

Distinct creep regimes of methane hydrates predicted by a monatomic water model

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The power-law creep properties of methane hydrates were measured experimentally two decades ago, but their microscopic explanation is still missing. Here we show, using molecular dynamics simulations spanning almost 2 orders of magnitude of stresses and 3 orders of magnitude of strain rates, that such power-law creep emerges in molecular dynamics simulations of polycrystalline methane hydrates using a monatomic water model, suggesting that only simplified molecular interactions and the concept of a hydrate polycrystal are needed for such power-law creep behavior to emerge. Damage patterns post-creep suggest that hydrates are strong because damage only occurs on crystal surfaces.

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Introduction. Gas hydrates are icelike crystalline compounds with a host lattice of water molecules enclathrating guest molecules [1]. Such hydrates form at high-pressure and low-temperature conditions, typically under the seabed or the arctic tundra at sufficient depth [2], but only in a relatively narrow section of the subsea due to the geothermal temperature gradient. Methane is the most common guest gas in nature; therefore, hydrates are considered as an energy resource [3,4], but the role of hydrates in marine sediments has also highlighted the risk of slope failures due to seawater warming [5] and how hydrates may facilitate methane gas migration through sediments by crustal fingering [6].

Since methane hydrates are a hydrogen-bonded lattice of water molecules with similar density and bond angles to ice [7], one would expect the mechanical properties of hydrates to be similar to those of ice. The elastic response is very close to that of ice, although it is isotropic [8]. The tensile strength also seems to be similar in experiments [9] and the fracture toughness in molecular dynamics simulations is similar to that of ice [10].

Ice creeps relatively easily, and polycrystalline ice follows Glen's law for polycrystalline ice [11,12], $\dot{\epsilon} = B\sigma^n$, with $n = 3$. Basal slip in monocrystalline ice scales with stress with a stress exponent of $n = 2$, but with a larger prefactor so that the basal slip is always faster than the slip of polycrystalline ice [13].

Polycrystalline methane hydrates turn out to be 20–30 times more creep resistant than polycrystalline ice near the water freezing point, and the difference increases with a de-

creasing temperature [14]. The same experiment shows that when described with a typical steady-state rheology equation of state [15], hydrates creep rates, $\dot{\epsilon}$, display two distinct stress scaling regimes, where $\dot{\epsilon} \sim \sigma^n$, with $n \approx 2$ for small stresses and $n \approx 4$ for large stresses. It was suggested that the relatively large unit cell of the methane hydrate molecular structure makes glide and climb motions of dislocations difficult, decreasing intracrystalline plastic deformation [14], indicating that the polycrystal scale is relevant for understanding the creep resistance of hydrates. Polycrystalline methane hydrates make up an important, sometimes mechanically crucial part of hydrate-bearing sediments [5]. Thus, an improved understanding of the creep properties of polycrystalline hydrates will also aid the understanding of the creep properties of hydrate-bearing sediments [16].

Experiments on polycrystalline hydrate shells [17] suggest that the tensile strength of hydrates has been previously overestimated, and also that there can be quantitative agreement between molecular dynamics simulations, experiments, and the field scale with appropriate grain size scaling. Linking the laboratory scale to the field scale is challenging because hydrates coarsen very slowly [18], resulting in grain sizes that are orders of magnitude smaller in the laboratory than in nature [19]. Natural massive hydrates are very rare, and they show more brittle behavior than laboratory-synthesized hydrates [20]. Previous molecular dynamics studies have revealed such phenomena as the Hall-Petch effect and the reverse Hall-Petch effect [21,22] for nanocrystalline hydrates under compression, tension [23], and shear [24]. Molecular dynamics simulations have also suggested a nonmonotonous dependence of ice content on the strength of polycrystalline hydrate-ice systems [25]. The creep rates of polycrystalline hydrates under high compression have been studied with molecular dynamics simulations [26] showing that steady-state creep of methane hydrates can be studied with molecular dynamics simulations. However, no previous molecular scale modeling studies have considered stress ranges that allow for

