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On cloud modelling and the mass accommodation coefficient of water

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Abstract

The mass accommodation coefficient of water is a quantity for which different experimental techniques have yielded conflicting values in the range 0.04–1. From the viewpoint of cloud modelling, this is an unfortunate situation, since the value of the mass accommodation coefficient affects the model results, e.g. the number concentration of activated cloud droplets. In this paper we argue that a mass accommodation coefficient of unity should be used in cloud modelling, since this value has been obtained in experimental studies of water droplet growth rates, a quantity which is explicitly described in cloud models. In contrast, mass accommodation coefficient values below unity have been derived from experimental results which are analyzed with different theoretical expressions than those included in cloud models.

1. Introduction

The mass accommodation coefficient α of water vapor molecules on liquid water has been studied experimentally and theoretically for decades with conflicting results. Recent experiments on droplet growth rates (Winkler et al., 2004) indicate a mass accommodation coefficient of unity or near unity, while results from droplet train flow reactors (Li et al., 2001) have yielded values on the order of 0.1–0.3. Even lower values, on the order of 0.04–0.1, were obtained with a technique measuring droplet evaporation rates in an electrodynamic levitation chamber (Shaw and Lamb, 1999) .

The mass accommodation coefficient is a quantity that affects among other things the results obtained with process models simulating cloud droplet growth. A mass accommodation coefficient below unity slows down droplet growth and causes the maximum supersaturation to increase. It has been shown that relatively large increases in cloud droplet number concentrations can result for small decreases in the value of α (Rudolf et al., 2001; Nenes et al., 2001). The values of mass accommodation coefficient applied in recent cloud model studies are between 0.04–1 (Kreidenweis et al., 2003), which undoubtedly causes differences in the model results. It is our purpose to point out that the droplet growth rate obtained in cloud model studies is only consistent with experimental results if a mass accommodation coefficient of unity is applied.

2. Discussion

The condensation theory used in cloud models is the so called transition regime condensation theory. The mass flux directed away from the droplet can be given in the form (Kulmala et al., 1993a,b)

$$I = \frac{-4\pi a(S - S_a)}{\frac{RT_\infty}{M_v\beta_M D(1+(S+S_a)p_{ve}(T_\infty)/2p)p_{ve}(T_\infty)} + \frac{S_a L^2 M_v}{R\beta_T K T_\infty^2}}, \qquad (1)$$

where a is the droplet radius, S is the gas phase activity at ambient (far from the droplet) temperature T_∞ and S_a is the activity over the droplet surface, R is the gas constant, M_v is the molecular weight of the condensing vapour, D is the binary (between vapour and the inert gas) diffusion coefficient at T_∞, p_{ve} is the saturation vapour pressure of the liquid, L is the latent heat of vaporization and K is the heat conductivity of the vapour-gas mixture at the ambient temperature and p is the ambient total gas pressure.

β_M is the transition regime correction for mass transfer (Fuchs and Sutugin, 1970)

$$\beta_M = \frac{1 + Kn}{1 + \left(\frac{4}{3\alpha_M} + 0.377\right) Kn + \frac{4}{3\alpha_M} Kn^2}, \qquad (2)$$

where the Knudsen number Kn is the ratio of the mean effective free path of the vapour molecules, calculated from the vapour diffusivity, to the droplet radius. α_M is now the mass accommodation coefficient. Correspondingly, β_T is the transitional correction factor for heat transfer

$$\beta_T = \frac{1 + Kn_T}{1 + \left(\frac{4}{3\alpha_T} + 0.377\right) Kn_T + \frac{4}{3\alpha_T} Kn_T^2}, \tag{3}$$

where α_T is the thermal accommodation coefficient. The Knudsen number Kn_T for heat transfer is defined analogously to Kn by replacing the mean free path of vapour by a length scale for heat transfer, which is provided by the mean effective free path of the carrier gas molecules calculated from the heat conductivity of the inert gas (Wagner, 1982). Clearly, α_M refers to water vapour molecules, while α_T refers (mainly) to inert air molecules. Note, that the transition regime corrections used in the present study in conjunction with the proper definitions of the Knudsen numbers (Fuchs and Sutugin, 1970) have been found to provide good approximations for molecular mass ratios ranging from values $\ll 1$ (light vapours) up to values exceeding 10 (Qu and Davis, 2001). Similar expressions must also be applied in multicomponent condensation calculations, see e.g. the treatment of nitric acid condensation during cloud formation by Kulmala et al. (1993b).

