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Sub-10 nm particle growth by vapor condensation – effects of vapor molecule size and particle thermal speed

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Abstract. The growth of freshly formed nanoparticles has been investigated. A new analytical expression based on a recently developed exact solution for the condensational growth rate has been derived. Based on the new growth rate, a new approximate but accurate analytical expression for growth time has been derived. The expression includes transition regime effects on growth, molecule size effects on the collision cross section and particle thermal speed effects on the relative collisional speeds – the last two of which are typically neglected, but may have significant effects when dealing with the growth of freshly nucleated particles. To demonstrate the use of the derived expressions, the contribution of sulphuric acid and organic compounds on sub 3 nm and sub 10 nm particle growth rates has been studied. For sulphuric acid also the effect of hydration as function of relative humidity has been taken into account. According to the new expression the sulphuric acid concentration needed for 1 nm/h growth in sub 3 nm range is ca. $1.5 \times 10^7 \, \text{cm}^{-3}$, which is a factor of 1.5 smaller than values typically used in aerosol physics based on standard model in kinetic regime.

1 Introduction

Atmospheric nucleation and subsequent growth of these freshly formed nanoparticles has been observed all around the world (Kulmala et al., 2004a). The actual formation of e.g. 3 nm or 10 nm particles has been shown to be dependent on the processes related to initial steps of the growth (Kulmala et al., 2004b). The growth of atmospheric particles has been shown to be mainly due to condensation of low volatile vapours (Kulmala et al., 1998), and it seems to be size dependent (Hirsikko et al., 2005). In situations of very high nucle-

ation mode particle concentrations also intramodal coagulation of the nucleated particles can contribute to the observed particle growth rates (Stolzenburg et al., 2005; Kulmala and Kerminen, 2008).

To date there are only a few reports of direct measurements of the chemical composition of atmospheric nucleation mode particles (see e.g. Smith et al., 2005, 2008). Because of the experimental challenges, various indirect methods to reveal the details of nucleation and initial growth have been designed. Analysis of growth is one important such tool. First of all, magnitudes of growth rates can be used to estimate condensable vapour concentrations (Kulmala et al., 2005). Similarly, if concentrations of vapours are measured, a detailed growth rate analysis will reveal the fractions by which the vapours participate in particle growth (Sihto et al., 2006) – thus giving also indirect information of chemical composition. Finally, for global modelling purposes, if semi-empirical particle formation rates are sought after, accurate and consistent ways to estimate growth rates and times are crucial since formation rates depend strongly on growth rates (Lehtinen et al., 2007).

When modelling growth of nanometre size particles, it is typical to use either a continuum regime expression together with a transition regime correction factor, e.g. Fuchs-Sutugin (see e.g., Kulmala et al., 2001), or approximate the growth with free-molecular regime theory (see e.g., Seinfeld and Pandis, 2006). These approaches assume that the condensing molecules have negligible size compared to the aerosol particles and the particles have negligible mobility compared to the vapour molecules. Such assumptions break down especially in cases where the condensing molecules are large and the particles small. To take these important effects into account, a modification to the widely used growth expressions was derived by Lehtinen and Kulmala (2003), based on analogy to coagulation theory.

In this paper we will revisit the exact expression for the condensation growth of atmospheric particles (Lehtinen and

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Kulmala, 2003), especially since the above mentioned incorrect assumptions are still widely used. Knowing the accurate dependence of the particle growth rate on vapour concentration and molecular properties is important in the smallest size ranges (sub 10 nm and particularly in sub 3 nm), since the initial growth of the particles in sub-10 nm size range is the most important step determining the fraction of nucleated particle reaching sizes of e.g. cloud condensation nuclei (∼50 nm and larger) (see e.g., Kulmala and Kerminen, 2008). We also derive a new approximate expression relating particle growth time and concentration of condensable vapours, and investigate the dependence of growth rate on mass of condensing vapour as well as on volume of vapour molecules and density of growing particles. Here we focus on sub 10 nm and particularly on sub 3 nm particles, since the most critical size range is just the size around 1 to 2 nm where atmospheric nucleation occurs (see Kulmala et al., 2007).

