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Interactive comment on “Prediction of cloud condensation nuclei activity for organic compounds using functional group contribution methods” by M. D. Petters et al.

Anonymous Referee #1

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This work presents a comparison between predicted and measured hygroscopicity, presented as CCN activation potential, for a set of important atmospheric functionalities. The comparison between the measured and predicted kappa values, in itself, is an interesting result and should be published at some level and could equally appear in ACP. My general feeling is that the tone regarding the novelty, and evaluation, of the model basis rather than the application needs to be addressed slightly before accepting for publication in GMD. I raise specific points in the following, with appropriate references, which I believe shouldnt require much effort and ultimately add to the presentation of the work.

First, on that general note, in the abstract there is the following text: ‘The model com-
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bines Kohler theory with semi-empirical group contribution methods.’ I would suggest, ‘Following previous methodologies in the literature, we test the ability of group contribution methods in Kohler theory to...’ but of course then add a statement that portrays the attempt to include LLE - ‘however, in our approach, we also attempt to account for LLE using’

Following this, in the introduction the authors state that ‘To obtain a prognostic understanding of the contribution of the organic fraction to indirect aerosol forcing in future climates, models need improved schemes that map simulated organic aerosol composition to hygroscopicity and CCN activity.’ I completely agree. However mapping this functionality from detailed chemical mechanisms is not easy. Group contribution methods present the ‘keys’ to performing this mapping, but selecting those keys from thousands to millions of compounds falls within the remit of chemoinformatics. For the compounds presented in this study, we are able to check the coverage provided by the selected UNIFAC groups. I would suggest qualifying this study with a statement similar to: ‘In this study, we test the ability of manually applying such methodologies to ..’

There is also the statement: ‘This work addresses the need for a model that can predict the contribution of a compound with known chemical structure to the CCN activity of a particle of known size. The proposed model uses the UNIFAC equations..’ On first glance, this sounds as if the approach of UNIFAC within Kohler theory is a new concept. There have been thermodynamic equilibrium models developed around group-contribution methods specifically due to the demand for enabling predictions over the wide range of atmospheric functionalities. This should be clear in the paper.

Section 2.2 Molar Volume

Barley et al (2012) reviewed the performance of various methods for predicting molar volume. What is the relative sensitivity of errors in molar volume to derived k using this method?

Barley, M. H., D. O. Topping and G. McFiggans, The Critical Assessment of Liquid

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Density Estimation Methods for Multifunctional Organic Compounds, J Phys Chem A 2013 Apr 15;117(16):3428-41. Epub 2013 Apr 15.

Section 2.4 Phase equilibrium

The authors are correct in that phase separation can occur, and there are a number of key papers in the literature focusing on the mechanics/numerics of treating this process alone. I find this section a little lacking in detail as it currently stands. For binary systems, it is quite easy to model. A simple root finding method can be used to assess the point of equal chemical potentials and then a calculation of the Gibbs energy used to determine the most stable state. The method proposed here needs to be proven to work from a select number of binary systems that exist in the literature, particularly as this process is then embedded within a Kohler curve designed for multicomponent solutions. For example, how does this perform for systems presented in Zuend et al 2010?

A. Zuend, C. Marcolli, T. Peter and J. H. Seinfeld, Atmos. Chem. Phys., 2010, 10, 7795– 7820.

Given that study used AIOMFAC, which for organic-water systems gives the same results as UNIFAC, these results should be reproduceable. By presenting this information, and also presenting the phase boundaries for the systems presented in the paper, even as supplementary material, one gets a feel for the importance of including, or not, LLE in these calculations.

I appreciate the focus of the paper is on organic systems, but what happens when inorganic ions are included in this? UNIFAC can account for ions, but without any organic-inorganic interactions beyond the short-range forces represented within the UNIFAC framework. The challenge when including inorganic-organic interactions in an LLE model becomes a numerical one since molality based terms can induce strongly deviating activity coefficients that can force any 'root finding' method to fail.

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Is the method for including LLE assumed to apply for multicomponent mixtures? Parameterised forms of LLE for multicomponent mixtures exist, based loosely on a collaborative dissolution approach or simply on O:C ratios, as benchmarked against more complex methods:

Song, M., Marcolli, C., Krieger, U. K., Zuend, A., and Peter, T.: Liquid-liquid phase separation and morphology of internally mixed dicarboxylic acids/ammonium sulfate/water particles, *Atmos. Chem. Phys.*, 12, 2691-2712, doi:10.5194/acp-12-2691-2012, 2012.

Topping, D, Barley, M and MCFiggans G: Including phase separation in a unified model to calculate partitioning of vapours to mixed inorganic–organic aerosol particles. *Faraday Discuss.*, 2013, 165, 273-288

Could a similar multicomponent or parameterised approach be built into your model? A simple ‘additive’ approach, as per combining kappa values, would not be guaranteed to work. I’m not suggesting the paper needs a full evaluation of multicomponent LLE, as experimental data would be scarce anyway. Nonetheless, there is currently no discussion as to any extension to mixed systems other than a statement at the end of the paper which suggests just combining k values in a mixing rule.

It is often interesting to assess errors associated with ‘forcing’ a model into specific states. For example, since an account for LLE is attempted here, why not include gas-particle partitioning depending on the Gibbs energy profile of each possible state? Is it more or less likely that gas-particle partitioning of organic semi-volatiles would represent a shift towards the most stable state under the same conditions? Zuend et al 2012 looked at the effect on gas-particle partitioning when forcing a one liquid state or allowing LLE to occur:

Zuend, A. and Seinfeld, J. H.: Modeling the gas-particle partitioning of secondary organic aerosol: the importance of liquid-liquid phase separation, *Atmos. Chem. Phys. Discuss.*, 12, 2199-2258, doi:10.5194/acpd-12-2199-2012, 2012.

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Line 18, page 7452: 'it is calculated'? 'it' being the number of stable phases?

The results in figure 2 are very interesting. It would benefit from error bars that are discussed in the supplementary material and model variants. Whilst it is clear in the text, it should also be clear in the figure that the predicted K in the figure is K-CCN. This figure should also have predicted K at 90%RH. Given the practice for inferring k from HTDMA's, and the inclusion of non-ideality with LLE in this paper, this would provide a very interesting set of points for the reader.

Summary and Conclusions:

Page 7463, last paragraph. This text needs a few caveats. 'It is feasible to perform offline computation of $\sim 10^6$ k's.' As far as I can tell, this is based on the information regarding computational cost and seems completely reasonable since you would treat every compound in a binary mixture. Computational time then is the only limit. As mentioned earlier, any automated selecting of the relevant functionalities needs checking against a database of compounds that cover combinations of functionalities. For example, by using the compounds within the Master-Chemical-Mechanism (MCM) database, how many compounds are 'fully' captured with the selected UNIFAC groups? The MCM would provide a nice checkpoint before moving onto using output from GECKO

In addition 'Once pure component k's are predicted, the evolution of the overall OA in k in mixed particles can be calculated quickly.'. How does this translate to a k value that has been inferred from a model that treats binary LLE? Is there evidence this holds across the range of compounds across chemical mechanisms or would it not be better to compare with multicomponent methods of LLE to test its suitability?

Interactive comment on Geosci. Model Dev. Discuss., 8, 7445, 2015.

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