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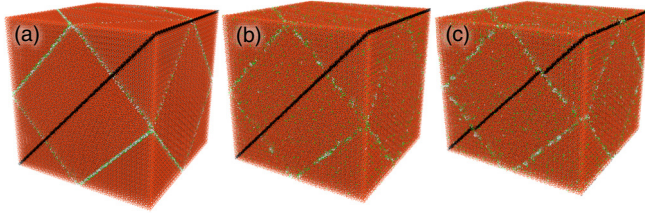


FIG. 1. Overview of the model system in this study. (a) Initial configuration of a methane hydrate polycrystal with 4 crystal grains, (b) relaxed configuration after 10 ns, and (c) system after being compressed for 10 ns. The particles are colored by their being identified as hydrate (red), interfacial hydrate (green) or not hydrate (white) by the CHILL+ algorithm [27]. Initially, the grain boundaries are visible, but upon equilibration they vanish to a large degree due to accommodations in the cage structure at the boundary. However, when the hydrate block is subjected to a stress, the grain boundaries reveal themselves again, indicating that the grain boundaries are involved in the deformation process. The black diagonal line is a tracer line with particle identities fixed at the first time step of the simulation. The discontinuity on the grain boundary after creeping indicates grain boundary sliding.

direct comparison with creep experiments, thus preventing direct comparison of power-law creep exponent from simulations with experiments.

We believe that what is missing is a modeling study that both reproduces the salient features of the original experiment, namely, the creep exponents, and simultaneously offers a window into the detailed mechanism of the creep resistance. Therefore, this study aims to reproduce the distinct creep exponents observed experimentally and to explore the underlying mechanisms of creep resistance in methane hydrates.

We target Durham *et al.*'s experiments [14] explicitly by molecular dynamics simulations of methane hydrate polycrystals. We choose molecular dynamics simulations since they contain the scale involved in mechanical failure. For water, this scale is the breaking of bonds between water molecules, and thus a monatomic water model can contain this behavior. We subject our systems to differential stresses from 10 to 300 MPa and find a creep behavior that is qualitatively consistent with experiments. We show that the creep is very well tracked by grain boundary sliding and that there is no intracrystalline damage or dislocation activity. Supporting simulations of amorphous hydrate suggest that the stress in polycrystals is carried by shear traction on grain boundaries in the low-stress regime, whereas some structural interlocking is necessary in the high-stress regime, where grain boundaries cannot carry the load.

Simulations. We modeled methane hydrate polycrystals by placing four randomly oriented, fully occupied, structure I methane hydrate single crystals into the Voronoi cells of a periodic fcc structure (see Fig. 1), with grain sizes ranging from 10 to 80 nm, using ATOMSK [28]. An example system is shown in Fig. 1(a). First, all systems were equilibrated for 10 ns at 270 K and 50 MPa, with an anisotropic Nosé-Hoover thermo-baro couple with damping times of $T_{\text{damp}} = 1$ ps and $P_{\text{damp}} = 10$ ps. We observed that the potential energy leveled out on a log-log plot, indicating relaxed grain boundaries. We then applied differential stress along the z direction of the

