

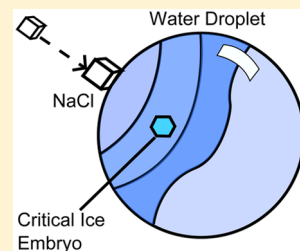
Contact Freezing of Water by Salts

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S Supporting Information

ABSTRACT: Water is unlikely to crystallize homogeneously at temperatures greater than -34 °C. Freezing at higher temperatures is heterogeneous—catalyzed by the presence of a second substance. If that substance is at an air–water interface, then the mode is called contact freezing, and it typically will trigger nucleation at a higher temperature than if the substances were wholly immersed within the liquid. We find that the impact of salt particles initiates freezing in experiments using water droplets at supercoolings of 9 to 16 °C. These results show that contact freezing nuclei need not be effective as immersion mode nuclei. We discuss our results in the context of proposed mechanisms of contact freezing. Finally, we use the time scales for diffusion of heat and of ions and the propagation of a sound wave through the droplet to estimate that contact freezing occurs within 10 ns of impact.



At atmospheric pressure, small quantities of pure water can be cooled to approximately -34 °C before crystallization spontaneously occurs; however, common experience shows that water will freeze at temperatures much closer to the melting point. Such freezing events are heterogeneous and are triggered by the presence of a second substance that acts as a catalyst, reducing the free-energy barrier between the metastable, supercooled water and ice. The degree to which the second substance catalyzes the phase transition varies considerably. Self-assembled monolayers of long chain alcohols can initiate freezing at a supercooling of only one degree,¹ while some mineral dusts may not become effective catalysts until just above the point at which water freezes homogeneously.²

Common experience also shows that if a soluble substance is dissolved in water, both the melting and freezing temperatures are reduced. (Note that while the melting point is a well-defined value, the freezing point is statistical, depending on the volume of water, the rate at which it is cooled, etc.) If both a soluble and insoluble substance are added, the soluble substance depresses the freezing point, but the insoluble substance will act to increase the characteristic freezing temperature of the solution.

The two most studied forms of heterogeneous freezing of water are the immersion/condensation mode, wherein the catalyzing substance is wholly immersed within the bulk water, and the deposition mode, in which an ice crystal forms on the surface of the catalyst directly from the vapor phase. If the catalyzing substance impinges upon the surface of the supercooled water, a third mode is possible, the so-called contact mode. Early work on the topic showed that aerosol particles, which hit a supercooled droplet of water, induced freezing at temperatures higher than if the same particles had been immersed within the droplet.^{3–5} More recent work has shown that the probability of a single aerosol particle initiating freezing upon colliding with a droplet of water at supercoolings of 15 to 25 °C is only 10^{-3} or lower;^{6,7} however, those

experiments also confirmed that for a single particle–droplet collision, contact freezing is more probable than is immersion freezing.

Why is freezing more likely when the catalyst impinges upon the air–water interface? Proposed mechanisms include subcritical ice embryos adsorbed to the surface of incoming particles,⁸ a momentary reduction in the free-energy barrier between water and ice as a result of the heat of wetting,⁹ an intrinsic reduction in the free energy barrier at a three phase contact line,^{10–13} and the presence of small scale features at the contact line.¹⁴ (See Ladino Moreno et al.¹⁵ for a more comprehensive review of theories and studies of contact nucleation.) Knollenberg proposed yet another mechanism for contact nucleation involving soluble substances, having recognized that most of the salts present in the atmosphere are endothermic upon dissolution.^{16,17} Salt impinging upon a water surface induces cooling in the surrounding liquid as heat is absorbed as the bonds within the salt are broken and the resulting ions hydrated. If the water is cooled below the eutectic point for the water–salt system, freezing is possible with the solid salt as a substrate. Alternatively, water may be cooled below its homogeneous freezing limit, inducing freezing before the ions from the dissolving crystal have diffused into the region that has been supercooled to that point.

Most contact freezing experiments have been with insoluble substances, motivated in part by the supposition that a substance likely to catalyze freezing when fully immersed within bulk water might also be likely to initiate freezing in the contact mode. Early work showed that silver iodide, sand, and clay triggered freezing at a higher temperature in the contact mode than in the immersion mode;³ however, in the same article, the authors briefly mention that salt and sugar were also

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contact nuclei, at -11 and -13.5 °C respectively. No discussion was offered as to the mechanism of freezing by a soluble substance. (Note that -11 °C is well above the eutectic point for water and NaCl.)

