We would like to thank Prof. Cantrell for his comments and suggestions, which helped us to considerably improve the manuscript. Specific answers and manuscript modifications related to his comments are given below in bold.

I believe the time is ripe for a review of contact freezing, and the authors have done a nice job of gathering and presenting the available material in a coherent, logical fashion. There have been several papers published in the last five years or so on the topic, there's renewed interest in the underlying theory, and most importantly, there are still many open questions. In fact, Figure 12 in the paper is one of the more compelling arguments I could offer as to why a review of the subject is warranted at this time. The available measurements of contact nucleation by dust show that almost no one's data agrees with anyone elses. Clearly there are open questions, and a review of this sort is valuable in highlighting and offering a critical perspective on them.

One of the strengths of the review is presentation of the various explanations and theories that have been offered to explain the fact that contact freezing is typically effective at higher temperatures than are the other modes. I have followed the same structure as the paper in my review, using the same headings as found in the paper, for the most part.

Introduction

pg. 7815, lines 12-14: "...contact freezing which is believed to initiate ice at the highest temperatures..." Biological particles are the highest temperature ice nucleators. Pseudomonas syringae catalyzes freezing at temperatures approaching -3 C [Levin and Yankofsky, 1983].
We did not mean to talk about the efficiency of single aerosol species. What we wanted to do was to introduce contact freezing as the pathway by which ice forms at the warmest temperatures. The sentence was changed to: "contact freezing which is believed to be the pathway by which ice forms at the warmest temperatures for a given IN type"

The sentence following that one is a little misleading in my opinion. I agree that scavenging processes could lead to contact nucleation. They could also lead to immersion nucleation. I don't think it is correct to say "The high freezing onset temperature due to contact nucleation could be partially attributed to scavenging processes..." Contact nucleation can be a result of scavenging processes, but I don't think we know enough about the mechanisms underlying contact nucleation to say that it is effective at higher temperatures <u>because of</u> the scavenging processes.
Scavenging processes could lead to immersion freezing if the aerosol particle that collided with a supercooled droplet did not cause any freezing. This may strongly depend on the particle penetration rates. As stated in section 3.1 "Gokhale and Goold Jr (1968) and Gokhale and Lewinter (1971) showed that the AgI particles remain at the droplet surface after the collision, i.e., there is no particle penetration into the droplet". This needs to be further investigated to confirm or refute these observations. It is very likely that this behavior is particle type dependent.
This sentence was changed to: "Although contact nucleation can be a result of scavenging processes, the reason of the high measured freezing onset temperatures is still unknown".

Theory behind contact freezing

Contact freezing is certainly convoluted with scavenging processes. That can also be said of immersion freezing. I think it would be useful to make that point here, as well as in the discussion in section 3.6.
This is now clarified in section 2. We did not make any change in section 3.6 since this is already explained and illustrated in Figure 15.

Freezing efficiency

Equation 1 is certainly correct, but it is worth noting that a droplet need not be falling to collect aerosol particles. Particles can diffuse to the droplet in still air.
The chance of particle diffusion was added to this sentence.

Theories about contact freezing

IN solubility

It isn't clear to me that partial dissolution should result in a decrease in IN activity. Fletcher even addresses this in the article where he says, "While this might in some cases increase their [the active sites'] activity, it is more generally likely that it will be reduced." There's no evidence to support that assertion in the remainder of the paper. If active sites can be destroyed as water partially dissolves a particle, why can't that process create sites as well?
We acknowledge that it is conceivable that active sites may be created as well, but we do not know enough about that.

I realize that the authors are reporting the information in the paper. However, I do not think it is out of line to raise such questions in a review, especially in an area such as contact nucleation, where there are so many open questions.
This point was added to this section in the revised manuscript.

Ice embryo formation and its size

I disagree with the criticism of Cooper's theory raised in the last sentence of the section (lines 13 to 15). (I realize that this criticism goes back to Pruppacher and Klett [1997], but I think the statement as it stands in this paper is too broad.) The criticism raised in Pruppacher and Klett [1997, pg. 340] is that water vapor density decreases rapidly as a droplet falls in subsaturated air, and water saturation is reached only at the droplet's surface. They go on to state that this implies a dependence on the relative humidity of the air and on the droplet size.
This statement was modified to be more precise.

Droplets need not be falling in subsaturated air for contact nucleation to be effective. Contact nucleation can happen in a cloud, where the relative humidity is quite high (even greater than 1). There are certainly interstitial particles in clouds that are potential contact nuclei.
We agree with this statement; however contact freezing can also take place in subsaturated conditions (e.g. at the cloud edges where entrainment can take place). At these conditions thermophoresis will be very important to enhance particle collision with supercooled drops.

