

Using magnetic resonance to validate predictions of the solid fraction formed during recalescence of freezing drops

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Abstract

Nuclear magnetic resonance (NMR) was used to validate a simple model (based on the Stefan number) for predicting the solid fraction formed during the recalescence of a supercooled liquid drop following nucleation. Experimental data were obtained using standard NMR techniques to measure the temporally resolved solid fraction of suspended drops following externally initiated nucleation. The results showed good agreement with the model predictions and also demonstrated the effectiveness of basic NMR techniques for obtaining such non-invasive data for the verification of solidification models.

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1. Introduction

Recalescence is the abrupt temperature rise of a liquid, caused by the release of latent heat from crystal growth initiated by nucleation in a supercooled liquid. The temperature jumps from the nucleation temperature to the equilibrium freezing temperature of the liquid, and a fraction of the liquid is consequently rapidly frozen. In bulk liquids the degree of supercooling is generally small so the solid fraction formed during recalescence is consequentially negligible. With the rapid solidification of bulk liquids (e.g. quenching of molten metals) and the freezing of small bodies of liquid (e.g. suspended drops or falling droplets as encountered during spray freezing operations [1]), a large degree of supercooling can be obtained before nucleation occurs and a significant solid fraction is then formed during rec-

alescence. Fig. 1, for example, shows the temperature transition of a 4 μ l drop of water freezing at the junction of a thermocouple in a cooling air flow [1]. This illustrates the high level of supercooling that can occur with the solidification of such drops. It can be seen that the droplet cooled to -21°C before nucleation. Recalescence is very rapid, with the droplet temperature rising from the nucleation temperature to the equilibrium freezing temperature of water (0°C) in less than 0.04 s. For any model to predict accurately the total freezing time of such a drop, the solid fraction formed during recalescence, needs to be incorporated into the model formulation.

One-dimensional heat conduction models have been developed for predicting the temperature transition and solid fraction formation during recalescence. In these models, the time evolution of the temperature and solid fraction was derived from the solid to liquid interface velocity, where the solid–liquid interface velocity was calculated from kinetic growth data or kinetic models [2–6]. Because of the very high growth velocities,

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Nomenclature

C_{pl}	liquid heat capacity
f_s	solid fraction formed during recalescence
k	proportionality constant
Ste	Stefan number
S	NMR signal intensity
t	time
T	temperature
T_f	equilibrium freezing temperature
t_R	repetition time between NMR spectrum acquisition
T_s	supercooled temperature
t_1	spin-lattice relaxation constant
t_2	spin-spin relaxation constant

Greek symbols

α	^1H density
ΔH_{fus}	latent heat of fusion
ΔT_s	degree of supercooling
ρ	density

Subscripts

l	liquid
s	solid
0	at the supercooled temperature, T_s
f	at the equilibrium freezing temperature, T_f

the numerical problem is often very unstable and solutions often consequently require large computational grids and small time steps or the use of integral profile methods e.g. [3,5]. Feuillebois et al. [7] however demonstrated the use of the Stefan number (Ste) to provide a much simpler means of predicting the solid fraction formed from recalescence.

The Stefan number (Ste) is defined as

$$Ste = \frac{C_{pl}(T_f - T)}{\Delta H_{fus}} \quad (1)$$

where C_{pl} is the liquid heat capacity, T is the temperature of the liquid, T_f the equilibrium freezing temperature of the liquid and ΔH_{fus} is the latent heat of fusion of the liquid. The Stefan number is thus a dimensionless representation of the ratio of the latent to sensible heat in a system; a formal derivation was first presented by

Gill et al. [8]. Assuming that the liquid instantaneously rises to the equilibrium freezing temperature, the Stefan number will represent the solid fraction formed during recalescence. The Stefan number can also be adjusted to compensate for the density difference between the solid and liquid phases. The solid fraction (f_s) formed from recalescence is therefore given by

$$f_s = \frac{C_{pl}\rho_l(T_f - T)}{\rho_s\Delta H_{fus}} = \frac{C_{pl}\rho_l(\Delta T_s)}{\rho_s\Delta H_{fus}} \quad (2)$$

where T_s is the supercooled temperature, ΔT_s is the degree of supercooling and ρ_l and ρ_s are the liquid and solid phase densities, respectively. The Stefan number has been used in a number of numerical models to predict the solid fraction formed from recalescence of drops [1,7–10]. This use has however, to the best of our knowledge, not been directly experimentally validated.

To experimentally measure the solid fraction in freezing liquids, thermograms [11] and differential scanning calorimetry (DSC) can be used. These methods are, however, not amenable to measuring the solid fraction formed from recalescence. This is because firstly they require comparatively large sample sizes, making it difficult to produce high supercoolings (they are difficult to apply to suspended drops) and secondly their data acquisition rates are normally not fast enough to resolve the solid fraction formed from recalescence and that formed by heat-transfer-driven freezing immediately following recalescence. With nuclear magnetic resonance (NMR) spectrometry, the above-mentioned problems can be overcome.

