A shift from the isobaric to the isochoric thermodynamic state can reduce energy consumption and augment temperature stability in frozen food storage

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ABSTRACT

Frozen storage of food comprises a large portion of global energy consumption, and in light of growing demand and increasing global temperatures, new solutions for increasing its energy efficiency are needed. Past efforts to improve refrigeration efficiency have focused primarily on improving the vapor-compression cycle and developing alternative heat pumps, but this study looks beyond the technology of cooling to the fundamental thermodynamics at play in the freezing of biological matter. Conventionally, food is frozen under isobaric conditions, e.g. at constant (atmospheric) pressure. Herein we use fundamental thermodynamic analyses to demonstrate that the process of freezing in an isochoric (constant volume) system requires up to 70% less energy compared to conventional freezing, and we develop novel phase change models to demonstrate newly discovered thermal effects that provide isochoric systems with exceptional temperature stability when exposed to ambient fluctuations (such as those encountered within freezers or during transportation), with the potential to substantially improve the energy efficiency of long-term storage and enhance preserved food quality. Our results show that a simple change in the thermodynamic state in which food is frozen and stored, from isobaric to isochoric, has the potential to substantially reduce the energy consumption of the global food storage industry, without the need to make major changes to existing refrigeration infrastructure.

1. Introduction

Cold storage is the most prominent method of preventing postharvest food losses and the spread of foodborne disease globally, with an estimated 1.6 billion refrigeration and freezing units deployed for this purpose. It accounts for roughly 8% of global electricity consumption (Coulomb, 2008; Coulomb et al., 2015) and given rapid population growth and the economic advancement of large developing countries, this number is expected to rise sharply in the near future (Coulomb et al., 2015). Furthermore, increasing global temperatures exacerbate the need for cold storage while simultaneously highlighting the importance of reducing its carbon footprint (James and James, 2010). It is thus recognized that increasing the energy efficiency of food cold storage processes should be a key goal for both the public and private sectors (Coulomb, 2008; Coulomb et al., 2015; IIR, 2009; James and James, 2010).

The efficiency of frozen food storage can be considered in two phases: the freezing efficiency and the storage efficiency. The freezing efficiency is characterized by the energy required to bring a mass of food to thermal equilibrium at a given subfreezing temperature. For water-based systems such as food, freezing is a much more energy intensive process than simple cooling—the energy required to freeze a unit mass of water (the latent heat of fusion) is nearly 100 times that required to cool the same unit mass one degree Centigrade. Thus freezers experiencing frequent additions of unfrozen mass, such as those used during industrial food processing, experience lower efficiencies than those used in domestic contexts (Geppert and Stamminger, 2013; Hasanuzzaman et al., 2009). The storage efficiency is characterized by the energy required to hold a mass of food at a desired subfreezing temperature over long periods, both at permanent storage sites and during transportation, and in the face of controlled and uncontrolled ambient temperature fluctuations. These fluctuations are a principal source of inefficiency in long-term food storage, and also contribute to various detrimental phenomena including moisture migration, bulk weight loss, disruption of microstructure, and poor retention of food-specific nutritional qualities (Bustabad, 1999; Gigiel and Collett, 1989; Lyu et al., 2017a; Martins et al., 2004; Năstase et al., 2017a; Ullah et al., 2014).

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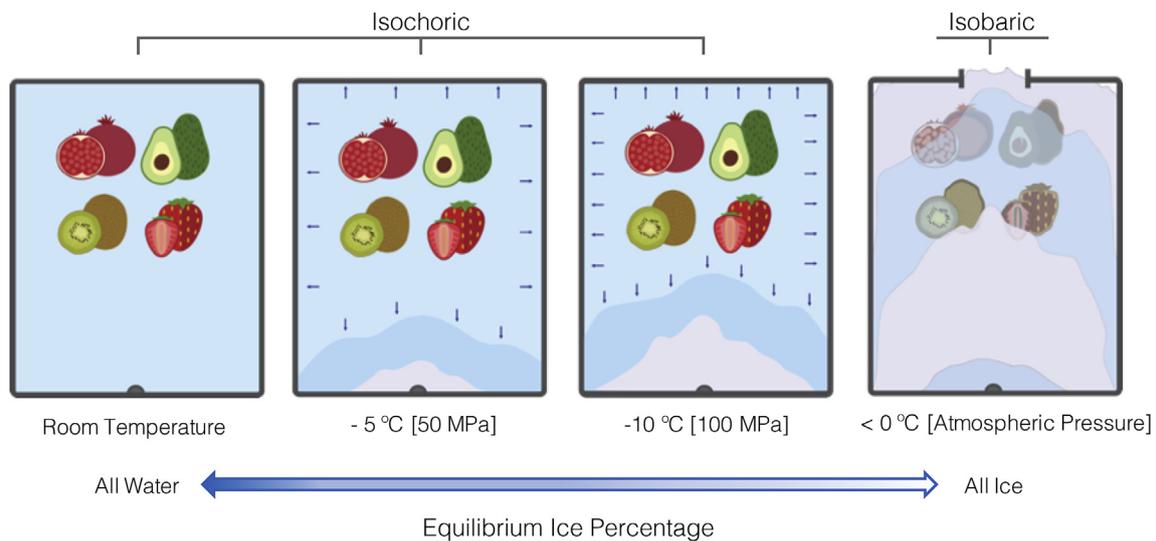
Fig. 1. Equilibrium states of isochoric systems at various temperatures and comparison to a standard isobaric system frozen at atmospheric pressure.