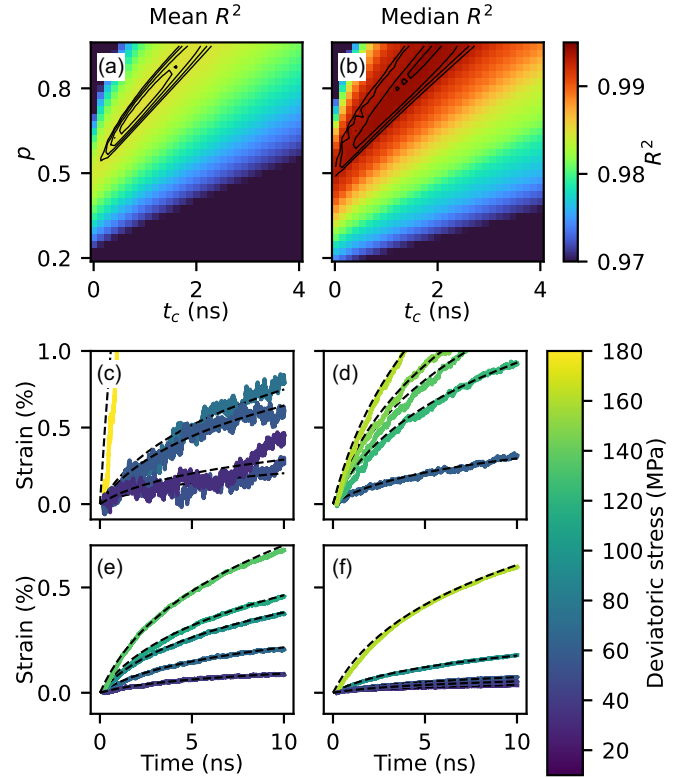


FIG. 2. Fitting the creep curves to the creep law [Eq. (1)]. Mean (a) and median (b) R^2 scores of fits to the creep law for varying values of t_c and p . Panels (c)–(f) show raw creep data from simulations (colored lines) and fits to the creep model (dashed lines) with $t_c = 1.5$ ns and $p = 0.85$. The panels (c)–(f) correspond to grain sizes of 10, 20, 40, and 80 nm, respectively.

simulation cell to induce creep. In this stage, the temperature was controlled by a Langevin thermostat with a damping time of 10 ps and the pressure was controlled by a Nosé-Hoover barostat with $P_{\text{damp}} = 10$ ps. The cell parameters of the barostat were updated every 10 ps to accommodate lateral expansion during creep. The confining pressure was 50 MPa, corresponding to the experimental setup of Durham *et al.* [14]. Forces were modeled using the mW monatomic force field [29,30]. Figures 1(b) and 1(c) show the polycrystal in the relaxed state and the state after compression and creep. Tracer lines aid the visual identification of grain boundary sliding from simulation snapshots.

The methane hydrate polycrystals responded by contracting in the direction of the applied stress. Example strain curves are shown in Figs. 2(c)–2(f). These strain curves show a decreasing creep rate with time, indicating a primary creep phase. To compare creep rates between simulations, we fit the curves to a standard power-law primary creep equation [31]. The phenomenology of this creep law has been observed in various materials, including Andrade's $\epsilon \sim t^{1/3}$ creep of metals [32] and the creep of ice [33]. This creep law has the general form $\dot{\epsilon} \sim (c + t)^{-p}$, which can be expressed as

$$\epsilon(t; A, p, t_c) = \frac{A}{1-p} (1 + t/t_c)^{1-p}, \quad (1)$$

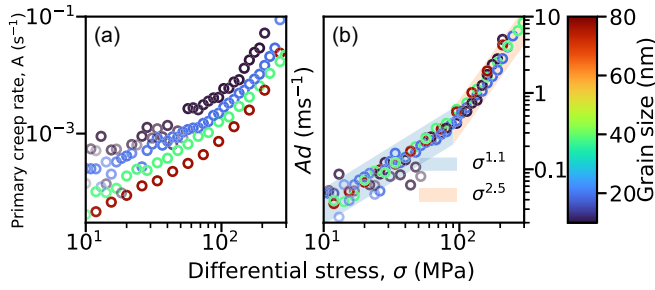


FIG. 3. Creep rates of polycrystalline methane hydrates from molecular dynamics simulations. Panel (a) shows the creep rate computed by fitting to Eq. (1) with $p = 0.85$ and $t_c = 1.5$ ns. Panel (b) shows a data collapse with a size dependence of $\dot{\epsilon} \propto \frac{1}{d}$.

