



## Review

## Enabling computer-aided food process engineering: Property estimation equations for transport phenomena-based models

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## ABSTRACT

During processing of a food, its temperature, moisture and other compositions, structure, etc., can change, continuously changing its physical properties. Realistic simulation of food processes require dynamic estimation of the food physical properties as they continue to change during the process. Having a few data points for a few states of the material, as is true for the majority of food properties data, is not sufficient for realistic process simulations. The goal of this article is a practical one: *it is to develop a concise resource for the equations that can estimate food properties as they change during processing*. Such a resource should make computer-aided food product, process and equipment design one step closer to reality by making the necessary input parameters available in one location and in a format that can be readily used in a simulation software. Several equilibrium, transport and electrical properties are included. The estimation equations for any property are chosen from among the most successful and accurate, staying away from property estimators that have theoretical basis but have not been as successful for food materials. For each property, implementation of its prediction equations in a computer model has also been discussed. Accuracy of each property estimation process have been included from the literature, showing most properties can be estimated to within 10% accuracy, sufficient for modeling purposes. Having such reasonable prediction models has the important implication that *unavailability of sufficient data, that is expected to be always true due to the variety and complexity of food materials and processes, is not a bottleneck for computer-aided food process engineering*.

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**Nomenclature**

| Symbol       | Description, units   | Greek symbols     |   |
|--------------|--|-------------------|---|
| $a_w$        | water activity, dimensionless  | $\lambda$         | latent heat, kJ/kg  |
| $A$          | Arrhenius factor   | $\mu$             | viscosity, kg/m s   |
| $b$          | constant for viscosity estimation, dimensionless                             | $\mu$             | chemical potential, kJ/kg   |
| $B$          | constant for water activity estimation, dimensionless                        | $\nu$             | specific volume, m <sup>3</sup> /kg   |
| $c$          | mass concentration, kg/m <sup>3</sup>  | $\epsilon$        | porosity, dimensionless   |
| $c$          | constant for bound water estimation, dimensionless                           | $\epsilon^0$      | initial porosity, dimensionless   |
| $C$          | stoichiometric charge, dimensionless   | $\phi$            | shrinkage–expansion coefficient, dimensionless                                  |
| $C_p$        | specific heat at constant pressure, J/kg K                                   | $\phi$            | shrinkage coefficient, dimensionless  |
| $C_v$        | specific heat at constant volume, J/kg K                                     | $\rho$            | density, kg/m <sup>3</sup>  |
| $C$          | molar concentration, kmol/m <sup>3</sup>                                     | $\rho_{app}$      | apparent density, kg/m <sup>3</sup> of total volume                             |
| $d_m$        | mean diameter, m   | $\alpha$          | volume of pores formed due to loss of water, m <sup>3</sup>                     |
| $d_i$        | sphericity factor for electrical conductivity estimation, dimensionless      | $\beta$           | volume of water and solids, m <sup>3</sup>                                      |
| $D$          | mass diffusivity, m <sup>2</sup> /s  | $\beta_e$         | constant for water activity estimation, dimensionless                           |
| $D_c$        | capillary diffusivity due to concentration gradient, m <sup>2</sup> /s       | $\nabla$          | gradient, m <sup>-1</sup>   |
| $D_T$        | capillary diffusivity due to temperature gradient, m <sup>2</sup> /s         | $\sigma$          | ionic conductivity, S/m   |
| $D_0$        | diffusivity at $X = 0$ , m <sup>2</sup> /s                                   | $\bar{\sigma}$    | conductivity of continuous phase, S/m   |
| $D_i$        | diffusivity as $X \rightarrow \infty$ , m <sup>2</sup> /s                    | $\sigma_{AB}$     | collision diameter, m   |
| $f$          | frequency, Hz  | $\psi$            | internal heat transfer term   |
| $f_k$        | distribution factor, dimensionless   | $\Omega_{D,AB}$   | function for estimating effective, diffusivity, dimensionless                   |
| $E$          | Arrhenius parameter, kJ/mol  | $\tau$            | tortuosity, dimensionless   |
| $\mathbf{E}$ | electric field, V/m  | $\tau$            | shear stress, Pa  |
| $g$          | gravity, m/s <sup>2</sup>  | $\tau$            | relaxation time, s  |
| $h$          | capillary head, m  | $\dot{\gamma}$    | shear rate, s <sup>-1</sup>   |
| $H$          | enthalpy, kJ/kg  | $\mu_0$           | magnetic permittivity of free space ( $4\pi \times 10^{-7}$ ), N/A <sup>2</sup> |
| $\mathbf{H}$ | magnetic field, T  | $\epsilon_0$      | electric permittivity of free space ( $8.85 \times 10^{-12}$ ), F/m             |
| $\dot{I}$    | rate of evaporation, kg/m <sup>3</sup> s                                     | $\epsilon$        | complex relative permittivity, dimensionless                                    |
| $j$          | parameter for thermal conductivity estimation, dimensionless                 | $\epsilon'$       | dielectric constant, F/m  |
| $k$          | permeability, m <sup>2</sup>   | $\epsilon''$      | dielectric loss factor, F/m   |
| $k$          | thermal conductivity, W/m K  | $\omega$          | angular frequency, rad/s  |
| $K$          | non-equilibrium evaporation constant in Eq. (11)                             |                   |   |
| $k_B$        | Boltzman constant, $1.38 \times 10^{-23}$ m <sup>2</sup> kg/s <sup>2</sup> K | <b>Subscripts</b> |   |
| $K_T$        | constant for temperature effect on viscosity, Pa s <sup>n</sup>              | $a$               | air   |
| $K_{TC}$     | constant for concentration effect on viscosity Pa s <sup>n</sup>             | $ai$              | initial apparent  |
| $L$          | length, m  | $app$             | apparent  |
| $m$          | mass, kg   | $ash$             | ash   |
| $m$          | molality, mol/kg   | $A$               | component A   |
| $M$          | molecular weight, kg   | $Asc$             | ascorbic acid   |
| $M_r$        | mass ratio, dimensionless  | $b$               | bulk  |
| $n$          | dissociation number, dimensionless   | $b$               | bound water   |
| $\bar{n}$    | mass flux, kg/m <sup>2</sup> s   | $bin$             | binary  |
| $\bar{n}$    | flow behavior index, dimensionless   | $B$               | component B   |
| $N$          | normality, mol/liter   | $c$               | capillary   |
| $p$          | pressure, partial pressure, Pa   | $c$               | condensed phase   |
| $P$          | pressure, Pa   | $carb$            | carbohydrates   |
| $\dot{q}$    | heat source, W/m <sup>3</sup>  | $Ca$              | calcium   |
| $\bar{q}$    | volumetric flux, m <sup>3</sup> /m <sup>2</sup>                              | $Cit$             | citric and isocitric acid   |
| $\bar{q}'$   | heat flux, W/m <sup>2</sup>  | $Cl$              | chlorine  |
| $\dot{Q}$    | Rate of heat generation, W/m <sup>3</sup>                                    | $disac$           | disaccharides   |
| $r$          | radius of the molecule, m  | $eff$             | effective   |
| $R_g$        | gas constant 8.315, kJ/kmol K  | $eq$              | equilibrium   |
| $S$          | Salinity, parts per thousand   | $exp$             | experimental  |
| $S_w$        | water, saturation = $\Delta V_w / \phi \Delta V$ , dimensionless             | $E_{mineral}$     | average or representative molecular weight of mineral                           |
| $S_g$        | gas, saturation = $\Delta V_g / \phi \Delta V$ , dimensionless               | $E_{acid/base}$   | average or representative molecular weight of acid/base                         |
| $t$          | time, s  | $f$               | freezing  |
| $T$          | temperature, ° C or K  | $fi$              | initial freezing  |
| $u$          | velocity, m/s  | $fw$              | free water  |
| $U$          | internal energy, kJ/kg   | $fat$             | fats  |
| $x$          | mass fraction, dimensionless   | $fiber$           | fibers  |
| $x^0$        | initial mass fraction, dimensionless   | $g$               | gas   |
| $X$          | moisture content, dry basis, kg of water/kg of total solids                  | $gr$              | gas, relative   |
| $V$          | total volume, m <sup>3</sup>   | $i$               | initial; also intrinsic   |
|              |  | $ice$             | ice   |

|                |                 |             |                 |
|----------------|-----------------|-------------|-----------------|
| <i>i,g</i>     | gas intrinsic   | <i>Oxa</i>  | oxalic acid     |
| <i>i,w</i>     | water intrinsic | <i>pa</i>   | parallel        |
| <i>ir</i>      | irreducible     | <i>prot</i> | proteins        |
| <i>K</i>       | potassium       | <i>P</i>    | phosphorous     |
| <i>l</i>       | liquid          | <i>r</i>    | relative        |
| <i>Lac</i>     | lactic acid     | <i>s</i>    | solid           |
| <i>Mal</i>     | malic acid      | <i>sat</i>  | saturated       |
| <i>m</i>       | material        | <i>se</i>   | series          |
| <i>m</i>       | mean            | <i>u</i>    | unfrozen water  |
| <i>Mg</i>      | magnesium       | <i>v</i>    | vapor           |
| <i>monosac</i> | monosaccharides | <i>vs</i>   | saturated vapor |
| <i>Na</i>      | sodium          | <i>va</i>   | vapor in air    |
| <i>NaCl</i>    | sodium chloride | <i>w</i>    | water,          |
| <i>Nit</i>     | nitrate         | <i>wr</i>   | water, relative |
| <i>o</i>       | oil             |             |                 |

## 1. Introduction

Design of food products, processes and equipment, for quality, safety and energy efficiency, is critically dependent on food properties. Quantitative knowledge of properties helps in a direct way by being part of computer models, in particular, physics-based computer models (see Fig. 1), that make design process more efficient. Indirectly, even when knowledge of properties is not part of a computer-based model, it can still help the design process in a qualitative manner. Elaborate physics-based models (as in Fig. 1) in computer-aided engineering are critically dependent, at a minimum, on estimated property data for various foods and their processing conditions. Although physics-based models have picked up speed in the recent years (e.g., see Bimbenet et al., 2007), they are generally pleading for property data.

Food materials are complex—they can be deformable/swellable capillary porous solid or complex liquid structures such as suspension, emulsion and colloids. In addition to this structure, properties of foods are generally dependent on composition, temperature (see Fig. 2) and even their histories. For such a complex material, measurement can seem to be an obvious choice. However, because of the above factors affecting property data, experimental techniques are far from being straight-forward, inexpensive, or low variability. Consequently, measured data points are particularly sparse, as can be seen in leading compilations (e.g., Rahman, 2009; Rao et al., 2005; Nesvadba et al., 2004; Saravacos and Maroulis, 2001). Even if such data sources were to get populated at a faster pace, it is practically impossible to come up with ways to cover every product and process combinations.

The alternative we are left with, in having quantitative data on properties, is to estimate them using predictive models. As a starter, we differentiate slightly between the terms *estimation* from *prediction*, which can be synonymous but estimation makes it more obvious that the results may be only approximate (Poling et al., 2001).

Estimation is particularly critical for food process modeling where the food material is always changing during a process, because of its temperature, moisture and other changes. For this article, *estimation* and *prediction* will be considered interchangeable. The book on generic properties of gases and liquids (Poling et al., 2001) provides insights into properties and their predictions but is not directly useful for estimating food properties. Like other advances in food processing, predictive models have also been improving. Publications on property modeling generally refer to a very small subset of the properties (e.g., Fikiin and Fikiin, 1999; Becker and Fricke, 1999). More importantly, publications on property modeling typically do not address the relationship of the property to various types of process models. Depending on the model formulation, a process model can require a significantly different version of the

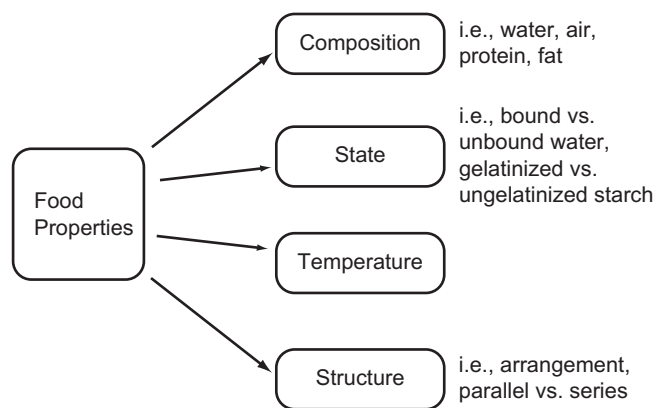


Fig. 2. Factors to consider in predicting food properties. In most cases, structure effect is not included in any simple manner but separate correlation is considered when the structure changes.

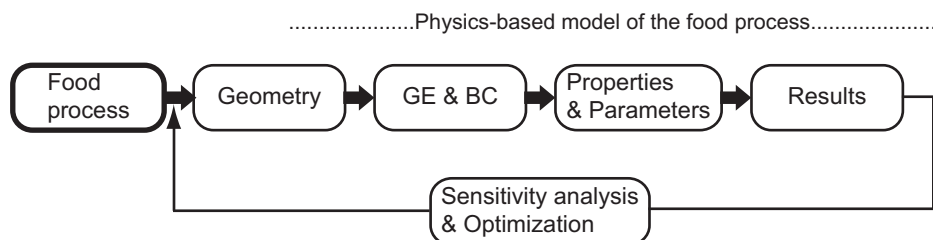


Fig. 1. A physics-based computer model replaces a physical process by its computer analog consisting of a geometry, governing equations (GE), boundary conditions (BC), and properties and parameters. Computer-aided engineering design is often interested in the sensitivity of the model to properties (and other components) in an effort to optimize the process. This is somewhat different from being interested in the exact output of the model for one specific condition.

property. Often, knowledge of how the property changes with temperature and composition during a process is required. Having the best of the predictive models available under one umbrella, showing clearly the relationship to the models, is deemed to be useful for the food process modeling community in particular and food product/process/equipment design community in general.

