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Interactive comment on "Reformulating the atmospheric lifecycle of SOA based on new field and laboratory data" *by* M. Shrivastava et al.

Anonymous Referee #1

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I thank the authors for providing a very detailed reply to my review. I would like to reiterate that I fully share the authors' interest in the questions discussed in the manuscript and think them of extreme importance to our field. This is exactly why I would like to see these questions addressed with utmost care and I hope the authors appreciate that. The authors seem to define two camps in discussing these important topics: the slow evaporation / high viscosity camp, and the liquid particles / fast evaporation camp. However the review is not taking sides in such a hypothetical debate as the issues are much more complex than that dichotomy, but rather is trying to point out inconsistencies or aspects that need to be improved in their interpretation, if they want to convince the scientific community of the soundness of their approach.

The length of the reply requires some time to digest and I would be happy to provide

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my detailed analysis in due time. However, several major points that I have raised in my review remain unanswered by the authors' reply and I hope they will take time to revisit them in a follow-up reply, if they wish to do so. Below I provide only a few examples that illustrate why I think the questions have not been answered.

In the reply the authors appear to alternate between two arguments, which are not necessarily connected and which have dramatically different implications for gas/aerosol partitioning. One argument is that the evaporation rates are so slow that they can be neglected in the chemical transport models. This argument does not require any knowledge of the particle physical state, intra-particle transfer limitations, etc. and does not necessarily contradict partitioning theory. Please note, I talk about validity of the theory, not validity of the assumption of equilibrium as derived from that theory. These are two very different things, which the authors seem to frequently confuse (see for example page 5, reply to #2).

The second argument involves the physical state of the particles, which the authors derive from the size dependence of particle evaporation, stability of two-phase particles, and back up with indirect evidence from other studies. This argument (i.e. inhibited intra-particle transport) does not necessarily require particle evaporation to be slow. For example, the Cappa and Wilson (2011) study referred to by the authors was performed at a very short residence time (15 s). However, this argument does have dramatic implications for application of the partitioning theory to calculations of kinetics of different processes involving particle/gas exchange. It implies that the bulk aerosol composition, as used in the Pankow theory, cannot be used for calculations of vapor pressures at the particle surface. Viscosity and diffusivity are linked; if particles are highly viscous, the intra-particle diffusion is slow. If the intra-particle transport is sufficiently limited, then the surface becomes virtually decoupled from the bulk with all the implications for evaporation kinetics and chemical reaction kinetics. One should bear in mind, however, that reaching thermodynamic equilibrium is still possible, if the intra-particle transport times are shorter than the atmospheric time scales. Whether or not

this is the case with ambient OA is the sixty four million dollar question.

However, setting aside the questions about the underlying evidence, some of which I will briefly address below, the proposed modeling approach still does not agree with basic physics. For example, the authors confuse evaporation rate with equilibration time scales. Quoting their response "Keep in mind that our evaporation rates were measured under organic vapor-free conditions. Under real atmospheric conditions, there would always be organic vapors present, and evaporation would be even slower. Under these conditions, how is one to calculate the gas particle partitioning, with the system being permanently far from equilibrium?" A slow evaporation rate under artificial conditions does not imply a longer equilibration time in real atmosphere. As a matter of fact, because organic vapor builds up in real atmospheric conditions, as the authors rightly point out, equilibration can be quickly attained, unlike in their experimental conditions where equilibrium is impossible to achieve due to the continuous stripping of vapor. Also, note that unlike evaporation rate, equilibration times do not depend on vapor pressures (see Seinfeld and Pandis, 2006). Thus, the first argument (i.e. that the models are wrong because aerosol never reaches equilibrium due to slow evaporation) simply does not hold. If one takes the second argument, the model has a major problem too. The equations provided in the Appendix do not hold for condensation (see eq.2 there), because the bulk composition is still used, which by the accepted definition of the problem is not accessible due to the very slow intra-particle diffusion. The authors' reply, unfortunately, does not resolve these problems.

The authors appear to be still confused about the size dependence of evaporation kinetics. In the free molecular regime dd_p/dt is size independent. Integrating leads to $d_p = d_0 - At$. Presenting it in the form of d_p/d_0 one gets $d_p/d_0 = 1 - At/d_0$ and, to compare to the graphs used in the paper, $(d_p/d_0)^2 = (1 - At/d_0)^2$. The same holds for any other power, with d_0, the initial particle size, still remaining in the right hand side. In the continuum regime $(d_p/d_0)^2$ also strongly depends on d_0, which the authors know very well according to Vaden et al. (2011). Thus, my argument still stands:

the free-molecular regime does not produce the kind of data the authors observe, nor does the continuum or transition regime, and independently of the type of material that the particles are composed of, be it liquid, solid, or glass. It does not matter how the authors define size independence: their data contradicts the basic transport theory.

The new discussion of the coating experiments provided in the reply was very informative. Unfortunately, neither the current manuscript nor Vaden et al. (2011) had as detailed a description of which classes or morphology of particles were used for which graphs. New information notwithstanding, the arguments remain unconvincing. The authors state, for example, that "the lower density fluid will always diffuse and reside on the surface of denser fluid" (top of page 28) which apparently comes from the buoyancy considerations. The question, however, is: how does it work for a spherical particle: what is top and what is bottom with respect to the center? Is it possible that there are multiple stable or metastable states, and that the change of configuration is not kinetically limited? A 4 nm coating on a 150 nm particle is ∼8%. Why then do the authors think that the particles have ∼20% of DOP trapped inside (middle of p.29 under #3)? What happened to the other 72%? Why is it that DOP dispersed inside SOA particles does not seem to evaporate together with the SOA material, etc., etc.?

As stated above, I will be happy to provide a detailed analysis of the authors' reply, but I hope the authors could revisit at the very least the points that I mentioned above. If the authors wish to do so, I would kindly ask to please refrain from attributing their logic and interpretations to me. No, I do not "trust their data" (middle of p.40), because I think it contradicts basic evaporation kinetics (see section 2 of the review); nor did I ever suggest replacing the existing VBS data with the authors data; nor did I ever agree that slow evaporation under the artificial experimental conditions necessarily means that equilibrium cannot be achieved in atmospherically-relevant timescales (see section 1 of the review); nor do I think that I neglect or contradict the available smog chamber data, one could actually point out that it is rather the authors' data that contradicts it, if one considers that much of the smog chamber data was collected at or near room

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temperature, etc., etc. These straw men that the authors attack have very little to do with my arguments.

I would also like to remind the authors that I am reviewing their manuscript and not several other papers, some unpublished, which they bring up as their arguments. In my review I had to revisit Vaden et al., because the current manuscript relies heavily on it, a fact the authors acknowledge in the reply, but somehow fault me for it. I thank the authors for reminding us of the high reputation and impact factors of some of the cited journals. However, I would like to point to a study showing a significant correlation between the journal impact factor and the number of retractions, which is briefly discussed in Science, V333, p.924. And in conclusion I would like to quote Galileo Galilei "In questions of science the authority of a thousand is not worth the humble reasoning of a single individual." Appeals to authority are still a logical fallacy.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 20107, 2011.