where A is a scaling factor relating to the magnitude of creep, p determines how much the creep rate decreases with time, and t_c is a delay timescale. We fit creep curves to this model by obtaining the creep magnitude factor A for each creep curve. To obtain comparable creep magnitudes across grain sizes and stresses, we need to fix p and t_c . Although these parameters are expected to vary a bit with the simulation conditions (e.g., compression and grain size) [31], fixing is necessary for comparison across simulations. We perform a grid search over the parameter ranges $t_c \in (0.1 \text{ ns}, 4 \text{ ns})$ and $p \in (0.1, 0.95)$ and score the parameter combinations by their R^2 values when fitting the creep curves to Eq. (1). After inspecting the R^2 data for each grain size separately, we chose not to use the data for the smallest grain size ($d \approx 10$ nm) when estimating t_c and p due to high fluctuations caused by the small system size for these data. Figure 2 shows the average and median R^2 values for all simulations with $d \geq 20$ nm, suggesting optimal values along a diagonal from $t_c = 0$ and $p \approx 0.5$ to $t_c \approx 2$ ns and $p \approx 0.9$. The highest R^2 values are found around $t_c = 1.5$ ns and $p = 0.85$, which we use for the subsequent analysis. The main trends of the stress-strain rate curves are relatively insensitive to the choice of (t_c, p) . Strain curves and fits to these strain curves are shown in Fig. 2, showing excellent agreement between the model and the simulations for all but the smallest grain size.

We use the strain rate magnitude value A from Eq. (1) as our measure of the creep rate for comparison across simulation conditions. Figure 3(a) shows the value of this creep magnitude value for different grain sizes and applied compressive stresses. Figure 3(b) shows the data of Fig. 3(a), but multiplied by the grain size. All strain rate magnitudes then collapse onto a common scaling function, showing that the creep rate is inversely proportional to the grain size. The stress-strain relationship in Figs. 3(a) and 3(b) seems to fall onto two main power-law regimes: $\dot{\epsilon} \sim \sigma^{1.1}$ for stresses below a critical value σ_c of approximately 100 MPa, and $\dot{\epsilon} \sim \sigma^{2.5}$ for stresses above 100 MPa.

Due to the limited simulation time of molecular dynamics simulations, we can only observe *primary creep*. However, by making assumptions about the creep process, we can estimate the creep exponents at the onset of secondary creep. In the limit where secondary creep lasts for a constant amount of strain, we infer secondary creep rates inspired by Budd and Jacka [33]: If there exists a constant strain ϵ_s where secondary

creep starts, the time it takes to reach this strain is

$$t(\epsilon_s) = t_c \left(\left[\frac{\epsilon_s(1-p)}{A} \right]^{\frac{1}{1-p}} - 1 \right). \quad (2)$$

The creep rate at this time can be expressed as

$$\dot{\epsilon}(t(\epsilon_s)) = \frac{A}{t_c} \left[\frac{A}{\epsilon_s(1-p)} \right]^{\frac{p}{1-p}}, \quad (3)$$

$$\dot{\epsilon}(t(\epsilon_s)) = A^{\frac{1}{1-p}} f(t_c, p), \quad (4)$$

with $f(t_c, p) = t_c [\epsilon_s(1-p)]^{\frac{p}{1-p}}$. This provides approximate limits for the secondary creep power-law exponents. By secondary creep, we mean the minimum creep as presented for example in Ref. [34]. In the lower limit, primary creep occurs for a finite amount of time, resulting in exponents of ≈ 1.1 and ≈ 2.5 . In the upper limit, primary creep occurs for a finite amount of strain, resulting in high exponents of ≈ 7 and ≈ 15 , which are very sensitive to the value of p and diverge in the limit of logarithmic creep. The relative magnitudes of the low-stress and high-stress exponents are similar to experiment; they differ by approximately a factor of 2 [14]. If, however, $p = 0.5$ and $t_c \rightarrow 0$, which is on the left end of the band of high R^2 values in Fig. 2(a), the stress exponents given that primary creep occurs for a finite amount of strain become 2.2 and 5, which are close to 2.2 and 4.5 as reported by Durham *et al.* [14]. Although the absolute values of the stress exponents at the onset of secondary creep are not well constrained, the contrast between the low-stress regime and the high-stress regime is well constrained, and their relative values are compatible with experiments.

