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Modeling and Validation of the Crystallization Process in Food Sprays

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Abstract

A freezing model for food sprays has been implemented into the computational fluid dynamics code *KIVA-3* and validated with experimental data. The model consists of three stages. In the first stage, the cooling of the droplet down to the freezing temperature is described as a convective heat transfer process in turbulent flow. In the second stage, when the droplet has reached the freezing temperature, the solidification process is initiated via nucleation and crystal growth. It is assumed that the droplet solidification starts on the drop surface and moves towards the center. This inhomogeneous structure is taken into account by a progress variable that accounts for the different heat capacities of the liquid and solid phases. After completion of the crystallization process, in stage three, the cooling of the solidified droplet (particle) is described again by a convective heat transfer process until the particle temperature is close to that of the gaseous environment. The freezing model has been validated by experimental data of a single cocoa butter droplet suspended in air. The subsequent spray validations were performed with data obtained from sprays of a cocoa butter melt in an experimental spray tower.

Introduction

In spray freezing, a liquid is injected into a cold gaseous environment where it breaks up into tiny droplets which subsequently solidify to form a powder. This process has been introduced to food processing by Meryman [1], and has been utilized by Windhab [2] to realize stable forms of food products that do not undergo structural changes after the crystallization process. Further, spray freezing provides fast cooling rates via rapid convective heat transfer, primarily due to the high surface-volume ratio. Therefore, small droplet size means more homogeneous temperature fields for freezing which results in a more uniform micro structure of the powder products.

In the confectionery industry there is a significant interest in understanding the crystallization of cocoa butter (CB) in the chocolate manufacturing process (cf. [3, 4]). CB fat powders are used as an ingredient in chocolate and are used as a seed powder for crystallization in the processing of chocolate masses. With a clearly defined crystalline structure of CB powder, better products with improved qualities, such as storage stability, melting behavior and consistency, can be obtained [2]. Consequently, the study of the CB solidification process is fundamental for the understanding of the resulting crystalline structure.

The crystallization process consists of a nucleation phase followed by crystal growth. The nucleation is the process where, at random locations throughout the liquid, molecules start clustering in a well-defined manner to form tiny crystals. Subsequently, during the crystal growth phase, these tiny crystal structures grow until the entire substance is solidified. During the crystallization process, the molecules arrange themselves into more ordered, lower energy states, and in this process release energy, called the latent heat.

For many substances, the crystallization process begins at temperatures which lie far below the melting point. This phenomenon is called supercooling and is typical for pure substances which lack nucleation agents. The initial crystallization process of a super-cooled liquid is very fast and consequently releases a large amount of latent heat which results in a sudden temperature increase, called recalescence. However, for CB

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the crystallization process starts as soon as the the melting or freezing temperature, T_f, is reached, and there is no supercooling or recalescence. The solidification process of such a substance can be described in three stages, as is the approach taken in this study.

The first stage is the cooling of the droplet which is modeled as a convective heat transfer process. Once the droplet reaches the freezing temperature, the solidification process is initiated via nucleation and crystal growth. In stage three, after completion of the solidification process, the cooling of the solidified droplet (particle) is described again by a heat transfer process until the particle temperature is close to that of the gaseous environment.

The model has been implemented into the three-dimensional computational fluid dynamics (CFD) code, *KIVA-3*. Model validations for a single droplet have been performed by simulating the experimental results of Gwie et al. [5]. In these experiments, a single CB droplet of 2 mm diameter is suspended in an airflow through a cylindrical chamber at gas temperatures of 277 K and 263 K. Subsequently, the model has been validated for freezing CB sprays by comparing simulation results with experimental results obtained at the Laboratory of Food Process Engineering at ETH Zurich.

Freezing Model

The freezing model presented in this paper consists of three-stages.

Stage 1: This stage is modeled on the principles of convective heat transfer. More precisely, the rate of decrease of the droplet temperature, T_d, is described by

$$\frac{\pi d^3}{6}\rho_d C_{p_d}\frac{dT_d}{dt} = -\pi d^2 h_0 (T_d - T_g), \tag{1}$$

where d is the droplet diameter, ρ_d is the liquid droplet density, C_{p_d} is the specific heat capacity of the liquid droplet, h_0 is the heat transfer coefficient and T_g is the ambient gas temperature. Equation (1) relates the rate of change of the droplet temperature to the heat that is transferred between the droplet and the ambient gas. The heat transfer coefficient is related to the heat flux, q_h, by

