



Massively-parallel molecular simulation studies of ice and clathrate-hydrate nanocrystal and precursor formation

(Chemical Sciences and Materials)

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Introduction: Clathrate hydrates are nonstoichiometric inclusion compounds in which a host lattice composed of water molecules encages small guest atoms or molecules in the cavities. Gas hydrates are found naturally in the ocean depths and permafrost, and can form blockages in gas transmission lines. Their growth kinetics are understood poorly. The aim of this study has been to investigate both ice and methane-hydrate nano-crystal nucleation and precursor formation.

Methods:

Non-equilibrium molecular dynamics (NEMD) simulations [1] have been performed for methane-hydrate precursor [2] and ice dissociation and growth [3]. The tetrahedrally-biased Stillinger-Weber-based single-site united-atom potential for water, and spherically symmetric two-body term only Stillinger-Weber-based potential for methane, dubbed 'mW', was used [2]. Water-methane interaction is also represented by the two-body terms of the Stillinger-Weber potential. An atomistic representation for water and methane was also used [1]. Clearly, the absence of electrostatics and explicit rotational motion limits the realism with which interfaces can be treated. The LAMMPS [1-3] and NAMD [1,3] software packages were used on IBM Blue Gene platforms for molecular- and atomistic-level representations, and scaling curves are shown in Fig. 1 for BG- L, P and Q for both representations in larger bulk hydrates. In general, there is an overall trend towards higher absolute performance and better parallel scaling to higher processor-counts as one progresses from BG/L to /Q, as well as the increasing system sizes that can be handled successfully with reasonable relative-performance considerations.

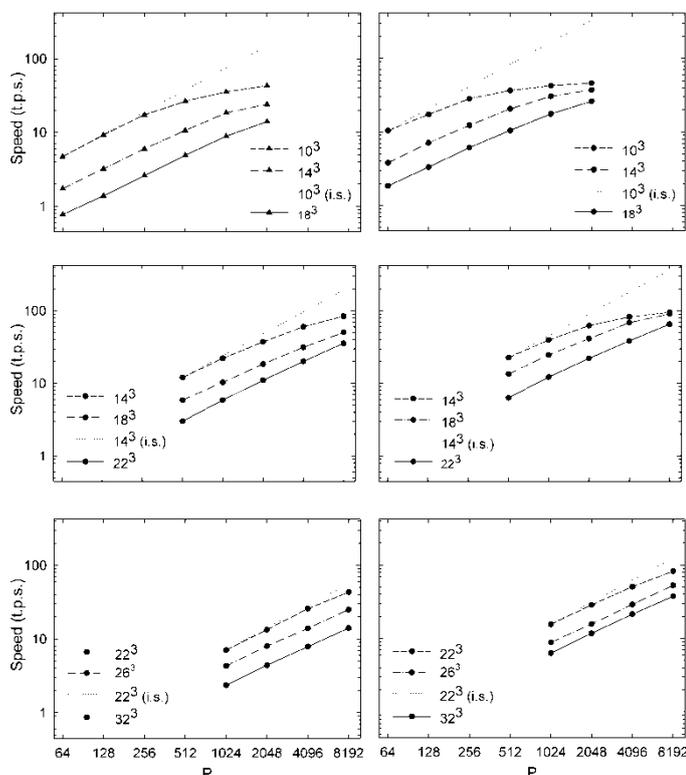


Figure 1 Time steps per second (t.p.s.) for BG/L (top), BG/P (middle) and BG/Q (bottom) for atomistic representation in NAMD (left) and coarse-grained set-up in LAMMPS (right). 'i.s.' denotes ideal scaling, for reference. 'P' denotes number of processes; this is understood to mean number of threads for LAMMPS on BG/Q (due to quad-threading with 64 threads per CPU thereon) [1].

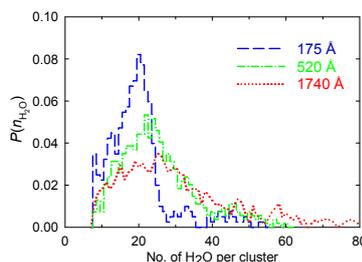


Figure 2 Probability distribution of number of waters in clusters after 400 ns in NEMD of planar interfacial systems of liquid water and liquid methane [2].

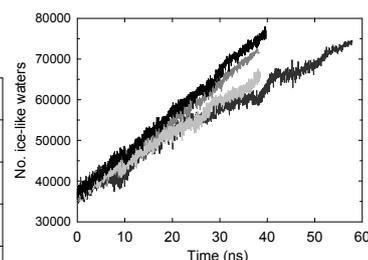


Figure 3 NPT mW growth of the 66 Å cluster is shown for systems increasing from 1 to 8.6 million molecules, with growth most rapid for the smallest system (in black, on left), and slowing as system size increases, with darkest grey on the right showing the 8.6 m system [3].

Discussion: Ice growth and decomposition was studied upon approximately spherical ice nano-particles of varying size surrounded by liquid water and at a variety of temperatures and pressures. The system box size was also varied for systems containing of the order of one million water molecules to almost ten million molecules, in order to establish system-size effects upon the growth and dissociation kinetics. It was found that there was a dependence upon system size on growth and dissociation, which points out the limitations of previous earlier simulation attempts in smaller simulation boxes (cf. Fig. 3).

Further, supercooled liquid water simulations were performed at various system sizes of the order to one to ten million water molecules, and the subtle re-arrangement of the structure and local density was explored as the system began to transition towards local ice-like conditions. Crucially, a system-size dependence was found upon these structural and dynamical rearrangements, which has been neglected in previous simulations.

The heterogeneous nucleation of ice nano-scale particles and the homogeneous nucleation of methane clathrate hydrates at water-methane interfaces were studied, again addressing the key question of the effect of system-size upon the results. It was found that both phenomena did depend on system-size, and that the subtle interplay between the frequency of box fluctuations and dilations with the underlying molecular rearrangements towards free-energy basins was quite important on influencing the outcome (cf. Fig. 2).

In the future, these studies of clathrate and ice nucleation, growth and dissociation will be continued, especially towards engineering applications, like using inhibitor compounds and temperature-/pressure-pulse strategies to regulate kinetics. Large-scale supercomputing is needed to study these complex non-equilibrium processes without being plagued by the tyranny of small systems and periodic boundary conditions affecting results adversely. Benefits to society will emerge from the greater understanding of these phenomena on a microscopic level, and the greater possibilities of devising kinetics-regulation strategies, e.g., to avoid pipeline blockage by hydrate plugs by inexpensive initial screening on supercomputing platforms, using molecular dynamics as an initial 'predictive' design tool.

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References:

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