Manuscript acp-2014-426: “Determination of interfacial parameters of a soluble particle in a nonideal solution from measured deliquescence and efflorescence humidities”

(submitted for publication in Atmos. Chem. Phys. by O. Hellmuth and A. K. Shchekin)

Reply to Referee Comments

February 8, 2015

1 General reply to referees #2 and #3

We thank both referees very much

- for the time they took to evaluate the paper and to recap potential readers perception of the essence of the paper and the supplement containing the calculus, and
- for the very stimulating and motivating for us assessment of the work that has been done inclusive for referees recommendations to improve the manuscript.

We did our best in the paper and its revision in the hope to find interested readers. The corrections and recommendations of the referees were found to be traceable and helpful to improve the manuscript.

Referee #2 added three ’minor’ remarks, referee #3 listed one ’minor’ remark and 6 specific remarks, which are *expressis verbis* ’not to be considered as mandatory, up to the author’s discretion’. All comments given by the referees have been considered in the revision as described below. Apart from this, referees attention is also directed to Section 6 below, in which some additional minor changes with respect to style, grammar, wording have been listed without changing the content of the paper.

2 Reference document for changes

All changes refer to the corresponding page number (e.g., P3 for page 3) and line number (e.g., L21 for line 21) in the PDF version in its accepted form from August 3, 2014, available online at `http://www.atmos-chem-phys-discuss.net/14/22715/2014/acpd-14-22715-2014.pdf`.

3 Specific reply to Referee #2

- R2: *Some minor remarks: - In the introduction, the authors talk about "stable nuclei" (page 2). This notation is misleading in the connection as it is used. Supercritical nuclei are as a rule not stable in the thermodynamic sense which is employed also at the same page but somewhat later.*

  Insertion on P3, L21:
  "These clusters need to reach a critical size (embryonic stage) in order to freely grow up to solid precipitates within the maternal solution droplet. The critical size of the embryo depends on temperature, supersaturation, and the droplet size."

- R2: *- I propose to change: A full derivation of the calculus → a comprehensive detailed outline of the calculus*

  Insertion on P10, L21:
  "A comprehensive detailed outline of the calculus can be found in the Supplement (SM)."

- R2: *- As possible candidate → A possible candidate*

  Correction on P27, L25:
  "A possible candidate for enhancement ..."

4 Reply to Referee #3

Referee's comments were considered in the following way:

1. R3: *It would be worthy to add a few introductory sentences (similar to those at the beginning of this review) showing importance of deliquescence and efflorescence for atmospheric models and processes and especially for climate models. This would emphasize the importance of this paper devoted to studies of these processes and for assessment of climate change.*

   Insertion on P3, L7:
   We have included the following, slightly modified paragraph from the referee report into the introduction with reference to the interactive comment given by the referee:

   "The importance of deliquescence and efflorescence (the notions of which will be explained below) for atmospheric models and processes, especially for climate models, originates from associated radiative effects (see Anonymous Referee 2014 and references given therein to, e.g., Cziczo and Abbatt 1999, Oatis et al. 1998, Xu et al. 1998, Lohmann and Feichter 2005, Khvorostyanov and Curry 2014, Sections 2.3, 2.5, 6.1, 11.1 therein): Deliquescence and efflorescence of aerosols impact the aerosol optical thickness, and in this way, the direct aerosol affect. It also influences activation of CCN into cloud drops and determines the 1st and 2nd indirect aerosol effects via cloud drops and, after subsequent freezing – several other indirect aerosol effects. Activated drops participate in cloud dynamical circulation. Due to downdrafts near the cloud edges such drops can be transported below the cloud bottom, where they may penetrate into the very dry environment (something similar can happen due to lateral entrainment of dry environmental air into cloudy air). Such drying may cause the reverse effect: evaporation of the drops to the sizes of CCN with strongly supersaturated solution concentration, which may in turn cause efflorescence and transformation of the aerosol particles to the state close to the original dry or slightly wetted CCN. When such particles are brought again into the cloud by the updrafts, they can grow again, may be activated and influence cloud microphysical and optical properties. Accounting for the significant variability of aerosol over the globe, it is obvious that any reliable estimates of aerosol impacts on clouds and climate change require physically appropriate theories of aerosol deliquescence and efflorescence."

