Self-preserving ice layers on CO₂ clathrate particles: Implications for Enceladus, Pluto, and similar ocean worlds

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ABSTRACT

Context. Gas hydrates can be stabilised outside their window of thermodynamic stability by the formation of an ice layer – a phenomenon termed self-preservation. This can lead to a positive buoyancy for clathrate particles containing CO₂ that would otherwise sink in the oceans of Enceladus, Pluto, and similar oceanic worlds.

Aims. Here we investigate the implications of Lifshitz forces and low occupancy surface regions on type I clathrate structures for their self-preservation through ice layer formation, presenting a plausible model based on multi-layer interactions through dispersion forces.

Methods. We used optical data and theoretical models for the dielectric response for water, ice, and gas hydrates with a different occupancy. Taking this together with the thermodynamic Lifshitz free energy, we modelled the energy minima essential for the formation of ice layers at the interface between gas hydrate and liquid water.

Results. We predict the growth of an ice layer between 0.01 and 0.2 µm thick on CO₂, CH₄, and CO₂ hydrate surfaces, depending on the presence of surface regions depleted in gas molecules. Effective hydrate particle density is estimated, delimiting a range of particle size and compositions that would be buoyant in different oceans. Over geological time, the deposition of floating hydrate particles could result in the accumulation of kilometre-thick gas hydrate layers above liquid water reservoirs and below the ice water crusts of their respective ocean worlds. On Enceladus, the destabilisation of near-surface hydrate deposits could lead to increased gas pressures that both drive plumes and entrain stabilised hydrate particles. Furthermore, on ocean worlds, such as Enceladus and particularly Pluto, the accumulation of thick CO₂ or mixed gas hydrate deposits could insulate its ocean against freezing. In preventing freezing of liquid water reservoirs in ocean worlds, the presence of CO₂-containing hydrate layers could enhance the habitability of ocean worlds in our Solar System and on the exoplanets and exomoons beyond.

Key words. planets and satellites: oceans – planets and satellites: interiors – planets and satellites: general

1. Introduction

Gas hydrates are important materials on Earth as well as on many planets and moons in our Solar System (Mousis et al. 2015; Bouquet et al. 2019). The ice-capped ocean-bearing moons Enceladus and Europa are two of the best examples beyond Earth where gas hydrates can be formed in their respective salty oceans (Schenk et al. 2018; Bouquet et al. 2019). Liquid water, gas hydrates, and complex molecules are potentially favourable for life within the Solar System and on exoplanets (Nimmo & Pappalardo 2016; Levi et al. 2017; Schenk et al. 2018; Khawaja et al. 2019; Harsono et al. 2020). Another example is Mars, where methane co-exists with subterranean water implying the existence of methane hydrates (Fonti & Marzo 2010).

Gas hydrates (also known as clathrates) are crystalline structures comprising water molecules arranged in cages that enclathrate guest gas molecules within them (Nguyen et al. 2020). As discussed by Takeya & Ripmeester (2008), these caged guest molecules are essential for hydrate formation, and the structure is thermodynamically stable only above a certain occupancy of gas molecules. These structures are furthermore stable only within a limited range of temperatures and pressures. As
one example, CH₄ gas hydrates turn out to be stable below the freezing temperature of water (e.g. at atmospheric pressure and temperatures between 240 and 273 K) (Takeya & Ripmeester 2008). The solution to this unexpectedly wide stability range seems to be that a thin, typically 1–2 μm (Falenty & Kuhs 2009), water ice layer forms on the surface (Takeya & Ripmeester 2008; Falenty & Kuhs 2009). Some gas hydrates (CH₄, CO₂, and N₂ type I hydrates, but not H₂S hydrates (Takeya & Ripmeester 2008)) are notably seen to be supported outside their normal window of thermodynamic stability by the formation of an ice layer — this phenomenon is termed ‘self-preservation’ or ‘anomalous preservation’ (Takeya & Ripmeester 2008; Falenty & Kuhs 2009), and has been observed in shallow permafrost (Shakhova et al. 2017, 2019; Chuvilin et al. 2018).

The formation of an ice layer on the hydrate is not only driven by kinetics as suggested by Falenty & Kuhs (2009), but it can also be driven by Lifshitz-force mediated equilibrium thermodynamics (Boström et al. 2019). Indeed, if the self-preserving ice layer effect on hydrates is spontaneous, as we find, this adds further support to the argument that gas hydrates may be stabilised in a way that was not previously understood.

The aim of this work is to present a model that offers a potential explanation for the occurrence of micron-sized water ice layers on CO₂ gas hydrate surfaces in cold water. Fundamentally, such layers of water ice on gas hydrates, if present, are important for the exploration and production of fossil fuels and they are vital for understanding the potential for methane contributions to greenhouse gases as the planet becomes warmer. We also point to the relevance of self-preservation ice layers in pipes with flowing natural gases, in seabed (Mahabadi et al. 2016), in sediments (Kwon et al. 2008), and in permafrost (Max 2003). In the current context, the role of Lifshitz energy can be important: The induced ice films may change the buoyancy of micron-sized CO₂-containing gas hydrate particles.

