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Growth of atmospheric nano-particles by heterogeneous nucleation of organic vapor

J. Wang, R. L. McGraw, and C. Kuang

Atmospheric Sciences Division, Brookhaven National Laboratory, Upton, NY 11973-5000, USA

Correspondence to: J. Wang (jian@bnl.gov)

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Abstract. Atmospheric aerosols play critical roles in air quality, public health, and visibility. In addition, they strongly influence climate by scattering solar radiation and by changing the reflectivity and lifetime of clouds. One major but still poorly understood source of atmospheric aerosols is new particle formation, which consists of the formation of thermodynamically stable clusters from trace gas molecules (homogeneous nucleation) followed by growth of these clusters to a detectable size (~ 3 nm). Because freshly nucleated clusters are most susceptible to loss due to high rate of coagulation with pre-existing aerosol population, the initial growth rate strongly influences the rate of new particle formation and ambient aerosol population. Whereas many field observations and modeling studies indicate that organics enhance the initial growth of the clusters and therefore new particle formation, thermodynamic considerations would suggest that the strong increase of equilibrium vapor concentration due to cluster surface curvature (Kelvin effect) may prevent ambient organics from condensing on these small clusters. Here, the contribution of organics to the initial cluster growth is described as heterogeneous nucleation of organic molecules onto these clusters. We find that the strong gradient in cluster population with respect to its size leads to positive cluster number flux. This positive flux drives the growth of clusters substantially smaller than the Kelvin diameter, conventionally considered the minimum particle size that can be grown through condensation. The conventional approach neglects the contribution from the cluster concentration gradient, and underestimates the cluster survival probabilities by a factor of up to 60 if early growth of clusters is due to both condensation of sulfuric acid and heterogeneous nucleation of organic vapors.

1 Introduction

Atmospheric aerosols have adverse effects on air quality and human health (Pope et al., 2002). They also contribute to urban and regional haze, leading to reduction in visibility (Hinds, 1999). On both regional and global scales, atmospheric aerosols strongly influence climate by scattering solar radiation and by serving as cloud condensation nuclei (CCN) to change the reflectivity, lifetime, and coverage of clouds (Finlayson-Pitts and Pitts, 2000; Seinfeld and Pandis, 2006; Twomey, 1977; Albrecht, 1989).

New particle formation in the atmosphere significantly influences the concentration of atmospheric aerosols, and therefore their impact on climate (Kerminen et al., 2005; Laaksonen et al., 2005; Spracklen et al., 2008). Model simulations show that nearly half of the global cloud condensation nuclei (CCN) in the atmospheric boundary layer may be formed through new particle formation (Merikanto et al., 2009). New particle formation is a two-stage process consisting of formation of thermodynamically stable clusters from trace gas molecules (homogeneous nucleation) followed by growth of these clusters to a detectable size of ~ 3 nm (McMurry et al., 2005; Kuang et al., 2010). Due to the high coagulation rate of clusters smaller than 3 nm with the pre-existing aerosol population, for new particle formation to take place, these clusters need to grow sufficiently fast to escape removal by coagulation (Kuang et al., 2010).

It is generally accepted that homogeneous nucleation in the troposphere involves sulfuric acid (Weber et al., 1996; Riipinen et al., 2007; Kuang et al., 2008). However, the concentration of gaseous sulfuric acid, while sufficient for the first step of homogeneous nucleation, is often insufficient to grow the resulting clusters (here, particles smaller than 3 nm are also referred to as clusters) fast enough to survive the coagulation scavenging by pre-existing aerosol population (Kuang et al., 2010). Observed growth rates of nucleated particles are often much greater than those based only on the condensation of sulfuric acid and associated inorganic compounds (Weber et al., 1997; Kuang et al., 2010, 2012; Mäkelä et al., 2001; O'Dowd et al., 2002; Iida et al., 2008), and modeling studies have indicated that condensation of low-volatility organic vapors contribute significantly to the initial growth of the clusters (Kulmala et al., 2004c; Paasonen et al., 2010). This enhancement is also supported by field measurements that show organics are often the dominant component of newly formed particles (Smith et al., 2008, 2010). However, thermodynamic considerations suggest that the strong increase of equilibrium vapor concentration due to cluster surface curvature (Kelvin effect) would prevent ambient organics from condensing on these small clusters (Kulmala et al., 2004a; Zhang and Wexler, 2002). Since freshly nucleated clusters are most susceptible to loss below 3 nm due to the high coagulation rate, the initial growth strongly influences the rate of new particle formation and ambient aerosol population.

Here, we extend the methodology of classical nucleation theory to describe the initial condensational growth of freshly nucleated clusters by organic vapor. The contribution of organics to the initial growth is treated as heterogeneous nucleation of organic molecules onto the clusters, and the number flux of clusters through a given size is examined using the same statistical thermodynamics treatment as in nucleation theory. We find that the strong gradient in cluster population with respect to size leads to positive cluster number flux, and therefore drives the growth of clusters substantially smaller than the Kelvin diameter, which is the critical embryo size for heterogeneous nucleation and is conventionally considered as the minimum particle size that can be grown through condensation. This conventional approach, which neglects the contribution from the cluster concentration gradient, substantially underestimates the initial growth of the clusters and the survival probabilities of these clusters to 3 nm or CCN sizes.

