1 **Effect of temperature abuse on frozen army rations. Part 1: Developing a heat transfer**
2 **numerical model based on thermo-physical properties of food**

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5 Authors:

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7 Karthikeyan J. S.^a, Kiran M. Desai^a, Deepti Salvi^a, Rieks Bruins^b, and Mukund V. Karwe^{a*}

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10 ^aDepartment of Food Science, Rutgers University,

11 65 Dudley Road, New Brunswick, NJ 08901, USA

12

13 ^bRutgers Food Innovation Center - North,

14 120 New England Avenue, Piscataway, NJ 08854, USA

15

16

17

18

19 *Corresponding author:

20 Tel: 1-848-932-5487

21 Fax: 1-732-932-6776

22 Email: karwe@aesop.rutgers.edu

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Abstract

Numerical simulation was carried out to predict the effect of external temperature conditions on thermal behavior of frozen US military rations, during storage and transportation. An army breakfast menu box containing beefsteaks, concentrated orange juice, peppers & onions, French toast, and Danishes, was selected for conducting this study. Thermo-physical properties of each food item were characterized using their composition and differential scanning calorimeter (DSC). Apparent heat capacity method was used to account for the latent heat of phase change during simulation of thawing and freezing. Numerically simulated results were experimentally validated using a gel-based model food system and the food items in the menu box. The average deviation between numerically predicted temperature and experimentally measured temperature for the model food system was approximately 1 °C and for the targeted food items the deviation ranged from 2 °C to 5 °C, depending on the food item.

Keywords: numerical simulation; frozen food; differential scanning calorimeter; apparent heat capacity.

1. Introduction

Most of the U.S. military operational rations consist of shelf-stable food items. The united group ration-A (UGR-A) is the only U.S. army ration that consists of perishable food items, which requires cold chain storage (Natick PAM 30-25, 2012). These rations are manufactured in the U.S. by different vendors and are frozen before shipping to army bases in various countries. According to the Combat Rations Network for Technology Implementation (The United States Department of Defense), cold chain transportation of these frozen army rations, via road and via sea, can take anywhere between 3 to 5 months. Different modes of transportation with loading, unloading, and storage in between, increase the possibility of temperature abuse on these frozen army rations, which might compromise their microbial safety and chemical quality (Moureh and Derens, 2000; Blond and Le Meste, 2004). It is imperative to have a technological solution for such frozen food items that would alert the end user, about the freeze-thaw cycles experienced by the food items due to possible temperature abuse and its overall impact on the safety and quality of food items, before they are consumed.

Temperature variation with time within a food item during freezing/thawing can be determined experimentally. However, experimental procedures are often too expensive and time consuming. In order to accurately predict the temperature variation from the numerical solutions of mathematical models, the physical changes that a food item undergoes during phase change have to be well understood. Since freezing or thawing is a heat transfer process with phase change, the Fourier equation for heat conduction (Eq. (1)) can be used to predict temperature distribution in a solid material.

$$\rho C_p \frac{\partial T}{\partial t} = \nabla(k \nabla T) + S \quad (1)$$

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72 where ρ is density (kg/m³), C_p is heat capacity (J/(kg·K)), T is temperature (K), t is time (s), k
 73 is thermal conductivity (W/(m²·K)) and S is a source term (W/m³) referring to distributed
 74 heat source or heat sink depending upon whether the product is being frozen or thawed,
 75 respectively (Ayasoufi et al., 2005). The simplest approach for solving Eq. (1) for a food
 76 system is to consider the food system as a bulk of material in which water and ice experience
 77 phase transition during a freeze-thaw process (Watzke et al., 2010). For a multi-component
 78 substance such as food, freezing or thawing does not occur at a fixed temperature. The latent
 79 heat will be released (during freezing) or absorbed (during thawing) over a range of
 80 temperature due to the changes in the concentration of solutes (Franke, 2000). The phase
 81 transition temperature range that separates the completely thawed and the completely frozen
 82 food is termed as the 'mushy' zone, which generally is characterized as the region with solid
 83 ice suspended in liquid water (Bhattacharya et al., 2002). In the mushy zone, the major
 84 thermo-physical properties: density, thermal conductivity and heat capacity, vary with
 85 temperature due to the changes in unfrozen water fraction and ice fraction. These thermo-
 86 physical properties can be assumed to be constant in completely thawed and completely
 87 frozen regions (Voller, 1997). Density and thermal conductivity of food items can be
 88 expressed as a function of temperature, based on the combination of the major constituents of
 89 individual food item (Hamdami et al., 2004a; Watzke et al., 2010). The challenge in solving
 90 Eq. (1) is the inclusion of sensible heat and latent heat of phase change in the mushy zone.
 91 For a food system, a method based on latent heat has to be developed, such that, a single
 92 energy balance equation is required for the entire domain consisting of coexisting solid,

liquid, and mushy zone. The most commonly used and reliable method is the apparent heat capacity (AHC) method (Pham, 2006; Kumar and Subhendu, 2009). In this method, latent heat is included in the sensible heat to produce a heat capacity curve with a large peak around the mushy zone, which lies between the temperatures T_1 (thawed side) and T_2 (frozen side), as depicted in the Fig. 1. The original heat transfer equation (Eq. (1)) is modified as Eq. (2), in which $C_{p(app)}$ is the apparent heat capacity (AHC) expressed in J/(kg·K).