In particular, we consider ice formation on CO₂ clathrates and its potential impact on different ocean worlds. The presence of both liquid water and gaseous CO₂ on the icy moon Enceladus have been inferred from measurements by the Cassini spacecraft (Schenk et al. 2018). Other ocean world candidates in the Solar System include Callisto, Europa, Ganymede, and Titan (Nimmo & Pappalardo 2016). Even the Kuiper belt objects (KBs) Pluto and Triton have been proposed to have a reservoir of liquid water (Stern et al. 2015; Nimmo & Pappalardo 2016). These icy Solar System bodies have been the focus during the exploration and search for potential candidates to host extraterrestrial life (Nimmo & Pappalardo 2016) in liquid water oceans. It is not unrealistic to assume a large number of habitable ocean worlds even when only a small fraction of the Universe is considered. Here we are interested in two such potential ocean worlds: Enceladus and Pluto. Depending on the material properties and sizes, ice-coated hydrate particles may enter the fissures in the Enceladean ice crust rather than sinking to the bottom of the ocean. From there, hydrates may enter fracture systems that feed Enceladus’ complex plume without destabilising. If they do not become trapped in deposits within the icy crust, hydrate particles may be directly ejected from the surface to the E-ring or fall back onto the surface of the south polar region. Notably, floating particles have sizes of the same order of magnitude as the observed ice particles in the E-ring around Saturn (Schenk et al. 2018). These could come from composite water-ice particles and also from less abundant self-preserving clathrate hydrates that are decomposed by solar winds into ice particles and gas molecules. Large amounts of stabilised hydrates are potentially trapped under or within the icy crust during transport. Such deposits may reactivate under changed conditions and have a delayed participation in the plume activity. As schematically indicated in Fig. 1, our model predicts that nanoscopic to microscopic ice coatings are essential for the CO₂ hydrate particles to be able to float in oceans. We propose that these floating particles could, in some ocean worlds, lead to thick CO₂ hydrate deposits forming below or in the ice crust, thereby redistributing CO₂ upwards, thus impacting the structural, thermal, and dynamical properties of the bodies. We propose that CO₂ deposits above the Enceladean ocean, particularly those closer to the surface, may be more prone to destabilisation and associated pressure-driven mass ejection via plumes and seeps. We also propose that the insulating hydrate layers on Pluto proposed and modelled by Kamata et al. (2019) will likely not be comprised of pure methane hydrates as suggested, but a mixture of ice-stabilised CO₂ hydrates with additional components involving CH₄ hydrates, mixed CO₂-CH₄ hydrates, and other hydrates. In the current work, we focus on CO₂ gas hydrates; however, we also briefly consider CH₄ hydrates and CO hydrates. There are several reasons to discuss these: The abundance of CH₄ is similar to that of CO₂ in Enceladus’ plumes and their thermodynamic disequilibrium is predicted to favour the formation of CH₄ from CO₂ in the satellite’s ocean (Waite et al. 2017). It is relevant that methane clathrates can thereby take part in feeding the plumes. On the other hand, CO molecules seem to be absent in the Cassini measurements of the composition of Enceladus plumes (Waite et al. 2017). However, it is one of the most abundant species observed in comets (Bockelée-Morvan & Biver 2017), and it could have been present in the building blocks of Enceladus initially. Notably, these two gas hydrates have been proposed to take part in a thermally insulating gas hydrate layer on Pluto (Kamata et al. 2019). We expect the general ideas presented here to be relevant for countless exoplanets beyond our Solar System (Levi et al. 2017; Taylor 1999).
2. Computational details

Following an idea presented by Elbaum & Schick (1991), according to which intermolecular dispersion forces can provide a vital contribution to ice pre-melting, Boström et al. (2019) recently investigated how these forces can also cause ice-cold water to freeze at some interfaces. Our present work considers a system with gas hydrate-ice-water. In order to model the energies involved in ice formation at gas hydrate-water interfaces, Lifshitz theory deploys dielectric functions for the materials involved, that is, electromagnetic spectra for ice, water, and gas hydrates. In particular, we replaced an old model (Elbaum & Schick 1991) for the dielectric function for ice-cold water with an improved new one (Fiedler et al. 2020).

The first material we needed to model was the CO₂ gas hydrates. At specific temperatures and pressures, known as quadruple points, clathrate structures can be formed when gas molecules are present in ice-cold water (Dickens & Quinby-Hunt 1994). Modelling dielectric functions for CO₂ clathrates were presented in a previous work (Boström et al. 2019). The modelling of the dielectric functions of CH₄ and CO₂ clathrates follows the same methodology (Boström et al. 2019), using clathrate structure parameters together with optical models (Fiedler et al. 2017) for the different gas molecules. In this paper, the material modelling is expanded to the full range of different gas molecular occupancies in the clathrate structure. This turns out to be an essential step and here we predict that a (surface) region with low occupancy of gas molecules is essential to obtain agreement with the experimentally observed ice layers discussed above (Takeya & Ripmeester 2008; Falenty & Kuhs 2009).

Secondly, the dielectric model for ice proposed by Elbaum & Schick (1991) remains reliable in the frequency range required for calculations of dispersion forces (Márquez 2019). Thirdly, two new parameterisations (Fiedler et al. 2020; Márquez 2019) for optical properties for water give similar Hamaker constants for ice-water related systems. We show in this work that by replacing the old model for the dielectric function of ice-cold water (Elbaum & Schick 1991) with the new model (Fiedler et al. 2020) for cold water near the quadrupole point of CO₂ clathrates, we obtain substantially better agreement with experiments (Takeya & Ripmeester 2008; Falenty & Kuhs 2009). The difference between the Elbaum & Schick (1991) model for water and the new water model is that the new one relies on optical data from a much wider frequency range, and also benefits from improved parameterisation techniques. In particular, the model for cold water presented by Elbaum & Schick (1991) has been seen to underestimate the strength of the dielectric function of cold water in optical and UV frequencies, primarily due to the unavailability of data at X-ray frequencies above 20 eV. The new model from Fiedler et al. (2020) includes all these new data.