2 Theory

2.1 Equation for particle growth rate due to vapor condensation

Here we derive an expression for the particle diameter growth rate resulting from condensation of single component vapor. We assume the particle to be spherical, and do not take into account any interaction forces between the particle and vapor molecules. The collision rate between aerosol particles and vapour molecules in the kinetic regime is

$$K_{\mathrm{kin}} = \frac{\pi}{4}(d_{\mathrm{p}}+d_{\mathrm{v}})^2 \left(\bar{c}_{\mathrm{p}}^2 + \bar{c}_{\mathrm{v}}^2\right)^{1/2} C_{\mathrm{v}}, \tag{1}$$

where d is diameter and $\bar{c}$ is thermal speed. Subscript "p" refers to particle and "v" to vapour molecule. In order to describe the situation also in continuum regime (i.e. when d_{p} is large), Eq. (1) must be multiplied with a correction factor γ. This factor is obtained by equating the generalized coagulation rate (see e.g., Seinfeld and Pandis, 2006),

$$2\pi(d_{\mathrm{p}}+d_{\mathrm{v}})(D_{\mathrm{p}}+D_{\mathrm{v}})\beta_{\mathrm{m}}, \tag{2}$$

with Eq. (1) multiplied by γ. Here D_{p} and D_{v} are the diffusivities of the particle and the vapour molecule, respectively, and β_{m} is the Fuchs-Sutugin transition regime correction factor for mass flux (see the Appendix for the definition of these). This way we obtain an expression for the collision rate between vapour molecules and particles of all sizes (see also Kulmala and Wagner, 2001):

$$K = \gamma K_{\mathrm{kin}} = \gamma \frac{\pi}{4}(d_{\mathrm{p}}+d_{\mathrm{v}})^2 \left(\bar{c}_{\mathrm{p}}^2 + \bar{c}_{\mathrm{v}}^2\right)^{1/2} C_{\mathrm{v}}, \tag{3}$$

$$\gamma = \frac{8(D_{\mathrm{p}}+D_{\mathrm{v}})}{(d_{\mathrm{p}}+d_{\mathrm{v}})\left(\bar{c}_{\mathrm{p}}^2 + \bar{c}_{\mathrm{v}}^2\right)^{1/2}} \cdot \beta_{\mathrm{m}} = \frac{4}{3} \cdot Kn \cdot \beta_{\mathrm{m}}. \tag{4}$$

The vapour molecule collision rate into particle can be converted to change rate of the particle volume V_{p}, assuming

that the volume of the vapor molecule is $V_{\mathrm{v}} = m_{\mathrm{v}}/\rho_{\mathrm{v}}$. Combining Eqs. (3) and (4), and converting the vapour molecule collision rate into particle diameter growth rate GR we get

$$GR = \frac{dd_{\mathrm{p}}}{dt} = \frac{\frac{dV_{\mathrm{p}}}{dt}}{\frac{dV_{\mathrm{p}}}{dd_{\mathrm{p}}}} = \frac{\gamma \frac{\pi}{4}(d_{\mathrm{p}}+d_{\mathrm{v}})^2 \left(\bar{c}_{\mathrm{p}}^2 + \bar{c}_{\mathrm{v}}^2\right)^{1/2} V_{\mathrm{v}} C_{\mathrm{v}}}{\frac{d}{dd_{\mathrm{p}}}\left[\frac{\pi}{6}d_{\mathrm{p}}^3\right]}$$

$$= \frac{\gamma \frac{\pi}{4}(d_{\mathrm{p}}+d_{\mathrm{v}})^2 \left(\frac{8kT}{\pi}\right)^{1/2}\left(\frac{1}{m_{\mathrm{p}}}+\frac{1}{m_{\mathrm{v}}}\right)^{1/2}\frac{m_{\mathrm{v}}}{\rho_{\mathrm{v}}}C_{\mathrm{v}}}{\frac{\pi}{2}d_{\mathrm{p}}^2}$$

$$= \frac{\gamma}{2\rho_{\mathrm{v}}}\left(1+\frac{d_{\mathrm{v}}}{d_{\mathrm{p}}}\right)^2 \left(\frac{8kT}{\pi}\right)^{1/2}\left(\frac{1}{m_{\mathrm{p}}}+\frac{1}{m_{\mathrm{v}}}\right)^{1/2} m_{\mathrm{v}} C_{\mathrm{v}}. \tag{5}$$

Here ρ_{v} is vapor condensed phase density, and m_{p} and m_{v} are particle and vapour molecule masses, respectively. Note that in the derivation of Eq. (5) we have not assumed the densities of the particle and the condensing vapor in liquid phase to be equal. If the particle density initially differs from the vapor liquid phase density, it reaches the vapor liquid phase density quite rapidly in the beginning of the growth (see also Kulmala et al., 1993).