2 Methods

Conventionally, the growth rate (GR) due to condensation is calculated from the difference between the concentrations of condensing species far from and at the particle surface corrected for the effect of particle curvature (Seinfeld and Pandis, 2006):

$$\frac{\mathrm{d}D_\mathrm{p}}{\mathrm{d}t} = \frac{1}{2D_\mathrm{p}^2}\left(D_\mathrm{p}+D_\mathrm{m}\right)^2 \bar{c}_\mu v \left[C_\infty - C_\mathrm{S}\exp\left(\frac{4\sigma v}{kTD_\mathrm{p}}\right)\right] \equiv \mathrm{GR}_\mathrm{cond}. \quad (1)$$

Here, D_p is the particle diameter, D_m is the diameter of the condensing molecule, $\bar{c}_\mu$ is the mean relative speed of the particle and condensing molecule, v is the volume of the condensing molecule, C_∞ is the concentration of condensing species far from the particle surface, C_S is the saturation concentration over a flat surface, and $\mathrm{GR}_\mathrm{cond}$ is the conventional condensational growth rate. The enhancement of the surface vapor concentration due to particle curvature (Kelvin effect) is described by the factor $\exp\left(\frac{4\sigma v}{kTD_\mathrm{p}}\right)$, where σ is surface tension, k is the Boltzmann constant, and T is absolute temperature. In Eq. (1), the term $\frac{1}{D_\mathrm{p}^2}\left(D_\mathrm{p}+D_\mathrm{m}\right)^2$ is included to account for the increase in collision diameter, which becomes non-negligible when the sizes of the particle and condensing molecule are comparable (Nieminen et al., 2010). Here we assume condensed organics do not form a solution with existing species in the particle (i.e., the Raoult's effect on equilibrium organic vapor pressure is neglected). Previous studies indicate that the early growth is often dominated by organics during NPF events, suggesting particles consisting mostly of organics. Therefore, the Raoult's effect on equilibrium organic vapor pressure may be modest over the particle size range of interest (Riccobono et al., 2012). The Kelvin factor increases exponentially with decreasing D_p and is huge for newly formed 1–2 nm clusters, reaching as high as 10^5 for typical ambient organic species (Zhang and Wexler, 2002; Kulmala et al., 2004a). As a result, the concentration difference $C_\infty - C_\mathrm{S}\exp\left(\frac{4\sigma v}{kTD_\mathrm{p}}\right)$ in Eq. (1) becomes negative, preventing organics from condensing onto the clusters (Zhang and Wexler, 2002). The particle diameter at which the quantity $C_\infty - C_\mathrm{S}\exp\left(\frac{4\sigma v}{kTD_\mathrm{p}}\right)$ equals zero is referred to as the Kelvin diameter. The Kelvin diameter, which is typically greater than 2 nm for ambient organic vapors, represents the minimum size at which particles would grow through condensation according to Eq. (1). In this traditional view, condensation of organic vapors cannot contribute to the growth of clusters smaller than the Kelvin diameter, and the resulting particle number flux, derived as $J_\mathrm{cond} = \frac{\mathrm{d}N}{\mathrm{d}D_\mathrm{p}}\mathrm{GR}_\mathrm{cond}$, is zero or even negative, where $\frac{\mathrm{d}N}{\mathrm{d}D_\mathrm{p}}$ is the particle number size distribution, and N is the number concentration of particles with diameters less than D_p. It has been suggested that other mechanisms, such as the lowering of vapor pressure through Raoult's law (Kulmala et al., 2004a, b) (nano-Köhler theory), heterogeneous chemical reactions (Zhang and Wexler, 2002), and adsorption of organics on cluster surface (Wang and Wexler, 2013) may help to overcome this large Kelvin effect by facilitating growth to above the Kelvin diameter, at which point the organic vapor can condense conventionally according to Eq. (1).

Here we do not attempt to dispute or ascertain the relative importance of various mechanisms for the early growth of nucleated clusters described in previous studies. Instead, we focus on an alternative mechanism that has not been considered. We show that the particle number flux calculated using the conventional condensational growth rate represents the total number flux only when the particle size is substantially greater than the Kelvin diameter. When the cluster size is smaller than or close to the Kelvin diameter, heterogeneous nucleation of organic vapors onto the clusters makes a second contribution that drives growth even for clusters smaller than the Kelvin diameter. This second contribution is due to the gradient in cluster concentration with respect to cluster size. It is not accounted for in conventional growth rate calculations, although it is included in classical nucleation theory. During the heterogeneous nucleation of organic vapors, the net flux from clusters with g condensed organic molecules to those with $g+1$, J_g is (Seinfeld and Pandis, 2006):

$$J_g = \beta_g f_g - \gamma_{g+1} f_{g+1}, \tag{2}$$

where f_g is the corresponding number concentration of the initial clusters (i.e., seed) plus g molecules of condensate, β_g is the size-dependent per-particle condensation rate, and γ_g is the size-dependent per-particle evaporation rate. Equation (2) can be rewritten to separate contributions to the flux from drift and diffusion in cluster size-space (detailed derivation given in Appendix A1):

$$J_g = \overbrace{f_g\left(\beta_g - \gamma_g\right)}^{\text{DRIFT}} \quad \overbrace{-\nabla_g\left[\frac{\left(\beta_g + \gamma_g\right)}{2} f_g\right]}^{\text{DIFFUSION IN CLUSTER SIZE SPACE}} \quad . \tag{3}$$

