Comment on acp-2021-830
Gabor Vali
December 15, 2021

This work is a welcome addition to a rather sparse set of experiments in which freezing of a population of water drops is observed at fixed temperatures. This comment refers principally to that part of the paper. The constant cooling and repeat freezing data are of good quality and are well analyzed.

Experiments at fixed temperatures need to have large sample sizes in order to meaningfully determine the time dependence of freezing and to separate the influences of the distribution of different INPs in the individual samples (drops) from the stochastic time dependence of nucleation[1]. Previous constant-temperature experiments that can be used for the purpose are those by Vonnegut (1948; Vt48), Vali and Stansbury (1966; VS66), Vali (1994; V94), Vali (2008; V08), Wright and Petters (2013,WP13a) and Wright et al. (2013; WP13b). There is no quantitative comparison with these earlier works in acp-2021-830; this comment is aimed at remedying that and to critique what is reported in the paper.

In all the experiments to be examined, sets of sample drops were cooled from above 0°C to the test temperature T_s, held at that temperature for a period time and then cooled again until all sample drops were frozen. In Vt48, the sample was plunged to the test temperature in an uncontrolled way. In subsequent works the rate of cooling was controlled[2].

The parameter best suited to discuss the results of the experiments is the rate of freezing, R_T, originally given as Eq. 3 in V94, and defined as

$$R_T(t) = -\frac{1}{N_{uf}} * \frac{\delta N_{uf}}{\delta t} \quad (1)$$

where N_{uf} is the number (or fraction) of the sample that is not frozen at time t. This function is a more explicit representation of observations than the fraction frozen versus time curves, though some trends can also be seen qualitatively in those curves.

Freezing rates as functions of time are shown in Fig. 1 for four constant temperature data sets. Panel (a) shows the freezing rate extracted from Fig. 5 of Vt48 with data from experiments with 64 water drops on a treated metal plate. Values of R_T were derived by reading numbers off the published graph and then using Eq. 1. Panel (b) is derived from Fig. 4 of Pound (1952) which shows the percent of tin droplets remaining liquid as they are held in a dilatometer at various temperatures for up to 250 minutes. The dilatometer measures the change in volume associated with the solidification. The published graph of percent unfrozen was used to read off changes over various time intervals and then Eq. 1 applied substituting percent unfrozen for N_{uf}. This is not totally valid as the tin droplets were not uniform in size, but the focus here is on the temporal change of R_T which will be relatively insensitive to this simplification. Panel (c) is based on the same data as Fig. 3 in V94, but for only one temperature and not normalized to the rate of freezing at the moment cooling stopped. Panel (d) is based on data in WP13a shown in their Fig. 5. The original data were kindly provided by the authors. Freezing rates were calculated using Eq 1 again making the simplification that the dispersion of droplet sizes in the emulsion used in these experiments doesn't alter the points to be made here.

The four data sets shown in Fig, 1 derive from rather diverse methods and are based on limited sample sizes. Yet, there are common features worth noting:

1. The freezing rate decreases with time in all cases. This is significant because it contradicts the prediction of a stochastic model of freezing of a population of drops assumed to have the same INP content. With that model the rate would remain constant while the temperature is constant.

2. The freezing rate is a function of temperature, as seen in panels (a) and (b) of Fig. 1. This is an expression of the general trend for INP numbers to increase with decreasing temperature.

[1] Another approach is repeated freezing of the same drop and observing the time it takes for freezing to occur.

[2] To simplify this comment, it is assumed that the reader is familiar with the fact that freezing temperatures of drops in a set are spread over a range of temperatures. Also for the sake of brevity, and in view of the relatively minor influence of the rate of cooling on freezing temperatures the impact of the history of the sample prior to arriving at T_s is ignored.