Recent efforts to address these issues have focused primarily on improving heat pump technology (Tassou et al., 2010). Though vapor-compression devices remain the most common choice for closed-loop cycling of heat, in light of their relatively low efficiencies and the environmentally harmful nature of the required refrigerants, many alternative technologies are being investigated, including those based on caloric effects, thermoelectric, thermoacoustic, and magnetic effects, air cycle and Stirling cycle refrigeration, etc (Tassou et al., 2010; Tušek et al., 2016). In this work however, a different approach is taken: instead of trying to increase the efficiency of discrete refrigeration technologies, a method is proposed to alter the fundamental thermodynamics at play in the freezing process itself, increasing the efficiency and temperature stability of cold storage regardless of the device used to facilitate it.

Isochoric (constant volume) cold storage systems have previously been suggested as a means to preserve organs for transplantation (Rubinsky et al., 2005; Wan et al., 2018; Zhang et al., 2018). More recently however, their potential for greatly enhancing the quality of foods stored at subfreezing temperatures has been demonstrated, with studies of sweet cherries (Bilbao-Sainz et al., 2018), tilapia (Năstase et al., 2017b), and potatoes (Lyu et al., 2017b) all demonstrating significant improvements in the quality of foods stored in isochoric systems compared to conventional freezing systems. Additional recent work further suggests that isochoric cold storage has the capacity to eliminate potentially harmful bacteria (Powell-Palm et al., 2018). Herein we present a theoretical study of two unique and previously unknown energetic behaviors of isochoric systems, with the potential to significantly improve the energy efficiency of frozen food storage in both the initial freezing and long-term storage phases. For the initial freezing phase, we demonstrate through fundamental thermodynamic analyses that up to 70% less energy is required to bring isochoric containers with relevant food contents to equilibrium at subfreezing temperatures compared to traditional isobaric containers. For the long-term storage phase, we develop a novel heat transfer model to reveal unique phase change phenomena that enable the coupling of latent and sensible heat effects, effectively increasing the thermal mass of a quantity of food held in an isochoric container by two orders of magnitude relative to the same quantity in an isobaric container. These phenomena provide isochoric systems with exceptional temperature stability when exposed to external temperature fluctuations, which in turn has been shown to reduce the energy consumption of long-term storage and substantially improve the quality of the preserved food.

The simple change in the thermodynamic state in which frozen food is stored, from isobaric to isochoric, requires relatively small changes to current worldwide refrigeration infrastructure, and has the potential to substantially and immediately reduce the energy consumption of frozen food storage while simultaneously improving the quality of the preserved food. The discoveries detailed herein present a novel path forward in the effort to improve global cold storage, rooted in the fundamental thermodynamics of isochoric freezing.

1.1. Principles of freezing in an isochoric system

The goals of cold storage of food are twofold: to reduce the rate of metabolism, the temperature-dependent process which drives biological degradation, and to provide an environment inhospitable to harmful microorganisms. Traditional freezing often achieves these goals, but at the cost of significant energy consumption, reduced food quality, and bulk weight loss. The root cause of these negative effects is the formation of ice crystals within the food matter, which cause mechanical damage, osmotic damage, dehydration, etc (Reid, 1996). Isochoric cold storage (ICS) was thus developed with the goal of protecting stored food matter from ice damage while retaining the beneficial effects of storage at temperatures below the freezing point of water.

The traditional thermodynamic premise upon which the modern freezing industry is built considers systems under isobaric conditions; systems at (constant) atmospheric pressure in which the two remaining state variables, temperature and volume, then vary in tandem. Within such a system, an unrestricted volume of water or aqueous solution (or the total water content within a given solid mass of food) will freeze almost completely when held below its phase transition temperature (freezing point). In an isochoric system however, the *volume* is held constant (physically constrained by a rigid container) and the *temperature* and *pressure* are left to vary in tandem. This fundamental remix of state variables leads to a very different freezing process.