As $\frac{\mathrm{d}N}{\mathrm{d}D_\mathrm{p}} = \frac{f_g}{\nabla_g D_\mathrm{p}}$, rewriting the particle flux as $J_g = \frac{\mathrm{d}N}{\mathrm{d}D_\mathrm{p}}\mathrm{GR}_\mathrm{eff} = \frac{f_g}{\nabla_g D_\mathrm{p}}\mathrm{GR}_\mathrm{eff}$ defines an effective growth rate GR_eff:

$$\mathrm{GR}_\mathrm{eff} = \frac{J_g}{\left(f_g/\nabla_g D_\mathrm{p}\right)} = \overbrace{\left(\nabla_g D_\mathrm{p}\right)\left(\beta_g - \gamma_g\right)}^{\text{DRIFT}}$$

$$\overbrace{-\frac{\nabla_g D_\mathrm{p}}{f_g}\nabla_g\left[\frac{\left(\beta_g + \gamma_g\right)}{2} f_g\right]}^{\text{DIFFUSION IN CLUSTER SIZE SPACE}} \quad . \tag{4}$$

The lead term on the right side of Eq. (4) describes the drift in the force field given by the gradient of the cluster free energy with respect to cluster size, and is essentially the conventional condensational growth rate described by Eq. (1) (details given in Appendix A2). The second term on the right is related to the gradient in cluster concentration with respect to cluster size. Note that traditional molecular diffusion theory describes the tendency of molecules to spread in space and is due to the gradient of concentration with respect to the space coordinate. As an analogy to traditional molecular diffusion, the second term is referred to as the contribution due to diffusion in cluster size space, with the size-dependent diffusion coefficient $\frac{\beta_g + \gamma_g}{2}$ (McGraw, 2001; Goodrich, 1964; Friedlander, 2000; Lifshitz and Pitaevskii, 1981). Similarly, this diffusion due to the concentration gradient spreads the cluster population along the size coordinate. The second term is significant when the cluster size distribution is steep (i.e., strong gradient in f_g with respect to cluster size), which occurs for clusters below or near the Kelvin diameter (conventional critical embryo size of the heterogeneous nucleation). As shown later, below the Kelvin diameter, the drift term results in evaporation to a smaller size since $\left(\beta_g - \gamma_g\right) < 0$; in this size regime, only the diffusion term makes a positive contribution to the number flux. Conventional growth rate calculations consider only the drift term, which underestimates the full growth rate because the diffusion contribution to growth is positive during new particle formation. This contribution becomes especially significant near or below the Kelvin diameter.

3 Results and discussions

The particle growth rate and its contributions from both drift and diffusion with respect to cluster size are calculated using parameters of gas-phase organic species (Table 1) that are within the typical ranges observed in earlier studies. Previous analyses of field measurements indicate ambient organic vapor concentrations (C_∞) between 1×10^7 and $3 \times 10^8\ \mathrm{cm}^{-3}$ (Paasonen et al., 2010; Kulmala et al., 2001), and saturation vapor concentrations (C_S) less than $\sim 10^5 - 10^6\ \mathrm{cm}^{-3}$ (Kulmala et al., 1998; Kerminen et al., 2000; Anttila and Kerminen, 2003). The conventional growth rate from Eq. (1), ($\mathrm{GR}_\mathrm{cond}$), the effective growth rate (GR_eff) based on the total flux J, and its resolution into the distinct contributions from drift and diffusion ($\mathrm{GR}_\mathrm{drift}$ and $\mathrm{GR}_\mathrm{diff}$) are shown in Fig. 1 as a function of cluster diameter. The total flux J is derived from equilibrium cluster distribution and β_g (Seinfeld and Pandis, 2006). $\mathrm{GR}_\mathrm{drift}$ agrees well with the commonly used $\mathrm{GR}_\mathrm{cond}$ based on Eq. (1). Both $\mathrm{GR}_\mathrm{cond}$ and $\mathrm{GR}_\mathrm{drift}$ decrease with decreasing D_p and reach zero at a Kelvin diameter of ~ 1.9 nm determined by the parameter values in Table 1. Therefore, according to the conventional formula, the smallest particle size that can be grown through the condensation of organic vapors is 1.9 nm in this case. The contribution from the diffusion term $\mathrm{GR}_\mathrm{diff}$ is determined by cluster size distribution f_g and the gradient of f_g with respect to g (i.e., the 2nd term on the RHS of Eq. 4). The cluster size distribution (Fig. A1, Appendix A3) is derived from β_g and γ_g under steady state (McGraw, 2001), a reasonable assumption for sizes near or below the critical embryo size of the heterogeneous nucleation (i.e., Kelvin diameter) (Seinfeld and Pandis, 2006), where $\mathrm{GR}_\mathrm{diff}$ is significant. Based on the method from Shi et al. (1990) and parameters from Table 1, the characteristic time to reach steady state is calculated as 87 s, which is substantially shorter than the typical time scale for variation of organic vapor concentration or the initial cluster (i.e. seed) population. Because f_g appears in both the numerator and denominator, only the shape of f_g (i.e., steady state cluster size distribution) is required to derive $\mathrm{GR}_\mathrm{diff}$. As D_p decreases, the negative gradient in f_g with respect to g becomes stronger, and therefore $\mathrm{GR}_\mathrm{diff}$ increases drastically. As a result, the overall growth rate GR_eff remains 5 % and 1 % of the maximum growth rate (i.e., 11 $\mathrm{nm\,h}^{-1}$, occurs at 3.5 nm in this case) at sub-Kelvin D_p of 1.68 and 1.57 nm,

Table 1. Parameter values for model organic species used in calculation of particle fluxes and growth rates.