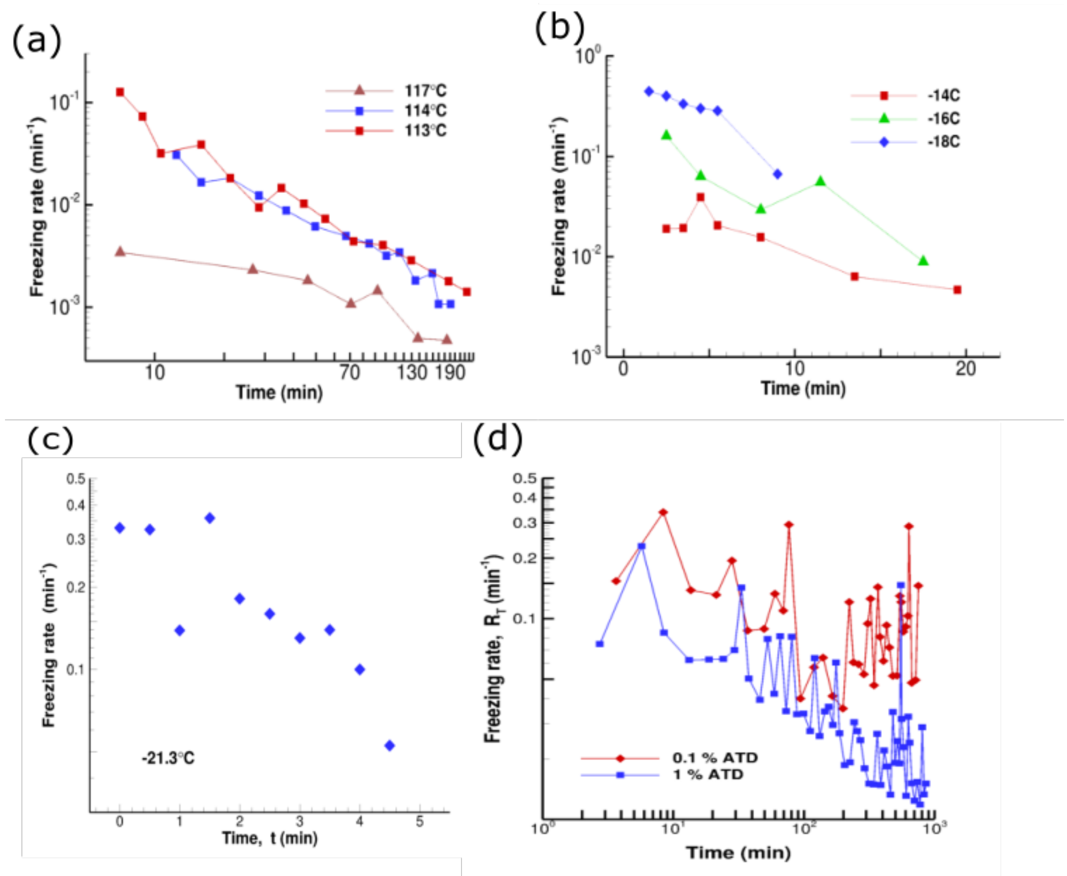

Figure 1. Freezing rate, $R_T(t)$ for four different data sets. (a) Vonnegut (1948), (b) Pound (1952), Vali (1994) and Wright and Petters (2013). See text for details.

3. The function best describing the time evolution of R_T is not necessarily an exponential. A roughly exponential decrease was suggested in V94 from a limited data set and for a water sample that was shown in cooling experiments to have an exponential dependence of the INP concentration on temperature. The data shown in Fig. 1 is insufficient to judge to what extent power functions might be better in panels (a) and (d). There is no *a priori* reason to expect a simple algebraic relationship. Because of the lack of a quantitative theoretical explanation, any algebraic expression must be considered at this time a parameterization of the empirical data.

Results in Fig. 8 and Fig. 10 of acp-2021-830 support the first point in the list above but references to some "natural time scale" and to fast and slow nucleation are not explained. Point 2 is not tested with the current data as only one isothermal temperature was used for each sample.

Regarding point 3, acp-2021-830 employs nested equations requiring three parameters ($\Delta N_{ice,\infty}$, C_i and α) to describe the fraction of drops frozen as a function of time. It is unclear what physical model is there to justify this approach. It also may be noted that the overall trend in Fig. 10, neglecting differences among samples, appears to be a power function similar to two of the panels in Fig. 1. It does confuse matters somewhat, that those examples were obtained for polidisperse drop populations. Incidentally, the large range of three orders of magnitude in R_T in Fig. 10 is somewhat surprising given what is seen in Fig. 8.

In general terms, the results in acp-2021-830 confirm that time is less important than temperature in heterogeneous freezing nucleation. The important issue is how to explain this (secondary) time dependence and to what extent the new data support earlier conclusions. At this point only a qualitative evaluation seems possible but at that level the current results are compatible with the three points listed above. It is less clear to what extent the authors agree with this interpretation of their data, since their analyses are not well explained.

Briefly, the three points listed above summarize aspects of the view of heterogeneous freezing nucleation developed in VS66, V94 and WP2013b. In these papers the freezing rate R_T is shown to be determined by two processes, one related to the stochastic time dependence of embryo growth, the other to the random distribution of INPs of different character in the sample drops. The first process leads to the site nucleation rate function with the characteristic temperature that anchors that function. The allocation of INPs of different characteristic temperatures in the sample drops is described by the nucleus spectrum[3].

The analyses given in ACP-2021-830 may be based on similar thoughts to those summarized in the preceding paragraph. If a closer agreement between the new data and those in earlier publication could be shown that would be a welcome reinforcement of the VS66/V94/WP2013b formulation. This is a crucial point to be clear about, as the interpretation of experiments as well as any effort to construct models of ice nucleation in complex systems like clouds or plants depend on this understanding.

The scheme presented in the paper for incorporating time dependence in cloud models follows the temperature shift approach suggested in V94 but without accounting for the rate of cooling. Regrettably, no comparison is offered with the TDFR parcel model of Vali and Snider (2015).

In all, the excellent device described in acp-2021-830 can certainly yield important inputs to studies of immersion freezing. Results in Section 3.1 show this; the presentation there suffers somewhat from the lack of quantitative error analyses. Only one test temperature in the isothermal experiments (Section 3.2) is a limitation but what data has been generated already is valuable and deserves a clearer presentation and more thoughtful analyses. The value of the parameterization in 3.2.2 could be evaluated by comparison with other, possibly simpler, solutions to the problem. Hopefully, these shortcomings will be corrected in a revised version of the paper and it will become clearer to what extent the results reinforce, or demand re-consideration, of earlier results.

(Dr. Markus Petters is thanked for data and for helpful discussion.)

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[3] Definitions are given in Section 4.7.2 of Vali et al. (2015) for the site nucleation rate, and in Section 4.3 for the nucleus spectrum. The combined process is described in Section 4.7.3.

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