**Magnetic-Field Effects on Methane-Hydrate Kinetics and PotentialGeophysical Implications: Insights from Non-Equilibrium Molecular Dynamics**

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We have conducted non-equilibrium molecular-dynamics (NEMD) simulation to show that externally-applied magnetic fields, including their reversals in direction, have important effects on gas-release dynamics from methane hydrates. In particular, we apply fluctuation-dissipation analysis in the guise of Onsager’s hypothesis to study hydrate kinetics at lower applied-field intensities, including temporary hydrate destabilisation in the wake of field-polarity switch; we scale down to the lowest practicable field intensities, of the order of 1 T. We conjecture, that these NEMD-based findings, particularly those involving polarity switch, may have ramifications for superchron-related Earth’s magnetic-field polarity swaps affecting methane release into the geosphere, although a good deal of further work would be needed to provide a more definitive causal link.

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**Introduction**

Clathrate hydrates are non-stoichiometric crystalline inclusion compounds in which a water host lattice encages small guest atoms or molecules in cavities (Makogen, 1997). Methane hydrates are the most widespread clathrate in Nature in the permafrost and relatively shallow continental-shelf ocean regions, and constitute a significant energy resource (Kvenvolden & Rogers, 2005; Boswell & Collett, 2011; Max & Johnson, 2016). In any event, global methane ‘exhalations’ from hydrates into the geosphere (Kvenvolden & Rogers, 2005) have been linked to the (much-questioned) “Clathrate-Gun” hypothesis, or other previously described alternatives (Max & Johnson, 2016; Ruppel & Kessler, 2017), in terms of acute heating effects from methane release on Earth’s climate over only thousands of years. While most authorities would agree that methane would cause warming upon release, some recent evidence suggests that mass methane releases (*e.g.*, from hydrates) would induce global *cooling*, due to an effect of enhanced CO2 uptake (Pohlm et al., 2017). Whatever the consequences of methane release from hydrate on warming or cooling, there is also evidence that the release of methane from hydrate deposits is relatively insensitive to short-term changes in climate (Hong et al., 2017). In contrast, modelling studies coupled with physical measurements of contemporary hydrate deposits suggest that the measurable growth and depletion of hydrate deposits occurs over geological time scales (>1 million years) in response to such environmental variation (Haacke et al., 2008). We hypothesise here that: *Global variation of hydrate release from marine deposits is linked to environmental changes that are either very infrequent or that occur over very long geological timescales.*

Naturally, a key question may be posed as to what nature of hydrate-stability-perturbing agents may plausibly come to the fore over geological timescales, potentially in some form of cycle, to induce methane exhalations? In terms of possibly cyclical, geological-scale agents, one intriguing, and completely unstudied, possible candidate lies in the Earth’s magnetic field, and its long periods of relative stability (known as superchrons) as well as its periodic polarity-reversal events (Jacobs, 1994). Is it possible that extraneous magnetic fields, when reversed, may lead to destabilisation of (methane) clathrates? If so, over what field-intensity range is this relevant? In the present work, we investigate magnetic-field effects on hydrate kinetics by non-equilibrium molecular dynamics (NEMD), and how may one bridge (sub-) microsecond timescales accessible by MD with geological time and scale down field strengths.

