



System-density fluctuations and electro-dissociation of methane clathrate hydrates in externally-applied static electric fields



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ABSTRACT

Non-equilibrium molecular-dynamics (NEMD) simulations of bulk methane clathrate hydrates have been conducted in a range of externally-applied static electric fields of up to $2.0 \text{ V}\cdot\text{nm}^{-1}$ in intensity, at 250 K and 60 atm. Studies into frequencies of system-mass-density fluctuations showed that these clathrates have two major modes: the dominant one is attributable to water molecules' librations and occurs at 720 cm^{-1} , regardless of applied fields. A more minor global density fluctuation arises at $10\text{--}12 \text{ cm}^{-1}$, due to the propagation of local-density fluctuations; again, this is independent of applied fields. A threshold intensity of $1.2 \text{ V}\cdot\text{nm}^{-1}$ was necessary to overcome the strong clathrate hydrogen-bonding network to produce any appreciable structural changes. Aside from variations in hydrate system density *per se*, a key interest in this study was (electro-) dissociation; a number of analysis methods were used to gauge this, including system-density and configurational-energy studies (and their respective autocorrelation functions and corresponding Fourier transforms), as well as radial distribution functions (RDFs) and density of states (DOS). In terms of electro-dissociation itself, a 'plateau' intensity of $1.6 \text{ V}\cdot\text{nm}^{-1}$ led to outright dissociation over the 0.5 ns timescales probed in the current study, where any field intensity above this level produced essentially identical dissociation outcomes: a marked loss of hydrate structure and increase in system configurational energy. RDF analysis of electro-dissociation indicates the collapse of the host lattice towards an amorphous structure and concomitant release of methane molecules from their now-collapsed cages to form a 'nano-bubble'. Upon post-dissociation field removal, it was found that this process was irreversible: the system transitions to an entirely new, less dense structure, featuring a phase-segregated methane nano-bubble within a liquid-like aqueous phase.

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1. Introduction

Methane clathrate hydrates are crystalline inclusion compounds, wherein a water host lattice encages methane molecules in cavities; the lattice is stabilised by the enclathration of the trapped methane solutes [1,2]. There are three known common clathrate-hydrate structures: (s)I, II and H. In type I hydrate, the unit cell is formed from two small 5^{12} pentagonal dodecahedral cavities and six slightly larger tetrakaidecahedral $5^{12}6^2$ cages, with 46 water molecules [1,2]. Methane hydrates are abundant *in situ*, occurring in Nature in the permafrost and in marine-sediment environments, typically adopting sI structure; this results in a methane content of up to 14.8% by mole ratio or 13.4% by mass, but more typically ~ 13 and 12%, respectively [1,2]. Recently, global

interest in methane clathrates has been dramatically increasing due to its potential to be a new source of natural gas, motivated in large part by energy and environmental considerations [3–5]. Indeed, the melting, or dissociation, of any clathrates can be dangerous as it leads to the sudden release of large volumes of methane which can cause sudden spikes in pressure [1,2]. Naturally, these allied gas-supply and environmental/safety concerns has led to a wide host of molecular-dynamics simulations studying methane-clathrate extraction methods, typically from marine-hydrate viewpoints [6]. More generally, molecular simulation has proved a rather invaluable tool in revealing much about equilibrium properties of clathrate hydrates, including structure [6–10], a 'resonant-scattering' picture of phonons and guest motion in cavities [11–13], hydrogen-bonding characteristics [14,15], and dynamical [7–22] and energetic properties [10,16]. Such molecular-simulations studies on dynamical properties have often focussed on vibrational properties of the host lattice and on the cavities, with 'overlapping' between these acoustic and optic modes, often interpreted in the context of resonant scattering

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[23]. Such an understanding of equilibrium dynamical properties and phonon scattering offered by molecular dynamics (MD) has indeed led to progress in recent years in enhancing our understanding of thermal-conduction processes in clathrate hydrates [24–28], together with “hopping”-mediated guest-diffusion processes of interest of energy- and gas- storage applications [29–33].

In any event, the application of external electric fields to gas hydrates is of much technological interest. For instance, in the inhibition of hydrate formation in natural-gas pipelines, aside from the use of either thermodynamic (e.g., methanol or ethylene glycol) or kinetic inhibitor additives injected into the gas stream, or localised application of higher temperature [1,2], external electric and electromagnetic (e/m) fields may serve to disrupt already-formed hydrates (e.g., as pipeline plugs or possibly *in situ* ‘natural’ hydrates) [1]. This is certainly more attractive than downstream ‘cleaning’ – extraction of inhibitors – at great operational and economic cost. Indeed, Makogon has commented on the effect of electric fields on hydrate crystals, devising an expression for the shift in thermodynamic equilibrium conditions caused by a static electric or magnetic field, concluding that the electric-field intensity would have to be of the order of 10^7 V/m (i.e. 10^{-2} V·nm⁻¹) to have any significant effect on equilibrium. Makogon also outlined a model for e/m field-induced melting of hydrate deposits from the porous rock of wells [1]. Rojey has reserved a U.S. patent on a system to inhibit/prevent the formation of clathrate hydrates in pipelines by means of exposure to a field of e/m waves set up by a network of emitters spaced along the length of a pipeline [34]. Rojey stated briefly that the e/m fields, of appropriate frequency and intensity, should prevent or minimise the organisation of water molecules to form a hydrogen-bonded crystalline lattice in a fluid containing an aqueous phase and hydrocarbons, disrupting the possibility of hydrate growth [34]. External electric fields would, and should, therefore, act as an alternative for gas-pipeline flow-assurance to more established practices of using additives [1]. Although e/m-field penetration depths in liquid water are of the order of ~1 cm, in gas, this extends for up to metres [34]; this, combined with repeated specular reflection along the pipe walls (in a ‘zig-zag’ fashion) serves to keep the amplitude relatively high over hundreds of metres, which is why Rojey’s patent mentions new field emitters every few hundred metres of pipeline. Unfortunately, however, there has been essentially no developmental work of these electric-field methods for gas-hydrate applications in the past 20 years reported in the open literature, with little industrial R&D taking place. This relative neglect of this intriguing flow-assurance proposition serves as a motivation to us to study further electric-field effects on hydrates.

