Methodology for Estimation of Nanoscale Hardness via Atomistic Simulations

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Abstract: Statistical mechanics has provided powerful techniques to measure mechanical properties of materials at the nanoscale and paved the way for bottom-up computational materials design. The introduction of such techniques in civil engineering applications, namely construction and geotechnical materials, remains limited to the elastic and fracture properties. This paper presents an atomistic approach to calculate the nanoscale cohesion, friction angle, and hardness. This method is based on the application of biaxial external deformation, or stress, in the weakest crystallographic direction in the material. The onset of the failure is characterized by investigating the unloading paths from several points on the stress-strain curve. Such calculations of the failure stress along different deformation paths provide multiple failure Mohr circles in the normal-shear stress space, which is found to provide a failure envelope akin to the Mohr–Coulomb failure criterion that is widely used for the plastic analysis of granular geomaterials. The failure envelope characterizes the nanoscale cohesion and friction angle, which in conjunction with continuum mechanics can be utilized to estimate the nanoscale hardness of layered materials. Application of this method to tobermorite and Na-montmorillonite crystals yields values that are close to the experimental measurements obtained using nanoindentation and atomic force microscopy techniques. DOI: 10.1061/(ASCE)NM.2153-5477.0000127. © 2017 American Society of Civil Engineers.

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Introduction

Computer simulations are becoming an indispensable part of the development of bottom-up approaches to materials design in the twenty first century. Such approaches based on the first principles of physics have been ubiquitously applied to nanomaterials (Bagri et al. 2010), metals (Bernal et al. 2015), glasses (Jund and Jullien 1999), ceramics (Blonski and Garofalini 1993), and recently have been applied to multiscale porous materials such as cementitious (Pellenq et al. 2009; Shahsavari et al. 2011) and geomaterials (Ebrahimi et al. 2012, 2014, 2016). The physical properties of multiscale porous materials have thus far been limited to elastic (Abdolhosseini Qomi et al. 2014), fracture (Bauchy et al. 2016, 2015; Brochard et al. 2015; Hantal et al. 2014), water dynamics (Qomi et al. 2014; Youssef et al. 2011), and thermal properties (Abdolhosseini Qomi et al. 2015). Despite the extensive research on plastic deformation in metallic materials (Aghaei et al. 2009; Khoei et al. 2009, 2011b), the study of inelastic deformation in layered materials continues to be limited, and the connection between experimental hardness measurement and the molecular simulations remains unknown.

Although in metals strength and hardness are typically associated with the mobility of dislocations and the interactions between them and grain boundaries, the molecular origins of strength properties of clay and cementitious materials remain elusive in the fields of cement, concrete, and geomechanics. Brinell (1901) conducted pioneering work to provide an empirical relationship between indentation hardness and material strength properties of solids. Subsequently, many contributions have been developed using mechanics solutions for indentation in cohesive solids (e.g., Chitkara and Butt 1992; Lockett 1963; Tabor 1948). In particular, in an attempt to address an underlying physics of strength in cohesive-frictional materials, Ganneau et al. (2006) provided a link between the intrinsic cohesion of materials’ friction angle and the hardness value measured in a nanoindentation experiment. Bobko et al. (2011) applied an inverse homogenization technique to back-calculate cohesive properties of clay on the basis of grid nanoindentation experiment on shale materials. The investigation of cohesive-frictional properties of pure clay minerals from the phyllosilicate group measured from nanoindentation (Zhang et al. 2009) proved to be close to the back-calculated values from inverse analysis of the results of nanoindentation experiments on shale samples (Bobko et al. 2009, 2011). Despite these efforts, the physical connection between intermolecular and intramolecular forces and the strength properties of layered materials has remained unexplored.

This paper uses tools of computational physics to establish a link between the molecular structure and strength properties of layered materials such as 11 Å tobermorite [Fig. 1(a)] and Na-montmorillonite clay with one layer of water [Fig. 1(b)] corresponding to basal layer spacing of 12 Å [see Ebrahimi et al. (2012) for the molecular construction of the sample]. As shown in Fig. 1, both crystals are composed of relatively rigid layers composed of calcium-silicate and substituted aluminosilicate groups, respectively. Both crystals contain soft interlayer spacing—interlayer galleries—which connects the rigid layers through ionic forces.