2.2 Analytical approximation of the growth equation

To obtain an estimate for the condensable vapour concentration corresponding to a certain growth rate, Eq. (5) needs to be integrated over the particle size range where the growth rate is determined. Equation (5) cannot be integrated analytically as such. However, if we approximate the last square root term in Eq. (5) with its Taylor series expansion, we obtain

$$\frac{dd_{\mathrm{p}}}{dt} \approx \tag{6}$$

$$\frac{\gamma}{2\rho_{\mathrm{v}}}\left(1+2\frac{d_{\mathrm{v}}}{d_{\mathrm{p}}}+\left(\frac{d_{\mathrm{v}}}{d_{\mathrm{p}}}\right)^2\right)\left(\frac{8kT}{\pi m_{\mathrm{v}}}\right)^{1/2}\left(1+\frac{1}{2}\frac{\rho_{\mathrm{v}}}{\rho_{\mathrm{p}}}\left(\frac{d_{\mathrm{v}}}{d_{\mathrm{p}}}\right)^3\right)m_{\mathrm{v}}C_{\mathrm{v}}$$

$$= \frac{\gamma m_{\mathrm{v}} C_{\mathrm{v}}}{2\rho_{\mathrm{v}}}\left(\frac{8kT}{\pi m_{\mathrm{v}}}\right)^{1/2}\left[1+2\frac{d_{\mathrm{v}}}{d_{\mathrm{p}}}+\left(\frac{d_{\mathrm{v}}}{d_{\mathrm{p}}}\right)^2+\frac{1}{2}\frac{\rho_{\mathrm{v}}}{\rho_{\mathrm{p}}}\left(\frac{d_{\mathrm{v}}}{d_{\mathrm{p}}}\right)^3\right.$$

$$\left.+\frac{\rho_{\mathrm{v}}}{\rho_{\mathrm{p}}}\left(\frac{d_{\mathrm{v}}}{d_{\mathrm{p}}}\right)^4+\frac{1}{2}\frac{\rho_{\mathrm{v}}}{\rho_{\mathrm{p}}}\left(\frac{d_{\mathrm{v}}}{d_{\mathrm{p}}}\right)^5\right]$$

where we have also expressed masses in terms of density and diameter.

Now, let's examine the magnitudes of terms in Eq. (6) (assuming $\rho_{\mathrm{p}}=\rho_{\mathrm{v}}$ for simplicity). If $d_{\mathrm{v}}=0.2d_{\mathrm{p}}$, the term in brackets is $1+0.4+0.04+0.004+0.0016+0.0002 = 1.4458$. In this case, taking two terms results in a 3.2% error and three in an 0.4% error in the growth rate compared to the exact formula of Eq. (5). If $d_{\mathrm{v}}=0.5d_{\mathrm{p}}$, the term in brackets is $1+1+0.25+0.0625+0.0625+0.0156 = 2.3906$, so taking two terms results in a 16% error and three terms in a 5.7% error in growth rate. Also, in the case of $d_{\mathrm{v}}=0.5d_{\mathrm{p}}$, if the

vapor liquid phase density would be $\rho_v = 2\rho_p$, approximation with three terms differs by 10% from the exact formula. Thus using an approximation with three terms of the Taylor series can be considered a rather good approximation in the sub 10 nm size range. Also, in the sub-10 nm size range the factor γ is very close to mass accomodation coefficient α_m. By additionally changing the derivative on the left hand side of Eq. (6) from d_p to d_v/d_p, we get

$$\frac{d\left(d_v/d_p\right)}{dt} = \frac{-d_v}{d_p^2}\frac{dd_p}{dt} \approx \tag{7}$$
$$-\frac{\alpha_m m_v C_v}{2\rho_v d_v}\left(\frac{8kT}{\pi m_v}\right)^{1/2}\left(\frac{d_v}{d_p}\right)^2\left(1+2\frac{d_v}{d_p}+\left(\frac{d_v}{d_p}\right)^2\right).$$

