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IS ICE NUCLEATION FROM SUPERCOOLED
WATER INSENSITIVE TO SURFACE ROUGHNESS?

James M. Campbell[1], Fiona C. Meldrum[2] and Hugo K. Christenson[1]*

[1]School of Physics and Astronomy, University of Leeds, Leeds LS2 9JT, UK.

[2]School of Chemistry, University of Leeds, Leeds LS2 9JT, UK.

ABSTRACT

There is much evidence that nucleation of liquid droplets from vapour as well as nucleation of crystals from both solution and vapour occurs preferentially in surface defects such as pits and grooves. In the case of nucleation of solid from liquid (freezing) the situation is much less clear-cut. We have therefore carried out a study of the freezing of 50 µm diameter water drops on silicon, glass and mica substrates, and made quantitative comparisons for smooth substrates and those roughened by scratching with three diamond powders of different size distributions. In all cases, freezing occurred close to the expected homogeneous freezing temperature, and the nucleation rates were within the range of literature data. Surface roughening had no experimentally significant effect on any of the substrates studied. In particular, surface roughening of mica – which has been shown to cause dramatic differences in crystal nucleation from organic vapours – has an insignificant effect on ice nucleation from supercooled water. The results also show that glass, silicon and mica have at best only a marginal ice-nucleating capability which does not differ appreciably between the substrates. The lack of effect of roughness on freezing can be rationalised in terms of the relative magnitudes of interfacial free energies and the lack of a viable two-step mechanism, which allows vapour nucleation to proceed via a liquid intermediate.

Keywords: ice nucleation, freezing, heterogeneous nucleation, topography

*corresponding author: e-mail h.k.christenson@leeds.ac.uk, tel. 441133433879

INTRODUCTION

One of the great open questions in crystallization is the role played by topography in promoting crystal nucleation. It is commonly believed that nucleation in real systems principally occurs heterogeneously on foreign substrates, and as few surfaces in nature are perfectly smooth, surface geometry is potentially a significant factor. Classical nucleation theory predicts a reduced energy barrier in tight concave features such as scratches or pits,[1] which is supported by simulations.[2-6] Whilst there is considerable evidence which suggests that topography is a vital factor in nucleation from solution and from vapour, there is almost no equivalent support for nucleation from the melt.

Nucleation from solution has received the most attention, and a range of organic and inorganic compounds have been shown to nucleate more favourably on roughened than on equivalent smooth surfaces.[7-10] Polymer films with surface nanopores are better nucleants than smoother polymeric films.[11-14] Highly porous materials can also be extremely efficient nucleators, but this requires pores of optimal diameters.[15-20] Studies of crystal nucleation from vapour have provided even more conclusive evidence for the involvement of topography. Chemical vapour deposition of diamond is greatly enhanced on roughened[21-23] as well as porous[24] silicon substrates, and nanoscale pits produced by focussed ion beams (FIB) have been used to direct Ge nucleation on silicon surfaces.[25] We have shown that several organic compounds nucleate preferably on roughened mica surfaces,[26] particularly in highly acute features.[27]

The effect of surface roughness on nucleation from the melt, by contrast, is unclear and there are few data in the literature. Conrad reported water freezing at higher temperatures on rougher surfaces of BaF_2,[28] but the large difference in experimental conditions between the rough and the smooth surfaces used leaves the result in some doubt. Studies of the freezing

of water droplets on superhydrophobic surfaces have either reported no influence of surface topography[29], or the conclusions are uncertain due to the difficulty of separating topographical from chemical effects.[30]

Here, we describe an investigation into the influence of surface topography on nucleation from the melt. We focus on the freezing of water, since this of great importance to a diverse range of phenomena, ranging from cryopreservation and freezing damage to ice formation in the atmosphere. Our work employs the droplet method of studying freezing, in which a large number of small isolated volumes are observed, with the expectation that a majority of them will be free from contamination.[31-36] A patterned hydrophobic monolayer with circular, hydrophilic domains was used to produce a regular array of drops of monodisperse and reproducible diameter. Nucleation on smooth mica, glass and silicon wafer surfaces was then compared to nucleation on those roughened by scratching with three different grades of diamond powder.[26] A rationalisation of the experimental results based on the relative magnitudes of interfacial free energies and the lack of a viable two-step mechanism is then presented.

EXPERIMENTAL SECTION

Substrates used were silicon (boron doped, 450-550 µm thick, Compart Technology), glass ("super premium" microscope slides, 0.9 mm thick, Fisher Scientific) and natural Muscovite mica cleaved on its (001) plane (Paramount Corp., N. Y.). Silicon substrates carried an oxide layer on their outer surface. Diamond powder of three different grades was used: "< 10 nm" (Aldrich), "< 1 µm" (Alfa Aesar) and "40-60 µm" (Alfa Aesar).