$$\rho C_{p(app)} \frac{\partial T}{\partial t} = \nabla(k \nabla T) \quad (2)$$

To determine AHC, a differential scanning calorimeter (DSC) is usually used. A DSC generated thermogram, in which the rate of heat transfer is plotted versus temperature for a small amount of sample, provides information on the energy released or absorbed in the form of latent heat during phase transition of that sample (Hamdami et al., 2004a; Sebnam et al., 2007; Le Reverend et al., 2009).

A mathematical model for a freeze-thaw process consists of partial differential equations governing the heat transfer in all three regions: unfrozen, frozen, and mushy. Analytical solution for these governing equations during phase change is impossible due to their complexity. Therefore, numerical methods based on a fundamentally sound theory, have to be used (Huan et al., 2003). The challenging step in simulating phase change of a food system is the description of non-linear thermal properties in time and space. In such cases, it has been shown that the finite element method (FEM) is the most suitable numerical method for obtaining converged solutions (Kumar and Subhendu, 2009).

Although prior research has been done to predict the thermal behavior of frozen foods and its influence on overall safety/quality, researchers have mainly focused on simpler geometries (Zuritz and Singh, 1985; Scott and Heldman, 1990; Elvira et al., 1996). A detailed study involving multiple food products in a complex geometry, including the effects of phase change on the overall thermal response and safety/quality, has not been carried out. Therefore, this research was focused on quantifying the effect of external time-varying temperature conditions on the thermal behavior of five different frozen food products inside a typical army menu box, taking into account the changes in their thermo-physical properties during phase change. The specific objectives were 1) to determine the apparent heat capacity and other thermo-physical properties of five different food items using their component data and a differential scanning calorimeter, and 2) to develop and validate a numerical model of the frozen army menu box containing those food items, to predict the heat transfer within the menu box with respect to external temperature conditions. Extension of this research which focused on predicting food safety during real-time temperature abuse scenarios by correlating the numerically simulated thermal behavior of food items to microbial growth kinetics is presented in a subsequent manuscript.

2. Materials and methods

2.1. Food description

Numerical model was developed for an army breakfast menu box, which contained beefsteaks, concentrated orange juice, peppers & onions, French toast, and Danishes (Fig. 2A). The composition of each food item, i.e., proteins, carbohydrates, fat, fiber was obtained from their nutrition labels provided by their respective vendors. Moisture content of each

food item was evaluated in triplicates by homogenizing the sample in a laboratory blender (Waring, New Hartford, CT) and using a moisture analyzer (Model no. MA30, Sartorius, Germany). The ash content of all the products was assumed to be 1%, based on literature (USDA, 1996). For numerical model validation, in addition to the selected food items, experiments were also carried out for a homogenous model food system. Freeze-thaw stable gelatin (No. G-2500, Sigma Aldrich) was used to create a cylindrical model food system (Fig. 2B). In the five chosen real food products, the moisture content of the high moisture food items (beefsteaks, concentrated orange juice, and peppers & onions) ranged from 60% to 90% (w.b.). Hence, the gelatin based model food system was made at 75% moisture content (w.b.) and 25% (w.b.) gelatin, to mimic the phase change behavior of real food items.

2.2. Differential scanning calorimeter (DSC) study

A differential scanning calorimeter (DSC) (Model no. DSC 823^e, Mettler Toledo, Columbus, OH) was used to analyze the enthalpy change of the food items during phase change. Five targeted food items and one model food system were analyzed in triplicates, during freezing and thawing in the temperature range of -30 °C to +30 °C, with the temperature change rate set at 10 °C/min (Le Reverend et al., 2009; Gras, 2013). Each food item was homogenized and a sample weighing around 10 mg was placed in a ME-27331 aluminum crucible to obtain a DSC thermogram. A typical DSC thermogram shows variation of heat flow per unit mass (W/g) as a function of temperature. MATLAB[®] (Version 2010a, Mathworks Inc., Natick, MA), was used to analyze the DSC thermograms and evaluate the thermo-physical properties. Evaluation of each property is explained below.

2.2.1. Initial freezing point and final thawing point

Initial freezing point is the temperature at which the phase change starts during the freezing process and the maximum heat flow value (W/g) is observed in the DSC thermogram. Final thawing point is the temperature at which the phase change is complete during the thawing process and the minimum heat flow value (W/g) is observed in the DSC thermogram.