Any realistic theory for self-preservation of gas hydrate must as a critical test be able to accommodate water ice layers of this kind. Within the old water model used by Boström et al. (2019), only nano-sized water ice layers were found on fully occupied CO₂ particles. No ice layers were predicted with lower occupancy of the gas molecules. However, our main result when using the improved water model is that we find a much more realistic micron-sized layer on low-occupancy to close-to-half filled gas hydrates. Such low occupancy regions could occur near the surface due to the diffusion of gas molecules. The stability of the system is then controlled by the slow diffusion rate for gas molecules through the ice layer.

The equilibrium ice layer comes from the free energy minimum for the layered structure shown in the schematic Fig. 2.

Lattice mismatches often occur at the interfaces between different gas hydrates, between the same gas hydrates with different densities, and between water ice and the gas hydrate. Such heterogeneous structures are known to exist in nature, and in fact ice layers on gas hydrates are observed but not fully understood (Takeya & Ripmeester 2008; Falenty & Kuhs 2009; Nguyen et al. 2015). Nguyen et al. (2015) present a path to understand this problem using molecular dynamics simulations for a gas hydrate-ice-air system and found that such transition layers are disordered, and they can typically be a few (commonly 2–3) water layers thick. The disordered interfacial transition layer between ice and gas hydrates when present relieves the pressure of mismatch and aids in understanding nucleation of gas hydrates on ice in the presence of gas. The effective thicknesses for such transitional layers are often negligible and hence do not need to be explicitly modelled. Hence the transitional layer does not affect our results, other than noting that its existence is critical in any model aiming to explain ice formation on gas hydrates be it either in gas or water.

We present in Fig. 3 the new dielectric function for ice-cold water (Fiedler et al. 2020), together with the model for ice from Elbaum and Schick (Elbaum & Schick 1991; Daniels 1971). We also show the dielectric function for CO₂ gas hydrate particles with empty (low occupancy) and fully (high occupancy) occupied structures. In our calculations for ice formation at the interface of a gas hydrate in contact with ice-cold water, we used a specific quadrupole point, which for CO₂ hydrate is at \( T = 273.1 \, \text{K} \) and \( p = 12.56 \, \text{bar} \) (Sloan Jr. & Koh 2007). The quadrupole point for CH₄ clathrates is \( T = 272.9 \, \text{K} \) and \( p = 25.63 \, \text{bar} \) (Sloan Jr. & Koh 2007) and for CO₂ clathrates it is at \( T = 272.0 \, \text{K} \) and \( p = 11.56 \, \text{bar} \) (Jäger et al. 2016). Away from the quadrupole point, additional thermodynamic effects must be considered. The model for the dielectric functions for gas hydrates was outlined by Boström et al. (2019). Ultimately, the equilibrium ice layer thicknesses on CO₂ clathrates is shown to depend on the gas occupancy, where \( N_g \) (between 0 and 8) is the number of gas molecules per 46 water molecules in the gas hydrate structure (\( N_g = 8 \) corresponds to fully occupied). The requirement for stable ice layers to form is that the Lifshitz energy for a layered system with gas hydrate-ice-water has short range repulsion that switches over to long range attraction with an energy minimum...
at a specific ice layer thickness. In general, the formation of both gas hydrate structures and self-preservation ice layers depend on various additional factors, including the amount of dissolved gases (Ninham et al. 2017; Azadi et al. 2020).

For the pre-melting of ice surfaces (Wettlaufer 1999), but not ice formation, electrostatic energies are important. While electrostatic energies are large near ice-water interfaces, they are independent of the ice layer thickness except for atomically thin ice layers and do not contribute to the interaction energy considered in this work (Boström et al. 2019). One pathway reported by Takeya & Ripmeester (2008) to synthesise ice coated self-preserved hydrate particles involves partial degassing of the outer part of a pure gas hydrate in an inert gas atmosphere or in vacuum during warming. Subsequent conversion of the outer emptied clathrate cells can be made to cubic, then hexagonal, and eventually annealed to form a continuous ice gas diffusion barrier on the underlying hydrate particle. In this case the source of the water for the ice layer originates from the particle. Formation of self-preserved hydrates in salt water was reported by Prasad & Kiran (2019). They confirmed self-preservation up to the melting point of ice in the three component system water-gas-NaCl for salt concentrations below a threshold of 0.5–1.5% NaCl. Self-preservation was inhibited at higher salt concentrations, including that of typical present-day sea water.

Salt effects in ice systems were recently studied by Thiyam et al. (2018) to model how ice particles below a certain size can be trapped under a water surface. It is well known that ice melting, for example, in Arctic regions (Armitage et al. 2020) can lead to substantial local reduction of the salt content in sea water. We argue that it is likely that, for example, the water below the ice cap on the moon Enceladus, as well as in the geysers channels that are leading the stream of water, gas, and particles out across the same ice cap, could have a much lower salt concentration compared to the deeper sea water. The limiting salt concentration for ice formation is linked to the lowering of the melting temperature of water ice in contact with salt water (Hall et al. 1988). Formation of ice layers in salt water is expected below a salt specific temperature. Some additional effects of salt ions on ice formation are discussed near the end of this work.

