Response to referee reports for, "A thermodynamic description for the hygroscopic growth of atmospheric aerosol particles" by Casterède and Thomson

We would like to thank the reviewers for their constructive and useful comments, which have illuminated several areas for improvement and clarification within our manuscript. We try to answer each reviewer question and utilize the suggestions in order to improve the manuscript, and have prepared a revised manuscript accordingly Below we explicitly address and/or point to changes in the text that address each of the items raised in the comments. The responses are presented in the context of the Reviewer comments (*italicized*), where our responses are preceded by bullet points and changes to the text are highlighted in blue.

To best illustrate the extent of the changes to the text the output of a latex difference file is also attached.

Anonymous Referee #1

Comment (1): Precondensation threshold

In the fit, the authors excluded the data that preclude a full monolayer of water ($l \leq 0.3nm$). Are you suggesting the monolayer sets a threshold for precondenation, below which the precondensation doesn't occur? Or this is only to optimize the fitting parameters? Id like to see more clear a structure of precondensation. Thus I would suggest to optimize e.g., extending the scale of Fig. 4 to lower RH (RH$<$ 50), and consider using log-scale of (gf-1) in the y axis. Figure 5 is a nice illustration but the visibility of the precondensation (core of this study) is not good.

• We do not suggest that a water monolayer is a threshold for adsorption, nor do we assume this condition to optimize fitting parameters. Certainly adsorption begins at the molecular scale and we cite literature in this regard ((Ewing, 2005)). However, implicit within the bulk theoretical formulation we propose is that the electrolyte dissolves into a bulk solution of uniform thickness. Although the theory might be used to estimate sub-monolayer coverages, a limit of our model is that sub-monolayer adsorption is not rigorously resolved.

We have changed the sentence in question to, "For physical consistency with the theoretical framework the best-fit solutions...". Furthermore, we add a reference (Peters and Ewing, 1997) to emphasize the point above.

As justified above the x-axis scales have been chosen to deemphasize the sub-monolayer region. However, the suggestion of adopting a log-scale (GF-1) is appreciated and the figure has been changed accordingly.

Comment (2): Non-prompt vs prompt

There has been discussions about the differences between the two experimental dataset used here (Haemeri et al and Biskos et al). Biskos et al. suggested a prompt deliquescence while non-prompt deliquescence was reported in Haemeri et al. That is Biskos found the gf of pre-deliquescenced well below 1.2 while Haemeri showed gf up to 1.4-1.6 before deliquescence. According to the proposed theory, is such high gf possible from a precondensation?

• In fact, Biskos et al. (2006) assert that the 'non-prompt' deliquescence observed by Hämeri et al. (2001) originates from an instrumental artifact or error. Moreover it is impossible with the information given to draw conclusions from the experimental data given the associated uncertainties. However, at high GF (1.4-1.6) the stabilizing effect of the intermolecular interactions becomes very small and we would expect the equilibrium to be a deliquesced state.

Comment (3): Prediction

I am thinking how the proposed method can be used to predict the precondensation. Now it seems that you have three adjustable parameters to fit the data, so how many experimental data do you need for a reliable fitting. As shown in Table 1, each size has its own fitting parameters. I am wondering if it is possible to have a universal parameter set that is applicable to all sizes. If so, the applicability of this method will be largely increased.

• We have presented the theory in its general form in order to demonstrate both its robustness and flexibility. Given that we hope others will be interested in applying the theory to a variety of systems, it seems most advantageous to maintain the generality. That said, for any particular system absolute parameters can be imposed or chosen to reduce the number of fitting parameters. How well this works depends upon how well those parameters can be independently ascertained and/or constrained. Furthermore, the well defined parameter set may vary between systems. For example, we can do such an analysis for the NaCl system with which we have made comparisons. We deem that discussion outside the scope of the main manuscript, but agree with the referee that it may be of interest to parties interested in utilizing the theoretical framework. Therefore we include a supplementary discussion of the NaCl fitting parameters at the conclusion of this document.

Comment (4): Technical suggestions

In Fig. 4, the lines represent the equilibrium RH for each gf based on modified Koehler equation. Since the experimental data shows the equilibrium gf rather than the equilibrium RH, I would suggest plotting the same parameters (equilibrium gf) to avoid confusion.

• For clarity, the theoretical lines represent the equilibrium between a given system size (layer thickness/particle size) and saturation condition. Mathematically it is most straightforward to calculate both the RH and GF from specified layer or particle sizes, but the means of calculation does not alter the equilibrium. The plots conform with how the experimental data was originally presented.

Anonymous Referee #2

As the authors note, several other works have been published that also present a theoretical treatment of pre-deliquescence (notably, Bruzewicz et al. 2011). I encourage the authors to more clearly state where their approach differs from others, and the advantages of using the refined Kohler model presented here over that of Bruzewicz et al.

• We agree with the referee that our work follows and extends previous work from other researchers. Notably Russell and Ming (2002) treat a system as we describe using a simple wetting argument to investigate the total free energy of a solid/liquid, liquid/vapor system versus a single interface solid/vapor system. Later Shchekin and Rusanov (2008) and through the years a number of collaborators more explicitly examine such systems but stop short of formulating a complete description of the intermolecular origin of what they ascribe to be a, “stabilizing disjoining pressure” (Shchekin et al., 2008, 2013; Hellmuth and Shchekin, 2015). Bruzewicz et al. (2011) observe NaCl nanoparticles but do not incorporate the particle geometry into their theoretical model, while again relying on a phenomenological model of the short range component of the interactions. Previously, we had attempted to clearly credit and outline the previous work in the final two paragraphs of § 1 but now also return to our models advantageous in the final discussion. There we have added the text:

The formulation of continuous dry particle dissolution and droplet growth as represented by Eq. 10 and presented in the figures has several advantages over previous treatments of such systems. First we treat the intermolecular interactions explicitly in order to minimize the use of bulk parameters to model the interfacial system. The interfacial free energy minimization is then carried out and incorporated into Köhler Theory as a simple additional term that continues to allow for analytical solutions. The approach is in contrast to other treatments of analogous systems that utilize ascribed or phenomenological descriptions of short range interactions (Shchekin and Rusanov, 2008; Shchekin et al., 2008; Bruzewicz et al., 2011; Shchekin et al., 2013; Hellmuth and Shchekin, 2015) and/or do not account for the full particle geometry (Bruzewicz et al., 2011) and thus the atmospheric context.

The inflection in some of the curves in Figure 4 warrants more explicit discussion because this behavior is not physically realistic and represents a limitation of the model. For example, in Fig. 4A, for the purple line, there are two GF values that correspond to 80% RH (at GF? 1.05 and GF? 1.3, the inflection point being ?85% RH). I was ultimately able to piece together where the inflection arises, but I encourage the authors to more explicitly discuss the trends shown in Figure 4 and their origins. Specifically, for example, I was looking for a sentence or paragraph in the discussion that explicitly stated "The inflection seen in Fig. 4 for small particles is due to..."

