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 the Editor

March 12, 2015

1 General response

We thank the editor very much for the fair and careful treatment of our manuscript and for the time he took for revision and editorial work associated therewith.

2 Reply to the technical comments of the editor from March 04, 2105

- Footnote 3. Please use other than Wikipedia for the reference to the eutectic temperature.

  Reply: Giving reference to more authoritative sources the footnote has been revised as follows:

  The eutecticum or “eutectic mixture” of chemical compounds or elements denotes the solidification products of homogeneous mixed melts at that chemical composition at which the melting point is lower than at any other chemical composition made up of the same ingredients (Wolf 1959, p. 763 therein). Similarly, Atkins (1994, pp. 254–255 therein) wrote that a liquid with eutectic composition freezes at a single temperature, without previously depositing solid A or B. A solid with the eutectic composition melts, without change of composition, at the lowest temperature of any mixture (see also Wedler 2004, pp. 364–365 therein). The composition of the eutecticum is known as the eutectic composition and the temperature at which it solidifies is known as the eutectic temperature. The name eutectic composition comes from Greek words for “easily melted” (Atkins 1994, p. 254 therein). Water and sodium chloride form a eutectic mixture. The eutectic temperature of aqueous sodium chloride solution amounts $\vartheta_{\mathrm{E}} = -21.2\,^{\circ}\mathrm{C}$, the eutectic mass fraction of solute 0.2242 (Brdička 1965, p. 513 therein).

- Section 4.1. Please add a paragraph change: Secondly, we determined...

  Reply: A paragraph change has been inserted on page 23, line 7.

- Move the sentence describing Figure 4 to the beginning of the paragraph starting with "The efflorescence radius, ".

  Reply: The sentence “Figure 4 displays the dependence of the solute ...” has been moved to the beginning of the embedding paragraph (i.e., on page 24, lines 23–30).

- page 25, line 15, Please start a paragraph at "Upon dehumidification..."

  Reply: A new paragraph starting with “Upon dehumidification ...” has been inserted on page 26 (!), line 15.

- Section 4.2. Please add a reference to Figure 9 already to the beginning of the paragraph.

  Reply: Now, Section 4.2.1 starts with the following sentence: ...

  “Figure 9, in comparison with Fig. 7, shows the influence of the solution surface tension on the hygroscopic growth factor.

  The derivation of the calculus relies on the assumption that . . ..”

- Section 4.2.3 Please remove comma before the word that in line 18.

  Reply: On page 29, line 18 the comma prior the word “that” has been removed.

- Section 5, point 3: Please also mention that the results deviate from Russell and Ming (2002).

  Reply: Regarding the comparison the our results with that obtained by Russell and Ming (2002) we have added a new item in the conclusions:

  Mirabel et al. (2000) proposed a scenario of prompt deliquescence of particles relying on the assumption that the particle being dry at the point of deliquescence. However, this assumption does not hold for crystalline sodium chloride, which adsorbs several monolayers of water prior to the onset of deliquescence. ‘Predeliquescent’ water adsorption is considered a significant effect especially for particles smaller than 400 nm. Russell and Ming (2002, p. 311 and references therein) argued that “for deliquescence points at higher relative humidities, the Gibbs free energy of the phase change should be predicted by difference of the dissolved particle compared to the wetted particle rather than to the dry crystal. The difficulty of this approach is that it requires describing the free energy of the adsorbed water layer and its interface, since the surface energy of a thin adsorbed layer on a crystal of unknown geometry is poorly constrained.” As a further challenge Russell and Ming (2002) stated the adequate description of the surface energy of the interior and exterior interfaces of the spherical shell of water enveloping the dry crystal. The authors quantified the potential impact of variation of surface tension for finite-molecule situations by consideration of size-dependent surface tension using simple Tolman length model. The generalised theoretical approach proposed in the present study considers the physical requirements formulated by Russell and Ming (2002).

