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Interactive comment on "Treatment of non-ideality in the multiphase model SPACCIM – Part 1: Model development" *by* A. J. Rusumdar et al.

Anonymous Referee #1

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Review of Rusumdar et al:

The paper presents a new approach to couple a generic group contribution activity coefficient model within the dynamic SPACCIM model. I fully support the author's scientific rationale for including non-ideality in general dynamic models. All too often the influence of non-ideality is ignored through considerations of computational expense at the danger of biasing sensitivity to other processes/composition dependent effects. I do however have a range of general and minor comments I believe the authors should respond to before consideration for publication. The work is clearly substantial, but the presentation of the new work is not clear to suggest the paper has the correct balance of material, which no doubt already exists. The minor comments generally revolve around typically vague statements, or professions of model improvements without ap-

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propriate contextualization.

General comments:

My general comments stem from section 2.3 and the apparent view from the abstract and introduction, that a new activity coefficient model has been developed to warrant the new reference 'SpactMod'. If the basis from AIOMFAC has indeed changed, this should be clearer in the document. However, on inspection of the presented equations, it seems to be the same theoretical framework as presented by Zuend et al (2008) in which case the model appears to be AOMFAC with new interaction parameters. Is this because you have not performed a full parameter refitting across all interaction terms that you have decided to re-brand the model? Section 2.3.1 covers the theoretical background behind activity models derived from the derivative of the Gibbs excess energy. I read this section with the assumption of an adjusted theoretical basis following a similar derivation. I appreciate the presentation of the background, but this section could be much shorter with reference to Zuend et al (2011) and (2008) and where the new parameters fit in the model, without the Gibbs excess terms. I note you have worked with the AIOMFAC developers in the acknowledgement but still find the presentation of already available derivations and lack of information regarding parameter refitting a pity. As I said in the introduction, I believe the work is useful and the presentation of the novelty of this work be reformulated.

Page 4174, line20. 'based mainly on AIOMFAC'. What do you mean by 'mainly'. This forms the crux of this section. By 'mainly' it seems you are referring to a reliance on the core of previously published interaction parameters rather than an extension of the theoretical basis. Is this correct?

Page 4180, line 26. 'it was found that [the] model produce[d] relatively better results in most cases in comparison with the parameters from standard UNFIAC only'. There are many aspects to this sentence. First, what statistics back this up? Does this cover a wide range of conditions and functionality? Where is the evidence? In addition,

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given that standard [parameters] in UNIFAC has been superseded by values fit to more recent and more comprehensive data sets, why is this surprising? It isn't clear based on the discussion, that needs re-writing. This falls into the same concern I have regarding presenting an activity coefficient model development in a sparsely populated scientific evaluation given the introduction of a 'new' model.

On the whole, I would have thought it much better to present a more thorough assessment of how the new interaction parameters were fitted, whilst accounting for, as best as possible, mitigation of both under and over-fitting. Indeed, I was expecting more figures showing the prescribed impact of the newly fitted parameters in simple mixtures and yet found only systems that can already be accounted for?

Minor comments:

Page 4146, line 7: 'newly considered non-ideality properties' is confusing. I presume you are referring to a study including non-ideality in the cloud model that has not been considered before. Please revise this sentence. I would suggest something like : 'The present study was aimed at presenting further development of the SPACIM model through treatment of solution non-ideality, which has never been considered before.'

Page 4156 line 20: This minor comment feeds into my general concerns in the general comments to follow. The note that AIOMFAC was selected as a 'base' model and extended by additional interaction parameters is clear. If the theoretical basis of said model, in any way has been similar altered, it must be stated here since it would justify the use of a bespoke name for such a framework.

Page 4156: '..the performance and the capability of the applied activity coefficient module were evaluated by. . .and results of other thermodynamic equilibrium models'. Please be clear here what exactly you mean by 'thermodynamic equilibrium models'. Models such as GFEMN, E-AIM, ADDEM, MOSAIC, whilst covering various scales of complexity, represent thermodynamic equilibrium models in that they search for the equilibrium end point. They rely on activity coefficient models, which technically should

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not be covered under the same model description.

