

Nucleation of vapours - molecular content of critical clusters and activation of nanoparticles

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Keywords: nucleation, molecular cluster, Kelvin equation, condensation particle counter.

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During the last years considerable advances in the study of gas to liquid phase transitions were achieved. Experiments on particle new formation have been extended down to molecular sizes (Winkler *et al.* 2008). Measurements of critical cluster sizes were performed pointing directly to the key step in the phase transition (Winkler *et al.* 2012). Atmospheric observations have demonstrated particle formation by nucleation to be a frequent phenomenon in the global atmosphere (Kulmala and Kerminen 2008). Wang *et al.* (2012) have pointed out that the initial growth of freshly nucleated small molecular clusters in the atmosphere can be described by heterogeneous nucleation. Despite of recent progress, however, nucleation processes are still among the least understood phenomena in aerosol science.

In this presentation we are providing an overview over some recent studies of nucleation and condensation processes at the Vienna expansion chamber system (Wagner *et al.* 2003).

New particle formation by homogeneous or by heterogeneous nucleation generally proceeds via molecular clusters of critical size, beyond which molecular clusters are likely to grow further to form new particles. Accordingly, critical clusters can be considered as the starting point of the nucleation process. The radius r^* of a critical cluster is related to the saturation ratio S and temperature T of a condensable vapour by

$$r^* = \frac{2\sigma M}{\rho RT \cdot \ln S} \quad (\text{Kelvin equation}),$$

where σ , ρ and M are surface tension, density and molar mass of the condensing liquid, respectively. This relation has been derived under the idealizing assumptions of the classical nucleation theory and its range of applicability needs to be tested experimentally. Under quite general assumptions Oxtoby and Kashchiev (1994) have derived the relation

$$\Delta N^* \cong \left(\frac{\partial \ln J}{\partial \ln S} \right)_T \quad (\text{nucleation theorem}),$$

which allows to approximately determine the (excess) molecular content ΔN^* of a critical cluster from the slope of experimental nucleation rate J vs saturation ratio S curves in a log-log plot. Recently Vehkamäki *et al.* (2007) have reformulated this theorem for application to heterogeneous nucleation. Possible limitations of the validity of the nucleation theorem have recently been discussed by Vehkamäki *et al.* (2012).

Homogeneous nucleation experiments (Strey *et al.* 1994) have provided information on the sizes of

critical clusters down to diameters of about 2nm in satisfactory agreement with the Kelvin equation.

Experiments on heterogeneous nucleation in n-propanol vapour by Winkler *et al.* 2008 allowed for the first time to bridge the scale from molecular clusters to nanoparticles. For charged seed particles an enhancement of heterogeneous nucleation and a significant sign preference were observed. The onset vapour supersaturations required for activation of charged and of uncharged nanoparticles were found to be well below the Kelvin prediction. As a consequence the term "Kelvin diameter" needs to be critically reconsidered and the fundamental detection range of Condensation Particle Counters is extended to smaller particle diameters.

Recently we performed experiments on heterogeneous nucleation on single ion molecules (Winkler *et al.* 2012). By means of the nucleation theorem we obtained critical cluster diameters strongly exceeding the diameter of the seed molecules, but in satisfactory agreement with the Kelvin-Thomson equation.

In experiments on the temperature dependence of heterogeneous nucleation (Schobesberger *et al.* 2010; Kupc *et al.* 2013) we surprisingly observed unexpected temperature trends for certain combinations of particle and vapour compositions. This seems to be evidence for strong molecular-scale interactions at the seed particle surface (McGraw *et al.* 2012).

This work was supported by the EC Seventh Framework Programme under the grant agreement no. 215072 (Marie Curie Initial Training Network "CLOUD-ITN") and by the Austrian Science Fund under project no. P19546 and L593.

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