Molecular Dynamics Simulation of Methane Hydrate Dissociation

Niall J. English
Research Associate, National Energy Technology Laboratory, Pittsburgh

Introduction:

The kinetic mechanisms of clathrate hydrate crystallisation and dissociation, on both a macroscopic and a molecular level, are understood rather poorly. Any investigations thereof tend to be at least an order of magnitude inferior in accuracy vis-à-vis experimental measurements or molecular simulation of equilibrium thermophysical properties. The objective of this molecular dynamics (MD) study was to investigate the microscopic details of methane hydrate (type I) break-up at 276.65 K and 69 bar, in an effort to complement the experimental work in macroscopic dissociation of methane hydrates at this temperature and pressure which was carried out at the National Energy Technology Laboratory.

Simulation Methodology:

The polarisable TIP4P-FQ potential was used to model water, whilst a non-polarisable model was in use for methane. Long-range electrostatics were handled by the Lekner and Ewald methods. MD simulations were performed in the NPT ensemble, using a multiple time step approach in the case of the Lekner technique (1.5 fs for Lennard-Jones and minimum image electrostatics and 15 fs for a full Lekner evaluation). The time step was 1.5 fs for the Ewald method.

Non-equilibrium crystal-liquid systems were generated, comprising of 1900 to 2700 molecules, corresponding in composition to 100, 90 and 80%-occupied methane hydrates, in two independent ways. In the first instance, labelled as the 'constrained melting' approach, a pure hydrate of desired composition was 'melted' at 600K, holding the position of a central, approximately spherical, hydrate 'crystallite' fixed, and then relaxing the resulting systems at 276 K / 69 bar. Secondly, in the 'implantation' technique, separate pure hydrate and melted liquid water-methane phases were prepared and relaxed at this temperature and pressure, and spherical hydrate implants were placed in the centre of the liquid simulation boxes, taking care to avoid molecular overlap. Four different crystallite sizes were used for each composition, ranging in radius from 10 to 12.5 Å.

Tie-in with Experiment:

NPT simulations were carried out at 3.5 °C and 986 psig to correspond to the point at which dissociation was first noted by the jump in pressure upon the application of the temperature increase in NETL's Hydrate Unit 1 after 160 hours (cf. Figure 1). Molecular simulations cannot hope to replicate quantitatively the actual break-up rate: they cannot take into account macroscopic mass transfer and hydrodynamic effects (e.g. agitation currents), nor can they examine multiple crystals with a characteristic size distribution, nor take into account the important issue of the kinetics of desolvation of the methane released from the liquid phase to the headspace in the reactor unit. Simulation does, however, offer an insight into the microscopic details of hydrogen bond rearrangement as the nanocrystals break up.

Note the 'memory effect' on the subsequent recrystallisation in Figure 1, i.e. the absence of any nucleation time for the methane gas release from the hydrate upon a temperature increase in the cell: it is possible that this attributable to the presence of residual, microscopic, metastable hydrate clusters observed at the end of break-up process in simulations (to be commented on further later).
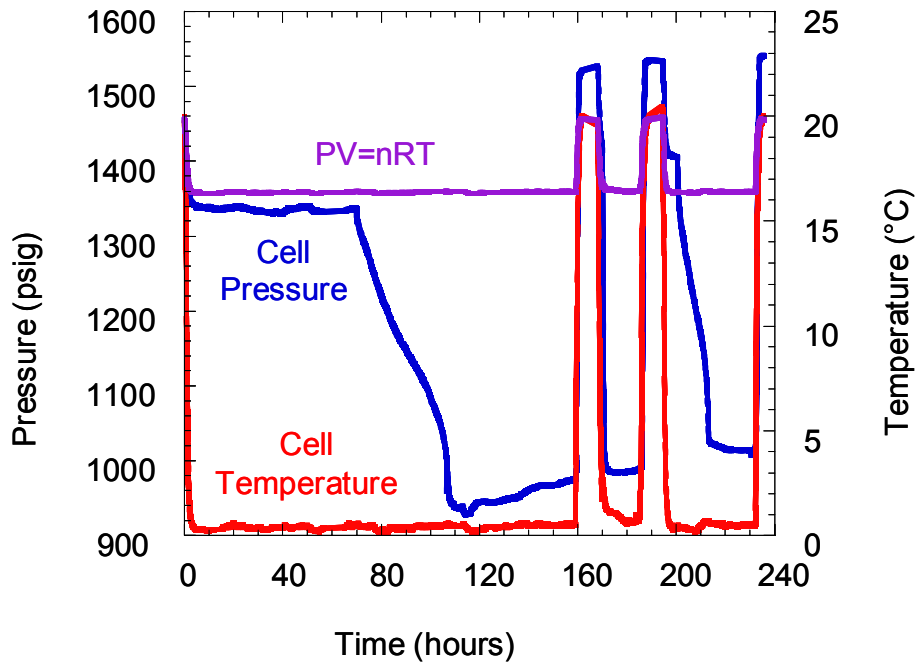