We have tested six soluble substances (KCl, KI, NaCl, NaI, NaOH, and KOH; chemicals were purchased from Alfa Aesar and Fisher Scientific and used as received) as contact nuclei, using a variation of the technique we developed for smaller particles of mineral dust and bacteria.^{6,18} In essence, the experiment is a cold stage with a temperature-controlled vertical tube above it. Because we wanted to test larger particles (25 μm to a few hundred micrometers diameter), the system is oriented vertically such that the test particles fall onto the test droplets. The distance fallen is such that particles reach terminal velocity and equilibrate with the air temperature within the tube. More detail is given in the [Experimental Methods](#) and the [Supporting Information](#).

In [Table 1](#) we report the threshold temperature, T_0 , as the lowest temperature at which collisions of our test compounds

Table 1. Threshold Freezing Temperature (T_0), 80% Freezing Temperature (T_{80}), Eutectic Temperature (T_{eutectic}), Heat of Dissolution ($\Delta H_{\text{dissolution}}$), and Density (ρ) of the Alkali Salts Tested for Contact Freezing Activity^a

substance	T_0 (°C)	$T_{80\%}$ (°C)	T_{eutectic} (°C)	$\Delta H_{\text{dissolution}}$ (kJ/mol)	ρ (g/cm ³)
NaI	-7	-13	-31.5	-7.53	3.67
KI	-8	-12	-23.2	20.33	3.1
NaOH	-11	-15	-28	-44.51	2.13
KOH	-11	-15	-62.8	-57.61	2.12
NaCl	-12	-15	-21.2	-3.88	2.16
KCl	-12	-13	-10.8	17.22	1.98

^aHeats of dissolution and densities are taken from the *CRC Handbook*,¹⁹ while the eutectics are taken from *Solubilities*.²⁰

with a supercooled droplet produced no freezing events. Below T_0 , all of the substances exhibited freezing. T_{80} is the temperature at which freezing occurred in four out of five tests. The eutectic temperature T_{eutectic} , heat of dissolution $\Delta H_{\text{dissolution}}$, and density ρ , are all taken from values reported in literature.

T_0 clearly shows a dependence on composition, and a decrease in the temperature leads to an increase in the probability that freezing will occur. The majority of tests are performed above the solute–water eutectic, with the exception of KCl. T_0 for KCl is below the eutectic; the equilibrium state is solid salt plus ice. It is possible in this case that ice could form directly from the vapor phase on the falling salt crystal, triggering freezing of the test droplet upon contact. However, we consider it more likely that the crystal began to dissolve as it fell through the droplet's vapor field, following Ostwald's rule of stages, resulting in a metastable solution of dissolved ions.

In these experiments, the collision of the aerosol particle with the test droplet must have triggered freezing. The particles cannot act as catalysts in the bulk liquid at these supercoolings because they would simply reduce the freezing point upon dissolution. (As noted above, KCl is the exception to this.) It has been suggested that the sites that catalyze freezing in the immersion mode (so-called active sites) are also the sites that trigger contact freezing, although it is not known why these domains would be effective at higher temperatures when at the air–water interface than when in the bulk.⁷ In the experiments

described here, the particles have no immersion mode active sites. Thus, freezing must be initiated by the collision. As further confirmation of this, we melted some of the droplets, then cooled them back to the temperature of the original contact freezing test. None of them froze when subjected to this procedure, corroborating our assertion that the phase transition is nucleated by the particles' impact.

We rule out the presence of sites upon the surface of the falling particles that catalyze freezing before they begin to dissolve because droplets have already begun to deliquesce when they collide with the test droplet. Droplets are allowed to reach thermal and evaporative equilibrium before a freezing test begins; the vapor field around it will cause falling particles to take up water and begin to deliquesce, forming a brine layer. Cooper⁸ estimated that a monolayer of water will form on a solid surface as it falls through a vapor field in 10^{-4} s; salt particles do begin to take up detectable amounts of water, even before deliquescence,²¹ so we are confident that the particles in our system have at least begun to deliquesce when they hit the droplet. (See the [Supporting Information](#) for an estimation of the time required for particles to form a layer of brine upon the surface.) In the case of NaI, NaOH, and KOH, the brine layer will be heated above the temperature of the ambient air due to exothermic dissolution and condensation. The condensation of water vapor and the associated release of latent heat will be partially offset in the case of the three endothermic salts. In any case, the particles that collide with the test droplet are not dry solids.