2. R3: *Classical nucleation theory usually uses a capillary approximation. Numerous attempts were made to improve or modify this approximation, especially for very small particles. The authors of this work introduce and use an alternative approximation of "disjoining pressure". However, its description is too short and not very clear. It would be worthy to add a few sentences on page 12 (22-26) with explanation of the physical meaning of "disjoining pressure", why it occurs, how it acts and how it is related to the traditional capillary approximation. Is capillary approximation a particular case of the "disjoining pressure" or there is no relations between them?*

   We agree with referee's suggestions. In response we have inserted the following paragraph on page 12, after line 22:

   "The disjoining pressure of a thin liquid film is the excess free energy density (free energy per unit volume), which originates from the overlapping of molecular interactions at both sides of the film when the film thickness decreases down to nanometric scales and the interfaces approach each other. It arises together with the nonuniformity of the middle part of the film. While the surface tension of a 'thick' film (considered as a 'bulk' liquid phase) is given by the sum of the surface tensions of both adjacent film interfaces, the principle of additivity of surface tensions cannot be applied any longer to a 'thin' film. Upon thinning a liquid film the interfacial layers on both sides of the film start to penetrate each other, leading to the emergence of an extra excess value, which must be additionally considered in the calculation of the film surface tension. The disjoining pressure decreases upon increasing the film thickness, and can be neglected in the limiting case of a thick film. The value of the disjoining pressure results from a superposition of contributions from different kinds of molecular interactions. The strengths of these interactions depend on the physical properties of the film phase and the ambient phases adjacent to the film. The shape of the functional dependence of the disjoining pressures on the film thickness results from molecular theory; the quantification of the disjoining pressure values requires experimental data and/or computer simulations. The notion 'disjoining pressure' (German: 'Spaltdruck') has been introduced by B. V. Derjaguin (e.g., Derjaguin 1955a,b; Derjaguin et al. 1987) to characterise the interaction-induced excess pressure appearing in a 'join'. The disjoining pressure is a signed value, i.e., it can effectively act as a 'disjoining pressure' (due to repelling forces) or as a 'joining pressure' (due to attractive forces). Details of the physical motivation of the concept of disjoining pressure and references for the specification applied here can be found in SM/Sections S.1.2 and S.1.7)."

3. R3: *Similar remark. On page 19 (22-33), eqs. 7 and 8, the 2 "cost functions" are introduced. Their introducing is also somewhat formal, and some comments are desirable here; it is "cost of what?", and what do they characterize?*

   We see the problem in using the notion "cost function" when there are no "costs" defined. Hence, this notion is somewhat misleading here and has been replaced by the following formulations:

   (a) P19, L2: "On this base, one can define a suitable physical constraint in form of an implicit function $\mathcal{F}^{(\sigma)}(\sigma_\infty^{(\alpha\gamma)}) = 0$, the numerical root of which is the sought-after interfacial energy $\sigma_\infty^{(\alpha\gamma)}$. The whole calculus reads: …"

   (b) P19, L18: "On this base, one can define another physical constraint in form of an implicit function $\mathcal{F}^{(l)}(l^{(\star)}) = 0$, the numerical root of which is the sought-after length scale $l^{(\star)}$: … The functions $\mathcal{F}^{(\sigma)}(\sigma_\infty^{(\alpha\gamma)}) = 0$ and $\mathcal{F}^{(l)}(l^{(\star)}) = 0$ serve as additional side conditions to close the model."

   (c) P21, L18: "... shows the function $\mathcal{F}^{(\sigma)}$ in dependence of ..."

   (d) P22, L4-5: ".. shows the function $\mathcal{F}^{(l)}$ in dependence of ..."