However, due to the small sample size (around 10 mg) needed to obtain a DSC thermogram; the moisture present in the sample gets saturated with the dissolved solids. This could lead to super cooling because of which determining the initial freezing point of the sample from a DSC thermogram can become difficult as pointed out by some researchers (Wang and Kolbe, 1991; Matuda et al., 2011). This anomaly in the DSC thermogram is observed only during the freezing process. Based on the previous studies, actual initial freezing point could be obtained experimentally (Wang and Kolbe, 1991; Hamdami et al., 2004b; Matuda et al., 2011). Such supporting experiments were carried out individually for each food item from the menu box undergoing freezing process, in a -18 °C freezer. Temperature history was monitored near the geometric center of each food item, using a 'T' type (copper-constantan) hypodermic needle probe of length 3.8 cm and diameter 0.81 mm (Model: HYP-2, Omega Engineering, Stamford, CT) and a data acquisition system. In the temperature history, the temperature range at which the time-temperature plot became plateau denoted the region of phase change and the first point of this plateau region was noted as the initial freezing point of that particular food item as suggested in literature (Hamdami et al., 2004a; Foong et al., 2010). For all the food items, DSC thermograms obtained during freezing process were shifted, such that the maximum heat flow value (W/g) lies at the

experimentally obtained initial freezing point.

2.2.2. Apparent heat capacity (AHC)

For a food item, from its DSC thermogram for thawing process and shifted DSC thermogram for freezing process, apparent heat capacity (AHC) in J/(kg·K), as a function of temperature was calculated, respectively, using Eq. (3) (Sebnam et al., 2007 and Matuda et al., 2011).

$$C_{p(app)} = \frac{\text{Heat flow rate } (\frac{W}{g})}{\text{Temperature change rate } (\frac{K}{s})} \times \frac{1000 \text{ g}}{1 \text{ kg}} = \frac{J}{kg \cdot K} \quad (3)$$

A cubic polynomial was fitted to the AHC data obtained using Eq. (3) as a function of temperature T. Fig. 1 depicts the theoretical AHC curve. By employing the cubic polynomial equation for the mushy zone ($T_2 < T < T_1$), AHC curve for each food item was developed as shown in the piecewise Eq. (4). Depending on the process, freezing or thawing, temperature T_1 is defined as the initial freezing point or final thawing point, respectively. For the completely thawed region ($T_1 < T$) and completely frozen region ($T < T_2$), the respective constant values of AHC, obtained from the DSC thermogram, were used.

$$C_{p(app)}(T) = \begin{cases} C_{p(app)} \text{ of frozen region} & T < T_2 \\ C_{p(app)} \text{ as a cubic polynomial} & T_2 < T < T_1 \\ C_{p(app)} \text{ of thawed region} & T_1 < T \end{cases} \quad (4)$$

2.2.3. Latent heat of phase change

Latent heat of phase change is the amount of energy absorbed or released during phase change per unit mass. The latent heat of phase change (J/kg) for each food item was calculated by evaluating the area under the AHC curve in the phase change mushy zone (region between T_1 and T_2 in Fig. 1) (Hamdami et al., 2004a).

2.2.4. Bound water fraction

Bound water fraction (x_b) is the fraction of water that remains unfrozen even at very low temperatures. The bound water fraction of each food item can be evaluated from its total moisture content and latent heat of phase change using Eq. (5) (Hamdami et al., 2004a).

$$\text{Bound water fraction} = \text{Total moisture fraction} - \frac{\text{Latent heat of phase change}}{L_o} \quad (5)$$

where L_o is the latent heat of fusion of water at 0 °C which is 333.3 kJ/kg.

2.2.5. Unfrozen water fraction and ice fraction

For each food item, for thawing and freezing processes, the unfrozen water fraction and ice fraction as a function of temperature were obtained separately. At the initial freezing point or final thawing point (T_1 in Fig. 1), unfrozen water fraction equals (x_{unf}) total moisture fraction (x_w) of food. During freezing, unfrozen water fraction reduces and follows the trend of AHC curve. At T_2 , the unfrozen water fraction was assumed to reach a constant value of bound water fraction (x_b). On the other hand, ice fraction (x_{ice}) will be zero at the initial freezing point (T_1), and while freezing it follows the trend of AHC curve and at T_2 it reaches its maximum value (Total water fraction x_w – bound water fraction x_b). The curves are similar

during thawing, but the process takes place in reverse order. MATLAB[®] was used to fit cubic polynomial functions to the nonlinear curves of unfrozen water fraction and ice fraction in the mushy zone as a function of temperature. Piecewise equations were generated for each food item, during thawing and freezing, separately, as given by Eqs. (6) and (7).

$$x_{unf}(T) = \begin{cases} x_b & T < T_2 \\ f_{unf}(T) \text{ as a cubic polynomial} & T_2 < T < T_1 \\ x_w & T_1 < T \end{cases} \quad (6)$$

$$x_{ice}(T) = \begin{cases} x_w - x_b & T < T_2 \\ f_{ice}(T) \text{ as a cubic polynomial} & T_2 < T < T_1 \\ 0 & T_1 < T \end{cases} \quad (7)$$

