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# Grain-size induced strengthening and weakening of dislocation-free polycrystalline gas hydrates

Jiayang Wu<sup>a</sup>, Bjørn Skallerud<sup>b</sup>, Jianying He<sup>b</sup> and Zhiliang Zhang<sup>b\*</sup>

<sup>a</sup>Department of Physics, Research Institute for Biomimetics and Soft Matter, Xiamen University, Xiamen 361005, China

<sup>b</sup>Faculty of Engineering Science and Technology, Norwegian University of Science and Technology, 7491 Trondheim, Norway

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## Abstract

Sediment-hosted gas hydrates have profound impacts on global energy sources and climate change. Their mechanical properties play a crucial role in gas recovery and understanding their evolution in nature, however, the deformation mechanisms of gas hydrates have not yet been elucidated owing to the difficulties in experimental measurements. Direct molecular dynamics simulations of the material instability of polycrystalline methane hydrates under mechanical loading have been carried out. The results show an unexpected ductile ultimate strength as a result of crossover from strengthening to weakening in polycrystals. The Hall-Petch type strengthening behavior arises from grain-junction mediated failure mechanism while the inverse Hall-Petch type weakening originates from grain boundary mediated deformation mechanism.

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## 1. Background

Natural gas hydrates, also called clathrate hydrates, typically form from freezing concentrated mixtures of gas molecules and water into an ice-like crystalline substance in which guest gas molecules are physically trapped inside solid lattice cavities of water molecules to deter hydrogen-bonded strain and breakage<sup>1-3</sup>. They occur abundantly underneath petro-production lines and in hostile environments such as seafloor sediments, arctic or permafrost regions<sup>4</sup>.

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\* Corresponding author. Tel.: +47 73592530.

E-mail address: [zhiliang.zhang@ntnu.no](mailto:zhiliang.zhang@ntnu.no)

<sup>5</sup>. There are three different crystallographic structures in gas hydrates and the cubic structure I (sI) is the most common one.

Despite the surging interests and worldwide research activities in gas hydrates, their mechanical properties and deformation mechanisms remain poorly understood. This lack of understanding attributes mainly to the remarkable difficulties in experimentally characterizing the deformation of hydrates and the limited availability and reproducibility of synthetic hydrates<sup>6</sup>. Recently, large-scale molecular dynamics simulations of polycrystalline sI methane hydrates under both tensile and compression loading have been performed<sup>7</sup>. The results show dislocation-free brittle failure in monocrystalline hydrates and an unexpected ductile ultimate/super strength as a result of crossover from grain-size strengthening to weakening in polycrystals. Unlike metallic materials, no dislocations were observed either inside the grains or at the grain boundary, and the existing dislocation based models can not be used to explain the observed phenomenon. In this paper, we for the first time present mechanics-based models to explain the dislocation-free Hall-Petch type and inverse Hall-Petch type behavior of polycrystalline gas hydrates.

## 2. Molecular dynamics simulation results

Two distinct types of microstructures were simulated by the molecular dynamics simulator LAMMPS. The nanograins were created by using a Voronoi construction<sup>8</sup> with the grain centers placed on a 3D periodic b.c.c. lattice. The as-constructed samples with size of Voronoi grain ranging from 5.61 to 28.1 nm contain approximately a total water and methane molecules varying from 93000 to 11700000. Both the host water and guest methane molecules were described with the monatomic model which represents each molecule as a single particle. Tetrahedrally short-ranged interactional functions of monatomic model of water (mW) with the form of the Stillinger–Weber potential mimic hydrogen-bonded water structures<sup>9</sup>. The water – methane and methane – methane interactions were modeled through the two-body term of the Stillinger–Weber potential<sup>10</sup>. Such a coarse-grained molecular model of water and methane is over twofold more efficient than atomistic models for reproducing a range of properties of liquid and solid phases of water and methane. Prior to the molecular dynamics simulations of uniaxial loading, polycrystalline methane hydrates were initially quasi-statically relaxed to a local minimum configuration via the conjugate gradient method. Subsequently, the relaxation was performed with simulation time 200 ps under cold and pressurized hydrate-forming conditions with NpT ensemble based on Nosé-Hoover barostat and thermostat, allowing unfavourable configuration in the grain boundaries to relax. The total consumption of the simulation time in this study is around 165 central processing unit years in the Norwegian Notur metacenter system for computational sciences. The atomic stress per atom was calculated according to the virial definition of stress using the forces on the atoms collected during the molecular dynamics process. Details about the simulation and calibration of the coarse-grained model against full atom simulations can be found in<sup>7</sup>.

The highlights of the molecular dynamics simulation can be summarized as follows. Firstly, new structures which are dissimilar to the base hydrate structure sI,  $0\text{CH}_4@5^{12}6^3$ ,  $2\text{CH}_4@5^{12}6^3$ ,  $1\text{CH}_4@5^{12}6^4$ ,  $2\text{CH}_4@5^{12}6^4$  were discovered at the grain boundaries. These new structures are necessary in order to structurally join the crystals together to form polycrystals. Obviously, due to either under- or over-occupancy these new grain boundary structures are greatly misshapen and thermodynamically less stable. Secondly, brittle failure was observed in monocrystalline gas hydrates while polycrystalline hydrates show unexpected ductile behavior. Unlike metallic materials, no dislocations either inside the crystals or at the grain boundaries were found. The ductile behavior of the gas hydrates mainly comes from the contribution of grain boundaries. Finally, it was shown that both the maximum tensile stress in tension and average flow stress in compression are strongly dependent on the grain size. Above a critical grain size about 15nm, the strength increases with the decrease of grain size. When the grain size is below the critical one, further refining the grains will reduce the strength. The crossover behavior for the cases with random grains are presented in Fig. 1, where the grain size in the abscissa represents the average value. The peak value of the flow stress at the crossover (called super or ultimate strength of the material) is around 180 MPa.

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