Scratching was performed by applying a small quantity of the powder to the tip of a nitrile rubber glove, and rubbing this back and forwards across the surface. Glass and silicon substrates were then cleaned by ultrasonication in 1% Decon 90 solution, followed by rinsing

in water, followed by ultrasonication in each of deionised water, acetone and deionised water, and were finally rinsed in ethanol before drying. Mica substrates were merely rinsed in water and ethanol to avoid damaging the more fragile material. On silicon and glass substrates, the scratching produces a large number of discrete linear grooves across the surface, with smaller grades generating a higher density of finer features. On mica, the whole surface is roughened and shredded. This occurs to a higher degree with larger grades, where an irregular and varied topography is observed. Electron micrographs are presented in Supplementary Figure S1.

Substrates were treated in an air plasma for two minutes (so as to introduce surface hydroxyl groups on mica[37] and increase their density, and to oxidise any pure silicon exposed by scratching) prior to the application of a monolayer of octadecyltrichlorosilane (Acros Organics, 95%). This was carried out by keeping the substrates in a sealed chamber above a pool of liquid silane held at 95 °C for 45 minutes. Substrates were then immersed in acetone for 24 hours to remove any polymerised silane. Advancing and receding contact angles on flat, coated mica substrates were observed to be 103±3° and 87±3°, respectively. A quartz photomask was used to pattern the substrates with a square array of round spots 50 µm in diameter, with 100 µm centre-to-centre nearest-neighbour separation. Substrates were placed on the mask and then exposed to deep ultra-violet light (λ = 254 nm) for 45 minutes, before immersing in acetone for another 24 hours to remove silane from the exposed areas.

The cell used for experiments is shown in Figure 1. Low temperatures are achieved through a constant liquid nitrogen flow, and controlled by supplying a varying voltage to counteracting electric heaters via an Omega CN7200 temperature controller. The substrate sits in a sealed chamber into which the microscope objective can be lowered, and a thermocouple directly below the substrate records its temperature with an estimated absolute accuracy of ±0.4 °C. The relative accuracy between different runs on like materials is better at an estimated ±0.2 °C. Water drop arrays are condensed from the atmosphere by slightly cooling the substrates with the chamber open. When the array is deemed by eye to be fully formed, it is covered in silicone oil (Sigma-Aldrich) to prevent further growth and the

chamber is sealed. Freezing is induced by rapidly decreasing the temperature to -15 °C and then slowly reducing the temperature by 1 °C/ min until all drops are seen to have frozen. A second run is then performed by raising the temperature to 15 °C for one minute, and then lowering the temperature again in an identical way. A camera takes micrographs every ten seconds. Freezing events are judged by eye, evidenced by a sudden increase in brightness in cross-polarised light (on silicon) or by the sudden appearance of structure within the drop (on mica and glass).

Figure 2 shows examples of arrays on each substrate. In each experiment there were about 100 drops in the field of view. Droplets that were visibly misshapen, mis-sized or which contained obvious particulate contamination were not considered.

RESULTS

Freezing studies were performed of arrays of water droplets generated on unscratched glass, silicon wafers and mica substrates, and the same types of substrates after they had been scratched with three different grades of diamond powder. Two runs were performed with each substrate.

Figure 3 shows the freezing data for the first run on each substrate, with the exception of the "40-60 µm"-scratched mica, where the second run is shown (the data for the first run were anomalous and has therefore been excluded, as explained below). On all substrates, the freezing rate sharply peaks at about -35 °C. However, the "< 1 µm" scratched silicon shows a different behaviour from all others, and a significant fraction of the drops freeze prior to this temperature. For this substrate, the freezing temperature of each drop on both the first and second run is shown as a "correlation plot" in Figure 4. It is evident that there is a strong positive correlation between the two runs: i.e. the drops which freeze at higher temperatures on the first run are the same that freeze at higher temperatures on the second (a perfect correlation would result in all points lying on a straight line of gradient one). As the scratches on the surface are abundant under every drop, if they are responsible for enhanced nucleation, then only a very small subset of them can be active. Alternatively, it cannot be ruled out that there could be some residual diamond powder or other contamination on the

substrates, which would make a small proportion of drops freeze at higher temperatures than they otherwise would.

A possible reason for the anomalous behaviour during the first run with the "40-60 µm"-scratched mica became apparent on closer inspection of the micrographs. This revealed that only drops adjacent to already frozen drops were freezing, which was not seen on other substrates. In only a single case was a drop seen to freeze before the four adjacent to it. It is almost certain that freezing events were spreading between drops, where this is possibly due to small volumes of liquid trapped in the many cavities of the highly rough surface. Upon a second run, very few drops were seen to freeze before the main freezing peak, as shown in Figure 5. This might be expected if freezing connects previously isolated small volumes, which are then pulled by surface tension into the larger drops upon melting.

Experiments were also performed on flat substrates of each material at a fixed temperature slightly above the main freezing peak. The results, shown in Supplementary Figure S2, exhibit an exponential decay of unfrozen drops, suggesting a single well-defined nucleation rate.[38]

DISCUSSION

All results are summarised in Figure 6, where the median freezing temperature of each run and the temperature range over which 68 % of the droplets freeze (34% on either side of the median, which is the percentage that falls within one standard deviation of the mean for a normal distribution) is shown. The median values for all samples are very close, and vary only from -34.8 °C to -35.3 °C (with the exception of the anomalous first run with "40-60 µm"-scratched mica). These results therefore clearly show that the type of surface roughness introduced into the substrates here has no effect on the freezing temperature.