Figure 1: Temperature and Pressure Evolution during Hydrate Formation and Dissociation Experiment

Relaxation Time and the Importance of the Liquid Phase:

It was found that there was a characteristic period of reorientational relaxation of the molecules in the interfacial liquid layer at the start of two-phase simulations involving the approximately spherical crystallite cores generated from the 'constrained melting' method of system preparation. This led to a delay in the onset of cluster dissociation, as water molecules in this layer rotated to lower their potential energy and to stabilise their hydrogen bond arrangements, resulting in an artificial increase in the cluster size (cf. Figure 2 for the case of 100%-occupied systems). Such a delay in break-up was not as evident for the implanted systems. Thereafter, the break-up rates were similar for both modes of system preparation, in terms of number of water molecules leaving the hydrate phase per unit time. For the four different crystal sizes investigated (i.e. 10 to 12.5 A radius), it was found that the dissociation rates were also similar (cf. Figure 2). This implies that the liquid phase is rate-controlling in the dissolution kinetics.
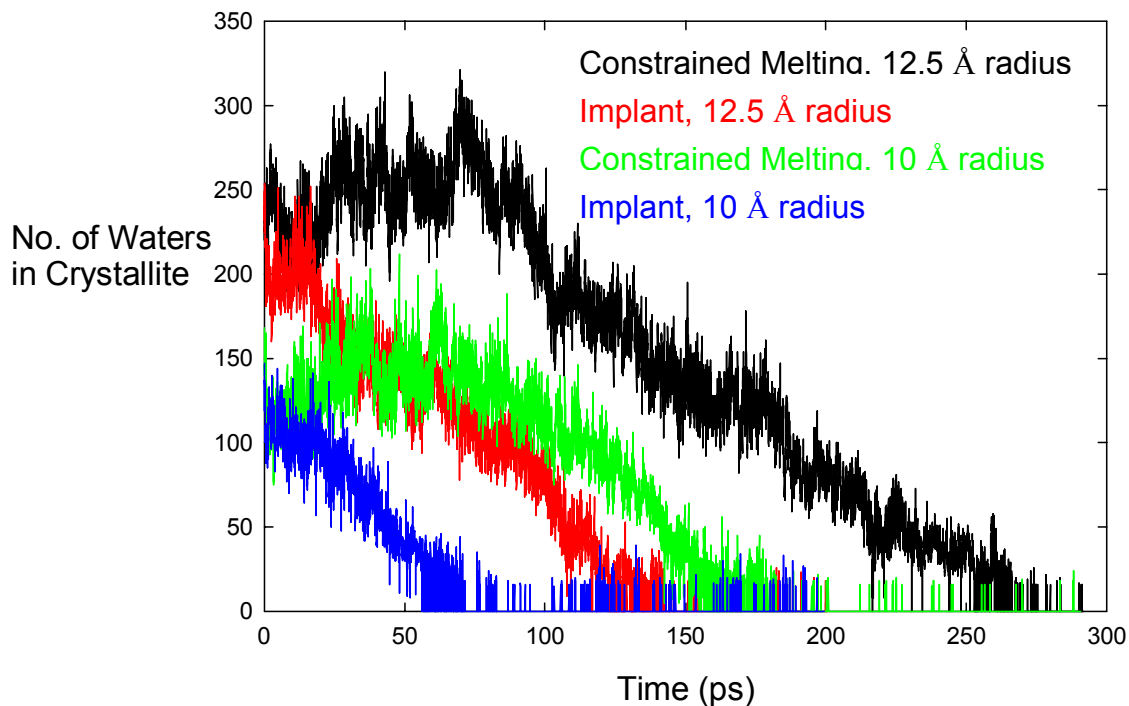
Figure 2: Number of Water Molecules in the Hydrate Phase as a Function of Time for Differently Sized Crystallites and Modes of System Preparation (100%-Occupied Systems)