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Based on this description, these crystals can be idealized as a repetitive stacking of soft and rigid layers as illustrated schematically in Fig. 1(c), which facilitates understanding failure mechanisms in layered materials. Upon application of the shear stress, two possible failure mechanisms can be envisioned. The first mechanism [Fig. 1(d)] entails sliding of the rigid layers against one another. The second mechanism [Fig. 1(e)] entails plastic deformation of the rigid layers that requires distortion of intralayer covalent bonds and therefore is not energetically favorable. This argument promotes the idea that the failure of layered materials is the result of interlayer stretching and sliding. This suggests that biaxial deformation at the crystal level is enough to unravel the fundamental strength parameters that are closely related to nanoscale hardness: cohesion and friction angle.

This paper is organized as follows. The next section reviews the two major approaches for obtaining stress-strain curves using atomistic simulation techniques and explains a methodology for obtaining the failure points along the stress-strain curve, i.e., the unloading approach. Following that is a detailed explanation of the procedure for calculating nanoscale cohesion, friction angle, and hardness. The penultimate section applies the aforementioned method to calculate molecular strength properties of two layered crystalline minerals, 11 Å tobermorite and montmorillonite, and compares the results with those of nanoindentation and atomic force microscopy (AFM). The final section closes the paper with some concluding remarks.

**Determining Stress-Strain Behavior and Failure Point via Atomistic Simulations**

The notion of materials strength is classically explored within the framework of continuum mechanics. Although the continuum approach can be powerful, it requires a priori knowledge of the material’s constitutive behavior, i.e., the relation between the stress and strain. Continuum plasticity and damage models describe the postfailure stress-strain behavior within a thermodynamically consistent mathematical framework. Researchers commonly parameterize these models using the available experimental data for a specific material. Atomistic simulation methods, however, provide an alternative approach that could supply the stress-strain relation and failure behavior of materials given a priori knowledge of the molecular structure of the material and interatomic interactions.

The molecular structures of crystalline minerals are extensively studied in the literature using X-ray diffraction (XRD) and are publicly available in the American Mineralogist Crystal Structure Database. Within the last two decades, several interatomic and intermolecular force fields such as the clay force field (CLAYFF) (Cygan et al. 2004) and the calcium-silicate-hydrate force field (CSHFF) (Shahsavari et al. 2011) have been developed to foster a more accurate prediction of the structure, elasticity, and adsorption properties of clay and calcium-silicate-hydrate systems, respectively. The relative success of atomistic simulation approaches, however, comes at the expense of the limited characteristic length scale controlled by the size of the periodic simulation cell. This implies that atomistic simulations cannot be used to study physical phenomenon with characteristic length scales comparable to or greater than the simulation cell.

There are two major atomistic approaches to calculate bulk mechanical properties of materials: molecular dynamics (MD) and local structure optimization (LSO). Researchers have widely used MD to study physical properties of materials at finite temperature by analyzing sufficiently long trajectories of atomic positions, velocities, and forces in the time domain. The use of the MD approach to study mechanical properties requires changing the simulation cell size in the time domain that entails extremely high strain-rates beyond the reach of experimental approaches or practical relevance. Hence the investigation of mechanical properties using MD method is usually accompanied by rate convergence studies to ensure elimination of spurious effects (Khoei et al. 2011a). Unlike the MD method, the study of mechanical properties using LSO is free of any rate effect. This is due to the concept of the harmonic vibration of atoms around the local energy minima on the energy landscape. Therefore the LSO approach is limited to relatively low temperatures, considerably below the Debye temperature, at which anharmonic effects can be safely neglected. Using the concept of phonons, i.e., individual lattice vibration frequencies, LSO can be extended to include thermal effects through quasi-harmonic approximation techniques. One can achieve this by incorporating vibrational entropy within the framework of Helmholz free energy optimization rather than the conventional internal energy or enthalpy minimization (Gale 1997; Gale and Rohl 2003). Although it is thermodynamically more elegant, free energy minimization proves to be computationally cumbersome and for the case of relatively stiff crystalline minerals is of limited practical significance (Abdolhosseini Qomi et al. 2012).
The LSO approach is adopted with internal energy or enthalpy minimization in calculations, while neglecting thermal contributions. There are two approaches to calculate the stress-strain behavior and failure point based on the finite difference technique: stress-controlled methods and strain-controlled methods. Although the former operates by incremental increase of external stress exerted on the lattice, the latter gradually increases the deformation along a prespecified deformation path. The following subsections explain these methods respectively in depth and provide examples of their applications on a $2 \times 2 \times 1$ supercell of 11 Å tobermorite.

