Atmos. Chem. Phys. Discuss., 11, C15433–C15440, 2012
www.atmos-chem-phys-discuss.net/11/C15433/2012/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "On the ice nucleation spectrum" *by* D. Barahona

D. Barahona

donifan.o.barahona@nasa.gov

Received and published: 17 February 2012

Thanks for the positive assessment. The comments are addressed below.

1 General Comments

`1. The concept of the nucleation time should be explained better in order to clearly differentiate it from the integration time t or the duration of an experiment, delta t_exp. In chapter 2 about general theory, it is not a priori clear that the introduction of a nucleation time scale and hence the approximation in equation (8) is justified, given the fact that J_hom usually depends strongly` on T and S. The justification of such an approach rather seems to be the result of the calculations in 3.1.1 and 3.2.2."

The difference between the nucleation timescale and the experimental time is precisely that the former takes into account the changing S_i and T fields, e.g, $\tau_{nuc} = \tau_{nuc}(S_i, T)$. Mathematically it can be shown that such timescale exist by expanding $ln[J(S_i, T)]$ in its Taylor series around S_i and T. The derivation of the general form of τ_{nuc} is presented in the revised paper. The derivation of the equations in sections 3.1.1 and 3.2.2. have also been expanded for clarity.

"‘2. In 3.2.3, it should be clearly stated that the dependence of the deposition ice nucleation spectra on different influencing parameters, as shown in Fig. 3, relies on the assumption that the nucleation rate coefficient J_{het} is constant throughout the surface of an individual ice nucleus"

Not true. The assumption that each particle can be characterized with a given J_{het} was only introduced to facilitate the explanation of the nature of the NPDF. It is neither a requirement of the theory nor of the expressions derived for homogeneous and heterogeneous ice nucleation.

The nucleation probability dispersion function (NPDF) represents the distribution of the nucleation coefficient (i.e., the number of ice germs present in a particle) normalized to a reference or "characteristic" state (in this case a uniform particle with area $\bar{s}_p$). Assumptions on J_{het} only apply to the reference state. If all particles have similar dependencies as the reference state then σ_φ is small, if they differ from it then σ_φ is large.

Section 2 has been rewritten to avoid confusion.

"In the general introduction in section 2.1.2, two different approaches are presented, one of which uses a surface distribution of active nucleation sites, and the other uses a nucleation rate coefficient. The derivations in section 3 are based on the latter approach, whereas the former is not considered further. This choice should be mentioned and motivated, since the choice of either assumption to describe heterogeneous nucleation can influence e.g. the results presented in Fig. 3."

This is a good point. Only empirical expressions for ρ_{as} exist, which are in general obtained using aerosol samples of unknown surface heterogeneity. This is a problem since the actual dependency of ρ_{as} on S_i and T maybe masked by variability in the surface properties of the aerosol sample. Thus a theoretical approach (i.e., CNT) is preferred.

However the two approaches presented in Section 2 are limits of variability rather than general definitions. Ice nucleation may occur either by surface adsorption or by the presence of active sites, and both may occur on the same particle. The equations in Section 2 have been rederived using this more general concept.

"3. In chapter 2.1.2, it seems that the second approach (with rho_s describing the IN surface) refers to the singular hypothesis about heterogeneous ice nucleation. However, the concept of preferential sites for ice nucleation on the surface of an IN can also be combined with the stochastic concept of a nucleation rate coefficient (e.g. Marcolli et al., 2007). Although adapting the formalism for deposition nucleation to further concepts involving active nucleation sites might be beyond the scope of this paper, it would be interesting if using such

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

descriptions would significantly change the dependency of f_f on T, S, etc."'

Actually the concept presented here is more general.

Consider the example of an hypothetical aerosol population in which each particle has two active sites and a wettable surface where in average one ice germ is formed by adsorption during a given experiment. To deal mechanistically with such complex population requires assumptions on the area of the active sites and the composition and structure of the adsorption surface. In the approach presented here, ice nucleation on such population is described by $\varphi = 3$, and the dependency of f_f on S_i, T and s_p obtained through relating to a reference state. In other words, in the approach presented here details of the micro-structure of each particle are not “hardwired” into f_f. This has been more clearly explained in the revised paper.

"4. On line 59-60 it is stated that existing models of describing the surface properties of a population of IN rely on idealized pictures of the particle surface structure. In what respect can the formalism presented here be considered as less idealized? In fact, the quantity "xi`` used in the NPDF seems to be based on the assumption of a constant contact angle throughout the surface of an IN. If this is true, then this formalism does not conceptionally differ from some of the concepts used in the stated literature. If this is not true, then more explanation is necessary to prevent misunderstanding."

