inter-layer space. Layer structure is progres-463 sively destroyed around the peak strength and during the softening zone. A relatively stable 464 damaged structure is found and related to the residual strength of crystal. As a first ap-465 proximation, the failure of crystal structure is generated by the collapse of inter-layer space 466 under compression in perpendicular direction and under extension in parallel direction. The 467 sheet bending is the principal failure mechanism under compression in parallel direction and 468 under extension in perpendicular direction. 469

A number of similar features have been observed between the atomistic behavior of 470 clay crystal and macroscopic responses of clayey rocks, in terms of effects of loading path 471 and orientation as well as mean stress on deformation and failure behaviors. Therefore, 472 numerical results from molecular simulations can provide useful atomistic interpretation of 473 macroscopic deformation and failure processes. However, macroscopic mechanical properties 474 of clayey rocks are also strongly affected by other factors such voids and inclusions at different 475 scales, and it is necessary to develop adequate multi-scale approaches. On the other hand, 476 the mechanical behavior of both NoMMT crystal and clayey rocks are also affected by water 477 content and temperature. These important issues will be investigated in our ongoing studies. 478

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