$$q_h = h_0 (T_d - T_g). \tag{2}$$

The heat transfer from the spherical droplet has been modeled using the Ranz-Marshall correlation

$$Nu = \frac{h_0 d}{K_g} = 2 + 0.6 Pr_d^{1/3} Re_d^{1/2},$$

where Nu is the Nusselt number, K_g is the thermal conductivity of the ambient gas, Pr_d is the droplet Prandtl number and Re_d the droplet Reynolds number. The droplet Reynolds and Prandtl numbers are given by

$$Re_d = \frac{\rho_g \|v_r\| d}{\mu_g} \quad \text{and} \quad Pr_d = \frac{C_{p_d}\mu_g}{K_g},$$

where ρ_g is the ambient air density, v_r is the relative droplet-gas velocity, $\|\cdot\|$ denotes the norm, and μ_g is the viscosity of the surrounding air.

In this study it has been assumed that there is no mass exchange between the droplet and the ambient air. This is because our interest is in applying the freezing model to understand the crystallization behavior of micron-sized droplets, where the mass transfer rates are much smaller than those of the heat transfer. Thus, in our simulations the diameter of the droplets remain constant during the solidification process.

Stage 2: Once the droplet reaches the freezing temperature, T_f, the crystallization process begins. For CB this freezing temperature has been chosen according to Loisel et al. [4] as $T_f = 291$ K. In our model we assume that the droplet starts solidifying from the outer surface towards the center. Hence, during the solidification process, the heat capacity of the semisolid droplet, $C_{p_{sd}}$, is taken to vary linearly from the liquid value of 2.2 kJ/kgK down to the solid value of 1.25 kJ/kgK.

On a graph of the temperature profile, the beginning of stage two is identified by a drastic decrease in the rate of change of temperature of the droplet, as can be seen in Fig. 1 for T_f = 291 K. This is a consequence of the release of latent heat caused by the rearrangement of the molecules to form the crystalline structure. As discussed in the introduction, there is no supercooling or recalescence during the freezing process of CB, and therefore, no sudden increase in the drop temperature occurs. The release of latent heat contributes to the heating of the droplet and in order to take this into account, Eq. (1) has to be modified to

$$\frac{\pi d^3}{6}\rho_d C_{p_{sd}}\frac{dT_d}{dt} = -\pi d^2 h_0(T_d - T_g) + L\rho_d\frac{\mathrm{d}V_f}{\mathrm{d}t}. \quad (3)$$

In the above equation $C_{p_{sd}}$ is the heat capacity of a semisolid droplet that varies linearly between the liquid and solid value, $\mathrm{d}V_f/\mathrm{d}t$ is the volumetric freezing rate and L is the latent heat of crystallization, which, according to Timms [6], has the value L=157 kJ/kg.

Stage 3: Once the droplet is completely solid, it begins to cool further based on the heat transfer model described in Eq. (1). Again, this point can be clearly identified on a temperature profile in the form of a distinctive change in the rate of decrease of the drop temperature, shown in Fig. 1 at 273 K. The cooling process continues until the droplet reaches the ambient temperature.

Table 1. Data used in the model validation for the single CB droplet case.

Parameter	Value
Droplet diameter [mm]	2
Droplet density [g/cm^3]	0.894
Initial droplet temp. [K]	318
Freezing temp. [K]	291
Ambient air temp. [K]	277/263
Ambient air pres. [bars]	1.0
Inflow air vel. [cm/s]	83.0

Table 2. Comparison between the simulation and experimental values [5] for the single CB droplet case at 277 K.

Parameter	Simulation	Experiment
Stage 1 cooling rate [K/s]	6.3	7–9
Initial stage 2 cooling rate [K/s]	0.5	0.2–0.4
Nusselt number (stage 2)	6.2	7–8
Heat transfer coef., h_0 [W/m^{2}K]	101	93–95

Model Validation for a Single CB Drop

The freezing model described in the previous section has been implemented into a modified version of the CFD code *KIVA-3* [7]. This code is equipped with additional models such as the Cascade Atomization and Drop breakup (CAB) model [8], and the *RNG k-ε* turbulence model as implemented by Han and Reitz [9]. The description of these models, along with the model parameters, are presented in the respective references. The other models used in the simulations are the standard *KIVA-3* models.