**Stress-Controlled Variable-Cell Enthalpy Minimization**

The original idea of variable-cell MD was proposed by Parrinello and Rahman (1981) and extended by Souza and Martins (1997) to study the possibility of crystal phase transitions under pressure. An arbitrary lattice is defined via a set of three lattice vectors, $a_i$, that can be put into matrix form $\mathbf{h} = [a_1, a_2, a_3]$. The nonsymmetric $\mathbf{h}$ matrix subsequently is transformed to a symmetric matrix $\mathbf{g} = \mathbf{h}^T \mathbf{h}$. In fractional coordinates, the position of the $i$th atom in its $k$th direction can be uniquely defined via its coordinates, $s_{ik}$, and matrix $\mathbf{g}$. Variable-cell energy minimization is closely related to the minimization of the generalized enthalpy, $\tilde{H}$, as follows (Souza and Martins 1997)

$$\tilde{H}(s_{ik}, g_{mn}) = U(s_{ik}, g_{mn}) + p_{ext} \sqrt{\det(g_{mn})} + \frac{1}{2} \tau_{mn} g_{mn}$$  \hspace{1cm} (1)

where $U$, $p_{ext}$, and $\tau_{mn}$ are, respectively, the lattice internal energy, the external pressure, and the $mn$th component of the deviatoric stress tensor, $\mathbf{\sigma}_{ext} = -p_{ext} \mathbf{I}_3 + \mathbf{\tau}_{ext}$, where $\mathbf{I}_3$ is the second-order unit tensor. Whereas the first term on the right-hand side indicates the internal strain energy, the second and third terms correspond to the linearized external work applied respectively by the volumetric and deviatoric external stresses to the system and hence are valid only in the limit of small deformations. It should be noted that the generalized enthalpy is minimum in a constant entropy–stress–number of particles thermodynamic ensemble, $(N, S, \mathbf{\sigma})$. Hence in this ensemble the generalized enthalpy should be minimum with respect to all lattice coordinates and parameters, $s_{ik}$ and $g_{mn}$, that yield

$$\frac{\partial \tilde{H}}{\partial s_{ik}} = \frac{\partial U}{\partial s_{ik}} = -F_{ik}^l = 0$$  \hspace{1cm} (2a)

$$\frac{\partial \tilde{H}}{\partial g_{mn}} = \frac{\partial U}{\partial g_{mn}} + \frac{1}{2} \sigma_{mn}^2 - \frac{1}{2} \sigma_{int}^2 + \frac{1}{2} \sigma_{ext}^2 = 0$$  \hspace{1cm} (2b)

where $F_{ik}^l = \text{net covariant force applied from the entire neighboring atoms on the } i\text{th atom in the } k\text{th direction}$, which can be thought of as a force component in the reciprocal lattice coordinates multiplied by $2\pi$ (Souza and Martins 1997). The covariant force is related to the lattice (real-space) force component as $F_{ik}^l = \gamma_{kl} F_{ik}$. The internal stress tensor, $\mathbf{\sigma}_{int}$, is defined according to the virial theorem

$$\mathbf{\sigma}_{int} = \frac{1}{\sqrt{\det g_{mn}}} \sum_k \sum_l (r_{ij}^l f_{jl}^i)$$  \hspace{1cm} (3)

where $r_{ij}^l$ and $f_{jl}^i$ are distance and force, respectively, between the $k$th and $l$th atoms in $i$th and $j$th directions.

Eqs. (2a) and (2b) are nonlinear functions of lattice coordinates and parameters, and hence should be solved iteratively via conventional numerical methods such as the updated Lagrangian method. With such an approach, $\mathbf{\sigma}_{ext}$ is applied in an incremental fashion, $\mathbf{\sigma}_{ext}^{i+1} = \mathbf{\sigma}_{ext}^i + \Delta \mathbf{\sigma}_{ext}$, and the reference configuration is updated to the last fully converged lattice structure, $\mathbf{h}^{i+1} = \sqrt{\mathbf{g}^{i+1}}$, where $\mathbf{g}^{i+1} = (\mathbf{h}^{i+1})^T \mathbf{h}^{i+1}$. Following the assumption of Cauchy and Born (Aghaei et al. 2009; Khoei et al. 2009, 2011b), in which lattice vectors are assumed to be small, the updated homogenous deformation gradient tensor, $\mathbf{F}^{i+1}$, describes the state of deformation in the $i$th deformed configuration stage compared to the undeformed body as (Aghaei et al. 2009; Khoei et al. 2009, 2011b; Qomi et al. 2014):