   (e) The notions 'cost function' appearing in Figs. 2, 3, 10, and 11 have been removed and replaced with "Function $\mathcal{F}^{(\sigma)}$ in dependence of" and "Function $\mathcal{F}^{(l)}$ in dependence of", respectively. The following sentences have been added in the captions of Figs. 2 and 3: "The sought-after value $\sigma_\infty^{(\alpha\gamma)}$ is the abscissa value corresponding to the functional value $\mathcal{F}^{(\sigma)}(\sigma_\infty^{(\alpha\gamma)}) = 0$, indicated by the solid horizontal line." Analogously: "The sought-after value $l^{(\star)}$ is the abcissa value corresponding to the ordinate value $\mathcal{F}^{(l)}(\sigma_\infty^{(\alpha\gamma)}) = 0$, indicated by the solid horizontal line." In Fig. 3 a reference to Table 2 has been added.

4. R3: *As I could understand, the baseline calculations in this work were performed at $T = 298\,\mathrm{K}$. Laboratory measurements show that there is a substantial temperature dependence of the deliquescence and efflorescence (e.g., Seinfeld and Pandis, 1998; Cziczo and Abbatt, 1999; Oatis et al., 1998; Xu et al., 1998), which is caused, in particular, by the temperature dependence of the surface tensions. In a recent work by Khvorostyanov and Curry, (2014, Chapter 11 therein), it was shown that these lab data can be reproduced based on extended CNT, and using appropriate reference points $\sigma(T_0)$ and temperature gradients of the surface tensions, $\mathrm{d}\sigma/\mathrm{d}T$. I guess, the theory of Hellmuth and Shchekin can be extended into a wider temperature range, and a short comment in Conclusions would be helpful on the possible T-extensions of this theory and appropriate necessary choice of the gradients ($\mathrm{d}\sigma/\mathrm{d}T$).*

   This is a good point. We are fully aware of the temperature dependence of deliquescence and efflorescence, which is of high importance for both theory building/verification and application. (One of the authors has just evaluated a study about temperature-dependence of the deliquescence humidity from molecular dynamics simulations). We agree with the referee that (next to other dependencies) the temperature dependence of both deliquescence and efflorescence deserves investigation within the framework of the presented theory. The current analysis was restricted to $T = 298\,\mathrm{K}$ because the empirical functions $\mathrm{DRH}(D_\mathrm{p})$ and $\mathrm{ERH}(D_\mathrm{p})$ for nanoparticles (both functions served as input parameters for the determination of interfacial properties) were only available for this temperature (at least, we were not aware of corresponding data at other temperatures). As we effectively did not perform any investigations on the temperature dependence, we cannot draw any specific conclusions. To meet referee's recommendation we have evaluated the additional references and added a new section "Remaining questions", in which this point has been adressed.

5. R3: *The authors concentrated in this work mostly on NaCl. Another aerosol, ammonium sulfate, may play an important role in formation of the upper-level clouds like cirrus. If the authors plan to perform similar study for ammonium sulfate (as Gao et al, 2006, 2007, made in 2 separate papers), it might be worthy to add such comment in Conclusions.*

   With respect to atmospheric applications, investigations of other aqueous systems involving, e.g., $(\mathrm{NH_4})_2\mathrm{SO_4}$, $\mathrm{NH_4Cl}$, and $\mathrm{NH_4NO_3}$ nanoparticles are of high interest. As argued before, owing to lack of own studies on this we will abstain from drawing conclusions, but instead give a comment in the new section "Remaining questions".

6. R3: *Can any recommendation be given, based on this work, for application of this theory in cloud or climate models? If so, this could be added in Conclusions.*

   No, for the time being we cannot (yet) give any specific recommendation for application of this theory in cloud or climate models. However, we agree with the referee regarding the importance of the applicational aspects. Therefore, we have included a comment in the new section "Remaining questions".

7. R3: *p. 23, 1st line. Is written "mass fanction", misprint. Should be "mass function".*

   Many thanks, referee. Has been corrected to "solute mass fraction".