This article is not intended to be an introduction to properties, for which the reader is referred to textbooks such as Bird et al. (2006) for transport properties or reference books covering many properties (Rahman, 1995, 2009; Rao et al., 2005; Perry and Green, 2008; Saravacos and Maroulis, 2001). When correlations over temperature, moisture or other parameter range are not available but point data are available (thermal conductivity at various temperature values, for example), linear interpolation is done between the two parameter values as needed during a simulation; this is standard in most computational software and does not need to be discussed here. The article is also not meant to reproduce in any significant way the property data or models available for standard materials available in many excellent handbooks (e.g., Perry and Green, 2008) or databases. For lack of space, we do not provide plots of the equations reported here, although such plots are useful in having a better picture of the variations.

Our approach and the organization of the manuscript are as follows. Exhaustive compilation of models for all needed properties would be unrealistic to achieve in this first attempt. Thus, we chose some of the most common structural, thermodynamic, transport and electrical properties that cover a great majority of the typical food processes. Models are described as functions of food group, composition, temperature, moisture content or combinations, as available. Wherever possible, models are mentioned for various categories of foods (such as for initial freezing point, thermal conductivity, and dielectric properties). Recently developed models with broader applicability and improved accuracy have been the preferred choice. Robustness of models have been included by providing accuracy data such as percentage error, whenever available. Attention is always paid to the primary intended use of this compilation—their incorporation in food process simulation. The expressions provided here are readily implementable in most commercial simulation software. We follow the sequence of porosity, density, initial freezing point, ice-fraction, water activity, specific heat, enthalpy, thermal conductivity, mass diffusivity, viscosity, dielectric properties and electrical conductivity.

## 2. Which properties?

Our focus in this article is transport phenomena-based modeling of food products and processes. Even so, the scope has to be

limited and thus the selection of properties was limited to the ones perceived to be the most in demand for transport phenomena-based models. Approaches to modeling can be categorized from the most elaborate (e.g., multiphase transport in porous media where separate phases are tracked) to semi-empirical (using parameters such as effective diffusivity where all phases are lumped together using an *effective* property). We hope to cover the properties needed for this entire range of modeling approaches. To make an easy connection between various physics and the relevant physical properties, a short and compact version of the governing equations for the two different physics of transport phenomena and electromagnetics (e.g., microwave and radiofrequency (RF) heating) are provided below.

### 2.1. Transport phenomena in porous media

The standard single phase continuum transport equations (for fluid flow, heat transfer and mass transfer) are not repeated here and the author is referred to books such as Bird et al. (2006). An enormous range of food processes involving solids can be viewed as involving transport of heat and mass through porous media. Processes already modeled using this formulation include drying, frying, microwave heating, meat roasting, puffing, and rehydration of solids. A porous media formulation homogenizes the real porous material and treats it as a continuum where the pore scale information is no longer available. In the most general version of the porous media formulation (for rigid porous media), individual phases of water, water vapor, air, and energy are tracked using their conservation equations.

$$\text{Water} \quad \frac{\partial c_w}{\partial t} + \vec{\nabla} \cdot (\vec{n}_w) = -\dot{I} \quad (1)$$

$$\text{Vapor} \quad \frac{\partial c_v}{\partial t} + \vec{\nabla} \cdot (\vec{n}_v) = \dot{I} \quad (2)$$

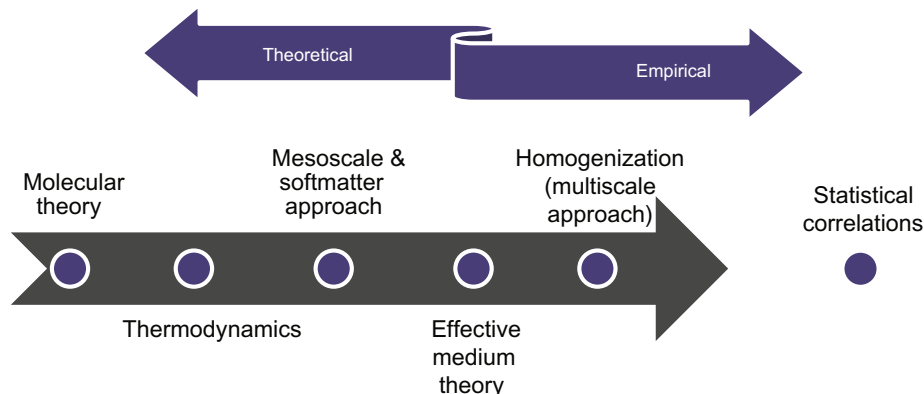
$$\text{Air} \quad \frac{\partial c_a}{\partial t} + \vec{\nabla} \cdot (\vec{n}_a) = 0 \quad (3)$$

$$\text{Energy} \quad (\rho C_p)_{\text{eff}} \frac{\partial T}{\partial t} + \sum_{i=w,a,v} (C_{p,i} \vec{n}_i) \cdot \vec{\nabla} T = \vec{\nabla} \cdot (k_{\text{eff}} \vec{\nabla} T) - \lambda \dot{I} + \dot{Q} \quad (4)$$

Here

$$\vec{n}_w = -\rho_w (k_w / \mu_w) \vec{\nabla} p_g - D_{w,cw} \vec{\nabla} c_w - D_{w,T} \vec{\nabla} T \quad (5)$$

is the flux of water due to gas pressure, moisture dependence of capillarity and temperature dependence of capillarity, respectively. Similarly, flux of water vapor is given by



**Fig. 3.** Models used to predict property can range from completely theoretical (often useful for only pure materials) to completely empirical (as is true for the majority of usable models for a complex material such as food). This article focuses on models based primarily on effective medium theory and statistical correlations such that they can be readily used for large groups of real food materials in process simulations.

**Table 1**  
Summary of physical properties with accuracy information.

| Property                | Equation No.    | Accuracy          | Measure of accuracy                    |
|-------------------------|-----------------|-------------------|--|
| Porosity                | (29)            | 0.033–10186       | root mean square deviation (RMSD)      |
| Bulk density            |                 |                   |  |
| Theoretical model       | (38)            | ≤4%               | percent error                          |
| Pure components         | (43)–(50)       | ±5%               | percent error                          |
| Specific Heat           |                 |                   |  |
| Pure components         | (68)–(76)       | ±5%               | percent error                          |
| Apparent                | (78)            | -                 |  |
| Ice fraction            | (56)            | ≤4.75%            | percent error                          |
| Initial freezing point  | (51)            | ±0.22 – ± 0.38 °C | absolute difference                    |
| Thermal conductivity    |                 |                   |  |
| Generic model           | (87)–(89)       | ≤0.02 W/m.K       | uncertainty in prediction (e)          |
| Fruits and vegetables   | (90)–(93)       | ≤10%              | percent error                          |
| Meat products           | (100)           | ≤10%              | percent error                          |
| Frozen foods            | (101) and (102) | 8%                | percent error                          |
| Component foods         | (105)–(112)     | ±10%              | percent error                          |
| Mass diffusivity        |                 |                   |  |
| Semi-empirical model    | (124)–(126)     | -                 |  |
| Empirical model         | (127)           | not reported      |  |
| Permeability            | (131)           | 0.95              | coefficient of determination ( $R^2$ ) |
| Viscosity               |                 |                   |  |
| Temperature effects     | (142)           | 0.99–1.00         | coefficient of determination ( $R^2$ ) |
| Concentration effects   | (143)           | 0.94–0.99         | coefficient of determination ( $R^2$ ) |
| Water activity          |                 |                   |  |
| Unfrozen foods          | (59)–(61)       | ≤2%               | percent error                          |
| Frozen foods            | (61)–(63)       | ≤1%               | percent error                          |
| Dielectric properties   |                 |                   |  |
| Salt solutions          | (145)           | ≤6%               | percent error                          |
| Cereal grains           | (156)           | 5–10%             | percent error                          |
| Meat products           | (158)           | 5–10%             | percent error                          |
| Fruits and vegetables   | (160)           | 6.2–13.22%        | percent error                          |
| Gums                    | (161)           | 0.91–0.92         | coefficient of determination ( $R^2$ ) |
| Frozen foods            | (164)           | -                 |  |
| Electrical conductivity | (166)           | 0.971–0.993       | coefficient of determination ( $R^2$ ) |

$$\vec{n}_v = -\rho_v(k_g/\mu_g)\vec{\nabla}p_g - \left(C_g^2/\rho_g\right)M_vM_aD_{bin}p_v/p_g^2\vec{\nabla}p_g - D_{v,cw}\vec{\nabla}c_w - D_{v,T}\vec{\nabla}T \quad (6)$$

due to gradients in gas pressure and water vapor pressure (decomposed into three separate effects representing the last three terms in Eq. (6)—binary diffusion, driven by liquid concentration and driven by temperature) (Halder et al., 2011). There is no distinct flow equation as the Darcy's law is used in water, water vapor and air transport equations as a replacement for the fluid flow or momentum equation. The set of equations are often solved by transforming the concentrations in terms of saturations. Concentrations are related to saturation,  $S_w$ , by

$$c_v = p_v(1 - S_w)\epsilon M_v/RT \quad (7)$$

$$c_a = (p_g - p_v)(1 - S_w)\epsilon M_a/RT \quad (8)$$

$$c_w = \rho_w\epsilon S_w \quad (9)$$

To complete the system, we need an additional equation. This additional information provides the rate of evaporation and can be formulated in one of two ways (Halder et al., 2011):

$$p_v = p_{v,eq}(X, T) \quad (10)$$

$$\dot{I} = K(\rho_{v,eq} - \rho_v)S_g\epsilon \quad (11)$$

Eq. 10 is the equilibrium relation for the material which relates the vapor pressure to moisture and temperature and Eq. (11) is an explicit expression for the evaporation rate  $\dot{I}$  used in a nonequilibrium formulation. Here,  $K$  is a material and process-dependent parameter signifying the rate constant of evaporation.

#### 2.1.1. Alternate equation for mass transport

Instead of the separate liquid transport equation (Eq. (1)) and the vapor transport equation (Eq. (2)), in the most common formu-

lation in food literature, these are combined into an effective “moisture” phase with the following equations

$$\frac{\partial c_w}{\partial t} = \nabla \cdot (D_{cw} \nabla c_w) \quad (12)$$

Here, the pressure gradient inside the food is zero due to atmospheric conditions and transport of liquid or vapor due to temperature gradients are small compared to liquid and vapor transport due to moisture gradients (Dhall and Datta, 2011). The diffusivity  $D_{cw}$  is due to liquid and vapor diffusion from gradient in water content, given by

$$D_{cw} = D_{w,cw} + D_{v,cw} \quad (13)$$

that includes capillary pressure dependence on moisture content (in  $D_{w,cw}$ ) and vapor pressure dependence on moisture content (in  $D_{v,cw}$ ). Here, the quantity  $D_{cw}$  would be equivalent to the commonly referred effective diffusivity,  $D_{eff}$ .

#### 2.1.2. Model inclusion

Eq. (12) is used extensively in food literature to model drying like processes. This  $D_{cw}$  (or  $D_{eff}$ ) is usually estimated by fitting experimentally observed drying curves and therefore includes all phases of moisture transport. Although it can be shown that liquid and vapor diffusivities can be combined into this  $D_{cw}$  used in Eq. (12) (Kolhapure and Venkatesh, 1997), in practice, even modes such as pressure driven flow and shrinkage would be included as this property is estimated from experimental data.

#### 2.2. Electromagnetic heating

Microwave, radiofrequency and other electromagnetic heating are described by Maxwell's equations of electromagnetics:



$$\vec{\nabla} \times \mathbf{E} = -j\omega\mu_0\mathbf{H} \quad (14)$$

$$\vec{\nabla} \times \mathbf{H} = j\omega\epsilon_0\epsilon\mathbf{E} \quad (15)$$

$$\vec{\nabla} \cdot \epsilon\mathbf{E} = 0 \quad (16)$$

$$\vec{\nabla} \cdot \mathbf{H} = 0 \quad (17)$$

where  $\mathbf{E}$  is the electric field intensity and  $\mathbf{H}$  is the magnetic field intensity. The complex relative permittivity,  $\epsilon$ , of the dielectric material (food) is given by:

$$\epsilon = \epsilon' + i\epsilon'' \quad (18)$$

where  $\epsilon'$  is the dielectric constant and  $\epsilon''$  is the dielectric loss factor—these two parameters being called the dielectric properties of materials. The heat absorbed by the food per unit time due to the electromagnetic heating is given by:

$$\dot{Q}(\vec{x}, t) = \frac{1}{2} \omega \epsilon_0 \epsilon'' |\mathbf{E}|^2 \quad (19)$$

This equation shows how the rate of heating depends on  $\epsilon''$ . The other property,  $\epsilon'$ , affects the heating rate through its effect on the electric field,  $\mathbf{E}$ .

### 3. Model types: theoretical, semi-empirical and empirical

Physical properties of every substance depend directly on the nature of their molecules. A complete understanding of molecular behavior, together with thermodynamics, should allow us to predict the physical properties of substances. But, such predictions are possible today only for very restricted situations and this approach is generally not possible for foods. A property estimate may be based on the most rigorous theories (molecular or thermodynamic) on one extreme and completely empirical (statistical correlation of experimental data) on the other (Fig. 3). Models based primarily on molecular theory, thermodynamics and the like (moving leftward in Fig. 3) will be termed as *theoretical* in this manuscript. Examples of such models outside of food can be seen in books such as Assael et al. (1996) and Poling et al. (2001). Although it can be the most instructive route to obtain properties, it is fair to generalize that the majority of such predictions are, for now, simpler systems than the food materials of our interest (see next paragraph for recent efforts for foods). A completely *empirical model* is simply a statistical correlation, without regard to underlying physics. This is the other extreme situation in contrast with theoretical models, shown on the right end of Fig. 3. Empirical models are useful when applied within parameter ranges that are very similar to those used to establish the correlations. A *semi-empirical model* is anywhere in between the completely theoretical and completely empirical model. Semi-empirical models often have the basic form that came from theoretical considerations (i.e., they are extensions of the theory) but has parameters that come from fitting experimental data. For all types of models and for especially the empirical and semi-empirical models, it is important to use the models within the narrow range of parameters in which they were developed.