None of the mechanisms^{15,16} of contact freezing listed above are consistent with these experiments, with the possible exception of one proposed by Fukuta, discussed in further detail below. The mechanism cannot depend on the presence of a solid surface,^{8,10,11,14} as there is no solid surface upon which a precritical ice embryo could form. The local cooling hypothesis, proposed by Knollenberg^{16,17} is also discarded because NaI, KOH, and NaOH are exothermic upon dissolution. Water in the vicinity of the aerosol particle's impact is heated, not cooled.

Eliminating most of the proposed contact freezing mechanisms and considering the fact that collisions of 10 μm diameter particles of NaCl with test droplets did not cause freezing in experiments we conducted with our flow-through system¹⁸ leads us to the size of the particles as a possible cause of the freezing. (A more detailed explanation of the tests with NaCl in the flow-through system is given in the [Supporting Information](#).) Larger particles fall at higher speeds and thus create a more pronounced mechanical disturbance upon collision with the droplet. [Figure 1](#) is a plot of the area equivalent diameter, D_{eq} , of dry particles that fell directly onto the microscope slides we use as substrates for the test droplets.

$$D_{\text{eq}} = \sqrt{\frac{4A_p}{\pi}} \quad (1)$$

where A_p is the projected area of a given aerosol particle on the slide. (The mass of salt that collided with the droplets in each of the freezing tests is shown in the [Supporting Information](#). Those masses are determined by measuring the volume of the residue left after the water evaporates.) The majority of the particles that collided with test droplets had diameters between 50 and 150 μm . The distributions for NaI and KI peak at smaller diameters because they are denser, and smaller particles still have the inertia to overcome the counterflow. [Figure 1](#)

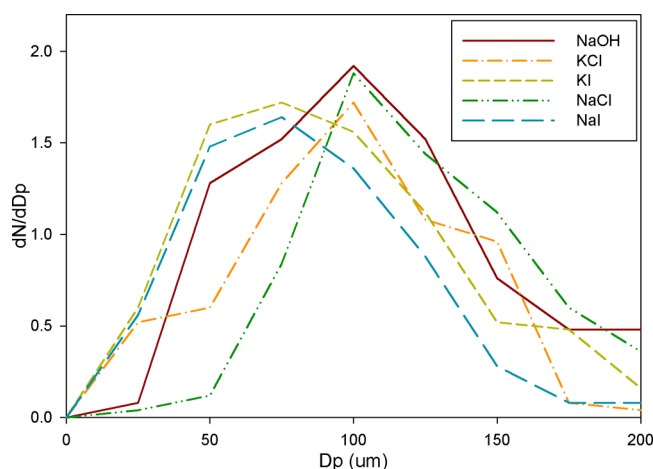


Figure 1. Area equivalent diameter of dry particles that fell through the system. From visual inspection, none of the particles had aspect ratios greater than 2. Because of the counterflow, less dense salts peaked at larger diameters. We were unable to obtain size distributions from KOH because the aerosol particles deliquesced.

shows that the variation in the size distributions among the compounds we tested is not dramatic, which indicates that differences in the sizes of the particles are unlikely to explain the differences in the threshold freezing temperatures that we observe.

