

Interactive comment on “The co-condensation of semi-volatile organics into multiple aerosol particle modes” by Matthew Crooks et al.

Matthew Crooks et al.

matthew.crooks@manchester.ac.uk

Received and published: 29 April 2016

0. “The co-condensation of semi-volatile organics into multiple aerosol particle modes. The authors have presented a new methodology and detailed set of non-linear equations to solve the co-condensation of organics into multiple modes. Although these mathematical equations and their derivations are presented in great details, their utility and atmosphere relevance is not clear. My major comment is that even after several reads, the paper mostly sounds like new and fairly involved algebraic mathematical formulations which are interesting, but why should atmospheric scientists care about these formulations?”

The paper initially presents a mathematical formulation for equilibrium absorptive partitioning theory to be used as an approximation for the dynamically condensation pro-

C1

cess that occurs in the atmosphere. The advantage of such a formulation is the algebraic nature of the equations rather than the differential equations that result from dynamic condensation. These algebraic equations depend on the instantaneous ambient conditions and do not need to be solved sequentially in time. Thus making their solution much less computationally expensive and therefore, when used in GCMs, can significantly reduce the computational expense. Even in situations when it is possible to dedicate sufficient time and computing power to solve the time dependent dynamic solution it is not necessarily the best route to take; quicker methods can allow more simulations to be carried out and therefore offer a better insight into the problem. We also do not believe that it is possible to solve every physical process using the most “accurate” (or complicated) means and some process always has to be lost or simplified in order to focus in on one or a few of particular interest.

Due to the non-linear nature of the equations, obtaining a solution is still a difficult task to carry out numerically. Non-linear solvers exist but require initial guesses for the solution and the more dimensions or unknowns that exist in the problem the better this guess has to be. In the current problem initial guess of zeros or ones is far from sufficiently accurate for any solver to converge and in a best case scenario will only find a local minimum. Starting with an initial guess far from the correct solution also increases the computational expense of the solution. The leading order solution offers a way to reduce the number of unknowns to 1. Single dimensional solvers are far more robust and require much less accurate initial conditions. The solution can additionally be calculated in a fraction of the time it takes to run a multidimensional solver. This solution, once found, can then be used as an initial guess for the multidimensional solver, therefore reducing computational expense. We additionally explore, however, how accurate this initial guess is as an approximation to the solution in its own right and find that in a range of scenarios the errors compared to the solution to the multidimensional solver solution are as low as 10-15% (see figure 8). This may be sufficiently accurate for many applications.

C2

We further suggest an alternative method to improving the accuracy of the leading order solution by perturbing the variables. Thus offering a semi-analytic method of increasing the accuracy without needing to use a multidimensional solver at all. This solution offers much improved accuracy (see figure 7) with greatly reduced computational expense compared to the multidimensional solver.

In summary, the applicability to atmospheric scientists is that our equilibrium partitioning may be able to replace hugely computationally expensive differential equation solvers in a range of work. In the case of GCMs this could make problems that have previously been thought of as too computationally expensive obtainable. In others, it may allow many more simulations to be carried out to span a wider parameter space and model many different scenarios.

1. "The condensation of semi-volatile organics on multiple modes is not a new formulation. This has been done in other models [e.g., Liu et al., 2012]."

It is not clear how [Liu et al., 2012] use multiple mode equilibrium partitioning. In section S1.1.3. SOA of their supplementary material they state "The condensation/evaporation is treated dynamically, as described below." – This suggests that the partitioning occurs dynamically and is not referencing an equilibrium partitioning, as proposed in the current work. Further to this, in Section S1.1.5. Condensation it says "Condensation of . . . the semi-volatile organics to various modes is treated dynamically, using standard mass transfer expressions" – this is similar to the dynamic parcel model that we are using to verify that our equilibrium partitioning theory calculates the correct condensed concentrations. Again, this is not an equilibrium partitioning theory.

We have changed "co-condensation" in line 85 of the original manuscript to "equilibrium absorptive partitioning" to try to stress the equilibrium aspect of the current work.

"The authors need to clearly make this distinction between their work and previous multi-mode partitioning studies"

C3

We still maintain that this is the first representation of multiple mode equilibrium absorptive partitioning and a review of existing equilibrium partitioning is presented. To further draw attention to the equilibrium aspect of this work and, in particular, the crucial element of the involatile constituent in the particles which makes this possible we have added the penultimate paragraph in the introduction.

2. "The title mentions co-condensation of semi-volatile organics. But it's actually co-condensation of organics and water on non-volatile core aerosol. The title needs to better reflect what is being presented. "

We don't understand this comment; it's not clear whether the issue is with the use of "co-condensation", "semi-volatile", multiple organics/water or the non-volatile component in the aerosol particles.

3. "What is the composition of the non-volatile core? Does it include inorganics such as sulfate, nitrate and also black carbon and non-volatile organic aerosol? The authors need to clearly define the composition of the core aerosol."

The core aerosol can take any composition but we assume that it is soluble through the van't Hoff factor; low solubility compounds such as black carbon can be modelled by using values close to zero. We also assume that it contributes to the partitioning of the SVOCs and water. In our particular examples we use ammonium sulphate and this is reflected in the material properties stated in table 3.

4. "If the core aerosol includes inorganics, the authors are implicitly assuming that the inorganic core aids the partitioning of semi-volatile organics e.g. see equation 3, where the non-volatile core is included in the calculation of COA. How is this assumption justified? The absorptive partitioning theory assumes well mixed solution [Pankow, 1994]. How can a core-shell model be well mixed? Also, several studies suggest that secondary organic aerosols (SOA) are under many conditions highly viscous semi-solids [Cappa and Wilson, 2011; Vaden et al., 2011; Virtanen et al., 2010], so they cannot be assumed to be well mixed. The authors need to clearly specify where their

C4

current formulation is not atmospherically relevant in the context of these studies."

We do indeed assume that the core aerosol aids partitioning and we also assume the particles are well mixed. Perhaps the confusion lies in the use of "core aerosol"; we are referring to the non-volatile constituent that exists before condensation, rather than a shell/core model with diffusion. We have changed references to "core" to "involatile"

A discussion of particle viscosity has been added in the third to last paragraph of the introduction.

5. "Section 7, page 18: The authors place large particles in the model first before adding small particles to improve the accuracy of their solution. How can this be applied in a regional or global 3D model, where many processes are happening simultaneously (such as nucleation, emissions, coagulation, condensation, transport etc.) so that at any time there are both small and big particles?"

This has been answered in detail in response to the first referee's first comment.

6. "Finally, does the author's new formulation include organic-inorganic interactions especially for aqueous aerosols? For example, I did not see hygroscopicity of the core and other organics include anywhere in their equations. Please clarify how the differing hygroscopicities, activities and aqueous phase reactions would affect your equations and their solutions."

The hygroscopicity, κ , as defined by [petters and kreidenweis 2007] can be used to derive equivalent values to the van't Hoff factor, ν , and vice versa. As such the hygroscopicity can be incorporated that way. We do not consider aqueous phase or gas phase reactions in our calculations.

Please also note the supplement to this comment:

<http://www.geosci-model-dev-discuss.net/gmd-2015-187/gmd-2015-187-AC2-supplement.pdf>

C5

Interactive comment on Geosci. Model Dev. Discuss., doi:10.5194/gmd-2015-187, 2016.

C6