• The inflection results for small particles when the strong Kelvin term effectively competes with the intermolecular interactions. However, one must remember the plotted curves represent equilibrium, and thus are not a direct prediction of what will be experimentally observed. In practice if the system humidity is gradually increased, when the inflection humidity is reached the particle is immediately exposed to a highly supersaturated environment relative to its equilibrium vapor pressure and thus will quickly grow until it reaches a new completely solvated equilibrium. In fact for small particles this very likely explains the fact that deliquescence appears spontaneous. Previously this was briefly addressed in the description of Fig. 4 but now we return to the point in the discussion. We add the text:

The model has the additional benefit of highlighting why, in practice, deliquescence is often observed to be an abrupt transition. The competition between the Kelvin term and the intermolecular forces results in an activation barrier (seen as the inflection points in Fig. 4 & Fig. 5), which when exceeded leaves a solvating particle in a highly supersaturated environment. As a result the particle grows suddenly until it reaches the new completely solvated equilibrium.

As is well-known, atmospheric aerosols are not single component and are mixed with organic compounds. The authors mention that "natural systems may require more complex treatments. . ." (p. 6, line 5) and also that the refined Kohler theory "remains general such that its application to more complex systems may yield deeper understandings of aerosol phase state and particle behavior" (p. 7, line 12), but there is not discussion of steps that may need to be taken to apply the refined Kohler theory to mixed organic/inorganic systems. I encourage more discussion here, as it would facilitate the application of their refinement.

• We have added the following text to the discussion:

Applying the model to more complex systems will also yield hurdles and likely make further approximations necessary, but as previously stated, may also lead to deeper insight. This model may allow some assessment of the relative importance of the short versus long range interactions and which quantities limit surface phase behavior. However, for mixtures and other materials each term of Eq. 10 would need to be re-evaluated. If bulk parameters that feed into the Köhler behavior (e.g., surface energy, water activity) are poorly constrained, strict physical interpretations will remain challenging.

Have the authors attempted to apply their refined Kohler theory to a system other than NaCl?

• In an ongoing collaboration with experimentalists the authors are studying a less atmospherically relevant system of butanol layers on nano-crystalline salts. However, implementing the theory for soluble particles beyond 1:1 electrolytes has not yet been treated. In that case each term in the manuscript's Eq. 10 would need to be re-evaluated, and as we state in the conclusion of §2, for more complex systems achieving analytical solutions would become challenging.

Much of the discussion and implications of the research are mentioned for the first time in the "Conclusions" section. This discussion would be better served in its own section. For example, the discussion surrounding Figure 6, which is currently called out for the first time in the conclusions, would be appropriate in a new section for "Discussion" or "Implications". This would enhance readability.

• The former "Conclusions" section has been split into Discussion and Conclusions sections.

The y-axis values in the inset to Figure 3 have commas rather than periods for the decimal point.

• The figure has been corrected.

I believe that on p. 1, line 14, the reference Davis et al. 2015b should be labeled as "a" (and Davis et al. 2015a should then be labeled "b").

• The reference has been corrected.

On p. 4, line 5, Van't Hoff and E-AIM models are mentioned without references. References should be provided.

• References have been added, such that the text now reads: "where a theoretical model (e.g., Van't Hoff – Zumdahl, 2005; E-AIM – Clegg et al., 1998; Friese and Ebel, 2010) or empirical parameterization can...".

The authors thank the reviewer for spotting the technical inconsistencies.

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Review Response Supplement

Discussion of Fitting Parameters for NaCl

In comment (3) Referee #1 wondered how the number of free fitting parameters could be reduced and how much more general one can make the theory by having a universal parameter set. Here we expand that discussion beyond what is relevant for the manuscript, but add it to the public discussion such that those seeking to apply the formulation within their own context might benefit.

A single parameter set can certainly be used for all sizes – and this is encouraged if one has well constrained, independent values for any of the parameters. Generally, surface charge and Hamaker constant should not depend strongly on the size of the initial particle, something which we also observe from the weak variations in the fitted values as presented in the main text in Table 1. However, the saturated equilibrium concentration C may have a size dependency. For example, using the three parameter fitting the brine concentration for the Biskos et al. (2006) data decreases as shown in Figure RS1. From such fitted values an empirical relationship for C can be derived, which in this case it takes the form of a decaying exponential (Figure RS1).

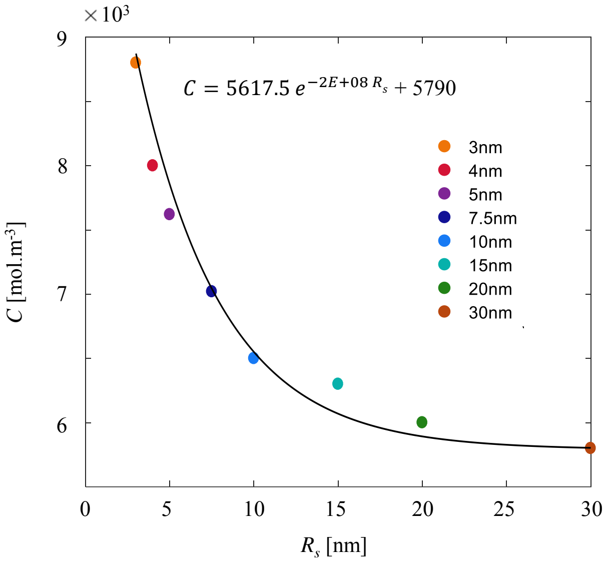
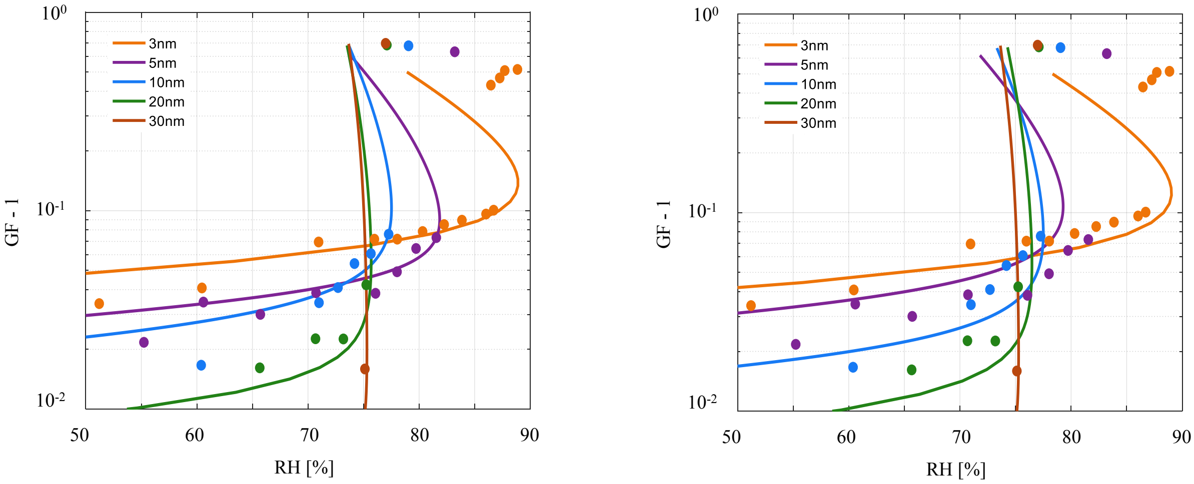


