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Letter to the Editor

Comments on the article: “Crystallization kinetics with nucleation phenomenon: Ice slurry system” by. T. Kousksou, A. Jamil, A. Arid, S. Jegadheeswaran, Y. Zéraouli, 2012, Int. J. Refrigeration, 35,7, 1921–1930

Commentaires sur l’article “Crystallization kinetics with nucleation phenomenon: Ice slurry system” de T. Kousksou, A. Jamil, A. Arid, S. Jegadheeswaran, Y. ZEraouli, RIF, 35,7, 1921e1930

1. Introduction

The article by Kousksou et al., 2012, is to explain the curve of the temperature on the axis of a cylinder of a few cm^3 filled with water or solutions, cooled, in a bath, down to a temperature low enough to observe supercooling and crystallization.

The main problem concerns the description of crystallization. In fact, the authors copy a description valid in the cases of highly viscous products such as polymers: in these cases, aggregates that appear by nucleation have a rate of development so low that other aggregates have time to form. So the crystallization kinetics is due to the nucleation of aggregates which multiply and grow slowly. This is tempered by the recoveries of the crystallized areas. This is expressed by the Avrami law which is mentioned but not used wisely.

NB: when I use the terms “slow” or “fast” it is in comparison to about the 10 min found for the crystallization time and no of picoseconds which are the life time duration of the germs of ice.

With the water and aqueous alcoholic solutions in question, the crystallization is so fast that it only takes one aggregate to cause crystallization of the entire sample. In reality, the energy due to the latent heat is sufficient to heat the sample suddenly to the equilibrium temperature. In fact, there is even a large excess of energy, only a portion of the sample is made of crystal, the other part being liquid at the temperature of thermodynamic equilibrium. Thus the explanation of the crystallization kinetics is the heat transfer due to the temperature difference between the region of the axis of the cell at the equilibrium temperature (at the fixed 0 °C for water) and the periphery of the cylinder whose temperature is the temperature of the bath, at this point lower (less than or equal to the crystallization temperature of the supercooled liquid). We can recognize the reasoning that we used with nodules in tanks (Bédécarrats et al., 1996).

The main author has used such a model (Kousksou et al., 2005).

This mechanism is also presented in the beginning of the article on page 5 and repeated later on page 8 without an understanding of the arguments over the interpretation of this work.

All goes in this model as if there could be perennial supercritical aggregates at temperatures lower than the equilibrium temperature.

Mathematically, if we forget its true physical meaning, $J(T)$ the probability of crystallization, is continuous in the entire model and one cooling, when this model is applied, should not induce a sudden change in temperature and even less a random character for the crystallization.

2. Details

2.1. General

- How the calculation starts? How can we have a sudden crystallization? Unless if the computing of the outdoor

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temperature at $r = R_0$ is not given by that of the bath $T_{\mathrm{bath}}(t)$ represented by the formula (14) [this formula can not be used for the lowest temperatures where the crystallizations occurs (see Fig. 6 $x = 0.22$)] but by the experimental temperature of the cell surface $T_{\mathrm{out}}(t)$ that suddenly changes due to the sudden crystallization in the cell. Let us reason in the case of pure water: the crystallization is observed at −6 °C and considering the function $J(T)$ in Fig. 3(a) of the text, $J(T) = 0.002\ \mathrm{s}^{-1}$. So, if this curve really represents the probability of crystallization of the sample (but I note below that the value derived from the authors' experiments given in Table 1 is not the same), it would take about 500 s (almost 8.5 min) for the near-certainty of the occurrence of a critical aggregate. Experiments show that it is faster than that. Numerical computations (whose details are not given) say nothing about the search for "entire" supercritical aggregates. If we assume, nevertheless, that the calculation has initiated crystallization, formula (20) tells us that the crystallization [because the term $J(T)$], although it induces warming, is almost stopped before 0 °C is reached … and therefore, there would be supercritical aggregates below 0 °C, which has never been observed.

