

**Hygroscopic growth
parameterizations**

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Aerosol hygroscopic growth parameterization based on a solute specific coefficient

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Abstract

Water is a main component of atmospheric aerosols and its amount depends on the particle chemical composition. We introduce a new parameterization for the aerosol hygroscopic growth factor (HGF), based on an empirical relation between water activity (a_w) and solute molality (μ_s) through a single solute specific coefficient ν_i . Three main advantages are: (1) wide applicability, (2) simplicity and (3) analytical nature. (1) Our approach considers the Kelvin effect and covers ideal solutions at large relative humidity (RH), including CCN activation, as well as concentrated solutions with high ionic strength at low RH such as the relative humidity of deliquescence (RHD). (2) A single ν_i coefficient suffices to parameterize the HGF for a wide range of particle sizes, from nanometer nucleation mode to micrometer coarse mode particles. (3) In contrast to previous methods, our analytical a_w parameterization depends not only on a linear correction factor for the solute molality, instead ν_i also appears in the exponent in form $x \cdot a^x$. According to our findings, ν_i can be assumed constant for the entire a_w range (0–1). Thus, the ν_i based method is computationally efficient. In this work we focus on single solute solutions, where ν_i is pre-determined with the bisection method from our analytical equations using RHD measurements and the saturation molality μ_s^{sat} . The computed aerosol HGF and supersaturation (Köhler-theory) compare well with the results of the thermodynamic reference model E-AIM for the key compounds NaCl and $(\text{NH}_4)_2\text{SO}_4$ relevant for CCN modeling and calibration studies. The equations introduced here provide the basis of our revised gas-liquid-solid partitioning model, i.e. version 4 of the Equilibrium Simplified Aerosol Model (EQSAM4), described in a companion paper.

1 Introduction

The gas-liquid-solid partitioning of atmospheric particles and precursor gases to large degree determines the composition and water uptake of atmospheric aerosol particles, which affect human and ecosystem health, clouds and climate (e.g. Künzli et al.,

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2000; IPCC, 2007). The most abundant aerosol species is water. The aerosol liquid water content (AWC) governs the size distribution, the atmospheric lifetime of both particles and interacting gases, and particle optical properties. Considering thermodynamic equilibrium, the AWC depends primarily on the available water vapor, ambient temperature (T) and relative humidity (RH). The AWC also depends on the particle hygroscopicity, which is the ability to absorb (release) water vapor from (to) the surrounding atmosphere. In particular the ability of salt solutes to dissolve causes hygroscopic growth (HG) of aerosol particles at subsaturated atmospheric conditions ($RH < 100$ [%]), where the equilibrium water uptake of atmospheric aerosols is generally limited by the available water vapor. For instance, sea salt particles can deliquesce at a very low RH of deliquescence (RHD) below 40 [%], because they contain a small amount of the very hygroscopic salt magnesium chloride ($MgCl_2$). Therefore, marine air is often much hazier than continental air at the same T and RH. The HG of atmospheric aerosol particles influences heterogeneous reactions, light extinction and visibility, and is important for the aerosol radiative forcing of climate (e.g. Pilinis et al., 1995). The HG and the associated AWC depends on the ionic composition of the particles, which in turn depends on the total AWC. Consequently, the HG and AWC involving gas/liquid/solid aerosol partitioning is difficult to measure or predict numerically, even though the complex thermodynamic system may be simplified by assuming phase equilibrium (e.g. Wexler and Potukuchi, 1998; Seinfeld and Pandis, 2006).

At the microscopic level two mechanisms of water uptake are important: (i) Adsorption of water on insoluble surfaces, whereby the fraction of surface area covered by adsorbed water is proposed as criterion for hydrophilicity (e.g. Naono and Nakuman, 1991). (ii) Absorption of water by soluble particulates, which are per definition hydrophilic. For atmospheric aerosols the absorption of water by soluble compounds is most important, and adsorption does not contribute much to the total AWC. Soluble and in particular hygroscopic particles take up water from the atmosphere for solute hydration. An increase in solute concentration (e.g. due to condensation of volatile compounds, coagulation, or chemical reactions) therefore either leads to additional

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water uptake, or to solute precipitation (causing a solid phase to co-exist with the aqueous phase), while a decrease of the solute concentration (e.g. due to evaporative loss or chemical reactions) is associated with the evaporation of aerosol water, so that ultimately at equilibrium the aerosol molality of a given aerosol composition remains constant at given T , RH and water activity (a_w).

The aerosol HG can be determined for certain solutes from laboratory a_w measurements (e.g. Tang and Munkelwitz, 1994), or calculated by considering the vapor pressure reduction that occurs by dissolving a salt solute in water – known as Raoult's law (Raoult, 1888) – if non-idealities of solution are taken into account (e.g. Warneck, 1988; Pruppacher and Klett, 2007). According to Köhler-theory (Köhler, 1936) and Raoult's law, the so-called Raoult-term, which considers the lowering of the equilibrium vapor pressure with increasing solute concentration at a given RH, is complemented by the so-called Kelvin-term, which accounts for the increase in the water vapor pressure due to the curvature of the particle surface. The modern Köhler equations allow to determine the equilibrium size of an aerosol droplet for a given dry size, chemical composition, RH and T , by accounting for the dissolution of gases into droplets, changes in surface tension, ion charges, or density of the droplet solutions (e.g. Reiss, 1950; Young and Warren, 1992; Konopka, 1996; Shulman et al., 1996; Laaksonen et al., 1998; Charlson et al., 2001; Russell and Ming, 2002; Mikhailov et al., 2004; Biskos et al., 2006a, b; Seinfeld and Pandis, 2006; McFiggans et al., 2006; Pruppacher and Klett, 2007; Rose et al., 2008; Mikhailov et al., 2009; Ruehl et al., 2010).

Three types of methods have been used to account for hygroscopic growth of atmospheric aerosols in general circulation models (GCMs): (i) the $f(\text{RH})$ method, (ii) Köhler-theory and (iii) thermodynamic equilibrium models. The $f(\text{RH})$ method (Charlson et al., 1992) scales particle optical properties as a function of RH. In a simplified manner, this method accounts for the hygroscopic nature of water-soluble aerosol particles and, hence, has been used for first-order estimates of aerosol HG and the corresponding radiative forcing of climate. The second method explicitly accounts for the hygroscopic nature, since the Köhler equation is based on the Raoult-term. However,

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both methods do not account for gas-liquid-solid partitioning and deliquescence that accompanies aerosol hygroscopic growth. Only models that also account for the gas-liquid-solid partitioning of single and mixed solute solutions are sufficiently comprehensive to calculate the RHD based HG factor (HGF) of single and mixed solutions, which usually includes various inorganic, organic and non-soluble compounds.

Here we first introduce new single solute solutions parameterizations for the aerosol HGF, which are based on a new representation of water activity, presented in Sect. 2. The equations provide the basis of our revised gas-liquid-solid equilibrium partitioning model, i.e. version 4 of the Equilibrium Simplified Aerosol Model (EQSAM4), which considers mixed solutions of various compounds important for atmospheric modeling. EQSAM4 is described in the companion paper. Our HGF parameterizations require for a given temperature only one solute specific coefficient, ν_i , to approximate a_w for the entire range of water activity (0–1). ν_i is pre-determined in Sect. 3 from our analytical equations with the bisection method using RHD measurements and applied to three cases: (a) flat surface, i.e. without Kelvin-term and sub-saturation ($RH < 100$ [%]), (b) curved surface, i.e. including Kelvin-term and subsaturation, and (c) supersaturation with Kelvin-term, i.e. $RH \geq 100$ [%]. The derived HGF and supersaturation results are compared with those derived from the thermodynamic reference model E-AIM (Wexler and Clegg, 2002; Clegg and Wexler, 2007) for two key compounds NaCl and $(\text{NH}_4)_2\text{SO}_4$, which are important for modeling of cloud condensation nuclei (CCN) and central for CCN calibrations (Frank et al., 2006, 2007) and CCN studies (Dusek et al., 2006; Rose et al., 2008). A comprehensive box model inter-comparison of major inorganic aerosol thermodynamic properties of mixed solutions predicted by EQSAM4 and EQUISOLV II (Jacobson et al., 1996, 1999) is subject of the revised publication of Xu et al. (2009).