To quantify grain boundary sliding, we use tracer particles on both sides of a selected set of grain boundaries. These tracer particles initially make up a straight line normal to the grain boundary [Fig. 1(b)], but grain boundary sliding splits these lines into two parts [Fig. 1(c)]. We fit a straight line to the positions of tracer particles on each side of the grain boundary and estimate the grain boundary sliding as the offset between these lines. The fit is done using the RANSAC algorithm [35] to exclude ambiguous particles near the boundary.

The major grain boundaries lie on a 45° slope in the polycrystal. If we define Δf_{RANSAC} to be the observed difference in the linear fits to tracer atoms on each side of grain boundaries, then the relationship between the overall contraction, Δl_z , of the box in the normal direction and the measured grain boundary sliding can be estimated in the two following simplified ways: (i) Pure shear sliding of grains, without any net transport of particles away from the grain boundary, results in $\Delta f_{\text{RANSAC}}/l_z = \epsilon$. (ii) If the sliding occurs only by the displacement of grain boundary material so that one grain sinks straight into another grain, the contribution is $\Delta f_{\text{RANSAC}}/l_z = \epsilon/2$.

Figure 4 shows the computed contribution of the grain boundary sliding to the overall strain as a function of the overall strain in all of the polycrystal simulations. It shows that grain boundary sliding tracks the overall strain well for all simulations up to a differential strain of 200–300 MPa, which is the upper limit of the indicated $\dot{\epsilon} \sim \sigma^{2.5}$ region in Fig. 3. Visual inspection of simulations at stresses higher than those shown in Fig. 3 clearly exhibit crushing of individual

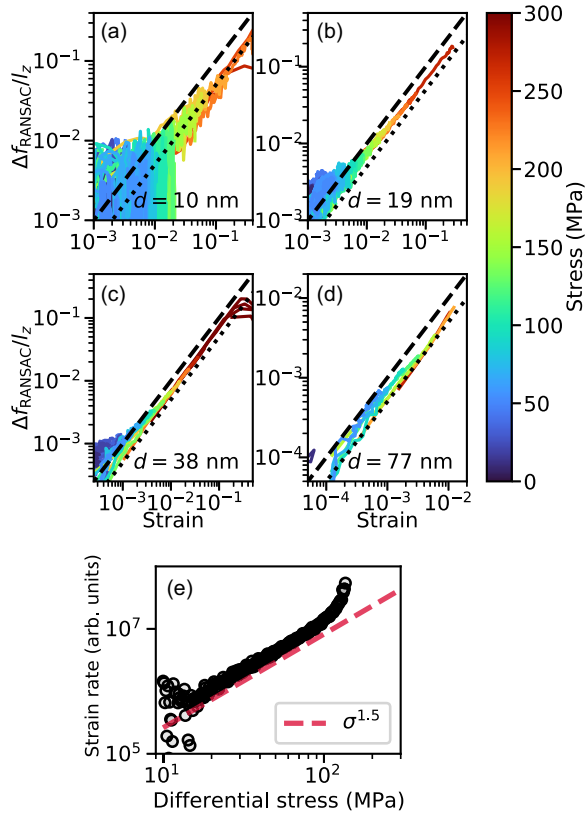


FIG. 4. Estimated grain boundary sliding contribution to strain as a function of the overall strain [panels (a)–(d)]. The black dashed line in panels (a)–(d) indicates $\Delta f_{\text{RANSAC}}/l_z = \varepsilon$ and the dotted line indicates $\Delta f_{\text{RANSAC}}/l_z = \varepsilon/2$. (e) Creep of amorphous hydrate as a function of applied shear stress. The loading condition is the same as the loading that the 45° grain boundaries experience during creep simulations of polycrystals.

grains, which is consistent with grain boundary sliding no longer tracking the creep deformation. The creep seems to be a combination of the contraction of grain boundaries and the displacement of grains by grain boundary sliding, since the observed grain boundary displacement Δf_{RANSAC} is between ε and $\varepsilon/2$.

