

Ideal Strength of Methane Hydrate using Density Functional Theory

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ABSTRACT

The ideal strength of methane hydrates or clathrates is investigated and quantified from first principles calculations. Methane hydrates are crystalline compounds in which hydrogen-bonded water molecules entrap methane at high pressures and/or low temperatures [1]. Although they exist abundantly almost all over the world, their mechanical properties are still under investigation. This is essential for detection and for risk assessment during production. Specifically, the ideal strength, defined as the stress at the elastic instability of a perfect crystal, sets an upper limit for strength, can be observed near crack tips, and is important in plastic deformation in terms of width of dislocations and stresses near dislocation sites [2,3].

Using Density Functional Theory (DFT), the linear and nonlinear elastic properties of methane hydrates are studied. Tests are performed to compute the ideal strength in characteristic lattice directions and under different modes of uniaxial, triaxial, and shear deformations. Stresses are applied incrementally, and the progression of the tests is followed with electron density plots that reflect the different effects on bonding between compression and tension. Moreover, the hydrogen bond strength and cage-to-guest size ratio are calculated to explain instability upon tension and compression, respectively. This analysis reflects the stabilization mechanism of methane hydrates through attractive forces between the water molecules and repulsive forces between the methane and water molecules. Hydrogen bond strength is quantified using the bond length, and the cage-to-guest size ratio was computed through electron density integration. It was found that methane hydrate can be up to 10 times stronger in compression compared to tension which reflects brittle behavior, and this agrees with experimental observation of increased brittleness as hydrate saturation increases in sediments [4]. Additionally, different slip systems were found almost equivalent which is attributed to the radial arrangement of bonds.

While these results are important due to their novelty and ab initio basis, their physical implications are far-reaching. Identification of the ideal strength and the shear planes along which deformation can most easily happen is significant for risk and crack analysis. Also, understanding the stabilization mechanism of methane hydrates through a balance of opposite forces can be extended to other guest molecules, like carbon dioxide, for comparison. Finally, these results complement our previous work on the elastic constants of gas hydrates [5].

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