Here it should be noted that the approximations leading to Eq. (7) effectively take into account only the size of the vapor molecule, as the effect of the particle diffusional motion was found to be of only minor importance in the preciding error analysis. Marking $x = d_v/d_p$ in Eq. (7) and integrating it we obtain

$$C_v = \frac{2\rho_v d_v}{\alpha_m m_v \Delta t}\cdot\sqrt{\frac{\pi m_v}{8kT}}\left[\frac{2x_1+1}{x_1(x_1+1)} - \frac{2x_0+1}{x_0(x_0+1)} + 2\ln\left(\frac{x_1(x_0+1)}{x_0(x_1+1)}\right)\right]. \tag{8}$$

In this expression $x_1 = d_v/d_{p,\text{final}}$ and $x_0 = d_v/d_{p,\text{initial}}$, so that if one is considering particle growth from $d_{p,\text{initial}}$ to $d_{p,\text{final}}$ in time Δt, Eq. (8) provides an easy to use relationship between particle growth time and the required vapour concentration. Kulmala (1988) (see also Kulmala et al., 2001) has derived a similar kind of formula connecting vapour concentration and particle growth time:

$$C_v = \frac{\rho_p}{D_v m_v \Delta t}\left(\frac{d_p^2 - d_{p0}^2}{8} + \left(\frac{4}{3\alpha} - 0.623\right)\frac{\lambda}{2}(d_p - d_{p0}) + 0.623\lambda^2\ln\frac{2\lambda+d_p}{2\lambda+d_{p0}}\right), \tag{9}$$

except that the effects of particle diffusion and vapour molecule finite size were neglected. Accordingly, the mean free path of the condensing vapour is calculated here as $\lambda = 3D_v/c_v$. Also, in Eq. (9) it is assumed that the particle density ρ_p is constant during the particle growth.

3 Results and discussion

3.1 Accuracy of the analytical approximation and comparison to the standard method

A comparison of the analytical approximation of Eq. (8) and the numerical integration of Eq. (5) is shown in Fig. 1, where the vapour concentration resulting in particle growth rate of $1\,\text{nm h}^{-1}$ is shown as function of vapour molecule mass. The results for growth over particle size 3 to 7 nm are very close to each other, the difference being less than 1% for the vapour molecule mass range 100–300 amu. For growth from 1.5 to 3 nm the range of vapour concentrations calculated by the approximation of Eq. (8) are between 1.7% and 4.7% higher
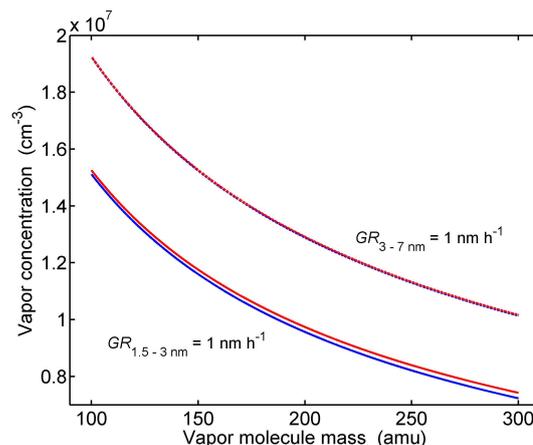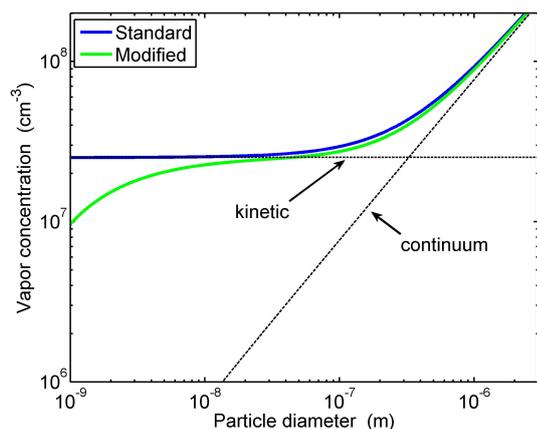

Fig. 1. The required vapor concentration for growth rate $1\,\text{nm h}^{-1}$ over particle size range 1.5–3 nm (solid lines) and 3–7 nm (dashed lines). The particle density and vapor liquid phase density are both assumed to be 1.83 g cm^{-3} (liquid phase density of sulphuric acid). Result using approximation of Eq. (8) is shown in red and result by numerically integrating Eq. (5) is shown in blue.

compared to the exact value. The difference increases with increasing vapour molecule mass.