**Methods**

NEMD simulations were performed in the absence and presence of external magnetic fields of a planar methane-hydrate interfaces with liquid water supersaturated with methane (*x*m ~6%) at 260 K. The level of liquid-phase supersaturation, an order of magnitude higher than the Henry’s Law Constant (English & Carroll, 2001; English et al., 2014), is needed to observe clear zero-field growth within reasonably accessible MD-simulation timescales of ~100 ns. The TIP4P water model was used for water-water interactions (Jorgensen et al., 1983) and the OPLS-AA potential for methane-methane interactions (Jorgensen et al., 1996), using the Sun-Duan *ab-initio*-fit water-methane interaction parameters, as validated by Mastny and de Pablo for TIP4P, rigid OPLS-AA methane and the Sun-Duan interaction parameters by a prediction of the melting point of (sI) methane hydrate at 400 bar to be within 287 and 302 K, vis-à-vis the experimental value of 297 K;14 this makes it a strong model for methane-hydrate thermodynamic properties. For ice, the TIP4P melting point is 230 K (Fernández et al., 2006). The cut-off radius for Lennard-Jones interaction parameters was 10 Å. The smooth particle mesh Ewald method (Allen & Tildesley, 2017) was used to handle long-range electrostatics, with a time step of 2 fs. For extended system dynamics in the NVT ensemble, light coupling to a Nosé-Hoover thermostat was used, with a thermostat relaxation time of 1 ps (Allen & Tildesley, 2017). Although the use of system-wide thermostats in non-equilibrium crystal-liquid systems (at temperatures below the zero-field freezing point) would be expected perhaps to lead to artificially rapid crystallisation, it was decided to employ this approach in the current study, as this had been used extensively in previous work on hydrate dissociation (English et al., 2015a), and it was desired that the results of this work be as comparable as possible to previous research. In addition, the optimal Nosé-Hoover thermostat inertia parameter is sensitive to natural temperature oscillations for translational and rotational modes of water, which would be expected to be affected to some extent by external magnetic fields. However, the precise details of this frequency-mode modulation is not known, so it was decided to use the 1 ps relaxation time for mild coupling. Future research to establish magnetic-field-induced mode affects in water, ice and hydrates would indeed be welcome.

Unfortunately, the phase diagram of water, or hydrates for that matter, has not been investigated systematically in magnetic fields - although the water phase diagram has been investigated in static electric fields, as discussed in the review of English and Waldron (2015b). It has been found that electric-field intensities required to shift water by a small fraction of 1 degree Kelvin were equivalent to external forces of the order of approaching 1% of the intermolecular forces. Now, given that the strong 100 kT fields used here lead to external (Lorentz) forces of the order of ~0.5%, one might imagine quite plausibly that this may lead to a phase-diagram shift by a fraction of 1 degree Kelvin, akin to the case for electric fields (English & Waldron, 2015b). Certainly, Makogon has found that external electric and magnetic field intensities need to lead to forces approaching some fraction of a percentage of intermolecular ones to have any real noticeable effect on thermodynamics (Makogon, 1997).

In the hydrate phase, the starting coordinates of the oxygen atoms in the unit cells of sI hydrate were taken from x-ray diffraction data (McMullan & Jeffrey, 1965). The initial unit cell lengths were 12.03 Å and the initial orientations of the water molecules were selected in a random manner so as to conform to the Bernal-Fowler rules (Bernal & Fowler, 1933) with vanishingly small total dipole moment. Methane molecules were placed in the cavities of each unit cell to allow for full occupation, *i.e.* 8 methane molecules. A 7x2x2 supercell was constructed by replication (with longest axis in the *z*-direction). The supercell was surrounded in the + and – *z-*directions by relaxed water ‘faces’ of equivalent cross-sectional area in the *x*-*y* plane, and of total length of approximately 200 Å along the *z*-axis to construct a planar-geometry crystallite. The mean system pressure was around 90 bar. The supercell is big enough to capture to a fair degree extended solid-liquid effects, given that simulations were performed under periodic boundary conditions.

Production-NEMD simulations were carried out for up to ~200 ns. In the case of externally-applied magnetic fields, these were along the laboratory +*y*-axis, using (English & MacElroy, 2004):

q*i* **v***i* **B**

 (1)

for charge-sites *i*, with a reversal in field direction to the -y-axis after 100 ns on some occasions (to mimic crudely a polarity switch). In terms of the magnetic-field intensity in eqn. 1, typical values of (non-Tokomak) ultra-strong (electro-) magnets are no more than ~100 T, with ~1-20 T magnets being typically the upper limit of those used in everyday industrial deployment. Given that the accessible timescales for NEMD are routinely no more than (fractions of) microseconds, it is necessary in the present work to employ larger field intensities (generally higher than 1 T) to have any possibility of observing tangible field effects over limited timescales, in terms of elucidation of underlying molecular mechanisms. In the NEMD formalism of eqn. 1 employed, the perturbation of Newton’s equation of motion handle perfectly and implicitly and current generated in a time-dependent magnetic field, in which the direction of external-field application is switched (*vide infra*).