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2 Aerosol hygroscopic growth parameterizations of single solutes

2.1 Köhler theory and models

Köhler theory relates the particle growth of a spherical droplet formed on a soluble particle to the ambient relative humidity (RH), which can be expressed as (e.g. Prupacher and Klett, 2007; Seinfeld and Pandis, 2006; Mikhailov et al., 2004, 2009; Rose et al., 2008):

$$\begin{aligned} \text{RH} &= \frac{\rho_{\text{w(g)}}}{\rho_{\text{w(g)}}^{\text{sat}}} \\ &= a_{\text{w}} \cdot K_{\text{e}} \\ &= a_{\text{w}} \cdot \exp\left(\frac{4 \cdot M_{\text{w}} \cdot \sigma_{\text{sol}}}{R \cdot T \cdot \rho_{\text{w}} \cdot D_{\text{wet}}}\right) \\ &= a_{\text{w}} \cdot \exp\left(\frac{4 \cdot M_{\text{w}} \cdot \sigma_{\text{sol}}}{R \cdot T \cdot \rho_{\text{w}} \cdot g_{\text{s}} \cdot D_{\text{s}}}\right) \end{aligned} \quad (1)$$

$\rho_{\text{w(g)}} [\text{Pa}]$ and $\rho_{\text{w(g)}}^{\text{sat}} [\text{Pa}]$ denote the partial pressures of water vapor of the ambient air at temperature $T [\text{K}]$ and at saturation at the same T . It is common to express the dimensionless fractional relative humidity $\text{RH} [-]$ as the saturation ratio $s = \text{RH} [-]$, with RH (not in italics) in [%]. In case of supersaturation, $\text{RH} > 100 [\%]$, it is customary to use the supersaturation S , which is defined as $S = (s - 1) \cdot 100 [\%]$.

The dimensionless term $a_{\text{w}} [-]$ is the water activity of the solution (droplet) and is referred to as the Raoult term (or volume contribution), since it accounts for an increase of the droplet volume (D_{wet}^3) with increasing RH with a $1/D_{\text{wet}}^3$ proportionality. $K_{\text{e}} [-]$ is the Kelvin (or surface) term, which accounts for a compensating effect with a $1/D_{\text{wet}}$ proportionality and the RH dependent surface tension $\sigma_{\text{sol}} [\text{J m}^{-2}]$ of the solution droplet; $R [\text{J mol}^{-1} \text{K}^{-1}]$ is the ideal gas constant and $T [\text{K}]$ the droplet temperature, $D_{\text{wet}} [\text{m}]$ is the ambient droplet diameter (geometric diameter = mass equivalent diameter

of a compact spherical droplet). With the assumption of “volume-additivity”, i.e. the volume of the solution droplet is given by the sum of the volumes of the dry solute and of the pure water contained in the droplet, D_{wet} can be expressed in terms of the dry mass equivalent diameter D_s [m] and the RH dependent mass equivalent growth factor g_s [-] of the droplet. g_s is defined as the ratio of wet to dry droplet diameter, and can be expressed in terms of the solute molality $\mu_s = n_s/m_w$ [mol(solute) kg⁻¹(H₂O)]:

$$g_s = \frac{D_{\text{wet}}}{D_s}$$

$$= \left(\frac{V_{\text{wet}}}{V_s}\right)^{1/3} = \left(\frac{V_w + V_s}{V_s}\right)^{1/3} = \left(\frac{V_w}{V_s} + 1\right)^{1/3} = \left(\frac{\rho_s \cdot m_w}{\rho_w \cdot m_s} + 1\right)^{1/3} \quad (2)$$

$$= \left(\frac{\rho_s}{M_s \cdot \rho_w \cdot \mu_s} + 1\right)^{1/3}$$

$V_{\text{wet}} = V_w + V_s$ [m³] is the total volume of the wet droplet with $V_s = m_s/\rho_s = n_s M_s/\rho_s$ and $V_w = m_w/\rho_w = n_w M_w/\rho_w$ [m³], i.e. the volumes of the initially dry solute and the associated pure water, respectively. m_s and m_w [kg] denote the corresponding solute and water masses, M_s and M_w [kg mol⁻¹] the molar masses, n_s and n_w [mol] the number of moles, and ρ_s and ρ_w [kg m⁻³] the densities, respectively. In the following g_s will be referred to as the hygroscopic growth factor (HGF) and applied to atmospheric aerosols.

2.1.1 Water activity representations – concepts

To clarify similarities and differences with previous work, we follow Rose et al. (2008) – in the following abbreviated as Rose08 (available at <http://www.atmos-chem-phys.net/8/1153/2008/>) – as they present a comprehensive overview of water activity representations on which the various present-day Köhler models are based. Rose08 have subdivided the water activity representations into 5 categories (see their Table 3), i.e.

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1. Activity parameterization (AP) models, e.g. Tang and Munkelwitz (1994), Tang (1996), Kreidenweis et al. (2005), which are of the type:

$$a_w = 1 + \sum_q a_q \cdot (100 \cdot \chi_s)^q \quad (3)$$

Tang and Munkelwitz (1994) and Tang (1996) have presented parameterizations for the activity of water in aqueous solutions derived from electrodynamic balance (EDB) single particle experiments as polynomial fit functions of RH dependent solute mass percentage ($100 \cdot \chi_s$). The solute mass fraction χ_s and the polynomial coefficients a_q [–] are listed e.g. in Table A2 of Rose08 to which we refer for a further discussion (also for 2–5).

2. Osmotic coefficient (OS) models, e.g. Robinson and Stokes (1959, 1965), Pitzer and Mayorga (1973), Brechtel and Kreidenweis (2000), which are of the type:

$$a_w = \exp\left(-M_w \cdot \Phi_w \cdot \sum_i \mu_i\right) = \exp(-M_w \cdot \Phi_s \cdot \nu_s \cdot \mu_s) \quad (4)$$

According to Robinson and Stokes (1959) (the book pages are online freely accessible at <http://books.google.de/books?id=6ZVqmqm-J9GkC&printsec=frontcover>) the water activity a_w is related to the total molality of all solute species $\sum_i \mu_i$ by the dimensionless molal osmotic coefficient of the aqueous phase Φ_w [–], where $\sum_i \mu_i$ can be expressed as $\nu_s \cdot \mu_s$ if the molal osmotic coefficient of the solute Φ_s is used in conjunction with the solute molality μ_s [mol kg⁻¹(H₂O)] and the solute's stoichiometric coefficient ν_s . M_w is the molar mass of water in SI-units [kg mol⁻¹]. Φ_w deviates from unity as the solution becomes non-ideal.

3. Van't Hoff factor (VH) models, e.g. van't Hoff (1887), Low (1969), Young and Warren (1992), which are of the type:

$$a_w = \frac{1}{1 + i_s \cdot n_s/n_w} = (1 + M_w \cdot i_s \cdot \mu_s)^{-1} \quad (5)$$

The van't Hoff factor i_s [-] is a constant, and similar to the stoichiometric coefficient (dissociation number) ν_s . deviations of i_s from ν_s can be attributed to solution non-idealities. The relation between i_s , ν_s and Φ_s can be approximated by a series expansion of the exponential term in Eq. (4) and can be approximated as (Kreidenweis et al., 2005):

$$i_s \approx \nu_s \cdot \Phi_s \quad (6)$$

4. Effective hygroscopicity parameter (EH) model of Petters and Kreidenweis (2007), which is of the type:

$$a_w = \left(1 + \kappa \frac{V_s}{V_w}\right)^{-1} \quad (7)$$

$V_s = n_s M_s / \rho_s$ and $V_w = n_w M_w / \rho_w$ are the volumes [m³] of the initially dry solute and pure water, respectively, with M_s and M_w [kg mol⁻¹] the molar masses of solute and water, respectively, and ρ_s and ρ_w [kg m⁻³] the densities of the initially dry solute and pure water, respectively. The dimensionless hygroscopicity parameter κ [-] parameterizes the composition dependent water activity of a solution droplet in analogy to the van't Hoff factor. κ and the van't Hoff factor i_s are related by:

$$\kappa = i_s \cdot \frac{n_s \cdot V_w}{n_w \cdot V_s} = i_s \cdot \frac{V_w}{V_s} = i_s \cdot \frac{\rho_s \cdot M_w}{\rho_w \cdot M_s} \quad (8)$$

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with v_s and v_w [mol m^{-3}] the molar volumes of the solute and of water, respectively.

Rose08 have used the Pitzer-Simonson-Clegg mole fraction based model AIM of Clegg et al. (1998a, b), Wexler and Clegg (2002) as a reference model (Clegg and Wexler, 2007), which is also based on osmotic coefficients, i.e. on Eq. (4), but combines the OS model with the universal functional group activity coefficient model (UNIFAC, Fredenslund et al., 1975).