Parameter	Value
σ	$0.04\,\mathrm{N\,m^{-1}}$
υ	$135\,\mathrm{cm^3\,mole^{-1}}$
T	$293.15\,\mathrm{K}$
C_S	$10^6\,\mathrm{cm^{-3}}$
C_∞	$10^8\,\mathrm{cm^{-3}}$

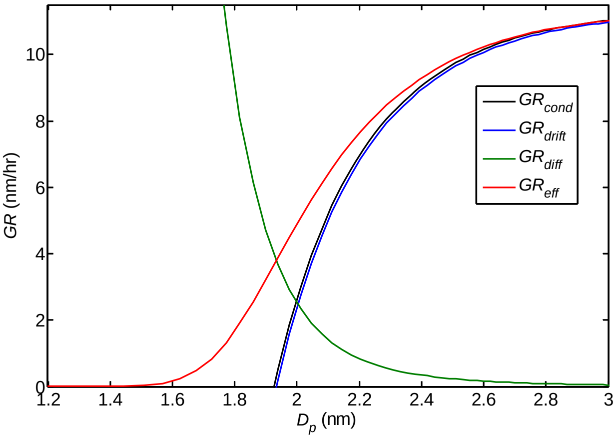

Fig. 1. Comparison of growth rates. The conventional growth rate ($\mathrm{GR_{cond}}$) based on Eq. (1), the effective growth rate ($\mathrm{GR_{eff}}$), and the contributions to $\mathrm{GR_{eff}}$ due to drift ($\mathrm{GR_{drift}}$) and diffusion in cluster size space ($\mathrm{GR_{diff}}$) as functions of cluster size. $\mathrm{GR_{cond}}$ and $\mathrm{GR_{drift}}$ vanish at the Kelvin diameter, and the difference between $\mathrm{GR_{eff}}$ (red) and $\mathrm{GR_{cond}}$ (black) is essentially the contribution from diffusion $\mathrm{GR_{diff}}$ (green). All growth rates are derived using the parameters listed in Table 1.

respectively. This indicates that the conventional approach substantially overestimates the minimum size of the particles that grow through condensation of organics. Furthermore, even at particle sizes just above the Kelvin diameter, $\mathrm{GR_{cond}}$ remains much smaller than the overall $\mathrm{GR_{eff}}$. As shown later, this translates into a significant underestimation of the cluster survival probabilities calculated using $\mathrm{GR_{cond}}$ alone. It is worth noting that while $\mathrm{GR_{diff}}$ depends only on the spectral shape of f_g, the corresponding particle number flux and the total flux J are linearly proportional to f_g. Assuming the cluster growth is dominated by the heterogeneous nucleation of organics, we calculate the concentrations of sub-Kelvin clusters between 1.5 and 1.7 nm, and between 1.7 and 1.9 nm as $5000\,\mathrm{cm^{-3}}$ and $250\,\mathrm{cm^{-3}}$, respectively, to reproduce the average new particle formation rate of $\sim 0.5\,\mathrm{cm^{-3}\,s^{-1}}$ observed from 14 March to 16 May 2011 in Hyytiälä, southern Finland (Kulmala et al., 2013). The magnitude of these cluster concentrations is broadly consistent with the average measurements in these size ranges (Kulmala et al., 2013).

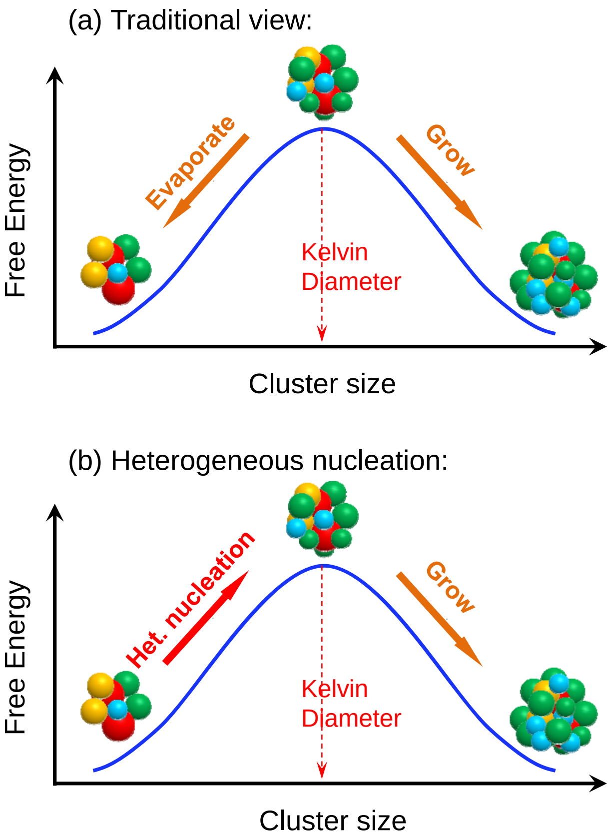

Fig. 2. (a) In traditional view, particles below the Kelvin diameter evaporate and only particles with diameter greater than the Kelvin diameter can grow through condensation; **(b)** based on heterogeneous nucleation theory, even particles below the Kelvin diameter can overcome the energy barrier and grow to larger sizes due to the net forward number flux.

