Comment on the manuscript "The size-dependent charge fraction of sub-3-nm particles as a key diagnostic of competitive nucleation mechanism under atmospheric conditions"

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1 Question of interest

Yu and Turco (2011) addressed the following question of interest: "How *conclusive* are conclusions, drawn from the estimation of apparent particle formation rates at a diameter of $D_\mathrm{p} = 2\,\mathrm{nm}$ from field measurements, with respect to the relative contribution of ion-mediated nucleation (IMN) to atmospheric new particle formation (NPF)?"

The authors critically re-evaluated field data, measured during selected NPF-event days within the framework of the BACCI/QUEST IV campaign 2005 in a boreal forest (Hyytiälä), which insinuated a relatively modest contribution of only $\approx 10\%$ of IMN to NPF. This relatively small contribution is based on previous evaluation of the size distributions of both charged and neutral particles down to $D_\mathrm{p} \approx 2\,\mathrm{nm}$, published in different papers. The authors demonstrated the untrustworthiness of conclusions/interpretations drawn from itself trustworthy observations and derivations of 2-nm phenomenological aerosol measurements. Most importantly, by means of an advanced modelling approach it was demonstrated, that an essential involvement of IMN is fully reconcilable with state-of-the-art atmospheric measurements.

2 Methodical approach

The authors defined the apparent ratio of ion-mediated NPF rate to the total NPF rate ("apparent fraction of nucleation to ions" $FJ_{D_\mathrm{p}}^{(\mathrm{ion})}$, Eq.(1)). Based on well-known principles of aerosol-dynamical balancing the authors re-derived the basic relations underlying the determination of apparent formation rates of both charged-type and all-type particles (at the diameter $D_\mathrm{p} = 2\,\mathrm{nm}$, $J_2^{(\mathrm{ion})}$ and $J_2^{(\mathrm{tot})}$ according to Eqs. (6) and (7)) from field measurements. This approach is completely sound and traceable.

Owing to the impossibility to measure particle size spectra down to near-critical cluster sizes, the authors realised an elegant idea: the employment of a sophisticated second-generation ion-mediated nucleation model of Yu (2006) to directly derive the net fluxes of both charged and neutral particles crossing the particle diameters of interest.

3 Discussion

Using the example of one selected NPF-event day out of the BACCI/QUEST IV campaign in spring 2005 (Julian day 117, April 17, 2005), the authors performed a detailed process analysis, which showed a (surprisingly to me) very strong size dependence of the apparent IMN fractions $FJ_{D_\mathrm{p}}^{(\mathrm{ion})}$ (see Figs. 2-4). I found the accompanying argumentation physically sound (what can be read in the text is reconcilable with what can be seen in the figures). It becomes clear, that the decrease of the diameter from super-critical sizes ($D_\mathrm{p} \approx 2\,\mathrm{nm}$) down to "near-critical" sizes ($D_\mathrm{p} \approx 1.5\,\mathrm{nm}$, still above the critical diameter!) is accompanied by a drastic increase of the $FJ_{D_\mathrm{p}}^{(\mathrm{ion})}$ values. The demonstrated behaviour of the IMN approach is self-consistent, and most importantly, reconcilable with available field measurements. On the base of the mechanistic process study of the NPF event on April 17, 2005, the authors extended their analysis to seven further event days of the above-mentioned campaign (Fig. 5). Finally, the overall outcome of the study can be easily captured by Figs. 6 and 7, showing a very strong size-dependence of the apparent formation rates of both charged and neutral particles as well as the corresponding $FJ_{D_\mathrm{p}}^{(\mathrm{ion})}$ values. The authors demonstrated, that the characteristic lifetime of charged particles against neutralisation is LOWER than the typical growth time, i.e., during the particle growth time the charged particles can be neutralised. Thus, indeed *"the size resolved, charge specific, kinetic analysis [...] shows explicitly how typical measurements may be inadvertently misinterpreted in favor of NCN (neutral cluster nucleation). Rather than the ≈ 10% ion contribution suggested in some earlier studies, [...] IMN processes account for closer to 100% of the new particles for the cases investigated."*

I mean, the result of the present study is interesting for several reasons:

- Seemingly "neutral particle formation" is completely reconcilable with an essential involvement of ions in the nucleation process.
- The kinetic IMN approach to new particle formation is in line with empirical findings showing the onset of nucleation at sulphuric-acid concentrations far below the threshold for binary homogeneous nucleation to occur. For mechanistic understanding of the role of ions in stimulating the nucleation process I want to refer to the instructive Fig. 1 in Lovejoy et al. (2004).
- By their very complex modelling approach the authors have brought forward the problem discussion in scientific "uncharted territory". Of course, as long as not all phenomenological findings are explained, the problem cannot be declared as solved. Unfortunately, by using very sophisticated process models, like the Yu (2006) IMN model, one cannot *a priori* exclude the possibility, that "the results might be right

for the wrong reason". However, I mean, despite of several uncertainties associated with sophisticated models (strong increase of the degrees of freedom due to involvement of further badly constraint processes), their use should be clearly favoured over the use of highly parameterised models. For example, in a mesoscale or global scale model the parameterisation of one process usually affects the parameterisation of other processes. Thus the independent use of an improved process submodel ("local upgrading") can easily downgrade the predictive power of the whole model ("global downgrading"), because the tuning of different parameterisations is disturbed be the supposed "improvement". This is a principal problem, which must be accepted to some degree. The only way to disconnect the interdependence of parameterisations is the stepwise reduction of parameterisations by replacing them with sophisticated process models.