An example of the difference between the approach used in this study and the standard one is shown in Fig. 2, where the vapour concentration needed to grow particles with growth rate of 1 nm/h is represented as function of particle size. The vapour has molecular properties of sulphuric acid, and the saturation vapour pressure is assumed negligible. It can be seen that both methods give similar results for large particles, approaching the continuum regime result where growth rate is inversely proportional to particle diameter. In sizes of few tens of nanometres the results start to differ. Below about 10 nm this difference increases significantly. The standard Fuchs-Sutugin approach gives growth rate independent of the particle size in accordance with the traditional kinetic (or free-molecular) expression. According to the modified approach, however, for 1.5–3 nm sized particles the vapour concentration resulting in growth rate 1 nm/h is 1.5×10^7 cm^{-3}, which is about half of that calculated according to the Fuchs-Sutugin approach.

3.2 Effect of vapour molecule properties and particle size on growth rate

Figure 3 shows the effect of vapour molecule mass on the growth rate from 1 to 3 nm resulting from a vapour concentration of 10^7 cm^{-3}. The growth rates are calculated both using the modified approach (Eq. 8) and the standard approach (Eq. 9), and we have taken into account the dependence of diffusivity on vapour molecule mass. It can be seen that while both approaches show an increase in growth rate with increasing vapour molecule mass, in the modified approach this effect on growth rate of sub 3 nm particles is
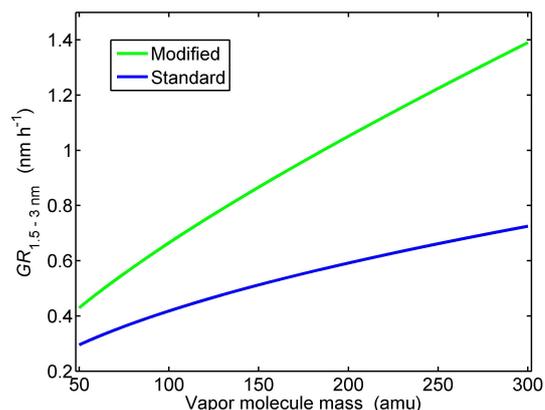
Fig. 2. Vapor concentration required for growth rate of 1 nm/h as function of particle diameter. Vapor is assumed to have molecular properties of sulphuric acid (molecule mass 98 amu and liquid phase density $1.83\,\mathrm{g\,cm^{-3}}$) and negligible saturation vapor pressure. Particle density is assumed to be equal to the vapor liquid phase density. "Modified" refers to the method of this study and "standard" to the Fuchs-Sutugin approach. Dashed lines show the kinetic (or free-molecular) and continuum regime results.

Fig. 3. Particle growth rate over 1.5–3 nm diameter range as function of condensing vapor molecule mass. Vapor concentration is $10^7\,\mathrm{cm^{-3}}$. Particle density and vapor liquid phase density are both assumed to be $1.83\,\mathrm{g\,cm^{-3}}$. "Modified" refers to the method of this study and "standard" to the Fuchs-Sutugin approach.