2.2.6. Density and thermal conductivity

The values for density and thermal conductivity of individual food components (fats, carbohydrates, proteins, ash, fiber, water, and ice) are listed in Table 1. To evaluate density of a food item as a function of temperature, mass fractions of all components (x) and their respective density values were used in Eq. (8) as described by Watzke et al. (2010). The thermal conductivity value for each food item was calculated from the volume fractions 'X' of the individual components and their respective thermal conductivity values using Eq. (9) as described by Kumar and Subhendu (2009).

$$\rho(T) = \frac{1}{\frac{x_i}{\rho_i} + \frac{x_{unf}(T)}{\rho_w} + \frac{x_{ice}(T)}{\rho_{ice}}} \quad (8)$$

$$k(T) = k_i X_i + k_w X_{unf}(T) + k_{ice} X_{ice}(T) \quad (9)$$

where the subscript i denotes non-water components and the subscripts w and ice denote water and ice, respectively. Eq. (6) for unfrozen water fraction and Eq. (7) for ice fraction were incorporated in Eqs. (8) and (9).

2.3. Numerical model

A finite element based commercial computational software, COMSOL Multiphysics® (Version 4.2, COMSOL Inc., Burlington, MA) was used to carry out the numerical simulation. The software was installed and run on a desktop computer (2.66 GHz Intel(R) Xeon(R) CPU processor, with a 24.0 GB RAM). The physical domain was discretized into computational domain to solve the governing equations along with imposed boundary conditions, so as to numerically predict the temperature distribution in the frozen army menu box. Usual practices such as grid refinement and stringent convergence criteria were followed to ensure the consistency, convergence, and accuracy of the numerical solution.

2.3.1. Geometry

The three dimensional geometry depicting five different food items inside the cardboard menu box is shown in Fig. 3A. The description of food items is as follows: (i) five uncooked beefsteaks, each measuring $(24.1 \times 17.8 \times 3.6)$ cm were individually packed in polystyrene film; all steaks were inside a cardboard box of dimensions $(39.4 \times 27.9 \times 14)$ cm, (ii) three cartons of concentrated orange juice of dimensions $(7 \times 7 \times 18.5)$ cm, (iii) two packs of peppers & onions with approximate dimensions of $(27 \times 15 \times 5.6)$ cm, (iv) twenty four individual cylindrical French toasts of length 15.2 cm and diameter 2.5 cm, inside a

cardboard box of dimensions $(31 \times 20 \times 13.5)$ cm, and (v) forty eight individual mini Danishes of diameter 7.6 cm and height 1.9 cm which were arranged in two rows, in a tray of dimensions of $(27 \times 19.6 \times 4.5)$ cm. Two trays of Danishes were packed in the menu box. The dimensions of packages and boxes, and the orientation and placement of the products in the menu box were standardized and this information was provided by the Combat Rations Network for Technology Implementation (The United States Department of Defense). Twenty four individual pieces of French toast in a box and forty eight individual Danishes in a tray were assumed as one block of French toast and one block of Danishes, respectively, with equivalent dimensions. For the gelatin based model food system, the gel sample in cylindrical shape was kept on its face with its axis in vertical direction (Fig. 3B).

2.3.2. Governing equations for numerical simulation

2.3.2.1. Heat transfer

The heat transfer model of the menu box was simulated using the physics *conjugate heat transfer model* available in COMSOL Multiphysics®. Heat transfer in a food system was solved based on the energy balance equation (Eq. (2)). The thermo-physical properties obtained from component data and DSC were used as the input to solve this equation.

The flow field of air in the headspace induced by the natural convection inside the menu box was included in the numerical simulation. The air gaps in the head spaces of beefsteak box, French toast box and Danishes boxes were very small, so the air there was assumed to be stagnant. Natural convective flow was considered only for the headspace of the menu box and the flow field was assumed to be laminar. The velocity of air at the inner

walls of the menu box was specified as zero. The conservation of momentum equation (Eq. (10)) was used for solving natural convective air flow.

$$\rho \frac{\partial u}{\partial t} + \rho(u \cdot \nabla)u = \nabla \cdot [-p + \mu(\nabla u + (\nabla u)^T)] + F \quad (10)$$

where ρ is density (kg/m³), u is velocity of air (m/s), t is time (s), p is pressure (Pa), and μ is dynamic viscosity (Pa·s), and T is temperature (K). F is the *volume force* term expressed in N/m³ used to account for gravity driven natural convective air flow in negative z direction (along the height of the box).

2.3.2.2. Boundary conditions

On the outer walls of the menu box which were exposed to the external temperature conditions, the boundary condition was defined by Eq. (11).

$$-n \cdot (-k\nabla T) = h \cdot (T_{ext} - T) \quad (11)$$

where n is surface unit normal vector, T_{ext} is external medium (air) temperature (K), and h is convective heat transfer coefficient (W/(m²·K)). For the simulation, the value of heat transfer coefficient h used was determined from experimental investigation as explained later in the section 2.4.