The mechanism described in Cooper [1974] does not require saturation with respect to water. If the particle encounters a humid environment, it will have water adsorbed to its surface. While it is true that a more humid environment will lead to more water adsorbed to the surface, the humidity doesn't have to be 1. Cooper does assume water saturation for the feasibility

calculations that he presents (see Cooper [1974], pg. 1834, second full paragraph), but the theory doesn't depend on a region saturated with respect to water. (The plots of theoretical FE in Figure 12 of this paper show that water saturation isn't required for Cooper's mechanism to work.)
We agree with you and revised our statement accordingly.

Cooper does make some estimate of the time scale required for the equilibrium population of deposition (and therefore contact) embryos to be established on the surface of a particle (see section 7b of Cooper [1974].) His estimate is less than 10^{-4} sec. Once an aerosol particle is close enough to a droplet to have a likelihood of colliding with it, it will almost certainly be within the same turbulent eddy (if the air is turbulent). In that case, the thermal velocity of the aerosol particle is a good estimate of the relevant closing velocity between particle and droplet. That's about 1 cm sec^{-1} for a particle of 500 nm diameter. If the relative humidity field around the droplet is 80% or more out to 10 mean free paths (gas phase), which is on the order of 1 μm (~ 100 nm x 10), then the particle will be in the high relative humidity environment for about 10^{-4} sec. Even in that extreme case, the particle should have a population of embryos on its surface.
We thank you for clarifying these points. The most relevant statements were added into this section in the revised manuscript.

I think the Comment on Cooper's original paper [Fukuta, 1975b] and Cooper's Reply [Cooper, 1975] are worth including as references in this section.
Both papers are now referenced in the revised manuscript.

Mechanical disturbances
As I understand Fukuta's proposed mechanism [Fukuta, 1975a], it does not depend on the energy of the collision. Inspection of Equations 7 and 8 (this paper, lines 3 and 4 on page 7823) show no obvious parameter that depends upon the aerosol particle's speed of impact, for example.
You are right. We corrected this in the revised manuscript.

The key element in Fukuta's mechanism is the alteration in the surface energy between the water and aerosol particle as it comes into contact with the air-water interface of the supercooled droplet of water. The total free energy barrier is lower because γ_{CL} is higher as a result of the restructuring of the adsorbed water on the particle as it comes into contact with the bulk water of the droplet. That restructuring results in a momentarily higher surface energy between the particle and liquid. The way Fukuta explains the mechanism, that restructuring is not a result of kinetic energy from the impact of the particle, but is instead a response of the water molecules adsorbed to the surface to the new environment - i.e. immersed in liquid water instead of air.
This clarification was added to the revised manuscript to reflect Fukuta's ideas.

Fukuta does not address this in his paper, but I see no reason why this mechanism wouldn't work if the particle were initially on the inside of the particle, and then diffused to the surface. The key element of the argument is a change in the environment. The structure of water interacting with the substrate (i.e. particle) would change as the particle emerged from the bulk.
We added a small note in section 2.3.3 where your suggested point was added.

Comparison of Fukuta's and Cooper's mechanisms[1]

The similarities are striking. Both mechanisms are framed in terms of water adsorbed to the surface of the potential contact IN. Both depend on the relative humidity. (Fukuta's mechanism doesn't explicitly address this, but a higher relative humidity implies more adsorbed water, which implies a greater potential for change in the surface free energy as the adsorbed water restructures.)

Cooper's mechanism explicitly predicts a size dependence. A larger surface provides a greater probability of forming the critical embryo necessary to trigger nucleation once the contact nucleus actually reaches the droplet's surface. Fukuta says that his mechanism is independent of the size of the particle (see Fukuta [1975a, 2nd point in section 5]), but I disagree. Figure 1 is a schematic of why. Water is adsorbed everywhere on the particle's surface; when the particle comes into contact with the surface of water, all of the adsorbed water will be changing structure, which is the critical point in Fukuta's mechanism. Thus, any part of the surface of the contact nucleus which comes into contact with the droplet may initiate freezing and so the efficacy of the particle as a contact IN should scale with its surface area.

[1] This heading does not correspond to one in the paper.