Page 4157, line 2: I agree activity coefficients should be mandatory but within the context of trying to determine, through process sensitivity studies, the uncertainty through their neglect is 'low enough' to be justified.

Page 4157, line 3: 'Modeled activity coefficients implicate that turnovers of chemical processes..'. What exactly do you mean by 'turnover'? The reader will presume this is somehow related to a time related constraint?

Page 4157, lines 5 -7. Similarly, please clarify what you mean by 'chemical ion processing'.

Page 4157, line 8:'..organic compounds are partly > 1..' This kind of statement appears in a number of places throughout the document. Partly? Do you mean that a certain % of activity coefficients are greater than unity? For what conditions? Can you please clarify this.

Page 4158 , line 18. Please introduce the relevant scale of activity coefficients at the very beginning [mole fraction or molality].

Page 4158, line 26'..ideal solution in aerosol models has to be abandoned and non ideal behavior has to be considered.' Again, I generally support you strong view on this issue. However, it should really be contextualized. You do refer to previous studies that suggest neglect of certain inorganic-organic interactions can lead to lower errors than an attempt at their inclusion. I would suggest adding the caveat that a range of sensitivity studies, from models that can account for composition dependent processes, need to be carried out to support either inclusion or neglect.

Page 4159, line8: '..effort has been devoted formerly to..'. Suggest removing formerly.

Page 4159, line 16: The comment on various numerical techniques based on energy minimization and their cost is slightly confusing. The cost of such schemes tends to derive not from the numerical core of that search, but from the cost of the activity

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coefficient model and the number of compounds used in calculations. Suggest adding more recent references here.

Page 4159, line 22.'Only very few models exist that treat partitioning to an efficient and accurate thermodynamics model'. Again, what do you mean by efficient thermodynamics model? Is SPACCIM particularly efficient? I would recommend, if this is the case, it is stated somewhere clearly. Also, MOSAIC and ADCHAM, for example, represent both extreme points in the modelling spectrum. MOSAIC was developed to face challenges associated with capturing thermodynamics in a regional model, whereas ADCHAM by appearance tried to include every process into a chamber based box model in one study.

Page 4159, line 25 onwards. Here the authors claim that interactions between organic compounds and inorganic components have remained elusive. This was true for some-time, but has improved significantly. The discussion on the range of organic compounds treated in up-to date activity coefficient models, specifically AIOMFAC, should be included here to put the argument into context. You have already included Zuend et al (2011) in the reference list, please include this in your discussion. It might be covered elsewhere so please make sure the text flows better in a new version. Indeed, I would consider grouping distinct discussions into the same part of the text: Existing activity models, current state of interaction matrices, why this study builds on these.

Page 4160, line 4 'is an object of intense research all along the last years'. Suggest 'has been the focus of many detailed studies'.

Page 4160, line 18: 'the kinetic description of non-ideality in SPACCIM is elaborated'. This another awkward sentence to read. I would suggest 'This paper is split into x sections. In section x, we described the inclusion of non-ideality into the SPACCIM model. . .etc'

Page 4161, line 18. Here you comment on the ability to account for a 'detailed' description of processing of gases and particles prior to cloud formation, during and after its

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life-cycle. Does this account for the effect of condensing components on the effected size distribution, thus micro physics, at the point of activation? Note there has been some papers discussing the impact of co-condensation on increased cloud droplet numbers.

Page 4161, line20:' An advanced coupling'. What is it 'advanced'? Are the other developments 'advanced'?

Page 4162, line 4:'The used chemical mechanism' is awkward. I would suggest 'the chemical mechanism used is provided as an input file'.

Page 4163, line 7, 'Mainly, the aqueous concentrations..'what do you mean by 'mainly'? Is this a dominant feature somehow of the model development? Please clarify.