2.3.2.3. Packaging material

For incorporating the effect of packaging materials, boundary condition termed as

thin thermally resistive layer was used, which solved Eqs. (12) and (13) accounting for the resistance provided by the packaging material to the heat flow.

$$-n_i \cdot (-k_i \nabla T_i) = -k \frac{(T_o - T_i)}{d} \quad (12)$$

$$-n_o \cdot (-k_o \nabla T_o) = -k \frac{(T_i - T_o)}{d} \quad (13)$$

where n is surface unit normal vector, subscripts o and i refer to the outside and inside of the resistive layer, respectively. Here, k is the thermal conductivity of the packaging material in W/(m·K) and d is the thickness of the packaging material in m. Individual beefsteaks, peppers & onions packs, French toast and one side of Danishes box were packed in expanded polystyrene (EPS). All the other boxes and concentrated orange juice cartons were made of cardboard. The thermal conductivity of EPS was specified to be 0.04 W/(m·K) and that of the cardboard box was 0.065 W/(m·K) (Kumar and Subhendu, 2009). The thicknesses of all the packaging materials were in the range of 0.5 mm to 1 cm.

2.3.3. Computational mesh

For numerical simulation purposes, the three dimensional menu box geometry (Fig. 3A) was mapped into tetrahedral elements using an inbuilt meshing option available in COMSOL Multiphysics®. The discretization was composed such that the regions of interest (food items) had finer meshes when compared to other regions of the geometry. Series of simulations with different mesh sizes were tried and the mesh size range was finalized based

on two aspects: 1. Temperature history predicted by a chosen mesh should be as accurate (less than 1% deviation) as the temperature history predicted by the finest mesh possible, and 2. Less computational time. Based on these two factors, to accommodate the complexity of the entire geometry, distance between proximate nodes was optimized and set in the range of 4.95 mm to 49.5 mm. The mesh size was relaxed (made coarse) only for the purpose of reducing computational time without significantly sacrificing the accuracy (<1%) of the results. The final mesh consisted of 23,019 domain elements, 7,221 boundary elements, and 1,012 edge elements. In the case of three dimensional gel based model food system (Fig. 3B), distance between proximate nodes of tetrahedral elements was optimized and set in the range of 0.419 mm to 3.35 mm, depending on the complexity of geometry. The final mesh consisted of 13,856 domain elements, 1,408 boundary elements, and 108 edge elements. The appropriate governing equations were solved for these finite elements at their nodes.

2.4. Experimental validation

Experiments were carried out to validate the developed heat transfer model. 'T' type thermocouple wires (for model food system) and 'T' type Omega hypodermic needle probes (Model. HYP-2) (for food items in the menu box) were inserted at predetermined locations, and the temperature variations with time were recorded using a data acquisition system.

Three sets of experiments used for validation were:

(1) Thawing experiments with the model food system: The frozen gel based model food system was allowed to thaw in ambient environment and inside an insulated box of dimensions $(49.5 \times 39.4 \times 30.2)$ cm. The experiment with the insulated box was conducted to analyze the effect of natural convective airflow in the headspace. Temperatures at four known

locations, along the axis of the gel sample, as shown in Fig. 2B, were recorded.

(2) Thawing experiment with the menu box: The frozen menu box with all the selected food items was allowed to thaw in ambient environment. Product temperatures were recorded at four known locations in four different food items. Due to the fixed orientation of food products inside the menu box (Fig. 3A), geometric centers for all the food items were not accessible to measure temperature history.

(3) Freezing experiments with individual food items: Thawed food items were allowed to freeze in a -18 °C freezer, individually. Product temperature was monitored near the geometric center of each food item.

In the numerical simulation of experimental cases, for thawing experiments (experiments 1 and 2) the initial temperature of the model food system and the menu box was set at -18 °C. For the freezing experiment (experiment 3) the initial temperature of individual food items was set at 10 °C. External temperature conditions were monitored during experiments and were imposed as boundary conditions in the numerical simulation. For experiments 1, 2, and 3, the external temperature conditions were set as 24 °C, 22 °C, and -18 °C, respectively.

Experiments were also used to estimate the heat transfer coefficient values of ambient environment over the outer walls of the menu box. In general, the heat transfer coefficient values for free convection of air ranges from 5 W/(m²·K) to 25 W/(m²·K) (Singh and Heldman, 2001). Based on this range, the heat transfer coefficient value of air over the outer walls of the menu box was varied in the numerical simulation, such that minimum error is

achieved between numerical prediction and experimental data. To evaluate the accuracy of the numerical model, experimentally obtained temperature data were compared with numerically predicted temperature variations, at predetermined locations. For experiment 1 these two data sets were compared for every 1 min, for experiment 2 the data sets were compared for every 30 min, and for experiment 3 the data sets were compared for every 15 min. These time intervals were chosen such that at least 50 data points were collected in each case. Average error was calculated based on the difference between experimentally obtained temperature data and numerically predicted temperature variation.