English and MacElroy have carried out non-equilibrium MD to assess how external e/m fields disrupt the formation of spherical methane-hydrate nano-crystallites [35]. They found that the shifting dipolar alignment inside the crystallite weakens the structural hydrogen-bonding arrangements, thereby leading to break-up (or inhibition of formation in the first place). Naturally, this is dependent on field intensity and frequency, with intensities of the order of 0.1–0.5 V·nm⁻¹ required to observe tangible results of inhibition within feasible MD simulation times. The ‘optimal’ frequencies for disruption were in the 20–200 GHz range (overlapping with the general hydrogen bond lifetimes). This confirms, to some extent [35], arguments advanced by Rojey [34]. In particular, e/m fields greater than 1.5 V·nm⁻¹ in root-mean-square (r.m.s.) led to “electro-dissociation” of hydrate nano-crystals, with the most rapid results in the 50–100 GHz range. However more recent non-equilibrium MD studies on bulk methane clathrates demonstrated that external e/m fields do not lead to “electro-dissociation” even with intensities approaching 2 V·nm⁻¹ (r.m.s.), at least on time-scales of the order of a nanosecond [36].

Luis et al. applied subsequently static electric fields to bulk methane hydrate, as opposed to spherical nanocrystals, and found that fields greater than 1.5 V·nm⁻¹ in intensity led to break up at a pressure of 2 MPa and temperature of 248 K [37]. Luis et al. then simulations were performed further electro-dissociation of bulk methane hydrate at 260 K and 8 MPa, and also at 285 K and 40 MPa, in static fields of 1–5 V·nm⁻¹ [38]. In both cases, fields greater than 1.5 V·nm⁻¹ led to dissociation, with formation of an (empty) ice-like and separate methane phase. Removal of applied fields led to ‘melting’ of the ice-like structure with separate liquid water and methane-gas phase [38].

Given that we have recently observed and studied temporal system-density fluctuations in liquid water [39], and methane hydrates [17], in which we established underlying (collective) frequency modes underpinning system-density variations, we now re-focus in the present study on bulk methane hydrates. However, based on Rojey’s patent [34] and English and MacElroy’s [35] and Luis et al.’s [37,38] more fundamental NE-MD work in both e/m and static electric fields, we are motivated by how external electric fields may influence or perturb these systemic vibrational modes of crystalline, phonon-type global-density fluctuations. In the present work, we assess via NE-MD the important effect of electric-field strength [40], up to and including field-intensity ranges (i.e., probably in the region of, and exceeding, 1.5 V·nm⁻¹) expected to induce electro-dissociation [35,37,38]. Therefore, we study temporal, system-density fluctuations, system configurational energies and structural quantities such as radial distribution functions (RDFs), as well as the translational and librational Density of States (DOS), of bulk methane hydrate for static-field intensities up to 2.0 V·nm⁻¹ before, during and after the onset of structural distortion and outright electro-dissociation (at least on limited MD time-scales of the order of a nanosecond used routinely today). Moreover, another key interest lies in gauging post-exposure system behaviour in strongly-perturbed cases, to assess the reversibility, or otherwise, of changes.

2. Methodology

Equilibrium and non-equilibrium (in-field, *vide infra*) MD was performed in cubic simulation boxes, for the various temperatures and system sizes, under constant-pressure, constant-temperature (NPT) conditions at ambient (0.1 MPa) pressure, using a light coupling to Melchionna’s modified form of the Hoover barostat with isotropic cell fluctuations and barostat and thermostat relaxation times of 0.4 and 0.1 ps, respectively [41]. A time step of 2 fs was used, with MD conducted under periodic boundary conditions (PBC). The Particle-Mesh Ewald method was used to handle long-range electrostatic interactions [26,42]. Normalised autocorrelation functions (ACFs) of the time-derivatives of the system density, as well as of the system’s configurational energy, were computed:

$$c^\alpha(t) = \langle \dot{\alpha}_i(t) \dot{\alpha}_i(0) \rangle / \langle \dot{\alpha}_i(0) \dot{\alpha}_i(0) \rangle \quad (1)$$

where α denotes density (m/V , i.e., the total mass of water and methane molecules per unit of system volume), or system’s configurational energy. The use of time-derivatives, $\dot{\alpha}$, in the definition has the advantage of being acutely sensitive to temporal fluctuations (e.g., periodic oscillations or ‘vibrations’) in the system density and configurational energy, allowing this to be probed conveniently and straightforwardly via power spectra (Fourier transformation) of their ACFs.

Owing to previous SPC-type models being used profitably in local-density fluctuation analysis in liquid water, and SPC for system-density-fluctuation analysis in liquid water [39] and methane hydrate [17], we employ here the SPC water model [43] with a OPLS-UA united-atom methane potential [44] and

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