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Technical note: Analytical formulae for the critical supersaturations and droplet diameters of CCN containing insoluble material

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Abstract. In this paper, we consider the cloud drop activation of aerosol particles consisting of water soluble material and an insoluble core. Based on the Köhler theory, we derive analytical equations for the critical diameters and supersaturations of such particles. We demonstrate the use of the equations by comparing the critical supersaturations of particles composed of ammonium sulfate and insoluble substances with those of model organic particles with varying molecular sizes.

1 Introduction

Köhler theory (Köhler, 1936) and its variants (Hänel, 1976; Shulman et al., 1996; Laaksonen et al., 1998; Sorjamaa et al., 2004) form the basis of our understanding of cloud formation. For example, sophisticated parameterizations (Abdul-Razzak and Ghan, 2004; Nenes and Seinfeld, 2003) that are used in global climate models to describe clouds make use of the theory. Recently, it has been suggested by Padró et al. (2007) that critical supersaturations measured using CCN counters can be used together with the Köhler theory to infer the solubility and the molecular size of the CCN material. This idea is based on the fact that in the case of completely water soluble CCN, analytical formulae are available for the critical supersaturation (S^*) and critical droplet diameter (D^*). Here we show that analytical formulae can be derived for S^* and D^* also when the CCN contains insoluble inclusions. We also demonstrate the use of these formulae by making calculations of S^* for particles consisting of ammonium sulfate and insoluble material, and compare them to S^*

of single component CCN that are composed of completely soluble materials with variable molecular size.

2 Theory

The supersaturation S for particles with an insoluble core can be calculated using

$$S = \exp\left(\frac{A}{D_p} - \frac{B}{D_p^3 - D_{p,0}^3}\right) - 1 \quad (1)$$

where D_p is the droplet diameter, $D_{p,0}$ is the equivalent diameter of the insoluble core, A/D_p is the curvature term, and $\frac{B}{D_p^3 - D_{p,0}^3}$ is the solute effect term. Details for parameters A and B are available in e.g. Seinfeld and Pandis (1998).

The critical diameter for particles can be determined by differentiating the Eq. (1) with respect to diameter and finding the roots of the obtained equation (e.g., Seinfeld and Pandis, 1998)

$$\frac{dS}{dD_p} = -\frac{A}{D_p^2} + \frac{3D_p^2 B}{(D_p^3 - D_{p,0}^3)^2} = 0 \quad (2)$$

Equation (2) can be re-arranged as

$$(D_p^3 - D_{p,0}^3)^2 = \frac{3BD_p^4}{A} \quad (3)$$

By taking square roots of both sides of Eq. (3), we obtain

$$D_p^3 - \sqrt{\frac{3B}{A}} D_p^2 - D_{p,0}^3 = 0 \quad (4)$$

The obtained cubic equation can be solved analytically, with the following solution for the critical diameter D^*

$$D^* = \frac{1}{6}\alpha_2^3 + \frac{2}{3}\left(\frac{3B}{A}\right)\frac{1}{\alpha_2} + \frac{1}{3}\sqrt{\frac{3B}{A}}, \quad (5)$$



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where

$$\alpha_1 = 12 \sqrt{81D_{p,0}^6 + 12D_{p,0}^3 \left(\frac{3B}{A}\right)^{\frac{3}{2}}} \quad (6)$$

and

$$\alpha_2 = \sqrt[3]{108D_{p,0}^3 + 8 \left(\frac{3B}{A}\right)^{\frac{3}{2}} + \alpha_1} \quad (7)$$

When D^* is substituted in Eq. (1), we obtain the critical supersaturation

$$S^* = \exp \left(\frac{A}{\frac{1}{6}\alpha_2 + \frac{2}{3}\left(\frac{3B}{A}\right)\frac{1}{\alpha_2} + \frac{1}{3}\sqrt{\frac{3B}{A}}} + \frac{B}{\left(\frac{1}{6}\alpha_2 + \frac{2}{3}\left(\frac{3B}{A}\right)\frac{1}{\alpha_2} + \frac{1}{3}\sqrt{\frac{3B}{A}}\right)^3 - D_{p,0}^3} \right) - 1. \quad (8)$$

It is important to note that when the equivalent diameter of the insoluble core of the particles is set to zero in Eqs. (5)–(7), the solution obtained is the same as obtained in case with no insoluble material in the droplet.