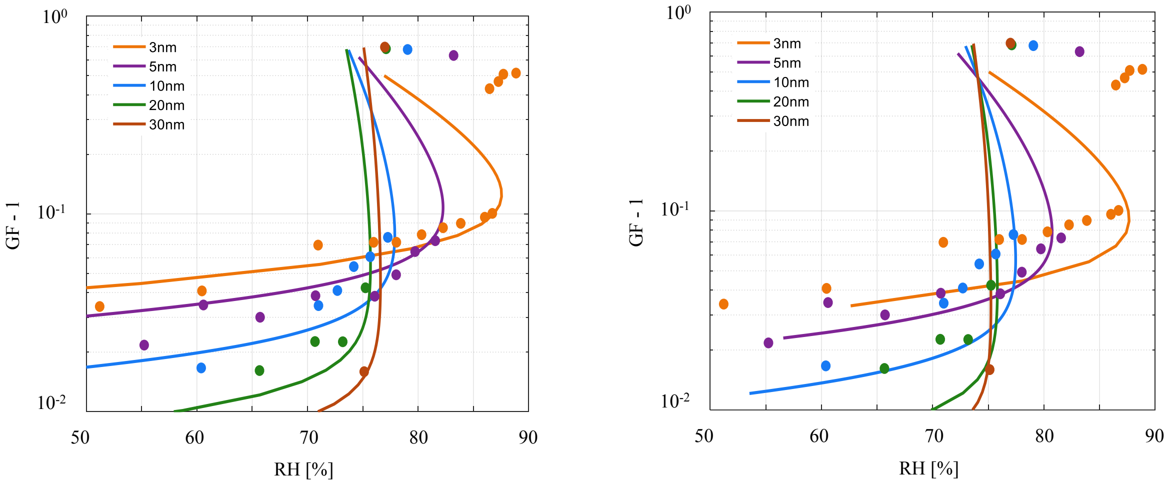
Figure RS1: Fitted concentration of the brine layer as a function of particle size for the Biskos et al. (2006) data, as taken from Table 1 in the main text.

In Figure RS2 a number of alternative equilibrium solutions are plotted based on different fitting procedures for a subset of the Biskos et al. (2006) data. What these plots make clear is that although, as one would expect, the best fits occur with the maximum three free parameters, fitting with up to two of the parameters fixed still yields high quality data representations. However, the quality of the data prediction is also clearly linked to how well quantified the parameters are. For the system we have presented, the breadth of independent information regarding surface charge, Hamaker constant, and equilibrium brine concentration, especially for the smallest particles is limited and thus using fixed literature values for q_s and A_h, while fitting the C value leads to poor data representations (as in panel (d)). Using fixed values for all three parameters yields even poorer results (not shown) which are clearly unphysical.



(a) Biskos et al. (2006) data reploted with the three-free parameter non-linear least squares, equilibrium solutions plotted in matching colors. Identical to Figure 4 in the main text.

(b) Theoretical equilibrium solutions reploted using fixed q_s and A_h, taken to be the average values as calculated from the Table 1 data in the main text, and a variable C as predicted from the presented empirical equation (see also Figure RS3).



(c) Theoretical equilibrium solutions again reploted. Here q_s and A_h are again taken to be the average values as calculated from the Table 1 data in the main text. C is treated as a free parameter and fit using a least squares minimization (see also Figure RS3).

(d) Alternative solution to Figure RS2c where q_s and A_h are fixed and assigned the reference values determined from the literature. C is again treated as a free parameter and fit using a least squares minimization (see also Figure RS3).

Figure RS2: Reploting Biskos et al. (2006) data as it appeared in the main text Figure 4 using, (a) 3 free parameters in identical manner to Figure 4, (b) 0 free fitting parameters, (c) 1 free fitting parameter with average values for fixed parameters, and (d) 1 free fitting parameter with fixed values taken from literature sources.

The table presented as Figure RS3 summarizes the quantities used to generate the plots in Figure RS2.

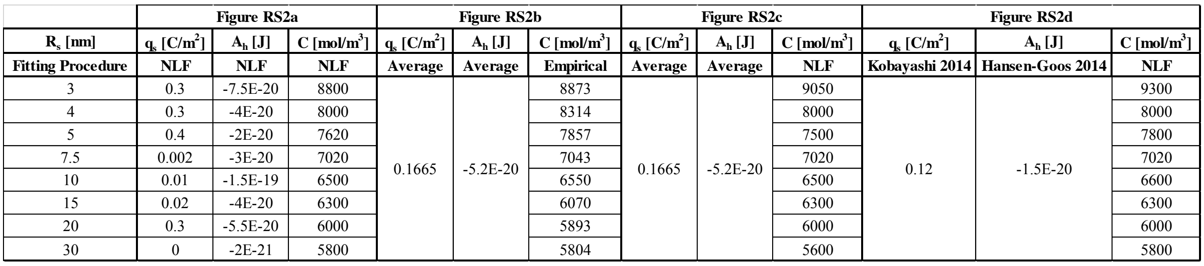


	Figure RS2a			Figure RS2b			Figure RS2c			Figure RS2d		
R_s [nm]	q_s [C/m^2]	A_h [J]	C [mol/m^3]	q_s [C/m^2]	A_h [J]	C [mol/m^3]	q_s [C/m^2]	A_h [J]	C [mol/m^3]	q_s [C/m^2]	A_h [J]	C [mol/m^3]
Fitting Procedure	**NLF**	**NLF**	**NLF**	**Average**	**Average**	**Empirical**	**Average**	**Average**	**NLF**	**Kobayashi 2014**	**Hansen-Goos 2014**	**NLF**
3	0.3	-7.5E-20	8800	0.1665	-5.2E-20	8873	0.1665	-5.2E-20	9050	0.12	-1.5E-20	9300
4	0.3	-4E-20	8000			8314			8000			8000
5	0.4	-2E-20	7620			7857			7500			7800
7.5	0.002	-3E-20	7020			7043			7020			7020
10	0.01	-1.5E-19	6500			6550			6500			6600
15	0.02	-4E-20	6300			6070			6300			6300
20	0.3	-5.5E-20	6000			5893			6000			6000
30	0	-2E-21	5800			5804			5600			5800