Fig. 4. Particle growth rate according to Eq. (5) as a function of particle size and molecular properties of the condensing vapor. Vapor concentration is $10^7\,\mathrm{cm^{-3}}$, and saturation vapor pressure is negligible. The vapor properties of free sulphuric acid and hydrated sulphuric acid molecules with one, two or three water molecules are used.

much stronger. Table 1 shows a comparison of the standard and modified approach in determining the condensable vapour concentration for different growth rates in 3–10 nm size range as well as the effect of vapour molecule mass, mass accommodation coefficient and temperature. Also the corresponding values for the size range 1.5–3 nm are shown.
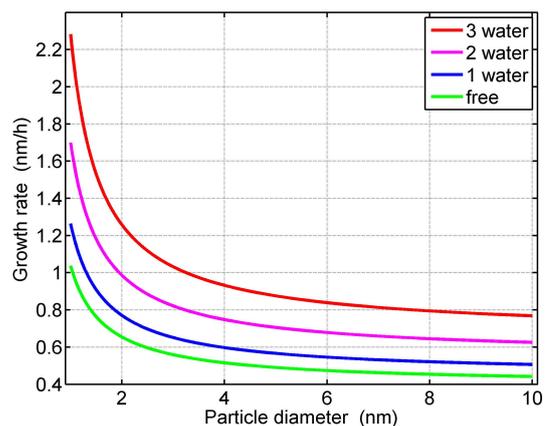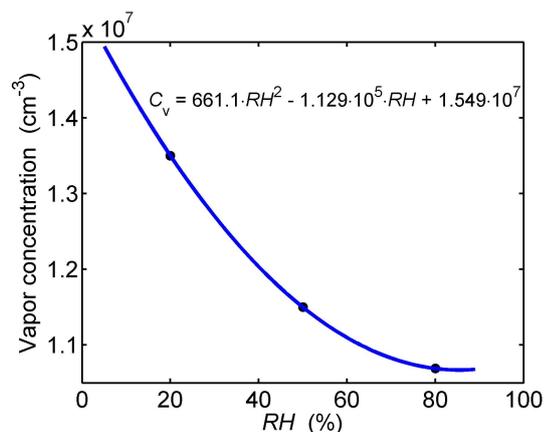
The molecular properties of atmospherically relevant condensing vapours (most probably oxidized organic compounds) are largely unknown. We studied the sensitivity of the growth rate to the molecular properties of the condensing vapour. Figure 4 illustrates the effect of sulphuric acid hydration on the growth rate. According to quantum chemical calculations (Kurtén et al., 2007), in atmospheric conditions most of the sulphuric acid molecules have either one, two or three water molecules attached to them. At 20% relative humidity more than half of the H_2SO_4 molecules have one water molecule attached to them. As RH increases, fraction of H_2SO_4 molecules bound with more than one water molecule increases, for example at RH=80% more than half of them has three water molecules and 10% of the clusters are expected to contain four water molecules. The growth rate due to condensation of sulphuric acid and three water molecules is increased by approximately 40% compared to condensation of free (unhydrated) sulphuric acid molecules.

3.3 Application to analysis of an atmospheric new particle formation event

From measurements of atmospheric new particle formation events we can analyze the growth rates of the newly formed particles. If there is measurement data or we can estimate the

sulphuric acid concentration, Eq. (5) can be used to calculate the growth rate explained by condensation of sulphuric acid. Typically in atmospheric observations, sulphuric acid concentrations can explain 5–30% of the observed particle growth rates below 10 nm (Birmili et al., 2003; Boy et al., 2005; Fiedler et al., 2005; Iida et al., 2008; Paasonen et al., 2009). Equation (8) can now be used to estimate the concentration of the other vapor or vapours contributing to the rest of the growth. This requires an estimation or prior knowledge of the molecular properties of the other vapor. Also, when calculating the contribution of sulphuric acid, hydration should be taken into account. In practice, one should determine based on relative humidity whether sulphuric acid

Table 1. The effect of vapor molecule mass, temperature and mass accomodation coefficient on the concentration of condensable vapor leading to particle growth rate GR. Particle density and vapor liquid phase density are both assumed to be $1.83 \, \text{g cm}^{-3}$. Growth rate is calculated over the size ranges 3–10 nm (2nd and 3rd columns from right), and 1.5–3 nm (1st column from right). Note that the values of C_v on the 3rd column from right differ from those given in Table 1 of Kulmala et al. (2001) because they have assumed particle density $1.0 \, \text{g cm}^{-3}$.