The model validations for the single drop simulations are based on the experiments of Gwie et al. [5]. The geometry used is a cylinder with a diameter of 2 cm and a height of 5 cm. There is an inflow of ambient air through a hole of diameter 3 mm at the center of the bottom face of the cylinder. The top face of the cylinder is configured as an open outflow boundary. A CB droplet of 2 mm diameter is suspended on the cylinder axis at the fixed distance of 2 mm from the inflow orifice. Air is injected with a velocity of 83 cm/s through the bottom hole, thus generating the relative drop-gas velocity responsible for the convective heat transfer. The experimental details are summarized in Table 1.

The computational mesh is a structured, hexahedral, polar mesh with a uniform axial cell distribution of 1 mm and a geometric radial cell distribution with a smallest cell size of 0.35 mm on the axis. The mesh is configured with $12 \times 20 \times 50$ cells in the radial, azimuthal and axial directions, respectively.

Two simulations have been performed, the first at the ambient air temperature of 277 K, and the second at 263 K. The temperature freezing profiles are shown in Fig. 1, and the comparison with the experimental values

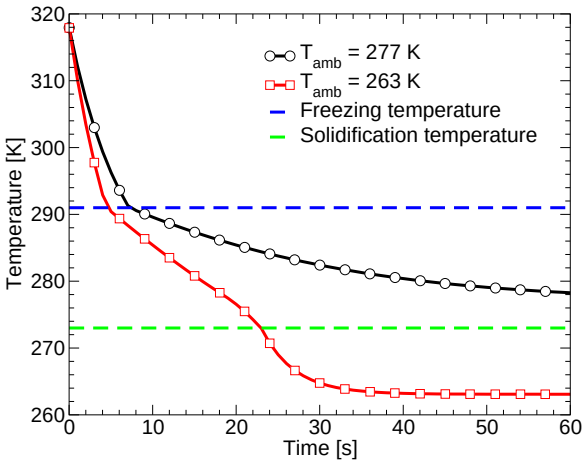

Figure 1. Temperature profiles of a 2 mm CB droplet, initially at 318 K, at the two different ambient temperature of 263 K and at 277 K.

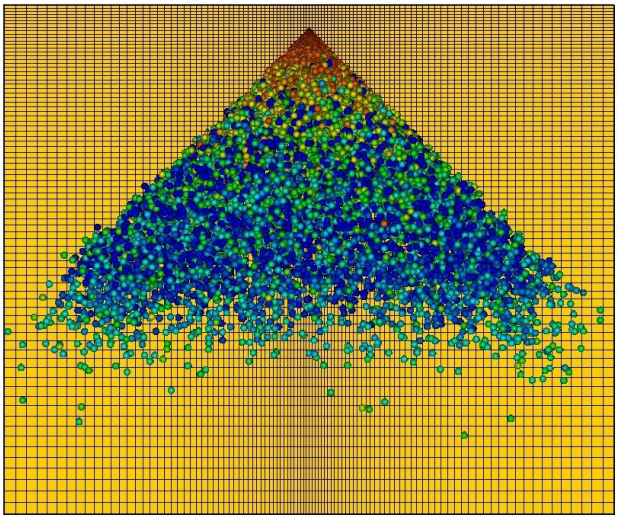

Figure 2. CB spray at an injection time of 40 ms. The particle temperatures scale ranges from 290 K (blue) to 320 K (red), and the gas temperature is 223 K.

for the 277 K case are shown in Table 2. As the table shows, the stage one droplet cooling rate, the solidification cooling rate of stage two, the Nusselt number and the heat transfer coefficient, h_0, are in close agreement with the experimental values.

The change in the rate of decrease of temperature at the freezing point of 291 K, observed in both simulations (cf. Fig. 1), is due to two competing phenomena. Initially, there is a continuous transfer of heat from the warm droplet to the environment. However, as the crystallization begins at 291 K, there is a release of latent heat of crystallization that contributes towards the increase of the droplet temperature. Nevertheless, since the rate of decrease of temperature is greater than the contribution due to latent heat, there is a net decrease in the temperature of the droplet.

For the 277 K ambient temperature case, the simulations and the experiments show that after 60 s the CB droplet has almost reached the ambient temperature of 277 K. However, the droplet is not completely solidified yet. This can be concluded because once the droplet is completely solid, there is a distinct decrease in the temperature profile, which indicates the beginning of stage three. This expected decrease, however, was not observed in the simulation, or in the experiment.