Figure RS3: Parameters used to plot Figure RS2. The parameters were determined in three different ways. **NLF**: Parameters are determined using a non-linear least squares minimization. **Average**: Average values calculated from corresponding NLF columns. **Emprical**: Values calculated from the empirical equation determined in Figure RS1: $C = 5617.5 \exp(-2 \times 10^8 R_s) + 5790$

A thermodynamic description for the hygroscopic growth of atmospheric aerosol particles

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Abstract. The phase state of atmospheric particulate is important to atmospheric processes and aerosol radiative forcing remains a large uncertainty in climate predictions. That said, precise atmospheric phase behavior is difficult to quantify and observations have shown that "precondensation" of water below predicted saturation values can occur. We propose a revised approach to understanding the transition from solid soluble particles to liquid droplets, typically described as cloud condensation nucleation – a process that is traditionally captured by Köhler theory, which describes a modified equilibrium saturation vapor pressure due to I. mixing entropy (Raoult's law) and II. droplet geometry (Kelvin effect). Given that observations of precondensation are not predicted by Köhler theory, we devise a more complete model which includes interfacial forces giving rise to predeliquescence, i.e., the formation of a brine layer wetting a salt particle at relative humidities well below the deliquescence point.

1 Introduction

The role of aerosols in the radiative budget of the planet is a source of large uncertainty in climate modeling and prediction (Stocker et al., 2013). One significant source of uncertainty comes from inadequate understanding of aerosol phase state in the atmosphere (Davis et al., 2015b). The phase behavior of atmospheric particles depends on both the environmental conditions (pressure, temperature, humidity, etc.) and the particle properties (Fig. 1). The phase state influences surface as well as bulk phase chemistry, cloud forming potential, particle deposition and other aspects of the global water and bio-/geochemical cycles. Thus fundamental knowledge of aerosol particle phase behavior is a key aspect to understanding and modeling atmospheric processes. For example, mixed phase clouds in the Arctic demonstrate a surprising persistence that is not predicted by the current understanding of ice-water saturation vapor pressure gradients and the resulting competition for H_2O (Wegener-Bergeron-Findeisen process) (Korolev, 2007; Martin et al., 2011; Morrison et al., 2012).

For soluble atmospheric particulate, Köhler theory is generally used to quantify and parameterize atmospheric phase state (Köhler, 1936). Köhler theory describes the equilibrium size of solution droplets in the atmosphere as determined by the satu-

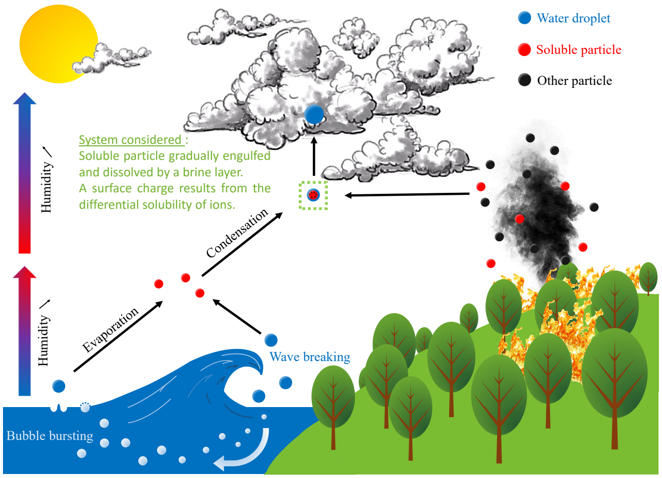

Figure 1. Soluble particles are ubiquitous in the atmosphere, with primary sources including biomass burning and the sea surface illustrated here. Solid salt particles, which can be directly emitted or form when solution droplets evaporate and effloresce, provide hygroscopic surfaces for cloud condensation nucleation.

ration vapor pressure, which depends upon component mixing (Raoult's Law) (Pruppacher and Klett, 1997) and the curvature of the interface (Kelvin or Gibbs-Thomson effect) (Thomson, 1871; Orr et al., 1958). For a fully soluble particle, implicit in the theory is a sudden transition from a dry (solid) particle to a saturated droplet. The relative humidity at the transition point is referred to as the deliquescence relative humidity (DRH). The Köhler model is useful because it provides a simple physical and mathematical description of nucleated condensation and can be modified to include compounds of limited solubility (Bilde and Svenningsson, 2004). As such it has remained the tool of choice in atmospheric models (Mirabel et al., 2000; Nenes and Seinfeld, 2003), although many measurements suggest that a precondensation of water even on pure soluble surfaces may occur below the DRH (Hämeri et al., 2001; Biskos et al., 2006; Zeng et al., 2013; Davis et al., 2015a; Cheng et al., 2015; Montgomery et al., 2015; Hsiao et al., 2016). For pure compounds, such observations are not predicted and thus hint that Köhler theory can be refined.

Here we suggest a theoretical refinement by considering the stability of a salt particle that is gradually engulfed and dissolved by a brine layer (Fig. 2). The model includes the understood bulk phase equilibria established by Köhler theory but invokes a transition region where meta-stable liquid layers exist on particle surfaces. The general shortcoming of Köhler theory for single component systems is the activated transition from dry particle to liquid droplet and the exclusion of an interfacial system that reduces the global free energy. The theory we propose herein evolves from previous explorations of wetting of soluble surfaces (Russell and Ming, 2002), where previous work has used bulk thermodynamics and ascribed disjoining pressures (also modeled using bulk properties or fitting parameters) to explore the stability of thin films on solvating particles (Shchekin and Rusanov, 2008; Shchekin et al., 2008; McGraw and Lewis, 2009; Shchekin et al., 2013). Other studies have used similar theoretical models to treat particle interfaces in the presence of substrate surfaces (Bruzewicz et al., 2011), or for terrestrial systems

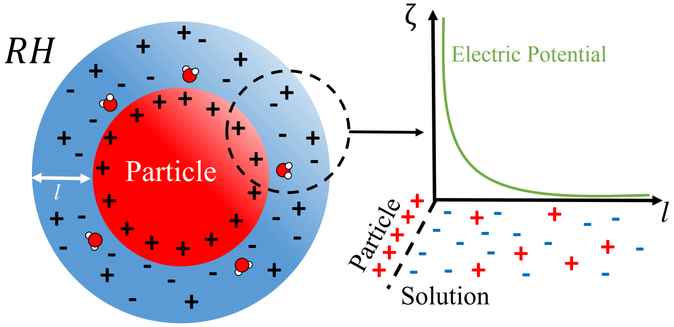

Figure 2. Schematic of the system considered herein – an idealized solvating atmospheric particle. The use of an idealized spherical geometry is justified by previous findings that NaCl crystal corner and step sites dissolve preferentially to surface sites, in a manner that quickly roughens and rounds faceted crystals (Chen et al., 2014).

like brine crusts where geometric effects can be excluded (Hansen-Goos et al., 2014). In this treatment we include terms to explicitly account for the intermolecular origins of the interfacial forces in a manner akin to surface melting (Dash et al., 2006).