The main mechanism for the growth of the particles through heterogeneous nucleation is also illustrated in Fig. 2. The conventional approach (i.e., $\mathrm{GR_{cond}}$) takes into consideration only the drift term, which is negative below the Kelvin diameter, since $\left(\beta_g - \gamma_g\right) < 0$. Therefore, in the conventional view, particles below the Kelvin diameter will evaporate because it is energetically favorable, and only particles above the Kelvin diameter (i.e., larger than the critical embryo size of the heterogeneous nucleation) can grow through condensation. In heterogeneous nucleation theory, for an individual particle that is smaller than the Kelvin diameter, the per particle evaporation rate is greater than the per particle condensation rate, i.e., $\gamma_g > \beta_g$. Therefore it is more likely for the individual particle to evaporate than to grow. However, because of the strong (negative) gradient in cluster population with respect to size ($f_g > f_{g+1}$), the total condensation flux (i.e., $\beta_g f_g$) is greater than the total evaporation flux (i.e., $\gamma_{g+1} f_{g+1}$) and the resulting net flux is positive (i.e., $J_g = \beta_g f_g - \gamma_{g+1} f_{g+1} > 0$). This net forward flux induced by heterogeneous nucleation can move sub-Kelvin particles over the energy barrier and allow them to grow to larger sizes. The impact of the gradient in the cluster size distribution on the number flux is previously established in both heterogeneous and homogeneous nucleation theories (Frenkel, 1946; Goodrich, 1964; Shizgal and Barrett, 1989; Ruckenstein and Nowakowski, 1990), and it is the very same principle in which gas phase molecules can overcome the energy barrier and form larger thermodynamically stable clusters during homogeneous nucleation (i.e., the first step of new particle formation).

It is worth noting that given the positive heterogeneous nucleation flux, $\mathrm{GR_{eff}}$ is greater than zero at all cluster sizes. Here we define $D_{\mathrm{p,lower}}$ as the particle size at which $\mathrm{GR_{eff}}$ is 1 % of its maximum value (the maximum $\mathrm{GR_{eff}}$ occurs at 3.5 nm in the above case), and $D_{\mathrm{p,upper}}$ as the particle size at which the relative difference between $\mathrm{GR_{eff}}$ and $\mathrm{GR_{cond}}$ decreases to 10 % (2.24 nm for the above case). The size range from $D_{\mathrm{p,lower}}$ to $D_{\mathrm{p,upper}}$ represents where the overall growth rate may be substantially underestimated if the contribution from $\mathrm{GR_{diff}}$ is not taken into consideration. Figure 3a shows $D_{\mathrm{p,lower}}$, $D_{\mathrm{p,upper}}$, and the Kelvin diameter as the ambient organic vapor concentration C_∞ increases from 1×10^7 to $3 \times 10^8\ \mathrm{cm^{-3}}$, a representative range suggested from earlier studies (all other parameters remain the same, as listed in Table 1). Similarly, the dependencies of the three diameters on surface tension σ are presented in Fig. 3b for σ ranging from 0.03 to 0.06 $\mathrm{N\,m^{-1}}$. As expected, the Kelvin diameter, or the critical embryo size for heterogeneous nucleation, decreases with increasing C_∞ or decreasing σ. The relative differences between $D_{\mathrm{p,lower}}$, $D_{\mathrm{p,upper}}$, and the Kelvin diameter increase as the Kelvin diameter decreases, suggesting a stronger impact from the diffusion term $\mathrm{GR_{diff}}$ (i.e., steeper gradient in cluster concentration respective to cluster sizes) for systems with smaller Kelvin diameter. Calculations are also carried out by varying the organics saturation vapor concentration and molar volume, and show similar results.

The contribution from $\mathrm{GR_{diff}}$ can have a significant impact on the overall $\mathrm{GR_{eff}}$ and therefore on the time required for clusters to grow to detectable sizes. The growth time directly controls the survival probability of freshly formed clusters, which is defined as the probability that a cluster will grow to a detectable size (nominally 3 nm) before being scavenged by the pre-existing aerosol (McMurry et al., 2005; Weber et al., 1997; Kerminen and Kulmala, 2002). Because freshly nucleated clusters are most susceptible to loss below 3 nm, the survival probability strongly influences the direct impact of atmospheric nucleation on the ambient aerosol population. As shown in Fig. 1, $\mathrm{GR_{diff}}$ contributes substantially to the overall growth rate $\mathrm{GR_{eff}}$ for clusters near or smaller than the Kelvin diameter. To examine its impact on the survival probability, we numerically solved the aerosol general dynamic equation for an aerosol population growing through simultaneous condensation and coagulation (Friedlander, 2000; Gelbard and Seinfeld, 1978; Kuang et al., 2008, 2009), explicitly accounting for the size-dependent growth rates in Fig. 1. Aerosol loss rates were determined exclusively from coagulation with the pre-existing aerosol, modeled with a size distribution typical of an urban aerosol (Jaenicke, 1993), and scaled to give a Fuchs surface area (A_{Fuchs}) of 330 $\mathrm{\mu m^2\,cm^{-3}}$, the average value for NPF events observed in Mexico City during the MILAGRO measurement campaign (Kuang et al., 2010). The effects of reduced cluster concentrations (due to coagulation) on the diffusion contribution to growth are neglected in this calculation. Early work on the multistate kinetics of nucleation in the presence of background aerosol (McGraw and Marlow, 1983) provides a model-tested criterion for when these effects are important. Empirically, it was found that when $A_{\mathrm{Fuchs}}/f_1 a_1 < 1$, here f_1 is the concentration of monomer and a_1 the surface area per monomer, cluster scavenging can be neglected, and classical nucleation theory, based on the same condensation and evaporation fluxes, applies even with scavenging by background aerosol present. An equivalent dimensionless parameter, L, was introduced by McMurry et al. (2005) for a different purpose, namely as a criterion for new particle formation in the sulfur-rich Atlanta atmosphere: new particle formation was typically observed when L was less than unity but not when L was greater. The combination of these independent findings suggests that when new particle formation is observed to occur, i.e., $L \approx A_{\mathrm{Fuchs}}/f_1 a_1 < 1$, so that the time scale for nucleation is less than the time scale for cluster scavenging, the latter process can be neglected. Conversely, when the scavenging rate is high and needs to be included, it is unlikely that new particle formation will occur anyway.