$$h_{mn}^{i+1} = F_{m}^{i+1} h_{np}^{0}$$  \hspace{1cm} (4)

where $\mathbf{h}^0$ is relaxed undeformed lattice vectors. The updated deformation gradient can be transformed to the more familiar updated Green–Lagrange strain tensor, $\mathbf{e}_{i+1}$, which is a rotation-independent measure of local relative deformation defined as

$$e_{mn}^{i+1} = \frac{1}{2} (F_{km}^{i+1} F_{kn}^{i+1} - \delta_{mn})$$  \hspace{1cm} (5)

where $\delta_{mn}$ is Kronecker delta. A set of $(e_{i+1}, \sigma_{ext}^{i+1})$ is sufficient to describe the stress-strain relation in a material with the aforementioned limitations. In terms of implementation, Gale (1997) and Gale and Rohlf (2003) implemented the case of isotropic external pressure along with the Broyden–Fletcher–Goldfarb–Shanno (BFGS) solver and rational functional optimization (RFO) in a general utility lattice program (GULP). Plimpton (1995) implemented enthalpy minimization for an arbitrary stress state with variants of conjugate gradient and line search algorithms in a large-scale atomic/molecular massively parallel simulator (LAMMPS).

To further describe the procedure for the stress-controlled variable-cell technique, this paper provides an example of uniaxial tensile loading of 11 Å tobermorite normal to the basal direction (Fig. 2). The external $\sigma_{ext}^{zz}$ is increased by 0.1-GPa increments and the generalized enthalpy is fully minimized at each stage. As presented in Fig. 2(a), following an initial linear behavior the $e_{zz} - \sigma_{ext}^{zz}$ relation increases and reaches a plateau at 2.5 GPa. At that point the crystal experiences unconstrained expansion due to the fracture propagation along the interlayer spacing (Bauschy et al. 2015). Unlike fracture mechanism studies, the interest here is not in the ultimate failure but rather in the onset of inelastic behavior, i.e., the yield point of the material. The easiest and most straightforward technique to locate the yield point is to perform an unloading analysis at various points along the stress-strain curve and to inspect whether the crystal springs back to its initial configuration. Three potential yield points were picked along the stress-strain curve, designated numerically in Fig. 2(a). The tensile stress was decreased incrementally to a stress-free state and the unloading stress-strain curves were plotted in Fig. 2(b). Upon unloading from Points 2 and 3, the sample experienced residual strain, which is indicative of an inelastic deformation allowing identification of Point 1 at 2.1 GPa as the yield point.

**Strain-Controlled Fixed-Cell Energy Minimization**

Unlike the stress-controlled variable-cell technique, the strain-controlled fixed-cell approach constrains the simulation box lattice vectors and only allows for the relaxation of the internal coordinates, $s_{ik}$. Such relaxation is achieved by minimizing internal energy through the process of eliminating external work parameters in Eq. (1) and only solving Eq. (2a). Setting Eq. (2a) to zero in all degrees of freedom is a nonlinear task that requires the steepest descent approaches, which at best is limited to the local minima. The practice of locating the global energy minimum is a tremendously challenging computational task and is beyond the scope of the present work. To solve such a nonlinear set of equations, an
updated Lagrangian approach is preferred in which the crystal lattice is incrementally deformed along a prescribed deformation path, $F_{\text{ext}}^{t+1} = F_{\text{ext}}^{t} + dF_{\text{ext}}$. The updated deformation gradient directly provides the updated Green–Lagrange strain tensor, $\epsilon_{\text{ext}}^{t+1}$, using Eq. (5). Furthermore, the relaxed coordinates at each relaxation step are used further to calculate the internal virial stresses, $\sigma_{\text{int}}^{t+1}$. A set of $(\epsilon_{\text{ext}}^{t+1}, \sigma_{\text{int}}^{t+1})$ is sufficient to describe the stress-strain relation in a material. Both GULP and LAMMPS have already implemented the fixed-cell optimization technique. Although the current version of GULP provides an analytical Hessian-based BFGS solver with RFO, it is limited to a small simulation cell that is composed of approximately a few thousand atoms. Furthermore, applying incremental deformation steps requires an additional script that runs GULP as an internal simulation engine. The current implementation of LAMMPS is scalable to many thousands of atoms and includes an internal fix to deform the simulation box. However, LAMMPS solvers are based on a conjugate gradient with numerical finite difference Hessians. This paper used the strain-controlled approach and utilized both software packages for fixed-cell simulations and verified that they yield almost identical results.