The geometric hydrate-ice-liquid distinction criteria of Báez and Clancy (1994) were employed to distinguish between the hydrate, ice lattices, and liquid-phase. This involves the calculation of an angular order parameter to quantify the tetrahedral nature of bonding for nearest-neighbour water molecules, followed by the recognition of five-membered rings of water molecules present in hydrate structures but absent in liquid water and ice. This allows a preliminary classification of hydrate-, ice- and liquid-like molecules, which is refined further by grouping hydrate-like molecules into clusters and taking into account the identities of neighboring water molecules.

**Results**

NEMD was run at 260 K, for which sustained hydrate growth occurs under zero-field conditions (cf. Figs. 1 & 2), with relatively aggressive liquid-phase methane supersaturation and a thermal “driving force” of ~25-30 K below the (accurately-predicted) methane-hydrate melting point for the potential models employed; the need for large temperature and supersaturation levels drivers in MD of hydrate kinetics is discussed in detail in English and MacElroy (2015). Above ~1 kT field intensity, there is a transition from hydrate growth to dissociation (cf. Fig. 2); this mirrors hydrate electro-dissociation-threshold findings of ~0.1-0.15 V/Å for electromagnetic (English & MacElroy, 2004) and static-electric (Waldron & English, 2018) fields. Naturally, as discussed in English et al. (2005) individual-run hydrate-content statistics, although revealing much in terms of fluctuation-dissipation information (cf. Fig. 1 & *vide infra*), must be averaged over many independent runs before one can extract kinetic rates with any confidence; this is done in Fig. 2 for a variety of external-field intensities, yielding relatively constant rates. Given that the Earth’s magnetic-field intensity is of the order of 0.025-0.065 mT (Gubbins et al., 2006), it is obvious that this is insufficiently high to retard methane-hydrate growth: for comparison, a 1 T field exerts a force on atoms of ~5 × 10-6 % of those typically present intrinsically in hydrate-liquid systems by virtue of interactions with other molecules. Therefore, over geological timescales and ambient fields, very appreciable hydrate deposits are developed in both marine and permafrost milieu (especially in a long superchron)(Haake et al., 2008). However, upon polarity switch, the field-direction reversal after 100 ns of NEMD is dramatic for more intense fields (cf. Fig. 3): there is a sudden additional rate of hydrate decomposition (a kinetic effect), as the abrupt direction shift in the field’s on-atom Lorentz forces lead to consequent induced molecular torques perturbing lattice-/cage- stabilising hydrogen-bond arrangements (especially at the hydrate-liquid interface)(English et al., 2005); after some 10-20 ns, the system ‘memory’ of the polarity switch is lost (Avena et al., 2015) and in-field hydrate kinetics (in the now-reversed fields) reverts, by and large, to its pre-‘shock’ kinetic-rate behaviour. Naturally, this temporary acceleration in hydrate decomposition (and methane release) is amplified in extent in larger field strengths, owing to greater levels of switch-induced mechanical work on molecules. Generally, it is difficult to assess any real change in the level of sudden, post-switch hydrate break-up from the background hydrate-content ‘noise level’ (especially in individual simulations, *e.g.*, cf. Fig. 1) below around 100 T, owing to on-atom Lorentz forces being less than ~5 × 10-4 % of average intrinsic-system forces, with induced molecular torques typically being less able to ‘compete’ mechanically with lattice-stabilising hydrogen-bond strengths. In any event, we stress that this polarity switch leads to a kinetic effect on hydrates, rather than altering its phase state and crystal structure in any way.

