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Interactive Comment

Interactive comment on "Mass transfer effects in hygroscopic measurements of aerosol particles" *by* M. N. Chan and C. K. Chan

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We would like to thank the referee, who gives very helpful comments in improving the paper.

Specific comments:
In its current form, the analysis is based almost entirely on results from lab and field measurements, with practically no theoretical background or discussion (or it is scattered around the text). At the very least, the manuscript should include one or two paragraphs where the authors would explicitly summarise the most plausible factors influencing (or hindering) the establishment of hygroscopic equilibrium (coverage of particle surface by surfactants, size, phase changes inside the particles etc.). How accommodation coefficient is related to these issues and how small it should be to have

influence on mass transfer?

The influence of particle size (diameter=D) on water mass transfer effects should be discussed more explicitly in the text. First, since the particle volume is proportional to D to the power 3 and condensation flux to D to the power 1-2, the time scale for achieving an equilibrium size goes as D to the power 1-2, unless there other are factors that are dependent on size. For example, different-size and type particles have a different probability to have surfactant layer of a certain thickness.

Response: We agree with the referee's suggestion to include a theoretical analysis on how the particle size and accommodation coefficient affect the time scale required for the particle to achieve equilibrium. We have added an equation and cited calculated results in the literature to show that particles can grow to their equilibrium size within seconds, when the accommodation coefficient is larger than 0.001. However, for particles with a much smaller accommodation coefficient such as in the case with a presence of surfactant on particle surface, the establishment of gas-particle equilibrium may be hindered. Another possibility leading to non-equilibrium growth is the internal mass transfer effects within the droplets, which have been reported in our previous EDB measurements of selected solutes.

The following paragraph has been added in Section 3 of the revised manuscript.

Theoretical analysis of the gas-particle equilibrium time scales for the water uptake for a non-volatile particle is available in the literature (Kerminen, 1997). In gas condensation, the flux of a species into a single particle, I_i, can be described by:

$$I_i(d_p) = \frac{2\pi D_i[C_i - C_{i,eq}(d_p)]}{1 + 2\lambda/\alpha_i d_p}$$

where d_p is the particle diameter, D_i is the gas-phase diffusion coefficient of the species, i, C_i and $C_{i,eq}$ are its concentration in the gas phase and over the particle surface, respectively, λ is the air mean free path, and α is the accommodation coefficient accounting for the imperfect accommodation of the species on the particle

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surface. Kerminen (1997) estimated the time required for the achievement of water equilibrium to be between 8x10^{-6}s and 0.1s for 100nm and 500nm particles at 90%RH and at 0°C and 25°C with different accommodation coefficients (0.001 to 1). The typical residence time of a few seconds in the RH conditioner in TDMA measurements is adequate for most equilibrium hygroscopic measurements. Significantly longer equilibrium time may be required when the accommodation coefficient is much less than 0.001. Chuang (2003) found that some atmospheric particles exhibited equilibrium time scale in the order of seconds to tens of seconds in their TDMA measurements. He estimated that the accommodation coefficients of these particles are in the range of 10^{-4} to 10^{-5}. This falls into the lower range of values reported in laboratory experiments using model aerosols with single component films. Atmospheric particles containing organic films resulting in an accommodation coefficient in the range of 10^{-4} to 10^{-5} may not achieve equilibrium in TDMA experiments.

Most researchers choose NaCl or $(NH_4)_2SO_4$ particles to verify the time scale for equilibrium measurements with the implicit assumption that the water vapor -particle equilibrium is also achieved for other particles, including atmospheric particles, in the same time scale (order of seconds). However, in addition to possibility of having particles of a very low accommodation coefficient, transport effects in very viscous can also hinder gas-particle equilibrium (Seinfeld, 1986; Kerminen, 1997; Chan et al., 1998). Chan and coworkers have experimentally shown that the achievement of equilibrium of some aqueous droplets can be hindered by the transport limitation inside the droplets in their EDB measurements. For example, Chan et al. (2000) found that there is a significant retardation of water evaporation (and growth) rate of magnesium sulfate ($MgSO_4$) droplets at high concentrations (at low RH). Using Raman spectroscopy, Zhang and Chan (2000) attributed this delay to the formation of contact ion pairs and chain structures in highly concentrated droplets of $MgSO_4$. Moreover, Peng et al. (2001) observed that glutaric acid particles took a significant longer time (∼10 hrs) to completely deliquesce, compared to other dicarboxylic acids and multifunctional acids particles (∼40min). This mass transfer limitation in the growth process was also observed in sodium pyruvate particles by Peng and Chan (2001). These significant retardations in growth or evaporation rates were not found for NaCl or $(NH_4)_2SO_4$ particles in their EDB measurements. Overall, mass transfer effects in hygroscopic measurements of ambient particles and laboratory generated particles are possible if the particles are not allowed to have sufficient time to achieve their equilibrium sizes in the RH conditioner. Residence time of a few seconds may not be adequate, depending on the nature of the particles.

Reference added in the revised manuscript Chan, C. K., Choi, M. Y., and Zhang, Y.: Observation of mass transfer limitation in evaporation of single levitated droplets J. Aerosol Sci., 31(S1), S989-990, 2000.

Minor/technical comments:
On page 4060 (line 17), it is stated that the manuscript focuses on TDMA and EDB measurements. In reality, the focus is on TDMA measurements, as EDB measurements are discussed only briefly.

Response:
We agree with the referee's comment and have changed the sentence. "We focus our discussions on TDMA measurements in this paper."

On page 4061 (line 2) the acronyms "AC" and "DC" should be defined.

Response:
We have defined the AC and DC in the revised paper. "An EDB utilizes a combination of an alternating current electric field and a direct current electric field to levitate single particles (Davis, 1997)."

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 4057, 2005.