| GR (nm h^{-1})	m_v (amu)	α_m	T (K)	C_v $(10^7 \, \text{cm}^{-3})$ (Eq. 9)	C_v $(10^7 \, \text{cm}^{-3})$ (Eq. 8)	C_v $(10^7 \, \text{cm}^{-3})$ (Eq. 8)
1	98	1	298	2.44	2.02	1.54
2	98	1	298	4.88	4.05	3.09
4	98	1	298	9.76	8.10	6.17
6	98	1	298	14.6	12.1	9.26
10	98	1	298	24.4	20.2	15.4
20	98	1	298	48.8	40.5	30.9
20	98	1	268	51.5	42.7	32.5
18	98	1	298	43.9	36.4	27.8
18	196	1	298	31.0	24.7	17.7
18	196	0.01	298	3084	2468	1780
18	98	0.01	298	4361	3644	2780
18	49	1	298	6168	53.4	42.7

Fig. 5. Concentration of hydrated sulphuric acid required for growth rate $1 \, \text{nm h}^{-1}$ over size range 1.5–3 nm as a function of relative humidity. Points represent the calculated sulphuric acid concentrations according to Eq. (8), when the relative humidity dependent hydration of sulphuric acid molecules has been taken into account. Solid line is a second order polynomial fit to the calculated points. In the fitting equation RH is given in percents.

is bound to one, two or three water molecules, and use the corresponding vapor properties in Eq. (5). Figure 5 depicts the required sulphuric acid concentration for growth rate of $1 \, \text{nm h}^{-1}$ in size range 1.5 to 3 nm as function of relative humidity. We have used the H_2SO_4-hydrate distribution data given by Kurtén et al. (2007), and calculated the density and mass of the average hydrated H_2SO_4 molecule in relative humidities 20%, 50% and 80%. A second order polynomial fit to these data points gives a simple formula for the sulphuric

acid concentration needed for growth rate 1 nm/h in this size range as

$$C_{H_2SO_4} = 661.1 \cdot RH^2 - 1.129 \cdot 10^5 \cdot RH + 1.549 \times 10^7 \, \text{cm}^{-3}. \quad (10)$$

As an example of this method, we analyze data on a new particle formation event measured at the SMEAR II station in Hyytiälä, Finland (for a description of the SMEAR II station and the measurements there, see Hari and Kulmala, 2005), and use also measured sulphuric acid data (the technique and results of the H_2SO_4 measurements by Chemical Ionization Mass Spectrometer are described in detail by Petäjä et al., 2009). Figure 6 shows size spectra of negative air ions measured on 5 May 2007 with the Neutral cluster and Air Ion Spectrometer NAIS (Kulmala et al., 2007). New particle formation starts around noon and lasts for several hours, and we also see the growth continuing for several hours. The growth rate of the particles can be determined by following the peak concentration in each size bin of the instrument and fitting a linear function to these points. The growth rate in the beginning of the event, from 1.5 to 3 nm, is 2.1 nm/h. The relative humidity during this time was 36%. Using Eq. (10), we can now calculate that the sulphuric acid concentration needed to explain this growth rate is $2.58 \times 10^7 \, \text{cm}^{-3}$. On the other, the old method (Eq. 9) gives $5.22 \times 10^7 \, \text{cm}^{-3}$ as the required sulphuric acid concentration corresponding to this growth rate, which means that there is a difference by a factor of roughly two. The median sulphuric acid concentration during the growth of the particles was $1.3 \times 10^6 \, \text{cm}^{-3}$, showing that on this day less than 10% of the observed growth rate can be explained by condensation of sulphuric acid. Assuming that the rest of the growth rate is caused by one additional vapor of
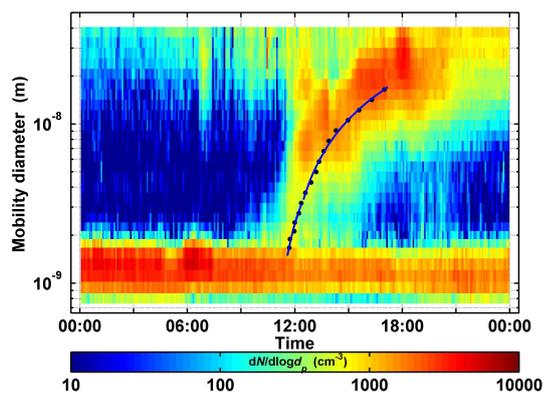
Fig. 6. Size spectra of negative air ions measured at Hyytiälä on 5 May 2007. Black dots represent locations of maxima of number concentrations in each size bin of the instrument. The solid line is a linear fit to those points. Growth rate of the particles is 2.1 nm/h in size range 1.5 to 3 nm, and 2.9 nm/h from 3 to 20 nm.

molecule mass 150 amu and liquid phase density $1.0\,\mathrm{g\,cm^{-3}}$, its concentration should be $1.18\times10^7\,\mathrm{cm^{-3}}$.