3. Dispersion free energies across the ice layer

One kind of contribution to the total free energy is the dispersion energy, modelled for planar multilayered systems by Lifshitz and co-workers (Dzyaloshinskii et al. 1961). This Lifshitz energy has found an increasing importance in technological applications such as microelectromechanical and nanoelectromechanical components (MEMS and NEMS), as these components gradually become smaller (DelRío et al. 2005; Stange et al. 2019). Dispersion forces are also used by living organisms, such as geckos walking in the ceiling (Autumn et al. 2000). The Lifshitz dispersion interaction has important implications for astrophysics. Here we suggest that the formation of ice layers induced by dispersion energies influences the influx and composition of icy particles via plumes onto the frozen surface of Enceladus and into the E-ring of Saturn. Furthermore, we propose that a large amount of floating ice-coated CO₂ hydrate particles could potentially result in an insulating gas hydrate layer above liquid water reservoirs at the lower edge of the icy surface on Enceladus and other icy Solar System bodies. Activity involving liquid water, with a proposed role for insulating methane and carbon monoxide hydrate layers (Kamata et al. 2019), has been inferred as a possibility to explain varying crater abundances (i.e. different surface ageing) on the icy dwarf planet Pluto (Stern et al. 2015; Nimmo et al. 2016; Nimmo & Pappalardo 2016). One of the reasons why the CO₂ molecule was discarded as a source for a potential insulating layer on Pluto (Kamata et al. 2019) was that its gas hydrate structure has a density which is too high to float, and rather than accumulate at the lower edge of the surface ice cap, the gas hydrates would sink to the bottom. As we point out in our result section, this could change in the presence of self-preserving ice layers.

We consider gas hydrates covered with an ice layer that are sufficiently large to be treated as locally planar. In this model, the surface force acting on the ice-water interface determines how the ice layer grows or melts. The corresponding potential is given by the Lifshitz free energy, whose density per unit area at temperature $T$ reads as (Ellingsen 2007; Esteso et al. 2020)

$$F(d) = \frac{k_B T}{2\pi} \sum_{m=0}^{\infty} \int_{0}^{\infty} dk^\parallel k^\parallel \left(1 - \frac{1}{\sigma_{\text{TE}}^2 + \sigma_{\text{TM}}^2} e^{-2\xi m^2 d}\right),$$

where $k^\parallel$ is the component of the wave vector $k = (2\pi/\lambda)\hat{\mathbf{k}}$ parallel to the surface, and $\xi_i = \sqrt{k^2 + \epsilon_i \omega^2 / \epsilon_0}$ (with $i = 1, \ldots, 4$ numerating the layer according to Fig. 2, $\xi_m = m \pi k_B T / h$ the Matsubara frequencies, the reduced Planck constant $h$, the Boltzmann constant $k_B$, and the speed of light $c$) is the imaginary part of the perpendicular wave vector component of the wave vector. The primed sum in the expression above denotes that the first term ($m = 0$) has to be weighted by 1/2. The photon polarisations $\sigma = \text{TE}$ (transverse electric) and $\sigma = \text{TM}$ (transverse magnetic). The multiple reflections between the interfaces lead to (Buhmann 2012; Ellingsen 2007)

$$\tilde{F}_{\sigma} = \frac{r_{\sigma}^{32} + r_{\sigma}^{12} e^{-2\xi d_o}}{1 + r_{\sigma}^{32} r_{\sigma}^{12} e^{-2\xi d_o}}.$$
4. Results: ice layers and buoyancy

We begin with the earlier unresolved problem (Boström et al. 2019), namely that for experimental conditions the ice film thickness needs to be much thicker than the nano-sized water ice films that were predicted in the past (Boström et al. 2019). This result is in contradiction to the well known experimental result discussed in the literature (Takeya & Ripmeester 2008; Fdently & Kuhs 2009). Theoretical calculations (Boström et al. 2019) applied the average experimental occupancy (not fully 100% occupied positions for the gas molecules) together with an older model of the dielectric function of ice-cold water (Elbaum & Schick 1991). This led to the problem that ice films were predicted ranging only up to a few nanometres thick for CO2 hydrate, with thickness d_h2O and the ice layer (ε_2) with thickness d, see Fig. 2.

The free energy (1) describes the action on the interface between the low occupancy hydrate layer (ε_2) with thickness d_h2O and the ice layer (ε_2) with thickness d, see Fig. 2.

\[
\sigma_{\perp}^{\perp} = \frac{\Delta \varepsilon_i}{\Delta \varepsilon_j} = \varepsilon_i \kappa_j - \varepsilon_j \kappa_i, \quad \sigma_{\perp}^{\parallel} = \frac{\Delta \varepsilon_i}{\Delta \varepsilon_j} = \varepsilon_i \kappa_j + \varepsilon_j \kappa_i. \tag{3}
\]

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Equilibrium ice layer thicknesses on homogeneous CO2, CH4, and CO gas hydrate particles at various gas occupancies are given in Table 1. There is no ice layer for a higher occupancy. A key point to observe is that use of the Elbaum and Schick model for cold water leads to the prediction that only partially full to fully occupied gas hydrate structures at the quadruple point can have thin (<4 nm) ice layers. In sharp contrast, the new water model requires low occupancy (for example, <38% for CO2) gas hydrate structures in order to have a Lifshitz interaction promoting ice formation. Here, a thick ice layer as thick as 245 nm is predicted. This influences self-preserving layers, the presence and absence of ice on CO2, CH4, and CO gas hydrates, and the buoyancy of these gas hydrate particles in cold water.