Since the creep of the hydrate polycrystals seems to occur through grain boundary sliding, we prepared a series of molecular dynamics simulations to investigate the shear creep behavior of amorphous methane hydrates, which is the structure of the grain boundary zone. We obtained relaxed microstructures of amorphous hydrates from a previous molecular dynamics study [36] and ran simulations under a combination of compressive stress in the vertical (z) direction and shear stress in the xz direction to mimic the stress condition of the amorphous zones in the polycrystal. The stress state was set to that on a 45° slope grain boundary in the polycrystal, corresponding to the slope of the main faces of the fcc grains. The value plotted on the first axis of Fig. 4 is $\frac{1}{\sqrt{2}}(\sigma_{zz} - P_c + \sigma_{xz})$, where P_c is the confining pressure. This is directly comparable to the differential stress in the polycrystal simulations. The simulations were run for 10 ns at 270 K with a Langevin thermostat and a Nosé-Hoover thermostat, both

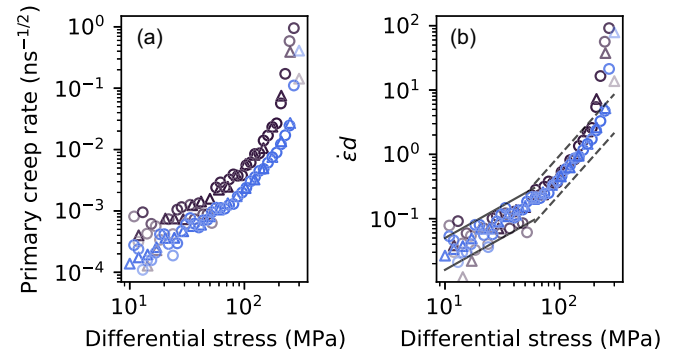


FIG. 5. Creep rates of polycrystalline methane hydrates from molecular dynamics simulations with 4 single crystal grains ($\circ$) and 32 grains ($\triangle$) for simulations with grain sizes of 10 nm (dark blue) and 19 nm (light blue). Panel (a) shows the creep rate computed by fitting to Eq. (1) in the main text. Panel (b) shows a data collapse with a size dependence of $\dot{\varepsilon} \propto \frac{1}{d}$.

with damping times of 1 ps and using the same interaction potential as for the polycrystal simulations.

The creep rates of amorphous hydrates, shown in Fig. 4(e), abruptly transitions from creep to immediate failure at a shear stress of 100 MPa. This is the same differential stress as that where the polycrystal system transitions from the low-power creep to the high-power creep. Thus, it seems that the grain boundaries hold the stress in the low-stress regime (<100 MPa) and that the transition to the high-power creep occurs when the grain boundaries cannot carry the traction. However, since the polycrystals do not run off like the amorphous system at 100 MPa, a different mechanism has to be responsible for holding the stress in the higher-stress regime. We suggest that this is due to geometrical locking between crystal grains, so that the system effectively behaves like a series of asperities in contact under high stress. This is in contrast to, for example, metals, where nonlinear creep-strain rate relationships are due to dislocations traveling through the crystals. We suggest this because we do not observe any material damage to the interior of grains in the high-stress (>100 MPa) regime. This can be inferred from the strain attribution in Fig. 4, but we have also verified this visually by looking at simulation trajectories. At extreme stresses, grains are eventually crushed, which can be seen in a few high-stress samples in Figs. 4(a) and 4(c), where the strain at some points increases without a corresponding increase in Δf_{RANSAC} . However, these samples are subjected to a stress higher than that where we indicate power-law creep in Fig. 2.

Effect of the number of crystals in the fcc-structured polycrystal. To verify that the size effects we observe in our molecular dynamics simulations are due to the size of the crystal grains, not due to the change of the size of the simulated system as the grain size increases, we ran a set of simulations with 32 fcc crystal grains in them. Figure 5 shows a comparison of creep rates between systems with 4 and 32 crystal grains. The computed creep rates in the simulations at the same *grain size* but different *number of grains* overlap, showing that the size dependence is indeed a grain size effect and not a system size effect.