The activity coefficient model describes the water activity by

$$a_w = f_w \cdot x_w = f_w \cdot (1 + M_w \cdot \mu_s)^{-1} \quad (9)$$

f_w [–] denotes the rational or mole fraction scale activity coefficient of water, which is included in this water activity representation model to account for non-ideal solutions and solutes that dissociate (partly or completely). x_w [–] is the mole fraction of water in the solution that at equilibrium contains the numbers of moles (amount-of-substance) n_w [mol] and n_s [mol] of water and solute, respectively. x_w can be mathematically described as:

$$x_w = \frac{n_w}{n_w + n_s} = \frac{1}{1 + n_s/n_w} = (1 + M_w \cdot \mu_s)^{-1} \quad (10a)$$

Analogously, the mole fraction of the solute x_s is given by

$$x_s = 1 - x_w = \frac{n_s}{n_w + n_s} = \frac{1}{1 + n_w/n_s} = \left(1 + \frac{1}{M_w \cdot \mu_s}\right)^{-1} \quad (10b)$$

i.e. satisfying the condition $x_s + x_w = 1$ for a binary solution (some solute and water).

x_w and x_s are related to the solute molality μ_s [$\text{mol(solute) kg}^{-1}(\text{H}_2\text{O})$] by

$$\mu_s = \frac{n_s}{m_w} = \frac{n_s}{n_w} \cdot \frac{1}{M_w} = \frac{x_s}{x_w} \cdot \frac{1}{M_w} = (M_w \cdot [1/x_s - 1])^{-1} = (M_s \cdot [1/x_s - 1])^{-1} \quad (11)$$

where $\chi_s = \frac{m_s}{(m_s + m_w)}$ [–] is the solute mass fraction, m_s and m_w [kg] the masses of solute and water, with M_s and M_w [kg mol^{-1}] the corresponding molar masses, respectively.

To consider cases for which the solution contains more than one solute, Eqs. (10a, b) is expressed in a more general form:

$$x_i = n_i / \left(\sum_j n_j \right) \quad (12)$$

n_i is the number of moles [mol] of component i , where $i = w$ for the solvent, or $i = s$ for the solute; $j = s_1, s_2, s_3, \dots, s_n, w$ is the summation over all $n + 1$ components in solution, so that $\sum_j x_j = 1$.

Equation (9) expressed in the general form yields the activity and the activity coefficient of solutes ($i = s$) or the solvent water ($i = w$), i.e.:

$$a_i = f_i \cdot x_i \quad (13)$$

f_i [-] is the rational activity coefficients and is defined on a reference state for which f_i is unity for infinite dilution (pure water), so that $f_i \rightarrow 1$ as $x_i \rightarrow 0$. f_i of the solute s is related to the molal-based activity coefficients γ_i by (Robinson and Stokes, 1959):

$$f_i = \gamma_i \left(1 + M_w \cdot \sum_i \mu_i \right) \quad (14)$$

with the summation in Eq. (14) over all solute molalities. M_w is the molar mass of water [kg mol⁻¹], μ_i the solute molality [mol kg⁻¹(H₂O)] given by Eq. (11).

The activity coefficients have been introduced to correct the solution molalities for non-ideality and to substitute earlier correction coefficients used in other a_w representations. Following Rose08, we will use the E-AIM model version III as a reference, which is available online (<http://www.aim.env.uea.ac.uk/aim/model3/mod3rhw.php>) (Wexler and Clegg, 2002; Clegg and Wexler, 2007), to be consistent with the reference (AP3) of Rose08 (see their Table 3).

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2.1.2 Water activity parameterization as a function of v_i

To parameterize the aerosol hygroscopic growth we introduce a new parameterization for the water activity, i.e. adding to the definitions summarized above. Since the computation of all the a_w representations is to some degree problematic – mainly since for all successful water activity parameterizations the correction coefficients are not independent of a_w –, we suggest here a new relation of a_w and the solute molality, μ_s , as a central aspect of our formulations. a_w and μ_s are related by a single solute specific coefficient v_i :

$$\begin{aligned} a_w &= \left(A + \mu_s^o \cdot M_w \cdot v_i \cdot \left[\frac{1}{\mu_s^o} \cdot \mu_s + B \right]^{v_i} \right)^{-1} \\ &= \left(A + \mu_s^o \cdot M_w \cdot v_i \cdot \left[\frac{1}{\mu_s^o} \cdot \frac{1}{M_s \cdot (1/\chi_s - 1)} + B \right]^{v_i} \right)^{-1} \end{aligned} \quad (15)$$

The terms v_i , A and B are dimensionless [–], while μ_s is the solute molality [mol(solute) kg⁻¹(H₂O)] defined by Eq. (11). A and B also depend only on μ_s and v_i , but for certain applications they can be neglected, i.e. $A = 1$ and $B = 0$, as demonstrated in Sect. 3. To match units with μ_s , we multiply μ_s on the rhs of Eq. (15) with an initial concentration of 1 mole of pure solute that dissolves in 1 kg of initially pure water, considering stoichiometry and molality scale, i.e. $\mu_s^o = 1$ [mol kg⁻¹]. M_w is the molar mass of water [kg mol⁻¹].

Similar to the VH concept, i.e. Eq. (5), and the activity coefficient concept, i.e. Eq. (9), we express the water activity a_w in terms of the solute molality μ_s and a solute specific correction coefficient. However, v_i introduced here is not only a linear correction factor, which is the case in other water activity representations, but appears also as a constant in the exponent of Eq. (15) in the form of $x \cdot a^x$. According to our findings v_i can be assumed constant for the entire a_w range (0 – 1). Hence, it suffices to determine v_i , e.g. with the bisection method, using any a_w value if the corresponding μ_s is known,

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e.g. at saturation. In case of saturation, a_w equals the RH of deliquescence (RHD) and μ_s is given through the relation Eq. (11) by the mass fraction χ_s^{sat} . Solubility values and the corresponding thermodynamic data are available for many compounds, e.g. in the CRC Handbook of Chemistry and Physics (2006).

2.1.3 RH of deliquescence (RHD) as a function of v_i

Here, we determine v_i from the compound's RH of deliquescence (RHD), since temperature dependent values are available for major compounds, which are relevant for atmospheric aerosol modeling. The RHD can be obtained as a function of v_i from Eq. (15) and Eq. (1), i.e. substitution of $a_w = \frac{\text{RH}}{K_e}$ yields:

$$\text{RH} = \frac{K_e}{\left(A + \mu_s^o \cdot M_w \cdot v_i \cdot \left[\frac{1}{\mu_s^o} \cdot \mu_s + B \right]^{v_i} \right)} \quad (16a)$$

and at saturation, where $\text{RH} = \text{RHD}$ and $w_s = \chi_s^{\text{sat}}$, Eq. (16a) can be expressed as:

$$\text{RHD} = \frac{K_e}{\left(A + \mu_s^o \cdot M_w \cdot v_i \cdot \left[\frac{1}{\mu_s^o} \cdot \frac{1}{M_s \cdot (1/w_s - 1)} + B \right]^{v_i} \right)} \quad (16b)$$

Thus, RHD values can be obtained with Eq. (16b) if w_s , v_i , A and B are known. In Sect. 3 we derive these yet unknown terms first from RHD measurements, by solving Eq. (16b) once, for example with the bisection method. The temperature dependency of the RHDs is obtained by (e.g. Wexler and Potukuchi, 1998):

$$\text{RHD}(T) = \text{RHD}(T_o) \cdot \exp \left[T_{\text{coef}} \cdot \left(\frac{1}{T} - \frac{1}{T_o} \right) \right] \quad (16c)$$

The T -dependent RHD values (with w_s at T) can be used to determine v_i by solving Eq. (16b) e.g. with the bisection method for the compounds for which RHD and w_s data are available. The procedure is described in Sect. 3.

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2.1.4 Solute molality (μ_s) as a function of v_i

According to our parameterization of water activity (a_w) the solute molality (μ_s) is also parameterized as a function of v_i and directly given by re-arranging Eq. (15):

$$\mu_s = \mu_s^0 \cdot \left(\left[\frac{1}{v_i \cdot \mu_s^0 \cdot M_w} \cdot \left(\frac{1}{a_w} - A \right) \right]^{\frac{1}{v_i}} - B \right) \quad (17a)$$

Using the relation of a_w and RH, Eq. (1), Eq. (17a) can be expressed in terms of RH, v_i and K_e , whereby K_e also depends on μ_s according to Eqs. (1–2). Thus, with $a_w = \frac{RH}{K_e}$ i.e.:

$$\mu_s = \mu_s^0 \cdot \left(\left[\frac{1}{v_i \cdot \mu_s^0 \cdot M_w} \cdot \left(\frac{K_e}{RH} - A \right) \right]^{\frac{1}{v_i}} - B \right) \quad (17b)$$

Equation (17b) can be directly solved, e.g. with the bisection method, while Eq. (17a) can also be analytically solved, since the K_e term is not relevant for flat surfaces. However, this also depends on the choice of the A and B terms. In case of a flat surface and subsaturation ($RH \leq 95$ [%]), K_e , A and B are neglected, i.e. $K_e = 1$, $A = 1$ and $B = 0$, and Eq. (17b) reduces to:

$$\mu_s = \mu_s^0 \cdot \left(\left[\frac{1}{v_i \cdot \mu_s^0 \cdot M_w} \cdot \left(\frac{1}{RH} - 1 \right) \right]^{\frac{1}{v_i}} \right) \quad (17c)$$

For applications up to $RH \leq 98$ [%], a slightly different representation of Eq. (17c) can be used, which only differs by a term B_{98} , i.e.

$$\mu_s = \mu_s^0 \cdot \left(\left[\frac{1}{v_i \cdot \mu_s^0 \cdot M_w} \cdot \left(\frac{1}{RH} - 1 \right) \right]^{\frac{1}{v_i}} - B_{98} \right) \quad (17d)$$

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Equations (17a–d) relate the solute molality μ_s to a_w and RH, depending only on the solute specific coefficient ν_j . Note that B -terms are needed only for high RH > 95 [%]. The A and B -terms are defined in Sect. 3. Whether Eqs. (17a), (17b), (17c), or (17d) should be used depends on the desired level of complexity and the scientific questions, which determine the RH regime, i.e. only Eq. (17b) accounts for the particle size. Equations (17a–d) can be applied in EQSAM4, while Eq. (17c) is equivalent to the one of EQSAM3, introduced by Metzger and Lelieveld (2007) by their Eq. (20), but limited w.r.t. Köhler theory to the subsaturated RH regime, with RH \leq 95 [%]. For these cases, the results of the four different representations of Eq. (17) are, however, rather similar. This is demonstrated in the next section.