It is not possible to say with any certainty whether the sharp increase in nucleation rate at about -35 °C is due to homogeneous or heterogeneous nucleation. The nucleation rates may be estimated from the fraction of previously unfrozen droplets that freeze between two successive micrographs, which is just the probability that there is one nucleation event per ten seconds in that total volume, calculated by assuming that each droplet is a spherical cap. The derived nucleation rates are within the range of literature results presented in Murray *et al.*,[39] although somewhat larger than the average of all data. For example, at -35.0 °C, our nucleation rates for all substrates are in the range from 2×10^5 to 2×10^6 cm^{-3}s^{-1}, compared to literature values in the range 1×10^4 to 2×10^6 cm^{-3}s^{-1}.[39] However, due to the sharp dependence of nucleation rate on temperature, the discrepancy could be almost entirely accounted for by our error in temperature (0.4 °C). Most importantly, the reasonable agreement with literature results gives us confidence that we would be able to detect any significant effects of surface roughness.

It is clear that no scratched substrate gave rise to a shift in the peak freezing temperature, and on only two substrates ("< 1 µm"-scratched silicon and "40-60 µm"-scratched mica) was there significant freezing before this peak. This is to be expected if freezing is homogeneous, as surface topography should not be a factor if nucleation occurs away from the surface. If, however, freezing is heterogeneous, it is clear that the substrate is only having a minor effect, as the freezing temperature is not far above the homogeneous limit. Discrimination between homogeneous and heterogeneous nucleation can in principle be made by studying the dependence of the nucleation rate on drop diameter, but would be extremely challenging in this experimental system. While we cannot of course state that topography is generally unimportant in nucleation from the melt, these results serve to suggest that the importance of topography may not be general (as appears to be the case in for example nucleation from vapour).

General arguments based on classical nucleation theory and the likely magnitudes of surface free energies support this conclusion. The increased rate of heterogeneous nucleation compared to homogeneous nucleation is strongly dependent on the effective contact angle θ of the nucleus on the substrate, and the reduction in the free energy barrier is proportional to the shape factor $S(\theta)$, where[40]

$$S(\theta) = \frac{(2 + \cos\theta)(1 - \cos\theta)^2}{4} \qquad (1)$$

From this it follows that the free energy barrier vanishes for $\theta = 0$ (wetting), and at $\theta = 90°$ it is exactly half of that for homogeneous nucleation ($\theta = 180°$ and $S = 1$). In a wedge or a conical pit the free energy barrier is reduced compared to the planar case, and it decreases with decreasing θ and ϕ, where ϕ is the internal wedge or cone angle (Figure 7).[1, 27, 41] For both a wedge and a conical pit the nucleation barrier vanishes for $\theta \leq (90° - \phi/2)$, but at high θ (above about 150°) the reduction in the barrier is negligible even at low ϕ. The contact angle is ultimately given by a relationship between three interfacial free energies; γ_{NM} between the nucleus and the medium, γ_{SM} between the (solid) substrate and the medium, and γ_{NS} between the nucleus and the substrate, where

$$\theta = \arccos\left[\frac{\gamma_{SM} - \gamma_{SN}}{\gamma_{NM}}\right] \qquad (2)$$

If the quantity $[\gamma_{SM} - \gamma_{SN}]$ in Eq. 1 is negative, i.e. the interfacial free energy between the substrate and the nucleus is larger than that between the substrate and the medium, the effective contact angle θ will exceed 90° and the nucleus will not wet the substrate. Regardless of whether the nucleation is from vapour, from solution or from the melt, γ_{SN} should be the same. Moreover, it is likely to be high, as are most interfacial free energies of

solid-solid interfaces. Since γ_{SM} between the substrate and the melt is likely to be less than γ_{SN} between the substrate and the nucleus, solid nuclei in the melt will generally have a large contact angle; this is in agreement with the common occurrence of interfacial premelting of solids.[42-43] By contrast, in solution, γ_{SM} may be larger or smaller than γ_{SN} depending on the specific interactions involved, whereas in vapour, γ_{SM} between the substrate and vapour is likely to be larger than γ_{SN}. It follows that solid nuclei in a liquid will generally have larger contact angles than those in vapour or in solution. The lowering of the free energy barrier by a surface wedge or conical pit should therefore be much less for nucleation from the melt than for nucleation from either solution or vapour.

There is also a second factor which may make topography relatively unimportant in nucleation from the melt. We have recently demonstrated experimentally that nucleation from vapour in a wedge may often proceed via a two-step process in which supercooled liquid first condenses,[44] and then a crystal nucleates from the supercooled liquid.[27, 45-47] Such a mechanism was proposed for atmospheric ice nucleation some fifty years ago by Fukuta,[48] but to our knowledge was never tested experimentally. However, subsequent to our work there has been renewed interest in such a mechanism in the atmospheric sciences literature,[49-51] and it has been suggested[47] that a similar mechanism might operate in systems where biominerals nucleate from solution via an amorphous precursor phase, e.g. calcium carbonate,[52] calcium sulfate[53] or hydroxyapatite.[54] From the melt, there appears to be no analogous process available.

