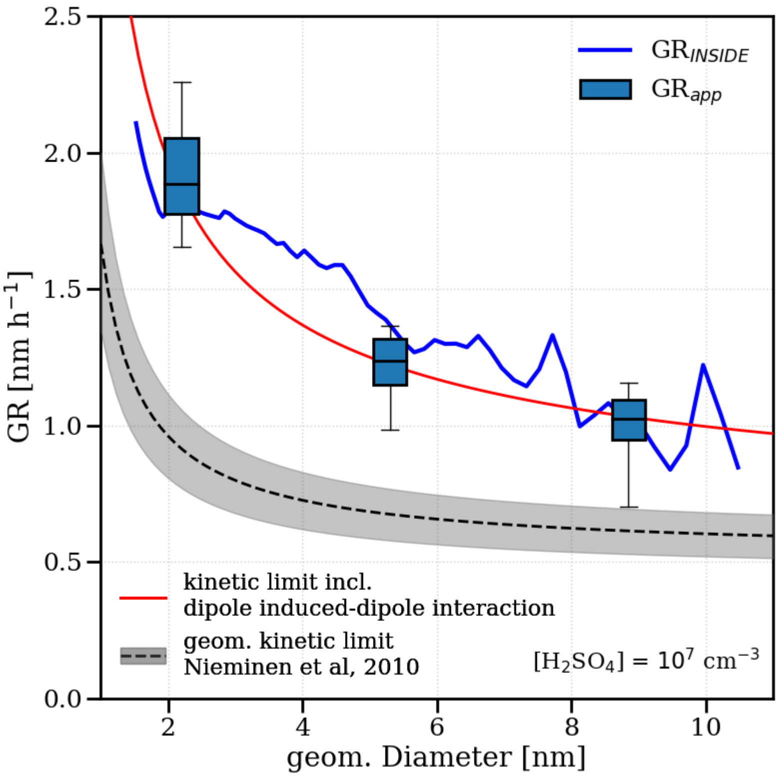
Response to Short Comment from Christopher Hogan on "Enhanced Growth Rate of Atmospheric Particles from Sulfuric Acid"

We thank Chris Hogan for thoroughly checking our manuscript on potential errors in the analysis. This will certainly help improving the quality and validity of the presented results.

First, it seems the authors equate the mobility diameter inferred from DMA measurements without correcting for the size of the gas molecule (or if they are correcting for gas molecule physical size, they are not stating this). As per Larriba et al (2011, doi: 10.1080/02786826.2010.546820), the physical diameter of a particle in air is ~0.3 nm smaller than the mobility diameter.

Indeed we used mobility diameter for our growth rate calculations, and collision kernels are typically given for mass diameters, which according to Larriba et al. (2011) are approximately 0.3 nm smaller. We appreciate that you pointed that out which will make our analysis certainly more correct. We will revise that throughout the manuscript and always specify which definition of diameter is used. In fact, we find a Hamaker constant of 5.3×10^{-20} J with the adjusted size range which is 20 % lower than before. Nevertheless, this is still within the general uncertainty of our Hamaker constant estimate and still in good agreement with earlier results. As can be seen from the below Figure (updated Figure 4, with geom. Diameter on x-axis), the effect of faster GRs than the hard sphere assumption is still significant.



Equation S1 has a factor of 2 in the numerator that is either not correct or not fully justified. The authors state that "k_{coll} is the kinetic collision frequency between particle and vapor, which is accounted for twice to include collisions in both ways." What does "both ways" mean? Why would something grow at twice the condensation rate? The authors appear to be using equations from Chan and Mozurkewich which have typographical errors in the original manuscript and are copied here.

Thanks for pointing this out, indeed a very good remark. This factor of 2 is indeed connected to the factor of 2 which appears in the collision rate and results from a wrong interpretation by the authors. As already noted the factors do cancel out, so there is no effect on the inferred GR. Apparently, we were following Chan & Mozurkewich (2001) too strictly in our derivation. We will correct for that in the revised manuscript, update our calculations and delete the sentence on the counting of the collisions.

The GR will be defined as:

$$GR = \frac{k_{coll} \cdot m_v \cdot C_v}{\rho \frac{\pi}{2} d_p^2} \qquad \text{(S1new)}$$

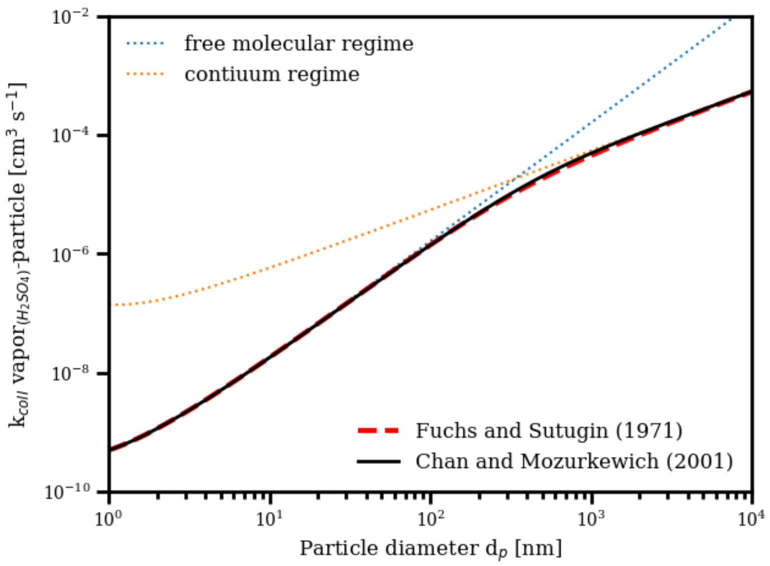
I think equation S2 is not correctly written, or at least, it has the wrong limits. When the ratio k_D/k_k (Knudsen number for collisions) is large, then it does correctly converge to k_k. However, it appears that as this ratio becomes very small, equation S2 would approach zero, when it needs to converge exactly to k_d to be an accurate transition regime kernel. In Chan and Mozurkewich (equations 27 and 28 of their paper), the do provide different expressions than what is given here.