Apart from that, I agree with the authors statements in their Section 3.4, e. g.: *"If the comprehensive theory provides explanatory results, then simplified models can be developed by investigating the relative importance of component processes and isolating the most important ones. The converse is not usually true. A simplified model, or highly approximated basis for analysis, cannot generally be extrapolated to reveal more detailed information and reach more fundamental conclusions. Moreover, a comprehensive model can be employed to carry out sensitivity studies that underscore the most critical uncertainties and point to the requirements for new data."*

4 Specific comments

In their Section 3.3, Yu and Turco (2011) derived an analytical expression for the apparent IMN fraction as a function of size (as shown in Fig. 6b). The authors presented their final expressions.

Employing the assumptions made by Yu and Turco (2011), I arrived at their Eqs. (9)-(11) via the following intermediate steps:

1. Both ion and neutral nucleation processes create thermodynamically stable particles at rates, $J^{(\pm)}_{D_{\mathrm{p},0}}$, having an initial diameter $D_\mathrm{p} = D_{\mathrm{p},0}$. Therewith, the fraction of new particles, that are initially charged (or formed due to IMN) at the diameter $D_{\mathrm{p},0}$, reads:
$$FJ^{(\mathrm{ion})}_{D_{\mathrm{p},0}} = \frac{J^{(\pm)}_{D_{\mathrm{p},0}}}{J^{(\pm)}_{D_{\mathrm{p},0}} + J^{(0)}_{D_{\mathrm{p},0}}} \ . \tag{1}$$

2. The particles nucleated on ions are subsequently neutralised due to charge recombination during their initial growth phase:
$$\frac{\mathrm{d}N^{(\pm)}_{D_{\mathrm{p},0}}}{\mathrm{d}t} \approx -\underbrace{\alpha_\mathrm{recomb}\, N^{(\mathrm{tot},\mp)}_{D_{\mathrm{p},0}}}_{=\,\tau^{-1}_\mathrm{recomb}} \cdot N^{(\pm)}_{D_{\mathrm{p},0}} \ .$$

Here, α_{recomb} denotes the ion–ion recombination coefficient, τ_{recomb} the characteristic time of recombination, and $N_{D_{\text{p},0}}^{(\text{tot},\mp)}$ is the total concentration of small (negative or positive) ions. Integrating this equation over the time interval $[t, t{+}\Delta t]$ yields:

$$N_{D_{\text{p},0}}^{(\pm)}(t+\Delta t) = N_{D_{\text{p},0}}^{(\pm)}(t) \cdot \exp\left(-\alpha_{\text{recomb}}\, N_{D_{\text{p},0}}^{(\text{tot},\mp)}\, \Delta t\right) \ .$$

During the time interval Δt, particles grow with a fixed diameter growth rate $\text{GR} = \text{d}D_\text{p}/\text{d}t$ from diameter $D_{\text{p},0}$ to $D_{\text{p},1}$:

$$\Delta t = \frac{D_{\text{p},1} - D_{\text{p},0}}{\text{GR}} \ .$$

Neglecting both coagulation scavenging of clusters as well as ion–neutral attachment, the number concentration of charged particles $N_{D_{\text{p},0}}^{(\pm)}(t+\Delta t)$ can be approximated by a truncated Taylor series:

$$N_{D_{\text{p},0}^{(\pm)}}(t+\Delta t) = \underbrace{N_{D_{\text{p},0}}(t) + \left.\frac{\partial N_{D_\text{p}}^{(\pm)}}{\partial D_\text{p}}\right|_{D_{\text{p},0}} \frac{\text{d}D_\text{p}}{\text{d}t}\Delta t}_{N_{D_{\text{p},1}}(t)} \ .$$

Therewith, one can write:

$$N_{D_{\text{p},1}}^{(\pm)}(t) = N_{D_{\text{p},0}}^{(\pm)}(t) \cdot \exp\left(-\alpha_{\text{recomb}}\, N_{D_{\text{p},0}}^{(\text{tot},\mp)}\, \Delta t\right) \ .$$

The time derivative of this equation yields the steady-state apparent nucleation flux of charged particles at diameter $D_\text{p} = D_{\text{p},1}$:

$$J_{D_{\text{p},1}}^{(\pm)} = J_{D_{\text{p},0}}^{(\pm)} \cdot \exp\left(-\alpha_{\text{recomb}}\, N_{D_{\text{p},0}}^{(\text{tot},\mp)}\, \Delta t\right) \ . \quad (2)$$