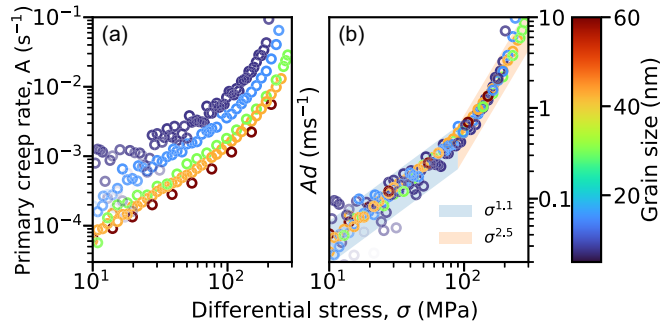


FIG. 6. Creep rates and data collapse of simulations of polycrystals generated from ten uniformly randomly placed Voronoi centers. The grain size d is the average grain size. The shaded blue and orange ranges in Fig. 6 represent the same creep rate values for $\dot{\epsilon} \propto \sigma^{1.1}$ and $\dot{\epsilon} \propto \sigma^{2.5}$ as shown in Fig. 3.

Distinct creep regimes are also observed with random shapes of grains. To verify that the observed distinct creep regimes do not rely on the details of the shape of the crystal grains in the polycrystal, we ran a series of simulations on polycrystals constructed from ten randomly placed Voronoi centers rather than four fcc-structured Voronoi centers. Figure 6 shows that the distinct creep regimes remain and that the magnitude of the creep rate is the same (we have not moved the shaded blue and orange areas relative to Fig. 3). In this case of randomly placed Voronoi centers, there is a distribution of grain sizes, with the mean grain size being reported on the x axis of Fig. 6. We report the equivalent grain size of a grain from the fcc packing, meaning that for the 10-grain system, the relationship between the system length and the grain size is $d = (\frac{4 \times V}{10})^{1/3}$. The number 4 in the nominator here comes from there being 4 grains in the minimal fcc system, while the grain size in the fcc system is equal to the length of the box, that is, $d = V^{1/3}$.

For reference, we have also included Fig. 7 which shows examples of creep curves and R^2 values of fitting to the creep law [Eq. (1)] for the random Voronoi center polycrystal system.

Discussion. We have identified two distinct stress-dependent creep regimes of polycrystalline methane hydrates using molecular dynamics simulations. In both regimes, the creep is tracked by grain boundary sliding, but based on simulations of amorphous hydrates, we suggest that the grain boundaries carry all the traction only in the low-stress regime, whereas grain corner contacts carry the stress and determine the creep rate at higher stresses. The grain-size dependence on the primary creep coefficient is $\dot{\epsilon}_{\text{primary}} \propto d^{-1}$ and indicates that primary creep depends on the ratio of the volume of the grain boundary to the total volume of the system, which is reasonable if the thickness of the unordered grain boundary zone is independent of the grain size and the creep is mostly controlled by the properties of this layer.

From Fig. 2(a), we find the primary creep rate for 80-nm grains at 30-MPa differential stress to be $A = 10^{-4} \text{ s}^{-1-p}$. Assuming that primary creep goes on for a few percent [14], say 5%, we obtain $\dot{\epsilon}(\epsilon = 0.05) = 1.6 \times 10^{-6} \text{ s}^{-1}$, which is in quantitative agreement with experiments (Fig. 8 in Ref. [14]). This estimate is sensitive to the specific value of ϵ_s , so this comparison is fragile and only indicates that the strain rates of