In conclusion, water drops on silicon, glass and mica surfaces were seen to freeze at a temperature close to the homogeneous limit, and this temperature was unaffected by scratching of the surface using diamond powders. Our data is therefore consistent with the existing literature which reports little effect of topography on crystal nucleation from the

melt. Topography aside, we have also demonstrated that mica, silicon and glass have little to no effect on ice nucleation, which is important to the use of these common experimental substrates in studying the freezing temperature of water. The results presented in this paper are therefore important to the wide range of phenomena which involve ice nucleation from the melt and in particular to our understanding of atmospheric ice nucleation. While the latter is widely believed to be promoted by atmospheric aerosols, existing studies have largely ignored the effects of topography.[55-56] The current data build on existing understanding to suggest that while topography may be important in promoting ice nucleation from vapour (deposition nucleation), it is not likely to play a significant role in nucleation from liquid water (immersion nucleation).

ACKNOWLEDGMENTS

Supporting Information Available: Scanning electron micrographs of smooth and scratched substrates. Plot of fraction of unfrozen droplets as a function of time at constant temperature. This material is available free of charge via the Internet at http://pubs.acs.org.
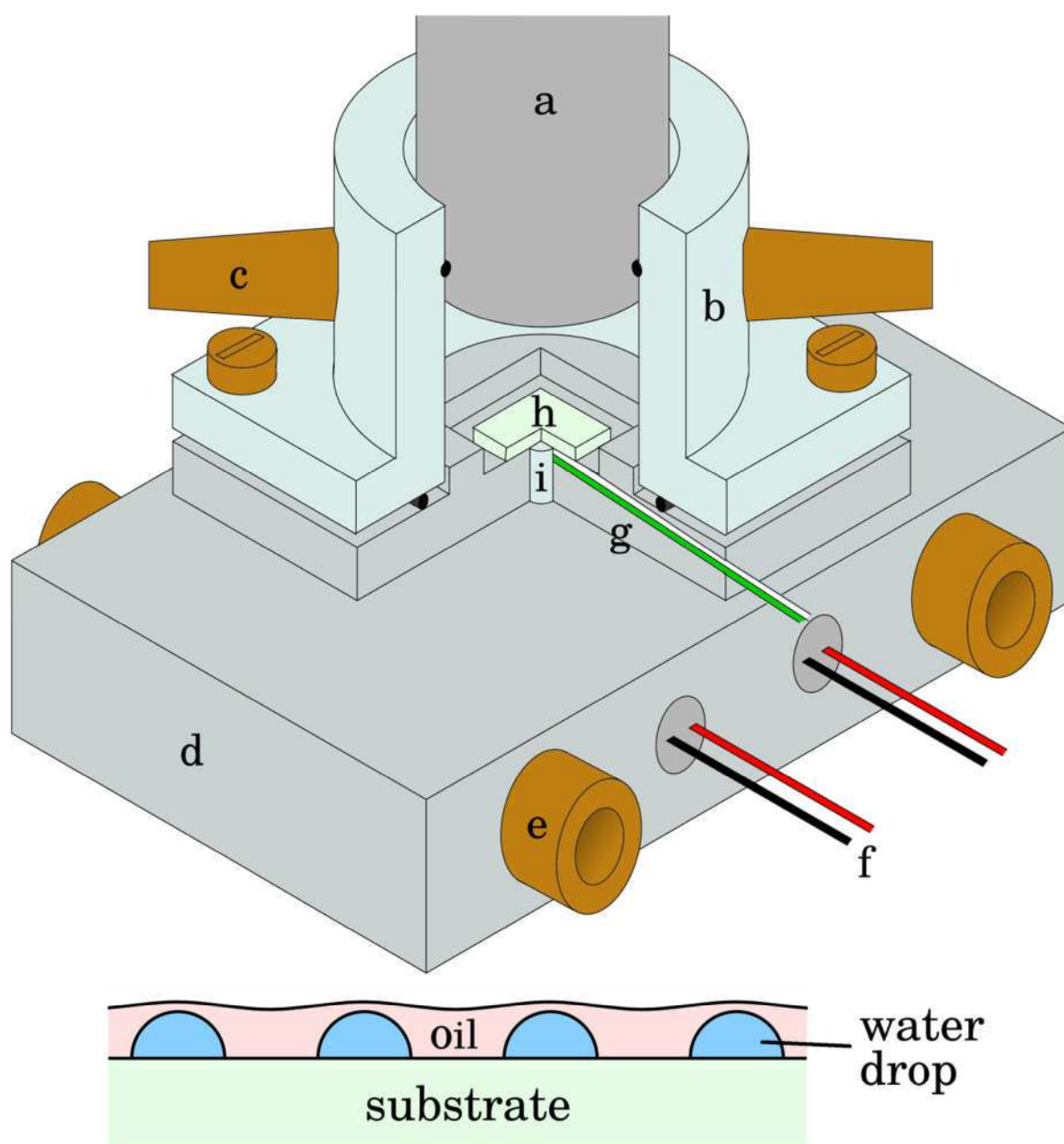