4 Conclusions

In this work we have investigated the condensational growth rate of aerosol particles smaller than 10 nm and particularly in sub 3 nm sizes. Based on our analyses, when calculating growth rates for sub 10 nm particles the effect on the collision cross section of the size of the vapor molecule as well as the effect of particle diffusional motion on the collisional relative speed need to be taken into account, which typically are neglected when dealing with atmospheric condensation. This enhancement of the mass flux results in growth rates up to a factor of about 1.5 higher than compared to the traditional free-molecular results. The derived analytical approximation connecting particle growth rate and growth time over a certain size range to the condensing vapor concentration was found to be fairly accurate compared to the exact numerical solution. This approximation includes both the above mentioned as well as transition regime effects on condensational growth.

Using the new expressions the contribution of different vapours – particularly sulphuric acid – on the total particulate growth can be determined. In case of sulphuric acid the contribution of water hydrates is also taken into account by an RH-dependent equation. This is crucial in order to understand the first steps of atmospheric new particle formation. After determining the sulphuric acid contribution on the growth rate, the contribution of other vapours e.g. low volatile organics can be found out. Such analyses provide very useful indirect information on nanoparticle chemical composition, in the absence of direct measurement methods.

Appendix A

The Fuchs-Sutugin transition regime correction factor β_m for mass flux is given by (Fuchs and Sutugin, 1971):

$$\beta_\mathrm{m} = \frac{1+Kn}{1+\left(\frac{4}{3\alpha_\mathrm{m}}+0.337\right)Kn+\frac{4}{3\alpha_\mathrm{m}}Kn^2}. \tag{A1}$$

Here Kn is the Knudsen number and α_m mass accommodation coefficient (assumed to be unity in this work). We have used the same modified form of the Knudsen number Kn as Lehtinen and Kulmala (2003):

$$Kn = \frac{2\lambda}{d_\mathrm{p}+d_\mathrm{v}}, \quad \lambda = \frac{3(D_\mathrm{p}+D_\mathrm{v})}{\left(\bar{c}_\mathrm{p}^2+\bar{c}_\mathrm{v}^2\right)^{1/2}}. \tag{A2}$$

The particle diffusion coefficient is calculated according to

$$D_\mathrm{p} = \frac{kTC_\mathrm{c}}{3\pi\mu d_\mathrm{p}}, \tag{A3}$$

where μ is the dynamic viscosity of air (approximately $1.84\times10^{-4}\,\mathrm{g\,cm^{-1}\,s^{-1}}$ at temperature 298 K and normal atmospheric pressure), and the Cunningham slip correction factor is given by $C_\mathrm{c}=1+Kn\cdot(1.257+0.4\cdot\exp(-1.1/Kn))$ (Seinfeld and Pandis, 2006). When calculating C_c for the particle the definition of Knudsen number is $Kn=2\lambda_\mathrm{v}/d_\mathrm{p}$. For vapour molecules we have calculated the diffusion coefficient from the semi-empirical formula presented in Poling et al. (2001):

$$D_\mathrm{v} = \frac{0.001T^{1.75}}{P\left(\Sigma_\mathrm{air}^{1/3}+\Sigma_\mathrm{v}^{1/3}\right)^2}\sqrt{\frac{1}{m_\mathrm{air}}+\frac{1}{m_\mathrm{v}}}, \tag{A4}$$

where m_air and m_v are molecule masses of air and the condensing vapour and P is pressure in units of atm. The diffusion volumes of air and the condensing vapour, Σ_air and Σ_v, are obtained by summing up tabulated atomic diffusion volumes (see Poling et al., 2001). For air molecules we have used values $m_\mathrm{air}=28.97$ amu and $\Sigma_\mathrm{air}=19.7$.

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