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# CHEMISTRY OF INTERFACES BETWEEN INORGANIC MINERALS AND POROUS CARBONS: IMPLICATIONS FOR THE MECHANICAL PROPERTIES OF GAS SHALE

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## Introduction

The role organic-rich shale plays in the production of fossil fuel has tremendously increased in the past decade thanks to recent technological developments that allow an efficient exploitation of this unconventional source rock. Gas shale is composed mostly of minerals but also a carbonaceous substance, called kerogen which is primarily responsible for hydrocarbon storage. As kerogen is encapsulated in a non-permeable mineral matrix, gas and oil recovery operates by means of hydraulic fracturing. One of the many challenges this technique is facing is controlling fracture propagation underground. Understanding how different gas shale components influence the fracture properties of the overall rock is thus of paramount importance for efficient well design. Yet, probing mechanical properties of different gas shale constituents is extremely difficult experimentally due to the very small size of these heterogeneities.

In this study, we make use of an alternative approach, based on molecular simulations, to elucidate fracture properties. We apply our methodology to illite, which is the most prominent clay constituent in gas shale, as well as to a composite of illite and a disordered porous carbon modelling kerogen.

## Methodology

The goal of this work is to simulate fracture propagation in our molecular systems and obtain fracture properties. Our approach is based on the energetic description of fracture mechanics. [1] Unlike the description based on the evaluation of stress intensity factors at the crack tip, this approach provides an unequivocal description of the system as all quantities involved can be calculated in molecular simulations. [2]

In the simulations, a mechanical load is applied to the system (in our case by prescribing the deformation) in every step, and the mechanical answer is measured (the average stress at the boundaries). Upon fracture propagation, the mechanical energy is released by creation of crack surface. The fracture energy, that characterizes the toughness of the system, is obtained by integrating the stress-strain curve of the process. Here we consider two different loading modes: in mode I, a tensile strain is applied normal to the crack orientation, whereas in mode II, a shear strain acts parallel to the crack. In both the pure illite and the composite systems, our focus is mainly on deformations on the 001

surface of illite, as clays are known to cleave primarily along this plane. To perform the molecular simulations, we chose to apply the ReaxFF reactive force field that is able to describe both intermolecular interactions and bond breaking and formation in an effective empirical way. [3,4]

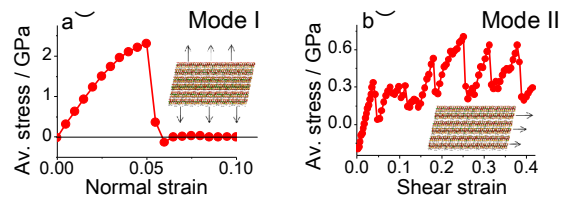
To simulate the organic phase in the composite system, we use the CS1000 molecular structure, which is a representative model of porous disordered carbon. [5] Bond formation was stimulated at the organic/inorganic interface by applying an annealing procedure starting from 600K and cooling the system down to 5 K with steps of 50 K, simulating every step for 2 ps.

## Results and Discussion

### 1) Fracture of pure illite

Illite was found to exhibit markedly different fracture behaviors depending on the loading mode. In mode I, the material displays a very brittle behavior and a very small fracture energy: it is two orders of magnitude smaller than what was found for silica in our previous study.[2] The fracture energy was found to be twice the surface energy (known as the Griffith criterion), which confirms the very brittle character of illite in this fracture mode.

In mode II, however, no fracture propagation is observed, that is, there is no fracture surface creation, and the mechanical energy is dissipated by the friction induced by clay layers sliding on each other. Technically, this means that the fracture energy (as well as the toughness) is infinity. These two different mechanisms were confirmed by evaluating the crack surface area upon loading by Conolly's method. **Figure 1** displays typical stress-strain curves obtained in different loading modes of illite.



**Figure 1.** Stress-strain curves obtained from molecular fracture simulations of illite in (a) mode I and (b) mode II. In mode I, illite exhibits a highly brittle behavior. In mode II, no fracture propagation is observed. Each stress drop in the stress-strain curve of mode II corresponds to one sliding event in the system.