Thus we extend previous work to combine and define, entropic, geometric and explicit intermolecular interactions that result in modified equilibrium vapor pressures above particle surfaces. We do so in a manner wherein achievable analytic solutions help to illuminate the underlying physicochemical processes that control the system, and may be used to benefit modeling at a range of scales. The implications of this work are far-reaching given that within the current state of understanding the existence of atmospheric aqueous surfaces is limited to deliquesced materials and/or coated insoluble particles. The model we propose herein suggests that aqueous surface layers may exist in some range of relative humidity (RH) below the DRH and thus resemble liquid droplet behavior for some processes and detection techniques.

2 Refinement of Köhler Theory

Köhler theory considers and balances the effects on droplet stability due to the interfacial curvature and soluble components (Farmer et al., 2015; Ruehl et al., 2016; Lohmann et al., 2016). Thus the equilibrium vapor pressure p_r at temperature T above a brine droplet of radius r is described by its departure from the analogous vapor pressure at the flat, pure water interface $p_{b\infty}$ at the same temperature,

$$\frac{p_r}{p_{b\infty}} = \frac{p_{sol}}{p_{b\infty}} \cdot \frac{p_r}{p_{sol}}, \tag{1}$$

where p_{sol} represents the equilibrium vapor pressure over the flat brine solution surface, also at temperature T. In detail the geometric term in (1) is given by the Kelvin equation,

$$\frac{p_r}{p_{sol}} = \exp\left(\frac{2\sigma v_{sol}}{R_g T r}\right), \tag{2}$$

where the surface free energy of the liquid/gas interface $\sigma \equiv \sigma(\rho_{sol})$ is a function of the bulk composition of the solution droplet as expressed by the solution density ρ_{sol}, R_g is the ideal gas constant, and v_{sol} is the molar volume of the solution. Likewise the modified equilibrium due to the addition of soluble components is given by the water activity,

$$\frac{p_{sol}}{p_{b\infty}} = a_w \tag{3}$$

where a theoretical model (e.g., Van't Hoff ~~,~~ – Zumdahl, 2005; E-AIM – Clegg et al., 1998; Friese and Ebel, 2010) or empirical parameterization can be chosen to best match the system of interest.

Thus from the combination of these effects the DRH is implicitly given when $r = \mathrm{R}_{\mathrm{DRH}}$ at the radius of the deliquesced droplet,

$$\frac{\mathrm{DRH}}{100} = a_w \exp\left(\frac{2\sigma v_{sol}}{R_g T \mathrm{R}_{\mathrm{DRH}}}\right). \tag{4}$$

This traditional Köhler formulation (4) for a fully soluble particle predicts the deliquescence point and, when r is allowed to evolve above $\mathrm{R}_{\mathrm{DRH}}$, the equilibrium relative humidity above the evolving brine droplet. However, in this formulation the sudden transition from a solid to liquid particle remains implicit.

Although the transition from solid to liquid solution may proceed quickly, it is important to consider whether or not there exists an intermediate state(s) of importance. Thus we consider whether a particle may be wetted by a thin film and what, if any, stability conditions may (de-)stabilize such a system. Such thin films are a common phenomenon and are generally treated within the rubric of adsorption or wetting (Schick, 1990), fields which incorporate many important applications from biology to surfactant physics (French et al., 2010).

Reformulating atmospheric particle dissolution as an interfacial problem leads to the system postulated in Fig. 2, where a charged soluble particle is engulfed and dissolved by a brine layer. However, in order for the interfacial system to endure it must yield some energetic benefit that can be captured by minimizing the global free energy of the system. Thus in addition to the bulk free energies tacit in Köhler theory (2) – (3) an interfacial contribution $\zeta(l)$ must be included. For thin films Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, which assesses the balance between short and long range intermolecular interactions, has been used to great success (Derjaguin and Landau, 1993; Verwey and Overbeek, 1948; Luo, 2007).

In the case of an ionic electrolyte a surface charge results from the differential solubility of ions (Kobayashi et al., 2014), while the solvated ions affect both the mixing entropy and the electric potential of the film. The ions in the brine layer are organized to offset the surface charge in a manner described by linearized Poisson-Boltzmann theory, where the characteristic falloff of the electric field is a *Debye Length* $\kappa^{-1} = \left((\epsilon\epsilon_o k_b T) / \left(e^2 N_A \rho_{sol}\right)\right)^{1/2}$, where ϵ_0 is the vacuum permittivity, ϵ is the relative permittivity of the brine, k_b is the Boltzmann constant, T is the absolute temperature, e is the elementary charge, and N_A is Avogadro's constant. Thus the contribution to the free energy is,

$$F_{elec}(d) = \frac{2q_s^2}{\kappa\epsilon\epsilon_0} e^{-\kappa l}, \tag{5}$$

where q_s is the surface charge and l is the thickness of the liquid layer. The colligative effect of the ions remains unchanged as in (3).

The long range dipole fluctuations in the system are volume-volume interactions and can be depicted to first-order as the non-retarded dispersion or van der Waals forces. Assuming that retardation is not important the van der Waals contribution to the free energy can be expressed as,

$$F_{disp}(d) = -\frac{A_h}{12\pi l^2}, \tag{6}$$

where the Hamaker constant A_h is determined for a given layered system (French, 2000). This formulation assumes a planar geometry, which given the relative scales of the layering versus the system size is taken as accurate to first order (French, 2000). For small nano-particles other considerations including the entire particle volume may become important as we discuss later.

The combined effects of the short and long range interactions captured by $F_{elec}(l)$ and $F_{disp}(l)$ yield a total interaction potential

$$\zeta(l) = F_{disp}(l) + F_{elec}(l), \tag{7}$$

whose derivative with respect to l, $\zeta'(l)$ represents the interfacial contribution to the free energy, and whose sign and strength will depend upon the material properties and geometry of the specific system.

To re-express Köhler theory including the effect of these intermolecular interactions we define an equilibrium vapor pressure over the curved brine surface p_ζ that includes the interfacial term, and thus in analogy to (1),

$$\frac{p_\zeta}{p_{b\infty}} = \frac{p_{sol}}{p_{b\infty}} \cdot \frac{p_r}{p_{sol}} \cdot \frac{p_\zeta}{p_r}. \tag{8}$$