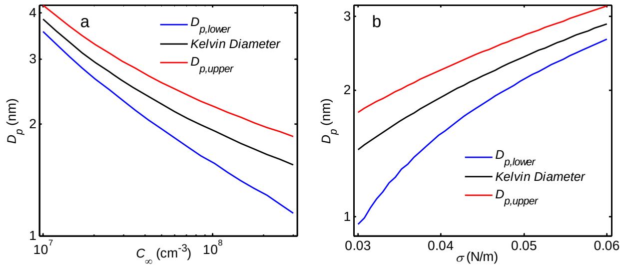

Fig. 3. Variation of $D_{\mathrm{p,lower}}$, $D_{\mathrm{p,upper}}$, and the Kelvin diameter over representative ranges of C_∞ **(a)** and σ **(b)**. All other parameters remain the same as listed in Table 1.

Here we assume that early growth of clusters is due to both condensation of sulfuric acid and heterogeneous nucleation of organic vapors during new particle formation events, and the survival probabilities are derived using $\mathrm{GR_{SA}}+\mathrm{GR_{cond}}$ and $\mathrm{GR_{SA}}+\mathrm{GR_{eff}}$, where $\mathrm{GR_{SA}}$ represents the growth rate attributed to sulfuric acid condensation, and $\mathrm{GR_{cond}}$ and $\mathrm{GR_{eff}}$ are the conventional growth rate and the effective growth rate due to organics presented in Fig. 1. Earlier field studies show that the growth enhancement factor Γ, defined as $(\mathrm{GR_{SA}}+\mathrm{GR_{cond}})/\mathrm{GR_{SA}}$, measured at 3 nm mostly ranges from 5 to 20 (Kuang et al. (2010); also note that $\mathrm{GR_{cond}}$ and

Table 2. The ratio of the cluster survival probability derived from GR_{eff} to that based on GR_{cond} under sulfuric acid and organics concentrations representative of NPF events. The survival probability is calculated for 1.5 nm thermodynamically stable clusters growing to form 3 nm particles.

Case #	C_∞ (organics, cm^{-3})	C_S (organics, cm^{-3})	$[H_2SO_4]$, (cm^{-3})	Growth rate enhancement	A_{Fuchs}, ($\mu m^2\ cm^{-3}$)	Ratio in cluster survival probability
1 (urban)	1.0×10^8	1.0×10^6	5.4×10^7	5	330	1.6
2 (urban)	1.0×10^8	1.0×10^6	2.4×10^7	10	330	4.6
3 (urban)	1.0×10^8	1.0×10^6	1.1×10^7	20	330	62
4 (remote)	1.0×10^7	1.0×10^5	5.4×10^6	5	33.5	1.6
5 (remote)	1.0×10^7	1.0×10^5	2.4×10^6	10	33.5	4.7
6 (remote)	1.0×10^7	1.0×10^5	1.1×10^6	20	33.5	66

GR_{eff} are essentially the same at 3 nm). The calculations are carried out for three sulfuric acid concentrations (5.4×10^7, 2.4×10^7, and $1.1 \times 10^7\ cm^{-3}$), which correspond to Γ values of 5, 10, and 20 for the value of GR_{cond} shown in Fig. 1. For thermodynamically stable clusters of 1.5 nm (Kulmala et al., 2007), the ratio of the cluster survival probability derived from GR_{eff} to that based on GR_{cond} is given in Table 2. The survival probability and therefore the rate of new particle formation are significantly underestimated when the conventional growth rate GR_{cond} is applied to organics. This underestimation of the survival probability becomes more severe with increasing Γ, as the relative contribution of organics to total growth increases, reaching factors of 1.6, 4.8, and 62 for Γ values of 5, 10, and 20, respectively.