Due to the crystallographic structure and density of ice 1, water expands as it freezes. Under isobaric conditions, the volume of the system will thus increase as the system freezes, to no further effect. In an isochoric system however, in which the volume is constrained, the ice cannot freely expand—and thus as it forms, a hydrostatic pressure develops in the system (Fig. 1). This pressure then depresses the freezing point of the solution, and so ice will continue to grow until the effective freezing point of the system is equal to the surrounding temperature (Fig. 2a). At this point a pressurized two-phase system will exist, with an unfrozen liquid portion and a frozen solid portion coexisting at a temperature below the atmospheric freezing point of the solution (Fig. 2b). Food matter can therefore be stored in the volume that remains liquid, protecting it from the harmful effects of freezing
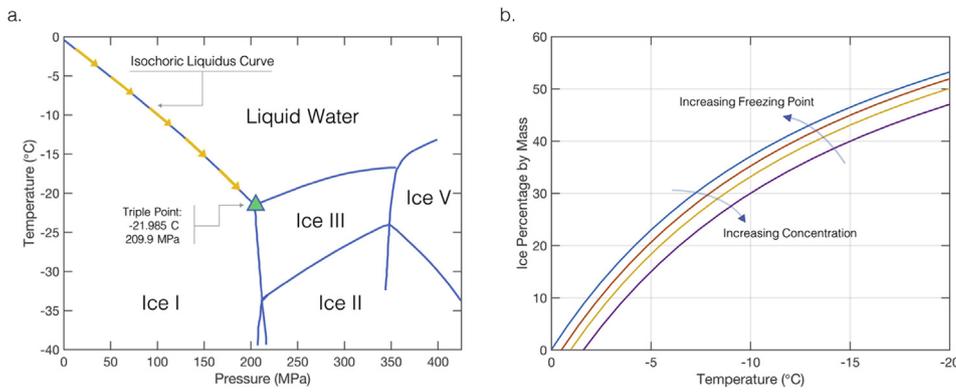
Fig. 2. Fundamental thermodynamic behaviors of isochoric systems. **a**, Phase diagram of pure water. The liquidus curve between liquid water, ice I, and ice III marks the equilibrium pressure that an isochoric system will experience at a given subzero temperature higher than the triple point. **b,** Percentage by mass of an equilibrium isochoric system that will be converted to ice as a function temperature, adapted from Rubinsky[15].

while enabling the desired reduction of metabolism that extends its edible lifetime. It should be noted furthermore that the equilibrium temperature-pressure relations experienced in an isochoric system follow precisely the liquidus curve between ice 1 and water up to the triple point (marked in Fig. 2a), naturally minimizing the pressure experienced within the system at a given subzero temperature (Rubinsky et al., 2005).

Though the energetic behaviors investigated in this work are theoretical in nature, numerous experimental isochoric containers have been fabricated for research purposes (see materials descriptions of (Bilbao-Sainz et al., 2018; Lyu et al., 2017b; Năstase et al., 2017b;

