

Report to the STSM Manager of the COST Action

Computational Study of Methane Hydrate Exposed to Microwave Fields in Marine Environment

Guest: Marco Lauricella

*Istituto per le Applicazioni del Calcolo, Consiglio Nazionale delle Ricerche, Rome,
Italy*

Host: Niall J. English

*School of Chemical and Bioprocess Engineering, University College Dublin, Belfield,
Dublin 4, Ireland*

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 probing the thermodynamic and kinetic stability of methane hydrate exposed to microwave field in order to promote the melting process in a marine environment with associated operational/economic benefits in terms of controlled methane release strategies. In particular, we are interested in investigating the interaction between the silica surfaces and the hydrate structures, which may provide changes in the local structure of water molecules near the liquid-solid interface, thus altering the stability of hydrate compounds (a key point in melting process investigation for methane release strategies). This last point is particular intriguing for developing new methane release strategies, and it is worth to remark that 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 study particularly timely.

During the STSM at UCD (from 07-03-2017 until 21-03-2017), we performed a computational study on hydrate stability in bulk two-phase system (fluid in contact with a silica solid phase) in presence of external electric field (static and microwave oscillating) by means of molecular dynamics simulations. To this purpose, we model a hydrophilic silica surface in contact with a block of methane hydrate mimicking a clathrate deposit in the deep ocean. High hydrophilic silica surfaces are likely the most common constituent of the marine rocks. 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

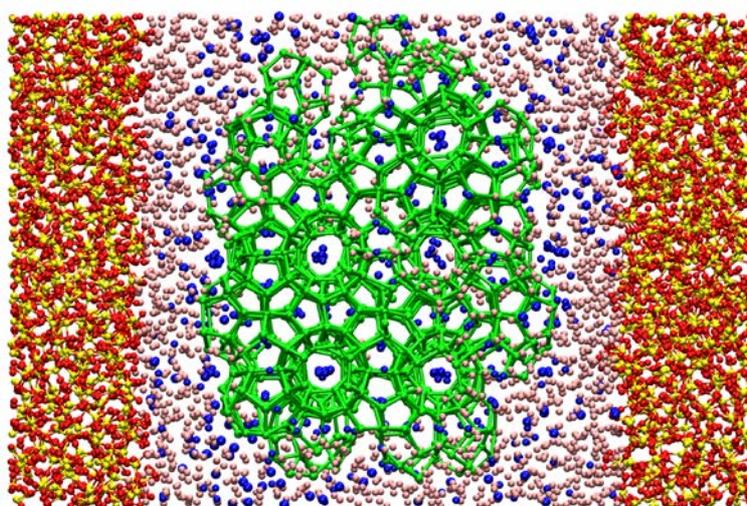


Figure 1: Snapshot of the obtained system showing a clathrate block (drawn in green) immersed in a solution of methane (blue) and water (pink) molecules. The silica bulk modeling a marine rock with a high hydrophilic surface is shown on both sides (oxygens drawn in red and silicons in yellow).

replicated 4 times, two and two along the axes x and y. The so obtained system was equilibrated for 1 nanosecond at 240 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 50x50x48 angstrom was added. Finally, we obtained a simulation box of approximately 50x50x73 angstrom, whose we count along z axis 25 angstrom of silica bulk and 48 angstrom of vacuum which will be later filled up with a 3x3x3 crystal unit (primitive) cell of methane hydrate bulk of structure I. The remaining vacuum space was randomly filled up with a mixed H₂O/CH₄ fluid (liquid phase) in ratio of 5.75 water molecules for each methane (the composition ratio observed in the clathrate structure I). The final system consists of 3280 water molecules and 560 methane. 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 Duan² with very good predictions of the relevant quantities characterizing a mixed H₂O/CH₄ fluid³ (e.g., density, diffusivity, etc.). The interactions 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 240 kelvin and 500 atmosphere. We have immediately observed a relaxation process involving the clathrate block and the methane/water solution at the interface of the crystalline phase during a preliminary molecular dynamics run of five nanoseconds by the Nosé-Hoover barostat method. The so obtained system (reported in Fig. 1) is the starting configuration for all the next simulations in presence of electric field. During the STSM at UCD,

several simulations were started to probe the hydrate stability under different conditions of external static electric field with intensity in a range 0.02– 0.5 V/Å. At the present, we are running a large series of oscillating microwave electric fields applied to the water-methane systems, started to record several melting phenomena providing promising results. The fields ranged in root-mean square (rms) electric field intensity from $E_{rms} = 0.02\text{--}0.5\text{ V/Å}$ and in frequency from = 1–100 GHz. In order to record the size of the hydrate crystal size we exploit the number of complete cages n_c . The number of connected cages, n_c is computed with a code developed by Jacobson *et al.*⁴ and based on the graph theory, where water molecules are the vertices of the graph and neighboring molecules, within a distance of 3.5 Å from each other, form its edges. Analysing the connectivity and ordering of the edges it is possible to identify complete clathrate cages^{5,6}.