Of course, empty clathrate structures are not stable, at least not in their bulk forms. A system of great interest is therefore a bulk material (with high occupancy of gas molecules) with a finite surface region where the depletion of a gas molecule has resulted in a low occupancy region. Here, the effect of such layered media influences the ice formation in ice-cold water. As an example, we first consider a surface region with an empty clathrate structure and a bulk region with a fully occupied structure. For thin ice layers, the free energy shown in Fig. 5 is not influenced by the bulk region while for very thick ice layers the inner region dominates. The basic theory has been well described in the general multilayered case in the book by Parsegian (2006). When the low occupancy surface region grows thicker, the result eventually approaches that found for homogeneous low occupancy clathrate structures. In Table 2, the ice thickness stabilising the CO2 gas hydrate is given for a surface region d_LiO at two fixed gas occupancy values. We take as examples a low occupancy surface region N_g=0 and a partially occupied surface region N_g=1. In both cases, the thicker the surface region is, the thicker the self-preserving ice layer. One should notice that already very thin surface depleted regions enable the formation of self-preserving ice layers.

As a direct application, the formation of ice layers on gas hydrate particles could have an important influence on the gas cycle of Enceladus. On this body, gases and particles are ejected from surface vents as plumes. The composition of these plumes have been measured by the Cassini spacecraft, and found to be dominated by water, various salts, and a large number of
Table 2. Self-preserving ice layer thickness $d$ for increasing values of low occupancy (LO) surface region thickness $d_{LO}$ with $N_g = 0$ (second column).

| Ice thickness, $d$ (nm) | $d_{LO}$ (nm) | $N_g = 0$ | $N_g = 1$ |
|-------------------------|---------------|-----------|-----------|
| 1                       | 3             | 3         |           |
| 5                       | 20            | 16        |           |
| 10                      | 40            | 32        |           |
| 50                      | 131           | 108       |           |
| 100                     | 182           | 149       |           |

Notes. As a comparison, we also give one example of a partially occupied surface region with $N_g = 1$ (third column). In these examples, the bulk region is taken as a fully occupied CO$_2$ clathrate structure.

volatile gases including CO$_2$, N$_2$, H$_2$S, and CH$_4$ (Waite et al. 2006; Postberg et al. 2011; Schenk et al. 2018). It has been postulated that gas hydrates could be important for the creation of the plumes as well as for the chemical composition of the ice layers beneath and in the interior (Bouquet et al. 2015; Matson et al. 2012, 2018). Matson et al. (2018) suggest that surface eruptions are sourced from CO$_2$ gas pockets and plume chambers above a subsurface water table less than 1 km under the uppermost ice layer. They propose that bubbles and gas dissolved in ocean water are the source of the CO$_2$ and do not consider floating CO$_2$ containing clathrate particles as a source.

Larger molecules (such as CO$_2$ and CH$_4$) form type I clathrate structures, while type II clathrate structures typically host smaller molecules (e.g. O$_2$ and N$_2$) (Sloan Jr. & Koh 2007). We note that CO hydrates initially can form type I structures that are metastable and convert to the stable type II structures on a timescale of weeks (Pétuya et al. 2019). A fully occupied type I CO$_2$ hydrate has a density greater than water, such that it sinks in water (McKay et al. 2003; Prieto-Ballesteros et al. 2005; Mousis et al. 2013; Safi et al. 2017). A layer of water ice can change the effective density and hence the buoyancy of gas hydrate particles (Boström et al. 2019; Thiyam et al. 2018). It was recently shown that geometry effects are small for concentric sphere ice systems when the size of the core is thick enough relative to the thickness of a coating layer (Parashar et al. 2019). This encouraged Boström et al. (2019) to take $d$ as the approximate thickness of each ice film at planar water-CO$_2$ gas hydrate interfaces with different gas molecular occupancy. Such a theory is expanded below to account for different occupancy (and mass density) in bulk and surface regions for the gas hydrate particle.

The average density ($\rho_{av}$) of an ice coated gas hydrate particle (approximated as a sphere with a low occupancy surface region) is

$$\rho_h = \rho_h\left(1 + \frac{d_{LO}}{r_h^3 - r_i^3}\right),$$

where $\rho_h$ is the average mass density of the layered gas hydrate comprising a high occupancy (HO) core with the radius $r_i = r_h - d_{LO}$ and a low occupancy (LO) surface region with the average thickness $d_{LO}$. Similarly, the average mass density of a mixed particle comprises an average of the gas hydrate interior ($\rho_h$) and a shell of water ice. The mass density of water in pure ice is $\rho_i = 0.9167$ g/cm$^3$, (Linde 2005) giving the number density of water molecules in pure ice as $n_i = 3.06 \times 10^{-2}$ Å$^{-3}$. The gas hydrate corresponds to water molecules and gas molecules in a specific structure with densities given in Table 3.

