Interactive comment on “The vapor pressures and activities of dicarboxylic acids reconsidered: the impact of the physical state of the aerosol” by V. Soonsin et al.

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Comments to Referee #2

The authors would like to sincerely thank anonymous referee #2 for his/her constructive comments. We have addressed the referee's concerns point-by-point as shown in the following. Our comments are given in italic.

General comments

Although the dicarboxylic acids have received considerable attention, the paper is important in the light of recent interest in glassy aerosols. It will also provide useful data for constraining activity models. However strong statements about the physical state observed in previous measurements are not backed up by the experimental evidence and other reasons are far more likely to be the cause of discrepancies. These must be changed before it can be accepted for publication and, whilst straightforward to address, constitute the grounds for the important major revisions I have requested. There are also a few additional considerations for determining the vapour pressures which I feel should be considered.

We believe to have strong evidence for the influence of physical state for our own measurements. Of course this allows only indirect conclusion on the physical state of previous measurements. We address the reviewer’s concern regarding this issue in detail below.

The physical state: The authors state that previous measurements may be compromised by amorphous and polycrystalline material. The work of Bilde, Riberio da Silva, Booth and Cappa all show the odd-even effect (the varying of certain solids state properties, e.g. VP, Tm delH(fus), with carbon chain parity), as this arises from the crystal structure its not clear how they would be anything other than crystalline solids. Also the Riberio da Silva malonic acid measurements cut across the onset temperature of one of the crystalline transition but still show a straight line ( lnP vs. 1/T ). The acid samples were recrystalised and dried in vacuo at 360K for several hours which would have removed any more volatile amorphous fractions (if they were present). The glutaric acid measurement is above one of the transition temperatures, but those of Bilde, Booth and Riipinen are (far) below it but the measurements still agree. This would suggest that either the polymorphic forms don’t affect the vapour pressure, and/or the measurements made were of the entirely crystalline form.

As the reviewer states, we can offer as explanation for the discrepancies between our
measurements and some literature data only, that some measurement of the vapor pressure of the solid acids reported in the literature, may be compromised by amorphous and polycrystalline material. This is the explanation which seems to be consistent with our own measurements of the solids. Let us repeat this discussion in detail: Our data for the solids also show the odd-even-effect. However, it is possible to observe an odd-even-effect as well, for example in TDMA data, if for some of the acids the aerosol particles effloresce during the experiment, while not in the case of all acids. Hence, unintentionally comparing vapor pressures of solid and liquid particles based on the assumption of a common physical state.

For malonic acid no efflorescence relative humidities have been reported in the literature simply because aqueous malonic acid particles do not effloresce in aerosol experiments. For glutaric acid the efflorescence relative humidities for micron sized particles reported in the literature range between 18% to 25% (Zardini et al., 2008) and 29% to 33% (Peng et al., 2001). In this study we even observed micron sized particles which did not effloresce at relative humidities as low as 5%. Thus it is at least conceivable that the particles remained in the metastable liquid state in the TDMA measurements of Bilde et al. (2003). Under this assumption our data agree extremely well with those of Bilde et al. for the supercooled melt as well as with the ones of subsequent publications of the same group (Riipinen et al. 2007).


The Cappa et al., (2007) data of the solids agree within error with our data of the saturated solutions for glutaric and succinic acid (if we allow for an error in the Cappa et al. data consistent with the one they state for glutaric acid). Since thermodynamics requires the solid to have the same vapor pressure as the saturated solution this again supports our data for the supercooled melt vapor pressures.

In addition our vapor pressures of the solids agree within error with those of the saturated solutions proofing the internal consistency of our measurements.

Clearly, the data of Booth et al., (2009) do not agree with our data but are substantially higher. The vapor pressures measured by Ribeiro da Silva et al., (1999) for malonic and glutaric are again substantially higher than ours. Also, it is evident from our Fig. 5 and Table 3 that the data of Ribeiro da Silva et al., (1999) do not agree with the ones of Salo et al.,( 2010), Bilde et al., (2003), and Cappa et al., (2007). Interestingly the Ribeiro da Silva et al., (2001) data for solid succinic acid are close to the ones of our saturated solution. (We include the data of Ribeiro da Silva et al., (2001) in our revised Fig. 10. Note that this is the acid with the lowest solubility which may lead to a “higher crystallinity” crystallization upon drying.