Powell-Palm et al., 2018)). A sample schematic of one such system is included in Fig. 3 below for clarity, adapted with permission from (Bilbao-Sainz et al., 2018). In practice, isochoric thermodynamic conditions can be achieved in any rigid container that can withstand high pressures (the exact magnitudes of which will vary depending on the target preservation temperature, according to the path highlighted in Fig. 2a). Food is typically stored in an isotonic solution inside the isochoric container (a saline solution for meats and fish or a sugar solution for fruits and vegetables, see Fig. 2b), and no air is allowed inside the chamber (due to its immense compressibility). While the research-grade isochoric containers used to date are typically built from thick-walled
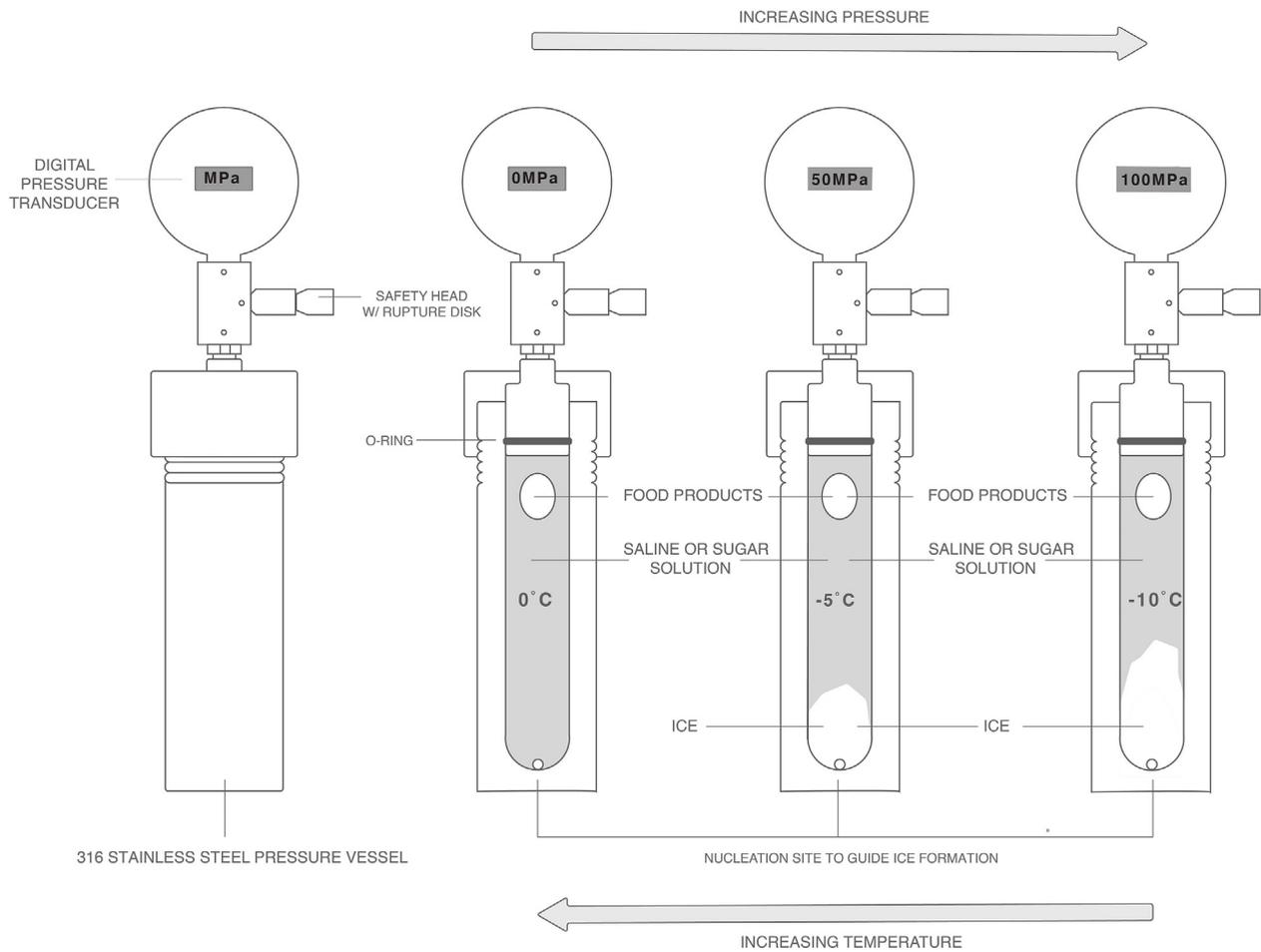
Fig. 3. Sample schematic of a research-grade isochoric container and the generalized isochoric freezing process. In a system of constrained liquid volume with rigid walls and no air pockets, ice expansion will generate hydrostatic pressure, which depresses the freezing point of the system. The pressure will continue to rise until the freezing point of the system becomes equal to the system temperature. At this point, liquid and solid phases will exist in equilibrium. Approximately 20% and 35% of the total volume will be frozen at $-5\,°C$ and $-10\,°C$, respectively.
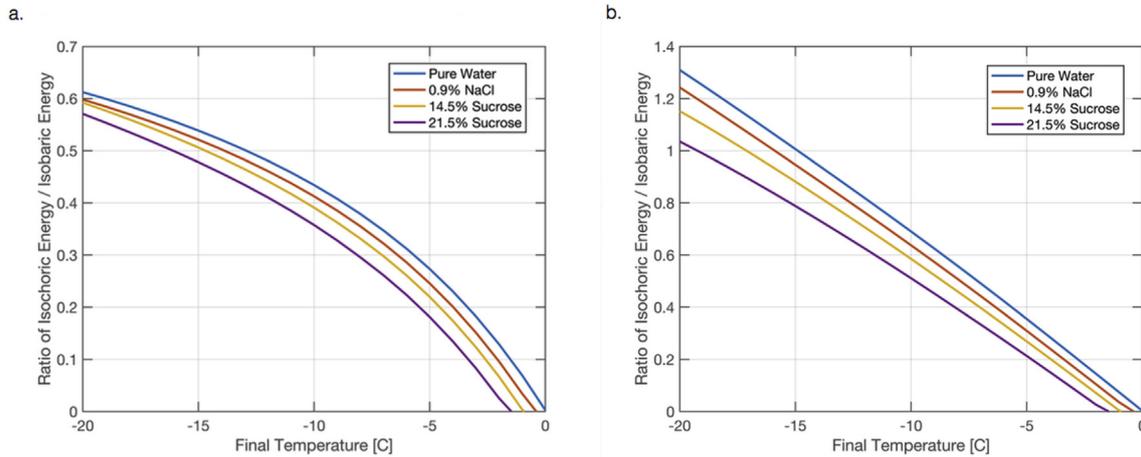
Fig. 4. Ratio of the energy required to bring a system to equilibrium at subfreezing temperatures between 0 and -20C under isochoric and isobaric conditions (isochoric/isobaric) for different solutions, including: pure water, saline solution of concentration equivalent to fresh meat or fish, sucrose solution of concentration equivalent to cherries (14.5 brix), and sucrose solution of concentration equivalent to pomegranate (21.5 brix). **a**, Ratios considering two systems of identical size. **b**, Ratios considering an isochoric system sized such that the portion remaining unfrozen at a given temperature is equal to the total size of the isobaric system.