5 New section in response to referee #3: "Remaining questions"

"In order to demonstrate the feasibility of combined thermodynamic theory and CNT to describe memory effects during humidification/dehumidification of soluble nanoparticles, the present approach had to be restricted to a special, well-characterised aqueous inorganic-salt solution under such thermohumid conditions, for which preferably all of the required thermophysical properties were available from authoritative sources. For such a reference system the aqueous sodium chloride solution at $T = 298\,\mathrm{K}$ has been chosen. However, even for this highly relevant and well-studied salt system there is still a great lack of quantitative insight into the properties of the NaCl surfaces such as the interfacial energy (see SM/Section S.3.6). Systematic simulations for the whole atmospheric temperature range, for the full size range of nanoparticles, for other aqueous salt solutions, and discussion of applicational aspects were beyond the scope of the current study. Nevertheless, owing to the practical relevance of these points we will add here some specific comments on remaining questions:

1. *Temperature dependence of deliquescence/efflorescence:* There is comprehensive phenomenological knowledge and theoretical analysis concerning the temperature dependence of both the deliquescence and efflorescence humidities (Khvorostyanov and Curry 2014, Chapter 11 therein). For example, for $(\mathrm{NH_4})_2\mathrm{SO_4}$ Cziczo and Abbatt (1999, Fig. 6 therein) reported a negative temperature coefficient of the deliquescent humidity, $\mathrm{d\,DRH}/\mathrm{d}T < 0$, in the temperature range $253-303\,\mathrm{K}$ with the following pairs of variates: $\mathrm{DRH} = (79.1 \pm 1)\,\%\mathrm{rh}\,@T = 298\,\mathrm{K}$; $(81 \pm 2)\,\%\mathrm{rh}\,@\,283\,\mathrm{K}$; $(82{\pm}2)\,\%\mathrm{rh}\,@\,273\,\mathrm{K}$; $(82{\pm}3)\,\%\mathrm{rh}\,@\,263\,\mathrm{K}$; $(83{\pm}4)\,\%\mathrm{rh}\,@\,254\,\mathrm{K}$. Similarly, also the temperature coefficient of the efflorescence humidity was found to be negative, $\mathrm{d\,ERH}/\mathrm{d}T < 0$, at least in the temperature range $253-298\,\mathrm{K}$ with the following pairs of variates: $\mathrm{ERH} = (33 \pm 2)\,\%\mathrm{rh}\,@T = 298\,\mathrm{K}$; $(37 \pm 3)\,\%\mathrm{rh}\,@\,273\,\mathrm{K}$; $(42{\pm}4)\,\%\mathrm{rh}\,@\,253\,\mathrm{K}$; $(41{\pm}6)\,\%\mathrm{rh}\,@\,238\,\mathrm{K}$. A detailed theoretical evaluation of the temperature dependence of deliquescence and efflorescence and additional references can be found in Khvorostyanov and Curry (2014, Chapter 11 therein). The theory evaluated in the present paper does not contain any restrictions concerning the applicable temperature range. However, the challenge in application of the model is the providence of the required experimentally determined thermophysical input properties in the extended temperature range, especially in the supercooled regime. For the surface tensions of pure water, aqueous sodium chloride, and ammonium sulphate solutions there are appropriate correlation functions available (e.g., Seinfeld and Pandis 2006, Section 17.1.3 therein, Kalová and Mares 2012, Khvorostyanov and Curry 2014, Section 4.4.5 therein). The temperature dependence of the solubility for different inorganic salts can be found in Seinfeld and Pandis (2006, Section 10.2.1 therein), however, without explicit information on the allowed temperature range for application. Based on the Khvorostyanov–Curry (KC) model of deliquescent-heterogeneous freezing Khvorostyanov and Curry (2014, Section 11.4.2, Eq. (11.4.9), Fig. 11.2 therein) derived a new equation for the temperature dependence of the solubility of inorganic salts. The authors demonstrated the applicability of this model to aqueous sodium chloride and ammonium sulphate solutions in the temperature range $-40\,^\circ\mathrm{C} \leq \vartheta \leq 100\,^\circ\mathrm{C}$. In addition, the temperature dependence of the relative deviation of the KC model predictions from measured data has been quantified. Similarly, Khvorostyanov and Curry (2014, Section 11.4.3, Fig. 11.3 therein) derived an expression for the temperature dependence of the water activity in the limiting case of an ideal solution. For an aqueous ammonium sulphate solution the authors found very good agreement of the KC predictions with measured water activities in the temperature range $240\,\mathrm{K} \leq T \leq 370\,\mathrm{K}$. Importantly, the empirical characterisation and theoretical description of several water–salt systems published in previous studies such as those performed by Khvorostyanov and Curry (2014, Chapter 11, Figs. 11.1–11.4, see also references therein) can be used as reference data for systematic model-to-model intercomparison studies. In the limiting case of 'thick' solution films (vanishing disjoining

