

Report to the STSM Manager of the COST Action

Methane Hydrate Simulations in Marine Environment

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Molecular simulations of methane hydrates in marine-sediment environments have been performed with at UCD acting as a host institution for STSM visits. In particular, the project was aimed to carry out molecular-dynamics simulation of methane hydrates in contact with silica surfaces, mimicking the marine environment. Our investigation is focused on two main problems which are strictly connected. The first is to probe the effect of solid surfaces on hydrate formation which may be attributed to changes in the local structure of water molecules near the liquid-solid interface, thus altering the pathways of hydrate formation. The second is to investigate the stability of clathrate deposited on silica surface also in presence of electromagnetic external fields, which can trigger the dissolution process in an effort to gauge methane-release strategies. The molecular dynamics is a versatile tool to investigate both the phenomena of formation and dissociation of hydrates in bulk two-phase system (fluid in contact with a silica solid phase).

During the 18-day STSM at UCD (26 Feb – 15 Mar '16), we focused my attention mainly on the first step of investigation: the nucleation of clathrate in contact with solid surface. To this purpose, we model an hydrophilic silica surface in order to promote the growth of methane hydrate and investigate the nucleation process of clathrate in deep ocean. High hydrophilic silica surfaces are likely the most common constituent of the marine rocks, and, moreover, silica surface can play the important role to stabilize adsorbed water molecules in complex clusters, which are the main precursors of the hydrogen bonded framework involved in clathrate compounds.

In order to prepare the two-phase system, we have assembled a silica layers (solid phase) for representing a slit pore of sedimentary rock. Thus, a piece of amorphous silica with dimension 25x25x25 Å previously relaxed at 1 atmosphere and 298 kelvin was replicated 4 times, two and two along the axes x and y. The so obtained system was equilibrated for 1 nanosecond at 260 K and 500 atm. The intra- and inter- molecular interactions were modeled by the CHARMM potential, specifically developed for silica bulks¹. Finally, the so obtained simulation box of approximately 50x50x25 was cut following the plane x-y at a z value equal 12.5 Å, and along the cutting surface a volume corresponding to a orthogonal box of dimension 50x50x42 angstrom was added. Finally, we obtained a simulation box of approximately 50x50x67 angstrom, whose we count along z axis 25 angstrom of silica bulk and 42 angstrom of vacuum which will be later filled up with a mixed H₂O/CH₄ fluid. Note that the cut was performed along the oxygen bridge connecting two

¹ Lopes, Pedro EM, et al. "Development of an empirical force field for silica. Application to the quartz-water interface." *The Journal of Physical Chemistry B* 110.6 (2006): 2782-2792.

silicon atoms of the silica bulk. Particular attention was paid in reconstructing the high hydrophilic surface of the silica bulk by using the following approach. A topological analysis of the silica bulk was performed by exploiting an ad-hoc (developed by me) Fortran code, which employ algorithms of the graph theory. Here, the graph is defined as the set of nodes and edges formed by silicon and oxygen atoms as nodes and their connecting bonds as edges. Then, we identify as star oxygen nodes all the oxygens connecting two silicon atoms which are at the opposite side with respect to the cutting surface. Hence, the vacuum space is added, and the star oxygen nodes replicated on both the surfaces (on both the side with respect to the cutting surface). Finally, an hydrogen was added on each star oxygen in order to obtain all hydrophilic hydroxide groups along the two surfaces. The so obtained surface is reported in figure 1. The high hydrophilicity is guaranteed by a rich presence of silanol groups including both silanediol and silanetriol groups. The vacuum space between the two silica surface was randomly filled up with a mixed H₂O/CH₄ fluid (liquid phase) with 160 CH₄ and 2660 H₂O molecules corresponding approximately to a ratio methane/water equal to 0.06, which is close to the critical value of solvated methane in water observed in our previous work on methane clathrate during the nucleation event². Note that the methane/water ratio is below the theoretical value expected in Structure I of methane Hydrate which is 0.14. The last fact represents an advantage in our case, since the clathrate phase is limited to a size which will be surely smaller than the simulation box, avoiding artifacts due to the periodic boundary conditions (we avoid the self-interactions of the clathrate phase with its specular image).