stainless steel cylinders, there is ample opportunity to design containers out of lighter materials (such as carbon fiber composites or hard phenolic thermosets), depending on the target temperature and pressure, and such containers need not employ a pressure transducer as pictured in Fig. 3. Essential to understanding the premise of isochoric food storage however is the fact that the thermodynamic conditions described above can be achieved by a very simple transition from an unconstrained volume to a constrained volume— no electricity or moving parts are required, simply ample rigidity and the absence of air within the container.

1.2. Thermodynamic model of isochoric freezing

In this work, the fundamental thermodynamics of isochoric freezing are examined to show that freezing an isochoric system to a given temperature is significantly less energy intensive than freezing a traditional (isobaric) system to the same temperature. For conceptual simplicity we consider herein a mass of water, but it should be noted going forward that these thermodynamic analyses can be applied to any solid food product with high water content (such as fruits or meats) or any liquid food product (such as milk or juices).

To bring a mass of water to equilibrium at a subfreezing temperature in a conventional isobaric system at atmospheric pressure, the following energetic quantities must be considered: the sensible heat required to bring the mass of water from some initial temperature to its freezing point (0 °C at atmospheric pressure), the latent heat required to freeze the mass of water at its freezing point, and the sensible heat required to bring the resulting mass of ice to the final subfreezing temperature. If the mass of water is assumed to be pre-chilled to 0 °C, the calculation simplifies to:

$$E = m_{total}L(T_0) + m_{total}\int_{T_0}^{T_1} c_{p\_ice}(T)dT \qquad (1)$$

where E is the energy required to reach equilibrium at a subfreezing temperature T_1, $L(T_0)$ is the latent heat of fusion for water evaluated at 0 °C, m_{total} is the total mass of system, and $c_{p\_ice}(T)$ is the temperature-dependent specific heat capacity of ice. Note that because under isobaric conditions the entire phase transition takes place at the freezing point, the temperature-dependent latent heat need not be integrated.

In an isochoric system however, the freezing point decreases as the phase transition progresses, due to the discussed development of internal pressure, and only a portion of the initial mass of water is able to freeze (Fig. 2B). In previous work, a thermodynamic method was

developed to calculate the percentage of the total system mass that is converted to ice as a function of temperature, henceforth referred to as $mp_{ice}(T)$ (see Methods for additional detail) (Rubinsky et al., 2005). Using this function to relate temperature to the mass percent of ice, an energy statement equivalent to eqn. (1) can be developed for an isochoric system:

$$E = \int_{m_1}^{m_2} L(T)dm + \int_{T_0}^{T_1} c_{P_{water}}(T) \times m_{total}(1 - mp_{ice}(T))dT$$
$$+ \int_{T_0}^{T_1} c_{P_{ice}}(T) \times m_{total}mp_{ice}(T)dT \qquad (2)$$

where it is first recognized that the differential mass dm in the integrated latent heat of fusion term can be rewritten as $dm = m_{total}mp'_{ice}(T)dT$, allowing integration over the temperature domain:

$$E = \int_{T_0}^{T_1} L(T)m_{total}mp'_{ice}(T)dT + \int_{T_0}^{T_1} c_{P_{water}}(T) \times m_{total}(1 - mp_{ice}(T))dT$$
$$+ \int_{T_0}^{T_1} c_{P_{ice}}(T) \times m_{total}mp_{ice}(T)dT \qquad (3)$$

Term by term, eqn. (3) thus represents: the integrated latent heat of fusion, the integrated sensible heat loss of the portion of the system that remains liquid, and the integrated sensible heat loss of the portion of the system that becomes ice.

