**Atmospheric
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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 for the valuable comments and suggestions. We have revised the manuscript and incorporated the change in the revised paper.

Main comment:
The hygroscopic growth depends, not only on the composition of the particles, but also on the size and shape of the particles. The shape is typically not known for the atmospheric aerosols, but the size is determined by classifying the aerosol with the first DMA. The size of particles both changes the equilibrium size (Kelvin effect) and also the time needed for the particle to grow to the final size. Since some of the experiments have been performed for particles of just some nanometers, these aspects needs to be considered.

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Response:
We agree with referee's comments. Referee 1 has also raised a similar comment on this issue. We have rewritten the section of 3. Equilibrium measurement. Owing to this analysis and re-discussion of the results referee has raised will be addressed in the revised manuscript and are additionally discussed in this section 3. In the revised section, we have addressed how the size of the particles determines the time required for the particle to achieve equilibrium in the hygroscopic measurements.

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 surface. Kerminen (1997) estimated the time required for the achievement of water equilibrium to be between 8×10^{-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

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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 ($\sim$10 hrs) to completely deliquesce, compared to other dicarboxylic acids and multifunctional acids particles ($\sim$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.

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Other comments:
Page 4060, line 19: An essential part of the setup is the humidifier of the sheath air of the second DMA. The details of the humidification/dehumidification of the particles differ for different setups and this aspect could be discussed further.

Response:
The point raised by the referee is well taken. Nevertheless, since our focus of the discussion is on the residence time, we would refer readers for the details of experimental setups including the sheath air to the literature. We do not discuss the humidification/dehumidification of the particles in the revised paper.

Page 4061, line 17: Hansson et al (1998) studied the uptake of water for NaCl particles coated with significant amounts of organic compounds. They observed very little effect even with thick layers of the organic compounds. It is not clear if this type of coating is possible in atmosphere and whether it can play any role in preventing the particle growth.

Response:
The types of coating studied by Hansson et al. (1998) have been detected in atmospheric aerosols (Duce et al., 1983; Gill et al., 1983). As mentioned by the referee, the coated NaCl particles can still be able to deliquesce and crystallize in presence of organic coating within the timescale of their TDMA measurement (10-20s). It is noted that since there is a rather large range of RH between two data points ($\sim$10%RH) in Hansson et al., it is not possible to clearly determine how the presence of organic coating affect the deliquescence and crystallization RH of NaCl particles. Since we did not discuss Hansson et al.'s work on Page 4061 and we do not know in what context we should include the above discussion, we will leave this comment in the discussion here.

Reference Duce, R. A., Mohnen, V. A., Zimmerman, P. R., Grosjean, D., Cautreels, W., Chatfeld, R., Jaenicke, R., Ogren, J. A., and Wallace, G. T.: Organic material in the

global troposphere, Rev. Geophys. Space Phys., 21, 921-952, 1983.

Gill, R. S., Graedel, T. E., and Weschler, C. J.: Organic films on atmospheric aerosol particles, fog droplets, cloud droplets, raindrops, and snowflakes, Rev. Geophys., 22, 903-920, 1983.

Page 4061, line 26: The work of Kerminen (1997) gives theoretical background for analysis of this study. The actual times for particles to reach the equilibrium size should be given and discussed here. This is important especially for particles of different sizes. In addition, the order of magnitude of the accommodation coefficient to be relevant slowing down the particle growth could be discussed further here.

Response:
Agreed. A similar comment was made by Referee 1. We have revised the manuscript accordingly. Pls refer to our response of Referee 1 for details.

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

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