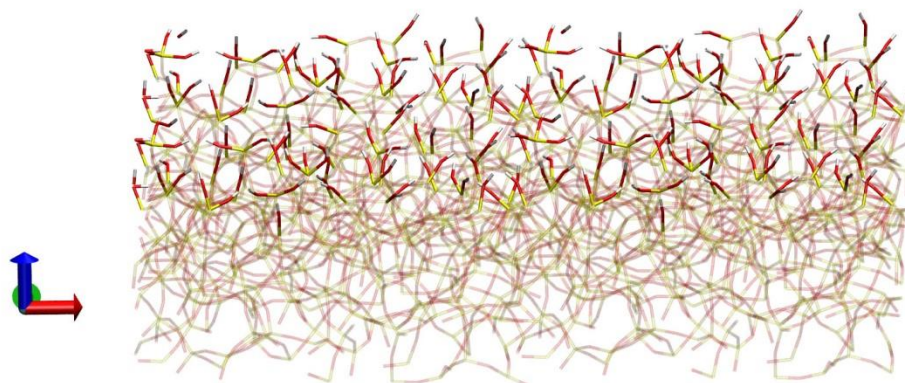


Figure 1: Snapshot of the obtained silica surface modeling a marine rock with a high hydrophilic surface . Note the presence of both Silanediol and Silanetriol groups enhancing the hydrophilicity.

Both water and methane was modeled by fully atomistic TIP4P/Sun-Duan model which is a mix of three developed potentials: the TIP4P for water, the fully atomistic OPLS-AA for methane, together with the optimized water-methane interaction parameters of Sun and Duan³ with very good predictions of the relevant quantities characterizing a mixed H₂O/CH₄ fluid⁴ (e.g., density, diffusivity, etc.). The interactions

² Lauricella, Marco, et al. "Methane clathrate hydrate nucleation mechanism by advanced molecular simulations." *The Journal of Physical Chemistry C* 118.40 (2014): 22847-22857.

³ Sun, Rui, and Zhenhao Duan. "Prediction of CH₄ and CO₂ hydrate phase equilibrium and cage occupancy from ab initio intermolecular potentials." *Geochimica et Cosmochimica Acta* 69.18 (2005): 4411-4424.

⁴ Waldron, Conor J., Marco Lauricella, and Niall J. English. "Structural and Dynamical Properties of Methane Clathrate Hydrates from Molecular Dynamics: Comparison of Atomistic and More Coarse-Grained Potential Models." *Fluid Phase Equilibria* (2015).

between fluid and solid phase were modeled by using the Lorentz-Berthelot combining rules. A cutoff radius of 12.0 angstrom was employed for the short-ranged interactions, and the Smoothed Particle Mesh Ewald (SPME) method was used for long-ranged electrostatic interactions.

The system composed of the two phases was equilibrated at 260 kelvin and 500 atmosphere. We have immediately observed a spinodal decomposition of the fluid phase in a methane liquid drop and a water liquid due to the poor miscibility of the two components (see Fig. 2). In such conditions, the observation of the nucleation phenomenon is a rare event and its sampling needs special techniques for speedup the exploration of the underlying free energy landscape. As a consequence, we start a metadynamics simulation to accelerate the observation of the clathrate nucleation at the amorphous silica surfaces.

Briefly, in metadynamics we introduce a set of collective variables (CV,) $\{\theta_i(\vec{r})\} i = 1, m$, where \vec{r} is the 3N-dimensional vector of the atomic positions and m the number of CVs. The atoms evolve driven by the physical potential, $U(\vec{r})$, plus a history-dependent bias potential, $V(\{\theta_i(\vec{r}), t\})$. This history-dependent potential is push the system to explore not previously visited state of the system accelerating the sampling of rare events as the nucleation. In this work we use two CVs. The first, C_{MM} , is the mean methane-methane coordination number, where C_{MM} is computed over a spherical shell with $rcut_{MM} = 8.5 \text{ \AA}$, corresponding to the first minimum of the pair correlation function in fluid methane. The second, C_{MW} is the mean methane-oxygen coordination number, where C_{MW} is computed over a spherical shell with $rcut_{MW} = 5.5 \text{ \AA}$. Note that in the last CV we consider all the oxygen both of water and hydrophilic silica surface.