1.3. Energy consumption during freezing

To evaluate the potential for energy savings, the ratios of the energy required to freeze identical masses in an isochoric system and an isobaric system were calculated. Fig. 4a presents these ratios as a function of final temperature for several solutions of relevance to the food industry. The energy required in an isochoric system is observed to be significantly less than that required for an isobaric system of identical mass. This phenomenon can be attributed to two physical effects: the reduction in total frozen mass and the temperature dependence of the latent heat of fusion of water. As established previously, at any subfreezing temperature higher than the triple point only a portion of the mass in an isochoric system will actually freeze (Fig. 2a/b), and thus there is a drastic reduction in the overall energy required for ice fusion. However, the energy required to freeze even that limited portion is also less than would be required for the same portion in an isobaric system,

because the latent heat of fusion decreases with temperature. This temperature dependence does not benefit isobaric systems because, as highlighted previously, the entire phase transition takes place at the atmospheric freezing point. In an isochoric system, the freezing point decreases as the phase transition progresses, and thus the energetic requirements of freezing are reduced. At a high level, in terms of latent heat, atmospheric isobaric systems naturally *maximize* the amount of energy required to freeze. Conversely, isochoric systems naturally reduce this energy.

As stated, a central goal of isochoric cold storage at subfreezing temperatures is the protection of preserved food matter from ice formation. However, in the scenario considered in Fig. 4a, the isobaric and isochoric system masses are equal, which implies that at subfreezing equilibrium some percentage of the isochoric system will be frozen. Thus in a practical food storage context, the effect of the isochoric system would be to protect only *some portion* of the preserved food matter from ice damage. While this scenario is certainly of industrial relevance, a means of conserving energy while reducing (rather than eliminating) damage, an additional comparison is required to evaluate the energy needed to protect the entire mass of food matter. A new isochoric system is thus considered, incorporating two mass terms: a food mass m_F, defined as the mass of food matter to be protected from ice formation, and a design mass m_D, defined as the total system mass required such that a portion equal to the food mass will remain unfrozen, or $m_D = \frac{m_F}{1 - m p_{ice}(T)}$. Substituting m_F and m_D for m_{total} in eqns. (2) and (3) respectively, the energy requirements are recalculated for an isobaric system of mass m_F and an isochoric system of mass m_D and presented in Fig. 4b. This figure reveals an interesting temperature threshold after which the effect of increased total mass overcomes the effect of ice reduction in the isochoric system, making it less efficient than the isobaric. It also further highlights the significant potential for energy savings in isochoric systems in the high subzero temperature range, where the difference in the total degree of ice formation will be most extreme between isochoric and isobaric systems. Differences observed between solutions in both figures are attributed to the freezing point depression that accompanies increased concentration (Lide, 2003).

1.4. Heat transfer with phase change model of isochoric freezing

A novel 1D phase change model is now developed to explore the effects of a steadily fluctuating external temperature on an isochoric system, after the completion of the initial freezing process (Fig. 5). The mathematical formulation of this problem for the solid phase is given as:

Solid Region: $\frac{\partial^2 T_s}{\partial x^2} = \frac{1}{\alpha_s}\frac{\partial T_s(x, t)}{\partial t}$ in $0 < x < S(t), t > 0$ (4)

$$T_s(x = 0, t) = T_D + A\cos(wt) \tag{5}$$

while the liquid phase is given as:

Liquid Region: $\frac{\partial^2 T_l}{\partial x^2} = \frac{1}{\alpha_l}\frac{\partial T_l(x, t)}{\partial t}$ in $S(t) < x < B t > 0$ (6)

$$\frac{dT_l(x = B, t)}{dx} = 0 \tag{7}$$

$$T_l(x, t = 0) = T_s(x, t = 0) = T_D \tag{8}$$

The coupling conditions at the interface are:

$$T_s(x = S(t), t) = T_l(x = S(t), t) = T_f(\bar{S}) \tag{9}$$

$$k_l \frac{\partial T_l}{\partial x}\bigg|_{x=S(t)} - k_S \frac{\partial T_s}{\partial x}\bigg|_{x=S(t)} = \rho L(T_f)\frac{dS(t)}{dt} \tag{10}$$

Here the subscripts s and l indicate properties of the solid and liquid regions respectively, and the parameters are: thermal conductivity k,

thermal diffusivity α, liquid density ρ, freezing point T_f, temperature-dependent latent heat of fusion $L(T_f)$, target storage temperature T_D, amplitude of external boundary temperature fluctuation A, frequency of external boundary temperature fluctuation w, and non-dimensional position of the freezing front $\bar{S} = S(t)/B$, in which B is the characteristic length of the system. These formulations resemble those of classic solidification problems in most regards, but feature two key adaptations to reflect isochoric conditions: In isobaric systems, the freezing point T_f is treated as constant, due to the fact that the entire solidification process is assumed to occur at the atmospheric T_f. Here (similar to the previous section), T_f varies as freezing progresses, in 1D as a function of the position of the freezing front $\bar{S}$. The relation $T_f(\bar{S})$ for pure water is calculated using the method of Rubsinky (see Methods) (Rubinsky et al., 2005). The temperature dependence of the latent heat $L(T_f)$ is also introduced, which is otherwise typically considered constant.