Examples of food property estimation covering this range from theoretical to empirical in Fig. 3 can be seen for partition coefficients using atomistic Flory–Huggins approach (Gillet et al., 2010), for state-diagram of starch using Flory–Huggins theory (van der Sman and Meinders, 2011), for initial freezing point and water activity using thermodynamics (van der Sman and Boer, 2005), for enthalpy and thermal conductivity of frozen meat and fish products using effective medium theory (van der Sman, 2008), transport properties using homogenization that is averaging of microscale properties (Ho et al., 2011) and finally statistical correlations (Choi and Okos, 1986). Note that of the examples just provided, the more theoretically-based ones are fairly new. In general,

the stronger the theoretical basis, greater is the potential reach of the estimation method but harder is the application to real systems. Like in other fields, most of the better estimation methods use equations based on the form of an incomplete theory with empirical correlation of the parameters that are not provided by that theory (making them semi-empirical). Introduction of empiricism into parts of a theoretical relation provides a powerful method of developing a reliable method, useful for estimation purposes. Thus, combing through the food property literature shows the best of the estimation equations that are readily usable today are necessarily semi-empirical to empirical and that is how the article will be organized.

### 4. Accuracy and choice among property models

An appropriate quote in this context can be “All models are wrong, but some are useful”. The most accurate method of property prediction may not be the best for the purpose of its inclusion in process modeling or engineering modeling in general, the context of this article. For example, in a complex process simulation that is already computationally demanding, the most accurate method of prediction can put additional unreasonably large computational overhead. For such reasons, for process modeling, simpler property estimation methods that require less parameters would be generally preferred over complex estimation methods that may be more accurate. The important point is that process modeling needs to be followed by sensitivity analysis of the process with respect to that property. Sensitivity analysis will allow the full benefit of the modeling process in design, instead of getting completely bogged down in property prediction details. Of course, if sensitivity analysis shows that the process is particularly sensitive to a property, one has typically no choice but to measure that property carefully over the needed range of conditions. Sampling of errors in property prediction models can be seen in Table 1 that lists the models discussed in this article. A very important point to note from this table is that we can predict most of the properties with an error of 10% or less—this is not that far away from the accuracy of typical experimental data.

Another important note in choosing the accuracy of a property model is that in the overall process modeling, as shown in Fig. 1, the total error in process calculation is contributed by each of the components, i.e., geometry, governing equations, boundary conditions, properties and other parameters. The contributions of each component to the total error depends also on the particular process, i.e., effect of thermal conductivity is not the same for a sterilization process as compared to a baking process. Thus, the need for accuracy in the properties data that is only one component of the overall process modeling should be seen in light of the level of accuracy available in all the other components of the process model shown in Fig. 1. If there are choices between several property models, the one chosen is a compromise between several factors—(1) it should be reliable over a range of temperature, composition and other conditions; (2) it should require as few input data as possible; (3) it should be as accurate as possible; and (4) it should have the least complexity in terms of modeling.

### 5. Composition data

Composition is one of the main parameters determining a property, as will be seen in this article. Many of the empirical and semi-empirical predictive models take the form of volume or mass weighted properties of the components making up the food. Whenever generic composition data is needed, it can be obtained from the USDA National Nutrient Database for Standard Reference, Release 19, which contains data for 7293 food items and up to 140

nutrients and other components. It is freely available and downloadable. Other sources of food composition data also exist (e.g., Souci et al., 2000). Combination of the composition database and generic models described in this article can provide a very powerful approach to estimate a property with little effort.

Pure component properties underlie much of the observed behavior of a complex material (Poling et al., 2001). Also, pure component property constants are often used as the basis for composition-dependent mixing rules for the composite or effective property. Thus, whenever appropriate, pure component properties are included for convenience.

## 6. Effective properties

Except for a few simple properties that do not depend on the structure of the material, effective property of a composite material (as is any food) depends on the type of property (or the physics) and the structure, and simple universal prediction equations for the effective properties of the composite material is not possible. Thus, the effective property equations will not have the same format for thermal conductivity and dielectric properties (see Eqs. (85) and (86) and Eq. (144), respectively, later). Entire branches of science have developed in predicting properties of a composite material. The process of obtaining effective properties from microscale information of the structure and composition is called homogenization (Guessasma et al., 2011) that is not the topic of this article. Thus, for Eqs. (1)–(4) in a porous media-based model, effective specific heat (that is composite structure independent) is estimated following Eq. (64) as  $C_{p,eff} = -x_g C_{p,g} + x_w C_{p,w} + x_s C_{p,s}$ , which is a simple volume average of the properties of the individual components, weighted by the volume fraction of the components. Although such averaged form of equation has been used for obtaining effective density and thermal conductivity in the same porous media models, this form may not be valid for all materials and under all processing conditions.

## 7. Porosity

Porosity can be defined as the ratio of the total volume occupied by the fluid to the total volume of bulk solid. Porosity of a food material  $\epsilon$ , can be defined as:

$$\epsilon = \frac{V_g}{V_g + V_w + V_s} + \frac{V_w}{V_g + V_w + V_s} = \epsilon_g + \epsilon_w \quad (20)$$

where  $V_g, V_w$  and  $V_s$  are the volumes of gas (air, water vapor), water and solid, respectively. Volumes of gas and liquid change as a process such as drying proceeds. Porosity affects most physical properties including mechanical and transport, as can be seen in Eqs. (7)–(9). As one phase is replaced by air, for example, moisture is replaced by air in drying, significant changes in porosity can occur that would change heat and mass transport in a critical way. Thus accurate estimation of heat and mass transfer requires predictive models of porosity with processing—most common situation being prediction of  $\epsilon_g$  and  $\epsilon_w$  with change in moisture content.

Porosity, although one of the quantitative measures of food structure, is both material and process dependent. Porosity depends on the time–temperature and time–moisture history of a particular food during processing and thus is affected by the transport processes as well as the mechanics of the deformation of the solid matrix. First-principle based models for porosity, therefore, would require detailed transport and hygro-mechanical models to predict changes in dimension during processing (e.g., see Scherer, 1990). Using such models, porosity can come out as a model output rather than a model input (Rakesh and Datta, 2011). In simpler

computation, of course, we can enforce a porosity change with process, primarily as function of moisture content. For such purposes, semi-empirical models exist that can be useful. The difficulty with prediction of porosity is the inability to predict shrinkage or collapse phenomena. Thus, the semi-empirical models derive their shrinkage/collapse information from curve-fitting of experimental data for the same material and process (Rahman, 2003; Khalloufi et al., 2009). One such model that takes into account the shrinkage/expansion coefficient to predict the porosity due to gas phase  $\epsilon_g$  is presented here (Rahman, 2003). The procedure involves calculating the material density (excluding gases) at any given moisture content.

$$\frac{1}{\rho_m} = \sum_i \frac{x_i}{\rho_i} \quad (21)$$

where  $x_i$  and  $\rho_i$  are the mass fraction and density, respectively of component  $i$ . As drying proceeds, the material loses moisture and as a result the mass fractions of the components change. The mass fraction of each component at any given moisture content during drying is given as (Eq. (22)):

$$x_i = \frac{x_i^0}{M_r} \quad (22)$$

where  $M_r$  is the mass ratio at any moisture content relative to the initial mass estimated using Eq. (23)

$$M_r = \frac{1 - x_w^0}{1 - x_w} \quad (23)$$

that is obtained from solids balance. Under ideal conditions, the volume of water removed during drying is replaced by the volume of water vapor and air, i.e., no shrinkage. In such cases, the volume occupied by gases formed due to the loss of water ( $\alpha$ ) and the volume of water and solids at any given moisture content ( $\beta$ ) is expressed as:

$$\alpha = \frac{1 - M_r}{\rho_w} \quad (24)$$

$$\beta = \frac{M_r}{\rho_m} \quad (25)$$

where, in the absence of initial porosity (due to gas phase), the volume fraction of gas phase is:

$$\epsilon'_g(X) = \frac{\alpha}{\alpha + \beta} \quad (26)$$

and, when the material has initial porosity ( $\epsilon_g^0$ ), the porosity under ideal conditions is expressed as:

$$\epsilon_g(X) = \epsilon_g^0 + (1 - \epsilon_g^0) \epsilon'_g(X) \quad (27)$$

Constant porosity and no shrinkage are often stated as key assumptions in models for drying. These assumptions could be used as initial estimations when experimental results are not available. The ideal porosity models can be extended to non-ideal situations by introducing a shrinkage/expansion coefficient ( $\phi$ ) as:

$$\epsilon''_g(X) = \frac{\phi \alpha}{\phi \alpha + \beta} \quad (28)$$

The shrinkage/expansion coefficient accounts for the deviations seen in the amount of pores formed to that of water evaporated during drying. The porosity under non-ideal conditions can thus be obtained as:

$$\epsilon_g(X) = \epsilon_g^0 + (1 - \epsilon_g^0) \epsilon''_g(X) \quad (29)$$

and the value of  $\phi$  can be estimated as a fitting parameter from Eqs. (28) and (29) as:



**Table 2**

Average molecular weight of food in each category (Boonsupthip et al., 2009).

| Category     | Molecular weight |           |
|--------------|------------------|-----------|
|              | Mineral          | Acid/base |
| Fruit        | 39.00            | 163.10    |
| Vegetable    | 39.00            | 163.10    |
| Meat         | 32.13            | 90.03     |
| Seafood      | 32.13            | 176.10    |
| Dairy (milk) | 32.13            | 192.10    |
| Cheese       | 32.13            | 90.03     |

$$\phi = \frac{\beta(\epsilon_g^o - \epsilon_{g,exp})}{\alpha(\epsilon_{g,exp} - 1)} \quad (30)$$

where  $\epsilon_{g,exp}$  is the actual measured gas porosity as a function of moisture content,  $\alpha$  and  $\beta$  are given by Eqs. (24) and (25). The model for  $\epsilon_g$  above certainly has advantages over completely empirical models, even though it has one fitting parameter ( $\phi$ ) that explains the deviations in the porosity values observed during drying. The model was tested using experimental data of apples (Lozano et al., 1980) and garlic (Madamba et al., 1994) and the root mean square deviation (RMSD) was found to be 0.186 and 0.033, respectively (Rahman, 2003; Khalloufi et al., 2009).

The porosity attributed to water,  $\epsilon_w$ , calculated as a function of moisture content comes from mass balance and is given as Eq. (31):

$$\epsilon_w = \frac{V_w}{V_s + V_w + V_a} \quad (31)$$

$$= \frac{m_w}{\rho_w} \frac{\rho_b}{m_b} \quad (32)$$

$$= \frac{\rho_b}{\rho_w} \left[ \frac{X}{1+X} \right] \quad (33)$$

The expression for  $\epsilon_w$  can be further simplified using bulk density relationship (Eq. (38)) described later to get an explicit expression of  $\epsilon_w$  in terms of moisture content and  $\epsilon_a$  as:

$$\epsilon_w = \frac{\rho_s}{\rho_w} (1 - \epsilon_a) \left[ \frac{X}{1 + \frac{\rho_s}{\rho_w} X} \right] \quad (34)$$

### 7.1. Model inclusion

Using the expressions of  $\epsilon_g$  (Eq. (29)) and  $\epsilon_w$  (Eq. (33)), the total porosity of the food material is calculated as a function of moisture content (Eq. (20)). It is this total porosity that is used in Eqs. (7)–(9). Inclusion of this moisture dependence of porosity will make it possible for porosity to change with processing.

## 8. Density

Density is defined as mass per unit volume and is one of the most important physical properties needed for process simulations. There can be many different types of density such as true density, material density, particle density, apparent density and bulk density, each one being defined differently (Rahman, 1995, 2009). The transport equations are generally based on bulk density. As with porosity, density of foodstuffs also changes with moisture content and thus accurate prediction of density with moisture content is important in process modeling.

### 8.1. Theoretical models

A first-principle based model for bulk density as function of moisture content has been presented in the context of drying (Khalloufi et al., 2010). The bulk density is calculated as:

$$\rho_b = \frac{m_w + m_s}{V_s + V_w + V_a} \quad (35)$$

$$= \rho_w \frac{V_w}{V_s + V_w + V_a} + \rho_s \frac{V_s}{V_s + V_w + V_a} \quad (36)$$

$$= \rho_w \epsilon_w + \rho_s (1 - \epsilon_w - \epsilon_a) \quad (37)$$

The porosity attributed to water,  $\epsilon_w$ , as a function of moisture content and that attributed to gas,  $\epsilon_g$ , in terms of the moisture content and shrinkage/expansion coefficient,  $\phi$ , is discussed in Section 7. Substituting these values, the equation for bulk density is written as

$$\rho_b = \rho_s (1 - \epsilon_g) \left( \frac{1 + X}{1 + (\rho_s/\rho_w)X} \right) \quad (38)$$

where  $\epsilon_g$  is the gas porosity that is a function of moisture content given, by either Eq. (27) or (29). In most bulk density calculations, the density of the solids,  $\rho_s$ , is generally obtained as a fitting parameter or is obtained experimentally (Khalloufi et al., 2010). The model could predict bulk density for a range of products (e.g., carrot, potato, apple, sweet potato, whole garlic, sliced garlic) and processing conditions (e.g., air, microwave plus vacuum drying) to within an accuracy of 4% or less.

#### 8.1.1. Model inclusion

During a process such as drying, moisture is lost (replaced by air or another component) and the bulk density in Eq. (4) evolves with the process. This bulk density will be calculated as a function of moisture content using Eq. (38).

### 8.2. Empirical models: pure materials

Density of water as a function of temperature is given by (McCabe et al., 2005)

$$\rho_w = 1001.4 - 0.1276(T - 273) - 0.0029(T - 273)^2 \quad 273K \leq T \leq 423K \quad (39)$$

Both air and water vapor are generally considered as ideal gases and the density of the gas phase is obtained using ideal gas law:

$$\rho_g = \frac{p_g M_g}{R_g T} \quad (40)$$

$$M_g = x_a M_a + x_v M_v \quad (41)$$

Here  $x_a$  and  $x_v$  are the mass fractions of air and vapor, respectively.