It is not surprising that the droplet is not fully solidified, despite the fact that its temperature of 277 K is considerably below the freezing temperature of 291 K. In fact, experimental observations reported by Loisel et al. [4] and Malssen et al. [10] confirm that the crystallization process of CB can occur over a wide range of temperatures, typically from 10 K below to about 25 K above the freezing temperature. Also, under different conditions, such as ambient temperatures and initial melt temperatures, various forms of crystalline CB can be realized. Further, depending on the size of the CB sample, some of these crystalline forms can be obtained from the initial liquid state in as early as a few seconds, while others can take as long as a few weeks [10].

In order to observe the abrupt change in the drop cooling rate after the solidifiaction process, the second simulation with the ambient temperature at 263 K was performed. As the temperature profile in Fig. 1 shows, this change in the cooling rate occurs after the droplet has reached a temperature of 273 K at about 23 s. In view of the fact that the current sample size is relatively small and that for spray investigations the droplets are even smaller (in the micron range), it is reasonable to assume that the droplet is completely frozen once it reaches a temperature of 273 K. Beyond this point, stage three of the freezing model is initiated, where the solid droplet cools to the ambient temperature of 263 K.

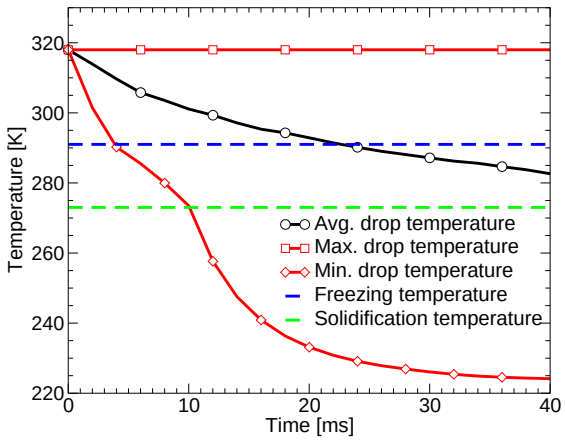

Figure 3. CB spray temperatures. The average spray temperature reaches the freezing temperature at 23 ms.

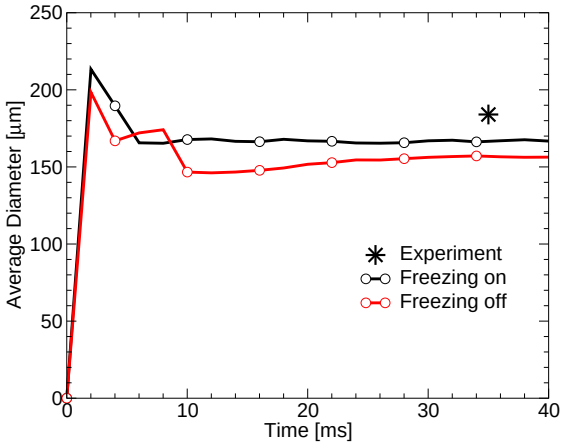

Figure 4. Average drop sizes of a CB spray with and without the freezing model.

Model Validation for a CB Spray

The geometry for the CB spray simulations is a cylinder with a diameter of 120 cm and a length of 100 cm, configured with a mesh of 53×30×85 cells in radial, azimuthal and axial direction. The cells in radial and axial direction follow a geometric distribution, where the smallest cell is at the nozzle exit at the top center, measuring 5 mm by 5 mm. The liquid CB is at a temperature of 318 K and has been injected with a pressure of 6 bar into the spray chamber by means of a hollow cone nozzle with an orifice of 0.5 mm and cone angles of 80^o and 12.5^o. The ambient gas temperature is 223 K and the pressure is 1 bar.

As discussed in the previous section, the droplets may not be completely solidified once they reach the freezing temperature. However, when the droplets reach the freezing temperatures, their outermost layer solidifies, which inhibits further droplet breakup or coalescence. Therefore, it can be assumed that the drop size distribution is stabilized once the droplets reach the freezing temperature.

The simulation duration was 40 ms, which is sufficient for most of the spray droplets away from the nozzle to reach the freezing temperature. This is illustrated in Fig. 2, which shows the spray at 40 ms in a vertical cut plane through the nozzle. It can be seen that most of the droplets in the lower half of the spray have already reached the freezing temperature and thus do not break up or coalesce anymore. In fact, as shown in Fig. 3, the average temperature of the entire spray has reached the freezing temperature of 291 K after 23 ms, whereas the average spray temperature is 283 K at the end of injection. Also, in the same figure, the maximum and minimum drop temperatures are shown. The maximum temperature of the droplets corresponds to the liquid temperature of 318 K. The minimum temperature, which most likely arises from one particular drop, reflects the nature of the temperature profile of the 263 K single droplet case in Fig. 1, and clearly shows the three freezing stages, but with much higher freezing rates.