In their Figs. 4, 5, and 10–12 Russell and Ming (2002) presented predicted hygroscopic growth factors of nanometric NaCl particles for their 'coated' and 'uncoated' deliquescence models, which at first glance differ from our predictions depicted in Figs. 7 and 9. Depending on the chosen model, Russell and Ming (2002, Fig. 4 for 15 nm dry diameter NaCl) distinguished several equilibrium regimes. For their 'coated particle model' the authors found stable and metastable equilibria for the wet particle, stable and unstable equilibria for the dry particle, unstable equilibria for partially wet particles, and deliquescence. For the 'uncoated particle model', the only difference in predicted equilibria is the onset of deliquescence at a lower relative humidity. Despite of the differences in the theoretical approaches and in the determination of the thermophysical properties, both approaches, i.e., that of Russell and Ming (2002) and the present one, describe the essential physical features of deliquescence of nanometric sodium chloride particles in agreement with available empirical findings. However, there are remarkable differences in the description of the heterogeneous nucleation pathway, i.e., in the hygroscopic growth of the partially wet particle. As the disjoining pressure is a continuous function of the film thickness, the predicted hygroscopic growth of the heterogeneous particle as shown in Figs. 7 and 9 reveals a smooth transition from the dry particle to the deliquescent point (stable equilibrium) and from the deliquescent point to the efflorescence point (conditionally stable equilibrium). In the approach of Russell and Ming (2002) these transitions show a more steplike behaviour. As the results of Russell and Ming (2002) and the ones presented here are both based on theoretical predictions, it is not possible to draw final conclusions regarding the predictive power of the employed theories with respect to the transitional behaviour in the heterogeneous regime. Nevertheless, both approaches appear to be reconcilable with available empirical findings on the hygroscopic growth of nanometric sodium chloride particles, i.e., available laboratory data cannot rule out one or the other prediction so far.

- Page 31, line 10-11: The object under study is phase transitions in nanoparticles. They are suspended in environmental conditions that can be considered macroscopic. But without the detailed measurements of the nanoparticle size (microscopic) at different conditions, one cannot determine the interface parameters. I suggest refrasing.

  Reply: We picked up this thought by adding a new item on page 31 as follows:

  The question of interest of the present study was the theoretical description of phase transitions of soluble nanoparticles. These particles are suspended in ambient air, which is thermodynamically controlled by macroscopic parameters, namely temperature and relative humidity. The empirical size dependence of deliquescence and efflorescence humidities on nanometric scales underlying the present approach underpins the great importance of high-accuracy measurements of nanometric particles under well-controlled thermohumid conditions. Such technically elaborate measurements are a prerequiste for (i) the estimation of interface parameters, (ii) for further enhancement of theoretical concepts to describe such systems, and (iii) for the assessment of the predicitive power of available models especially in the heterogeneous nucleation regime.

- Section 6. Please add few paragraph breaks for easier reading; page 33, line 15; line 23; line 34; page 34, line 13; page 34, in section 2. Thermophysical properties: . . . the calculus via the activation energy . . .

  Reply: Yes, we see. Thanks for that hint. Paragraph breaks have been inserted now.

- Figure 1: Please add a reference to Biskos et al. to the figure caption.

  Reply: A reference to Biskos et al. (2006) has been added to the caption of Fig. 1.

- Figure 6: Please remove text "Ostwald-Freundlich equilibrium" and move it to the figure caption.

  Reply: The figure title “Ostwald-Freundlich equilibrium” has been removed to the figure caption.

- Figure 7 & 9: Distinguish the two heterogeneous nucleation pathways in Figure legend.

  Reply: The two heterogeneous nucleatioin pathways have been distinguished in the caption of figure 7 correspondingly. On page 26, lines 25-30 have been updated according to changed annotation.

- Figure 10: Please clarify legend. Figures are left and right.

  Reply: Thanks. Legend has been clarified correspondingly.

- Figure 11: & 12 Add σ_∞ corresponding to two curves in figure legend.

  Reply: The annotations $\sigma_\infty^{(\alpha\beta)} = 0.083\,\mathrm{J\,m^{-2}}$ and $\sigma_\infty^{(\alpha\beta)} = 0.072\,\mathrm{J\,m^{-2}}$ have been added to distinguish graphs 1 and 2 correspondingly.

- Further changes:
  - Addition of a reference to Ally and Braunstein (1998) on page 19, line 14.
  - On page 26 , line 32: replacement of “thermohygric” by “thermohumid”.
  - Update of acknowledgements.

References

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