3. Results and discussion

3.1. DSC thermograms

DSC thermograms generated for the five targeted food items are shown in Fig. 4A and B, for freezing and thawing, respectively. Latent heat released during freezing was represented by positive peaks (Fig. 4A), and during thawing, negative peaks were observed (Fig. 4B), due to absorption of latent heat (Le Reverend et al., 2009). Since, only water undergoes phase transition in this temperature range, the height of the peak is proportional to the available water in the system, for phase change (Hamdami et al., 2004b). For beefsteak and for concentrated orange juice, though both had approximately the same moisture content (~ 61% to 63% w.b.), heat flow peak of beefsteak was taller. From the compositional data, shown in Table 2, it can be seen that beefsteak had 0% carbohydrates, and concentrated orange juice had approximately 37% carbohydrates. In the presence of carbohydrates water can form hydrates and decrease the available water for phase change (Park, 2008). This suggested that beefsteak had less bound water, so most of its water fraction had undergone phase change unlike concentrated orange juice which had high amount of soluble sugars

(Park, 2008; Thanatuksorn et al., 2008). In the case of Danishes, no noticeable peak was observed; this may be due to its comparatively low moisture content (21% w.b.) (Hamdami et al., 2004b). In general, phase change process cannot be clearly observed in baked products because of their complex system, that has polymers (like starches and proteins) and low molecular weight solutes (like sodium chloride) dispersed in liquid water (Cauvain and Young, 2008). For all the food items, DSC thermograms during freezing had narrower peak width when compared to long tailing peak while thawing. This indicated that during thawing, phase change occurred over a wider temperature range and more gradually when compared to freezing, as observed previously in the literature (Sahin and Sumnu, 2006; Le Reverend et al., 2009). DSC thermograms were obtained for gelatin based model food system during thawing process; they are not presented in this manuscript for brevity.

3.2. Thermo-physical properties

3.2.1. Initial freezing/final thawing point

Freezing thermograms (Fig. 4A) showed that, freezing process took place in the unusual range of -12 °C to -24 °C. We know from textbook knowledge that this cannot be true. To obtain the actual initial freezing point, freezing experiments were done for five food items. The results of freezing experiments for beefsteak are discussed in this paper. Fig. 5 represents the temperature history of the beefsteak, during the freezing experiment, at a known location. The graph can be divided into three regions: temperature drop in the thawed phase, plateau phase change region and temperature drop in the frozen phase (Hamdami et al., 2004a; Foong et al., 2010). The temperature drop in thawed phase and frozen phase were due to constant sensible heat removal. As can be seen from Fig. 5, in the phase change

region, freezing of beefsteak started at -1.9°C (initial freezing point) and was completed at -3.6°C . The temperature drop in the phase change region was small due to large amount of latent heat released to freeze available water in the beefsteak (Foong et al., 2010). The DSC thermogram obtained during the freezing process (Fig. 4A) of beefsteak was shifted such that the peak is at the initial freezing point (-1.9°C), as suggested in literature (Wang and Kolbe, 1991, Hamdami et al., 2004b). Similarly for all the food items, the freezing process DSC thermograms were shifted to their actual initial freezing points. The initial freezing points obtained from experimental data and the final thawing points obtained from DSC thermograms, are given in Table 3. The initial freezing point of the food samples were in the range of -1°C to -5°C , with the lowest being -4.5°C for concentrated orange juice, and highest being -1.2°C for French toast. The initial freezing point range agrees with the values previously reported in the literature (Hamdami et al., 2004b; Cengel, 2007). Based on the colligative property (depression of freezing point), due to high amount of soluble sugar content, concentrated orange juice had the lowest initial freezing point and final thawing point (Thanatuksorn et al., 2008). Initial freezing point of the model food system was not evaluated, as we did not simulate its freezing process.

3.2.2. Apparent heat capacity (AHC), latent heat of phase change, and bound water fraction

Apparent heat capacity (AHC) curves were plotted using Eq. (3), with the temperature change rate of 10 K/min . The latent heat of phase change, i.e., the area under the curve was approximately same for a given food item, in thawing and freezing AHC curves. Hence, the latent heat of phase change was assumed to be a constant for a particular food item. The latent heat of phase change and the bound water fraction, calculated from Eq. (4),

for the four food items and one model food system, are given in Table 3. Calculated latent heat of phase change and bound water fraction for each food item, were in the range of values previously reported in the literature (Potter and Hotchkiss, 1998; Cengel, 2007; Park, 2008). As mentioned earlier Danishes did not show any phase change. When comparing the high moisture food systems: peppers & onions (85% w.b. moisture) and gelatin gel (75% w.b. moisture), the latent heat of phase change was higher in gelatin gel. This may be due to the homogenous nature of gelatin system and less bound water fraction, whereas in the heterogeneous peppers & onions system, the possibility of water entrapped in the food matrix might be higher, although this is just a speculation.

