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Advantages of isochoric freezing for food preservation: A preliminary analysis☆

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ABSTRACT

Motivated by an interest in developing more efficient and economical methods for long-term preservation of food in a frozen state, we have explored the concept of isochoric (constant volume) freezing. In this theoretical study, we have developed a new set of equations that describe the process of freezing in the isochoric system. Unlike isobaric systems, in isochoric systems, the pressure is not constant and affects the phase transition temperature in a way prescribed by equilibrium thermodynamics. Fundamental thermodynamic principles, were used to derive an equation that facilitates the calculation of the temperature of the change of phase interface during the freezing process as a function of the quality of the system (the extent of freezing). A simple one-dimensional case study demonstrates the advantages of isochoric freezing of food. These advantages include the ability to freeze only part of the system at recommended food storage temperature, which results in substantial energy savings and conditions that will likely lead to stored food of better quality.

1. Introduction

Feeding the world population is made possible by advances in food preservation technology. Cooling has been used in food preservation, for food storage and to avoid food spoilage, for centuries. Low temperatures reduce deleterious chemical reactions in food and inhibit growth of microorganisms and other pathogens. In theory, lowering the temperatures has a beneficial effect on food preservation. A temperature of −18 °C, or less, is recommended for long-term storage of foods [1]. However, biological matter is mostly water, and lowering the temperature to below the freezing temperature of water produces a marked change in the physical state of the food. The ice crystals that form intracellularly and extracellularly affect the texture of the thawed food and the quality of the preserved food.

Freezing of a food product is a process in which heat is extracted from the outer surface of the product by a cooling medium. In a conventional freezing process, ice nucleation starts at the outer surface of the product, in contact with the cooling medium, and the ice propagates towards the interior of the product from the exterior as a function of the outer surface, thermal boundary conditions and the properties and dimensions of the frozen material. In general, freezing with high freezing velocities results in smaller ice crystals [2]. The smaller the ice crystals the better is the biologically matter morphologically preserved, and the higher is the quality of the preserved food product [3]. The American inventor Clarence Birdseye who developed the quick-freezing process of food preservation in 1929 first recognized the value of rapid freezing for food preservation [4]. Rapid freezing is commercially referred to as "flash freezing" or "cryogenic." It is a process in which food is very quickly frozen at extremely cold, cryogenic temperatures. The freezing speed directly influences the ice nucleation process and ice crystal size. Therefore, in flash freezing, the food is usually rapidly immersed in a cryogen such as liquid nitrogen at −196 °C, or a mixture of dry ice (solid CO_2) and ethanol [5]. Once flash frozen, the foods are moved to a conventional mechanical freezer with a temperature closer to the freezing point (−20 °C for long-term storage).

While flash freezing provides the highest quality frozen foods, it has limitations. Regardless of the cooling medium, the freezing interface must propagate from the exterior in contact with the coolant, to the interior. The freezing interface velocity slows towards the interior. Therefore, small ice crystals cannot form uniformly throughout the frozen food. In flash freezing, they will be small near the outer surface of the freezing object, but increase towards the interior. While flash

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Nomenclature

a	coefficient in Eq. (7)
b	coefficient in Eq. (7)
c	specific heat, J/kg K
C	concentration, M
d	coefficient in Eq. (7)
D	mass diffusivity, m/s^2
IP	percentage volume of ice in the system (%)
k	thermal conductivity, W/m K
R	energy ratio, Eq. (18)
Ste	Stefan number, Eq. (17)

Greek

α_1	thermal diffusivity in ice, m^2/s
λ	partition coefficient in freezing of solutions
θ	dimensionless temperature, Eq. (16)
ζ	dimensionless distance, Eq. (16)
τ	dimensionless time, Eq. (16)

Subscripts

1	frozen domain
2	liquid domain
init.	initial
o	initial conditions

Superscripts

o	boundary

freezing is the most rapid method of freezing, currently known, the process of freezing in many commercial products takes several hours. During this period the temperature in the interior, unfrozen volume, can be above the freezing point [6] and conducive to microorganism proliferation. Flash freezing is also energetically wasteful because the frozen food is first frozen to cryogenic temperatures, but stored at high subzero temperatures. The difference in temperatures between the processing temperature and storage temperature is wasted energy. Furthermore, while the quality of food frozen with flash freezing is high, the device technology is expensive, as it requires systems designed around cryogenic temperatures. There are also other freezing systems referred to as "mechanical freezing". They are much less expensive. Mechanical freezers were, in fact, the first to be used in the food industry and are used in the vast majority of freezing/refrigerating lines. They function through a conventional refrigeration cycle and operate at temperatures of about −20 °C. While less expensive, mechanical freezers cannot freeze to achieve the small ice crystals that characterize foods frozen with flash freezing.