This has been covered in points 1 to 3. To prevent misunderstanding Section 2 have been rewritten including a more detailed description of the physical basis behind the theory.

2 Specific Comments

```
"Line 69: Add ``approximately'' to ``singular behavior''.
If the ice nuclei followed strictly singular behavior,
then fluctuations in the ice embryo size would lead to
negligible spread in freezing temperatures, which
is not the case according to..."
```

```
"Line 124: I think if the upper limit of integration
in eq. (7) is t, then the variable in the integral should
be different, for example t'. This also holds for more
equations of the same kind."
```

This has been corrected

```
Line 114: How exactly is n_c in eq. (6) defined? Shouldn't
the left side of eq. (6) also be a differential?
```

n_c is the total derivative of f_f, i.e, $n_c = \mathrm{d}t\frac{\mathrm{d}f_f}{\mathrm{d}t}$. However the equation is not used further in this study and has been removed.

```
Line 136. Please give a precise reference (including the
equation number in Pruppacher and Klett (1997)) for rho_s.
```

`Does rho_s represent the surface density of sites that nucleate ice at specific conditions (T,S) according to the singular hypothesis, or is it a function of e.g. contact angle, as introduced by Marcolli et al. (2007)? Furthermore, I suppose that rho_s should also be written instead of rho_as as in eq. (9, 10, 11) and several other places.`

The equation has been removed in the revised version of the paper, where a more general definition of φ is used. ρ_{as} is the surface density of active sites according to the singular hypothesis. This has been clarified in the paper. The symbol is suppose to be ρ_{as}; all the typos have been removed.

`Line 146: Is the proportionality in eq. (11) valid independently from the functional form of the NPDF?`

It is not proportionality what is depicted but rather functionality. To avoid confusion Eqs. (11) and (13) have been removed.

`Line 181: The derivation of equation (20) from eq. (18) and (19) is not clear, and should become comprehensible to the reader. More steps would probably help, and the cooling rate gamma has not been introduced up to this point.`

Equations (18) to (20) have been rederived and clearly explained, starting from a general definition of τ_{nuc}.

`Line 221: The sentence ''The NPDF allows a finite probability. . .'' does not make sense to me. Explain better.`

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

The statement has been removed. The relation between actives sites and nucleation by adsorption is now explained in Section 2.

`Line 241: The sentence ''To assure physical consistency. . .'' needs further explanation, and probably a reference to eq. (22).`

The steady state surface concentration is determined by equality between the incoming and outgoing molecule fluxes. Increasing Δg_d decreases the desorption flux and must increase $c_{1,s}$. Thus Δg_d must be positive in Eq. (22). This explanation has been included in the revised paper.

`Line 275: On the right hand side of eq. (34), where has the prefactor 1/sqrt(f) gone that is present in eq. (26)? Furthermore, it should be mentioned that Deltag_g has to be evaluated at f=1.`

The prefactor has been neglected on the basis that the exponential term dominates the variation in J_{het}. I agree, Δg_g must be evaluated at $f = 1$. This has been corrected in the revised paper.

`Line 277: In eq. (35), f should be a function of theta, but the derivative should be evaluated at the characteristic theta. I guess this would be mathematically more rigorous.`

Indeed. This has been corrected.

`Line 279: The step from eq. (35) and (36) is not comprehensible to the reader. Give more details.`

In essence this results from dividing the equation by $\bar{\varphi}$ and separating the constants out of the expression, keeping only terms involving $\frac{\theta}{\bar{\theta}}$ within the functionality. These steps are now explicitly shown.

`Line 340: Is it justified to speak about a ''previously` `unidentified behavior of homogeneous freezing''? I think it is immediately clear from CNT that the presence of small droplets limits the frozen fraction.`

The sentence refers to the the effect of dispersion in the droplet size distribution on the ice nucleation spectrum. It is shown that T at the freezing point is generally not affected by dispersion but rather it is the form of the spectrum at high f_f what is affected. The fact that $varr \approx 0.4$ represents a limit above which the effect of droplet size variability on f_f is significant is a new finding.

The sentence has been rewritten to avoid confusion.

`Line 362: Along the lines of general comment number 2, one might add here that since an alternative description of deposition nucleation using a distribution of active sites would probably be closer to the singular hypothesis than the formalism developed in the present manuscript (assuming a constant contact angle on individual IN), the observed temporal dependence of the frozen fraction might be considered as an upper limit for temporal effects.`

As mentioned above, the developed formalism does not rely on the assumption of a constant contact angle on individual IN. Temporal effects at constant S_i and T on f_f, and cooling rate dependency and variable S_i and T are not necessarily related. The revised paper includes a new section where temporal effects are discussed.

`Technical comments:`

All technical comments have been addressed.