Using these equations, S^* of particles including insoluble material can be calculated without iteration. These equations can be applied, for example, in cloud activation parameterizations, which use Köhler equations in order to calculate the number of activated droplets. Thus, Eqs. (5)–(7) can be used e.g. including insoluble material in the cloud activation parameterizations (e.g. Twomey, 1959; Nenes and Seinfeld, 2003; Abdul-Razzak and Ghan, 2004) which use the Köhler equations to calculate the effective maximum saturation ratio of the air parcel and the critical diameter to calculate number of activated droplets for a size distribution using sectional size classes.

While Khvorostyanov and Curry (2007) also present the expression for S^* and D^* when insoluble material is present, they use approximation in the derivation of the critical radii. Furthermore, their equation for the critical radius is applicable only for particles with extremely small soluble fraction.

Figure 1 illustrates the relative error of the approximations in S^* by Khvorostyanov and Curry (2007) when compared to the analytical solution given here in Eq (8). The relative error is calculated for particles 50 nm in diameter assuming that the soluble compound in the particle is NaCl together with an insoluble core. The solid curve is the relative error for the approximation which takes into account the insoluble core and the dashed curve is the relative error for the approximation that assumes the insoluble core to be negligible. From Fig. 1 it can be seen that the approximation which takes into account the insoluble core is valid only when the amount of soluble material is extremely small ($<10^{-5}$).

In a recent paper by Sorjamaa and Laaksonen (2008) a CCN activation theory was developed that accounts for the

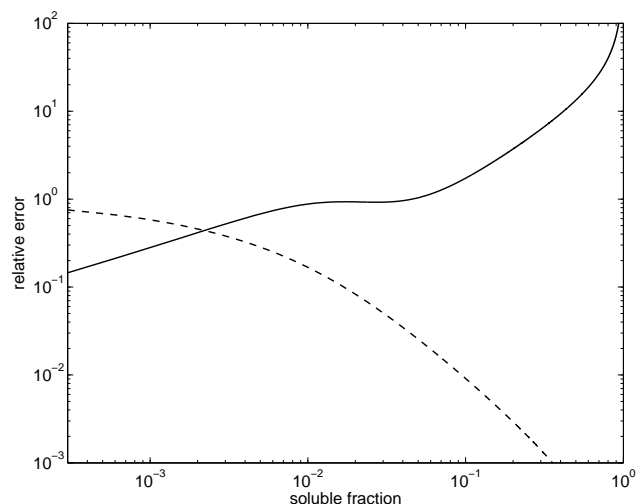


Fig. 1. Relative error in the critical supersaturation using approximations by Khvorostyanov and Curry (2007) compared to the analytical solution given here in Eq. (8). The solid curve is the relative error of Eq. (31) and the dashed curve is the relative error of Eq. (29) by Khvorostyanov and Curry (2007)

effect of water vapour adsorption on insoluble particles. The main difference between the theories of Sorjamaa and Laaksonen and the present theory is that an adsorption layer consists of pure water whereas in our treatment the water layer is assumed to be an aqueous solution. In principle, a theory could be developed which contains both an adsorption term and a Raoult term, describing the activation of an insoluble particle covered with a small amount of soluble matter. However, such a theoretical treatment is out of the scope of the present paper.

3 Example calculations

It has become customary to calculate so called “soluble fractions” for ambient particles based on hygroscopicity measurements (see Lehmann et al., 2005): if the growth factor of the particles at some given relative humidity is lower than that of ammonium sulfate, the soluble fraction indicates the volume fraction of ammonium sulfate in the dry particle assuming that it is composed of ammonium sulfate and insoluble matter. Here, we demonstrate the use of the above equations for S^* and D^* for such particles, and compare them to the S^* and D^* calculated for particles that are composed of substances that are completely water soluble, but less hygroscopic than ammonium sulfate.