### 8.3. Empirical models: food materials

Densities of solid food materials mainly depend on composition and temperature. The following empirical correlations (Eqs. (43)–(50)) have been widely used (Choi and Okos, 1986). They do not require the detailed analysis mentioned under theoretical models above but they are completely empirical, based on the procedure described under empirical models for thermal conductivity (Section 14). The bulk density of the composite food is computed from its individual component densities and their mass fractions as

$$\frac{1}{\rho_b} = \sum_i \frac{x_i}{\rho_i} \quad (42)$$

The densities of individual components,  $\rho_i$  are given by ( $-40^\circ\text{C} \leq T \leq 150^\circ\text{C}$ ):

$$\rho_a = 12.847 - 3.2358 \times 10^{-3}T \quad (43)$$

$$\rho_w = 9.9718 \times 10^2 + 3.1439 \times 10^{-3}T - 3.7574 \times 10^{-3}T^2 \quad (44)$$

$$\rho_{ice} = 9.1689 \times 10^2 - 0.1307T \quad (45)$$

$$\rho_{prot} = 1.3300 \times 10^3 - 0.5184T \quad (46)$$

$$\rho_{carb} = 1.5991 \times 10^2 - 0.31046T \quad (47)$$

$$\rho_{fat} = 9.2559 \times 10^2 - 0.41757T \quad (48)$$

$$\rho_{fiber} = 1.3115 \times 10^3 - 0.36589T \quad (49)$$

$$\rho_{ash} = 2.4328 \times 10^3 - 0.28063T \quad (50)$$

This method has limited applications as it does not take into account the porosity effects or the interaction between phases. Also, the expressions above are simply results of statistical correlation between experimental data and the individual densities; thus the use of Eqs. (43)–(50) cannot be compared directly with Eq. (38). See also discussion under Section 12.3.

## 9. Initial freezing point

Initial freezing point is the temperature at which the first ice crystals appear as temperature is lowered. Initial freezing point of food systems are lower than that of water due to several dissolved constituents. The vast majority of raw foods, owing to their high moisture content, have their freezing point between 0 and  $-4^\circ\text{C}$  (Rahman, 2009).

### 9.1. Semi-empirical approach

Several models for prediction of initial freezing point,  $T_{fi}$ , have been developed based on food composition (Schwartzberg, 1976; Chen et al., 1990; Singh and Mannapperuma, 1990; Miles et al., 1997; Hartel, 2001; Boonsupthip and Heldman, 2007; Boonsupthip et al., 2009). The method developed by Boonsupthip et al. (2009) based on average molecular weights of food components for different categories of food products, i.e., fruits, vegetables, meat products, dairy products (milk and cheese) is:

$$\frac{1}{T_{fi}} = \frac{1}{T_{f0}} - \frac{R}{\lambda_{ice}M_w} \ln \left( \frac{(x_w - x_b)/M_w}{(x_u - x_b)/M_w + \sum_i (x_i/M_i)} \right) \quad (51)$$

where  $T_{f0}$  is the freezing temperature of pure water (273.15 K),  $x_w$  is the mass fraction of total amount of water,  $x_b$  is the mass fraction of bound water (see Section 10),  $x_i$  is the mass fraction of key food components,  $M_w$  is the molecular weight of water, and  $M_i$  is the molecular weight of key food components. The mass of various components are calculated based on the total mass of food excluding the amount of ice. Eq. (54) was used to calculate the amount of bound water.

$$\sum_i \frac{x_i}{M_i} = \frac{x_{prot}}{M_{prot}} + \frac{x_{carb}}{M_{carb}} + \frac{x_{fiber}}{M_{fiber}} + \frac{x_{monosac}}{M_{monosac}} + \frac{x_{disac}}{M_{disac}} + \frac{x_{Na} + x_{Mg} + x_P + x_{Cl} + x_K + x_{Ca}}{M_{E,mineral}} + \frac{x_{Nit} + x_{Oxa} + x_{Lac} + x_{Mal} + x_{Asc} + x_{Cit}}{M_{E,acid/base}} \quad (52)$$

The above equation comes from categorizing the solutes into—(1) low-molecular carbohydrates (mono- and disaccharides); (2) minerals (sodium, potassium, magnesium, chlorine, phosphorous, and calcium); and (3) acids/bases (nitrates, oxalic acid, lactic acid, malic acid, ascorbic acid, and iso-citric/citric acid). Average molecular weights for categories 2 and 3,  $M_{E,mineral}$  and  $M_{E,acid/base}$ , are shown in Table 2. The molecular weight of proteins ( $M_{prot}$ ), carbohydrates ( $M_{carb}$ ), fibers ( $M_{fiber}$ ) in the above equation are assumed a value of 50000 while molecular weight for mono-saccharides ( $M_{monosac}$ ) and

disaccharides ( $M_{disac}$ ) are 180.16 and 342.29, respectively. The initial freezing point,  $T_{fi}$ , predicted using Eq. (51) for 212 foods with standard composition data in the literature (Souci et al., 2000), has an absolute difference (AD) lying between  $\pm 0.22$  and  $\pm 0.38^\circ\text{C}$  when compared with experimental results.

Eq. (51) is simpler and more robust over previous models (e.g., Schwartzberg, 1976; Chen et al., 1990) by not requiring detailed composition data. It does not have any fitting or empirical parameter that needs to be estimated from experimental values. It is readily implementable in a commercial software as part of estimation of ice-fraction.

## 10. Estimation of ice-fraction

Foods freeze over a temperature range as the water in the food has many dissolved constituents whose concentration increases as some of the water freezes. Estimation of frozen fraction or ice-fraction is useful, in turn, in other property estimations involving frozen or partially frozen foods.

### 10.1. Semi-empirical model

Of the many models in literature (for e.g. Heldman, 1974; Schwartzberg, 1976; Chang and Tao, 1981; Miles et al., 1983; Pham, 1996; Fikiin and Fikiin, 1999; van der Sman, 2008) for estimating ice-fraction, the most widely used model is based on Raoult's Law and Clausius–Clapeyron equation as:

$$x_{ice} = (x_w - x_b) \left( 1 - \frac{T_{fi}}{T} \right) \quad (53)$$

where  $x_w$  is the fraction of water,  $x_b$  is the fraction of bound water, and  $T_{fi}$  is the initial freezing point, discussed in Section 9. The amount of bound water can be estimated using the following empirical equation (Schwartzberg, 1976):

$$x_b = cx_s \quad (54)$$

where  $c$  is a product category specific empirical constant and  $x_s$  is the sum of solids mass fraction i.e. proteins, carbohydrates, lipids, ash and fibers (Schwartzberg, 1976; Chen, 1985b; Pham, 1987; Mannapperuma and Singh, 1989). The range of values of  $c$  proposed for different food categories are: 0.24–0.27 for meats and fish, 0.18–0.25 for vegetables, 0.15–0.20 for glucose, 0.3 for sucrose, 0.11 for egg products, 0.13 for bread and 0.40 for Tylose gel (Schwartzberg, 1976; Chen, 1985b; Pham, 1987). Alternate models for estimation of bound water content are also available for specific groups of food products, for example, the following equation was used based on protein and carbohydrate mass fractions for meat products (van der Sman and Boer, 2005):

$$x_b = 0.299x_{prot} + 0.10x_{carb} \quad (55)$$

The  $x_b$  value is substituted in Eq. (53) to compute  $x_{ice}$ .

### 10.2. Empirical model

Completely empirical models of ice fraction have been developed. For example, the following equations (Tchigeov, 1956, 1979) estimate ice fraction for meats, fish, milk, eggs, fruits and vegetables with sufficient accuracy (Fikiin, 1998):

$$\frac{x_{ice}}{x_w} = \frac{1.105}{1 + (0.70138 / \ln(T_{fi} - T + 1))} \quad (56)$$

This equation is valid in the range  $-45 \leq T \leq T_{fi}$  and  $-2 \leq T_{fi} \leq -0.4$  where  $T_f$  and  $T$  are in  $^\circ\text{C}$  and it has an average absolute prediction error of 4.75%.

### 10.2.1. Model inclusion

Ice-fraction estimations are required in various other thermo-physical property calculations such as water activity, specific heat, enthalpy and thermal conductivity. Both Eqs. (53) and (56) are fairly general and simple as they have been used for a number of food products (Fikiin, 1998).

## 11. Water activity

Water activity is an intrinsic parameter of a food system. It is expressed as (Van Den Berg and Bruin, 1981):

$$a_w = \left( \frac{p_v}{p_{v,sat}} \right)_T \quad (57)$$

where,  $p_v$  is the vapor pressure of water in the food and  $p_{v,sat}$  is the vapor pressure of pure water at the same temperature ( $T$ ) of the food. The theoretical estimation of  $a_w$  comes from thermodynamics which involves the concept of chemical potential of water (Eq. (58)):

$$\mu = \mu_0 + RT \ln a_w \quad (58)$$

where  $\mu$  is the chemical potential. For ideal solutions, the famous Raoult's law is used to obtain the water activity as the mole fraction of water in the solution. But food systems are far from being ideal and the  $a_w$  of foods are evaluated based on the types of solutes present: electrolytes, non-electrolytes, or both (Vega-Mercado et al., 1994).

### 11.1. Semi-empirical models: unfrozen foods

For most foods, water activity can be determined by their salt content ( $\text{NaCl}$  and ash content). For such cases, it is assumed that there are no interactions between different ions and contributions of different salts in Eq. (58) are additive (Sereno et al., 2001), i.e.

$$a_w = a_{w,ash} a_{w,NaCl} \quad (59)$$

The ash content ( $x_{ash}$ ) of a food material is a mixture of various minerals excluding the amount of sodium chloride ( $x_{NaCl}$ ). The contribution to water activity from ash follows from Raoult's Law:

$$a_{w,ash} = \frac{x_w}{x_w + n_{ash} M_w x_{ash} / M_{ash}} \quad (60)$$

and for  $a_{w,NaCl}$ , a modified form of Pitzer equation is used (Eq. (61)). Pitzer equation describes the behavior of dissolved salts in water (Chen, 1990; van der Sman and Boer, 2005).

$$\frac{1}{a_{w,NaCl}} = 1 + M_w (\beta_e + B m^n) m \quad (61)$$

Here, the  $M_w$  is the molar mass of water (18 g/mol),  $M_{NaCl}$  is the molar mass of sodium chloride (58.15 g/mol), and  $M_{ash}$  is the effective molar mass of ash (72 g/mol). The dissociation number,  $n_{ash}$  (in Eq. (60)) equals 2. The molality of  $\text{NaCl}$  is given by  $m = M_{NaCl} x_{NaCl} / x_w$  and the constants in Eq. (61) are:  $\beta_e = 1.868$ ,  $B = 0.0582$ , and  $n = 1.618$  (van der Sman and Boer, 2005).

### 11.2. Semi-empirical models: frozen foods

Estimating water activity for frozen foods involves calculating the free water that is available to dissolve the solutes. The ice and bound water phases are unavailable for dissolving the solutes. Hence water activity is based on free water given by Eq. (62):

$$x_{fw} = x_w - x_{ice} - x_b \quad (62)$$

Expressions to calculate  $x_{ice}$  and  $x_b$  have been discussed in Section 10. Again, from Raoult's Law the contribution to  $a_w$  from ash is given as:

$$a_{w,ash} = \frac{x_{fw}}{x_{fw} + n_{ash} M_w x_{ash} / M_{ash}} \quad (63)$$

and the contribution from sodium chloride, is estimated using Eq. (61). The values of  $a_{w,ash}$  and  $a_{w,NaCl}$  are substituted back in Eq. (59) to get the water activity of frozen food systems. This method of estimating water activity was carried out for meat, fish and related products (van der Sman and Boer, 2005, van der Sman 2010) and good agreement with experimental data was obtained.

### 11.2.1. Model inclusion

In the equations for multiphase transport model (see Eq. (10)) and its boundary conditions, water activity would be needed to obtain vapor pressure,  $p_v$ , using Eq. (57). Water activity can also be needed to predict mass diffusivity using Eq. (123). Unlike many other properties, water activity measurement has become routine and therefore the modeler can strongly consider measured data.

## 12. Specific heat

Specific heat,  $C_p$ , of a material is defined as the amount of heat required to raise the temperature of a unit mass of the material through one degree. Specific heat is required for transient heat transfer modeling, for example. Foods and biological materials are generally processed under conditions of constant pressure, thus  $C_p$  as opposed to  $C_v$  is often the appropriate specific heat.

### 12.1. Theoretical models

Specific heat is commonly estimated based on the mass fractions ( $x_i$ ) of the individual components and their corresponding specific heats ( $C_{p,i}$ )

$$C_p = \sum_i x_i C_{p,i} \quad (64)$$

### 12.2. Empirical models: pure components

Specific heat of pure water as function of temperature is given as (Tanaka, 2000)

$$C_{p,w} = 4.02 + 1.6 \times 10^{-3} (T - 273.15) + 0.41 \times 10^{-3} \exp(1685/T) \quad (65)$$

where  $T$  is in K and  $C_{p,w}$  is in kJ/kg K. Specific heat of pure ice as function of temperature is given as (Dorsey, 1940):

$$C_{p,ice} = 2.12 + 7.8 \times 10^{-3} T \quad -20^\circ\text{C} < T < 0^\circ\text{C} \quad (66)$$

where  $T$  is in  $^\circ\text{C}$ . The specific heat of water vapor as function of temperature is given by (Lewis, 1987):

$$C_{p,v} = \left[ 32.22 + 0.192 \times 10^{-2} (T - 273) + 1.054 \times 10^{-5} (T - 273)^2 - 3.594 \times 10^{-9} (T - 273)^3 \right] \frac{10^3}{M_v} \quad (67)$$

where  $T$  is in K.

### 12.3. Empirical models: unfrozen foods

Of the many empirical models in literature, perhaps the most used is the one by Choi and Okos (1986) where the  $C_{p,i}$  values come from empirical equations noted in Eqs. (68)–(76).

$$C_{p,w} = 4.1762 - 9.0862 \times 10^{-5}T + 5.4731 \times 10^{-6}T^2 \quad 0^\circ\text{C} \leq T < 150^\circ\text{C} \quad (68)$$

$$C_{p,w} = 4.0817 - 5.3062 \times 10^{-3}T + 9.9516 \times 10^{-4}T^2 \quad -40^\circ\text{C} < T < 0^\circ\text{C} \quad (69)$$

$$C_{p,prot} = 2.0082 + 1.2089 \times 10^{-3}T - 1.3129 \times 10^{-6}T^2 \quad (70)$$

$$C_{p,fat} = 1.9842 + 1.4733 \times 10^{-3}T - 4.8008 \times 10^{-6}T^2 \quad (71)$$

$$C_{p,carb} = 1.5488 + 1.9625 \times 10^{-3}T - 5.9399 \times 10^{-6}T^2 \quad (72)$$

$$C_{p,fiber} = 1.8459 + 1.8306 \times 10^{-3}T - 4.6509 \times 10^{-6}T^2 \quad (73)$$

$$C_{p,ash} = 1.0926 + 1.8896 \times 10^{-3}T - 3.6817 \times 10^{-6}T^2 \quad (74)$$

$$C_{p,ice} = 2.0623 + 6.0769 \times 10^{-3}T \quad (75)$$

$$C_{p,a} = 1.006 \quad (76)$$

These empirical correlations were developed from a large collection of literature data on measured specific heat and standard chemical compositions of these foods (i.e., compositions are not necessarily obtained from the same study as the specific heat). Thus, the categories “protein”, “fat”, etc., in the correlations above do not necessarily stand for any particular well defined chemical composition. For frozen foods, ice fraction should also be considered along with other components. These equations predict the specific heat capacities over the range of  $-40$  to  $150^\circ\text{C}$ , with a prediction error of less than 5%.