In a second set of calculations we examine the impact of the growth due to diffusion in size space (GR_{diff}) on the survival probability under more pristine conditions. In these calculations, the H_2SO_4 concentrations in the above calculations are reduced by a factor of 10 to 5.4×10^6, 2.4×10^6, and $1.1 \times 10^6\ cm^{-3}$, respectively. The concentration $1.1 \times 10^6\ cm^{-3}$ is near the lower end of sulfuric acid concentration ranges observed during new particle formation events in remote locations (Kuang et al., 2010). The concentration and saturation concentrations of organic vapor are also reduced by a factor of 10 to maintain the same growth rate enhancement Γ. If the original organics concentrations are maintained, the growth rate enhancement will be too large and inconsistent with field observations, and the impact due to GR_{diff} will be even greater, as the growth due to organics will have an even larger contribution to the total particle growth. For the pristine conditions, the survival probability is derived using a pre-existing aerosol size distribution with a typical shape of a rural aerosol (Jaenicke, 1993), but scaled to give an average Fuchs surface area of 33.5 $\mu m^2\ cm^{-3}$ for the new particle formation events observed at Hyytiälä during QUEST IV campaign (Kuang et al., 2010). For thermodynamic stable clusters of 1.5 nm, the ratio of the survival probability derived from GR_{eff} to that based on GR_{cond} is similar to that under a more polluted environment, and ranges from 1.6 to 66 as Γ increases from 5 to 20. Importantly, for a given new particle formation event, the ratio of survival probabilities to 3 nm also represents the ratio in production rates of particles at larger sizes, such as cloud condensation nuclei (CCN, ∼ 100 nm), because GR_{cond} and GR_{eff} are essentially the same for particles larger than 3 nm.

4 Conclusions

We have shown that for typical organic vapors in the atmosphere, the diffusion of clusters in size space (GR_{diff}) can have a significant positive contribution to the overall particle growth during new particle formation events. This diffusion contribution can lead to substantial growth for sub-Kelvin clusters, which may be one of the mechanisms that allows ambient organics to contribute to the growth of freshly formed clusters despite the strong Kelvin effect. The conventional approach, which neglects this diffusion contribution, underestimates the early growth rate of clusters. Assuming early growth of clusters is due to both condensation of sulfuric acid and heterogeneous nucleation of organic vapors, we show the growth rate calculated using the conventional approach may lead to an underestimation of cluster survival probability to 3 nm or CCN size by a factor of up to 60. Given its importance, this contribution of cluster diffusion in size space to initial particle growth needs to be included when modeling the rate of new particle formation and the subsequent production of CCN – a critical determinant of aerosol indirect effects on climate.

Appendix A

A1 Contributions to heterogeneous nucleation flux

The separation of the heterogeneous nucleation flux into "drift" and "diffusion in cluster size space" contributions is described in a number of earlier works in classical nucleation theory (Frenkel, 1946; Goodrich, 1964; Shizgal and Barrett, 1989; Ruckenstein and Nowakowski, 1990) and textbooks

(Friedlander, 2000; Seinfeld and Pandis, 2006). A similar separation is also given in McGraw (2001). The separation of the flux following earlier works is briefly described below (Goodrich, 1964; Ruckenstein and Nowakowski, 1990). The net flux from clusters with g condensed molecules to those containing $g+1$ condensed molecules is (Seinfeld and Pandis, 2006):

$$J_g = \beta_g f_g - \gamma_{g+1} f_{g+1}. \tag{A1}$$

Based on the continuum approximation, J is approximated as a continuous function of g, and the gradient in J_g with respect to g is given by

$$\frac{dJ_g}{dg} = J_g - J_{g-1} = \beta_g f_g - \gamma_{g+1} f_{g+1} - \beta_{g-1} f_{g-1} + \gamma_g f_g. \tag{A2}$$

Performing a second order Taylor expansion of the 2nd and third term of the right hand side of Eq. (A2) gives

$$\begin{aligned}\gamma_{g+1} f_{g+1} &= \gamma_g f_g + \frac{d}{dg}\left(\gamma_g f_g\right) + \frac{1}{2}\frac{d^2}{dg^2}\left(\gamma_g f_g\right)\\ \beta_{g-1} f_{g-1} &= \beta_g f_g - \frac{d}{dg}\left(\beta_g f_g\right) + \frac{1}{2}\frac{d^2}{dg^2}\left(\beta_g f_g\right).\end{aligned} \tag{A3}$$

Combining Eqs. (A2) and (A3) gives

$$\begin{aligned}\frac{dJ_g}{dg} &= \frac{d}{dg}\left(\beta_g f_g\right) - \frac{1}{2}\frac{d^2}{dg^2}\left(\beta_g f_g\right) - \frac{d}{dg}\left(\gamma_g f_g\right)\\ &-\frac{1}{2}\frac{d^2}{dg^2}\left(\gamma_g f_g\right) = \frac{d}{dg}\left[\left(\beta_g - \gamma_g\right) f_g\right] - \frac{1}{2}\frac{d^2}{dg^2}\left[\left(\beta_g + \gamma_g\right) f_g\right]\end{aligned} \tag{A4}$$

Integrating the above Eq. (A4) gives the desired separation of the flux into contributions from the drift in the force field and diffusion in cluster size space:

$$\begin{aligned}J_g &= f_g\left(\beta_g - \gamma_g\right) - \frac{1}{2}\frac{d}{dg}\left[\left(\beta_g + \gamma_g\right) f_g\right]\\ &= \overbrace{f_g\left(\beta_g - \gamma_g\right)}^{\text{DRIFT}} \quad \overbrace{-\frac{1}{2}\nabla_g\left[\left(\beta_g + \gamma_g\right) f_g\right]}^{\text{DIFFUSION IN CLUSTER SIZE SPACE}} \quad .\end{aligned} \tag{A5}$$