pressure), all simulations should agree for the same thermophysical input data. The main focus of the present model is on the description of thin-film systems, allowing the treatment of size effects of deliquescence and efflorescence, which are very important in the early stages of water uptake. Additional empirical and modelling data for the temperature-dependence of deliquescence and effloresecene in the limiting case of bulk systems can be used, e.g., to formulate additional mathematical constraints for the determination of hygroscopic and interface properties of ambient aerosol systems (see item 4). Further efforts in this direction should also aim at the demonstation, that different theoretical approaches to solve identical questions of interest (the same chemical composition and size of the aerosol system under the same thermohumid conditions) are physically reconcilable and consistent among each other.

2. *Thermophysical properties:* The solute supersaturation, $S^{(\alpha)} = a_{\mathrm{s,effl}}/a_{\mathrm{s,sat}}$, defined as the ratio of the salt activity at efflorescence, $a_{\mathrm{s,effl}}$, to the saturated activity at deliquescence, $a_{\mathrm{s,sat}}$, has been reported to exceed values of $20-30$ (depending on the inorganic salt) at the point of homogeneous efflorescence (Khvorostyanov and Curry 2014, pp. 548, 551 therein). Such high values pose a great challenge regarding the molality range of experiments to determine the solution viscosity, which enters the calculus via the activiation energy in the kinetic prefactor of the homogeneous efflorescence rate. For example, available table values for the viscosity of an aqueous sodium chloride solution are usually restricted to molalities not exceeding the saturation molality, $m \leq m_{\mathrm{s,sat}} = 6\,\mathrm{mol\,kg^{-1}}$ (see SM/Section S.3.5). Hence, the application of these table values to highly supersaturated states, occuring at the point of homogeneous efflorescence, is necessarily based on extrapolation with unknown uncertainty.
   In the present study, the determination of the solvent and solute activitites is based on the Ally–Braunstein statistical mechanics theory of multilayer adsorption for highly concentrated solutions in combination with an empirical solvent activity as function of molality (see SM/Section S.3.1). For the solvent activity a molality dependence has been used, the validity of which is restricted to $T = 298\,\mathrm{K}$. Hence, application of the calculus to the aqueous sodium chloride system at temperatures $T \neq 298\,\mathrm{K}$ requires corresponding revision of the solvent activity formula or at least quantification of the uncertainty of extrapolated activities and the associated model sensitivity.
   For the solubility of the sodium chloride solute a temperature-dependent bulk value has been used (see SM/Section S.3.4). For the time being nothing conclusive can be said about a possible size-dependence of this quantity and the model sensitivity against such dependence.
   Sources of experimental data and formulations of thermophysical properties for application of the theory to supercooled states down to the eutectic temperature are the IAPWS pool of thermophysical properties (`http://www.iapws.org/`), the new Thermodynamic Equation Of Seawater-2010 (TEOS-10, `http://www.teos-10.org/`), and the FREZCHEM database (`http://www.dri.edu/frezchem`).