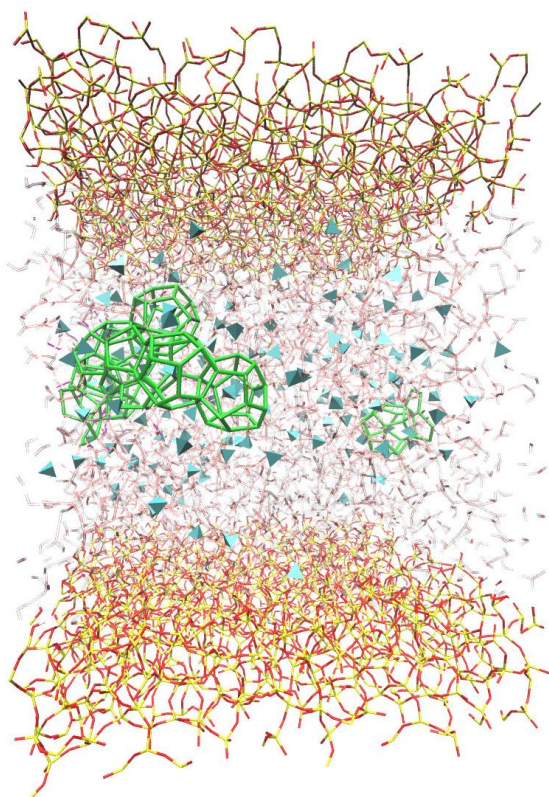


Figure 3: Snapshot of a nucleation event during a metadynamics simulation. The hydrogen bond structure related to the clathrate phase is drawn in green, while the methane represented as tetrahedral polyhedra.

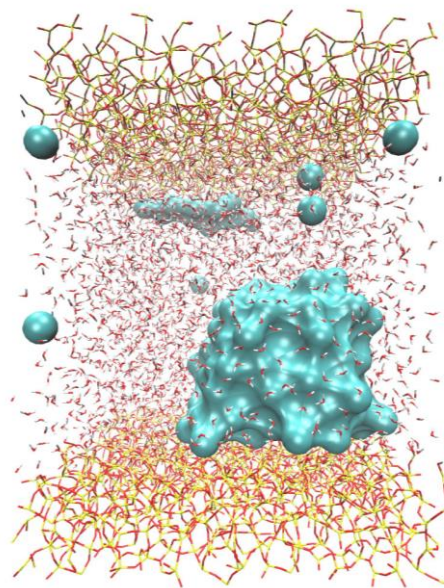


Figure 2: Snapshot showing the spinodal decomposition of the liquid phase in two: a drop of methane in cyan deposited on the silica surface, and the aqueous phase.

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During the STSM at UCD, a metadynamics simulation was started to observe the nucleation events. We started to record several crystallization phenomena providing promising results. As example we report snapshot of a nucleation event in our system. In Fig. , an initial seed of methane hydrate close to the critical size is reported, where the hydrogen bond structure is colored in green while the methane molecules spread in the system are represented as tetrahedron polyhedra.

We plan to identify reactive paths of the nucleation phenomena, and to perform a systematic investigation of the mechanism of methane-hydrate nucleation in the heterogeneous environment of silica surfaces and compare these to the homogeneous environment, providing useful insights on nucleation phenomena in both homogeneous and marine environments. This is helpful in the context of elucidating hydrate-nucleation phenomena with a view to potential exploitation of marine-hydrate gas resources.