We exploit, in Fig. 6, the equilibrium distances for Lifshitz free energies evaluated above for each combination of surface region thickness and ice layer thickness in the specific example of a fully occupied ($N_g = 8$) CO$_2$ clathrate structure coated with an empty ($N_g = 0$) clathrate structure. The 0.01–0.2 μm thick ice layer on homogeneous type I CO$_2$ hydrate particles that we found above using the new water model suggests that micron-sized instead of nanometre-sized (Boström et al. 2019) particles may...
float in the ocean under the ice cap on Enceladus. However, both the density of the ice-free gas hydrate particle and the additional equilibrium thickness $d$ of the ice layer depend on the internal structure of the gas hydrate particle. Depending on the surface structure of the clathrate particle, the transition from sinking to floating driven by buoyancy is predicted to occur for typical particle sizes ranging from 0.02 to 2 μm. The critical composition of such particles corresponds to a mass fraction of high-occupancy hydrate (in the core of the particle) of around 50% (see Fig. 7).

As can be read directly from the graph, the approximate critical high-occupancy-hydrate mass fraction in particles corresponds, in every case, to a critical floating and sinking value of 0.5, below which particles float. We use this as the upper estimate for the high-occupancy-hydrate composition of particles that are able to float in an ocean of density $\rho = 1.0 g cm^{-3}$. This number can be used to provide estimates for how the thickness of an insulating hydrate layer is related to the available amount of CO$_2$ in each specific ocean world. As can be inferred from the mass densities in Table 3, CH$_4$ hydrates will float and CO hydrates are close to the floating-sinking transition in water. Even in the absence of self-preserving ice layers, both are likely to float in ocean water. It is noteworthy that all three gas hydrates considered could have gas molecule depletion layers in their surface regions. According to our calculations, this would favour water-ice formation in surface regions of these three gas hydrates, in which case we would expect to also observe all three gases in the Enceladean plume. We note that CO$_2$ and CH$_4$ are indeed observed, however CO is not. This is consistent with the hypothesis of Mousis et al. (2009b) that light gases volatilised from planetesimals in the Kronian nebula, eliminating CO (along with Ar and N$_2$) before the formation of Enceladus. Kamata et al. (2019) propose that floating gas hydrates could prevent Pluto’s ocean from freezing over geological time by forming a thermally insulating, non-convective layer atop the ocean. They hypothesise that CO$_2$ hydrates would sink on Pluto, not accounting for a stabilising ice layer, and therefore they invoke methane and CO hydrates as the insulating hydrates, being naturally buoyant.

We estimate the same layer thickness (10 km on Pluto) as proposed by Nimmo et al. (2016); Kamata et al. (2019), but built from pure CO$_2$ hydrates stabilised by an ice layer with a composition having an upper limit of 50% pure CO$_2$ hydrate. This requires around 1% of the estimated total amount of CO$_2$ available on Pluto, estimated from H$_2$O:CO$_2$ ratios in the solar nebula (Mousis et al. 2009a; Eistrup et al. 2019) to be bound within the layer. Such a layer on Pluto would be around 50% less insulating than a pure hydrate due to the mixing with water ice. It would also likely be substantially less viscous than a pure hydrate layer given that the water ice would be the continuous phase, at least initially. Nonetheless, taking the stabilisation of mixed CO$_2$-CH$_4$-CO floating hydrates into account may have important implications for the long-term stability of liquid layers on ocean worlds in our Solar System and beyond.

Next, we give an estimate for the upper limit of thickness of a corresponding hydrate layer on Enceladus. If we consider that all of the CO$_2$ emitted from the plumes of Enceladus were sourced from a CO$_2$ hydrate layer on Enceladus, then the integrated thickness over time can be calculated to be 2–20 km. In other words, 2–20 km of CO$_2$ hydrate would have decomposed and been emitted from the surface via plumes. This is based on a rate of plume emission of 100–350 kg s$^{-1}$ (Postberg et al. 2018a) and a mass fraction of CO$_2$ in the plume of 0.3–0.8% (Waite et al. 2017) calculated over 4.6 billion years. Using a similar argument, the emitted methane originating from methane hydrates would correspond to a methane layer 2–18 km thick, which has a mass greater than the amount of methane predicted from a solar nebula composition. This can be explained by thermo-dynamic disequilibrium between oxidants in Enceladus’ ocean and hydrothermally derived H$_2$, which has been proposed to favour the formation of CH$_4$ from CO$_2$ on Enceladus, (Waite et al. 2017). If we instead calculate the case where all CO$_2$ forms a global hydrate layer, the thickness of the CO$_2$ hydrate layer before emission would have ranges of 67–350 km (considering the CO$_2$/water ratio to be cometary, Le Roy et al. 2015; Eistrup et al. 2019; Bockelée-Morvan & Biver 2017), or around 160 km (considering the CO$_2$/water ratio to be that of the solar nebula, Mousis et al. 2009a; Eistrup et al. 2019). Clearly given these assumptions, only a small fraction of the total available CO$_2$ would be required to form significantly thick deposits on Enceladus, or other ocean worlds with similar mass ratios of H$_2$O:CO$_2$ and where other sinks of CO$_2$ occur, such as conversion to CH$_4$ and carbonation at the ocean and rock interface. These are obviously upper limit estimates for the thickness of a gas hydrate layer on Enceladus, and this does not account for an insulating layer in flux, constantly growing and decreasing by adsorption of gas hydrates and emission of gas hydrates and gas molecules. The same mechanism applies to both CO$_2$ and CH$_4$ hydrates, the latter being positively buoyant at all occupancies. Both gases are observed in similar concentrations in the plume. Likely CO$_2$/CH$_4$ mixed hydrates are involved. The important point is that a reasonably thick layer of stabilised hydrate may have formed during Enceladus’ lifetime. Such a hydrate layer would have implications for the thermal insulation on the Enceladean ocean via impacting conductive and convective heat transport.