This seems to be a misunderstanding. We provide the exact same expression as Chan & Mozurkewich (2001), just the factor of 2 in the collision rate for the continuum regime is placed at a different position:

Term	Discussion paper	Chan & Mozurkewich with $a_{i/j} = d_{v/p}/2$	Revised version
k_k	$\frac{\pi}{8}(d_v + d_p)(\bar{c}_v^2 + \bar{c}_p^2)^{1/2}E(\infty)$	$\frac{\pi}{8}(d_v + d_p)(\bar{c}_v^2 + \bar{c}_p^2)^{1/2}E(\infty)$	$\frac{\pi}{4}(d_v + d_p)(\bar{c}_v^2 + \bar{c}_p^2)^{1/2}E(\infty)$
k_D	$2\pi(D_v + D_p)(d_v + d_p)E(0)$	$\pi(D_v + D_p)(d_v + d_p)E(0)$	$2\pi(D_v + D_p)(d_v + d_p)E(0)$
k_T	$k_k \cdot \left(\sqrt{1 + \left(\frac{k_k}{k_D}\right)^2} - \left(\frac{k_k}{k_D}\right)\right)$	$k_k \cdot \left(\sqrt{1 + \left(\frac{k_k}{2k_D}\right)^2} - \left(\frac{k_k}{2k_D}\right)\right)$	$k_k \cdot \left(\sqrt{1 + \left(\frac{k_k}{2k_D}\right)^2} - \left(\frac{k_k}{2k_D}\right)\right)$

However, these equations would also have the same issue, (an incorrect limit). The authors should look at the transition regime expressions of Fuchs or Dahneke (or more recent developments) to see how the transition regime equation must be constructed to converge to the correct limits.

First, we want to point out that the formulation of the transition regime correction is in any case not dramatically affecting our results as we were analysing sub-10 nm growth rates, which should be entirely dominated by the free molecular regime. On line 128 in the main text we underline that already. However, we are also confused by the statement of the wrong limits. Also Sceats (1987) used a similar expression and claims it reaches the correct limit (Eq. 7 in Sceats work). For the case considered in our manuscript (fixed vapor size and varying particle size) we also find that the limits are correct. This can be seen from the below Figure (similar to Figure 4 a in the current manuscript), which shows the collision kernel of a sulfuric acid molecule with a particle of diameter d_p. Both the transition regime expression by Fuchs & Sutugin (1971) and the one used by Chan & Mozurkewich (2001) are approaching the correct limits and yield quite similar results. Note, that we adjusted the expression of Chan & Mozurkewich by the wrong factor of 2 as shown in the above Table under "Revised version". We therefore see no further reason to fundamentally change our analysis, but we will once again cross-check all our calculations and equations before submitting a revised version of our manuscript.



Aside from the issues with equation S2, use of the equations of Chan and Mozurkewich alone, which come from the theoretical derivations of Sceats, may not be accurate. More recent theoretical investigations of van der Waals enhancement in collision rates (doi: 10.1063/1.4742064) suggest that for a given Hamaker constant, Sceats overestimates the enhancement factor in the free molecular limit. The noted reference discusses more tractable approaches which agree with collision rates from trajectory calculations.

We appreciate this comment pointing us towards other approaches in literature. We will try to make use of them in the revised version of the manuscript, to crosscheck our analysis.

Equations S4 for E(0). I think the authors should show that this functional form follows exactly from the Fuchs integral for the enhancement factor in the continuum/diffusive regime, which is an exact integral and typically easily calculable for a given potential interaction. Similarly, it is not clear that equation S3 follows from analyzing ballistic regime in the appropriate manner. The authors should be aware that the equations in Chan and Mozurkewich do not appear in the original Sceats paper, as far as I can tell they are a regression fit to results in Sceats's work (from his plots).

We agree with Chris Hogan, that the manuscript needs some deeper explanations on how the work of Chan & Mozurkewich (2001) relates to other work and we will clarify some of the derivations in the revised version of the manuscript.

It would seem more reasonable for the authors to use a different approach either in lieu of or in addition to the equations of Chan and Mozurkewish, i.e. for the authors to either compare to the equations of Ouyang et al (doi: 10.1063/1.4742064) and/or of Fuchs & Sutugin (doi: simple but accurate: 10.1016/0095-8522(65)90031-0). In the free molecular limit, Ouyang et al follow Fuchs's approach but integrate across the velocity distribution, while Fuchs assumes a single approach speed.

We understand that the Chan & Mozurkewich (2001) approach might be oversimplified and that more recent developments on that exist. As already mentioned above, Chan & Mozurkewich (2001) was used as the blueprint for this analysis and we might have followed it too rigorously. Adding another approach will certainly help improving the quality of the manuscript and will be done in the revised version of the manuscript. However, we also want to point out that these different derivations will only influence the result of the inferred Hamaker constant, which is anyways subject to systematic uncertainties which are difficult to reduce with the chosen approach. We will comment this point separately in our reply to Ref.2. In this context, we want to emphasize that this manuscript is about the observation of growth rates faster than expected from a hard sphere assumption under pure, well-controlled and atmospherically relevant conditions, which seem to have a global impact. This was also the reason to choose Atmos. Chem. Phys. for dissemination instead of a journal which focusses more on pure Physical Chemistry and collision kinetics.