#### 12.4. Semi-empirical models: frozen foods

Specific heats of foods that are completely frozen can be estimated following procedure just mentioned. During a freezing or thawing process, since freezing of foods occur over a temperature range, latent heats will be involved. Although different from specific heat, for heat transfer modeling in freezing and thawing, an efficient approach is to define an apparent specific heat that includes both specific heat and latent heat:

$$C_{p,app} = \frac{\partial H}{\partial T} \quad (77)$$

Following the discussion in the previous section, the composite specific heat of the frozen food material can be written as (Datta and Rakesh, 2009)

$$C_{p,app} = x_w \left( (1 - x_{ice})C_{p,w} + x_{ice}C_{p,ice} + \lambda_{ice} \frac{\partial x_{ice}}{\partial T} \right) + (1 - x_w)C_{p,s} \quad (78)$$

where  $C_{p,s}$  is the specific heat of dry solids,  $C_{p,w}$  is the specific heat of water,  $C_{p,ice}$  is the specific heat of ice,  $\lambda_{ice}$  is the latent heat of fusion (Eq. (82)). Substituting for the frozen fraction term,  $x_{ice}$ , as discussed in Section 10, one can get the apparent specific heat of the frozen material.

##### 12.4.1. Model inclusion

The effective specific heat of the food, needed in the energy balance equation (Eq. (4)), is obtained by using Eq. (64) together with Eqs. (67)–(76). This combination of equations is the most commonly used prediction method for specific heat of unfrozen foods in the modeling literature (Hwang and Gunasekaran, 2010). In modeling freezing or thawing, apparent specific heat defined by Eq. (78), that is conceptually based on Eq. (64), is used with the heat conduction equation.

### 13. Enthalpy

Enthalpy of a substance is defined as the sum of specific internal energy,  $U$ , and the product of pressure,  $P$ , and specific volume,  $v$ , as  $H = U + Pv$ . Enthalpy information is needed in modeling where an

enthalpy formulation is used or, more commonly, to obtain specific heat or apparent specific heat (that includes latent heat, see Section 12.4) of food as a composite material. Above freezing point, enthalpy consists of only sensible energy whereas below freezing temperatures, enthalpy also consists of latent heat.

#### 13.1. Theoretical models: unfrozen foods

Enthalpy of unfrozen foods can be obtained simply as a weighted average of the enthalpies of pure components, i.e., water, fat, carbohydrates, proteins, fiber, ash and salts (Mannapperuma and Singh, 1988). The enthalpy expressed in mass fractions,  $x_i$ , is given as:

$$H(T) = \sum_i x_i H_i(T) \quad (79)$$

and the enthalpy of individual components can be expressed as:

$$H_i(T) = \int_T C_{p,i}(T) dT \quad (80)$$

Specific heats have been discussed in Section 12. This procedure will work readily for enthalpies of unfrozen foods.

#### 13.2. Theoretical models: frozen foods

For frozen foods, the total enthalpy of the food material is the sum of the sensible heat portions of total solids, unfrozen water and ice along with the latent heat.

$$H = H_s + H_u + H_{ice} + x_u \lambda_{ice} \quad (81)$$

The latent heat of fusion of pure ice is not constant over the temperature range of freezing; its temperature dependency is given by (Cogné et al., 2003).

$$\lambda_{ice} = (333.802 + 2.1165T) \times 1000 \text{ J/kg} \quad (82)$$

where  $T$  is in  $^\circ\text{C}$ . In order to predict the enthalpy of a frozen food product, the thermal energy of the individual components are integrated over the needed temperature range, using  $-40^\circ\text{C}$  as reference at which the enthalpy is set to zero (Heldman, 1982):

$$H(T) = \int_{-40}^T x_s C_{p,s} dT + \int_{-40}^{T_{fi}} x_u C_{p,w} dT + \int_{T_{fi}}^T x_u C_{p,w} dT + x_u \lambda_{ice} + \int_{-40}^{T_{fi}} x_{ice} C_{p,ice} dT \quad (83)$$

where  $x_s, x_u$  and  $x_{ice}$  are the mass fractions of component solids, unfrozen water and ice, respectively,  $C_{p,s}, C_{p,w}$  and  $C_{p,ice}$  are the specific heats of component solids, water and ice, respectively, and  $T_{fi}$  is the initial freezing temperature (see Section 9).

##### 13.2.1. Model inclusion

Enthalpy is not used directly in the transport equations presented here but used indirectly to calculate apparent specific heat, for example, using Eq. (77). However, in alternate enthalpy formulation of energy equation that is used in freezing and thawing calculations (Agnelli and Mascheroni, 2001), enthalpy can be used in a direct manner in numerical calculations.

### 14. Thermal conductivity

Thermal conductivity of a material represents its ability to conduct heat through it, and is defined by the Fourier's law of heat conduction:

$$\vec{q}'' = -k \vec{\nabla} T \quad (84)$$



where  $\vec{q}''$  is the heat flux,  $k$  is the thermal conductivity, and  $\vec{\nabla}T$  is the temperature gradient. Composition, structure, and processing conditions (e.g., temperature) of the food are among the most important factors governing the thermal conductivity of foods. A number of predictive models exist in literature to estimate the thermal conductivity of foods.

#### 14.1. Theoretical models

Elementary kinetic theory approach, that can be used to derive approximate but reasonable values for viscosity and diffusion coefficients for ideal gases, is not as accurate in predicting thermal conductivity (Poling et al., 2001). More detailed (than elementary kinetic theory) theoretical models for thermal conductivity are available only for simple gases and even for simple liquids, estimation is empirical. Theoretical models for thermal conductivity involves treating the material as a mixture of its various components and developing a relation for the thermal conductivity of the mixture (composite material) as a function of thermal conductivity of the individual components. The simplest of such models are the series (Eq. (85)) and the parallel (Eq. (86)) model

$$\frac{1}{k_{eff}} = \sum \frac{\epsilon_i}{k_i} \quad (85)$$

$$k_{eff} = \sum \epsilon_i k_i \quad (86)$$

where  $k_{eff}$  is the effective thermal conductivity of the composite material using either series or parallel models, respectively,  $k_i$  is the thermal conductivity of the individual components or phases and  $\epsilon_i$  are the volume fractions of individual phases. Individual  $k_i$  can be a function of temperature. Such simple theoretical predictive models have been used successfully only for liquid foods (Murakami and Okos, 1989) but they have not been generally accurate for solid and porous foods.

#### 14.2. Semi-empirical models: unfrozen foods

Semi-empirical models are partly based on theoretical models for predicting thermal conductivity such as the series and the parallel models described above.

##### 14.2.1. Generic model for unfrozen porous foods

A generic model for predicting the thermal conductivity of unfrozen porous foods is provided by Carson (2002). This model is the well-known Maxwell model modified to introduce additional weighting parameter  $j$  (0 to 1) as:

$$k_{eff} = k_c \frac{\left(\frac{j^2}{1-j^2}\right)k_c + k_a - \left(\frac{j^2}{1-j^2}\right)(k_c - k_a)\epsilon_a}{\left(\frac{j^2}{1-j^2}\right)k_c + k_a + (k_c - k_a)\epsilon_a} \quad (87)$$

This additional parameter  $j$  accounts for differences in structure between different types of porous materials so that a single equation can effectively predict the thermal conductivity. Qualitatively,  $j$  is a measure of 'heat conduction pathways' in the material (Carson et al., 2005). The effective thermal conductivity is obtained by following a step by step procedure given as follows (Carson et al., 2006):

1. Combine  $k_{prot}$ ,  $k_{fat}$ ,  $k_{carb}$ , and  $k_{ash}$  (Eqs. (105)–(112)) using Eq. (86) to produce  $k_s$
2. Combine  $k_s$  and  $k_w$  using Eq. (88) to produce  $k_c$  (effective thermal conductivity of the condensed phase):

$$k_c = \frac{1}{4} \left( (3\epsilon_w - 1)k_w + [3(1 - \epsilon_w) - 1]k_s + \sqrt{[(3\epsilon_w - 1)k_w + (3(1 - \epsilon_w) - 1)k_s]^2 + 8k_s k_w} \right) \quad (88)$$

3. If the food is fibrous/anisotropic, obtain the distribution factor  $f_k$  if available (Chen et al., 1998; Murakami and Okos, 1989) or calculate it using Eq. (93) (for fruits and vegetables only) and use Krischers model to calculate  $k_{eff}$  from  $k_a$  and  $k_c$  (Eq. (89)):

$$k_{eff} = \frac{1}{\frac{1-f_k}{(1-\epsilon_a)k_c + \epsilon_a k_a} + f_k \left( \frac{1-\epsilon_a}{k_c} + \frac{\epsilon_a}{k_a} \right)} \quad (89)$$

4. Or, if the food may be considered isotropic on a macroscopic scale, use Eq. (87) to calculate  $k_{eff}$  from  $k_a$  and  $k_c$ . For foam or sponge-like material having internal porosity, the expected value of  $j$  is chosen between 0.68 and 0.82 and for a particulate material (external porosity),  $j$  value is chosen between 0.4 and 0.7.

The temperature dependence is included by making the individual component thermal conductivities functions of temperature by using Eqs. (105), (105)–(112). Using the above algorithm, the uncertainty in prediction of thermal conductivity for isotropic, internal porosity, non-frozen foods was reported to be less than or equal to 0.02 W/m·K when a fixed value of  $j$  (=0.75) was used (Carson et al., 2006).

##### 14.2.2. Unfrozen fruits and vegetables

A semi-empirical generic model that works for fruits and vegetables (Maroulis et al., 2002) that uses shrinkage coefficient,  $\phi$ , and a structural factor,  $f_k$ , as empirical parameters with both the series and parallel models, is given by Eqs. (90)–(93).

$$\frac{1}{k_{eff}} = \frac{1-f_k}{k_{pa,eff}} + \frac{f_k}{k_{se,eff}} \quad (90)$$

where  $k_{pa,eff}$  and  $k_{se,eff}$  are values calculated from the parallel and series models, respectively, given by

$$k_{pa,eff} = \epsilon_s k_s + \epsilon_w k_w + \epsilon_a k_a \quad (91)$$

$$k_{se,eff} = \frac{1}{\left( \frac{\epsilon_s}{k_s} + \frac{\epsilon_w}{k_w} + \frac{\epsilon_a}{k_a} \right)} \quad (92)$$

The quantity  $f_k$ , accounting for structural factors and given by

$$f_k = 0.996(1 - \epsilon_a + k_a/(k_w)_r)(T/T_r)^{0.713} x_w^{0.285} \quad (93)$$

has been used for a number of fruits and vegetables (Rahman et al., 1997). Here,  $T_r$  is the reference temperature 273 K,  $T$  is the absolute temperature in K,  $x_w$  is the mass fraction of water (wet basis),  $\epsilon_a$  is the porosity and  $(k_w)_r$  is the thermal conductivity of water at  $T_r$ . Ranges of parameters for which the equation is valid are given by  $5 < T < 100$  °C,  $0.14 < x_w < 0.94$  and  $0 < \epsilon_a < 0.56$ , respectively. The volume fractions in Eqs. (91) and (92) are given by Eqs. (94)–(96):

$$\epsilon_a = 1 - \frac{\rho_a}{\rho_t} \quad (94)$$

$$\epsilon_w = \frac{X}{1+X} \frac{\rho_a}{\rho_w} \quad (95)$$

$$\epsilon_s = \frac{1}{1+X} \frac{\rho_a}{\rho_s} \quad (96)$$

Densities  $\rho_t$  and  $\rho_a$  are calculated using Eqs. (97) and (98):

$$\rho_t = \frac{1+X}{\left( \frac{1}{\rho_s} + \frac{X}{\rho_w} \right)} \quad (97)$$

$$\rho_a = \frac{1+X}{\left( \frac{1+X_i}{\rho_{ai}} + \phi \frac{X-X_i}{\rho_w} \right)} \quad (98)$$



Shrinkage coefficient  $\phi$  represents the effect of air phase or pores in the food. Its value is obtained by fitting the experimental volume vs. moisture content curve:

$$v = v_i - \phi \frac{(X_i - X)}{\rho_w} \quad (99)$$

where  $v$  is the specific volume at dry basis moisture content  $X$ ,  $X_i$  is the initial moisture content (dry basis), and  $v_i$  is the specific volume at  $X = X_i$ . Eq. 90 was tested for the literature data available for apples and the maximum error was found to be less than 10% for a wide range of temperature and moisture content values. The authors (Maroulis et al., 2002) report this model as a generic one for fruits and vegetables.

#### 14.2.3. Meats and related products

Thermal conductivities of meats and meat products in the temperature range  $-40$  to  $30$  °C have been predicted using six different models and it was shown that except for the series model, all models were sufficiently accurate (Pham and Willix, 1989) having a prediction error of less than 10%. As an example, one of these five models that had good predictive capability is reproduced here (Maxwell–Eucken model).

$$k_{eff} = k_s \frac{2k_s + k_w - 2(k_s - k_w)\epsilon_w}{2k_s + k_w + (k_s - k_w)\epsilon_w} \quad (100)$$

where  $k_s$  is obtained by combining  $k_{prot}$ ,  $k_{fat}$ ,  $k_{carb}$ , and  $k_{ash}$  (Eqs. (105)–(112)) using Eq. (86).