Figure 1. Above: cut-away illustration of the sample cell and cooling stage: (a) microscope objective; (b) Perspex walls; (c) gas inlet/outlet; (d) aluminium base; (e) liquid nitrogen pipes; (f) PID-controlled electric heaters; (g) thermocouple, terminating just below substrate; (h) substrate; (i) Perspex optical port, added after experiments with silicon substrates. Below: illustration of water drops and oil layer on substrate.
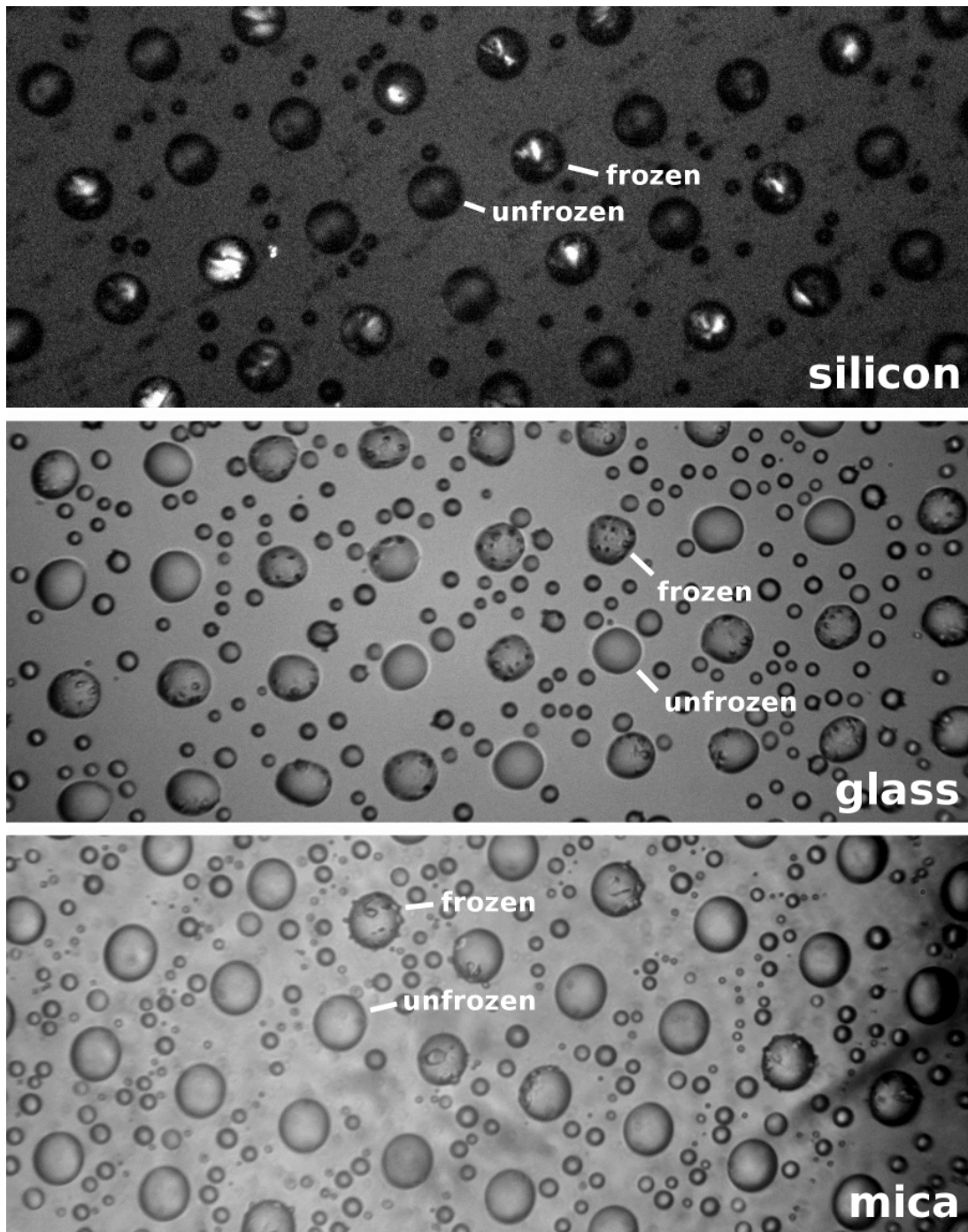
Figure 2. Droplet arrays under oil on smooth silicon, glass and mica, showing both frozen and unfrozen drops. On silicon, frozen drops are identified by appearing bright in cross-polarised illumination, on glass and mica they are identified by the sudden appearance of structure within the drops.
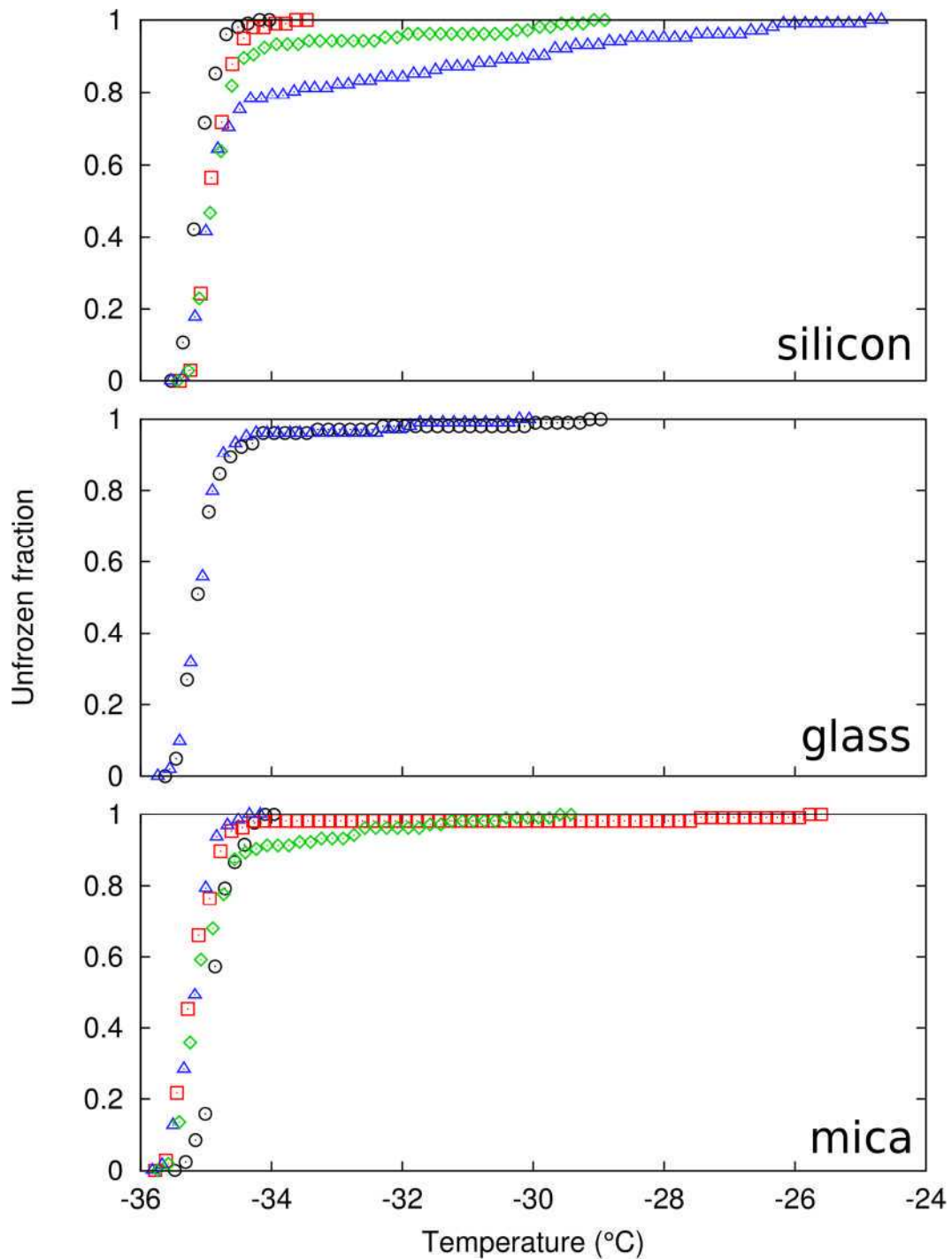