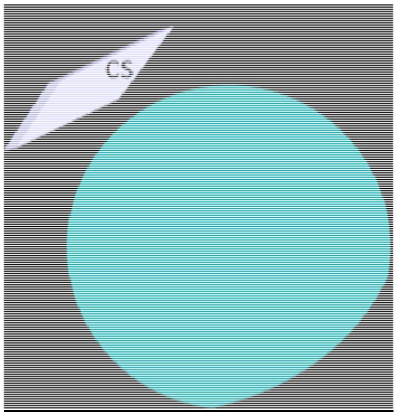

Figure 1: Schematic of an idealized contact nucleus approaching a super-cooled droplet of water. (Not drawn to scale.) The surface labeled CS will have water adsorbed to it. In both Cooper's and Fukuta's proposed mechanisms, nucleation can be initiated anywhere on that surface which comes into contact with the droplet's surface. Therefore, both mechanisms predict a dependence on the size (i.e. surface area) of the contact nuclei.

We thank you for sharing your thoughts and ideas with us. The above mentioned similarities between these two theories are now added to section 2.3.

Three phase contact

I think that discussion of work by R. Sear [Sear, 2007] is warranted in this section as well as that by Djikaev and Ruckenstein [2008]. Sear shows that nucleation is favored at the three phase contact line. The results are based on thermodynamic arguments, but include kinetic aspects as well. Though the work is in the context of spins (a Potts model), Sear makes the case that the results are general.

The results from Sear [2007] are now discussed in this section of the revised manuscript.

Since this review first appeared, Gurganus et al. have a new paper [Gurganus et al., 2013]. They have done a more comprehensive analysis and still see no preference for nucleation at the three phase contact line.
This paper is now referenced in the revised manuscript.

Experimental results and discussion

Cold plate

There are two types of cold plate experiments described in this section. There are static cold plate experiments like those described in Shaw et al. [2005] and Fornea et al. [2009] and then there are more dynamic experiments where the droplets are supported on a cold stage, but the aerosol particles impact the droplet from the air, like, for example, Fukuta [1975a] and Bunker et al. [2012]. (Bunker et al. [2012] is not listed in Table 2.)
The Bunker et al (2012) study was added to Table 2. In the revised manuscript we distinguish between the static and the dynamic cold plate.

The first sentence of the second paragraph of this section (pg. 7825, lines 5-6) is true of the static experiments, but isn't necessarily true of the second type. Cold plate experiments do observe fewer freezing events (i.e. fewer droplets) than do flow through cloud chambers, for example. However, the cold plate experiments where aerosol deposit to the droplet from the air can access freezing efficiencies of 10^{-4} and lower. In those cases, the statistics of the number of particles which interact with the droplet is greater than most other techniques.
A clear distinction of the statistics between the static and dynamic cold plate is now made. The advantages of the dynamics and static cold plate are also defined in the revised manuscript.

pg 7826, line 7-9: "The IN efficiency..." I think this statement is more appropriate in section 3.5.
This sentence was moved to section 3.5 as suggested.

Electrodynamic balance (EDB)

The authors are probably aware of the two papers from the KIT group that have recently appeared, Hoffmann et al. [2013a,b]. I find the discussion of collision efficiency and freezing efficiency in the context of pg. 7829 hard to follow. Collision efficiency, defined on page 7817, is the fraction of particles in the volume swept out by a falling droplet which are actually collected by the droplet. The freezing efficiency, FE is then (see Equn 3) the ratio of number of frozen droplets to the number of particles collected. I disagree with the statement "The RH_w dependence of contact nucleation is hard to understand as the collision efficiency (Sect. 2.1 and Fig. 2) decrease with increasing RH_w due to thermophoresis." The collision efficiency affects the number of particles that the droplet collects, but the freezing efficiency explicitly accounts for that. The freezing efficiency may be 1 or 10^{-6} regardless of what the collection efficiency is.
References to the Hoffmann et al. [2013a,b] papers were added in this section and also in several other parts of the revised manuscript.
We think that the above mentioned statement ("The RH_w dependence of contact nucleation is hard to understand as the collision efficiency (Sect. 2.1 and Fig. 2) decrease with increasing RH_w due to thermophoresis.") is correct. The FE is independent of the collision efficiency. To derive FE from experimental data (FF) we need to know the CE though.

What this formula really means is that the FF depends on the number of collisions and therefore CE.

The authors discuss the dependence of FE on the relative humidity elsewhere in the paper. Cooper's mechanism should depend on RH_w, as should Fukuta's. The curves from theory in Figure 12 are also functions of RH_w. From that point of view, the dependence on RH_w is readily explained.
We agree that the RHw dependence is discussed in several parts of the manuscript. However, it is necessary to add this discussion here since Svensson et al (2009) is the first laboratory study reporting the effect of RHw on FE. In addition to it, the CE theory could not support the observations made by Svensson et al (2009) as mentioned in the above comment.