#### 14.3. Semi-empirical models: frozen foods

Thermal conductivity of frozen non-porous (insignificant air phase or low air porosity) foods involves estimating the ice content of the food material, as discussed in Section 10. Once the ice content is obtained, we can follow the procedure described in Section 14.2.1 with ice as one of the components. Prediction models of thermal conductivity for frozen, porous foods are scanty in literature owing to their complex microstructures. A generic 3-step prediction model that is based on food's microstructure is provided here (Cagne et al., 2003; Carson, 2006). First, parallel model (Eq. (86)) is used to combine the thermal conductivities of the liquid water and the components of food solids,  $k_{pa}$ ; the resulting thermal conductivity is then combined with the thermal conductivity of ice using the De Vries model (Eq. (101))

$$k_{eff} = k_{pa} \frac{1 - \epsilon_{ice} + \epsilon_{ice}F(k_{ice}/k_{pa})}{1 - \epsilon_{ice} + \epsilon_{ice}F} \quad (101)$$

where  $F$  is given by:

$$F = \frac{1}{3} \left[ 1 + 0.18 \left( \frac{k_{ice}}{k_{pa}} - 1 \right) + 0.82 \left( \frac{k_{ice}}{k_{pa}} - 1 \right)^2 \right]^{-1} \quad (102)$$

to produce the thermal conductivity of the condensed phase. Here,  $k_{pa}$  is obtained using Eq. (86). Finally, the thermal conductivity of the condensed phase is combined with the thermal conductivity of air using the Maxwell–Eucken model by replacing  $k_w$  and  $\epsilon_w$  with  $k_a$  and  $\epsilon_a$  in (Eq. (100)) to give the overall thermal conductivity. This has been used to predict thermal conductivity of ice cream that has discrete air bubbles, fat globules and ice crystals, with an error in prediction of less than 8% (Cagne et al., 2003). It has also been used for partially baked french bread as a high porosity model food (Hamdami et al., 2004).

#### 14.4. Empirical models: pure materials

Data for pure components (water, water vapor, air), needed for above predictions or otherwise, are available from standard literature (Perry and Green, 2008). For dry air, the following correlation

$$k_{dryair} = 2.43 \times 10^{-2} + 7.98 \times 10^{-5}T - 1.79 \times 10^{-8}T^2 - 8.57 \times 10^{-12}T^3 \quad (103)$$

has been shown to work (Maroulis et al., 2002) in the temperature range  $0$ – $100$  °C. For moist air, thermal conductivity as functions of temperature,  $T$ , and relative humidity,  $RH$ , can be used from Luikov (1964)

$$k_{moistair} = 0.0076 + 7.85 \times 10^{-4}T + 0.0156RH \quad (104)$$

The validity of the model is within the temperature range of  $20$ – $60$  °C and relative humidity range of  $0$ – $1$ .

As described under specific heat (Choi and Okos, 1986), a set of completely empirical correlations developed between literature data (from many sources) and food composition data (taken from the standard source of USDA composition database) have been used most widely:

$$k_w = 0.57109 + 1.762 \times 10^{-3}T - 6.7036 \times 10^{-6}T^2 \quad (105)$$

$$k_{ice} = 2.21960 - 6.2489 \times 10^{-3}T + 1.0154 \times 10^{-4}T^2 \quad (106)$$

$$k_{prot} = 0.17881 + 1.1958 \times 10^{-3}T - 2.7178 \times 10^{-6}T^2 \quad (107)$$

$$k_{fat} = 0.18071 - 2.7604 \times 10^{-3}T - 1.7749 \times 10^{-7}T^2 \quad (108)$$

$$k_{carb} = 0.20141 + 1.3874 \times 10^{-3}T - 4.3312 \times 10^{-6}T^2 \quad (109)$$

$$k_{fiber} = 0.18331 + 1.2497 \times 10^{-3}T - 3.1683 \times 10^{-6}T^2 \quad (110)$$

$$k_{ash} = 0.32961 + 1.4011 \times 10^{-3}T - 2.9069 \times 10^{-6}T^2 \quad (111)$$

$$k_a = 0.025 \quad (112)$$

From the above thermal conductivities of the individual components, the effective thermal conductivity of the composite food material is predicted using Eq. (86). Note that the component equations (Eq. (105)–(112)) will have to be used (rather than such correlations from other sources) in combination with Eq. (86) to be consistent with the empirical prediction equations of Choi and Okos (1986). The temperature range for which these correlations were developed is ( $-40$  and  $150$  °C).

##### 14.4.1. Model inclusion

In the Energy equation (Eq. (4)), the effective thermal conductivity value is obtained from any one of Eqs. (86), (87), (89), (90) or (100), depending on the category of the food material. Note that the general series model (Eq. (85)) is typically not used (Carson, 2006).

Prediction of effective thermal conductivity of unfrozen, non-porous foods (for example liquid foods) is fairly straightforward since the effective thermal conductivity is only a function of components' thermal conductivities and their volume fractions (series and the parallel models). The accuracy in prediction lies within  $\pm 10\%$  (Carson, 2006). For porous and/or frozen foods, accurate estimation of porosity and ice fraction is required which have their own associated errors. Typically, an empirical parameter is introduced to account for variations in composition and structure. Eqs. (105)–(112) have been used extensively by modelers and have a prediction error of 5%. This error can increase for porous and/or frozen foods where error in estimation of porosity and ice fraction can also contribute. For design purposes, a prediction error of  $\pm 10\%$  in thermal conductivity estimation is considered acceptable (Nesvadba, 1982). Models proposed above are well within this accepted limit.

## 15. Mass diffusivity

Mass diffusivity of a material measures its ability to allow transport of a mass species through it due to the driving force of concentration gradient of the species. Mass diffusivity is defined by the Fick's law:

$$\vec{n}_A = -D_{AB} \vec{\nabla} c_A \quad (113)$$

Here,  $\vec{n}_A$  is the flux of component A,  $D_{AB}$  is the diffusivity of A in B, and  $\vec{\nabla} c_A$  is the concentration gradient of A. Although originally formulated for molecular diffusion, diffusivity,  $D_{AB}$ , can be due to many different mechanisms of transport that are analogous to molecular diffusion. For example, in transport of one gas in another or for transport in the liquid phase,  $D_{AB}$  typically refers to molecular diffusion (a random walk process) whereas for water transport in an unsaturated solid,  $D_{AB}$  stands for capillary diffusivity of water in solid. Often many different modes of transport are lumped into the  $D_{AB}$ , without clear identification of the modes, leading to  $D_{AB}$  being referred to as effective diffusivity (denoted as  $D_{eff}$ ).

Moisture diffusivity is a strong function of moisture content, temperature and structure (void fraction, pore structure and distribution) of the material. Moisture diffusivity in the food literature often lumps one or more transport mechanisms (capillary diffusion of liquid water, molecular diffusion of vapor) and separating the effective diffusivity into distinct contributions from any one transport mechanism is generally difficult from literature data.

### 15.1. Theoretical and semi-empirical models: molecular diffusivity in simple gases and liquids

Temperature and other parameter effects on molecular diffusivities can be obtained from standard equations such as the following one for diffusivity of gases

$$D_{AB} = \frac{0.001858 T^{3/2} (1/M_A + 1/M_B)^{1/2}}{P \sigma_{AB}^2 \Omega_{D,AB}} \quad (114)$$

where  $T$  is the absolute temperature,  $M_A$  and  $M_B$  are molecular weights of species A and B, respectively,  $P$  is absolute pressure in atm,  $\sigma_{AB}$  is the collision diameter in Å, and  $\Omega_{D,AB}$  is a dimensionless function of the temperature and the intermolecular potential. An application to binary diffusion of vapor in air that would be of particular interest to food process simulations is given as a function of pressure and temperature (Vargaftik, 1975):

$$D_{eff,g} = \frac{2.13}{P} \left( \frac{T}{273} \right)^{1.8} \quad (115)$$

where  $P$  is pressure in Pa and  $T$  is absolute temperature in K.

Diffusion in simple liquids (those composed of diatomic or tetrahedral molecules) is described most commonly by the Stokes–Einstein equation

$$D_{AB} = \frac{k_B T}{6\pi\mu r} \quad (116)$$

where A is the diffusing species, B is the fluid through which diffusion is taking place,  $k_B$  is Boltzmann's constant,  $T$  is the absolute temperature in K,  $\mu$  is the viscosity in Pa·s and  $r$  is the radius of the molecule in meters. While this equation is strictly applicable only in cases where the diffusing molecule is large compared to the surrounding solvent molecules, it has proven useful for solute–solvent pairs in which the radius,  $r$ , is only two to three times the solvent radius (Saltzman, 2001). For small solute molecules that are identical to solvent, Eq. (116) is modified as:

$$D_{AB} = \frac{k_B T}{4\pi\mu r} \quad (117)$$

Diffusion through solids, of interest in food applications, can be divided into two parts: diffusion of gas through a solid and diffusion of liquid through a solid. We can divide the food materials into non-porous gels and porous materials. Gas diffusion through solid is typically molecular diffusion through the gas filled pores of the solid. For gas diffusion through the pores of a solid, the effective gas diffusivity,  $D_{eff}$ , is related to the molecular diffusivity of the gas by the expression

$$D_{eff} = \frac{D_{AB}}{\tau} \quad (118)$$

where  $D_{AB}$  is the molecular diffusivity of gas A through gas B (that occupies the pores in the solid) and  $\tau$  is the tortuosity of the pores in the solid. Liquid diffusion through solid is typically capillary diffusion where diffusivity can vary strongly with moisture content.

### 15.2. Semi-empirical models: effective diffusivity of moisture in solid foods

In a moist food, water transport can be in both liquid and vapor form. Often both these transport modes are combined in an effective diffusivity value. A large number of empirical models have been developed based on drying kinetics, sorption or desorption kinetics and moisture profile analysis, as summarized by Marinou-Kouris and Maroulis (1995) and Zogzas and Maroulis (1996). However, generic models in estimating moisture diffusivity as a function of moisture and temperature values are rare. In one such attempt (King, 1968), Fick's second law was used to model heat and mass transfer in hygroscopic porous body. All the internal mass transfer mechanisms were lumped together in effective diffusivity and, in the absence of internal temperature gradients,  $D_{eff}$  is given by (Eq. (119)):

$$D_{eff}(X, T) = \frac{XD'p_v}{\rho_s RT} \left( \frac{P}{(P - p_w)} \right) \left( \frac{\partial a_w}{\partial X} \right)_T \quad (119)$$

In the above equation,  $D_{eff}$  relates the moisture content to the vapor pressure which is the driving force for diffusion.  $D'$  is obtained by multiplying the porosity of the material with Eq. (118). However, desorption of a material requires heat to be consumed to vaporize the moisture, thus making the drying of hygroscopic porous materials an interaction of heat and mass transfer. The effective diffusivity term can also be expressed to include internal heat transfer as (Eq. (120)):

$$D_{eff}(X) = \frac{XD'p_v}{\rho_s RT} \left( \frac{P}{(P - p_w)} \right) \left( \frac{\partial a_w}{\partial X} \right)_T \left( \frac{\psi}{1 + \psi} \right) \quad (120)$$

where

$$\psi = \frac{k_{eff} R R_v T^3}{(\Delta H_d)^2 D' a_w p_v} \quad (121)$$

where  $k_{eff}$  is the effective thermal conductivity,  $\Delta H_d$  is the molar heat of desorption,  $R_g$  is the universal gas constant and  $R_v$  is a constant (82.1 atm cm<sup>3</sup>/mol K).

The model has several underlying assumptions as discussed in King (1968). However, the advantage of this model is the ease in which the effective moisture diffusivity can be calculated based on fundamental transport properties (Rossen and Hayakawa, 1977).

### 15.3. Semi-empirical model: capillary diffusivity of moisture in solid foods

When the food has a significant amount of moisture, effective diffusivity is essentially the capillary diffusivity of liquid water. Theoretically, it should be possible to predict capillary diffusivity

from data on permeability and capillary pressure using the following equation from porous media literature (e.g., Datta, 2007):

$$D_{w,cw} = \frac{\rho_w^2 k_i g}{\mu_w} \frac{\partial h}{\partial c} \quad (122)$$

where  $D_{w,cw}$  is capillary diffusivity (see Eq. (13);  $D_{w,cw}$  is essentially the same as  $D_{eff}$  for high moisture foods),  $\rho_w$  is density of water,  $k_i$  is intrinsic permeability of the matrix,  $g$  is the acceleration due to gravity,  $\mu_w$  is viscosity of water, and  $h$  is the matric potential for water in the food matrix. The matric potential for food materials is difficult to measure directly but its estimation from water activity data has been made using the Kelvin's equation

$$h = \frac{RT}{\rho_w g V_m} \ln a_w \quad (123)$$

where  $a_w$  is the water activity, obtained experimentally. Alternatively,  $h$  has also been estimated using Leverett function that is a generic empirical relation between capillary pressure and saturation for vegetables during dehydration (Wang and Chen, 1999). However, accuracy of prediction using Leverett's function was not clear from this work.

Eq. 122, together with Eq. (123), has not been used to predict capillary diffusivity directly due to difficulties in obtaining (experimentally or using predictive equations) the various parameters (Datta et al., 2012). In particular, the intrinsic permeability,  $k_i$ , is hard to predict. Thus, predictive models for capillary diffusion of water through food is restricted to empirical and semi-empirical models described in the following section.

Instead of effective diffusivity in a diffusion equation, an equivalent formulation used for transport in a porous medium is the Richard's equation. This equation has been used to predict transport of water in food as a capillary solid where Eq. (123) is used to predict capillary pressure and the transport parameter hydraulic conductivity as a function of capillary pressure (Trotyot et al., 2011; Wallach et al., 2011). Richard's equation has also been used to model water transport in soaking of tea leaves (Weerts et al., 2003) but as just mentioned, prediction of permeability was still a problem. Thus, semi-empirical prediction of effective diffusivity at high moisture content (which is the same as capillary diffusivity), starting from water activity data, has not matured. Such diffusivity data as function of moisture content being extremely important and so little of it is available in the literature, water activity based prediction model provided in this section can serve at least a starting point for a simulation.

The paragraphs above concern liquid water transport driven by water content characterized by  $D_{w,cw}$ . In the simulation of a moisture transport process, if the material will reach significantly lower moisture such that vapor diffusion will become significant, vapor transport driven by water content, characterized by  $D_{v,cw}$  (see Eq. (13)), will need to be considered as well. For such situations, it is recommended to use Eq. (119) or another equivalent expression for effective diffusivity given by Kolhapure and Venkatesh (1997).