To further explore the difference in the freezing efficacy of the compounds, we plot in Figure 2 the highest temperature at

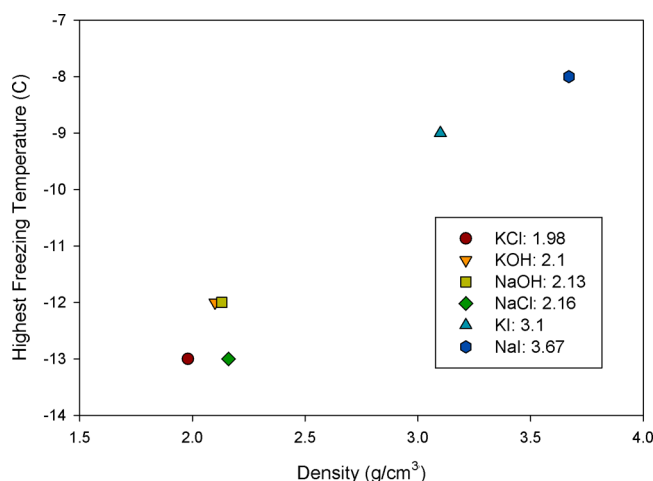


Figure 2. Highest temperature at which freezing was observed ($T_0 - 1$ °C), plotted as a function of the density for all the compounds tested.

which freezing was observed ($T_0 - 1$ °C) for each substance as a function of the density. It scales almost linearly. The most obvious conclusion is that the fall speed is determining T_0 , given that the sizes of the particles are similar, but the densities vary. The lack of correlation with the heat of dissolution leads us to believe chemistry is not playing a dominant role in the freezing process.

The left panel of Figure 3 shows calculated terminal velocities as a function of diameter and density. The velocities of the particles cover approximately a factor of 50, from the smallest, least dense particles, to the largest, most dense. For example, a 25 μm diameter particle of KCl has a terminal velocity of 4 cm/s, while a 200 μm diameter particle of NaI has

a terminal velocity of 200 cm/s. At the time of collision, the particles are moving at or near terminal velocity. Recall, however, that the particles are taking up water as they fall through the droplet's vapor field, so they are accelerating slightly. The calculated kinetic energy carried by particles of a given diameter and density is plotted in the right panel of Figure 3. The natural energy scale for this problem is the magnitude of the Gibbs free-energy barrier to nucleation, ΔG , which Sanz et al.²³ have estimated as $515k_B T$ or 1.84×10^{-18} J for homogeneous nucleation at a supercooling of 14.5 °C. Nearly all particles with a diameter larger than 50 μm carry this energy. If the energy of a particle-droplet collision were such that it somehow triggered freezing, we should see no dependence on the particles' composition.

However, our results do suggest that the collision can introduce energy to the metastable liquid in a way that promotes nucleation. Fukuta⁹ argued that perhaps a transient zone of increased free energy is responsible for the fact that contact mode freezing typically occurs at higher temperatures than does freezing in the immersion mode. As surfaces come very near liquid water, vapor molecules will adsorb to the solid. Upon being plunged into the bulk, these molecules must reorient to accommodate for hydrogen bonds with the liquid structure. The energy associated with that reorientation is the difference in the free energies of the adsorbed molecules and the bulk water, that is, the heat of wetting. Fukuta proposed that the transient increase in free energy at the interface might temporarily lower the free-energy barrier to nucleation in the adjacent layers. Hence the only requirement for an increased nucleation rate upon contact is the continual subduction of adsorbed vapor molecules into the bulk.

In the context of classical nucleation theory, the Gibbs free-energy difference upon creation of an ice embryo upon a substrate (e.g., an aerosol particle) is usually written as²⁵

$$\Delta G = -V_i \Delta \mu + A_{i,l} \sigma_{i,l} + A_{i,s} \sigma_{i,s} - A_{i,s} \sigma_{l,s} \quad (2)$$

where V_i is the volume of the ice nucleus, $\Delta \mu$ is the free-energy difference per volume between ice and liquid, $A_{i,l} \sigma_{i,l}$ is the free energy cost of the ice–liquid interface, and $A_{i,s} \sigma_{i,s} - A_{i,s} \sigma_{l,s}$ is the change in free energy upon replacing an area of the substrate in contact with the liquid with one in contact with the ice embryo. Fukuta noted that the final term in eq 2 is where the transient increase in the free energy due to wetting would manifest itself, as $\sigma_{l,s}$ is increased, lowering ΔG in total. In the experiments described here, the first two terms in eq 2 remain, but the remaining ones are questionable because the particles start to deliquesce before they make contact with the test droplet; however, it is clear that some transient effect, which is a consequence of the collision (e.g., the pressure wave which radiates out from the site of the impact), results in a lower energy barrier and higher nucleation rate.