3. *Refinement of the theory:* The current theory is based on the assumption that, among others, the vapour/solution surface tension is independent of the solution concentration. In reality, the surface tension of an aqueous solution depends on the solution molality (e.g., Seinfeld and Pandis 2006, Section 17.1.3 therein, Khvorostyanov and Curry 2014, Section 4.4.5 therein). The uncertainty originating from the neglect of the molality dependence of the solution surface tension is needed to be quantified. However, the consideration of the molality dependence of the surface tension requires a rederivation of the whole calculus and will lead to the appearance of additional terms in the generalised thermodynamic equilibrium equations.
   Another challenge is the generalisation of the theory to a multicomponent three-phases system, e.g., for application to describe formation of secondary organic aerosols in the film phase.

4. *Other binary aqueous solutions of unary salts and organo-salt mixtures:* The variety of atmospherically relevant aerosols containing either pure inorganic salts or mixtures of inorganic salts with organic compounds is very large, whereat mixed states of hygroscopic particles have to be considered as the atmospheric normal case. In view of high importance of water uptake by such systems for cloud droplet activation, there are multitudinous studies on the deliquescence and efflorescence (e.g., Cziczo and Abbatt 1999, Xu et al. 1998, Oatis et al. 1998, Khvorostyanov and Curry 2014), and hygroscopic growth of 'pure' and 'mixed' particle systems (e.g., Michel Flores et al. 2012, Sjogren et al. 2007, Stock et al. 2011). The present theory allows the simulation of water adsorption of unary salts from the first monolayer and the reverse process, water desorption until homogeneous efflorescence, provided the required thermophysical properties and interface parameters are available. As emphasised previously, a special challenge is the determination of the disjoining pressure. Employing measured DRH and ERH values, it was demonstrated here how these interface parameters can be estimated. With retainment of the basic assumptions of the present theory, this monocomponent approach can be extended to mixed hygroscopic particles by consideration of the Zdanovskii–Stokes–Robinson (ZSR) relation for the growth factor of mixtures (e.g., Michel Flores et al. 2012, Sjogren et al. 2007, Stokes and Robinson 1966, Stock et al. 2011), which provides an additional constraint for the estimation of interface parameters for mixed particles within the framework of the present approach. The combination of the current theory with the ZSR relation opens a semi-empirical way to derive interface parameters for atmospherically relevant mixed aerosol systems from both measured volume fractions of the pure components in the mixture (e.g., using Aerosol Mass Spectrometer) and hygroscopic growth factors of these mixed systems (using Hygroscopic Tandem Differential Mobility Analyser) (personal communication by L. Poulain, TROPOS Leipzig, December 19, 2014). In turn, provided that the relevant interface properties are available with sufficient accuracy, the present model can be used to predict the size- and temperature-dependent hygroscopic growth factors of mixed particles.

5. *Application in aerosoldynamical and microphysical models:* Provided all necessary thermophysical and interfacial properties of the chemical substances of interest can be acquired, the application of the present calculus in a bin-resolved aerosoldy-

namical or microphysical model requires (a) the implementation of an efficient numerical solver for the solution of the coupled transcendental equations describing the humidity growth factor and the chemical composition of the aerosol system as function of both temperature and relative humidity, or alternatively, (b) the precalculation of look-up-tables with the corresponding values (eventually complemented by an effective interpolation routine).
In order to decide which of the multiple (and equitable) thermodynamic states (size and composition) a certain particle will adopt under specific thermohumid conditions during its lifetime, one must not only know the actual temperature and humidity but also their history, i.e., the 'memory' of the aerosol system must be carried along the simulation, notwithstanding that only equilibrium states are considered.
In context with the specification of the time resolution of a host model which incorporates the calculus an analysis of the characteristic time scales to establish the Gibbs–Kelvin–Köhler and Ostwald–Freundlich equilibria for the specific systems of interest is required."