In terms of addressing the important contribution of this STSM activity towards MIGRATE WG 2's goals, the following key points are of relevance:

- elucidation of formation mechanisms (especially thermodynamic and kinetic aspects) allows for devising inhibition strategies based on detailed microscopic understanding/insight;
- important, and largely positive, assessment of the proof-of-concept prototyping capability of state-of-the-art molecular simulation to yield insights into thermodynamic and kinetic stability (*e.g.*, nucleation timescales, spinodal decomposition) without the upfront need to observe these phenomena in a marine environment and associated operational/economic challenges;
- detailed and rich potential to apply, in future, external perturbations (*e.g.*, microwave fields) to perturb and inhibit hydrate-slurry agglomeration in seabed-to-surface recovery channels.

The results of this STSM project will be the topic of one forthcoming publication in a peer-reviewed journal. Further, the work will be presented by Dr. Niall English at the American Institute of Chemical Engineers (AIChE) Annual Meeting, which will be held in San Francisco on November 13-18, 2016. The title is: *'Methane-hydrate nucleation in marine environments: insights from molecular-dynamics strategies exploring free-energy landscapes'*. Naturally, Dr. English will discuss MIGRATE, and WG2's broad goals, as a backdrop and introduction to this talk.

I look forward to continuing my collaboration in marine-hydrate research with Dr. English and bolstering MIGRATE efforts in this arena, building on and consolidating my already-established collaborative relationship on methane-hydrate simulation with Dr. English. He and I have four co-published journal articles on methane hydrates and several others in preparation. He and I also plan to leverage supercomputer time on foot of this STSM project.

In terms of closing thoughts building on the rich STSM discussions that Dr. English and I had recently in Dublin, the idea of using electromagnetic fields to induce marine-hydrate dissociation, or inhibit formation thereof, will be intriguing to investigate. Indeed, the soon-to-expire status of Rojey's 1997 US patent on microwave-inhibition of hydrate formation, together with a lack of published data, renders this particularly timely. This may allow us to pursue a future STSM in this area, provide the budge available allows for this.



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21st April 2016

Re: Letter of acceptance of COST-MIGRATE-STSM report, and remarks on STSM success

Dear Dr. Lauricella,

It gives me great pleasure to accept your STSM report for your recent highly productive and successful visit to work with me here in the Materials, Energy and Water Simulations (MEWS) Group here at Chemical Engineering in UCD. Your molecular-simulation studies of nucleation in a marine-sediment environment, and free-energy pathways leading to this, have really established a workable intellectual capacity here at UCD and also within MIGRATE Working Group 2 to tackle the microscopic details of these processes. I think that your visit has stimulated some very interesting developments in marine-hydrate molecular simulation, and will help to boost Europe's leadership in this field of research.

More specifically, in terms of addressing the important contribution of this STSM activity towards MIGRATE WG 2's goals, the following key points are of relevance:

- elucidation of formation mechanisms (especially thermodynamic and kinetic aspects) allows for devising inhibition strategies based on detailed microscopic understanding/insight;
- important, and largely positive, assessment of the proof-of-concept prototyping capability of state-of-the-art molecular simulation to yield insights into thermodynamic and kinetic stability (*e.g.*, nucleation timescales, spinodal decomposition) without the upfront need to observe these phenomena in a marine environment and associated operational/economic challenges;
- detailed and rich potential to apply, in future, external perturbations (*e.g.*, microwave fields) to perturb and inhibit hydrate-slurry agglomeration in seabed-to-surface recovery channels.

I look forward to continuing our collaboration in marine-hydrate research, building on and consolidating our already-established collaborative relationship on methane-hydrate simulation (with our four co-published journal articles and several others *in statu nascendi*). Certainly, I will look forward to presenting this work at the upcoming AIChE meeting in San Francisco in mid-November, and developing a journal-article version in the future, together with leveraging supercomputer time therewith. In particular, the idea of using electromagnetic fields to induce marine-hydrate dissociation, or inhibit formation thereof, will be intriguing to pursue in future. Indeed, the soon-to-expire status of Rojey's 1997 US patent on microwave-inhibition of hydrate formation, together with a lack of published data, renders this particularly timely. This notion has been discussed in MIGRATE WG 2 meetings, and may allow us to pursue a future STSM in this vein (budget allowing, of course).

Yours sincerely,

Niall English

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