This study introduces a new freezing technology that can operate at mechanical freezer temperatures and yield food preservation with a quality that may be superior to flash freezing, in an energy economical process. The technology is named, isochoric freezing. Conventional freezing processes occur at constant pressure, isobaric, because this is the common thermodynamic state on earth. Our group has recently developed the fundamental thermodynamics of phase transformation of aqueous solutions in an isochoric, constant volume, system [7,8,9,10]. This study will expand on the previous work and explore the kinetic process of freezing in an isochoric system. This is a theoretical study that will introduce the mathematical formulation, and discuss the concept and principles of isochoric freezing. The value of this technology for frozen-food preservation, will become evident from the analysis of a simple case study.

2. Isochoric freezing mathematical model

Consider the general isochoric solidification problem. There is a constant volume, V, and domain, Ω, comprised of two time dependent domains $\Omega_1(t)$ and $\Omega_2(t)$ which represent, the solid phase region and the liquid phase region, respectively, such that $\Omega = \Omega_1(t) \cup \Omega_2(t)$. The outer boundary of the solid domain $\Omega_1(t)$, Γ_1, is fixed. This ensures the constant volume (isochoric) nature of the problem. The boundary between domains $\Omega_1(t)$ and $\Omega_2(t)$, $\Gamma_2(t)$, is the moving change of phase interface common to both domains. The outward normal unit vector at any point on $\Gamma_2(t)$ is, n. Our problem is to determine the transient location of $\Gamma_2(t)$, and the temperature distribution in domains $\Omega_1(t)$ and $\Omega_2(t)$.

The process of freezing in an isochoric system has certain unique attributes, that are different from conventional freezing in an isobaric system. Whereas in an isobaric system, the temperature of the change of phase interface between ice and water is constant and independent on the location of the change of phase interface and on the thermal history during freezing, in an isochoric system the temperature on the change of phase interface is dependent on the thermal history and the location of the interface. When freezing occurs in an isochoric system, any incremental change in the location of the change of phase interface changes the pressure of the system. In a simplistic explanation, the changes are related to the difference in density between ice and water. When a certain volume of water solidifies, the decrease in density upon freezing will elevate the pressure in the closed volume system. We assume that for the time scale of solidification processes, this change in pressure is instantaneous and uniform in the entire isochoric system. This change in pressure will instantaneously change the temperature on the change of phase interface, in such a way that the ice/water interface temperature is at the thermodynamic equilibrium value at the new pressure. In isobaric solidification the temperature of the change of phase interface is known and constant and the location of the interface is unknown. In isochoric solidification, the temperature on the interface and the location of the interface are both unknown and must be found as part of the solution. Therefore, the analysis of isochoric solidification processes requires additional equations that will correlate between the location of the change of phase interface, the pressure and the temperature on the change of phase interface. Specifically, the isochoric problem also requires the solution of the set of thermodynamic equilibrium equations which define the internal pressure P(t), in the constant volume domain, V, as a function of the extent of freezing. Biological matter contains solutes, and the general formulation of isochoric freezing in a solution should also include a mass transfer equation for solute transport [2].

The analysis of an isochoric freezing system requires the solution of the following set of equations:

The conservation of energy equation in the frozen region:

$$\nabla \cdot (k_1 \nabla \mathrm{T}_1) = \rho_1 c_1 {}^{\partial \mathrm{T}_1}\!/_{\partial \mathrm{t}} \ \text{in } \Omega_1(\mathrm{t}) \tag{1}$$

The conservation of energy equation in the unfrozen region:

$$\nabla \cdot (k_2 \nabla \mathrm{T}_2) = \rho_2 c_2 {}^{\partial \mathrm{T}_2}\!/_{\partial \mathrm{t}} \ \text{in } \Omega_2(\mathrm{t}) \tag{2}$$

The conservation of mass equation in the unfrozen region:

$$\nabla \cdot (D \nabla C) = {}^{\partial C}\!/_{\partial \mathrm{t}} \ \text{in } \Omega_2(\mathrm{t}) \tag{3}$$

The conservation of energy on the change of phase interface:

$$\rho L v_n = k_1 {}^{\partial \mathrm{T}_1}\!/_{\partial \mathrm{n}} - k_2 {}^{\partial \mathrm{T}_2}\!/_{\partial \mathrm{n}} \ \text{on } \Gamma_2(\mathrm{t}) \tag{4}$$