6 Other changes in the manuscript

1. P5, L13, insertion of an additional reference:
   Khvorostyanov and Curry (2014)

2. P25, L8, addition of paragraph:
   These three points represent the three possible (and equitable) thermodynamic states the aerosol system can adopt at $(T, \mathrm{RH}){=}(298\,\mathrm{K}, 78\,\%\mathrm{rh})$. The first minimum at about $(R'_\mathrm{N}, R){\approx}(4.5\,\mathrm{nm}, 6.5\,\mathrm{nm})$ corresponds to the existence of a thermodynamically stable heterogeneous droplet, the second minimum at about $(R'_\mathrm{N}, R) \approx (0\,\mathrm{nm}, 8.8\,\mathrm{nm})$ to a thermodynamically stable homogeneous solution droplet, and the saddle point at about $(R'_\mathrm{N}, R){\approx}(3\,\mathrm{nm}, 8.8\,\mathrm{nm})$ to the existence of conditionally stable heterogeneous droplet. The latter is thermodynamically stable against small fluctuations of R'_N and R along a trajectory across the 'valley', but thermodynamically unstable against small fluctuations of R'_N and R along a trajectory across the 'ridge'. For detailed analysis of this conditional stability the reader is referred to Shchekin et al. (2013).

3. Addition to caption of Fig. 8:
   One can see two minima in the formation work, which are separated by a saddle point. These three characteristic points represent the three equitable thermodynamic states the aerosol systems can adopt at $(T, \mathrm{RH}){=}(298\,\mathrm{K}, 78\,\%\mathrm{rh})$. The first minimum at about $(R'_\mathrm{N}, R){\approx}(4.5\,\mathrm{nm}, 6.5\,\mathrm{nm})$ corresponds to the existence of a thermodynamically stable heterogeneous droplet, the second minimum at about $(R'_\mathrm{N}, R){\approx}(0\,\mathrm{nm}, 8.8\,\mathrm{nm})$ to a thermodynamically stable homogeneous solution droplet, and the saddle point at about $(R'_\mathrm{N}, R){\approx}(3\,\mathrm{nm}, 8.8\,\mathrm{nm})$ to the existence of conditionally stable heterogeneous droplet.

4. P25, L11, new: The derivation of the calculus relies on the assumption ...

5. P26 (L14, L16, L22, L23); P27 (L12, L17), Table 1, Figs. 10–12: Symbols (old) $\sigma^{(\alpha\gamma)}$ and $\sigma^{(\beta\gamma)}$, respectively, were replaced with new symbols $\sigma_{\infty}^{(\alpha\gamma)}$ and $\sigma_{\infty}^{(\beta\gamma)}$, respectively.
6. Item 7 of the conclusion has been moved to the new section "Remaining questions".
7. The referees are mentioned in the acknowledgement.
8. The reference to Bontjer (2006) has been updated (last access 06 February 2015) in the reference list.
9. Figures 2,3, 11, 12 have been revised by replacing the labels of their ordinates.
10. Changes in the Supplementary Material:
    (a) P7, missing word: "... is the surface tension ..."
    (b) P14, Eq. (S-43): placing a comma into the equation array
    (c) P36, Fig. 6: In this figure symbol sizes and thicknesses have been enhanced.
    (d) P39, item1: setting a bracket: $\sigma_{\infty}^{(\alpha\beta)}=(0.083\pm0.002)\,\mathrm{J\,m^{-2}}$

7 Final remarks

We are open for any further comments, discussions, or additional requests concerning the revised and changed parts of the paper. Editor and referees are expected to bring forward corresponding wishes.

References

Anonymous Referee: Interactive comment (RC C9360) on "Determination of interfacial parameters of a soluble particle in a nonideal solution from measured deliquescence and efflorescence humidities" by O. Hellmuth and A. K. Shchekin, Atmos. Chem. Phys. Discuss., 14, C9360–C9364, `http://www.atmos-chem-phys-discuss.net/14/C9360/2014/acpd-14-C9360-2014.pdf`, 2014.

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