3 Parameter determination

To solve our water activity parameterization, i.e. Eq. (15), the dimensionless terms ν_j , A and B are required. Here, A and B have been empirically determined to best match the reference results of E-AIM – the explicit derivation is beyond the scope of this work and will be presented separately. A and B are defined to only depend on the solute specific coefficient, ν_j , and on the solute molality μ_s , i.e.:

$$A = (1 + \nu_j \cdot \mu_s \cdot M_w) \cdot \exp\left(-M_w \cdot \mu_s^0 \cdot \nu_j \cdot \left(\frac{\mu_s}{\mu_s^0}\right)^{\nu_j}\right) \quad (18)$$

$$B = \left(1 + \frac{1}{\nu_j \cdot \mu_s \cdot M_s}\right)^{-1} \cdot \left(\nu_j \cdot \frac{\mu_s}{\mu_s^0}\right)^{-\frac{1}{\nu_j}} \quad (19)$$

As A and B depends on μ_s and ν_j , we additionally define an alternative B -term for Eq. (17d) with RH \leq 98 [%], which only depends on ν_j :

$$B_{98} = 10^{\left[\frac{2}{\nu_j} - 2\right]} \quad (20)$$

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To solve Eqs. (15–20), v_i must be known. If v_i can be assumed constant for the entire range of water activity a_w (0–1), it should be possible when Eq. (1) is used to determine v_i for any particle dry diameter (D_s) at given temperature (T) from the saturation point, i.e. also for the case where a_w equals the RH of deliquescence (RHD). In this case, we can solve Eq. (16b) directly with a root finding algorithm, notably the bisection method; see e.g. Numerical Recipes (<http://www.nr.com/>) in Fortran 90, Second Edition (1996), page 1185 (an online version is freely available at: <http://apps.nrbook.com/fortran/index.html>). To constrain the bisection method when solving Eq. (16b) we use the T -dependent RHD and w_s values, i.e. for the left hand-side at $T_o = 298.15$ [K] RHD = 0.7528 [–] for NaCl_(cr) and RHD = 0.7997 [–] for (NH₄)₂SO_{4(cr)}, and calculate v_i as follows:

1. Given $w_s = \chi_s$, we first calculate μ_s^{sat} from Eq. (11);
2. A is a function of v_i and calculated from $\mu_s = \mu_s^{\text{sat}}$ and M_w using Eq. (18);
3. B is a function of v_i and calculated from $\mu_s = \mu_s^{\text{sat}}$ and M_s using Eqs. (19) or (20);
4. We finally determine v_i by solving Eq. (16b) with the bisection method by using μ_s^{sat} from step 1, A and B from step 2 and 3 and assuming $K_e = 1$. Given v_i and μ_s , Eqs. (17a–d) can be solved for a_w and RH, if at step 1 the HGF is additionally calculated from Eq. (2). Apart from this, the procedure of solving Eqs. (17a–d) is the same as to determine v_i .

Note that the choice of A and B in Eqs. (18–20) depends on the application. At T_o the following values for NaCl_(cr) and (NH₄)₂SO_{4(cr)} are: mass fraction solubility $w_s = 0.2647$ [–] and $w_s = 0.4331$ [–], molar masses $M_s = 0.05844$ [kg mol⁻¹] and $M_s = 0.1321$ [kg mol⁻¹], and densities $\rho_s = 2170$ [kg m⁻³] and $\rho_s = 1770$ [kg m⁻³], respectively.

Once v_i has been determined, Eqs. (17a–d) can be either solved for RH for a given solute molality μ_s , e.g. from Eq. (11) or reference model calculations, or vice versa

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as done in the companion paper (i.e. GCM application where the RH is usually prescribed). The hygroscopic growth factor (HGF), the saturation (s) and supersaturation (S) can then be obtained from μ_s with Eq. (2) and Eq. (1), respectively, by using Eq. (15) to solve the associated a_w of Eq. (1). Note that this combination of Eq. (15) and Eq. (1) yields Eq. (16a), and if the RHD is substituted by the RH it yields Eq. (16b).

For consistency with Rose08, we also compare our results with the parametric calculations of E-AIM. Rose08 provided in their electronic supplement $a_w - \mu_s$ values in the a_w range 0.97–1, which we have connected with the E-AIM web-output, with a_w and μ_s obtained by running the E-AIM model version III (<http://www.aim.env.uea.ac.uk/aim/model3/mod3rhw.php>), to cover the remaining a_w range from the RHD to 0.97 by keeping the large number of the Rose08 AIM data points above 0.97. We have then calculated from these E-AIM $a_w - \mu_s$ values our reference HGF from Eq. (2), and reference RH from Eq. (1), by assuming (for the sake of simplicity) volume additivity, and a constant pure water surface tension of the solution, $\sigma_{\text{sol}} = 0.076 \text{ [N m}^{-2}\text{]}$, and the pure water density $\rho_w = 997.1 \text{ [kg m}^{-3}\text{]}$. For a discussion of σ_{sol} and the volume additivity of Eq. (1) we refer to Rose08, who provide a comprehensive sensitivity analysis to various parameters affecting Eq. (1).

3.1 Bulk particles – flat surface

To compare our water activity parameterization with the E-AIM reference data and to test the sensitivity w.r.t. different combinations of A and B , we solve Eqs. (17a–d) for two key compounds, $\text{NaCl}_{(\text{cr})}$ and $(\text{NH}_4)_2\text{SO}_{4(\text{cr})}$, considering four cases:

1. Equation (17a): using the A - and B -terms, but no K_e -term.
2. Equation (17b): same as (1) but considering the K_e -term as our best a_w estimate.
3. Equation (17c): same as (1) but without the A - and B -terms as our simplest a_w estimate.
4. Equation (17d): same as (3) but with a different B -term than (1) and (2).

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Table 1 gives an overview of the equations applied for the four different cases, i.e. solute molality, μ_s -models. Note that Eqs. (17a–d) can be used to calculate either a_w , RH or μ_s . Here we prescribe μ_s and calculate a_w and RH, while in the companion paper we prescribe RH and calculate μ_s from Eqs. (17a–d). The RHD and the derived v_i values are listed in Table 2 for the four cases listed in Table 1. These data, together with a Fortran 90 program to reproduce our results are provided in the Supplement. Figures 1 and 2 firstly compare our four RH calculations as a function of HGF for the simplest case of flat surface, i.e. particles with a sufficiently large dry diameter in the subsaturated RH regime, so that the Kelvin-term can be neglected for the aerosol HGF calculations. Then, the four cases shown in Table 1 should yield similar results if the corresponding v_i values listed in Table 2 are used to solve Eqs. (17a–d). For each case (equation), we calculate the RH by prescribing the E-AIM μ_s values of two single solute solutions: (1) pure sodium chloride, $\text{NaCl}_{(cr)}$, and (2) pure ammonium sulfate, $(\text{NH}_4)_2\text{SO}_{4(cr)}$, assuming a sufficiently large dry particle diameter (geometric diameter = mass equivalent diameter for a compact spherical droplet), i.e. $D_s = 1 [\mu\text{m}]$, so that the Kelvin term is negligible. The HGF is shown for the deliquescence branch of the hysteresis curves, i.e. considering an initially dry solute that entirely deliquesce when the RH exceeds the solute’s RHD. Figure 1 shows the HGF for the RH range, $\text{RHD} \leq \text{RH} \leq 97 [\%]$, while Fig. 2 shows the complementing results for the RH range, $97 \leq \text{RH} \leq 100 [\%]$, to highlight possible differences in the “quasi” ideal solution range close to RH 100 [%], where the water activity approaches unity.