The problem formulated above was solved using an approximate finite difference approach, (see Methods), ultimately yielding transient temperature profiles for an isochoric system exposed to external periodic temperature fluctuations.

1.5. Temperature stability results

Steady temperature fluctuations were calculated for dimensionally identical isobaric and isochoric systems of pure water at thermal equilibrium for varying input parameters, including the amplitude A and frequency w of the external temperature oscillation, the desired storage temperature T_D, and the characteristic length of the system (Fig. 6a – 6c). Calculations for isochoric systems use the specialized model formulated in the previous section, because even at a steady subzero temperature, an isochoric system will consist of two phases in thermodynamic equilibrium with a liquid/solid phase boundary between them. In isobaric systems however, at subzero-temperature equilibrium the entire volume will have frozen, eliminating the need to consider a phase boundary and enabling use of standard steady-periodic slab solutions.

Using the data showcased in Fig. 6, the effective amplitude of the temperature fluctuation experienced at the center of each system was measured, and ratios of isochoric to isobaric amplitudes are presented in Fig. 7a and b. Both figures reveal that isochoric systems experience **up to an order of magnitude less** internal temperature fluctuation than isobaric systems, and both show a consistent dependence on system size. This is a general reflection of the underlying principal governing the observed temperature stability: because the temperature of an isochoric system held at subzero °C equilibrium will always equal its phase change temperature, the majority of any imparted energy change will be consumed directly by phase change, not sensible temperature change. Thus, as the mass available for freezing increases, the energetic weight of this phase change buffer increase accordingly.

Fig. 7a showcases the dependence of the amplitude ratio on the frequency of the applied external temperature fluctuation, suggesting that isochoric systems are increasingly protected against temperature swings as the frequency increases. While food matter will typically encounter lower frequencies (cycles of two or three hours) during long-term storage, exposure to high frequency temperature changes is often experienced during transitions in storage conditions/locations, as food matter moves through the distribution process (Ndraha et al., 2018; Zhang et al., 2009). In Fig. 7b, the applied external amplitude appears not to appreciably affect the internal amplitude ratios, but sensitivity to the desired storage temperature is observed, with relative isochoric stability decreasing as T_D decreases. This behavior results from the temperature dependence of the latent heat of fusion, as discussed for the thermodynamic model; because the energy required for phase changes decreases with temperature, the temperature buffer afforded to an isochoric system by continuous phase change also decreases with temperature.
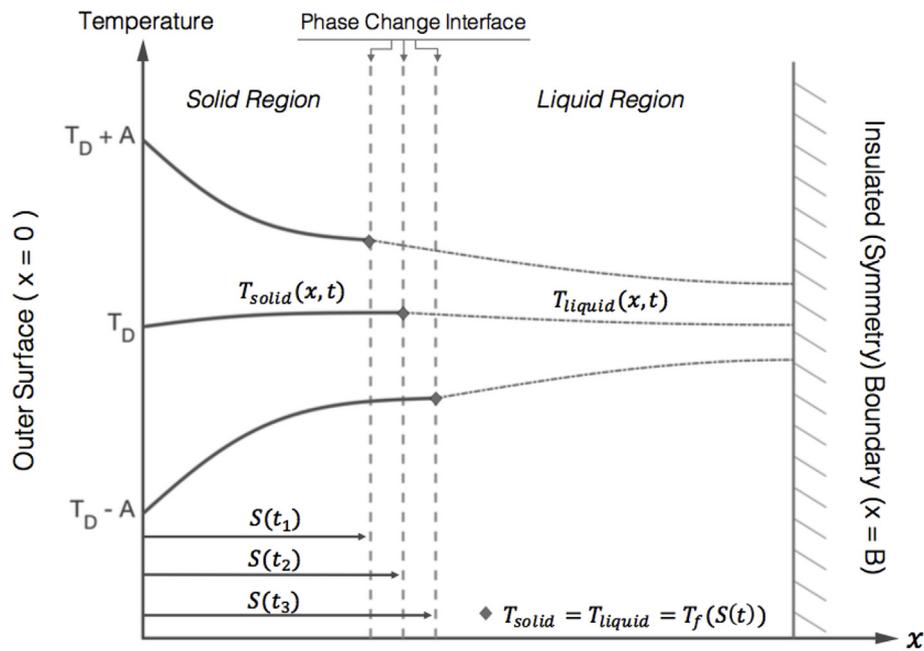
Fig. 5. Isochoric Phase Change Model: A finite, one-dimensional, two-phase system is considered, bounded by an outer surface with an oscillating prescribed temperature and an insulated (symmetry) boundary. The time-dependent position of the phase change interface is marked by $S(t)$. The domain $0 < x < S(t)$ represents the solid (frozen) region, and the domain from $S(t) < x < B$ represents the liquid (unfrozen) region. The temperature at the interface is the phase change temperature of the system, which varies with interface position.