However, lower external-field strengths (scaling down, somewhat more towards geological levels) may still conceivably lead to less immediately discernible effects on hydrate kinetics: on a ‘rare-event’ basis, statistical weakening of even a moderate additional level of cage-stabilising hydrogen bonds may lead to sizable changes in underlying hydrate kinetics, particularly for incomplete cavities at the hydrate-liquid interface (English et al., 2005), during geological field-polarity cycles, or, more especially, in superchrons’ wakes. Obviously, using direct, deterministic NEMD, it is not possible to gauge accurately tangible effects of lower field intensities (*e.g.*, ~1-100 T, or perhaps lower still) over periods of only (fractions of) microseconds amenable to modern-day molecular simulation, in terms of distinguishing with statistical precision from zero- (or ambient-Earth-) field kinetics. In an effort to address this pressing and difficult quandary, we turned to fluctuation-dissipation statistical mechanics, in the guise of Onsager’s hypothesis for hydrate kinetics (English et al., 2005; English & Clarke, 2013), which applies well to the reasonably slow underlying hydrate kinetics studied here over multiple-nanosecond intervals (English et al., 2005). Here, in denoting the instantaneous number of guest (methane) molecules as *N*(*t*), and the corresponding underlying average in any multiple-nanosecond interval as *N*’(*t*), the instantaneous number fluctuation may be defined as Δ*N*(*t*) = *N*(*t*) - *N*’(*t*). The normalised autocorrelation function (ACF) of Δ*N*(*t*) is

*C*(*t*) = 〈Δ*N*(*t*)Δ*N*(0)〉/〈Δ*N*(0)Δ*N*(0)〉 (2)

Onsager’s hypothesis states that fluctuations about the (*de-facto*) equilibrium state decay on average according to macroscopic laws, so that one may infer from crystal-size fluctuations at near-equilibrium conditions underlying kinetic rates at non-equilibrium conditions (*e.g.*, in lower-intensity external fields) (Tepper & Briels, 2001; English et al., 2005; English & Clarke, 2013;). Within this framework, it may be investigated if ACF decay towards ‘background-noise’ levels beyond a certain short-time transient may be treated as (approximately) negative-exponential, *i.e.*, *C*(*t*) = *A* exp(-*t* ⁄ τ); if so, it has been established that the underlying hydrate-crystallisation rate (whether growth or decomposition) is inversely related to the relaxation time, τ (Tepper & Briels, 2001). In Fig. 4, we depict typical individual-run behaviour of *C*(*t*) in 1-100 T fields, for which there is underlying growth not greatly slower than the zero-field case (and not readily statistically discernible therefrom). The general post-dissipation noise amplitude is seen from inspection be around 0.15, with approximately exponential decay evident in Fig. 4’s inset. Averaging exponential fits to background noise over independent runs down to background-noise level, as before (cf. Figs. 2 & 3), yields τ of 35.4 ± 2.4, 49.5 ± 2.9 and 58.2 ± 3.2 ps for 1, 10 and 100 T, respectively. This corroborates more clearly the general trend of increasing field strength in reducing the hydrate-growth rate (and increasing the fluctuation relaxation time) to ~90% level of certainty from pairwise *t*-tests. It was found that below 1 T, it was not possible to find any clear-cut difference vis-à-vis zero- (or lower-) field kinetics using Onsager analysis.

It is true that applied fields of the order of 1 T – 1 kT correspond to the upper range of magnetic-field intensities used typically in experiments and industrial and strong-electromagnet applications. Therefore, some of the stronger fields applied in the present work do correspond to experiments may be, in principle, amenable. However, in terms of the Earth’s typical (sub-)mT magnetic-field intensity *per se*, we have used the Onsager hypothesis to suggest, albeit not admittedly conclusively, that scaling down applied-field intensities in that direction may be of relevance to lower, more geologically relevant fields. We admit readily that this is problematic and less than clear-cut or fully convincing – indeed, perhaps ‘heroic’. However, we conjecture that over long time periods of aeons, *i.e.*, many millions of years, such field effects could have cumulative effects on hydrate build-up or release; the quotidian example of a compass needle aligning readily and instantly with the Earth’s magnetic field, or wildlife’s sensitivity to magnetic-field variations (*e.g.*, avian navigation)(Muehsam & Pilla, 2009), underscores the sensitivity of the geosphere to ambient magnetic fields. One may, perhaps justifiably, assume that thermal noise would negate any effect of sub-mT magnetic-field reversal on the formation of methane hydrates at the atomic scale. However, such an assumption is not clear-cut, especially when considering aggregate, planet-wide effects summing over molecular-level phenomena over geological times in between field reversals. Indeed, recent studies have shown that, certainly from a theoretical standpoint, such field strengths can be effective in moderating ion/ligand motion, independently of thermal-noise strength (Muehsam & Pilla, 2009).