Although we can only speculate at this time as to the mechanism of contact freezing in our experiments, we can place limits on the time scale in which the freezing takes place. We start by assuming that the nucleation event occurs under the “most likely” conditions, when the water droplet is coldest and before any ions diffuse into the region in which the critical nucleus forms. We see freezing for both endothermic and exothermic heats of dissolution, so we rule out the possibility that dissolution forms a locally cold region that facilitates the formation of a critical embryo. The critical embryo must form before any heat from the exothermic compounds propagates into the pure water. We also rule out the possibility that the

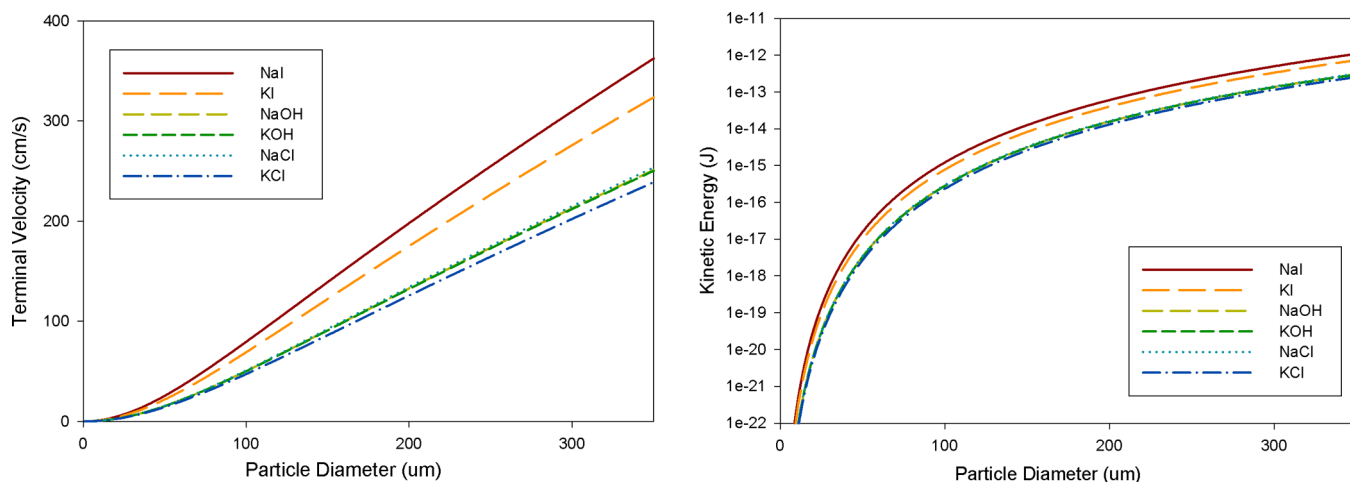


Figure 3. Left: Terminal velocity of spheres of the specified density as a function of the diameter. Terminal velocity is calculated numerically from expressions for terminal velocity as a function of the drag coefficient.²² The salt particles are nonspherical, so the actual velocity will be slightly below the values shown here.²² Right: The kinetic energy follows directly from the terminal velocity, proportional to v_{TS}^2 and D_p^3 .

critical embryo forms on the salt surface itself, as in the case of deposition nucleation, because of the brine layer that forms as the particles fall through the droplet's vapor field.

The time scale for diffusive processes can be estimated as

$$\tau = \frac{L^2}{D} \quad (3)$$

where L is a characteristic length and D is the diffusion coefficient. The diffusion coefficient for ions in water²⁶ and the thermal diffusivity of water¹⁹ are $D_{\text{ions}} = 2 \times 10^{-5} \text{ cm}^2/\text{s}$ and $D_{\text{thermal}} = 0.0014 \text{ cm}^2/\text{s}$, respectively. The other time scale to consider is the time required for a pressure wave to travel the distance L . The pressure, or mechanical, time scale is then simply $\tau = L/v_{\text{sound}}$, where we have taken $v_{\text{sound}} = 1400 \text{ m/s}$. (The variation in the speed of sound with temperature plays a negligible role here.)