Figure 3. Fraction of unfrozen drops with decreasing temperature on smooth and scratched silicon, glass and mica substrates: (black circles) smooth; (red squares) scratched with "< 10 nm" diamond powder; (blue triangles) scratched with "< 1 µm" diamond powder; (green diamonds) scratched with "40-60 µm" diamond powder. Only one of two runs on each substrate is shown.
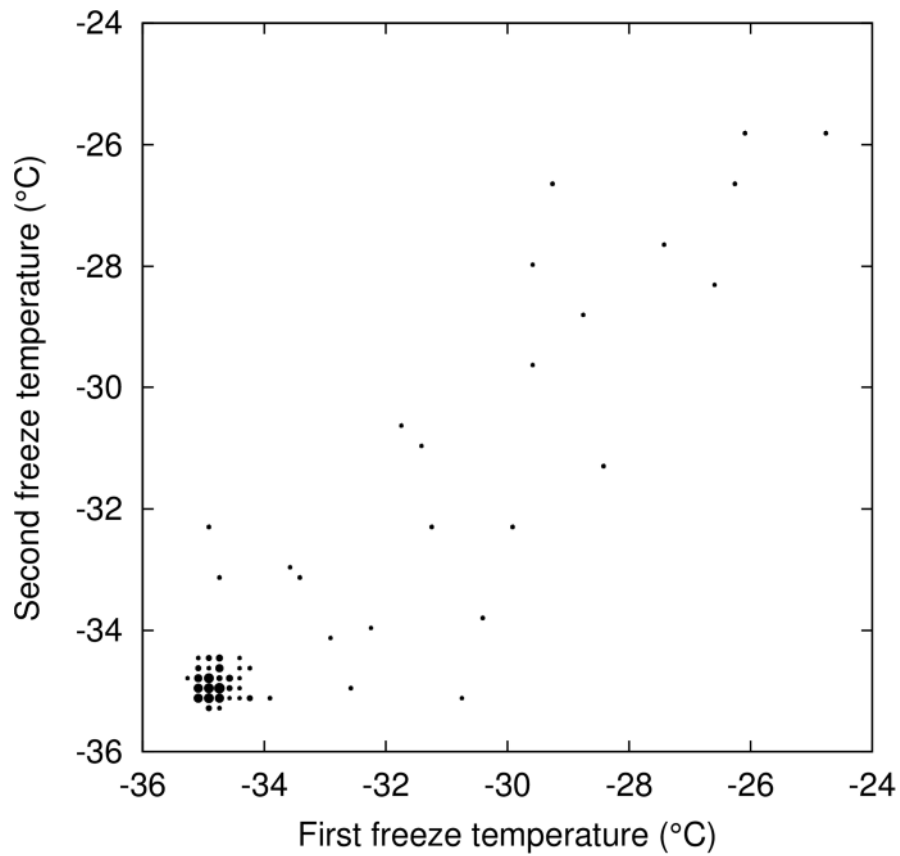
Figure 4. Freezing temperature of each drop on the first and second run on silicon scratched with "< 1 µm" diamond powder, where this shows a strong correlation. The area of each point is proportional to the number of drops it represents.
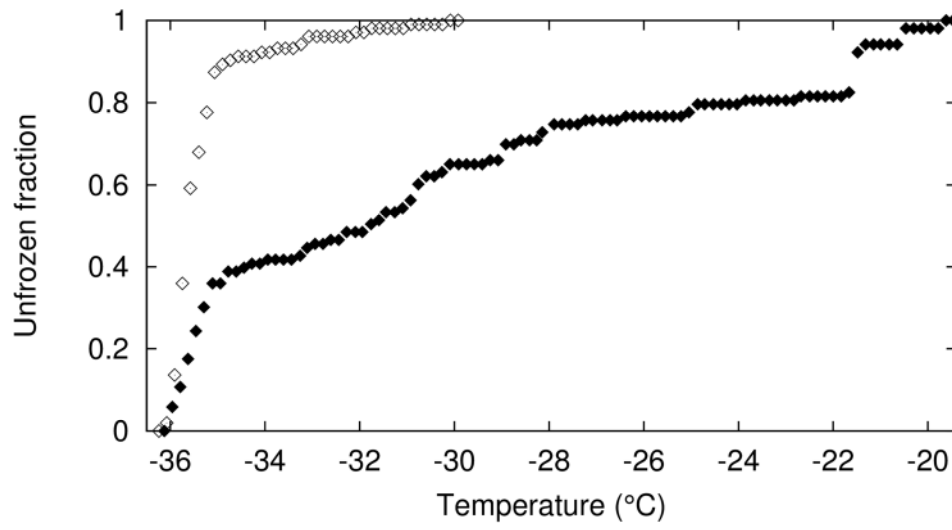
Figure 5. Fraction of unfrozen drops with decreasing temperature on the first (filled symbols) and second (unfilled symbols) run on mica scratched with "40-60 µm" diamond powder.