According to Figs. 1 and 2, the results based on Eq. (17a) and Eq. (17b) are almost identical for the entire RH-range, which indicates that for this case the Kelvin-effect is indeed negligible. And for $\text{RH} < 95 [\%]$, all four cases, i.e. Eqs. (17a–d), agree well with the reference. In the RH range, $95 < \text{RH} \leq 98 [\%]$ the results of Eq. (17d) (using the simplified B -term) are still close to those of Eq. (17a–b) and E-AIM, while the results of Eq. (17c) without the A - and B -terms deviate noticeably. But when the RH exceeds 98 [%] the results of Eq. (17d) also start to deviate from our reference. Only the results of Eq. (17a–b) agree well with the E-AIM results close to RH 100 [%]. But for these high

RH values, and for submicron aerosol particles in general, the Kelvin-term becomes important anyhow, so that only our most complete parameterization Eq. (17b) can be used for further evaluation.

3.2 Submicron sized particles – curved surface

In the case of submicron sized particles ($D_s < 1$ [μm]), surface curvature becomes important for the aerosol hygroscopic growth calculations. Equation (17b) includes the Kelvin-term and will be used to calculate the HGF of submicron sized particles with Eq. (2) using the above v_i values listed in Table 2 for Eq. (17b). Figure 3 compares the HGF obtained with Eq. (17b) with E-AIM for $\text{RH} \leq 97$ [%] and the four different dry particle diameters $D_s = 0.05$, $D_s = 0.1$, $D_s = 0.5$ and $D_s = 1$ [μm]. Figure 4 complements Fig. 3 for the high values within the subsaturated regime, i.e. $97 \leq \text{RH} \leq 100$ [%]. Note that a_w , and the derived HGF results of E-AIM, do not directly depend on the Kelvin-term K_e . We plot the HGF versus $\text{RH} = a_w \cdot K_e$ following Rose et al. (2008), which yields a dependency of the E-AIM results on K_e , but also shifts the RHD (of E-AIM) to a higher water activity (due to $a_w \cdot K_e$). We can reproduce this shift in RHD if the Kelvin-term is considered in the RHD calculations using the v_i determined from the flat surface case. The estimated size dependent RHD values are obtained by calculating the RHD with Eq. (16b) using the v_i values listed in Table 2 for Eq. (17b), which is the only equation of Eq. (17a–d) that accounts for a size dependency by including the K_e -term. The size dependent RHD estimates are shown in Table 3 for the different dry particle diameters.

According to Figs. 3 and 4 the results of Eq. (17b) agree well for different particle sizes in the subsaturated RH regime. It also appears that the results capture the decrease of the HGF for nanometer size particles reported by measurements provided by Biskos et al. (2006a, b). Note that we have not applied a shape correction factor, and used for simplicity a constant surface tension of pure water (as mentioned above) for the K_e -term calculation for both Eq. (17b) and E-AIM. For a discussion of these parameters we refer to Biskos et al. (2006a, b), Rose08, Harmon et al. (2010) and Wang et al. (2010) (and references therein). In the next section we focus on the remaining RH regime of water vapor saturation and supersaturation, i.e. $\text{RH} \geq 100$ [%].

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3.3 Supersaturation – Köhler curves

To evaluate the upper RH limit where the parameterizations may still be valid, we compare the results obtained from Eq. (17b) with E-AIM for the case of water vapor saturation and supersaturation, i.e. $\text{RH} \geq 100$ [%]. The supersaturation S [%] is defined as $S = (s - 1) \cdot 100$, with s obtained by solving Eq. (1) as a function of wet diameter, D_{wet} , using Eq. (17b). For E-AIM we again use $\text{RH} = a_w \cdot K_e$, following Rose08. Figure 5 completes the RH range shown in Figs. 3 and 4, and shows that the results of Eq. (17b) are comparable to E-AIM from the RHD to supersaturation for pure $\text{NaCl}_{(\text{cr})}$ and $(\text{NH}_4)_2\text{SO}_{4(\text{cr})}$ particles and different dry particle diameters, i.e. $D_s = 0.05$, $D_s = 0.1$, $D_s = 0.5$ and $D_s = 1$ [μm]. These results are also comparable to Fig. 15.5 of Pandis and Seinfeld (1998), which describe their approximation for ideal solutions. Figure 6 shows the critical supersaturation S_c , which complements Fig. 5. S_c is given by the maximum S . The results are comparable to Fig. 15.6 of Pandis and Seinfeld (1998) and Fig. 10 of Rose08. Note that Fig. 6 covers a diameter range 5–500 [nm], which is extended compared to Rose08 (their Fig. 10 shows 20–200 [nm]), so that our maximum critical supersaturation is about 10 [%] for 5 [nm] $\text{NaCl}_{(\text{cr})}$ particles. Note that these high critical supersaturations are merely shown to evaluate the Eq. (17b) method. To bring the results closer to our artificial help lines in the log–log diagram, it was necessary to assume for the 5 [nm] particles (and only for 5 [nm]) for $\text{NaCl}_{(\text{cr})}$ and $(\text{NH}_4)_2\text{SO}_{4(\text{cr})}$ a shape factor of 1.15 and 1.14, respectively, which was used to calculate the Kelvin-term with Eq. (1) for E-AIM, Kappa and the Eq. (17b) method. For all other particle sizes no shape factor was applied.

4 Discussion

We presented aerosol hygroscopic growth parameterizations that provide the core of our revised gas-liquid-solid partitioning model, i.e. version 4 of the Equilibrium Simplified Aerosol Model (EQSAM4), which is described in greater detail in the companion

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paper. EQSAM4 is part of our aerosol chemistry-microphysics module (GMXe), the latter being coupled to the EMAC atmospheric chemistry-climate model (Pringle et al., 2010), and will be used to study the aerosol hygroscopic growth of single and mixed solutes. Thus, a requirement is that the parameterizations are both sufficiently accurate and computationally efficient, so that large-scale, long-term and high-resolution atmospheric chemistry-climate simulations are feasible.

1. *Simplified HGF calculations:*

as demonstrated in Sect. 3, our empirical representation of water activity, a_w , by Eq. (15), and the derived equations for the solute molality μ_s , Eqs. (17a–d), can help estimate the HGF of atmospheric aerosols. Our results compare well with the reference calculations of E-AIM for typical RH (a_w) values, relevant to conditions in the atmosphere. HGF estimates, as calculated from Eq. (2) and based on the complete a_w representation, Eq. (17b), which includes the Kelvin-effect, also applies to submicron sized particles (e.g. Russell and Ming, 2002; Biskos et al., 2006a, b), i.e. with a dry diameter D_s below 0.5 [μm]. The results agree well with the κ -method of Petters and Kreidenweis (2007) for the ideal solution cases, but agree more closely with E-AIM for concentrated solutions. Both, the κ and ν_i method only require one coefficient per compound, and agree relatively well w.r.t. the CCN activation of the aerosols according to Köhler theory (e.g. Charlson et al., 2001; McFiggans et al., 2006) down to dry diameters D_s below 0.05 [μm]. Only for $(\text{NH}_4)_2\text{SO}_4$ particles the S_c obtained from the κ -method agrees more closely with E-AIM, but the steep increase in supersaturation agrees less w.r.t. E-AIM and at 0.005 [μm] also the S_c obtained by the ν_i method appears closer to E-AIM when the same κ and ν_i values are assumed for all particles sizes. For simplicity and clarity, we have neglected here potential effects of surface tension and other size effects, though they can be included when needed. For a discussion we refer to e.g. Rose08 and references therein.

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**2. The advantage of Eqs. (17a–b):**

compared to most other representations of water activity (briefly summarized in Sect. 2) our approach requires only one empirical coefficient ν_i to cover a wide range of a_w from concentrated solutions at low RH, around the compound's RHD, up to ideal solutions at large RH and CCN activation. The κ -method of Petters and Kreidenweis (2007), which also requires only a single parameter, is limited to ideal solutions and not optimally valid for concentrated solutions as confirmed by Figs. 3 and 4. The advantage of our parameterizations Eqs. (17a–b), compared to our Eqs. (17c–d), is that they can be applied to concentrated and ideal solutions, since they include the additional A - and B -terms. Equation (17b) can be further applied to the supersaturated RH regime, because it includes the Kelvin term. However, the A -, B - and K_e -terms depend on μ_s , which makes Eqs. (17a–b) more complex to solve in case RH or a_w is prescribed. Nevertheless, despite this self-dependency, also Eq. (17a–b) can be directly solved when using ν_i by a root-finding method, such as the bisection method used in this study.

3. The advantage of Eqs. (17c–d):

compared to our more comprehensive parameterizations Eqs. (17a–b), our simpler parameterizations Eqs. (17c–d) are limited to the subsaturated RH regime; Eq. (17c) to approximately $\text{RH} \leq 95$ [%]; Eq. (17d), which includes a simplified B -term defined by Eq. (20), to approximately $\text{RH} \leq 98$ [%]. This actually covers the most important RH range for atmospheric aerosols, useful for many applications especially in GCMs. And for CCN activation, Eq. (17b) can be used. The advantage of using Eqs. (17c–d) is that the HGF of single or mixed compound solutions can be analytically and non-iteratively obtained for a given RH, by using a single constant ν_i value per compound and various particles dry sizes, since our calculations do not depend on the aerosol liquid water content.