The objective of this study was thus to use NMR spectrometry to obtain experimental data describing the freezing of supercooled drops, to determine whether the simple Stefan number analysis is adequate for predicting the solid fraction formed from recalescence of supercooled water.

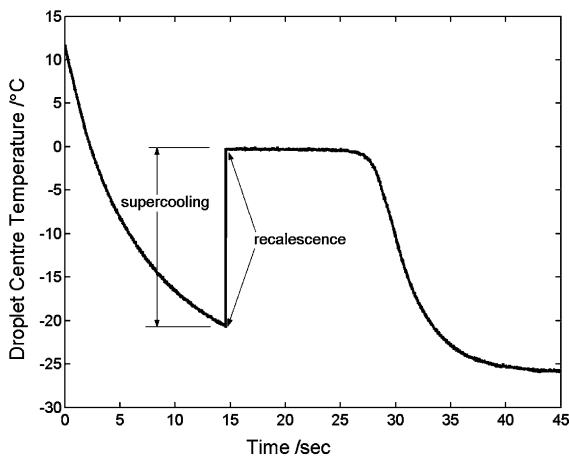


Fig. 1. Temperature transition of a freezing 4 μl droplet of water in a -25°C air flow.

2. Materials and methods

2.1. Experimental method

Experiments were performed in a Bruker DMX 300 NMR spectrometer featuring a 7.04 T vertical bore magnet fitted with a 5 mm diameter ¹H birdcage radio frequency (RF) coil and a Bruker BVT 3000 temperature control unit. The temperature of the sample was controlled via a heater/cold airflow apparatus attached to the bottom of the magnet, and a T-type thermocouple connected to the Bruker BVT 3000. The accuracy of the temperature reading of the thermocouple, relative to the actual temperature of the liquid sample, was calibrated against the temperature-dependent NMR spectral chemical shift of methanol to ±0.4°C, down to a temperature of −20°C [12].

For each experiment, 4 μl of micro-filtered de-ionised water was placed and thus suspended from the tip of a disposable glass pipette. The pipette was then inserted into the RF coil inside the magnet and the temperature lowered to the selected supercooled value. NMR spectra sampling was started and after several seconds, nucleation in the drop was initiated by dropping a small piece of the ice-nucleating agent, silver iodide, into the top of the pipette. NMR sampling was stopped once a sharp drop in the signal indicated that nucleation and recalescence of the water had occurred. This was repeated for a range of supercoolings from 5 to 13 K.

2.2. NMR method

A simple time-resolved pulse-acquire sequence, employing a 90° RF pulse, was used to resolve the spectra. For the time resolution or repetition time (*t_R*) between spectral acquisitions, the magnitude of the acquired ¹H NMR signal, *S*, will be:

$$S = k\alpha \left(1 - \exp \left[-\frac{t_R}{T_1} \right] \right) \quad (3)$$

where *k* is a proportionality constant, *α* is the ¹H density in the sample and *T₁* is the spin-lattice relaxation time of the water. If the signal is acquired at a time *t* = 20 μs after the 90° pulse only the water ¹H are effectively sampled. This is because the spin-spin relaxation time of ice, *t₂* is approximately 5 μs, so that the signal of the ice ¹H will have virtually completely decayed after 20 μs, whilst the decay of the water ¹H signal will be negligible. The spin-lattice relaxation time, *t₁* of water is dependent on the temperature: there will consequently be a change in *S* during recalescence due to the rise in the water temperature. Assuming that the solid fraction formation and temperature rise during recalescence occurs within the repetition time, *t_R* (355 ms was used here), the solid fraction, *f_s*, formed from recalescence can be calculated with:

$$f_s = 1 - \frac{S_f}{S_0} \left(\frac{1 - \exp \left[-\frac{t_R}{t_{1(s)}} \right]}{1 - \exp \left[-\frac{t_R}{t_{1(f)}} \right]} \right) \quad (4)$$

where *S₀* is the ¹H signal at the supercooling temperature, *T_s* (before recalescence), *S_f* is the ¹H signal after recalescence (assumed to be at the equilibrium freezing temperature of water *T_f*), and *t_{1(s)}* and *t_{1(f)}* are the ¹H spin-lattice relaxation times at the supercooling temperature, *T_s*, and at the equilibrium freezing temperature of water, *T_f*, respectively. The ¹H spin-lattice relaxation time, *t₁* of water for supercooled temperatures was measured with an inversion-recovery pulse sequence [13].