In these last sentences, I am mostly referring to the peripheral zone but, considering the thermal conductivity of water, the temperature change on the axis should not be sudden (intuitively we can say that the curve would resemble the inverse of the final part of end cooling which represents a return to the equilibrium of the whole sample). Not only it is sharp but it goes back to the melting temperature of 0 °C … and the formula (20) indicates that there is no more crystallization since $J(T) = 0$ at thermodynamic equilibrium.

In case of pure water, the liquid–solid equilibrium is an indifferent state, that is to say (fixed pressure) that there is no link between the quantities of each phase in equilibrium and the melting temperature. However, in this case of a phase change very fast, we can admit that if we consider the crystallization fast enough to assume that, in the first moments, it would be an adiabatic transformation, we obtain an equilibrium between of water at 0 °C and a quantity of ice equal to 1.25% per degree of supercooling (c_L/L_F). With a supercooling of 6 K, there is 92.5% water and 7.5% of ice only. The authors are very vague with respect to the initial conditions and have they considered or not this point to define $T(r,0)$ and $\chi_{ic}(r,0)$? If it is the case, they have not solved the model as presented but another according to the reported above (Bédécarrats et al., 1996) describing the evolution of the quantity of ice by an energy balance.

As regards the binary solutions, the variance of the system is 2, and the problem is different: in equilibrium there is a relation between the temperature and χ_{ic}. This is the formula (2). I do not realize what is the formula used by the authors to describe the evolution of χ_{ic}, for example to build the Figures 8. If it is this formula (2) which is used, under these conditions, the resolution is not the one described but again by using a heat balance. If it is the formula (20) which is used, as noted for the pure water, we would be in the case of supercritical aggregates remaining for a long time in a supercooled liquid which is not possible with such water-ethanol solutions.

2.2. *On the identification*

- The determination of the probability function $J(T)$ by an identification method (classical inverse method or genetic algorithm) is an acceptable way, provided that the experiment is the result of a statistical description of the random nature of the crystallization of liquids supercooled (see for example the work on the emulsions by Gibout et al. (2007), cited by Kousksou et al. (2012)). Here, the identification is done by one sample and one crystallization.
- It would have been interesting to have more details on the method of identification by genetic algorithm. In particular, how is it deduced information from (i) the very sharp ascending part of the curve, where there are very few experimental points (sometimes no more than 2) and (ii) the almost flat part (independent of temperature) [pure compound and solution $c = 0.02$] where it is not possible to identify a function of temperature such as $J(T)$? It keeps only the final part of the peak, which itself represents the return to thermal equilibrium and therefore has nothing to do with $J(T)$. Finally, how are used the experimental results at R_0? In fact what is R_0? According to the formula (13), it would be the inner radius of the copper cylinder. In reality, the thermocouple junction is located on its outer surface showing also the "violence" of the release of heat: should we not also consider the energy needed to warm copper and the adjacent layers of the liquid of the bath?

2.3. *On the results of the identification*

- excessive variation of B with concentration: in this term (formula (16) in the text), only σ the surface tension between ice and solution should change with concentration but certainly not with such a ratio $(974{,}000/62{,}157)^{1/3} = 2.5$. In addition it is generally observed that the surface tension decreases with increasing concentration of the solution and not the reverse. The remark by Chégnimonhan et al. (2010), cited by Kousksou et al. (2012), seems more appropriate.
- the effect of viscosity can play only on A. If we adopt the formula given by Turnbull (1956) (cited by Kousksou et al. (2012), A is substantially inversely proportional to the viscosity. It is true that the increase of the concentration of the solution increases its viscosity. We should then have a value of A decreasing with concentration. This is the reverse of what is given in Table 1.
- adjusted R: It is very surprising, given that most of this thermal resistance (according to the formula (13) it is rather the inverse of a heat transfer coefficient) is due to the thickness of the copper and the contact between the copper and the bath, there is such a difference between the experiments due to a change in concentration of the solutions or the effect of temperature. Why such a change (50%) between the pure water and the solution of mass fraction 0.02? Note: the value of R in the formula (13) should be expressed in KW and values of Table 1 are given in $\mathrm{m}^2\ \mathrm{KW}^{-1}$ and thus we do not know what the true authors' calculations for comparison are. In addition this value of R could have been determined, for example, on the part of

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