**Discussion**

We have deployed NEMD and fluctuation-dissipation analysis to study hydrate kinetics in external magnetic fields, including temporary hydrate destabilisation in the wake of field-polarity switch, scaling down to the lowest practicable field intensities. In terms of geological time, the Onsager hypothesis provides an elegant framework, which can, in principle, be extrapolated to longer (>1M year) times and lower field intensities of the order of the terrestrial magnetic field. However, in practice, more advanced non-equilibrium statistical methods would be required to provide a more robust scaling network. Incidentally, although temperature change will have an important effect on hydrate *kinetics* (English et al., 2005; English & Clarke, 2013; English & MacElroy, 2015), there would have to be very large temperature swings to affect *in-situ* hydrate stability *per se*, as opposed to kinetics of formation or dissociation.

We are relatively agnostic about wider geological ramifications of this work, in that any extrapolations towards our original superchron-and-polarity-switch motivations are necessarily tenuous. Certainly, outside of superchrons, the Earth’s magnetic field has been shown to undergo reversals at a frequency of typically less than 1 million years – a veritable “Dance of the Aeons”; however, over the last 60 M years, the frequency of field reversal is approximately 1.55 per million years (Jacobs, 1994). Further, outside of superchrons, it is also evident that relatively low magnetic field fluctuations – rather than reversals – occur over the Earth’s surface at much higher, measurable frequencies in the recent past (Korte et al., 2005).

The critical finding from our analysis, is, therefore, that this field flux represents a considerable input of mechanical work that may destabilise hydrate deposits over post-reversal geological time periods. We propose that further research should be instigated therefore to assess the relative impact of this process.

Further, the absence of this periodic energy input during the 10M+ year period of a superchron would lead to the accumulation of hydrate deposits that, even after one field-reversal event, would be prone to partial destabilisation during the reversal-adjustment period. Very provocatively, it may be conjectured that field-polarity switches may trigger dramatic climate effects: methane release to the geosphere may lead to worldwide debate about warming or cooling (Pohlm et al., 2017), and, with that, melting ice caps or ice ages respectively, dramatic sea-level change and mass (marine, leading also to terrestrial) extinctions (Orth et al., 1986; Renne et al., 2013) - with a substantial wipe-out of marine organisms in tandem with massive sea-level drops due to Earth’s cooling and expansion of the ice caps (Brenchley et al., 2001). The end-Permian mass extinction, for example, can be linked to proximity to superchron-reversal cycles in the polarity of the Earth’s magnetic field within approximately a 10-million-year margin of error of the initiation of these multi-million-year-duration events, with insightful evidence of concomitant “field-swapping” timing (Courtillot & Olsen, 2007). Although deep-mantle plumes have been proposed as the mechanistic causative link between these mass-extinction and superchron-reversal phenomena(Courtillot & Olsen, 2007), it is equally possible to consider epic methane releases from dissociating hydrates as a cause. This provocative proposal should, however, be tempered by the widely-accepted view that most extinctions can be linked to strictly biotic effects (Bambach et al., 2004). Further, the Cretaceous-Paleogene boundary mass extinction (*circa* 75-60 mya), may be regarded as an outlier to our theory, certainly (the apex at 66 mya of this event being *c.* 20 my from the end of the Cretaceous long normal superchron), and here the link between this mass extinction and Chicxulub bolide impact is presently widely accepted (Schulte et al., 2013). Despite the uncertainty of mass extinction events’ precise duration, they appear from the geological record to range over millions of years, with, as yet, no proposal that they are linked to common causal events (Jacobs, 1994). We note with interest that the end of a normal superchron near the end of the Cretaceous (*c*. 118-81 million years ago) and two reverse superchrons – Carboniferrous-Permian or Kiaman (*c.* 312–262 mya) and Ordiovician or Moyero (*c.* 502–470 mya). The Kiaman is the longest reverse superchron in the Paleozoic era, and ended at approximately 262 mya. The apex of the late-Permian extinction is at approximately 250 mya, but was probably initiated at 254 mya – less than 10 my after the end of the Kiaman (Sahney & Benton, 2008). The end-Permian extinction event is also considered to be preceded by one or two smaller extinction events (the end-Guadalupian and Olsen’s extinction): the events occurring in a combined sequence of about 30 million years (Jacobs, 1994; Sahney & Benton, 2008). It is therefore starkly apparent that the end-Permian mass extinction, as the greatest extinction event in Earth’s history, was also linked chronologically to perhaps the end of the longest superchron since the start of the Paleozoic era.