The Role of System Composition:

       The break-up rates were slightly more sluggish for the two-phase systems with lower methane compositions in both phases (i.e. 80 and 90%-occupied), compared to the fully saturated system (cf. Figure 3), suggesting that the more complete hydrogen bonding networks formed in the liquid phase for a lower methane occupation inhibit more readily the break-up of the more rigid hydrogen bonding structure in the hydrate phase.
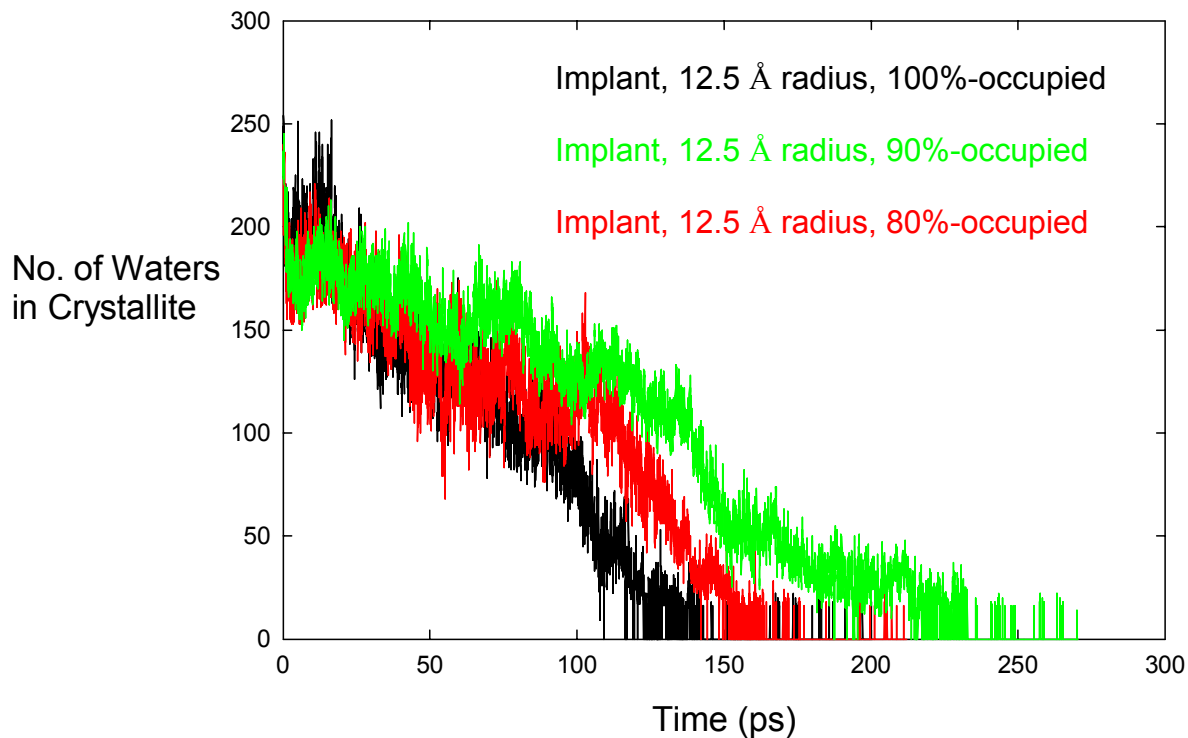
Figure 3: Dissolution of Nanocrystals as a Function of System Composition

The Effect of System Size:

It was found that placing identical implants in progressively larger liquid systems (ranging from a total system size of 1900 to 2700 molecules) did not alter the eventual dissolution rates dramatically, but tended to reduce any initial 'relaxation time' (cf. Figure 4 for the case of 80%-occupied systems).