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4. Determining ν_j :

to determine ν_j , any of the ν_j -based equations, i.e. Eqs. (15–17d), could be solved with a root finding method, e.g. bisection, by prescribing a pair of water activity (a_w) and solute molality (μ_s) values of an $a_w - \mu_s$ diagram. Such a data pair can be either obtained from detailed calculations or measurements. Using for instance RHD and solubility (w_s) measurements, both values are directly known and related by ν_j through Eqs. (16a–b), i.e.: a_w by $\text{RHD} = \text{RH} = a_w \cdot K_e$ through Eq. (1), and μ_s by w_s through Eq. (11). Hence, in this work we have determined ν_j by solving Eq. (16b) using a measured RHD for $\text{NaCl}_{(\text{cr})}$ and $(\text{NH}_4)_2\text{SO}_{4(\text{cr})}$ and assuming a flat surface, i.e. $K_e = 1$, as described in Sect. 3.

5. Constant ν_j :

in all cases we have used a solute specific coefficient, i.e. ν_j , determined from the solute's RHD. According to the comparison with the E-AIM reference calculations, it appears that a constant ν_j suffices to estimate the compound's HGF with Eqs. (17a–d) for a wide RH range and various particle sizes. Note that we express the water activity a_w in terms of the solute molality μ_s and a solute specific correction coefficient, similar to the VH concept, i.e. Eq. (5), and the activity coefficient concept, i.e. Eq. (9). However, ν_j introduced here is not only a linear correction factor, which is the case in other water activity representations, but is also used in the exponent of Eq. (15) in form of $x \cdot a^x$. Apparently, even our simplest a_w estimate based on Eq. (17c) yields reasonably accurate results for the subsaturated regime, $\text{RH} \leq 95$ [%], but the Kelvin-term must be neglected. The advantage of using ν_j is that it allows to directly solve Eqs. (17a–d), i.e. either Eqs. (17a–b) with e.g. the bisection method, or Eqs. (17c–d) analytically without iterations. In all cases, ν_j allows to easily compute the HGF for a wide RH range with Eq. (2) when using Eqs. (17a–d). Thus, for our purpose, i.e. application in EQSAM4, the proposed ν_j based equations suffice, and complicated calculations of solution densities, activity coefficients, or osmotic coefficients, as described in the overview article of Rose08, are not required here.

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**6. Uncertainty range for HGF and S_c calculations:**

an indication of the uncertainty of our best estimates based on Eq. (17b) is given by a comparison of Figs. 5 and 6 with the corresponding Fig. 10 of Rose08. According to our Fig. 5, a relatively large difference appears for the supersaturation estimate for $D_s = 0.05$ $(\text{NH}_4)_2\text{SO}_4$ particles. In the logarithmic plot of Fig. 6, these differences are less obvious, and the Fig. 10 of Rose08 even shows a larger deviation relative to the results of E-AIM for the various other a_w based S_c estimates. Thus, the comparison of our Fig. 6 and their Fig. 10 shows that our best estimate based on Eq. (17b) lies well within the uncertainty range given by the a_w representations discussed in Rose08.

7. From single to mixed solute solutions:

our example calculations are shown for single solute solutions. But the v_i based equations are also applicable for mixed solutions, if e.g. the widely used additive approach of partial water masses of single solutes in mixed solutions (ZSR-relation; Zdanovskii, 1948; Stokes and Robinson, 1966), or other approaches, e.g. CSB (Hanford et al., 2008) are used to obtain the mixed solution water content. Our v_i approach even simplifies the calculation for the mixed solution molality and water content, since our Eqs. (17a–d) do not depend on the water content. Thus, the mixed solution water content and the corresponding HGF can be more easily calculated with Eqs. (11) and (2). Especially by considering the Kelvin term, our v_i based equations can substantially simplify the calculations, since in this case (multidimensional) iterations would be required otherwise. The mixed solution RHD, often referred to as mutual deliquescence relative humidity, MDRH, (Wexler and Seinfeld, 1991), for which all salts are simultaneously saturated with respect to all components, will be considered in our revised gas-liquid-solid partitioning model, i.e. version 4 of the EQUilibrium Simplified Aerosol Model (EQSAM4), described in the companion paper.

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8. *Relation to other concepts through a_w :*

the relationship of our ν_i -based a_w parameterizations to the various other concepts and a_w representations is given by a_w itself. The water activity is the central thermodynamic property from which all other properties can be derived – the various relations, which are most important for atmospheric aerosol research, are briefly summarized in Sect. 2. The relation of ν_i to the EQSAM3 concept introduced by Metzger and Lelieveld (2007) is given by our Eq. (17c) for the solute molality μ_s , which equals their corresponding equation Eq. (20), with $\nu_i = \nu_e/\nu_w$. Both equations are limited w.r.t. to Köhler theory to $\text{RH} \leq 95$ [%] though only depend on solute specific constants. Thus, in the EQSAM3 context, ν_i may be also directly related to an effective dissociation and the solute solubility.

5 Conclusions

We have introduced a new parameterization of the water activity (a_w) of single solute solutions, which only requires an empirical solute specific coefficient, ν_i . ν_i can for instance be determined from RHD measurements or reference calculations through the various relations presented. One advantage of the ν_i concept is that it requires only a single coefficient to parameterize the solute molality for a wide range of water activities, while other concepts require solution dependent coefficients. The derived HGF parameterizations can be used up to high relative humidity and size ranges, from nanometer sized particles to cloud condensation nuclei (CCN). Another advantage is that the water uptake for mixed solutions can be more easily obtained from our ν_i based equations, since the solute molality calculated with Eqs. (17a–d) does not depend on the water content of the solution, so that the mixed solution water content can be more easily obtained with e.g. the ZSR-relation. This work provides the equations on which the revised EQSAM4 model builds, which considers mixed solutions of various compounds important for atmospheric modeling described in a companion paper and evaluated for various mixed solution cases in the revised publication of Xu et al. (2009).

Supplementary material related to this article is available online at:
[http://www.atmos-chem-phys-discuss.net/11/24813/2011/
acpd-11-24813-2011-supplement.zip](http://www.atmos-chem-phys-discuss.net/11/24813/2011/acpd-11-24813-2011-supplement.zip).

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Table 1. Overview of the applied cases using four different solute molality, μ_s -models.

μ_s -model	a_w	$K_{(e)}$ -term ^a	A-term	B-term	ν_i from
Eq. (17a)	Eq. (15)	no	Eq. (18)	Eq. (19)	Eq. (16b)
Eq. (17b)	Eq. (15)	yes	Eq. (18)	Eq. (19)	Eq. (16b)
Eq. (17c)	Eq. (15)	no	$A = 1$	$B = 0$	Eq. (16b)
Eq. (17d)	Eq. (15)	no	$A = 1$	Eq. (20)	Eq. (16b)
Eq. (2)	E-AIM ^b	yes	–	–	–

^a Through Eq. (1), ^b similar as AP3 of Rose08 (see their Table 3).

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Table 2. ν_i [–] and RHD values at $T_o = 298.15$ [K] and $D_s = 1$ [μm] for the cases of Table 1.

Solute	ν_i -Eq. (17a)	ν_i -Eq. (17b)	ν_i -Eq. (17c)	ν_i -Eq. (17d)	RHD ^a
NaCl _(cr)	1.737506	1.737506	1.408369	1.384214	0.7528
(NH ₄) ₂ SO _{4(cr)}	1.661410	1.661410	1.335281	1.305553	0.7997

^a RHD measurements (values of Fountoukis and Nenes, 2007).

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Table 3. Estimated^a RHD values for different D_s with ν_i from Table 2 using Eq. (17b) of Table 1.

D_s [μm]	0.05	0.1	0.5	1	flat surface ^b
$\text{NaCl}_{(\text{cr})}$	0.7704	0.7616	0.7545	0.7537	0.7528
$(\text{NH}_4)_2\text{SO}_{4(\text{cr})}$	0.8238	0.8117	0.8021	0.8009	0.7997

^a Using Eq. (16b) with the K_e -term from Eqs. (1–2) and the A and B -terms from Eqs. (18–19);

^b Reference RHD that have been used to determine the ν_i values for Eq. (17b) (shown in Table 2).

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Table 4. List of greek symbols.

Greek Symbol	Name	Unit
ν_i	solute specific coefficient, Eq. (15) (introduced by this work)	[-]
ν_s	stoichiometric coefficient of solute (\pm ion-pair)	[-]
γ_i	molal-based coefficients	[kg(H ₂ O)] mol ⁻¹
μ_s	molality of solute	[mol kg ⁻¹ (H ₂ O)]
μ_s^o	reference molality of 1 mole of solute (considering stoichiometry)	[mol kg ⁻¹ (H ₂ O)]
μ_s^{sat}	saturation molality of solute	[mol kg ⁻¹ (H ₂ O)]
$\sum_i \mu_i$	summation over all solute molalities	[mol kg ⁻¹ (H ₂ O)]
Φ_s	molal or practical osmotic coefficient of solute	[-]
Φ_w	molal or practical osmotic coefficient of water	[-]
ρ_s	density of solute	[kg m ⁻³]
ρ_w	density of water	[kg m ⁻³]
σ_{sol}	surface tension of the solution droplet	[J m ⁻²]
χ_s	solute mass fraction, referring to the solute's dry mass	[-]
χ_s^{sat}	solute mass fraction, referring to the solute's dry mass at saturation	[-]

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Table 5. List of symbols.

