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Discussions

Interactive comment on "A 3D particle Monte Carlo approach to studying nucleation" *by* Christoph Köhn et al.

Anonymous Referee #2

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The authors present a Monte Carlo scheme for simulating the evolution of a set of particles in a spatial volume, designed to represent sulphuric acid monomers and their clusters. The particles combine together when a stochastic spatial move takes them within an overlap distance of one another, and they fragment with the emission of a monomer according to a stochastic thermal evaporation process.

In my opinion, there are numerous problems with this manuscript and I cannot recommend publication.

The authors state in the introduction that the technique might possibly provide 'new insights into the process of nucleation'. However, I am not persuaded that this has been achieved, and the authors do not enlarge on this claim in the conclusions. The MC method presented is essentially a numerical implementation of the stochastic evolution

of a cluster size distribution, and I suspect that the outcomes are consistent with much less elaborate treatments, such as a simple Becker-Doering rate equation approach. Namely, the events are infrequent in the situations considered (and probably do not give rise to spatial correlations between potential collision partners) and are dominated by single monomer attachment and detachment processes rather than cluster-cluster collisions. If the reported cluster size distributions were compared with the results of such a rate equation scheme, involving the solution of a few ODEs for a set of spatially averaged cluster populations, I would expect to find the outcomes compatible. This would have been a very useful benchmarking procedure to assess the value of using a 3D approach.

The updating of the configuration is not entirely clear. In a couple of places, the authors refer to the velocities of the particles. However, the dynamics, in equation (1), seems to involve stochastic moves in spatial position only. What is the purpose of considering the velocities? Is the update a combination of ballistic motion and diffusive jumps? The discussion seem to imply only diffusion.

Furthermore, the selection of the direction of diffusive motion does not seem right. The spherical polar angles theta and phi are sampled uniformly from their respective ranges (page 3, line 10). This is fine for phi, but the angle theta should be sampled nonuniformly (in proportion to sin(theta)) in order to provide a uniform sampling of the 4 pi of solid angle. Uniform sampling of theta improperly favours the polar regions of a globe rather than the equator and if this is indeed the scheme implemented, then the particles will tend to diffuse up and down (with respect to the z axis of the simulation cell) and not sideways. Since the MC scheme is intended to be physically representative, this is a significant drawback. But perhaps this is a typo in the manuscript.

The authors are apparently unaware that other 3D 'brute force' numerical simulations have previously been carried out to investigate the process of nucleation. These have involved molecular dynamics rather than (kinetic) Monte Carlo configurational evolution, but the aim is very similar, as is the computational expense. Recent papers (2014-

16) by Diemand, Angelil and the Tanakas should be consulted, and older studies by Wedekind et al (2006-2007).

The authors seek to compare their results with experimental values of nucleation rates for sulphuric acid clusters of radius 0.85 nm, even though no clusters of this size are generated in their simulations. In order to make this assessment, they fit an exponential function (equation (8)) to the cluster size distribution at each timestep and extrapolate to the target size. This is not a convincing approach since it is likely to introduce large uncertainty. But even if there were reason to use such a function, the nucleation rate is not a mean population at a certain size divided by the elapsed time, as given in equation (9); instead it is a current or flow of clusters through that size. In an asymptotic stationary state, the definition used by the authors would produce a nucleation rate of zero. Only if there were a maximum size cluster in the scheme, receiving clusters from the size below but not losing them to sizes above or below (i.e. equivalent to a cluster sink), would such a definition be appropriate. The extracted nucleation rates are stated to be compatible with experimental values of sulphuric acid, within error bars, but the statistical errors quoted in Table 1 are very large, and the claim of consistency is weak.

Finally, I have reservations about the assumed evaporation rate in equation (7). The authors have introduced a factor of R_1/R on the grounds that the saturated vapour pressure over a curved interface is lower than that over a flat interface, such that the evaporation rate should increase as the radius decreases. But it is the Kelvin term (the exponential in equation (7)) that represents this effect: I do not see why a new factor is required. The Kelvin term is a consequence of the capillarity approximation used in the construction of the excess free energy of cluster formation from monomers, and so the extra factor corresponds to a non-classical term (in the sense of an addition to Classical Nucleation Theory (CNT)) in the excess free energy. The introduction of such a new term has not been justified.

In passing, setting the evaporation rate equal to the Kelvin form ought to lead to a nucleation rate consistent with CNT, at least in some circumstances, and this would also

be a useful benchmark exercise. Another useful benchmark would be to compare the simulations at 200 K with known analytical results for a Brownian coagulation model.

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