Conclusions

Clearly, the above, no-doubt controversial polarity-switch/extinction-origin hypothesis, underpinned mechanistically by *en-masse* methane release from field-switch-induced hydrate dissociation after ample methane-hydrate build-up during superchrons, does represent a gross extrapolation of the present NEMD-simulation results and a bold, jarring foray into the unknown. Further work is of course needed to support this conjecture, which we codify here as the “Belfast hypothesis”. More specifically, a future investigative conceptual framework would include a parallel statistical study of prehistoric temperature, atmospheric methane/CO2 levels and sea-level data, using times-series auto- and cross- correlation analysis with magnetic-field intensity and direction data. Curating such reliable and comprehensive data with reasonable time accuracy and precision may, at best, allow for some degree of statistical correlation to be established between these phenomena and properties; however, since there is no firmly-established estimate of *in-situ* hydrate deposits even in today’s world (Makogon, 1997), this will clearly be nigh impossible to estimate for geological pre-history. Candidly, the outlook for either confirmation or falsifiability of this conjecture is thus limited and unpromising by lack of plausible and relevant data, and the quality thereof. In any event, even with such accurate and precisely-timed sea-level, magnetic-field, temperature and methane/CO2 data, this idealised conceptual framework may suffer ultimately in the sense of the very ability to either confirm or reject unambiguously the mechanistic role of hydrates being the actual source of sizable methane release or build-up during (actually, after) respective periods of field-polarity flux and stability. *Post hoc ergo propter hoc?* Indeed, this is a “chicken-and-egg” question of the Ages, meaning we may perhaps only aspire to glimpse fleetingly the beguiling “Dance of the Aeons”. Without further confirmation, the prospect for which we have conveyed our relative pessimism, we advocate that this bold and provocative hypothesis, although intriguing and perhaps even enjoyable as an intellectual exercise, cannot currently be tested experimentally.

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Figure Captions

1. Typical behaviour of number of evolution of hydrate-like methane molecules during individual runs, for in-field decomposition, at 260 K.
2. Averaged evolution of number of hydrate-like methane molecules, over 16 independent runs for in-field break-up and over 32 for zero-field growth, at 260 K. The field-strength threshold for inducing hydrate decomposition at 260 K is above ~1 kT.
3. Averaged evolution of number of hydrate-like methane molecules for in-field decomposition over 16 independent runs, featuring field-direction reversal at 100 ns. The loss of ‘memory’ after accelerated hydrate decomposition over ~20 ns is noteworthy, with re-establishment of essentially the same pre-switch decomposition rate.
4. Typical behaviour of individual-run normalised autocorrelation (ACF) of the fluctuations in number of hydrate-like methane at 260 K, sampled from 20 ns intervals with the underlying level of guests subtracted therein by quadratic regression (cf. Methods). The general amplitude of noise after dissipation is seen from inspection in this case to be around 0.15. The inset shows a log-linear plot with evidence of negative-exponential decay before background noise is reached. Faster decay is suggestive of a faster growth rate (which is the case for lower intensity fields).

Fig. 1



Fig. 2



Fig. 3



0.2



Fig. 4