To further describe the procedure for the strain-controlled fixed-cell technique, this paper provides an example of uniaxial tensile deformation, $\mathbf{F} = \mathbf{I} + 0.2\epsilon_z \otimes \epsilon_z$, of 11 Å tobermorite along the normal to the basal direction, Fig. 3. The external deformation gradient $F_{\text{ext}}^{\epsilon_z}$ was increased by 0.001 increments and the energy was fully minimized at each stage. As shown in Fig. 3(a), the $\epsilon_{\text{ext}}^{\epsilon_z} - \sigma_{\text{int}}^{\epsilon_z}$ relation increased almost linearly until it reached the nonlinear regime at 0.032 strain. It should be noted that the strain-controlled fixed-cell method provides postpeak behavior that was absent in the variable-cell technique. To identify the precise location of the yield point, a numerical unloading procedure was performed at four designated locations along the loading path in Fig. 3(a). The unloading was performed by incrementally decreasing the deformation gradient applied to the cell vectors down to the initial undeformed configuration while monitoring the internal stress. As shown in Fig. 3(b), the unloading from Point 1 at the very end of the linear regime sprang back to the original configuration with no apparent residual stress. However, the unloading paths from two to four paths lead to residual stress at the zero strain, indicating that the material deformed plastically during the loading process. It is suggested that the failure threshold be assigned to the last point that exhibits reversible behavior on the stress-strain curve. Because the system is still elastic, this can be regarded as a conservative choice. However, a slight perturbation will incur irreversible deformation in the molecular structure of the crystal. In fact, the maximum error associated with such a selection is equal to the size of the strain increment. Reducing the size of the strain increment can decrease this error, but such a solution is limited by the computational cost. Therefore there is a trade-off between the accuracy and the computational cost. For these reasons, Point 1 was assigned as the yield point in the system for this particular deformation path.

![Fig. 2](image1.png)  
Fig. 2. Analysis of failure in a stress-controlled numerical experiment using incremental tensile loading, $\sigma_{zz}$, in 11 Å tobermorite: (a) stress-strain curve for tensile loading using enthalpy optimization technique; (b) stress-strain loading and unloading curves to determine failure point.

![Fig. 3](image2.png)  
Fig. 3. Analysis of failure in strain-controlled numerical experiment using incremental strain normal to the basal direction in 11 Å tobermorite: (a) stress-strain curve for incremental unidirectional stretching using energy minimization technique; (b) stress-strain loading and unloading curves to determine failure point.

**Hardness Calculation Methodology**

Due to the layered nature of tobermorite and clay minerals, these materials exhibit lower strength along their basal direction. This is...
directly attributed to the lack of interchain Si–O or Al–O covalent bonds that can effectively transfer stress between the layers. This suggests that the failure analysis should focus on $\epsilon_{zz}$ and the other two relevant shear strains, $\epsilon_{xz}$ and $\epsilon_{yz}$. The responses of tobermorite and clay minerals along these two shear paths are almost identical because they both exhibit shear localization at the interlayer spacing. Therefore the six-dimensional failure spaces reduce to a two-dimensional space. This considerably decreases the number of computations required to calculate failure and hardness via atomistic simulations. Subsequently, as shown in Fig. 4, three independent deformation paths are considered in $\epsilon_{zz} - \epsilon_{zz}$ space. Each deformation path is a linear combination of $\epsilon_{zz}$ and $\epsilon_{xz}$ in which a mutual application of shear deformation along with tensile or compressive deformation simulates the confinement effect at the atomic-scale. A successful simulation requires careful consideration of two technical points. First, as depicted schematically in Fig. 4, the $\epsilon_{zz} - \epsilon_{zz}$ space is divided into three regions: tension-dominated, shear-dominated, and pressure-dominated domains. This classification highlights the importance of the confining stress on the failure mechanism and hardnes magnitude. In fact, different experimental setups explore mechanical properties at different confining pressures. For instance, whereas atomic force microscopy (AFM) and nanoindentation measure mechanical properties with shear contributions under the tip (Bobko et al. 2011; Zhang et al. 2009), high-pressure XRD measures the properties at high confining pressure (Moon et al. 2013; Oh et al. 2012). Furthermore, the failure mechanism at the nanoscale is at a length scale below the scale of friction and wear, describing how solid bodies are rubbed against each other.