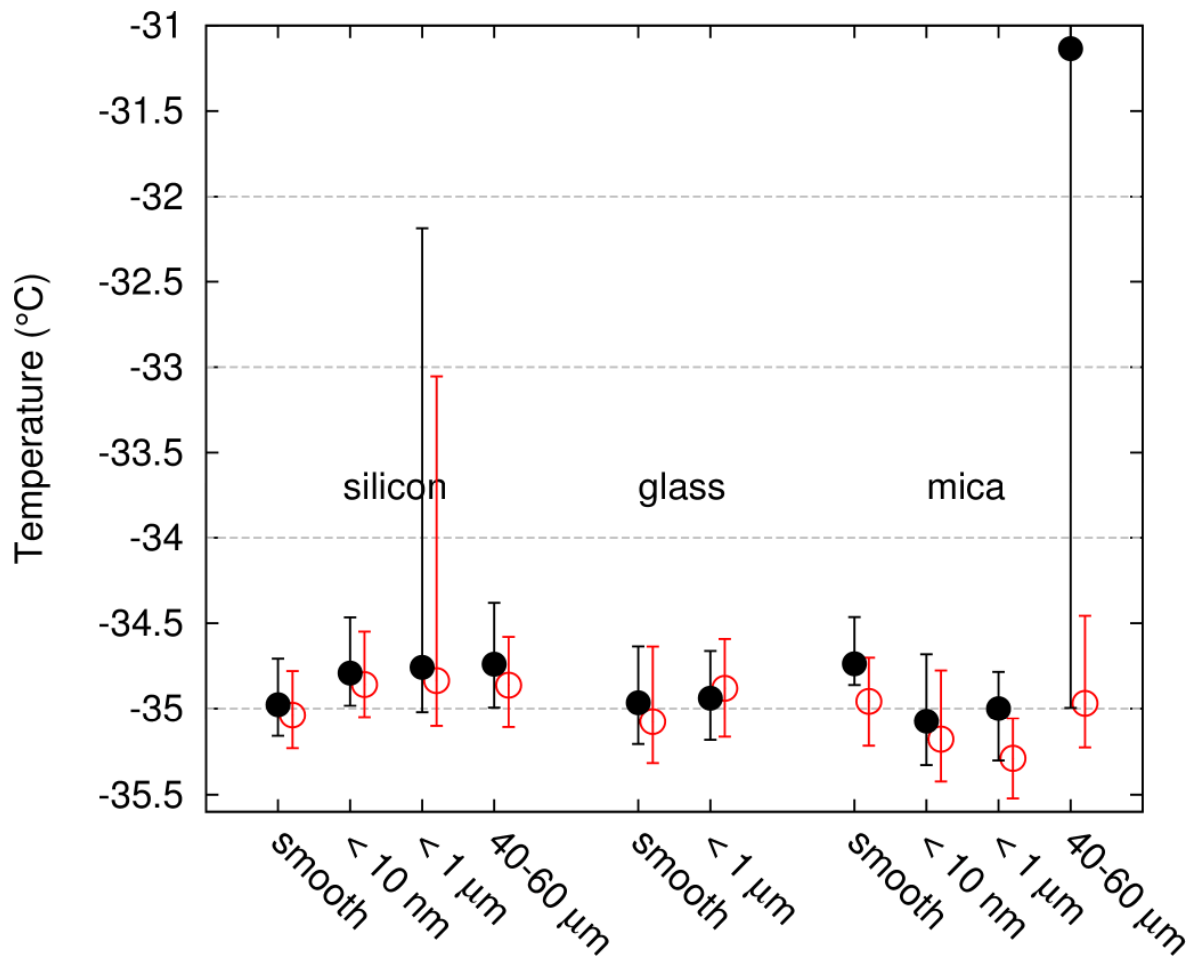**Figure 6** Median freezing temperatures (circles) with the data within 34% of the median contained within the upper and lower bar for first (filled black circles) and second (open red circles) runs on all surfaces, smooth or scratched with the different diamond powders as indicated. The large spread in values for silicon "< 1 μm" and the first run with mica "40-60 μm" is discussed in the text.
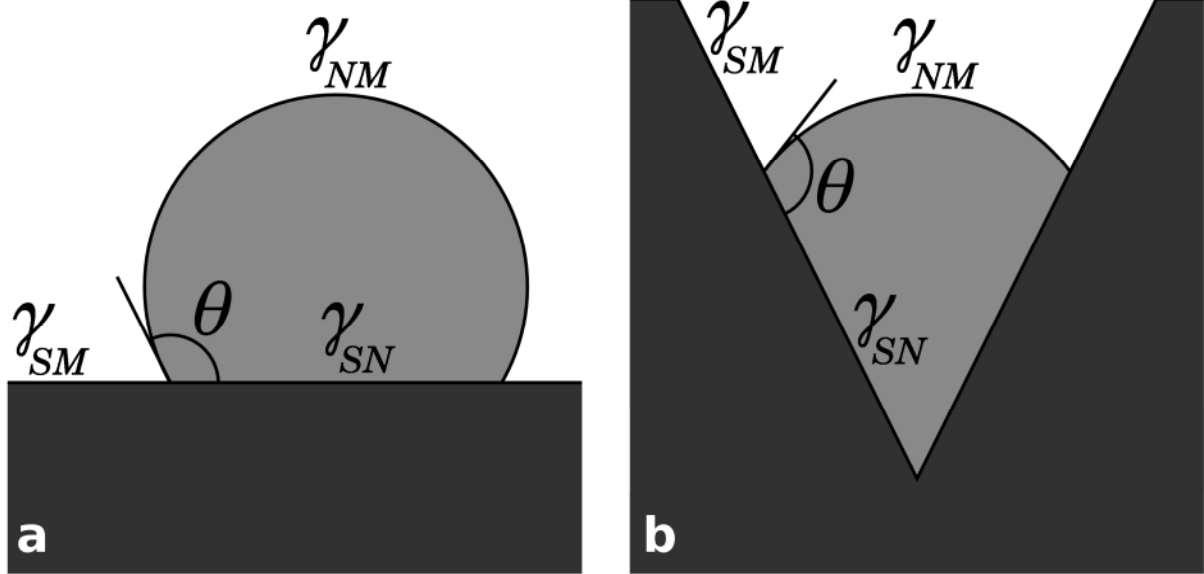
Figure 7   Schematic of a critical nucleus on (a) a flat surface and (b) in a conical or linear wedge. θ is the contact angle of the nucleus on the substrate and γ_{NM}, γ_{SN}, γ_{SM} are the nucleus-medium, nucleus-substrate and substrate-medium interfacial free energies, respectively.

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