In calculations of the condensational growth, the equations for mass and heat fluxes are coupled and knowledge of the droplet temperature is required in order to calculate the mass flux. The above expression for the mass flux takes approximately into account the correct droplet temperature due the latent heat release and under atmospheric conditions the formula very precisely gives the same results as the full coupled equations used by Winkler et al. (2004) (see also Vesala et al., 1997). Furthermore, Fladerer et al. (2002) have shown that the formula is applicable to all growth regimes and to initial conditions of high supersaturation, for which it was not expected to work properly.

Winkler et al. (2004) carried out experiments on the growth rates of water droplets observing growth kinetics in an expansion cloud chamber system. They studied liquid droplets nucleated on Ag particles and growing due to condensation of supersaturated water vapour using the experimental system presented in detail by Wagner et al. (2003). Vapour supersaturation is achieved by adiabatic expansion in a computer controlled thermostated expansion chamber resulting in well defined uniform thermodynamical conditions in the measuring volume. Growth of droplets is observed using the constant-angle Mie scattering (CAMS) detection method (Wagner, 1985) providing absolute, time-resolved and non-invasive simultaneous determination of droplet diameter and number density. Winkler et al. (2004) compared their results with theoretical calculations employing the transition regime condensation correction by Fuchs and Sutugin (1970) with different values of the mass accommodation coefficient. They found agreement only for mass accommodation coefficients in a certain range around unity.

The droplet train apparatus of Li et al. (2001) is based on a fast-moving monodisperse, spatially collimated train of droplets interacting with the gas-phase species ($H_2^{17}O$ or D_2O) in trace quantities. The liquid water itself is in equilibrium with its vapor, and the uptake of the trace isotopic species (which is of course out-of equilibrium) does not significantly perturb the bulk phase or the surface of the liquid. Mass accommodation coefficients are obtained from the determination of uptake (condensation) of gas phase isotope in trace amounts combined with calculations using a theory which describes the transport of vapor molecules from the gas phase to the air-water interface, and transfer of the species across the interface, i.e. a different theory than that used by Winkler et al. (2004) , and in the cloud models. Attempts have been made to reconciliate the above results (Morita et al., 2004, Davidovits et al., submitted, 2004[1]) but so far without success. Both the growth rate and droplet train experiments are carefully designed, and almost an order of magnitude difference in the mass accommodation coefficient seems quite high.

The lowest experimental values measured for α in recent years, between 0.04–0.1, were obtained by Shaw and Lamb (1999). They measured the evaporation rate of droplets suspended in an electrodynamic levitation system within a controlled envi-

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[1] Davidovits, P., Worsnop, D. R., Jayne, J. T., Kolb, C. E., Winkler, P., Vrtala, A., Wagner, P. E., Kulmala, M., Lehtinen, K. E. J., Vesala, T., and Mozurkewich, M.: Mass Accommodation coefficient of water vapor on liquid water, J. Geophys. Res., submitted, 2004.

ronment. They used the homogeneous freezing nucleation rate as a way to measure droplet temperatures (Pruppacher and Klett, 1997). However, this technique might be prone to errors since the homogeneous nucleation theory is still a complex, unsolved problem (see e.g. Seinfeld and Pandis, 1998).