Figure 4 is a plot of the three time scales as a function of distance from an impact of an aerosol particle with a test droplet. The plot shows that ions diffuse into the droplet slowly, leaving diffusion of heat and the time for the pressure wave to propagate as limits for a nucleation event. Because the freezing event is triggered by the impact of the particle with the droplet and the fact that a collision has occurred is carried at the speed of sound, the lower bound is set by the time for the pressure wave to reach a given distance away from the impact. Heat released as exothermic compounds dissolve raises the temperature of the water, decreasing the nucleation rate and setting the upper bound for the time scale in which the nucleation even could be triggered. The lower plot in Figure 4 shows the time scales if the freezing event takes place within 100 nm of the impact. The size of the critical nucleus at a supercooling of 14.5°C is $\sim 6 \text{ nm}$.²³ Close to the point of impact, nucleation must be quite rapid, on the order of 10^{-8} seconds.

Much of the research in contact freezing has been motivated by its possible relevance for ice initiation in Earth's atmosphere. The results presented here will not be directly relevant for that because there are very few salt crystals with a size of hundreds of microns at elevations relevant for ice formation; however, the fact that contact nuclei need not be effective as immersion mode nuclei should be relevant in the search for a more comprehensive description of freezing by atmospheric aerosol.

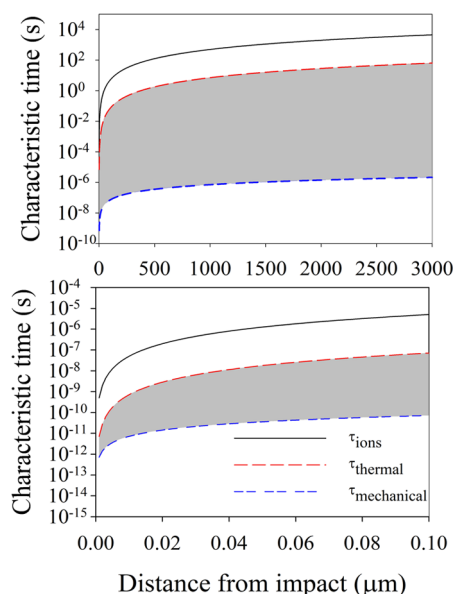


Figure 4. Upper panel: The three characteristic time scales as a function of the distance from an impact of an aerosol particle with a test droplet. The test droplets are $\sim 3 \text{ mm}$ (i.e., $3000 \mu\text{m}$) in diameter. The shaded region shows the bounds for the time scale for nucleation. Lower panel: If the nucleation event takes place within 100 nm of the point of impact, the time scale for nucleation is on the order of 10^{-8} s .

More generally, our results suggest that the kinetic energy from a mechanical disturbance can contribute to a reduction in the free-energy barrier to nucleation, enhancing the probability of a phase transition.

In summary, we have shown that collisions of simple ionic substances with moderately supercooled water will trigger freezing. This effect must depend on the collision itself, as the substances we have used as freezing catalysts would depress the freezing point upon dissolution into the bulk. In other words, we have shown that contact freezing nuclei need not be effective as immersion mode nuclei because none of the catalysts described here will act as freezing nuclei in the immersion mode. These results are consistent with only one of the many mechanisms proposed to explain why contact freezing is typically more likely than freezing in the immersion

mode. Furthermore, because we can estimate time scales for competing processes in the systems we have tested, we can place stringent limits upon the time scale in which contact freezing must be initiated.

EXPERIMENTAL METHODS

Our technique for quantitative measurement of contact freezing of water initiated by the impact of aerosol particles composed of simple ionic substances is based on the same principle as our previous measurements of contact freezing by dusts and bacteria.⁶ Measurement of contact freezing differs from the measurement of other modes of heterogeneous nucleation in that the surface of a supercooled droplet of water must come into contact with an aerosol particle and the subsequent freezing event detected. For quantitative assessment, the number of aerosol–droplet interactions before freezing must be known.