Assuming that the thermodynamic equilibrium condition at the solution – vapor interface is set by the free exchange of water molecules $\frac{\partial G}{\partial N_v} = \frac{\partial G}{\partial N_l}$ and that near deliquescence temperature is constant, an expression for p_ζ can be calculated by considering the difference in chemical potentials between the solvated and layered states,

$$p_\zeta = p_r \exp\left(\frac{v_{sol}\zeta'(l)}{R_g T}\right), \tag{9}$$

where the details of the derivation as presented in Hansen-Goos et al. (hereafter, HG14) (Hansen-Goos et al., 2014) are included in the supplementary material for completeness. Thus (8) can be rewritten as,

$$\frac{p_\zeta}{p_{b\infty}} = \frac{RH}{100} = a_w \exp\left(\frac{2\sigma v_{sol}}{R_g T r'}\right) \exp\left(\frac{v_{sol}\zeta'(l)}{R_g T}\right), \tag{10}$$

$$\text{where, } r' < \mathrm{R_{DRH}} \rightarrow r' = \mathrm{R_s} + l - \frac{l}{\beta}, \tag{11}$$

$$r' \geq \mathrm{R_{DRH}} \rightarrow r' = r, \tag{12}$$

Thus at $r' < \mathrm{R_{DRH}}$ the system size evolves like $\mathrm{R_s} + l - \frac{l}{\beta}$, which captures the change in radius due to condensation and dissolution, where a linear solvation is assumed. The exact solution considering the volume/volume equivalence of dissolution requires numerically solving a 3^{rd} degree polynomial and yields a negligible correction factor. The growth factor at DRH is

$\beta = \mathrm{R_{DRH}}/\mathrm{R_s}$, where the dry particle radius is $\mathrm{R_s}$. At $r' \geq \mathrm{R_{DRH}}$ the entire particle is dissolved and thus r is the solution droplet's radius and the theory re-converges to classical Köhler theory as $\zeta'(l)$ vanishes.

Equation (10) is a general result describing the equilibrium vapor pressure over a dissolving salt particle, from the dry particle state to the totally dissolved state. Although herein we treat an idealized monovalent electrolyte system using modified DLVO theory to constrain the functional behavior of $\zeta'(l)$, natural systems may require more complex treatments that would likely yield a host of interesting behavior, and simultaneously strain the ability to achieve analytical and/or computational solutions.

3 Applying refined Köhler theory

It is instructive to use the refined Köhler formulation (10) to model a NaCl particle, as might represent an idealized marine aerosol. Although considerable information concerning bulk salt solutions is available it is difficult to assess the applicability of these values to thin brines. For example, the assumptions that the interfacial brine layer is a saturated solution whose thickness is controlled by electrostatic interactions may not be self-consistent. The ion availability within a saturated NaCl brine will allow efficient charge screening and thus a very short Debye Length should result. That said the uncertain theoretical parameters, q_s, A_h, κ^{-1}, and brine concentration C can also be used as fitting parameters in order to illuminate the range of possible physical behavior.

Here for an idealized case we choose to apply (10) to a sodium chloride particle of a representative atmospheric diameter $\simeq 0.8\,\mu$m in the accumulation mode (Lewis and Schwartz, 2004; Lohmann et al., 2016). The growth factor is assumed such that the particle will lead to a solvated brine droplet of radius $1.36\,\mu$m, and for consistency with previous work we choose a temperature of 20° C and a saturated concentration of $[\mathrm{NaCl}]_{sat} = 5.4$ mol L^{-1} (Haynes, 2012), which is also used to calculate the Debye length. The value for surface charge $q_s = 0.12$ C m^{-2} is taken from Kobayashi et al. (2014), while the HG14 value $A_h = -1.5 \times 10^{-20}$ is used, and the expression for the water activity of a NaCl solution is taken from Tang et al. (1997). The result is illustrated in Fig. 3, where both the classical Köhler behavior and the refined model of pre-deliquescent hygroscopic growth are captured. With the refined interfacial model the DRH is captured ($\approx 75\%$ RH) as reported in many previous studies (Tang and Munkelwitz, 1994; Metzger et al., 2012; Laskina et al., 2015), but near the deliquescence transition (Fig. 3, zoom) a wetted interface is predicted below DRH when considering the balance of the intermolecular interactions.

The result suggests that observations of pre-condensation in the existing literature (Hämeri et al., 2001; Biskos et al., 2006; Cheng et al., 2015) may also be explained by a metastable interfacial equilibrium. In Fig. 4 the theoretical model is compared to measurement data from Hämeri et al. (2001) and Biskos et al. (2006). Each of the solid lines in Fig. 4 correspond to non-linear least-squares solutions to fit the data, where the identified fitting parameters are presented in Table 1.

For physical consistency ~~the~~ with the theoretical framework the best-fit solutions have been calculated excluding data points that preclude a full monolayer of water ($l \leq 0.3$ nm) and excluding the data points that represent the fully solvated particles (Growth Factor ≥ 1.2 in Fig. 4). Although sub-monolayer water adsorption is observed (Peters and Ewing, 1997), implicit in this theory is a bulk solution layer of uniform thickness. In all cases the data is well represented within a narrow window of the fitting parameters and the best-fit solutions also serve to demonstrate the impact of the parameters on the shapes of the curves.

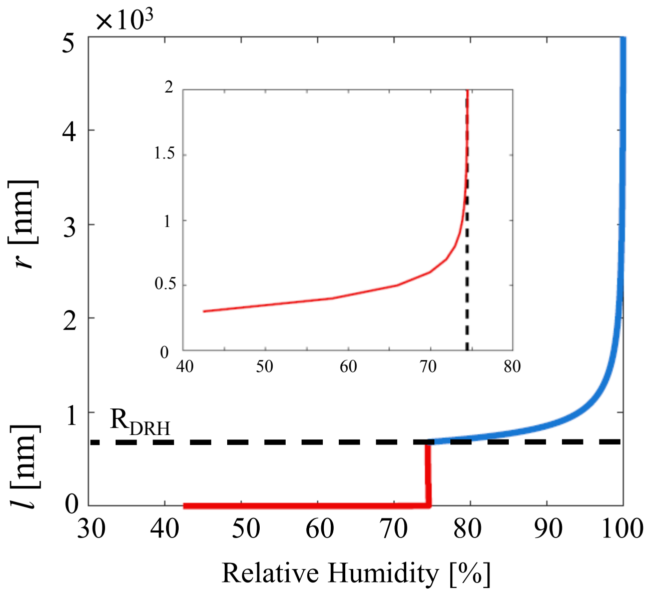

Figure 3. Model of the growth of the solvating surface of a 0.8 μm accumulation mode NaCl particle as outlined in the text. Below deliquescence ($\lesssim 75\%$ RH and in zoom) the metastable brine layer behavior is governed as in Eq. (10) – red curve. Above deliquescence the layer thickness l becomes the radius r of the growing solution droplet as is captured by classical Köhler theory (Eqs. (1)–(4) and Eq. (10) for $r' = r$, where the interfacial term has vanished; blue curve).

Furthermore, the best fit solutions agree well with values extracted from the literature, listed in the first row of Table 1 and used previously to construct Fig. 3, where their sources are referenced.