Empty hydrates are generally considered unstable, although these have been isolated under particular laboratory conditions (Jacobson et al. 2009; Falenty et al. 2014), while partially empty hydrates are well known. At the molecular scale, the low-occupancy hydrate layer is therefore more likely considered to be thinner, with structural stabilisation coming from hydrogen bonding with the inner high-occupancy particle core and the
outer ice coating. This would tend to favour large populations of buoyant, ice-coated, nano-sized CO$_2$ hydrate particles at the lower end of the distribution, that is to say 20 nm, whose particle number would be $10^6$ times higher compared to two micron particles at the higher end of the distribution, assuming the same number of nuclei. Further, at a critical density for buoyancy of 1.003–1.03 g cm$^{-3}$ depending on the ocean density, the 20 nm fraction has a specific surface area of around 150 m$^2$ g$^{-1}$ compared with just 1.5 m$^2$ g$^{-1}$ for two micron particles, and at just 0.1% volume fraction in the sea water, the particle number is $3 \times 10^{19}$ m$^{-3}$. Such particles could enter the plume feed via a sea-spray mechanism (Postberg et al. 2018b). In doing so, these would present a large specific surface area that could act as nucleation sites for ice and salt crystallisation from the liquid phase of the spray droplets and be trapped in the cores of particles ejected to the E-ring or deposited back on the surface of Enceladus (Postberg et al. 2018b).

5. Discussion

Our model for anomalous stabilisation of gas hydrates via Lifshitz free energy thermodynamic minima may not be directly transferable to the situation for hydrates in the ocean of Enceladus due to differences in temperature influenced by salinity and under varying pressures at different depths (Glein et al. 2018). Notably, one important effect of salt is to change the freezing point depression of water (Hall et al. 1988; Glein et al. 2018). We stress that the freezing point for water decreases weakly with added salt. While temperatures are very low at the surface of Enceladus, the presence of liquid water under the ice cap, notably at an estimated 0.05–0.2 M NaCl concentration and basic pH (Postberg et al. 2008, 2009, 2011, 2018b; Glein & Waite 2020), indicates ocean water with a temperature close to 273 K (Glein et al. 2018). The estimated water temperature in the ocean on Enceladus is in fact remarkably close to the quadruple point temperatures that we use in the present work. Postberg et al. (2008, 2009, 2011, 2018b) (see also Schenk et al. 2018) used the results from a cosmic dust analyser (CDA) to account for three distinct types of ice particles in the plume. The first had almost pure water ice, the second also carried organic compounds, and the third was rich in salt. There were also nanoparticles rich in silicon that were supposed to originate as inclusions in the second and third ice type. One of the most reliable measurements reported by Waite et al. (2017) suggests a true composition (in contrast to an impact-modified composition) with an abundant presence of H$_2$O, H$_2$, and CO$_2$. There has also been reports of CH$_4$, NH$_3$, and other gases present in measurements (Waite et al. 2017). A comparison between the results from CDA and laboratory experiments further enabled Postberg et al. (2008, 2009, 2011, 2018b) to put limits on the concentrations of different salt species in the ocean on Enceladus.

The freezing point depression is weak at the salt concentration levels predicted for the ice-capped ocean on Enceladus. This is important since it suggests that our theoretical model for self-preservation can also be relevant in the presence of salt, but at slightly lower temperatures. At these concentrations, the added salt ions have only small effects on the dielectric function of water so an approximation of the ice layer thickness would not be dramatically affected by changes in optical properties of the materials. This is also the case for oceans on Earth. Similarly, effects from different NaCl salt concentrations on the melting temperature of CO$_2$ clathrates were explored by Darling (1991). Improvements of our theory to temperatures away from the quadruple point of the gas hydrate structure can be considered by expanding the recent work of Esteso et al. (2020) (see also references therein), while relevant salt effects on ice-water interfaces were discussed by Thiym et al. (2018). Even so, here, trends are estimated to be similar in the ocean on Enceladus, especially in subsurface water reservoirs just below the water-ice cap (where melted water from the ice cap potentially could reduce the salinity). In addition, low salt conditions are expected to occur when the water-dominated liquid plume mixture passes through holes in the water-ice cap coating the ocean. The surface of Enceladus is almost entirely made of pure water ice except near its south pole in the region of the geysers, and especially in the region called the ‘tiger stripes’, where there are some light organics, CO$_2$, and amorphous and crystalline water ice (Brown et al. 2006). It seems very likely (Schenk et al. 2018) that the origin of the CO$_2$ abundance in this area is linked to the geysers and therefore directly related to the ocean composition.

It is known that the observed blue colour of the Saturn E-ring, in contrast to the red colour of Jupiter’s dusty rings or Saturn’s G-ring (Nicholson et al. 1996; de Pater & Lissauer 2015), suggests water-ice particles in the ring to have an average size of the order of 1 μm (Baum et al. 1981; Hillier et al. 2007; Schenk et al. 2018; Catling & Kasting 2017). Measurements by the Cassini spacecraft, within the Cassini-Huygens mission (Schenk et al. 2018; Hillier et al. 2007), confirmed the size range for particles. They also showed that CO$_2$, directly after water, is one of the most common species in the plume near the south pole of Enceladus (Schenk et al. 2018). Furthermore, CO$_2$ gas hydrate particles of different sizes ranging from nano-sized to micron-sized can be ejected (Matson et al. 2018), together with much more abundant water-ice particles via plumes onto the surface and partially also into outer space providing material for the E-ring around Saturn.