Symbol	Name	Unit
A	A -term, Eq. (18) and introduced with Eq. (15)	[-]
B	B -term, Eq. (19–20) and introduced with Eq. (15)	[-]
a_w	water activity (Raoult-term)	[-]
D_s	dry droplet diameter of the solute	[m]
D_{wet}	wet droplet diameter of the solution	[m]
f_w	rational or mole fraction scale activity coefficient of water	[-]
g_s	hygroscopic mass equivalent (diameter) growth factor	[-]
i_s	van't Hoff factor of solute	[-]
K_s	surface or Kelvin-term of the solution	[-]
m_s	crystalline mass of solute	[kg]
m_w	aqueous mass of water (solvent)	[kg]
M_s	molar mass of solute	[kg mol ⁻¹]
M_w	molar mass of water	[kg mol ⁻¹]
n_s	moles of solute	[mol]
$\sum_i n_{s,i}$	summation over all moles of solutes	[mol]
n_w	moles of water	[mol]
$p_{w(g)}$	water vapor	[Pa]
$p_{w(g)}^{sat}$	vapor pressure at saturation (at given T)	[Pa]
RH	relative humidity in percent (as used in text)	[%]
RH	fractional relative humidity (as used in equations)	[-]
s	saturation ratio	[-]
S	supersaturation	[-]
S_c	critical supersaturation in percent	[%]
T_{coef}	dimensionless temperature coefficients for the RHD	[-]
T_o	reference temperature in Kelvin	[298.15 K]
T	temperature in Kelvin	[K]
T	temperature in degree Celsius	[°C]
w_s	mass fraction solubility, referring to the solute's dry mass required for saturation	[-]
x_s	mole fraction of solute	[-]
x_w	mole fraction of water	[-]

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Table 6. List of names and abbreviations.

Abbreviation	Name
sat	superscript, indicator for saturation
(cr)	subscript, phase indicator for anhydrous (solid=crystalline=cr) phase
(aq)	subscript, phase indicator for aqueous phase
(g)	subscript, phase indicator for gas phase
AWC	Aerosol liquid Water Content
EQSAM4	EQilibrium Simplified Aerosol Model, version 4
EMAC	ECHAM MESSy Atmospheric Chemistry-climate model
$f(RH)$	$f(RH)$ method (Charlson et al., 1992)
GCMs	General Circulation Models
HG	Hygroscopic Growth
HGF	hygroscopic Growth Factor
H-TDMA	Hygroscopicity tandem differential mobility analyzer
IPCC	Intergovernmental Panel on Climate Change
\log_{10}	decadal logarithm
log	natural logarithm
RH	Relative Humidity
RHD	Relative Humidity of Deliquescence
UNIFAC	Universal functional group activity coefficient model (Fredenslund et al., 1975)
ZSR-relation	Zdanovskii-Stokes-Robinson mixing rule (Zdanovskii, 1948; Stokes and Robinson, 1966)

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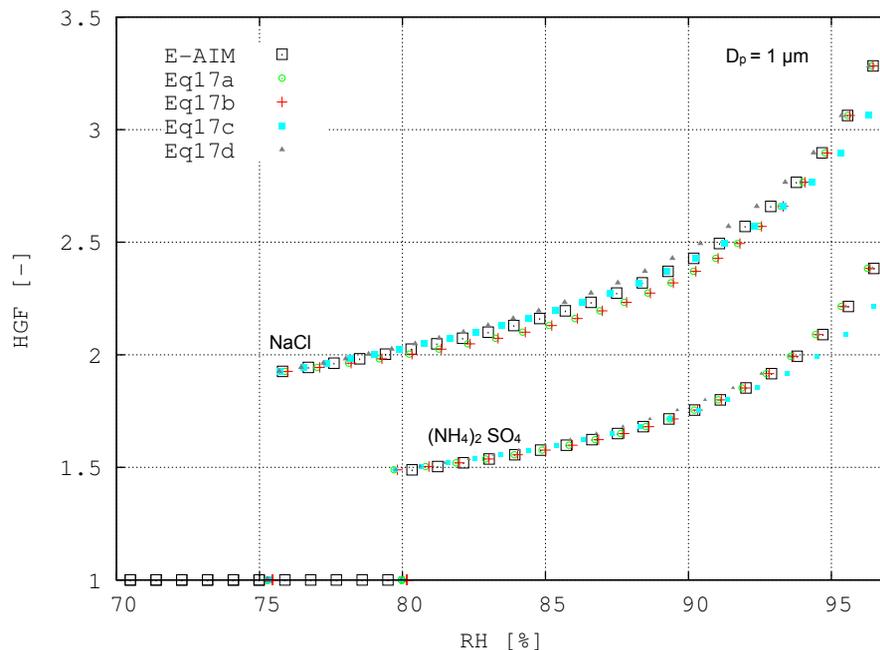


Fig. 1. Hygroscopic mass equivalent (diameter) growth factor (HGF) for pure $\text{NaCl}_{(\text{cr})}$ and $(\text{NH}_4)_2\text{SO}_{4(\text{cr})}$ particles with a dry diameter $D_s = 1 \mu\text{m}$ for $\text{RH} \leq 97$ [%], showing the four different solute molality, μ_s -models, summarized in Table 1, in comparison to the results of E-AIM.

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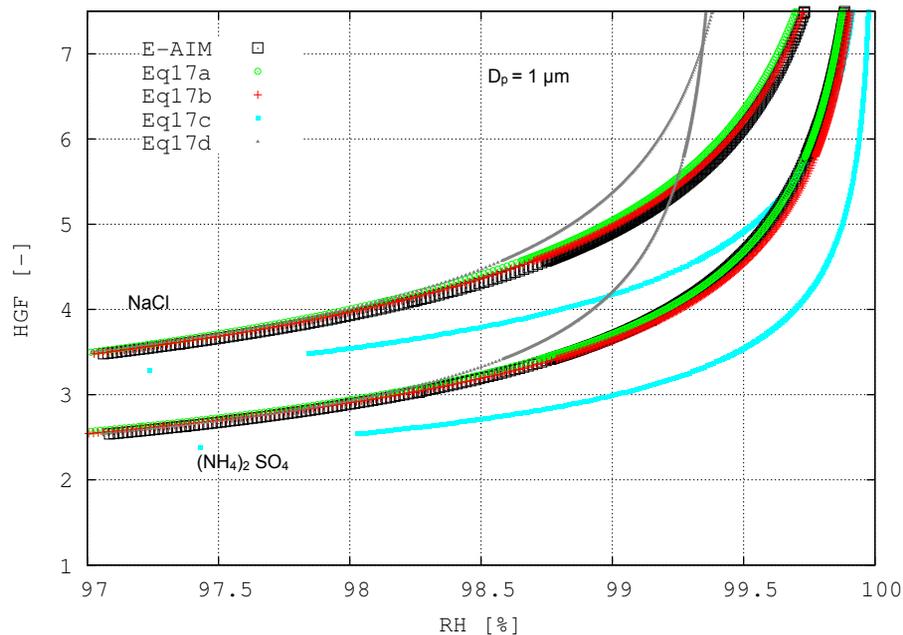


Fig. 2. Same data as Fig. 1 but for RH values within the subsaturated regime, i.e. $97 \leq \text{RH} \leq 100$ [%].