3.2.3. Unfrozen water fraction, ice fraction, density, and thermal conductivity

Fig. 6 shows the unfrozen water fraction as a function of temperature for four food items during freezing. At the respective initial freezing points of each food item, the values of unfrozen fraction were at their maximum, i.e., total moisture content. As the temperature decreased, due to phase change, unfrozen water fraction reduced and the curves approached constant bound water fraction values of each food item (Hamdami et al., 2004a). These curves were used to generate piecewise equations for unfrozen water fraction during freezing, as a function of temperature. Similarly piecewise equations for ice fractions were generated. For each food item, the equations for freezing and thawing processes were developed separately. With these equations and the data from Table 1 and Table 2, the density and the thermal conductivity values of each food item, as a function of temperature were evaluated using Eqs. (8) and (9). Depending on the process, freezing or thawing, these equations were used accordingly in the numerical simulation.

3.3. Experimental validation

3.3.1. Thawing experiments with the model food system

Fig. 7 and 8 show the comparison of temperature history obtained from experiment and numerical simulation for frozen gelatin gel suddenly exposed to ambient conditions and inside an insulated box, respectively, at four selected locations. On comparing the results for all locations in both the cases, the maximum deviation between predicted and experimentally obtained temperature data was around 5 °C and the overall average deviation was approximately 1 °C. This shows that the numerical model was in reasonably good agreement with experimental data, considering many sources of variability in the physical properties and the process.

As discussed earlier, the temperature data can be divided into three regions: initial temperature rise in the frozen phase, plateau phase change region, and temperature rise in the thawed phase. The change of slope around the 0°C in experimental data (dashed lines) represents the completion of phase change, i.e., the final thawing point (Hamdami et al., 2004a; Foong et al., 2010). The temperature rise trend agreed with experimental results in most of the temperature range except in the final temperature rise zone (thawed region). This may be because of the high temperature change rate (10 K/min) used in DSC study, which can generate imprecise curves (Le Reverend et al., 2009). High temperature change rate was chosen because of time limitations involved in obtaining DSC thermograms for large number of samples. Since, AHC curves and other thermo-physical properties were evaluated from DSC thermograms; some deviation between simulated and experimental data was expected.

3.3.2. Thawing experiment with the menu box

Frozen menu box at $-18\text{ }^{\circ}\text{C}$, as described in Fig. 3A, was exposed to a constant ambient temperature of $22\text{ }^{\circ}\text{C}$ and results of predicted temperature distribution throughout the box are shown in Fig. 9. In the figure, the colors represent temperature levels, blue being the coldest and red being the warmest; temperature range varies in both the figures. At time $t=0$ (Fig. 9A), the box was completely frozen, so represented in blue color. In the simulation, once the menu box was exposed to $22\text{ }^{\circ}\text{C}$, the temperature of air in the headspace of the menu box started rising. For all the food items, corner regions thawed first. Depending on the position, orientation (how close the food item is located to the walls of the menu box), the initial freezing point, the latent of phase change and other thermo-physical properties, the food items thawed in the following order: Danishes, concentrated orange juice, peppers & onions, French toast, and beefsteak. At $t=25\text{ h}$ (Fig. 9B), all the food items except the topmost beefsteak (beefsteak 3) were thawed completely.

Fig. 10 shows the comparison of temperature history obtained from experiment and numerical simulation, for four food items at known locations. Predicted temperature for beefsteak (Fig. 10A), had an average deviation of approximately $2.5\text{ }^{\circ}\text{C}$, when compared with the experimental data. These deviations were most likely due to the challenges in real-time temperature measurement. It was observed that the position of the thermocouple got disturbed due to softening of the beefsteak tissue, during thawing. Similarly, in the case of concentrated orange juice (Fig. 10A); the fluctuations in experimental data (black dotted line) could be due to the natural convection in the thawed concentrated orange juice, which was

not considered in the simulation. This could be the reason for an average deviation of 4 °C between predicted and experimentally obtained temperature data for concentrated orange juice. In both these cases, numerical simulation under-predicted the temperature before the final thawing point and over-predicted the temperature after the food item was completely thawed. Similar trend was previously observed by Leung and Chan (2009). This discrepancy may be attributed due to ignoring the effect of temperature on density and thermal conductivity of individual food components, as mentioned in Table 1. The results for peppers and onions (Fig. 10B) showed better agreement between the numerical predictions and experimental data, with an average deviation of 2 °C. Results for French toast (Fig. 10B) showed an average deviation of 5 °C. This high deviation may be mainly due to the assumption of simplified geometry, in which twenty four individual French toasts were considered as one rectangular slab.

As expected, the deviation between simulated and experimentally obtained temperature history for the real food items was greater than that for the model food system. This can be attributed to the fact that model food system was homogenous and gelatin is freeze-thaw stable whereas real food system is complex and heterogeneous in nature. As mentioned earlier, the deviation may also be due to high temperature change rate used during DSC study and the assumptions made in the numerical simulation such as simplified food geometry and undisturbed thermocouple location throughout the experiment.

The experiments were also used to determine the heat transfer coefficient values of ambient environment (air) on the outside of the box, which can be used for simulating real-

time temperature abuse scenarios. The heat transfer coefficient values of $20 \text{ W}/(\text{m}^2 \cdot \text{K})$ on the exposed sides of the box and $5 \text{ W}/(\text{m}^2 \cdot \text{K})$ on the base were finalized, since these values gave minimum error in the product temperature prediction.