For small particles ($R_s \lesssim 5$ nm) the Kelvin term is strong enough to compete with the intermolecular forces and thus the system retains an activation barrier until DRH or above (McGraw and Lewis, 2009), as shown in Figs. 4–5. ~~A~~ In practice a small dry particle would ~~first~~ be subjected to reversible uptake of water due to intermolecular attraction until it suddenly dissolves into a brine droplet when the deliquescence activation barrier is overcome. However, at short length scales the veracity of the bulk approximations and several other simplifying assumptions of this model must be questioned. For example, the high brine layer concentrations predicted for small particles may be indicative of the model limitations. Although the model represents the data remarkably well even where it might be expected to fail, in those cases it might be better to approach the activation problem in terms of adsorption theory (Langmuir, 1918) or using molecular dynamics simulations (Lovrić et al., 2016).

The refinement of Köhler theory we have proposed, yields a smooth meta-stable transition from solid to aqueous phase atmospheric particles. It captures observed behavior for specific compounds, yet remains general such that its application to more complex systems may yield deeper understandings of aerosol phase state and particle behavior.

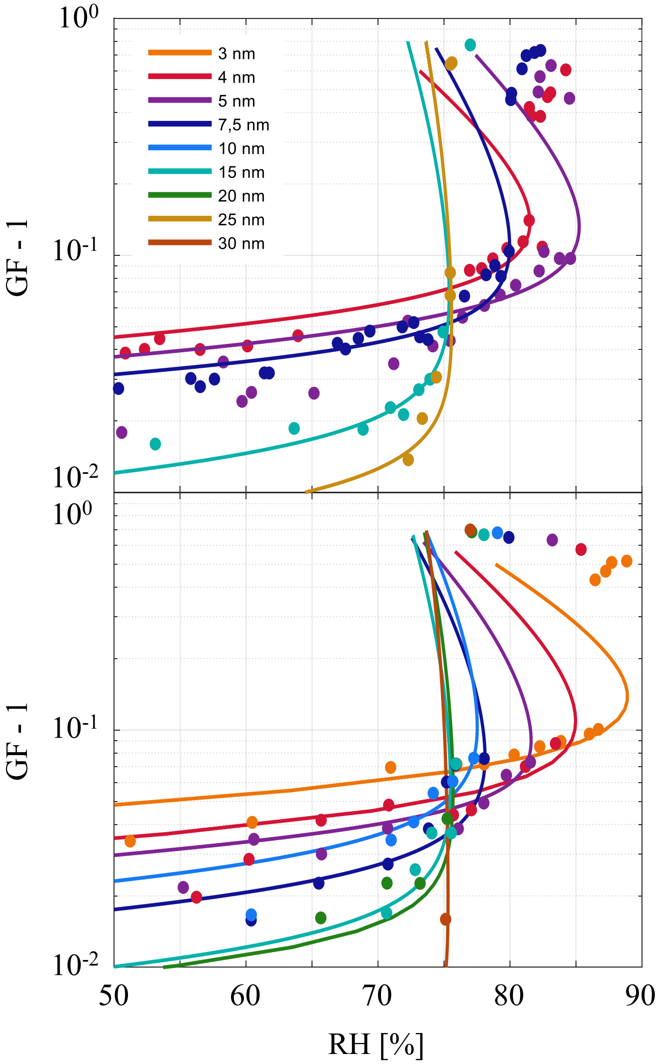

Figure 4. Measurement data points of NaCl particle hygroscopic growth under incrementally increasing RH. Colors correspond to different initial dry particle radii indicated in the legend and the growth factor (GF) is the ratio of the measured radius to the dry radius (GF-1 scaling is used to suitably present data on logarithmic scale). (a) Lines represent theoretical fits to data presented by Hämeri et al. (2001). (b) Theoretical fits to data presented by Biskos et al. (2006). In all cases fitting parameters are presented in Table 1. Given the experimentally prescribed increasing humidities, particles that grow beyond the activation barrier set by the strong Kelvin effect (cf. Fig. 5) are observed at RH exceeding the equilibrium value.

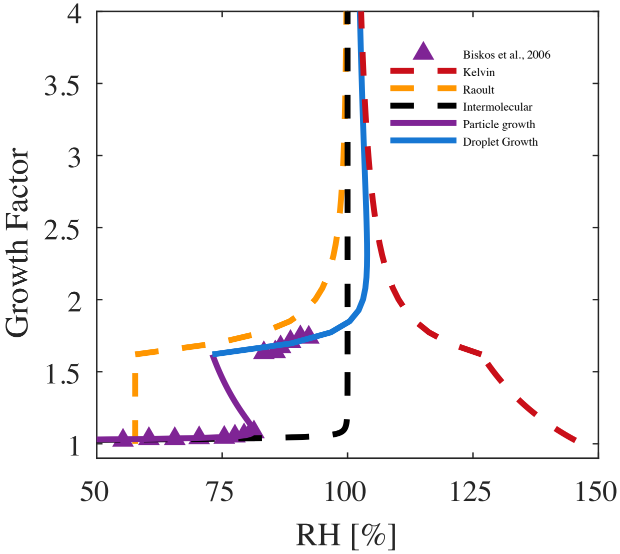

Figure 5. The evolution of the individual terms in Eq. (10) are shown for a solvating 5 nm NaCl particle. For such small particles the Kelvin term dominates yielding an activation barrier as illustrated by the inflection in the layer growth (magenta) curve. One also observes that the Raoult term (yellow curve) is onset only after the solid particle dissolves ($\mathrm{R_{DRH}}$) and that the intermolecular interactions are very short range (black curve).

4 Discussion

Real particles in the atmosphere tend to be more complicated than idealized theories of solvation can easily capture. Atmospheric particulates that assist nucleation are often internally mixed and include varying quantities of soluble/insoluble, organic/inorganic materials etc (Zardini et al., 2008; Seinfeld et al., 2016). Furthermore, theoretical adaptations of Köhler theory have been used to capture particle mixing state; for example “modified-Köhler theory" (Bilde and Svenningsson, 2004) and “κ-Köhler theory" (Petters and Kreidenweis, 2007). However, these remain limited to predicting critical supersaturations and droplet evolution. Our contribution is general in that it predicts the complete evolution from the dry particle through a meta-stable equilibrium characterized by a growing thin film. Such films are not only consistent with droplet deliquescence but also with previous observations of water absorption and ionic mobility at RH far below the DRH $(35\% \leq \mathrm{RH} \leq \mathrm{DRH})$ (Ewing, 2005; Verdaguer et al., 2005; Wise et al., 2008). The implication is that given the correct intermolecular force balance, the surface of any soluble-material-containing atmospheric particle may “pre-deliquesce” and thereby contribute to an as yet unquantified aqueous reservoir.