It ought to be noted that the number of water molecules left in the residual, metastable, cluster after the dissociation of the original nanocrystal, which is detected by the geometric hydrate recognition criteria, is about twenty (cf. Figures 2, 3 and 4): this coincides with the number of water molecules in a pentagonal dodecahedral [5][12] cavity (and also in the coordination layer in a solvated methane molecule in the liquid state), and hence relates directly with the memory effect observed in the NETL experiment (cf. Figure 1).
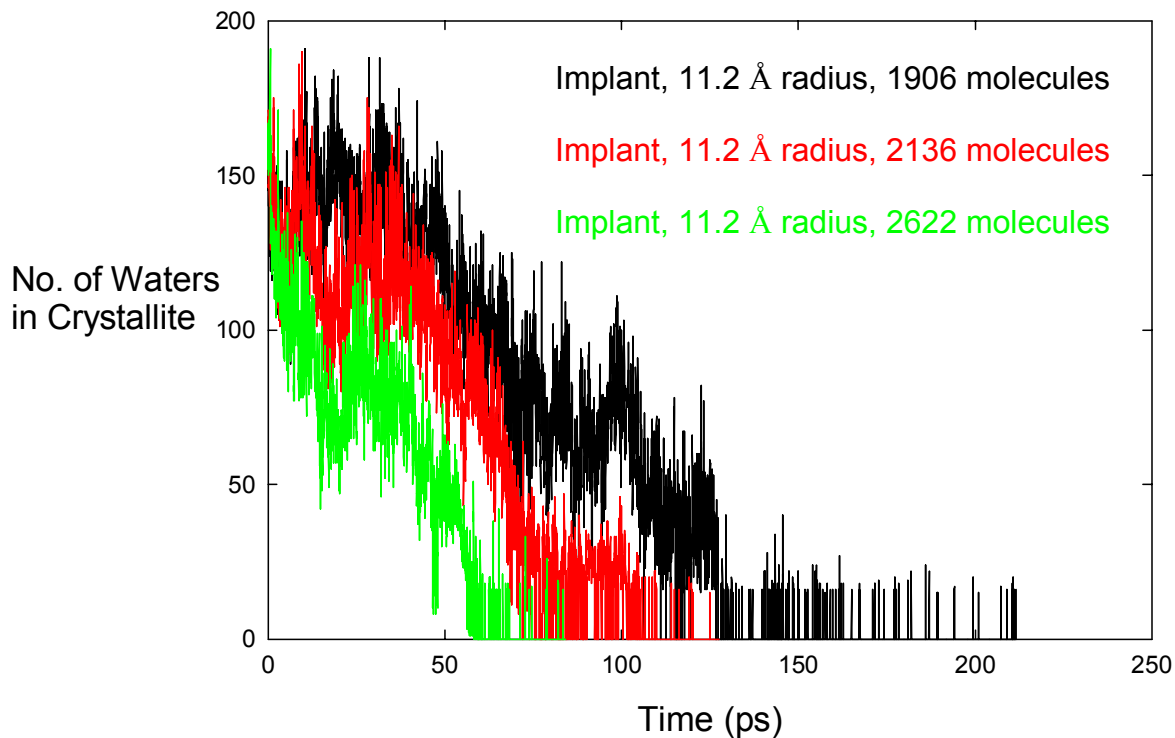
Figure 4: Influence of System Size on Break-up Kinetics of Crystallites for 80%-Occupied Systems

Break-up Statistics and the Influence of Electrostatics:

To assess the statistical uncertainty in dissociation rates, two additional simulations were performed for similar starting configurations for implants in 100, 90 and 80%-occupied nanocrystals of identical size (but with randomised velocities), for both the largest and smallest system sizes. Similar break-up rates were obtained.

To study the effect of different long-ranged electrostatics implementations on the results, the Ewald method was used and it was found that the nanocrystals dissociated at approximately twice the rate relative to the Lekner technique. It has been noted in the past that minimum image electrostatics lead also to faster dissolution rates: it would appear that less rigorous treatments of long-ranged electrostatic interactions do not model the diffuse phase boundary in crystal-liquid systems as well as the 'definitive' Lekner technique.