



Rethinking the first nucleation theorem in atmospheric nucleation

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The first nucleation theorem is a very useful tool in experimental studies of vapor-liquid nucleation, as it relates the derivative of the nucleation rate with respect to saturation ratio to the critical cluster size of the system. In other words, one can measure the nucleation rate of a system at various saturation ratios (holding all other variables constant), and learn information concerning the structure of the critical nucleus. This is an invaluable tool, as it's quite difficult to probe the structure of the critical nucleus directly. It has been well-established that the theorem is accurate for systems with a single maximum in the free energy profile. In the case of other systems, however, the case is not so clear. In particular, if there is also a local minimum on the free energy surface in addition to the global maximum. This is often the case in ion-induced nucleation, where the addition of multiple neutral molecules (such as water) serve to stabilize the ion before the free energy barrier to nucleation. It has been argued that the first nucleation theorem can still be used in this case, either without modification or with a minor systematic modification, although in-depth exploration is lacking in the literature.

Through the use of the Atmospheric Cluster Dynamics Code (ACDC), a collection of Perl and MATLAB scripts, we have solved the system of differential equations for various fictitious free energy profiles displaying a free energy maximum and one (or zero) free energy minimums, including one directly applicable for ion-induced nucleation. The fictitious free energy profiles were produced for single-component water nucleation, while the ion-induced case is the quasi-one-component water + ion nucleation system. In addition to the first nucleation theorem, a formula derived by McGraw and Wu was also used, which is a more general expansion of the first nucleation theorem. Given that these formulas were both derived under the assumption that only monomers can collide and evaporate from clusters, and given that this same restriction is not present in explicit solution of the differential equations deriving the system, both cases were tested by ACDC (allowing only monomer collisions/evaporations, and allowing all collisions/evaporations). In order to compare to the experimental case, we explored the possibility of holding various concentrations constant while computing the derivative of the nucleation rate with respect to the saturation ratio: the monomer concentration, the concentration of the cluster at the free energy minimum, and the total concentration of molecules in the system. We have found that the first nucleation theorem holds true for the case where there is no free energy minimum (as expected). For a fictitious free energy profile with one free energy minimum, the first nucleation theorem predicts incorrect results, regardless of the quantity held constant. For a curve produced by considering the ion-induced nucleation of water, the first nucleation theorem was found to give decent results when the concentration of the cluster located at the free energy minimum was held constant, but not as good of results in the other two cases. These results have a significant impact on the determination of critical cluster composition from experiments in atmospheric nucleation.