3.3.3. Freezing experiments with individual food items

In this case, individual food items undergoing freezing process in a -18°C freezer were analyzed. For simulation, as mentioned earlier, shifted AHC freezing curves were used. On comparing the results near the geometric center of four food items (except Danishes), the average deviation between predicted and experimentally obtained temperature data was approximately 2°C (Karthikeyan, 2013). The comparative results of freezing experiment are not presented in this manuscript.

4. Conclusions

Numerical simulation was carried out to predict the effect of external temperature conditions on thermal behavior of frozen US military rations, during storage and transportation. An army breakfast menu box containing beefsteaks, concentrated orange juice, peppers & onions, French toast, and Danishes, was selected for conducting this study. Component data and differential scanning calorimeter (DSC) were used to determine the thermo-physical properties of five different food items. Effect of phase change: freezing and thawing, on these properties were evaluated. A numerical model was developed based on the evaluated thermo-physical properties to predict the heat transfer of a frozen U.S. army breakfast menu box containing those five food items. Experimental investigation showed that the average deviation in predicting the thermal behavior of food items in the menu box

during thawing ranged from 2 °C to 5 °C. Since DSC did not estimate the initial freezing points of the food items accurately, the freezing DSC thermograms were shifted according to the results of freezing experiments. Based on this adjustment thermo-physical properties were evaluated and used in numerical simulation of freezing process. The average deviation in numerical temperature prediction from the experimental data was 2 °C, during freezing. A generic numerical simulation technique was developed which can be used to predict heat transfer in any food system experiencing phase change, under varied external temperature conditions. Specifically, it can be used for frozen foods that are more susceptible to temperature abuse during very long duration of transportation. For these food items, estimating the extent of spoilage from the time-temperature history alone is difficult. Hence, temperature history obtained from this model can be combined with the microbial or chemical kinetics, to predict the food safety and quality as a function of external temperature conditions. This work was extended to predict the microbial safety of the food items in the army menu box during real-time temperature abuse scenarios, which is presented in detail in a separate manuscript (Part 2).

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Table 1

Density and thermal conductivity of individual food components. Temperature dependence of these properties was assumed to be negligible in this study.

	Fat	Carbohydrates	Protein	Ash	Fiber	Water	Ice
Density (kg/m ³)	925.5	1599.1	1329.9	2423.8	1311.5	997.18	916.89
Thermal	0.18071	0.20141	0.17881	0.32961	0.18331	0.5711	2.2196

Conductivity

(W/(m·K))

(Watzke et al., 2010; Kumar and Subhendu, 2009)

Table 2

Component fractions of food items in the menu box

	Fats	Carbohydrates	Proteins	Fiber	Ash	Water
Beefsteak	0.142	0	0.196	0.025	0.01	0.627
Concentrated orange juice	0	0.3662	0.0126	0.0012	0.01	0.61

Peppers & onions	0.0235	0.0941	0.012	0.0104	0.01	0.85
French toast	0.17	0.41	0.06	0.01	0.01	0.34
Danishes	0.1714	0.5429	0.057	0.0067	0.01	0.212

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727 **Table 3**

728 Thermo-physical properties of all food items which undergo phase change during
729 freezing/thawing, evaluated using DSC and supporting experiments.

Initial freezing point (°C)	Final thawing point (°C)	Latent heat of phase change (kJ/kg)	Bound water fraction (x_b)
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Beefsteak	-1.9	-0.5	153.18	0.17
Concentrated orange juice	-4.5	-2.5	123.21	0.24
Peppers & onions	-3.2	-1.9	229.77	0.16
French toast	-1.2	-1	86.58	0.08
25% gelatin gel		-0.7	240.43	0.03

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Fig. 1. Theoretical apparent heat capacity curve

FIGURES

Fig. 2A. Five food items displayed in their respective packages

Fig. 2B. Model food system - 25% (w.b.) gelatin gel

Fig. 3A. 3D geometry of the menu box containing five food items

Fig. 3B. 3D geometry of the model food system

Fig. 4A. DSC thermograms obtained during freezing

Fig. 4B. DSC thermograms obtained during thawing

Fig. 5. Temp. history of beefsteak, during freezing

Fig. 6. Unf. water fraction as a function of Temp., (freezing)

Fig. 7A. Exp. validation of gel thawing at amb. temp. (1 & 2)

Fig. 7B. Exp. validation of gel thawing at amb. temp. (3 & 4)

Fig. 8A. Exp. validation of gel thawing inside a box (1 & 2)

Fig. 8B. Exp. validation of gel thawing inside a box (3 & 4)

Fig. 9A. Temperature distribution prediction at $t=0$

Fig. 9B. Temperature distribution prediction at $t=25$ h

Fig. 10A. Exp. validation of beefsteak and orange juice(thawing)

Fig. 10B. Exp. validation of peppers & onions and French toast