A2 Comparison of $\mathrm{GR}_{\mathrm{drift}}$ and $\mathrm{GR}_{\mathrm{cond}}$

The size-dependent per-particle condensation rate β_g is given by (Seinfeld and Pandis, 2006):

$$\beta_g = \frac{\pi}{4}\left(D_\mathrm{p} + D_\mathrm{m}\right)^2 \bar{c}_\mu C_\infty. \tag{A6}$$

The size-dependent per-particle evaporation rate is related to the condensation rate by (Seinfeld and Pandis, 2006):

$$\gamma_g = \frac{\beta_{g-1} C_\mathrm{S}}{C_\infty} \exp\left[\frac{\sigma\left(a_g - a_{g-1}\right)}{kT}\right], \tag{A7}$$

where a_g is the surface area of the growing cluster consisting of the initial cluster (seed) and g monomers of condensate.

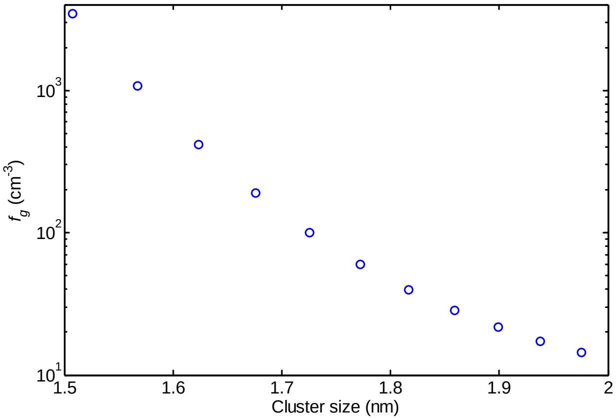

Fig. A1. An example of steady state cluster size distribution at sub-Kelvin size range derived using parameters from Table 1.

Letting D_s denote the size of the initial cluster, the size of the growing cluster is:

$$D_\mathrm{p} = \left(D_\mathrm{s}^3 + g D_\mathrm{m}^3\right)^{1/3}.$$

Given its small volume, addition of a monomer leads to a small increase in cluster diameter. Employing the continuum approximation at large g, we have

$$\begin{aligned}a_g - a_{g-1} &= \nabla_g a = \nabla_g\left[\pi\left(D_\mathrm{s}^3 + g D_\mathrm{m}^3\right)^{2/3}\right]\\ &= \frac{2}{3}\pi\left(D_\mathrm{s}^3 + g D_\mathrm{m}^3\right)^{-1/3} D_\mathrm{m}^3 = 4\frac{1}{6}\pi D_\mathrm{m}^3\left(D_\mathrm{s}^3 + g D_\mathrm{m}^3\right)^{-1/3}\\ &= \frac{4v}{D_\mathrm{p}}.\end{aligned} \tag{A8}$$

Similarly, the gradient of the size of the growing cluster is given by

$$\begin{aligned}\nabla_g D_\mathrm{p} &= \nabla_g\left[\left(D_\mathrm{s}^3 + g D_\mathrm{m}^3\right)^{1/3}\right] = \frac{1}{3}\left(D_\mathrm{s}^3 + g D_\mathrm{m}^3\right)^{-2/3} D_\mathrm{m}^3\\ &= \frac{\frac{\pi}{6} D_\mathrm{m}^3}{\frac{\pi}{2} D_\mathrm{p}^2} = \frac{v}{\frac{\pi}{2} D_\mathrm{p}^2}.\end{aligned} \tag{A9}$$

Inserting Eq. (A8) into Eq. (A7), γ_g can be written as

$$\begin{aligned}\gamma_g &= \frac{\beta_{g-1} C_\mathrm{S}}{C_\infty} \exp\left(\frac{\sigma \nabla_g a}{kT}\right) \approx \frac{\beta_g C_\mathrm{S}}{C_\infty} \exp\left(\frac{\sigma \nabla_g a}{kT}\right)\\ &= \frac{\beta_g C_\mathrm{S}}{C_\infty} \exp\left[\frac{4\sigma v}{kT D_\mathrm{p}}\right].\end{aligned} \tag{A10}$$

Combining Eqs. (A6), (A9), and (A10), we can show that the traditional condensation growth rate is essentially the contribution of drift term to the total growth rate:

$$\begin{aligned}\mathrm{GR}_\mathrm{drift} &= \left(\nabla_g D_\mathrm{p}\right)\left(\beta_g - \gamma_g\right)\\ &= \frac{1}{2D_\mathrm{p}^2}\left(D_\mathrm{p} + D_\mathrm{m}\right)^2 \bar{c}_\mu v\left[C_\infty - C_\mathrm{S} \exp\left(\frac{4\sigma v}{kT D_\mathrm{p}}\right)\right] = \mathrm{GR}_\mathrm{cond}.\end{aligned} \tag{A11}$$

A3 Steady state cluster size distribution f_g

The steady state cluster size distribution f_g is derived from β_g and γ_g using parameters from Table 1. It is worth noting that $\mathrm{GR}_{\mathrm{diff}}$ depends only on the spectral shape of f_g, whereas the corresponding flux and the total flux is linearly proportional to the value of f_g. The steady state cluster distribution shown in Fig. A1 corresponds to a total flux of $0.5\,\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$, the average value observed during NPF events from 14 March to 16 May 2011 in Hyytiälä, southern Finland (Kulmala et al., 2013).

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