

Interactive comment on “A model for particle formation and growth in the atmosphere with molecular resolution in size” by K. E. J. Lehtinen and M. Kulmala

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This paper describes a model on the molecular scale which is used to calculate results for two nucleation events observed at Hyytiälä in Finland. The novelties in the model and the results are interesting and merit publication, but first the authors need to recognize the limitations of the model and improve the comparison with the data.

MAIN POINTS

1. The collision rate used in the paper may be an improvement over the "traditional" expression commonly used for calculations in atmospheric aerosol science, but it is not unique in extension to molecular sizes. For example, general forms are given by Oh

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and Sorensen (1997) which extend down to molecular sizes.

2. The claim in the paper that the discrete coagulation equations (4) are exact is not necessarily correct. At a molecular level, these equations are "birth" or "growth" equations (Goodrich 1964a, Clement and Wood 1979) in which particles only grow; no emission occurs. When an aerosol particle is in equilibrium with the surrounding vapour, the emission rate of monomers is equal to the growth rate. Emission terms cannot be neglected unless the ambient vapour pressure or vapour molecule concentration is much larger than its equilibrium value. This is certainly not the case for particles of very small sizes below or near a nucleation barrier, and may not be for larger sizes and the condensation of semi-volatile species, e.g. water, in the atmosphere. The relevance to the present application is that the region of very small size is included, and that the condensing species may be semi-volatile organics.

Thus emission rates of molecules are probably not negligible in the present context, although they almost certainly are for emissions of larger clusters. The basic equations at a molecular level are then the "birth and death" or "growth and decay" equations (Goodrich 1964b, Clement and Wood 1980), which are also familiar in the nucleation context as Becker-Döring equations. The continuous approximations to these equations have the form of Fokker-Planck equations for which several versions have been suggested (see Shizgal and Barrett 1989). Both the basic equations and their Fokker-Planck approximations contain diffusion in size space which produces a real physical mechanism for spreading the particle size distribution, as opposed to the spurious diffusion arising in the fixed sectional method for numerical solution of the general dynamical equation (Friedlander 2000). This equation does not contain any size diffusive terms, an approximation which may be generally justified at large sizes, but possibly not for the nm sizes considered here.

I am not suggesting that the authors amend their paper to include the emission terms in their calculations, but the paper should recognize their existence and the resulting possible lack of exactness.

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3. Calculations. The bases for the calculations are not explained in this paper. How was the nucleation rate chosen? Was an initial background aerosol for coagulation taken from experiment?

4. Comparison with observations. A constant value was chosen for the vapour concentration for condensation. It was previously shown that the condensing species for Finnish nucleation events was likely to be produced by photochemical reactions, and that an estimate for this concentration would be the radiation intensity divided by the molecular removal rate onto the observed aerosol (Clement et al., 2001). This ratio should be obtainable from observations on the two days in question, and plots during the days would provide an experimental check on the validity of the constancy of the concentration.

TECHNICAL CORRECTIONS

1. Eq.(3). The velocities, c , are not defined and nor is the formula used for the diffusivity.

2. In two references the title of the paper is not given.

3. In Kerminen and Kulmala, the journal should be J. Aerosol Science.

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