Our model suggests an alternative mechanism for the source of the CO$_2$ collecting in the subsurface lakes postulated by Matson et al. (2018). They considered bubbles and CO$_2$ gas dissolved in water as the source of the CO$_2$ pocket driving the plumes. Our model suggests that buoyant, ice stabilised CO$_2$ hydrates, or mixed gas hydrates (CO$_2$ and CH$_4$, for example), may be able to reach the water reservoir below the cap ice and

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**Fig. 7.** Graph of CO$_2$ hydrate particle density as a function of high-occupancy-hydrate content in each particle. The five lines correspond to five different high-occupancy-core radii, $r_c = r_o - d_{LO} = 20, 50, 100, 500,$ and 1000 nm, with each point in each respective line representing the five scenarios of differing low-occupancy-hydrate thickness given in Cols. 1 and 2 of Table 2.
above the water table. Some fraction of these hydrates could then destabilise, for instance through collisions breaking the thinner, stabilising ice layers, or by subsequent infiltration of warmer water from hot spots (Matson et al. 2007; Hsu et al. 2015; Bouquet et al. 2015). Such destabilised hydrates could feed either the CO₂ seeks further from the plumes, forming CO₂ frost patches, or drive plume activity through pressurisation under the ice cap, resulting in CO₂ and/or CO₂ hydrate particles being ballistically vented to fall back to the surface or to escape into the E-ring. The amount of CO₂ gas in bubbles or dissolved in water is relatively low in contrast to the relatively high amount in CO₂ gas hydrates (Safi et al. 2017), thus stabilised hydrates could act as a richer source of CO₂ than dissolved gases in the up-welling ocean water.

When the pressures and temperatures of the local environment on Enceladus change at different depths in the ocean, one would expect that this could lead to the leakage of gas molecules via diffusion in the interfacial region of each particle. Particles with sizes up to around a few micrometers with a bulk region built by high occupancy type I gas hydrates and a substantial interfacial region with low occupancy can have a thin film of water-ice. For such systems, arguments can be made that large particles dominated by bulk regions may sink, while other particles, where the surface region is thick enough to generate a self-preserving water-ice layer, have the potential to float. With positive buoyancy, these particles could, over geologically long time periods, lead to substantial hydrate deposits at the top of the ocean or in the overlying ice crust. From our model, we consequently predict that the fraction of particles that sink through the ocean gradually diminishes through a feedback mechanism. As CO₂ is removed from the ocean by deposition as stabilised hydrates above the ocean, the sinking fraction decomposes near the hot rocky core and, if it does not react near the rocky core material (producing carbonates or CH₄, for example), it can be fed back to the ocean to form a new population comprised of both sinking and floating hydrates. This cycling could continue until the sinking population becomes depleted through the source being removed to the deposits above the ocean or within the icy crust.

We have discussed that near-surface deposits in the crust could lead to CO₂ and or hydrate emissions to the surface through seeps or to the surface or E-ring via plumes. As for CO₂-containing hydrate deposits at the top of the ocean, these may accumulate to thick sequences of strata over geological time measured in billions of years. Such layers have been postulated as effective insulators on Pluto as a way to explain why Pluto’s ocean has not frozen (Kamata et al. 2019). Buoyant hydrates including ice stabilised CO₂ hydrates discussed here may form thick sequences of thermally insulating, high viscosity strata that can limit heat flow to the surface and may be a general phenomenon in the hydrosphere of ocean worlds through the proposed stabilisation mechanism.

By floating to the top of the ocean surface, ice-coated CO₂-containing hydrates can form deposits underneath or within the icy crusts of ocean worlds. Reasonably thick deposits of stabilised hydrates may have formed during the lifetime of Enceladus and Pluto, and in the case of the less tidally disrupted Pluto, these may have formed a continuous global insulator, albeit less thermally insulating than a layer made of pure hydrate. On Enceladus, these deposits would be expected to be subject to tectonic and thermal destabilisation. Nonetheless, the self-preservation of mixed CO₂-methane floating hydrates may have important implications for the long-term evolution and dynamics of ocean worlds in our Solar System and beyond.

6. Conclusions

Using the most reliable, experimentally derived dielectric properties of ice and water, we obtain theoretical results that predict relatively thick, sub-micron scale ice coats on partially degassed hydrates in ice-cold water pointing to a previously unconsidered mechanism for gas hydrate self-preservation and buoyancy. We predict that nano- to micron-sized ice coated type I CO₂ clathrates can float in the water columns of ocean worlds, forming regional or global deposits on top of these oceans, underneath or within the ice layers. Further, we predict that self-preservation also occurs for CO and CH₄ hydrates just as it does for CO₂. Ice-coated type I CO₂-containing mixed gas hydrates will also float.

Over millions to billions of years, CO₂-rich hydrate layers may grow to a significant thickness. When such layers are global, they could provide thermal insulation against freezing of that respective world’s ocean or, if local or regional, they could destabilise to drive and feed ejecta plumes, as seen on Enceladus. The proposed model presented here for floating CO₂-containing hydrates is expected to be applicable to the liquid water columns of other ocean worlds within our Solar System, from Europa to Triton and to a significant fraction of the rapidly increasing list of extra solar planetary bodies and their moons that have yet to be discovered.

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A54, page 9 of 10

M. Boström et al.: Self-preserving ice layers on CO₂ clathrate particles