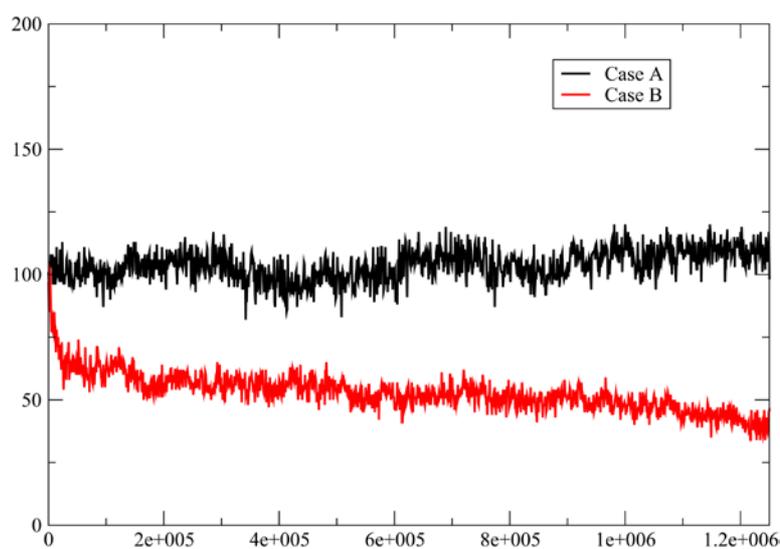


Figure 2: The number of complete cages, n_c , versus time (in femtoseconds) for the case A (zero field applied) and case B (external static field of intensity 0.2 V/Å).

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.

² 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.

³ 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).

⁴ Jacobson, L. C., Hujo, W., & Molinero, V. (2009). Thermodynamic stability and growth of guest-free clathrate hydrates: a low-density crystal phase of water. *The Journal of Physical Chemistry B*, 113(30), 10298-10307.

⁵ Lauricella, M., Meloni, S., English, N. J., Peters, B., & Ciccotti, G. (2014). Methane clathrate hydrate nucleation mechanism by advanced molecular simulations. *The Journal of Physical Chemistry C*, 118(40), 22847-22857.

As example of the collected results, we report in Fig. 2 the number of cages, n , as function of the simulation time, t , detected in two different runs: the first in absence of external electric field (case A), and the second with a static electric field of intensity 0.2 V/\AA (case B), both in NVE ensemble. In Fig. 2, the profile of the number of cages, n , shows two completely different trends for the cases under investigations. In the case A, we observe a slowly but evident crystal growth process due to the significant driving force for crystallization at the actual thermodynamic conditions of temperature and pressure. In the case B, we note a clear melting process showing that we are beyond the critical intensity of the applied electric field at which point crystal dissolution became possible.

We plan to identify the critical values in terms of intensity and frequency of the applied external electric field in order to exert a better control on the melting process of methane hydrate in marine environment. This is helpful in the context of developing new strategies for releasing natural gas from gas hydrate deposits. This aim matches some of the main objectives in the WG 2. In particular, 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 melting mechanisms in presence of external electric field for devising new releasing 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 instability (*e.g.*, melting timescales) without the upfront need to observe these phenomena in a marine environment and associated operational/economic challenges;

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 in upcoming international conferences providing a broad visibility for the MIGRATE action and WG2's goals, as a backdrop and introduction to these talks.

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 two *in statu nascendi*. In such framework, the STSM program is an excellent opportunity to lead to a strengthening of this collaboration, and, moreover, a closer partnership between the host and my home institution. The idea of using electromagnetic fields to induce marine-hydrate dissociation will be intriguing to investigate also in the context of inhibition of methane hydrates in marine environment. This may consent us to pursue a future STSM in this area, provide the budget available allows for this.

⁶ Lauricella, M., Meloni, S., Liang, S., English, N. J., Kusalik, P. G., & Ciccotti, G. (2015). Clathrate structure-type recognition: application to hydrate nucleation and crystallisation. *The Journal of chemical physics*, 142(24), 244503.