#### 15.4. Semi-empirical models: generic model of calculating effective diffusivity of moisture in solid foods

In one semi-empirical model (Maroulis et al., 2001), a food material is thought of as a uniform mixture of (1) its dried counterpart (phase a), and (2) its wet counterpart with infinite moisture (phase b). The diffusivity of the food could then be estimated using a two-phase structural model as:

$$D_{eff}(X, T) = \frac{1}{1+X} D_{X_0}(T) + \frac{X}{1+X} D_{X_i}(T) \quad (124)$$

where  $D_{eff}$  is the effective moisture diffusivity in  $m^2/s$ ;  $D_{X_0}$  is the moisture diffusivity of the dried material (phase a) in  $m^2/s$ ;  $D_{X_i}$  is the moisture diffusivity of the wet material (phase b) in  $m^2/s$ ;  $X$  is the material moisture content (dry basis); and  $T$  is the material temperature in  $^{\circ}C$ . Here, the diffusivities of both phases depend on temperature and can be estimated using an Arrhenius-type model as:

$$D_{X_0} = D_0 \exp \left( -\frac{E_0}{R} \left( \frac{1}{T} - \frac{1}{T_r} \right) \right) \quad (125)$$

$$D_{X_i} = D_i \exp \left( -\frac{E_i}{R} \left( \frac{1}{T} - \frac{1}{T_r} \right) \right) \quad (126)$$

where  $T_r = 60^{\circ}C$  is a reference temperature,  $R_g$  is the universal gas constant; here  $D_0$  is the diffusivity at moisture  $X = 0$  and at temperature  $T = T_r$ ;  $D_i$  is the diffusivity at moisture  $X \rightarrow \infty$  and temperature  $T = T_r$ ;  $E_0$  is the activation energy for diffusion in dry material at  $X = 0$ ;  $E_i$  is the activation energy for diffusion in wet material at  $X \rightarrow \infty$ . The adjustable parameters for a large number of foods (corn, pasta, rice, wheat, apple, banana, carrot, garlic, onion, potato and some model foods) are available in Maroulis et al. (2001).

Empirical and semi-empirical equations, developed from individual experimental data, will have to remain an important source for moisture diffusivity. An example of such relation, the effective diffusivity of water in starch based systems is (Marousis et al., 1991):

$$D_{eff} = 10^{-10} \left( 4.842 + 0.5735X - 4.34 + 34.2(\epsilon^3/(1-\epsilon)^3) \right) \exp(-4.5/RT) \quad (127)$$

where  $D_{eff}$  is the effective water diffusivity (in  $m^2/s$ ),  $X, \epsilon$  and  $T$  are moisture content (dry basis), porosity (as a function of moisture content) and temperature of the food material, respectively.

## 16. Permeability

Permeability quantifies the material's ability to allow pressure driven (or bulk) flow of fluids through it. Permeability is defined by Darcy's law of transport through a porous medium as:

$$\vec{q} = -\frac{k}{\mu} \vec{\nabla} p \quad (128)$$

where  $\vec{q}$  is the volumetric flux,  $k$  is the permeability,  $\mu$  is viscosity, and  $\vec{\nabla} p$  is the pressure gradient driving the flow.

Extent and nature of pores in the material and the transport properties of fluid are the most important factors governing the permeability of foods. Unlike most other properties noted in this article, very little data exists for permeability (Goedeken and Tong, 1993) and no predictive model is known for food products. Permeability,  $k$ , is further broken into intrinsic permeability,  $k_i$ , and relative permeability,  $k_r$ , given by the following expression:

$$k = k_i k_r \quad (129)$$

The intrinsic permeability,  $k_i$ , represents the permeability of a liquid or gas in fully saturated state. Thus, for use in Eqs. (5) and (6),  $k_w = k_i k_{wr}$  and  $k_g = k_i k_{gr}$ .

### 16.1. Intrinsic permeability: theoretical and empirical equations

Models with limited success exist in relating intrinsic permeability to the structure of the material—no such relation exists for food materials. A typical expression for permeability as it relates to porosity in a packed bed of solids is given by the well known Kozeny-Carman equation

$$k_i = \frac{d_m^2}{180} \frac{\epsilon^3}{(1-\epsilon)^2} \quad (130)$$

where  $d_m = 6/A_s$  is a mean diameter for the particles in the bed,  $A_s$  is the specific area ( $A/(1 - \epsilon)$ ) of the porous media. This relation is unlikely to succeed in directly predicting permeability from structural information, as has been tried for bread (Chaunier et al., 2008), but the relation has been used to fit experimental intrinsic permeability data for apple as a function of porosity, given by (Feng et al., 2004)

$$k_i = 5.578 \times 10^{-12} \frac{\epsilon^3}{(1 - \epsilon)^2} \quad (131)$$

in the range porosities given by  $0.39 < \epsilon < 0.77$  with a  $R^2$  value of 0.95. Here,  $k$  is in  $\text{m}^2$ . Thus, scaling of permeability with porosity, as given by Eq. (130), may be possible for other situations, starting from measured value of permeability for a particular porosity. Some measured data for permeability are available as a starting point (Chaunier et al., 2008; Feng et al., 2004; Datta, 2006).

Although intrinsic permeability is supposed to be constant for the material and represent the effect of the solid matrix (and not fluid), it has to be modified in low pressure conditions or low permeabilities. In low pressure, i.e., under partial vacuum, gases experience “slip flow” due to the pore radius approaching the mean free path of the particle, also known as the Klinkenberg effect. In porous media with “low” intrinsic permeability or low pore pressures, the gas intrinsic permeability is expected to be much greater than that of the liquid and a correction factor for intrinsic permeability is given by (Tanikawa and Shimamoto, 2009).

$$k_{i,g} = k_{i,w} \left( 1 + \frac{0.15(k_{i,w})^{-0.37}}{P} \right) \quad (132)$$

where  $k_{i,g}$  and  $k_{i,w}$  are the gas and water intrinsic permeabilities ( $\text{m}^2$ ), respectively, and  $P$  is the pore pressure (Pa).

## 16.2. Relative permeability: empirical equations

Standard expressions also exist for relative permeability as a function of saturation in the material. A widely used expression for relative permeability of gases as function of saturation is given by

$$k_{gr} = \begin{cases} 1 - 1.1S_w & S_w < 1/1.1 \\ 0 & S_w > 1/1.1 \end{cases} \quad (133)$$

Similarly, a widely used expression for liquid permeability as a function of saturation is given by

$$k_{wr} = \begin{cases} \left( \frac{S_w - S_{ir}}{1 - S_{ir}} \right)^3 & S_w > S_{ir} \\ 0 & S_w < S_{ir} \end{cases} \quad (134)$$

Here,  $S_{ir}$  is the irreducible saturation that is often assumed. See, for example, the work of Nasrallah and Perre (1988) and Ilic and Turner (1989) where a value of 0.09 was assumed. In food applications, values of 0.08 have been assumed (Halder et al., 2007).

### 16.2.1. Model inclusion

Permeability data is perhaps the most difficult to obtain, among the properties included here. There is very little measured data available (small amount of data available for potato (Ni and Datta, 1999), meat (Datta, 2006) and bread (Goedken and Tong, 2006) and only one prediction equation is available (for apple) with porosity (Eq. (131)). Thus, the only choice seems to be to start from one of the measured data points for a material that may be close, followed by sensitivity analysis.

## 17. Viscosity

Rheological or flow properties of fluid foods can vary widely. Simplest of the fluid foods are Newtonian fluids, described by the equation

$$\tau = -\mu \dot{\gamma} \quad (135)$$

where  $\tau$  is the shear stress in the fluid at any point  $x$  where the shear rate is  $\dot{\gamma}$ . The proportionality constant,  $\mu$ , is called the viscosity of the fluid. Many liquid foods are more complex and cannot be described by Eq. (135)—these are called non-Newtonian fluids. A common type of non-Newtonian fluid in the context of food materials is the power-law fluid described by

$$\tau = m(-\dot{\gamma})^{\bar{n}} \quad (136)$$

where  $m$  is called the flow consistency index and  $\bar{n}$  is called the flow behavior index. Viscosity is often a strong function of composition and temperature. The field of food rheology is advanced and major treatise on food rheology exist (e.g., Rao, 1999) that discusses flow properties of Newtonian and non-Newtonian fluids; these details simply cannot be included in this article. Thus, in the paragraphs below, we give a flavor of the type of models that describe how rheological properties of simple (homogenous, no phase change) fluids vary with temperature and composition. Estimation of viscosity for liquids from theoretical basis alone is difficult, unlike for gases where significant theoretical basis exists for estimation of their viscosities (Poling et al., 2001). Thus, completely theoretical models for complex fluids as food materials is unlikely.

### 17.1. Empirical models: effect of temperature on simple materials

Viscosities of water and air as function of temperature are given by (McCabe et al., 2005):

$$\mu_w = 2.74 \times 10^{-6} e^{(1735.5/T)} \quad (137)$$

$$\mu_g = 0.017 \times 10^{-3} \left( \frac{T}{273} \right)^{0.65} \quad (138)$$

Here,  $T$  is temperature in K and  $\mu_i$  ( $i = w, g, o$ ) is the viscosity in Pa s. Viscosity of gases is nearly independent of pressure within the ideal gas region. Viscosity of undegraded soybean oil used for frying has been modeled as a function of temperature as (Tseng et al., 1996)

$$\mu_o = 5.12 \times 10^{-6} e^{(2215.65/T)} \quad (139)$$

They also provide how the constants in Eq. (139) will change with degradation of oil during the heating process.

### 17.2. Empirical models: effect of temperature on complex foods

Both viscosity or apparent viscosity (in case of Newtonian fluids, at a specific shear rate) can be treated as a function of temperature using an Arrhenius type relationship (Steffe, 1996; Rao, 2005):

$$\mu_{app} = A e^{E/RT} \quad (140)$$

where  $T$  is absolute temperature, and  $A$  and  $E$  are determined from experiment. This model has been used for liquids in general for almost 100 years and improvements over this model exist (Poling et al., 2001). Magnitudes of activation energy have been tabulated for various foods (Rao, 2005; Steffe, 1996). An alternative, but easier to use approach, is to write the above equation in terms of a reference temperature for which the viscosity is known

$$\ln \left( \frac{\mu}{\mu_r} \right) = \frac{E}{R} \left( \frac{1}{T} - \frac{1}{T_r} \right) \quad (141)$$



Eq. (141) can be used to find viscosity at any temperature knowing the viscosity,  $\mu_r$ , at temperature  $T_r$  (in °C). For power law fluids, the effect of temperature has been included in the model in several ways, one of these is (Harper and El-Sahrigi, 1965)

$$\mu_{app} = K_T \exp^{(E/RT)} \dot{\gamma}^{\bar{n}-1} \quad (142)$$

where  $K_T$  is a model constant and  $\bar{n}$  is an average value of flow behavior index over the entire range of temperature (°C). The constants  $K_T$ ,  $\bar{n}$  and  $E$  are determined from experimental data at few temperatures.

When the food goes through phase change, (for example, when gelatinization occurs in heating of starch solution), the effect of temperature is quite complex. For example, the apparent viscosity can be dependent on time–temperature history, as shown in the model of Dolan and Steffe (1990). Inclusion of such a complex rheological model can provide realistic flow and heat transfer calculations but it can be numerically challenging to implement. For such complex situations, apparent viscosity obtained directly from experiment can be included in numerical modeling of the flow and heat transfer process (Yang and Rao, 1998).

### 17.3. Empirical models: effect of concentration

For a given fluid food, viscosity increases as the concentration of total solids in the food increases. Over a limited range of concentration, effects of temperature and concentration on apparent viscosity at a constant shear rate can be combined as (Vitali and Rao, 1984)

$$\mu_{app} = K_{TC} \exp^{(E_a/RT)} C^b \quad (143)$$

where  $K_{TC}$ ,  $E_a$  and  $b$  are determined from experimental data. As an application example, Chin et al. (2009) used Eqs. (142) and (143) to investigate the effect of temperature and juice concentration on the rheological properties and flow characteristics of pummelo juice concentrates. The constants in the above equations were obtained as fitting parameters.

#### 17.3.1. Model inclusion

In single phase fluid flow modeling using a computational software, either viscosity or apparent viscosity (for non-Newtonian fluids) data is entered as viscosity input data or, the software may be capable of including the quantities  $m$  and  $\bar{n}$  in Eq. (136) directly. For multiphase model, as in Eqs. (5) and (6), corresponding viscosities of liquid or gas are assumed to be Newtonian, which should be reasonable at the typically low velocities in biological tissues or possibly even in a highly porous material as in bread during baking.

## 18. Dielectric properties

Dielectric properties of foods (dielectric constant ( $\epsilon'$ ) and dielectric loss factor ( $\epsilon''$ )) provide information about the food's interaction with electromagnetic energy during dielectric heating such as microwave or radiofrequency heating. These two properties are therefore required to model the electromagnetic portion of such heating processes, governing equations for which are Eqs. (14)–(18). As with many other food properties, first principle based predictive equations for dielectric properties as functions of temperature, composition and frequency are not available. Empirical and semiempirical correlations in literature are also scanty (as compared to data on thermal conductivity, for example) for food materials. These correlations have been restricted to a particular group of food products or even one particular food type (Sun et al., 1995; Calay et al., 1994; Sipahioglu and Barringer, 2003; Kumar et al., 2007; Hu et al., 2008). For calculations based on single

values, Sosa-Morales et al. (2010) have carried out a compilation of data points for several food materials (fruits and vegetables, flour, dough and bread, nuts, coffee grains, meats, fish and seafood, dairy products, eggs and egg products and liquid fluids) and Lizhi et al. (2008) for edible oils and fatty acids. Here, available predictive equations for specific groups of food products are discussed.