Freezing efficiency results inter-comparison

This is the most relevant section as far as comparison of results from different experiments. The frozen fraction is of very limited utility because the number of aerosol particles which have been deposited to the droplet is unconstrained. This is known from studies of immersion freezing, for example. In my lab, I see threshold freezing temperatures of -3 C in the immersion mode for kaolinite, but the concentration of dust in water is such that the mixture looks like strong coffee with cream in it. If I wanted a threshold freezing temperature relevant for the atmosphere, I'd use data from Murray et al. [2011], for example, where the concentration of dust in water is much lower.
It should also be noted that there is still some ambiguity in the data shown in Figure 12 because in a few cases (Svensson et al. [2009] and Pitter and Pruppacher [1973]), the size, and therefore the surface area, of the particles that hit the test droplets are not well known. Hoffmann et al. [2013a] argue that freezing efficiency scales with the surface area.
We agree than the number of particles within a liquid a droplet (or the contained particle surface area) may strongly affect the threshold freezing temperatures on immersion freezing. That is one of the reasons to add section 3.6 in our manuscript. The limitations when comparing contact and immersion freezing are presented and a new approach to better compare these two modes is introduced. We agree with the ambiguity in the data shown in Figure 12 since both studies (Svensson et al. [2009] and Pitter and Pruppacher [1973])) used polydisperse aerosol particles whereas the other studies presented in Figure 12 used monodisperse particles. This is shown in Table 1.

The most striking part of Figure 12 is that the data is quite scattered, spanning eight orders of magnitude over 30 degrees. Clearly there's some room for improvement! I think it would also be worth noting that not only does the data not agree so well in the few areas where the temperature range of different experiments overlap, but the temperature dependence indicated by the data is strikingly different. The shallow slope seen in the data from Pitter and Pruppacher [1973] is quite different from the sharp temperature dependence exhibited by data in the high RH range for Svensson et al. [2009].
The agreement or discrepancies between the theoretical and experimental activation slopes is now described in more detail as suggested.

The data from Pitter and Pruppacher [1973] are shown as three separate curves, corresponding to three separate estimates of the number of kaolinite particles which collided with the test drops in their wind tunnel. They estimate in the paper that each droplet collected a few thousand particles before freezing. I recommend plotting their data as the best guess with an uncertainty to show the range they state. The other data on the plot correspond to experiments, not to experiments with different estimates of the number of collisions. It will help readers interpret the figure if all the data is treated in the same manner.

The blue stars in Figure 12 show the estimated FE values using the frozen fractions reported by Pitter and Pruppacher [1973] and assuming N_{coll} = 1000. This value is the best guess for this data set (the authors reported that a drop of 325 μm radius captured several thousand particles during the time the clay particles passed by the drop). In addition, we also calculated the FE values assuming higher (10^4) and lower (1) concentrations for N_{coll} to understand the sensitivity FE on N_{coll}. We added that to Figure 12.

This is the section where I would include the statement made on pg. 7826, comparing results from cold plate studies to other techniques. It is quite difficult to make comparisons between the techniques at this time because the temperature ranges barely overlap, and other experimental conditions are also not well constrained.

The paragraph was slightly modified and the suggested sentences were moved to this section.

Contact freezing versus immersion freezing

Papers by Roberts and Hallett [1968] and Niemand et al. [2012], which explicitly cite the fraction of particles that were active as ice nuclei in the immersion mode as a function of temperature, are relevant for this section. The numbers they cite are quite useful to put the numbers from Figure 12 into context.

The suggested references were added to the revised manuscript.

Conclusions

The mechanisms for contact nucleation proposed by Cooper [1974] and Shaw et al. [2005] are offered as the "... the most promising ideas." for mechanisms without explanation. I have no quarrel with the authors offering their opinion. (I think a carefully reasoned, expert opinion is one of the benefits of a good review.) In this case, I would like to hear why the authors believe these two mechanisms are the most promising. What is it about the mechanisms offered by Fukuta [1975a], for example, that make them unpromising?

An explanation is provided in the revised manuscript. Additionally, we also added Fukuta's theory noting the similarities between Cooper's and Fukuta's mechanisms.

pg. 7841, lines 7-10: Not all cold plate experiments used large particles. The static ones do, but the dynamic ones like Bunker et al. [2012] and Fukuta [1975a] use much smaller particles.

This sentence was corrected to indicate that it refers to the static cold plate only.

Editorial and minor comments

- The reference for Fletcher [1970] includes the journal section "Notes and correspondence:" as part of the title of the article.

This was corrected

- pg. 7826, line 6: "... very low calculated FE (~ 1.0^{-5}) ..." Should be "... very low calculated FE (~ 10^{-5}) ..." (i.e. no decimal place)

This was corrected

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