Both tobermorite and montmorillonite samples were subsequently deformed following the aforementioned deformation paths, Paths 1, 2, and 3 for montmorillonite and Paths 1, 2, and 4 for tobermorite, in a strain-control fashion. To eliminate the rate effect, all simulations were performed using the strain-controlled fixed-cell energy minimization technique. Similar to Fig. 3, the stress-strain response was plotted accordingly for each individual deformation path. As illustrated previously, the failure analysis identifies the conservative strain, $(\epsilon_{zz}^c, \epsilon_{xz}^c)_{\text{ext}}$ and stress, $(\sigma_{zz}^c, \sigma_{xz}^c)_{\text{int}}$, at which the material fails upon loading at a particular deformation path. Because the deformation is confined in the other axial directions and is subjected to the Poisson effect, a planar stress evolves in the material while undergoing constrained biaxial deformation. The planar stress is direction-independent, $\sigma_{zz}^c = \sigma_{yz} = \sigma_{pl}$, due to the isotropy within the intralayer of two crystals. Therefore the stress tensor at failure point, $\sigma_{\text{int}}$, can be viewed as

$$\sigma_{\text{int}} = \begin{bmatrix} \sigma_{pl}^c & 0 & 0 \\ 0 & \sigma_{pl}^c & \sigma_{yz}^c \\ 0 & \sigma_{yz}^c & \sigma_{zz}^c \end{bmatrix} \quad (6)$$

The failure stress tensor can be stated in terms of principle failure stress components $(\sigma^c_1 = \sigma^c_2 = \sigma^c_{III})$ by finding the eigenvalues of the failure stress tensor. Therefore the principle stresses can be written as

$$\sigma^c_1 = \sigma_{pl}^c \quad (7a)$$

$$\sigma^c_{II} = \frac{1}{2} \left[ -\sqrt{(\sigma_{pl}^c - \sigma_{zz}^c)^2 + 4\sigma_{pl}^c \sigma_{zz}^c} \right] \quad (7b)$$

$$\sigma^c_{III} = \frac{1}{2} \left[ \sqrt{(\sigma_{pl}^c - \sigma_{zz}^c)^2 + 4\sigma_{pl}^c \sigma_{zz}^c} \right] \quad (7c)$$

Using the Mohr representation, the principle components of the stress can be identified as the intersection of Mohr circles with the $\sigma$-axis. The maximum and minimum of principle stresses for the $k$th deformation path are $\sum_{j} \sigma^c_j$ and $\sum_{k} \sigma_k$, respectively. These $k$th principle stresses and enclosing Mohr circles define the limit stress state at which the atomic structures of tobermorite and montmorillonite undergo an irreversible deformation. As shown in Fig. 5, a set of Mohr failure circles on independent deformation paths can define the failure mechanism and the plastic limit of the material. Fig. 5 shows that both crystals followed a Mohr–Coulomb-like failure criterion at the atomic scale. Application of Mohr–Coulomb in mechanics of granular materials is prevalent due to proper description of intergranular friction. However, the increase in strength of layered minerals at compressive domain is attributed to the confinement effect. There is no dissipative mechanism, such as friction or wear, active at the interlayer spacing. The increase in the shear strength at higher pressures is caused mainly by the elastic confinement effect making the propagation of the shear band harder for materials at higher pressures.

