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Long time scale simulations of transitions in and on the surface of solids

Diffusion and chemical reactions in and on the surface of solids are typically activated events, i.e. the system needs to climb over an energy barrier in order for the atoms to rearrange. A typical "fast" event on laboratory time-scale may have an energy barrier of half an electron volt and occur thousands of times per second. In a direct classical dynamics simulation (solving Newton's equations of motion) such an event is, however, impossibly slow even when simple interaction potentials are used, requiring thousands of CPU-years because of the small time step required for faithful representation of atomic vibrations. A different approach is needed for the simulation of atomic systems on laboratory time-scales. We present an extension of the kinetic Monte Carlo (kMC) algorithm - adaptive kMC - where the mechanism and rate of transitions are found within the harmonic approximation to transition state theory [1]. A search method based on the finding just the lowest frequency normal mode [2] is used to search for saddle points on the potential energy rim surrounding the basin corresponding to a given state of the system. In this way, the need for a predefined event table and lattice approximation typically employed in kMC simulations is eliminated. Application of this algorithm to the dissociation of boron clusters in silicon will be presented [3]. There, atomic forces evaluated by density functional theory are fed directly into the adaptive kCM algorithm. An interstitial mediated mechanism for the breakup of the highly stable B3I cluster, involving a B3I2 intermediate, gives good agreement with experimentally measured activation energy while direct dissociation has much higher barrier. Another application that will also be mentioned is multiple time scale simulations of the growth of an Al(100) surface using an empirical EAM potential. There, a screen saver has been developed and used to distribute the computations on more than a hundred PCs (see <http://eon.chem.washington.edu>). The simulations show that concerted processes involving multiple atoms are remarkably effective in smoothening the surface even at a very low temperature where adatom diffusion on the flat Al(100) terrace is inactive.

[1] G. Henkelman and H. Jonsson, *J. Chem. Phys.*, 115, 9657 (2001).

[2] G. Henkelman and H. Jonsson, *J. Chem. Phys.*, 111, 7010 (1999).

[3] Blas Uberuaga et al., *Physica Status Solidi B*, 233, No. 1 (2002)

(These and other recent publications from the group are available at www.hi.is/~hj)