Figure 2 shows how S^* of an assumed organic CCN behave compared to particles of ammonium sulfate plus insoluble substance (AI-particles). The molecular volume of the organic substance is 1.5 times the molecular volume of ammonium sulfate, and it is assumed that the organic does not

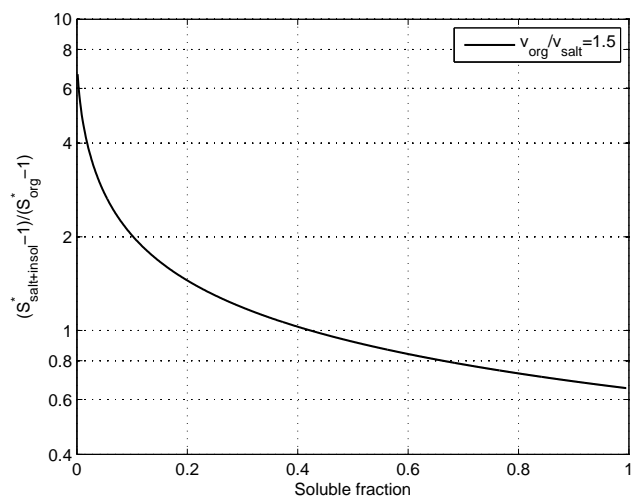


Fig. 2. Ratio of critical supersaturation for particles consisting ammonium sulfate and insoluble compounds $S_{\text{salt+insol}}^*$ to that of organic S_{org}^* as a function of soluble fraction in particles consisting ammonium sulfate and insoluble compounds.

dissociate in the aqueous solution. For simplicity, it was assumed that the surface tensions of both the organic and the AI solution droplets are equal to surface tension of water. The diameter of the insoluble core is 50 nm, and the amount of ammonium sulfate in the AI particles is varied. The dry size is also varied so that the dry diameter of the AI-particle and the organic particle are in each case the same. The y-axis of Fig. 2 indicates the ratio of S^* of the AI-particle and the organic particle, and the x-axis indicates the ratio of salt volume to insoluble volume in the AI-particle. It can be seen that when the soluble fraction is approximately 0.42, the critical supersaturations are equal.

Figure 3 focuses on organic particles that have the same critical supersaturations as the AI-particles. Here the x-axis indicates again the soluble fraction of salt in the AI-particles while the y-axis indicates the volume of the organic molecule relative to that of ammonium sulfate needed to produce the same S^* for the AI and the organic particles. This calculation, easy to perform using the newly derived equations, shows that two very different types of CCN with the same dry size can exhibit equal S^* . It is interesting to note that also the critical diameters are almost equal for the particles shown in Fig. 3

To conclude, the above calculations suggest that very different types of particles can show similar behavior in instruments such as CCN counters. While this may not be a big surprise, our newly derived equations provide an easy way of exploring what the quantitative effects of different sized insoluble core particles are for critical supersaturations and droplet diameters.

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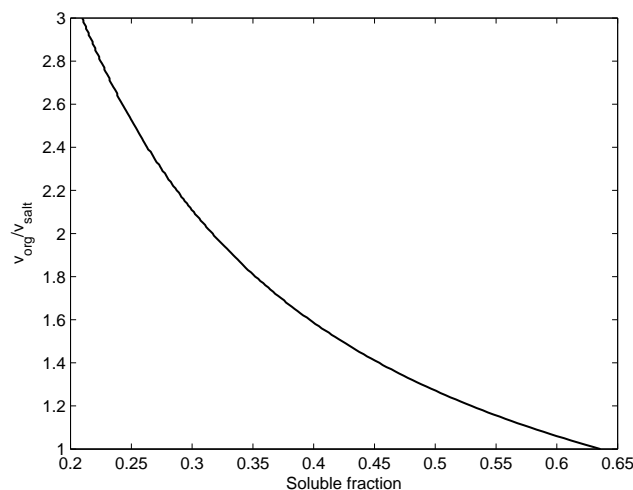


Fig. 3. Volume ratio of particles consisting ammonium sulfate and insoluble compounds to organic particles with equal critical supersaturation as a function of soluble fraction.

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