Our basic approach, shown schematically in Figure 5, is to allow aerosol particles to settle at terminal velocity onto a

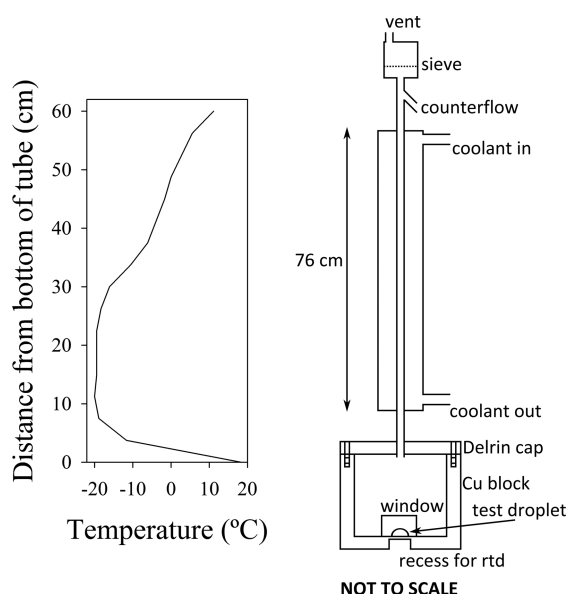


Figure 5. Schematic cross section of the vertically oriented contact freezing system and the temperature profile within the drop tube. The high temperatures near the bottom of the fall tube are an artifact of having the copper chamber open while measuring the temperature profile. Note that the schematic is not to scale.

supercooled droplet. We do this for two reasons. The first is so the speed of impact is known. The second is so the vapor field around the droplet is steady until the aerosol particles pass through it. This is unique from other designs, where, for example, the particles are introduced to the air upstream of the droplet and carried to it by an airflow.^{3,18}

The basic elements of the technique are a particle hopper, a fall tube, and a cold stage. Particles in the hopper are roughly size selected using a brass mesh of known size. Those smaller than the mesh size fall into the tube. A counter flow is used to reject smaller particles ($D_p < \sim 50 \mu\text{m}$). Note that because particles are rejected in the counterflow based on the aerodynamic diameter, which depends on the density of the particles, the size rejected depends on the chemical composition of the particles.

Larger particles (not rejected by the counterflow) fall through the 1/4 in. o.d. tube onto the droplet. The section of the tube above the droplet is jacketed by a hollow PVC pipe filled with coolant. The coolant is kept at a constant temperature with a circulating liquid chiller (Julabo, CF40) to reduce the difference between the aerosol and droplet temperature. The temperature profile is shown in Figure 5.

The test droplets sit directly under the drop tube in a milled copper block, which serves to stabilize the temperature. The block is thermostated with a Peltier element (Ferrotec) driven with an Accuthermo temperature controller (FTC 100). The temperature of the droplet is inferred from an rtd that sits in a recess directly underneath it. The air temperature is also monitored with a type-K thermocouple. The temperature readings of the rtd and thermocouple in the sample chamber were calibrated against the melting point of a droplet of pure water.

The test droplets are 5 μL and sit on a silanized glass slide (Hampton Scientific). Freezing events are detected by focusing a HeNe laser through the droplet onto a photodiode. Upon freezing, the opacity of the droplet changes dramatically, resulting in a corresponding decrease in signal at the photodiode. Freezing is also confirmed visually by opening the chamber after a freezing event is registered by the photodiode.

Because we have used soluble substances, the size distributions of the particles that fall onto the droplets are determined in separate experiments in which a test droplet is not on the cold stage. The aerosol particles fall onto one of the glass slides, which is then removed from the cold stage and examined with an optical microscope. The cross-sectional area of the particles on the slide is determined from an analysis of digital images, using ImageJ. The diameters we report are the area equivalent diameters, derived from the cross sectional area using eq 1. We were able to derive distributions for five of the six substances used. We were unable to obtain reliable distributions for KOH because the particles deliquesced even in the low relative humidity of the lab.

We cannot derive size distributions of the particles that actually fall onto the test droplets because they dissolve. In those cases, we derive the mass of salt that impacted the droplet by removing it from the cold stage, allowing it to evaporate, and then examining the residue of salt left behind. The area equivalent diameter of the residue is derived in the same way as previously outlined. The approximate thickness of the deposit is obtained by turning the slide 90° and imaging the deposits again. Further details of the experiment and sample preparation are given in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

This material is available free of charge via the Internet at <http://pubs.acs.org/>. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.5b01531.

Further details of the sample preparation and other details of the drop tube experiment, experiments with NaCl conducted in the flow-through system, and the time scale for deliquescence. (PDF)

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Notes

The authors declare no competing financial interest.

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