Figure 1 shows the experimental results of Winkler et al. (2004) for droplet growth, as well as theoretical growth curves calculated using the transition regime condensation theory, and mass accommodation coefficients ranging from 0.04 to 1. It is clear that only values near unity yield theoretical predictions consistent with the growth rates. Accordingly, the full coupled droplet growth equations accurately predict observations of droplet growth kinetics in an expansion cloud chamber system (Winkler et al., 2004), when the accommodation coefficients α_M and α_T are set to 1. Thus the usage of expressions (1–3) with α_M and α_T=1 is a physically rigorous and consistent approach to estimate the condensational growth. We stress rigor, since many atmospheric scientists are apparently unaware of the recent developments in the condensational growth theories and apply fundamentally incorrect expressions deviating from that given above, and very recently discusssed by Pines et al. (2004) and Vesala et al. (2004). We stress consistency, since the same theory used in the interpretations of the experiments must be fully applied in subsequent atmospheric models. Therefore, as long as the transition regime condensation theory is used in cloud models, the accommodation coefficients should be set to unity. Lower values can lead to too high cloud drop number concentrations, as indicated in Table 1.

3. Conclusions

At present, it is not clear whether the real value of α is near 1 or below. If the latter case proves to be correct, this must be associated with a deficiency of the currently used transition regime corrections for droplet growth rates. Whatever the case, the rigorous transition regime growth theory combined with a water vapour thermal and mass accommodation coefficients of unity yields excellent predictions of experimental droplet growth rates. For this reason, the use of mass accommodation coefficient values lower than 1 in cloud models together with the rigorous droplet growth theory is inconsistent and should be avoided.

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Table 1. The effect of accommodation coefficient on cloud drop number concentration (CDNC) calculated using a cloud parcel model. The aerosol size distribution is lognormal, with a mean diameter of 50 nm, standard deviation of 1.7, and number concentration of 3000 cm^{-3}. The updraft velocity is 1.0 m/s and temperature 273 K.

α	CDNC (cm^{-3})
0.04	1595
0.1	1221
1	873

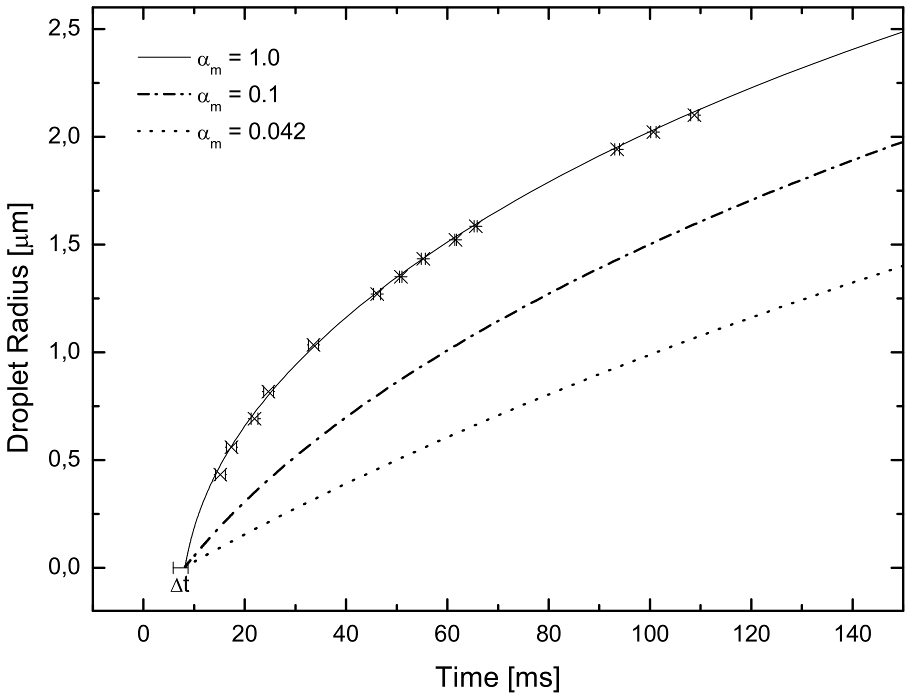

Fig. 1. Experimental results of Winkler et al. (2004) for droplet growth. Theoretical growth curves calculated by means of the transitional drop growth theory (Fuchs and Sutugin, 1970) for mass accommodation coefficients between 0.04 and 1.