The average drop sizes are shown in Fig. 4 for the simulations with the freezing model off and on, along with an experimental value. The agreement between the experimental value and the freezing simulation is quite good. Further, it is seen that the average drop size without the freezing model is smaller than with the freezing model switched on. This is because once the droplets reach the freezing temperature, they no longer breakup, and hence tend to be larger. Note that the drop coalescence plays a less important role, because hollow cone sprays are not very dense away from the nozzle, and therefore, the coalescence activity is small.

Summary and Conclusions

A three-stage freezing model has been developed and implemented into a modified version of the three-dimensional CFD code *KIVA-3*. The initial liquid cooling stage is based on a convective heat transfer model

until the droplet reaches the freezing temperature. Subsequently, the droplet enters the solidification stage in which there is a gradual crystallization of the droplet. Once the drop is completely solidified, then the solid droplet cools down to the ambient temperature via a convective heat transfer process.

The model has been validated with experimental data for a single CB drop suspended in an air flow, as well as for a freezing CB spray. The single CB drop simulation at the ambient gas temperature of 277 K showed good agreement with the experimental data, but, as in the experiments, the drop was not completely frozen when it reached the ambient gas temperature. An additional single CB drop simulation at the ambient temperature of 263 K showed that the solidification process is complete after the droplet has reached a temperature of 273 K. After this, the cooling rate was again considerably increased until the droplet reached the ambient gas temperature. In both single drop simulations, the cooling behavior was qualitatively the same for the first two stages, except that the colder domain exhibited larger cooling rates.

The spray simulations were conducted for a hollow-cone spray at the ambient temperature of 223 K, lasting for 40 ms. At the end of the simulation, the average spray temperature reached 283 K, which still lies above the temperature of 273 K when a single droplet has completed its solidification process. However, the freezing temperature of 291 K for the average spray was reached after 23 ms. Since the drop breakup and coalescence stop after droplets reach the freezing temperature, the drop size distribution of the spray will not change thereafter. Simulations with and without the freezing model have shown that the average drop size for the freezing spray is about 5% larger than without the freezing model. Also, the average drop size of the freezing spray is in better agreement with the experimental value than the non-freezing value.

A more detailed analysis of the freezing model and its effect on the other spray parameters is part of on-going studies.

References

1. Meryman, H., "Sublimation Freeze Drying without a Vacuum," *Science*, Vol. 130, 1959, pp. 628–629.
2. Windhab, E. J., "New Developments in Crystallization Processing," *Thermal Analysis and Calorimetry*, Vol. 57, 1999, pp. 171–180.
3. Metin, S. and Hartel, R., "Crystallization Behavior of Blends of Cocoa Butter and Milk Fat or Milk Fat Fractions," *Thermal Analysis*, Vol. 47, 1996, pp. 1527–1544.
4. Loisel, C., Keller, G., Lecq, G., Bourgaux, C., and M., O., "Phase Transition and Polymorphism of Cocoa Butter," *American Oil Chemists Society*, Vol. 75, 1998, pp. 425–439.
5. Gwie, C., Griffiths, R., Cooney, D., Johns, M., and Wilson, D., "Microstructures Formed by Spray Freezing of Food Fats," *American Oil Chemists Society*, Vol. 83, 2006, pp. 1053–1062.
6. Timms, R., *Confectionary Fats Handbook: Properties, Production and Application*, The Oily Press, Bridgewater, England, 2003.
7. Amsden, A. A., "KIVA–3: A KIVA Program with Block-Structured Mesh for Complex Geometries," Tech. Rep. LA-12503-MS, Los Alamos National Laboratory, March 1993.
8. Tanner, F. X., "Development and Validation of a Cascade Atomization and Drop Breakup Model for High-Velocity Dense Sprays," *Atomization and Sprays*, Vol. 14, No. 3, 2004, pp. 211–242.
9. Han, Z. Y. and Reitz, R. D., "Turbulence Modeling of Internal Combustion Engines Using *RNG k-ε* Models," *Combustion Science and Technology*, Vol. 106, 1995, pp. 267–295.
10. Malssen, K., Langvelde, A., Peschar, R., and Schenk, H., "Phase Behavior and Extended Phase Scheme of Static Cocoa Butter Investigated with Real-Time X-Ray Powder Diffraction," *American Oil Chemists Society*, Vol. 76, No. 6, 1999, pp. 669–676.