3. According to Eq. (3), the net fluxes of particles crossing the diameters $D_{\text{p},0}$ and $D_{\text{p},1}$ read:

$$\text{PL}_{\text{growth}}^{(0,\pm)} = J_{D_{\text{p},0}}^{(0,\pm)} - J_{D_{\text{p},1}}^{(0,\pm)} \ .$$

Assuming

$$\text{PL}_{\text{growth}}^{(0)} \approx -\text{PL}_{\text{growth}}^{(\pm)} \rightsquigarrow J_{D_{\text{p},0}}^{(0)} - J_{D_{\text{p},1}}^{(0)} \approx J_{D_{\text{p},1}}^{(\pm)} - J_{D_{\text{p},0}}^{(\pm)}$$

according to Figs. 4a and 4b, one obtains by virtue of Eq. (2) the steady-state apparent nucleation flux of neutral particles at diameter $D_\text{p} = D_{\text{p},1}$:

$$\begin{aligned} J_{D_{\text{p},1}}^{(0)} &\approx J_{D_{\text{p},0}}^{(0)} + J_{D_{\text{p},0}}^{(\pm)} - J_{D_{\text{p},1}}^{(\pm)} \\ &\approx J_{D_{\text{p},0}}^{(0)} + J_{D_{\text{p},0}}^{(\pm)} \left[1 - \exp\left(-\alpha_{\text{recomb}}\, N_{D_{\text{p},0}}^{(\text{tot},\mp)}\, \Delta t\right)\right] \ . \end{aligned} \quad (3)$$

4. Therewith, the apparent ion nucleation fraction of particles with the diameter $D_\mathrm{p} = D_{\mathrm{p},1}$, reads:

$$
\begin{aligned}
FJ^{(\mathrm{ion})}_{D_{\mathrm{p},1}} = \frac{J^{(\pm)}_{D_{\mathrm{p},1}}}{J^{(\pm)}_{D_{\mathrm{p},1}} + J^{(0)}_{D_{\mathrm{p},1}}} &= \frac{J^{(\pm)}_{D_{\mathrm{p},0}} \exp\left(-\alpha_\mathrm{recomb}\, N^{(\mathrm{tot},\mp)}_{D_{\mathrm{p},0}}\, \Delta t\right)}{J^{(\pm)}_{D_{\mathrm{p},0}} + J^{(0)}_{D_{\mathrm{p},0}}} \\
&= FJ^{(\mathrm{ion})}_{D_{\mathrm{p},1}} \exp\left(-\alpha_\mathrm{recomb}\, N^{(\mathrm{tot},\mp)}_{D_{\mathrm{p},0}}\, \Delta t\right) , \qquad (4) \\
\frac{FJ^{(\mathrm{ion})}_{D_{\mathrm{p},1}}}{FJ^{(\mathrm{ion})}_{D_{\mathrm{p},0}}} &= \exp\left(-\alpha_\mathrm{recomb}\, N^{(\mathrm{tot},\mp)}_{D_{\mathrm{p},0}}\, \frac{D_{\mathrm{p},1} - D_{\mathrm{p},0}}{\mathrm{GR}}\right) ,
\end{aligned}
$$

For typical conditions, Yu and Turco (2011) employed the following parameters:

Parameter	Value
α_recomb	$\approx 1.6\times10^{-6}\,\mathrm{cm^3 s^{-1}}$
$N^{(\mathrm{tot},\mp)}_{D_{\mathrm{p},0}}$	$\approx 1000\,\mathrm{cm^{-3}}$
$\mathrm{GR}_\mathrm{estimate}$	$\approx 1.9\,\mathrm{nm\,h^{-1}}$
$[D_{\mathrm{p},0}, D_{\mathrm{p},1}]$	$[1.5\,\mathrm{nm}, 2\,\mathrm{nm}]$

The characteristic lifetime of a charged particle against neutralisation (τ_recomb) is smaller than the characteristic growth time (τ_growth):

$$
\tau_\mathrm{recomb} = \frac{1}{\alpha_\mathrm{recomb} N^{(\mathrm{tot},\mp)}_{D_{\mathrm{p},0}}} \approx 10\,\mathrm{min} < \tau_\mathrm{growth} = \frac{D_{\mathrm{p},1} - D_{\mathrm{p},0}}{\mathrm{GR}} \approx 15\,\mathrm{min} .
$$

Therefrom it follows, that within the characteristic growth time charged particles can be neutralised.

5 Minor corrections

- p. 11291, line 5 (typo): “relative humidity”
- p. 11293, line 28: The BACCI/QUEST IV reference day was April 17, 2005 (but not April 27).
- p. 11297, lines 26-28: The message of this sentence should be checked! The characteristic time scale of recombination is SMALLER then the characteristic time scale of growth, $\tau_\mathrm{recomb} < \tau_\mathrm{growth}$, i.e., during the particle growth time the charged particles can be neutralised. I suspect, the verb “exceed” is not correctly used in line 27.

6 Overall assessment

I found this paper both practically relevant and scientifically very interesting. Together with the critical comments of the reviewer Jeffrey Pierce and authors reply it allows better insight into the origin of the surprisingly large differences of the present study to that of Manninnen et al.

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