Also note that data for vapor pressures of the solid acids available in the literature scatter much stronger between different setups when compared to the scatter of the vapor pressures measured in the liquid. This again may be taken as an indication that even upon drying at high temperatures the solids are not all the same but deviate from a perfect crystalline structure.

In summary we are convinced that our data provide convincing indication that measurements of the vapor pressures of the solid short chain dicarboxylic acids may be compromised by amorphous material or strong defects in their crystalline structure.
Therefore we recommend using liquid phase measurements for determination of vapor pressures.

**Activity Model:** The choice of activity model is an important factor in determining the vapour pressure using evaporation-type measurements. UNIFAC is known to be problematic for certain small molecules so use the authors use UNIFAC-Peng, but the Peng parameters are fitted to electrodynamic balance measurements so it seems somewhat circular as any systematic errors from EDB VP measurements may also affected the activity coefficients determinations. Koponen et al. explored the sensitivity of their evaporation based measurements and found that alternating between UNIFAC Dortmund and Van Laar activity models caused a difference in vapour pressures of two orders of magnitude for malonic acid, a sensitivity which decreases significantly as the chain length gets longer. This would suggest that the sensitivity of oxalic acid measurements to the choice of activity model even greater, and is far more likely to be the cause of most discrepancies between measurements. The authors should do a sensitivity comparison for oxalic and malonic acids with some other activity models, e.g. Van’t Hoff, AIOMFAC, UNIFAC-Dortmund.

We agree with the reviewer that applying wrong activities of the acids in the analysis for obtaining vapor pressures from evaporation rates of aqueous droplets can lead to substantial errors in the obtained vapor pressure. For this very reason we derived the acid activities directly from our measurements prior to the analysis of the vapor pressures. This is explained in detail in Section 3.1. We include the van Laar parameterization and UNIFAC Dortmund parameterization in the revised version of Fig. 2 of the manuscript which is copied as Fig. 1 of this comment. (Details of this figure: Data at T=290.9 K; T=281.3 K; T=303.2 K: Dotted line: Raoult’s law; Olive line: UNIFAC Dortmund parameterization taken from Koponen et al. (2007); Dark cyan line: van Laar parameterization by Koponen et al. (2007); Green line: UNIFAC parameterization by Ming and Russell (2002); Blue line: parameterization by Clegg and Seinfeld (2006a); Red line: UNIFAC parameterization by Peng et al. (2001). Mole fractions are on the basis of undissociated glutaric acid.) We intend to include both parameterizations also in the figures of malonic and succinic acids.

Clearly, our data agree best with the UNIFAC Peng and the Clegg and Seinfeld parameterization. UNIFAC Dortmund and the van Laar parameterization of Koponen et al. do not agree with the data. If we use the Ming and Russell (2002) parameterization (even though it does not agree with our data) instead of the UNIFAC Peng it leads to a supercooled vapor pressure of $p^\circ_{L}=(7.3\pm2.2)\times10^{-4}$ Pa (Ming & Russell), instead of $p^\circ_{L}=(9.3\pm2.7)\times10^{-4}$ Pa (UNIFAC-Peng). The difference between both is still within the error. We conclude that our analysis allow to constrain the error due to uncertainties of the acid’s activities to a range negligible to all the other errors.

**Solid state:** The authors state that the edb allows unambiguous identification of solids via the monitoring of the angular scattering pattern. What would happen if a solid particle was spherical, could this be distinguished?

The angular scattering pattern allows only detecting deviations from spherical symmetry, however it is extremely sensitive in detecting any deviation. From our experience any crystalline particle will be detected easily and also mixed phase particles (solid inclusion in an aqueous droplet), see Braun and Krieger 2001. Amorphous solids, e.g. glassy particles, retain their spherical symmetry. However, the glass transition temperatures of short chain dicarboxylic acids are below the temperature range of our measurements.

**Saturated solution:** Why do the saturated solution vapour pressures show the odd-even dependence? I would have thought they’d be closer to the supercooled melt VP?
Differences between sub-cooled & solid: Other Workers, e.g. Booth & Koponen & Riipinen use the Prausnitz equation to correct between sub-cooled & solid. It would be interesting to compare the differences measured here with the calculated ones from thermochemical data. I think it will provide a useful check on the validity of using the Prausnitz eqn, and the thermochemical data used.