### 18.1. Theoretical and semi-empirical equations

An example of a theoretical or a semi-empirical equation for dielectric property prediction is that for a two-component mixture, where  $\epsilon'$  represents the effective dielectric constant of the mixture and is given by (Landau and Lifshits, 1960; Looyenga, 1965)

$$(\epsilon')^{1/3} = \epsilon_A (\epsilon'_A)^{1/3} + \epsilon_B (\epsilon'_B)^{1/3} \quad (144)$$

Here,  $\epsilon'$  is the effective dielectric constant of the mixture,  $\epsilon'_A$  is the dielectric constant of the medium in which particles of permittivity  $\epsilon'_B$  are dispersed, and  $\epsilon_A$  and  $\epsilon_B$  are the volume fractions of the respective components, with  $\epsilon_A + \epsilon_B = 1$ . This equation has been useful for predicting dielectric constant of cereal grains (Nelson, 1983; Nelson, 1994). Dielectric loss values in such studies are generally empirically correlated using linear or quadratic regression.

### 18.2. Semi-empirical models: salt solutions

Salt solutions are the simplest systems whose properties have relationship to those for foods. For saline water, well known equations exist (Stogryn, 1971) for dielectric properties, written as a complex quantity as:

$$\epsilon' + j\epsilon'' = \epsilon_\infty + \frac{\epsilon_0^* - \epsilon_\infty}{1 - j2\pi\tau f} + j \frac{\sigma}{2\pi\epsilon_0 f} \quad (145)$$

where  $\epsilon_0^*$  and  $\epsilon_\infty$  are the static and high-frequency dielectric constants of the solution, respectively,  $\tau$  is the relaxation time,  $\epsilon_0$  is the permittivity of free space ( $8.854 \times 10^{12}$  F/m),  $\epsilon_\infty$  is a constant having a value of 4.9,  $\sigma$  is the ionic conductivity of the dissolved salts (here NaCl) in mho/m, and  $f$  is the frequency. The values needed in Eq. (145) are given by:

$$\epsilon_0^*(T, N) = \epsilon_0^*(T, 0) a(N) \quad (146)$$

$$2\pi\tau(T, N) = 2\pi\tau(T, 0) b(N, T) \quad (147)$$

$$a(N) = 1.000 - 0.2551N + 5.151 \times 10^{-2}N^3 \quad (148)$$

$$b(N, T) = 0.1463 \times 10^{-2}NT + 1.000 - 0.04896N - 0.02967N^2 + 5.644 \times 10^{-3}N^3 \quad (149)$$

$$\epsilon_0(T, 0) = 87.74 - 4.0008T + 9.398 \times 10^{-4}T^2 + 1.410 \times 10^{-6}T^3 \quad (150)$$

$$2\pi\tau(T, 0) = 1.1109 \times 10^{-10} - 3.824 \times 10^{-12}T + 6.938 \times 10^{-14}T^2 - 5.096 \times 10^{-16}T^3 \quad (151)$$

$$N = S(1.707 \times 10^{-2} + 1.205 \times 10^{-5}S + 4.058 \times 10^{-9}S^2) \quad (152)$$

$$\sigma_{NaCl}(T, N) = \sigma_{NaCl}(25, N)(1.000 - 1.962 \times 10^{-2}\Delta + 8.08 \times 10^{-5}\Delta^2 - \Delta N(3.020 \times 10^{-5} + 3.922 \times 10^{-5}\Delta + N(1.721 \times 10^{-5} - 6.584 \times 10^{-6}\Delta))) \quad (153)$$

$$\sigma_{NaCl}(25, N) = N(10.394 - 2.3776N + 0.68258N^2 - 0.13538N^3 + 1.0086 \times 10^{-2}N^4) \quad (154)$$

Here,  $T$  is the water temperature ( $0 < T < 40$  °C),  $N$  is the normality of the solution ( $0 < N < 3$ ) and  $S$  is the salinity in parts per thousand and is valid for  $0 < S < 260$ , and  $\Delta = 25 - T$ . The model was tested on experimental results of Hasted and Elsabeh (1953) and good agreement was obtained between predicted and experimental observations.

### 18.3. Empirical models: cereal grains

Dielectric properties of cereal grains (corn, wheat, barley, oats, rye and soybeans) as functions of frequency, moisture content and bulk density are given by (Kraszewski and Nelson, 1989):

$$\epsilon' = \left(1 + \frac{0.504x_w\rho_b}{\sqrt{x_w} + \log f}\right)^2 \quad (155)$$

$$\epsilon'' = 0.146\rho_b^2 + 0.004615x_w^2\rho_b^2(0.32\log f + 1.743/\log f - 1) \quad (156)$$



The model, within the frequency range of 5–5000 MHz and moisture range of 8–26% wet basis, was tested for a wide range of literature data with average errors between 5% and 10% in comparison with experimental values.

#### 18.4. Empirical models: meat and meat products

Dielectric properties of meats (raw beef, beef juice, raw turkey and turkey juice) were correlated to temperature (K), moisture content (wet basis) and ash (Sun et al., 1995):

$$\epsilon' = X_w(1.0707 - 0.0018485T) + x_{ash}(4.7947) + 8.5452 \quad (157)$$

$$\epsilon'' = X_w(3.4472 - 0.01868T + 0.000025T^2) + x_{ash}(-57.093 + 0.23109T) - 3.5985 \quad (158)$$

where  $X_w$  is the moisture content (wet basis) and  $x_{ash}$  is the mass fraction of ash. The dielectric constant model has a correlation coefficient  $R^2 = 0.97$  with maximum error in prediction as low as 5% and the dielectric loss model has  $R^2 = 0.997$  with errors in prediction less than 10%. Dielectric properties of fish and seafood are generally in the same range as that of meats.

#### 18.5. Empirical models: fruits and vegetables

Dielectric properties of various fruits and vegetables have been reported in a number of studies (Kuang and Nelson, 1997; Sipahioğlu and Barringer, 2003; Sosa-Morales et al., 2010). Overall predictive equations were developed by combining the data for different fruits and vegetables to express the dielectric properties as a function of temperature, ash (wet basis) and moisture content (wet basis) as (Sipahioğlu and Barringer, 2003):

$$\epsilon' = 38.57 + 0.1255 + 0.456x_w - 14.54x_{ash} - 0.0037x_wT + 0.07327x_{ash}T \quad (159)$$

$$\epsilon'' = 17.72 - 0.4519T + 0.001382T^2 - 0.07448x_w + 22.93x_{ash} - 13.44x_{ash}^2 + 0.002206x_wT + 0.1505x_{ash}T \quad (160)$$

The average percent error of prediction was 6.20% for the dielectric constant and 13.22% for dielectric loss factor.

#### 18.6. Empirical models: gums

Gums are major carbohydrates present in foods along with starches and sugars. Predictive models, expressing both the dielectric constant and the loss factor of gums in powdered form as a function of moisture, temperature and stoichiometric charge of the molecule are given as (Prakash et al., 1992):

$$\epsilon' = 2.1256 - 0.00125CT + 0.0010Tx_w - 0.01565x_wC + 0.00220x_w^2 \quad (161)$$

$$\epsilon'' = 0.1295 - 0.00370Cx_w + 0.0004367Tx_w - 0.000993x_w^2 - 0.14469C^{1/3} \quad (162)$$

Here,  $T$  is the temperature (°C),  $x_w$  is the moisture content (% wet basis) and  $C$  is the stoichiometric charge (moles of charge/kg). Methods to obtain  $C$  have been discussed in Prakash et al. (1992). For Eqs. (161) and (162),  $R^2$  values are 0.91 and 0.92, respectively.

#### 18.7. Semi-empirical models: frozen foods

Dielectric properties of frozen food materials have been reported in literature (Bengtsson et al., 1963; Bengtsson and Rismon, 1971). But there are very few data points in the partially frozen range, where the properties can be strong functions of temperature, ice and salt content. Modeling of microwave thawing, for

example, requires properties in the partially frozen range as different regions in the food will be thawed to different extent at any given time. For the entire frozen range (−40 to 0 °C), correlations for dielectric property and loss factor for Tylose, a food analog whose property can be close to that of beef, are given as follows (Chamchong and Datta, 1999):

$$\epsilon' = 56.98x_u + 3.4402(1 - x_u) \quad (163)$$

$$\epsilon'' = 33.79x_u + 0.7450(1 - x_u) \quad (164)$$

where  $x_u$  is the fraction of unfrozen water at any temperature, estimated as described in Section 10.

##### 18.7.1. Model inclusion

In a transient simulation of microwave and radio-frequency heating, when the temperature is changing significantly and the dielectric properties vary significantly with temperature, coupling of electromagnetics and heat transfer would be obtained by simply including dielectric properties as function of temperature in a two-way coupled simulation. The two situations where dielectric properties are particularly strong functions of temperature are thawing and heating of salty foods such as a soup. In some materials like raw potato, the dielectric properties do not change significantly with temperature and thus two-way coupling of electromagnetics and heat transfer may not be needed, i.e., constant dielectric properties and a one way coupling where heat transfer follows electromagnetics would be sufficient. Likewise, if there is significant change of moisture during the heating process (as would be in drying), coupled simulation will be necessary with properties as function of moisture content.

## 19. Electrical conductivity

Electrical conductivity of a food is a measure of how well the electric current (direct or low frequency) flows through it. Electrical conductivity is the inverse of electrical resistivity and is expressed in S/m (Siemens/m). Electrical conductivity is needed, for example, to compute the rate of heat generation in modeling Ohmic heating (Dealwis and Fryer, 1992). Eq. 19 relates electrical conductivity,  $\sigma$ , to the rate of conductive heat generation, since

$$\epsilon''\epsilon_0 = \frac{\sigma}{\omega} \quad (165)$$

##### 19.1. Semi-empirical models

For a two-phase food system consisting of a liquid phase (also known as the continuous phase) and a phase consisting of solid particles (dispersed phase), the effective electrical conductivity can be obtained from (Zhu et al., 2010):

$$\sigma = \frac{\left(\sum_{i=1}^N \epsilon_i \sigma_i \frac{d_i \bar{\sigma}}{(d_i - 1)\bar{\sigma} + \sigma_i}\right)}{\left(\sum_{i=1}^N \epsilon_i \frac{d_i \bar{\sigma}}{(d_i - 1)\bar{\sigma} + \sigma_i}\right)} \quad (166)$$

Here,  $N$  is the number of material components,  $\sigma_i$  and  $\epsilon_i$  are the electrical conductivity and volume fraction of component  $i$ , respectively,  $\bar{\sigma}$  is the electrical conductivity of the continuous phase, and  $d_i$  is a factor related to the sphericity of the solid particles with a value of  $d_i = 3$  as recommended by Wang et al. (2006). Effective electrical conductivity of various solid particles (carrot, potato, radish, beef muscle, pork muscle and salted ham) dispersed in the continuous phase (5% starch solution, 0.1–1.5% salt concentration), predicted by Eq. (166), had a regression coefficient ( $R^2$ ) between 0.971 and 0.993 (Zhu et al., 2010), showing reasonably good prediction.

## 19.2. Empirical models: foods

Electrical conductivity of foods is often modeled as increasing linearly with temperature (Sastry, 2005):

$$\sigma = \sigma_0(1 + mT) \quad (167)$$

where  $\sigma$  is electrical conductivity,  $\sigma_0$  is reference electrical conductivity, and  $m$  is the temperature coefficient obtained from experiments. The values for the empirical constants in Eq. (167) has been noted for many foods such as for hydrocolloids (Marcotte et al., 2000). Effect of composition, including inert suspended solids and non-electrolyte solutes, have been modeled (Sastry, 2005). Correlations of conductivity with temperature are available for individual food such as meats and related products (e.g., Palaniappan and Sastry, 1991b; Wu et al., 1998; Zhu et al., 2010), fruits and fruit juices (Palaniappan and Sastry, 1991a, Castro et al., 2003; Castro et al., 2004; Amiali et al., 2006), and vegetables and related products (Palaniappan and Sastry, 1991b, Wang and Sastry, 1997b, Tulsian et al., 2008; Zhu et al., 2010).

### 19.2.1. Model inclusion

Although the same comments apply as for microwave and radio frequency heating in Section 18, temperature dependence of conductivity is generally quite significant and needs to be considered in modeling. As noted in Section 18, lack of linear or other correlation (as discussed below) is no obstacle to modeling as experimental data of conductivity vs. temperature can be directly included in a numerical software as a table where needed and data at a particular temperature can be interpolated during the computation.

## 20. Other Properties

For space reasons, many other properties are not included here. For example, psychrometric properties that are equilibrium properties of air–water vapor mixture, are often quite useful in modeling. Equations that describe these properties and thus can be included readily in the model are given in a number of sources (see, for example, <http://www.ageng.ndsu.nodak.edu/envr/PsycEqns.htm>).

## 21. Summary and the future

Despite the serious scarcity of measured thermophysical data that would be needed in physics-based modeling of food processes, computer-aided food process engineering can continue its rapid growth based on semi-empirical and empirical composition-based property prediction models that are available today. Most of these property prediction models have been validated against measured properties with an error of 10% or less. In design, we are often interested in “what if” scenarios where it is more important to see trends as we vary model parameters (e.g., physical properties) as opposed to the most accurate answer for a specific situation. This is easily achieved in computer-aided food process engineering through sensitivity analysis of model. The properties needed for such modeling approach often would not have need for greater accuracy than what is offered by many of the property modeling techniques presented in this article. The level of accuracy needed for engineering applications depends also on the level (rough screening vs. final stages) of design, reliability of the rest of the methodology used and sensitivity of the process to a particular property (Towler and Sinnott, 2008). Many of the property models presented here, as well as others in the literature make sufficient predictions for both the research objectives they intend to investigate and those resources available for investigation.

Another practical development that would greatly reduce the effort of computer-aided food process engineer hunting for data is to include the chosen food property prediction equations as part of the built-in property databases in computational software as is possible today (see, for example, thermophysical property prediction equations built into COMSOL Multiphysics, [www.comsol.com](http://www.comsol.com)). The equations provided in this article are one step away from achieving this.

Property prediction models will only improve in the future, not just through more improved approaches in semi-empirical predictions, but through more revolutionary (at least for the food world) simulations mentioned in Section 3. Of particular interest is multi-scale simulation where microscale continuum-based simulation is made to obtain average or effective properties that are used in macroscale simulation, as has been done for transport properties (Ho et al., 2011), and mechanical properties (Kanit et al., 2006) with promise in areas such as cereal (Guessasma et al., 2011).

The authors hope that this selected compilation would help remove one of the major bottlenecks in computer-aided food process engineering, that of obtaining properties as function of process parameters. Improved models in the future will possibly replace the ones in this article but these are satisfactorily usable today for most design and research applications.

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