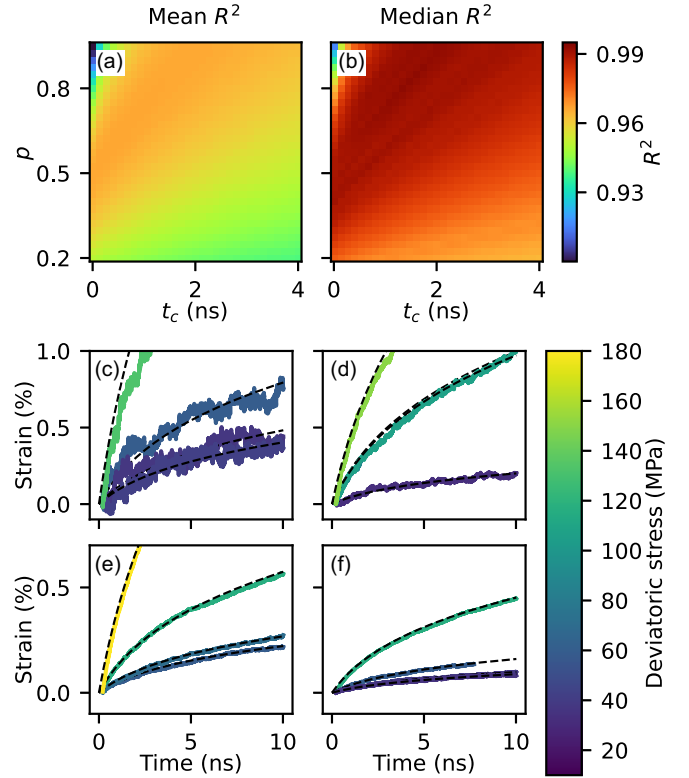


FIG. 7. Fitting the creep curves to the creep law [Eq. (1)]. Mean (a) and median (b) R^2 score of fits to the creep law for varying values of t_c and p . Panels (c)–(f) show raw creep data from simulations (colored lines) and fits to the creep model with (dashed lines) $t_c = 1.5 \text{ ns}$ and $p = 0.85$. The panels (c)–(f) correspond to grain sizes of 10, 20, 40, and 80 nm, respectively.

our model *can* take on values within the numerical range of experiments. The stress of the transition between the power-law regimes occurs at around 100 MPa, rather than 30 MPa as observed in experiments at this temperature. A quantitative discrepancy is expected when using a monatomic water model. The lack of explicit hydrogen atoms results in an elevated mobility of water molecules which shows up, for example, in the diffusion of water into a dense supercooled state at low temperatures [29].

All simulations in this study were run at 270 K. Temperature is an important parameter controlling mechanical properties of hydrates, both in the laboratory [14] and in simulations [10,24]. However, the simulations for this study were computationally expensive, and we therefore had to prioritize varying the stress with high resolution and running all simulations at a single temperature that was compatible with the experiment we targeted [14]. The grains in our simulations are smaller than those in natural samples and thus the results need to be interpreted with caution. A possible avenue for future research is to develop an up-scaled, for example phase-field, model for the creep of polycrystalline hydrates on a larger scale, which has been done previously for polycrystalline ice [37]. Since the mW model is a coarse-grained model, it is generally less accurate than all-atom models. It would therefore be useful to run simulations using an all-atom model like TIP4P/Ice [38] or even machine-learning potentials like DeepMD [39] or Allegro [40]. However, this would require

substantial computational resources, far beyond what was available for the present study.

A result in this study is that the crystal grains stay intact during creep, with no dislocation activity inside the crystal grains. This is in contrast to what is known for pure ice [11], where basal glide is an integral part of the deformation of polycrystals. The absence of such an intragrain mechanism in hydrates is consistent with our observation of a lower-stress exponent.

Conclusion. The stress-strain rate relationship of methane hydrates that was shown experimentally by Durham *et al.* [14] has lacked a mechanistic explanation. In this article, we have shown that such behavior can be obtained in molecular dynamics simulations of methane hydrate polycrystals using a coarse-grained water model. The simulations showed primary creep rate exponents of 1.1 and 2.5 for stresses below

and above roughly 100 MPa, respectively, and the creep is tracked by grain boundary sliding. We suggest that the grain boundaries carry the load in the low-stress ($\dot{\epsilon} \sim \sigma^{1.1}$) regime, whereas some other mechanism, likely geometrical interlocking, is needed to carry the load at higher stresses ($\dot{\epsilon} \sim \sigma^{2.5}$). Only the surfaces of hydrate grains are damaged, thus there is no intricate mechanism involving dislocations in the interior of the grains. This therefore presents further evidence that the creep resistance of hydrates compared with ice is due to the absence of intragrain dislocation activity [14], so that the material can only creep due to sliding of grain boundaries and tearing of crystal corners.

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