3. Results and discussion

Fig. 2 shows the time-resolved ¹H signal for a 4 μl water drop nucleated at −10°C. Prior to nucleation, the signal decays to a steady-state value after several acquisitions, due to the repetition time, *t_R* (355 ms), being shorter than the spin-lattice relaxation time, *t₁* (1390 ms). The steady state signal at 3 < *t* < 15 s represents the signal from the water at the supercooled temperature (i.e. no solid or ice present). The subsequent rapid drop in the signal indicates that nucleation and recalescence have occurred. After recalescence, the more gradual signal decrease signifies the onset of heat transfer driven freezing of the water. In Fig. 2, the points *S₀* and *S₁* used in the calculation of *f_s* (Eq. (4)) are shown: *S₁* is the first acquisition point after the sudden signal drop and *S₀* is the last point before the sudden signal drop.

Fig. 3 shows the *t₁* of water measured as a function of temperature for a supercooled water droplet in the

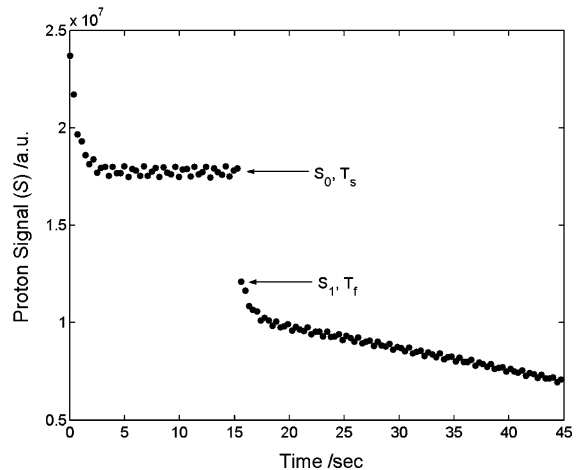


Fig. 2. Time-resolved integrated ¹H signal for a 4 μl of water undergoing nucleation and recalescence at −10°C.

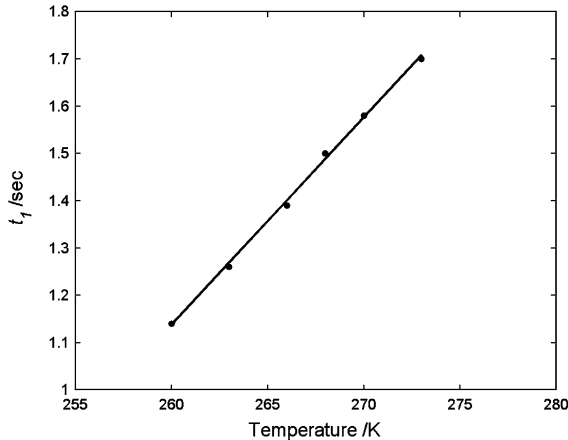


Fig. 3. Spin lattice relaxation time, t_1 of water at supercooled temperatures in a 7.04 T magnetic field. Solid line shows regressed linear fit: $t_1 = 0.044T - 10.29$ ($R^2 = 0.99$).

7.04 T magnet. Using the measured values of S_0 and S_1 and the appropriate values of t_1 (from Fig. 3), Eq. (4) was used to determine the solid fraction, f_s , formed during recalescence. The results are presented in Fig. 4, for a number of droplets frozen over a range of supercoolings, ΔT_s . Also shown in Fig. 4 is the solid fraction predicted by the Stefan number model (Eq. (2)). The results show good agreement between the experimental and model predictions, and no systematic error is evident. The discrepancy becomes more significant (>5%) at lower supercoolings, where the main contributor to this error is most likely the uncertainty

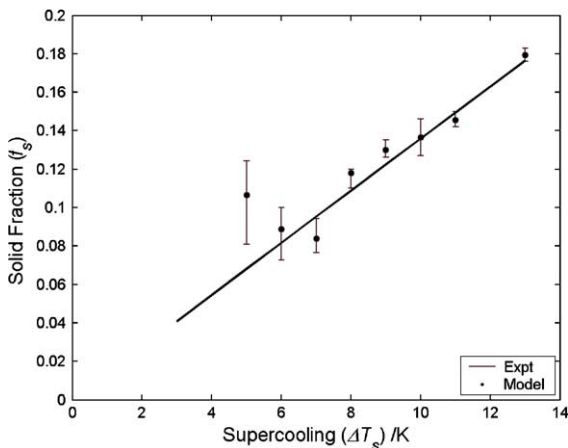


Fig. 4. Solid fraction, f_s , formed from recalescence for different degrees of supercooling of water. The solid line indicates the prediction of the Stefan number. There is good agreement with the experimental data.

in the temperature measurement of the actual drop ($\pm 0.4^\circ\text{C}$).

4. Conclusions

The NMR results demonstrate for cases with 7–18 wt% freezing presented here, that the simple Stefan number model is adequate for predicting the solid fraction formed from recalescence. Clearly this effect needs to be accounted for in any model of the subsequent heat-transfer driven freezing of the drop, which is the focus of ongoing work. In this respect, the study also indicates that NMR has considerable potential for generating experimental data (e.g. solid fractions as a function of time) that can be used to verify models of such solidification in drops.

Acknowledgment

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