Heterogeneous Nucleation on Nanometer and Sub-Nanometer Sized Charged Atomic Clusters

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Condensation of vapour molecules on nanoparticles and clusters plays a crucial role in a number of industrial and environmental processes.

An important factor affecting vapour condensation on nanoparticles in the nanometer range is their charge (Wilson, 1897, Nadykto *et al*, 2003). The presence of charge creates an electric field in the vicinity of the particles that lowers the free energy barrier required for nucleation. As a result charged clusters can be activated at lower supersaturation levels than the neutral.

Although theory can predict this difference in the nucleation process for charged and neutral particles, it is not yet fully understood why positive particles require higher supersaturation level than negative particles in order to become activated.

Heterogeneous nucleation studies can be performed with the use of a Condensation Particle Counter (CPC). This instrument is commonly used as an aerosol nanoparticle detector, providing concentration measurements. It relies on the condensation of vapour molecules on to the particle surface, by creating a supersaturated environment from which particles pass through. This leads to the formation of a liquid droplet around the particle, large enough to be detected optically.

In this study, we report measurements of the detection efficiency of a commercial ultrafine butanol based CPC (3025, TSI, Inc., St. Paul, MN), in the sub 3 nm singly charged particles range.

The experimental setup for measuring the detection efficiency consisted of a spark discharge generator (SDG), a half-mini DMA (M. Attoui *et al.*, 2013) an aerosol electrometer and the CPC.

The SDG has been used to generate small singly self-charged silver atomic clusters, of 5 atoms or less. The generation and production of these small clusters will be presented in another abstract for the EAC 2013.

The CPC was operated at increased temperature difference between saturator and condenser, in order to improve the detection efficiency for small sub-nanometer particles. The operation of a boosted-CPC can be found in literature (Kuang et al.2011). As shown in Fig.1, the boosted CPC is capable of detecting sub-nanometer sized atomic clusters.

A clear alternating trend is observed, as the cluster size decreases. For clusters of inverse mobility (1/Z) larger than ~ 0.8 Vs/cm^2, presence of negative charge shows higher detection efficiency than positive one. Meanwhile, for clusters of 1/Z< 0.8 Vs/cm^2, the trend is reversed. Moreover, very small positive clusters are activated with the same efficiency, regardless of the decreasing size. This comes in contrast with the classical theory of heterogeneous nucleation, in which nucleation rate should decrease with decreasing particle size.

The ability of negative particles, with sizes larger than ~1 nm, to activate at a lower supersaturation has been observed elsewhere (Winkler *et al.*¸2008). A possible explanation for this phenomenon involves the ion-dipole molecule interaction. Non-symmetrical polar molecules will orientate on the particle surface according to the particle polarity. This leads to a difference in the structure of positive and negative nucleating embryos.

In such small cluster sizes, it is expected that a thermodynamic approach of nucleation will not be sufficient to interpret experimental data. Indeed, a theory involving a quantum description of the cluster dynamics seems to be more accurately approaching the nucleation process, for small sub 3nm atomic clusters (Nadykto *et al*, 2006).

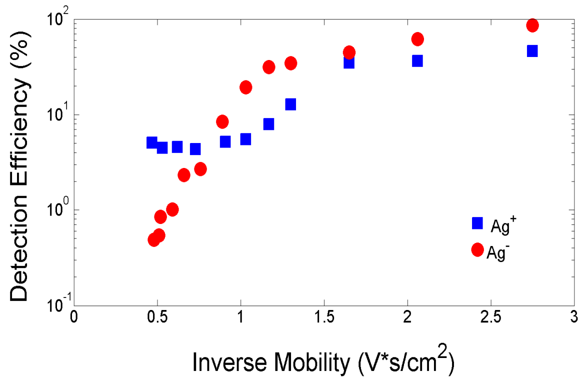

Figure 1. Measured detection efficiency of positive and negative atomic clusters suspended in N_2.

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