~~We note that given the approximations~~ The formulation of continuous dry particle dissolution and droplet growth as represented by Eq. (10) and presented in the figures has several advantages over previous treatments of such systems. First we treat the intermolecular interactions explicitly in order to minimize the use of bulk parameters to model the interfacial system. The interfacial free energy minimization is then carried out and incorporated into Köhler Theory as a simple additional term that continues to allow for analytical solutions. The approach is in contrast to other treatments of analogous systems that utilize ascribed or phenomenological descriptions of short range interactions (Shchekin and Rusanov, 2008; Shchekin et al., 2008; Bruzewicz et a and/or do not account for the full particle geometry (Bruzewicz et al., 2011) and thus the atmospheric context. The model has the additional benefit of highlighting why, in practice, deliquescence is often observed to be an abrupt transition. The competition between the Kelvin term and the intermolecular forces results in an activation barrier (seen as the inflection points in Fig. 4 & Fig. 5), which when exceeded leaves a solvating particle in a highly supersaturated environment. As a result the particle grows suddenly until it reaches the new completely solvated equilibrium. Thus, there may be implications for non-equilibrium particle growth in the atmosphere.

Unfortunately, approximations remain inherent in the model, for example the fitted concentrations of the brine layers increase with decreasing particle size. These predicted equilibrium concentrations may seem physically unrealistic for very small particles, which could be due to the geometric limitations of our model – the dispersion forces are derived assuming interactions between flat, parallel interfaces. But it is also possible that the model is compensating for other physical effects not taken into account in this study (such as surface depletion), effects that could lower the chemical potential of the liquid phase for very small sizes. ~~The model does illustrate that due to the enduring activation barrier for small particle dissolution, those particles which manage to exceed the barrier will immediately be in a domain of strong supersaturation relative to their equilibrium. Thus, there may be implications for non-equilibrium particle growth in the atmosphere.~~Applying the model to more complex systems will also yield hurdles and likely make further approximations necessary, but as previously stated, may also lead to deeper insight. This model may allow some assessment of the relative importance of the short versus long range interactions and which quantities limit surface phase behavior. However, for mixtures and other materials each term of Eq. (10) would need to be re-evaluated. If bulk parameters that feed into the Köhler behavior (e.g., surface energy, water activity) are poorly constrained, strict physical interpretations will remain challenging.

Given the importance of aerosol phase state there may also be significant implications to even a limited RH range where stable aqueous interfacial films exist. Most obvious is the significance for contributions to aqueous phase chemistry (Martin, 2000). However, there are also potential cloud and climate scale impacts that deserve some investigation. The radiative absorption cross-section of pre-deliquescing particles may significantly change their optical properties as has been shown for aerosol – particle mixtures (Ackerman and Toon, 1981), and especially for particles that include soot (Jacobson, 2000). There are also implications for understanding mixed phase cloud stability given that the equilibrium vapor pressure above a pre-deliquescence layer can be much lower than the analogous vapor pressure above a liquid droplet (Fig. 6).

Mixed phase clouds are inherently unstable given that air saturated with respect to water is supersaturated with respect to ice, and in fact most precipitation globally originates from mixed phase processes (Mülmenstädt et al., 2015). However, particularly in the Arctic and sub-Arctic regions the unexplained persistence of mixed phase clouds has consequential climate impacts (Morrison et al., 2012). Simply put the equilibrium vapor gradient innate between supercooled liquid droplets and ice crystals is greatly diminished if droplets are replaced by pre-deliquesced particles (Fig. 6), while to some observational techniques the two morphologies may be indistinguishable. A potential result is slower growing ice crystals and thus a longer

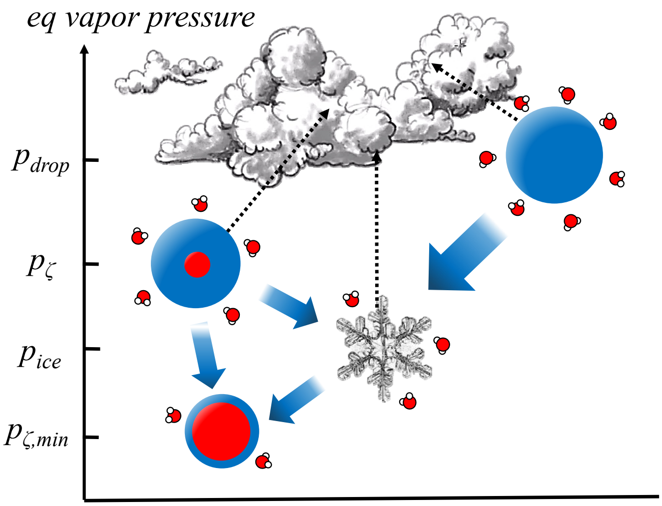

Figure 6. Schematic of the equilibrium vapor pressures over droplets, pre-deliquesced particles, and ice particles where gradients lead to Wegener-Bergeron-Findeisen processing. The range of equilibrium vapor pressures above pre-deliquesced thin films straddle the equilibrium vapor pressure over ice p_{ice}, resulting in a more stable co-existance between ice and pre-deliquesced particles, relative to liquid droplets.

lifetime for mixed phase clouds. Although a complete understanding of mixed phase must also involve particle dynamics (Sullivan et al., 2016), pre-deliquescing particles may play a contributing role and recent studies suggest that there exist more sources for dry soluble particles than previously thought (Davis et al., 2015b).

5 Conclusions

This study has introduced a refinement of Köhler theory that tracks a soluble atmospheric particle from its dry state to the solvated droplet equilibrium. The model presumes that from molecular scale adsorption to the growth of thin liquid films, the interface can be stabilized by the intermolecular interactions in a system. Although, the details of real atmospheric systems would be subject to a strict bookkeeping, even the highly simplified model proposed here captures many important parameters, like equilibrium vapor pressure and liquid layer thickness, that could contribute to better parameterizations for aerosol-cloud interaction modeling efforts.

Author contributions. The authors have contributed equally to this work.

Competing interests. The authors declare that they have no conflict of interest.

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Table 1. Fitting parameters yielding curves in Fig. 4 where superscripted letters correspond to figure panel.

$\mathrm{R_s}$	q_s [C m^{-2}]	A_h [J]	C [moles m^{-3}]
standard values	0.12 (Kobayashi et al., 2014)	-1.5×10^{-20} (HG14)	5400 (Haynes, 2012)
$3nm^{(b)}$	0.3	-7.5×10^{-20}	8800
$4nm^{(a)}$	0.3	-9×10^{-20}	8270
$4nm^{(b)}$	0.3	-4×10^{-20}	8000
$5nm^{(a)}$	0.1	-9×10^{-20}	7050
$5nm^{(b)}$	0.4	-2.5×10^{-20}	7620
$7.5nm^{(a)}$	0.6	-9×10^{-20}	6700
$7.5nm^{(b)}$	0.002	-3×10^{-20}	7020
$10nm^{(b)}$	0.01	-15×10^{-20}	6500
$15nm^{(a)}$	2.7×10^{-6}	-5×10^{-20}	6300
$15nm^{(b)}$	0.02	-4×10^{-20}	6300
$20nm^{(b)}$	0.3	-5.5×10^{-20}	6000
$25nm^{(a)}$	0.1	-5×10^{-20}	5850
$30nm^{(b)}$	0	-0.2×10^{-20}	5800