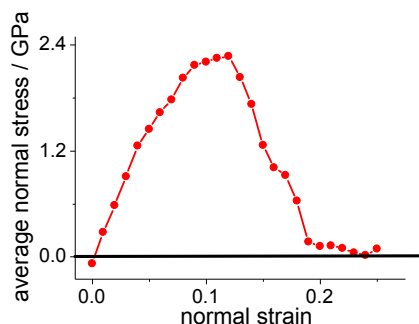
The distinctly different behaviors can be understood by considering the lack of chemical bonds between clay layers where the cohesion is only provided by weak electrostatic interactions. This means that none of the releasing mechanisms (fracture propagation or friction) involve chemical bond breaking. This is confirmed by the fact that no initial crack creation is needed in any loading modes. Based on these facts, it is possible to use a non-reactive potential to simulate the different mechanical loadings in the system. To this end, we repeated some simulations with the ClayFF potential. [6] The calculations showed the same behaviors and qualitatively similar fracture energy values in mode I loading.

## 2) Fracture of illite/kerogen composites

In the first step, bond formation at the kerogen/illite interface was studied as resulted from the annealing procedure. To this end, radial distribution functions (RDFs) were calculated to check the existence of possible bonds. A combined analysis of RDFs revealed bond formation between illite and CS1000 via Si-O-C and Al-O-C bonds, but ruled out the possibility of direct chemical bonds between surface Al or Si atoms of illite and C atoms of CS1000. As a consequence of bond formations between the two phases, the surface of illite gets reconstructed and the surface siloxane bonds get reorganized forming low-membered rings.

In the second part, fracture analysis of the prepared kerogen/illite interface was carried out. In one set of the calculations the system was loaded without any initiated crack, whereas in another set of calculations a crack was created in the interface.

The results showed that fracture propagation can occur both at the interface and the clay phase depending on the relative strength of the interface compared to illite: if the interface is weaker than illite, the fracture will occur in the interface. **Figure 2** shows a typical stress-strain curve in the crack free system. The comparison of this figure to **Figure 1** reveals that even though the fracture propagation occurs in illite, the material shows significant ductility as well as a much larger surface energy (5 times larger than in the pure case). This observation provides molecular structure based explanation for the apparent toughening of organic rich shale compared to the organic-free case.



**Figure 2.** Stress-strain curve of kerogen/illite composite systems without an initiated crack in the system. Even though the fracture propagates in the clay phase, the system displays a much more ductile behavior than pure illite as well as a much larger fracture energy. This is related to the fact that mechanical energy is dissipated in the ductile organic phase upon loading the system. This mechanism can provide explanation for the observed toughening of organic-rich shales.

## Conclusions

In this work the fracture properties of pure illite and illite/kerogen composites were studied by means of molecular simulations. For pure illite, markedly different fracture behaviors were observed depending on the loading mode. In mode I, illite shows a very brittle behavior with very low toughness, whereas in mode II, no fracture propagation occurs, but the mechanical energy is dissipated by friction induced by clay layers sliding on each other. Technically this means a super plastic behavior with infinite fracture toughness.

In illite/kerogen composites, first the possibility of chemical bond formation induced by an annealing procedure was explored. It was found that chemical bond formation can occur between illite and the CS1000 structure used to model kerogen. A detailed fracture study of this composite system showed that fracture propagation can occur either in the kerogen phase or in the interface depending on their relative strength. In cases where the interface is stronger, hence fracture occurs in illite, a very ductile behavior was observed in mode I, as opposed to the very brittle behavior of pure illite. The observed fracture energy is 5 times higher compared to the pure case.

Both the friction based dissipative mechanism of the mode II loading of pure illite and the toughening of illite/kerogen composite systems due to the ductile organic phase can provide explanations for the apparent increased fracability of argillaceous and organic-rich shales.

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