140g Superheated Homogeneous and Heterogeneous Bubble Nucleation Rates Using Npt and Np$_{ZZ}$T Molecular Dynamics: Effects of Surface Interactions

Brian Novak, Edward J. Maginn, and Mark J. McCready

Performance of gas-evolving electrodes and boiling heat transfer surfaces could be substantially improved if it were possible to control the gas bubble nucleation process. While surface geometry is known to play an important role, at least at some length scales, if gas or vapor can be trapped, the effect of chemical interactions between liquid and solid is not known. This study examines this question by comparing vapor nucleation rates of for Lennard-Jones argon near a Lennard-Jones fcc solid with different solid-fluid interaction strengths and with the purely homogenous fluid rates.

A molecular dynamics approach is used employing an NPT ensemble with 2500 atoms for the homogenous case and the NP$_{zz}$T ensemble with 2302 fluid and 648 solid atoms for the heterogeneous case. The normal stress (P$_{zz}$) on an upper (“opposing”) wall potential is controlled by moving the position of the wall potential. Nucleation is achieved by quickly ramping up the set temperature of equilibrated configurations. The method used by Bartell[1] to calculate nucleation rates from sets of nucleation times is used.

In all calculations, the set pressure or normal stress is $P^* = 0.01$ (4.23 bar). Dimensionless values use the fluid-fluid parameters. For the smooth solid surfaces, three cases are considered by varying ε_{fs}, the solid-fluid interaction parameter, from ½ the value of the fluid-fluid parameter ε_{ff} (most repulsive) up to 1.518 times the fluid-fluid value. For $\varepsilon_{fs}/\varepsilon_{ff} = 0.5$, nucleation is fastest due to the the relative solid-fluid repulsion which enables void formation. The nucleation rates vary from 1.6×10^{34} m^{-3}s^{-1} to 1.0×10^{35} m^{-3}s^{-1} for T* from 1.091 to 1.124 (132 to 136 K) and the free energy of forming bubbles larger than the critical size is $\Delta G^* = 90$ (91 kJ/mol). For $\varepsilon_{fs}/\varepsilon_{ff} = 1.0$ the nucleation rates vary from 1.2×10^{33} m^{-3}s^{-1} to 4.9×10^{34} m^{-3}s^{-1} for T* from 1.107 to 1.124 and the free energy is 298. For $\varepsilon_{fs}/\varepsilon_{ff} = 1.518$, the nucleation rates vary from 1.8×10^{33} m^{-3}s^{-1} to 3.2×10^{34} m^{-3}s^{-1} for T* from 1.111 to 1.124 and the free energy is 294. The nucleation rates and energies in the second and third case are nearly the same which suggests that the limit of the effect of the fluid-solid interactions on nucleation has been reached.

As expected from classical theories, nucleation is easier in all three heterogeneous cases compared with the homogenous case. The nucleation rates vary from 1.7×10^{33} m^{-3}s^{-1} to 7.8×10^{34} m^{-3}s^{-1} for temperatures between 1.186 and 1.194 and the free energy is 632.

The results show a large enough change in nanoscale void formation rates caused by chemical interactions to suggest that experiments to determine the effect on bubble formation could be worthwhile.

[1] L.S. Bartell, *J. Phys. Chem. A*, **106**(45), 10893 (2002).