If the vapor pressures of the solid acids show an odd-even alternation the vapor pressures of the corresponding saturated solution have to show the same dependence because thermodynamics requires the vapor pressure of the crystalline stable solid to be the same as the one of the saturated solution. In our approach we need the solubilities of the acids in order to interpolate our vapor pressure measurements to the concentrations of the saturated solution. As explained in the text those solubilities are known to high accuracy. Alternatively we may use thermophysical data to calculate the vapor pressure of the solid from supercooled melt data and those rely on the accuracy of the enthalpy of formation at the melting point and the change in heat capacity upon melting. Taking the thermophysical data from Koponen et al. (2007) and Eqs. (11-13) of Prausnitz et al. (Prausnitz, J. M.; Lichtenhaler, R. N.; de Azevedo, E. G. Molecular thermodynamics of fluid phase equilibria, 3rd ed.; Prentice Hall, Inc.: Englewood Cliffs, NJ, 1999.) or Eq. (1) of Cappa et al. (2008) and his thermophysical data, yields:

<table>
<thead>
<tr>
<th></th>
<th>Malonic</th>
<th>Succinic</th>
<th>Glutaric</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p^{L}/p^{S}$ (observed)</td>
<td>8.1</td>
<td>113</td>
<td>16.6</td>
</tr>
<tr>
<td>$p^{L}/p^{S}$ (Prausnitz)</td>
<td>18.3</td>
<td>39.0</td>
<td>3.8</td>
</tr>
<tr>
<td>$p^{L}/p^{S}$ (Cappa)</td>
<td>12.2</td>
<td>114</td>
<td>4.7</td>
</tr>
</tbody>
</table>

Since there are no data available neither for the triple point temperature of the acids nor for the enthalpy of fusion at the triple point temperature we used the usual practice of substituting them by the normal melting point temperature and the enthalpy at the melting temperature. Since the ratio of the pressures is an exponential function of the scaled enthalpy and the heat capacity upon melting it depends critically on the corresponding values. This can be seen by comparing the Cappa et al. factor with the one from the Prausnitz equation and the Koponen et al. data. We cannot explain the larger discrepancy for glutaric acid, but suspect it relates to the approximations involved for the acid with the lowest melting point in our study.

**Kinetics:** Water has been shown to bind much more strongly on defect sites of crystals (Laux et al; Davies and Cox). What would the implication be of the observed loss of water from your crystal be? i.e. can there be in effect two loss rates of water, one from a defect site and one from a non defect site? Also, do you need to assume an uptake coefficient or accommodation coefficient.

This is an interesting suggestion. It could be one explanation for what we see in our evaporation rate for the solids (Fig. 4 and Fig.9). However, since we do not have any information about the detailed morphology or defect structure or liquid inclusions in our solid particle we can only speculate about this at present. This is another important point raised by the reviewer. In our evaluation of the evaporation rates we assume the accommodation coefficient to be equal to one. Since our particles are of a size of typically several micrometers and we are in the continuum regime, that assumption does not influence much our derived pressures as long as the accommodation coefficient is larger than about 0.05, see figure below. It shows the ratio of modified gas phase diffusion constant versus accommodation coefficient according to Pruppacher and Klett (Microphysics of Clouds and Precipitation, 2nd edition, Kluwer, Dordrecht, 1997, pp. 904, Eqs. (13-14)). For the aqueous solutions the accommodation coefficient is most likely larger than 0.1. Since we observe consistent vapor pressures for the solid acids when compared to the saturated solutions this may be taken as an indication that also the accommodation coefficient of the solids are of this order of magnitude. See Fig. 2
of this comment.

Minor comments.

- Cappa et al., have also measured malonic acid (see ref) P298 solid 2.2x10^-4 Pa.

We have added P298(solid) of malonic acid from Cappa et al., 2008 as suggested by the referee.

- There is a paper recently out that is probably worth comparing with, Pope et al., EDB measurements and optical tweezers.

The Pope et al., 2010 will be included in the revised version.

- p20528 ln14 proves rather than proofs

We have changed “proofs” to “proves” as suggested by the referee.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 20515, 2010.

Fig. 1. Glutaric acid activity versus mole fraction of glutaric acid. For details see text.
Fig. 2. Ratio of modified gas phase diffusion constant to gas phase diffusion constant versus accommodation coefficient for particles with different radii.