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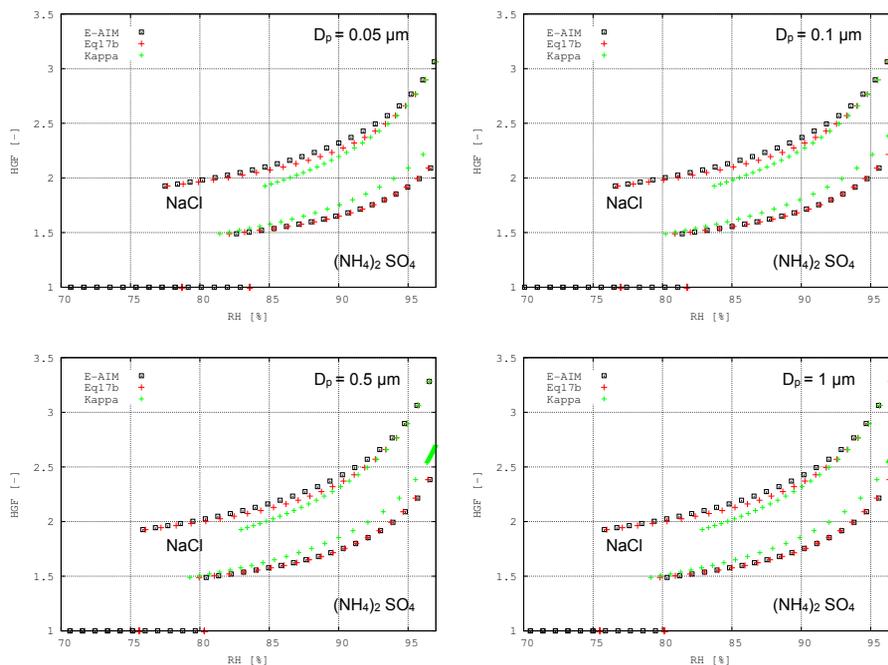


Fig. 3. Same as Fig. 1, but for dry particle diameter $D_s = 0.05$ (upper left), $D_s = 0.1$ (upper right), $D_s = 0.5$ (lower left) and $D_s = 1$ [μm] (lower right) comparing Eq. (17b) with E-AIM for $\text{RH} \leq 97$ [%]. For comparison, the results using the κ method of Petters and Kreidenweis (2007) are also included, obtained by solving Eq. A30 of Rose08 using $\kappa = 1.28$ for $\text{NaCl}_{(\text{cr})}$ and $\kappa = 0.61$ for $(\text{NH}_4)_2\text{SO}_{4(\text{cr})}$. Note that it is not possible to obtain HGF results below to the RHD for $\text{NaCl}_{(\text{cr})}$ with the κ -method using $\kappa = 1.28$.

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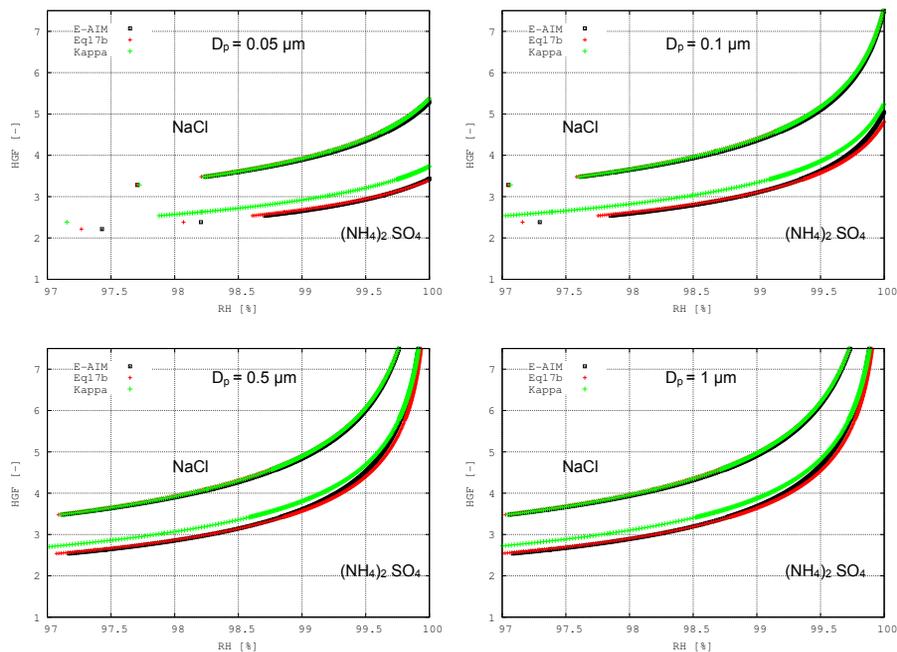


Fig. 4. Same as Fig. 3 but for high RH values within the subsaturated regime, i.e. $97 \leq \text{RH} \leq 100$ [%].

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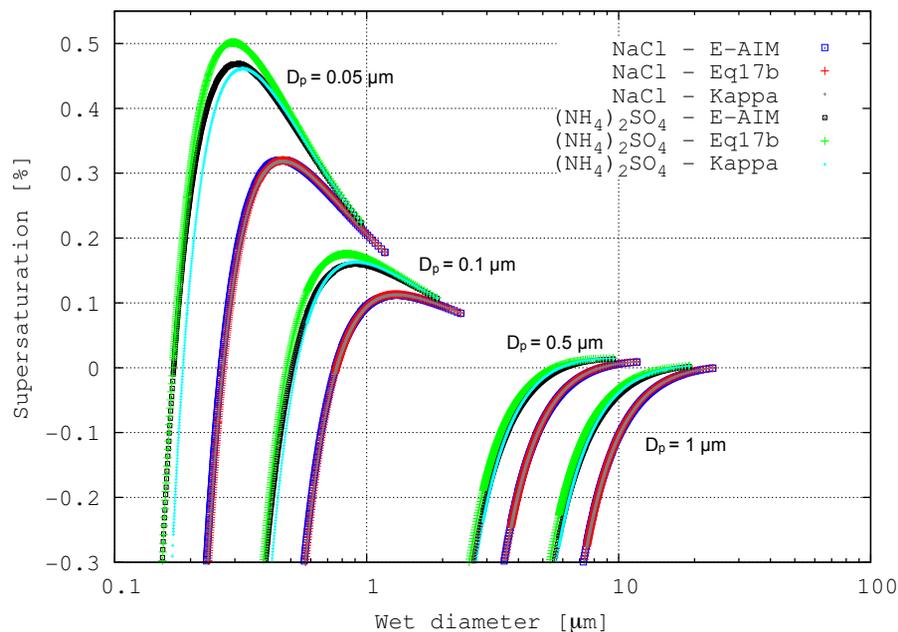


Fig. 5. Wet particle diameter, D_{wet} , as a function of supersaturation for pure NaCl and $(\text{NH}_4)_2\text{SO}_4$ aerosols with different dry diameters, i.e. $D_s = 0.05$, $D_s = 0.1$, $D_s = 0.5$ and $D_s = 1$ $[\mu\text{m}]$ as shown in Figs. 3 and 4. S is defined as $S = (s - 1) \cdot 100 [\%]$ and s is obtained from Eq. (1) for both our results using Eq. (17b) and the reference calculations using the E-AIM data of Rose 08. For comparison, the results using the κ method of Petters and Kreidenweis (2007) are also included, which are obtained by solving Eq. A30 of Rose08 using $\kappa = 1.28$ for $\text{NaCl}_{(\text{cr})}$ and $\kappa = 0.61$ for $(\text{NH}_4)_2\text{SO}_{4(\text{cr})}$.

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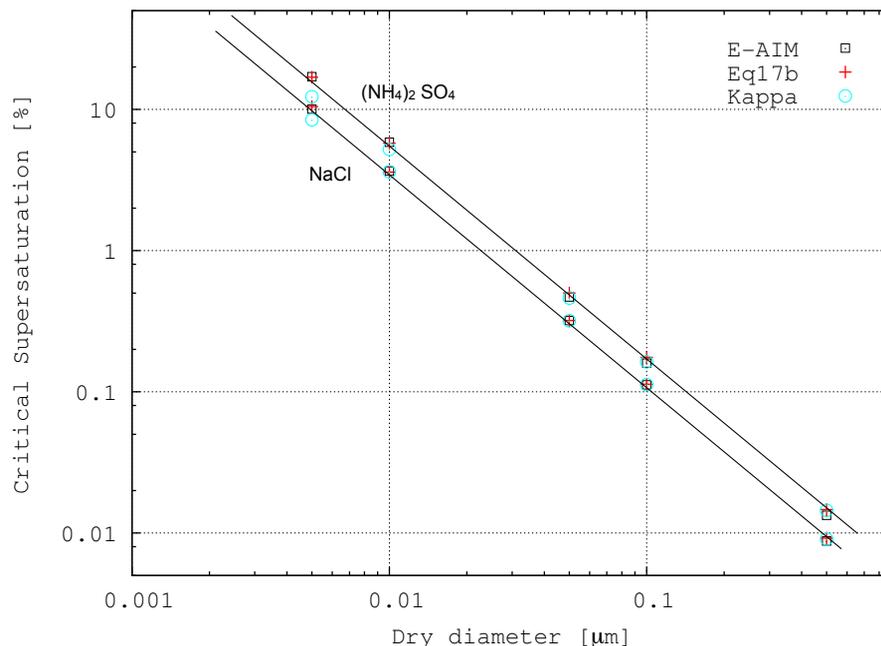


Fig. 6. Critical supersaturation as a function of dry diameter, D_s , for pure NaCl and $(\text{NH}_4)_2\text{SO}_4$ particles with different diameters, i.e. $D_s = 0.005$, $D_s = 0.01$, $D_s = 0.05$, $D_s = 0.1$ and $D_s = 0.5$ [μm], complementing Fig. 5. Note, the black solid lines are artificial help lines; the lower line and points correspond to NaCl, the upper ones to $(\text{NH}_4)_2\text{SO}_4$.

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