In particular, in the case of cementitious and clay minerals, the failure envelope is linear in the stress domains relevant to the nanoindentation experiment. Therefore layered crystals at the nanoscale can be described as a cohesive-frictional material characterized by the cohesion ($C$) and friction angle ($\phi$). Cohesion is the strength of the crystal at zero confinement pressure. Following Ganneau et al. (2006), the hardness ($H$) of a cohesive-frictional material can be stated as

$$\frac{H}{C} = \frac{\delta(\phi, \theta)}{\tan \phi} = \frac{1}{\tan \phi} \sum_{k=1}^{N} |a_k(\theta) \tan \phi|^k \quad (8)$$

where $\theta$ = indenter apex angle; $a_k$ = fitting parameters for a given indenter geometry; and $N = \text{maximum order of the polynomial}$. If the friction angle is on the order of $5^\circ$ or less, $\tan(\phi)$ becomes negligible, and as a result the hardness can be approximated by $5.8C$.  

**Fig. 4.** Schematic illustration of the deformation paths in two-dimensional strain space relevant to the failure of the layered materials: the strain space can be dissected to tension-dominated, shear-dominated, and pressure-dominated zones, which emphasizes the role of the confining pressure on manipulating the location of the failure point; in the nanoindentation experiment, the failure mode is rather shear-dominated and hence this work considers deformation Paths 1–4; double-sided arrows indicate that the location of boundaries between these domains are dependent on the type and strength of interactions between interlayer and intralayer atoms; Paths 1, 2, and 3 are used for montmorillonite and Paths 1, 2, and 4 are used for tobermorite.
Application in Layered Tobermorite and Clay Minerals

This paper employed the aforementioned method to calculate the cohesion, friction angle, and hardness for 11 Å tobermorite and Na-montmorillonite Clay (Fig. 5). Both CSHFF and CLAYFF were used to model tobermorite and Na-montmorillonite samples. Both systems were deformed in strain-controlled fixed-cell energy minimization fashion in three deformation paths. Yield stresses were calculated and corresponding Mohr circles were plotted in the Mohr \(\sigma-\tau\) plane. Subsequently, a linear failure envelope was constructed tangent to three Mohr circles. For the case of 11 Å tobermorite, the cohesion was approximately 1 GPa and the friction angle was approximately 10°. Using Eq. (8), this yielded a hardness value of 8.9 GPa, which is very close to the experimental values of 8.1 ± 1 GPa reported by Abdolhosseini Qomi et al. (2014). The experimental results were calculated using coupled statistical nanoindentation and wavelength dispersive spectroscopy to couple chemistry and mechanical properties (Krakowiak et al. 2015).

For the case of montmorillonite clay, the calculated friction angle was approximately 3.2°. Using AFM, Bucholz et al. (2012) reported an experimental friction angle of 1.7° for pyrophyllite and Liu et al. (1998) reported a friction angle between 0.1 and 7.4° for mica (depending on the lateral scan size and scan rate of AFM). The calculated friction angle for montmorillonite (3.2°) falls between the reported experiments on those clay minerals. It should be reiterated that the small friction angle reported here and in AFM and is not related to the macroscopic friction angle, which mainly is due to the dissipation of energy by rotational motion of clay platelets at the mesoscale and microscale. The atomistic cohesion is 0.27 GPa for montmorillonite, which yields a hardness of 1.56 GPa. There is no direct measurement of hardness for montmorillonite crystals. The closest experimental value on a relatively similar system was reported for rectorite, with a hardness value of 0.73 ± 0.17 GPa. Bobko et al. (2011) reported a range of values from 0.58 to 1.1 GPa for clay-rich shale materials using inverse analysis of nanoindentation data.

Conclusions

This paper presented a new approach to calculate the nanoscale friction angle, cohesion and hardness for layered crystal. The method is based on the application of biaxial deformation or stress along different paths that linearly combine normal and shear components along the weakest crystallographic direction of the material. The stress-strain relation can be determined either via stress-controlled variable-cell enthalpy optimization or strain-controlled fixed-cell energy minimization. Subsequently, either unloading technique or the close investigation of acoustic velocities determines the failure stress. Determination of the stress state at different deformation paths provides different failure Mohr circles in the \(\sigma-\tau\) stress space, which can be used to identify the failure envelope. This linear failure envelope characterizes the friction angle and cohesion at the nanoscale that can be used in conjunction with Ganneau’s model to determine hardness of the layered material at a given indenter apex angle. This technique was applied to both tobermorite and montmorillonite to show that the predictions were close to the experimental data published in the literature. This method has the potential to be further developed for estimation of strength properties of multiscale porous materials across length scales with minimal modifications.

References