Page 4164, line 13. Here you introduce the reliance on Henry's law coefficients. Given the drive to include non-ideality in the model, how do you know, for a wide range of atmospheric compounds, that Henry's law coefficients are more constrained that pure component vapour pressures? Do Henry's law coefficients cover the same range of functionality that has driven you to extend activity coefficient model interaction parameters?

Page 4166, section 2.2.3. I have a few issues when reading the section regarding terminology. You introduce a saturation vapour pressure, but relate this to the molality of the compound in question. I believe you should be referring to an equilibrium vapour pressure above the solution droplet? Saturation vapour pressure relates to the vapour pressure above a solution of the pure component [liquid or solid depending on the reference state]. Indeed, you then go on to refer to a 'saturation vapour mole concentration.' This does seem to be the case since you then express the [equilibrium] vapour pressure to the concentration in the gas phase at the same conditions.

Page 4168 line 25. 'Eq1 is used to determine the equilibration of water between the liquid and vapour phase'. Does this mean you do not account for a dynamic conden-

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sation of water to the condensed phase?! If so, this could have significant implications for the prescribed micro-physics couldn't it? Perhaps I have misunderstood this.

Page 4169, line 12. Please define precisely. Does mean other developments are not particularly precise?!

Page 4169, line 13:'Both effects are primarily appointed by the particle composition..'. Suggest replacing 'primarily appointed' by 'influenced'.

Page 4170, section 2.2.6. I have many issues with this section, which will need a significant re-write. Please add a reference for the 'almost' linear approximation. What exactly do you mean by 'almost'? Inclusion or neglect of surface tension has been the focus of many studies since the paper by Facchini et al (1999). I found it odd that there is not, at least, a brief discussion as to why this particular equation was used. It is not enough to simply chose it based on convenience as it isn't clear what effect it might have on your results. This particular formulation would lead to a significant decrease in surface tension at the point of activation. On the other hand, the studies of Sorjamaa et al 2004/Topping et al 2007/Prisle et al 2012 to name a few have since question the true meaning of surface tension, based on solving the Gibbs adsorption isotherm. The general study of Prisle et al 2012 indicated that using a range of models that can account for this effect can remove the previously held view of a significant impact from a decrease in surface tension but with appropriate caveats in the discussion. These studies need to be included in any discussion of any inclusion, or neglect, of a surface tension effect.

N. L. Prisle , A. Asmi , D. Topping , A.âĂŘI. Partanen , S. Romakkaniemi , M. Dal Maso , M. Kulmala , A. Laaksonen , K. E. J. Lehtinen , G. McFiggans , H. Kokkola: Surfactant effects in global simulations of cloud droplet activation. Geophys. Res. Lett., 39, L05802, doi:10.1029/2011GL050467. Topping, D. O., McFiggans, G. B., Kiss, G., Varga, Z., Facchini, M. C., Decesari, S., and Mircea, M.: Surface tensions of multi-component mixed inorganic/organic aqueous systems of atmospheric signifi-

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cance: measurements, model predictions and importance for cloud activation predictions, Atmos. Chem. Phys., 7, 2371-2398, doi:10.5194/acp-7-2371-2007, 2007. Sorjamaa, R., Svenningsson, B., Raatikainen, T., Henning, S., Bilde, M., and Laaksonen, A.: The role of surfactants in Köhler theory reconsidered, Atmos. Chem. Phys., 4, 2107-2117, doi:10.5194/acp-4-2107-2004, 2004.

Page 4176, line 8 'are described same as original AIOMFAC', Suggest 'described as they are in..'

Page 4177, lines17 – 19 really do not make sense. What exactly are you referring to with regards the statement:'compensation of these inaccuracies is controlled by this simplification'. Please revise this.

Page 4180, line 22 'are also comprised in the SR part'. Replace comprised with 'included'.

Interactive comment on Geosci. Model Dev. Discuss., 8, 4155, 2015.