2. Discussion

The thermodynamic considerations of Fig. 4 reveal that freezing efficiency is substantially increased in isochoric systems, based principally on the naturally reduced ice formation inherent to water-based systems of constrained volume. At $-5\,°C$, storage in an isochoric container designed to fully isolate food matter from ice crystallization (Fig. 4b) could yield up to a 70% decrease in the energy required to freeze meat or fish, with even greater savings available for high sugar foods such as fruits and berries. Furthermore, in an industrial context, these savings represent a lower bound, as they consider only traditional slow freezing; in industry, many foods are first frozen via flash freezing, an energy intensive method employing deep cryogenic temperatures to reduce the size of ice crystals in the interior of the frozen matter (Birdseye, 1924), and then allowed to warm back to typical freezer temperatures. Because no ice will form within food stored in an isochoric system, such processes would prove unnecessary preceding isochoric storage, yielding further energy savings.

Isochoric cold storage was also found to provide exceptional temperature stability relative to isobaric storage (Fig. 7a and b), reducing the temperature fluctuation experienced by stored food matter by up to an order of magnitude. This stability is the product of a thermodynamic behavior unique to isochoric systems which has not been previously investigated: in an isochoric system, the phase change temperature will always equal the bulk system temperature at equilibrium, effectively coupling latent and sensible heat consumption at all subzero temperatures. In other words, any input of energy into a subzero-temperature isochoric system will cause phase change, no matter the precise subzero value. This differs fundamentally from conventional isobaric systems, in which phase change will only occur at the fixed atmospheric phase change temperature ($0\,°C$ for pure water), and functions to effectively increase the thermal mass of the isochoric system by two orders of magnitude, or the ratio between the latent heat of fusion and sensible heat capacity of water.

The use of phase change as a buffer against temperature change is well-established in the field of thermal management, and furthermore, exterior phase change materials (PCMs) have recently been proven to increase the efficiency of vapor-compression freezers by increasing thermal mass and reducing the amount of time the compressor must run (Mastani Joybari et al., 2015). These exterior PCMs must be tailored to a specific system based on freezing point however, and introduce new complexity to freezer design. By comparison, the thermal mass effects discovered in this study show that an isochoric system behaves like an inherently optimized version of a traditional phase change material, in which the phase transition temperature dynamically varies alongside the system temperature, maximizing the amount of energy consumed by phase change relative to temperature change for a given energy input. Isochoric storage thus offers the unique advantage of effectively transforming *stored food* contents into phase change materials; in conventional isobaric systems, the stabilizing effects of phase change are lost after initial freezing around $0\,°C$, but in isochoric systems, phase change and temperature change are permanently coupled. Under isochoric conditions, water itself (including that found within solid food products) becomes an effective phase change material (PCM) at all temperatures between $0\,°C$ and the triple point, capable of significantly stabilizing temperature and increasing efficiency.

Various studies on increasing the efficiency of refrigeration systems by employing PCMs have demonstrated that by roughly halving temperature fluctuation, energy consumption can be reduced on the order of 10% (Azzouz et al., 2009; Cheng et al., 2011; Elarem et al., 2017; Sonnenrein et al., 2015). While a rigorous study of long-term storage efficiency is outside the scope of the present work, the order-of-magnitude reduction in temperature fluctuation seen herein suggests that long-term isochoric cold storage has the potential for exceptional additional energy savings. Furthermore, increased temperature stability has been shown to yield a plethora of other advantages, including resilience during power outages (of particular importance to the economically disadvantaged countries estimated to require the largest future growth in refrigeration infrastructure (Coulomb et al., 2015)), increased ability to avoid power consumption during peak hours, reduction of food spoilage, and protection of food contents from moisture migration, freezer burn, weight loss, and loss of nutritional value (Bustabad, 1999; Gigiel and Collett, 1989; Martins et al., 2004; Mastani Joybari et al., 2015; Ullah et al., 2014).
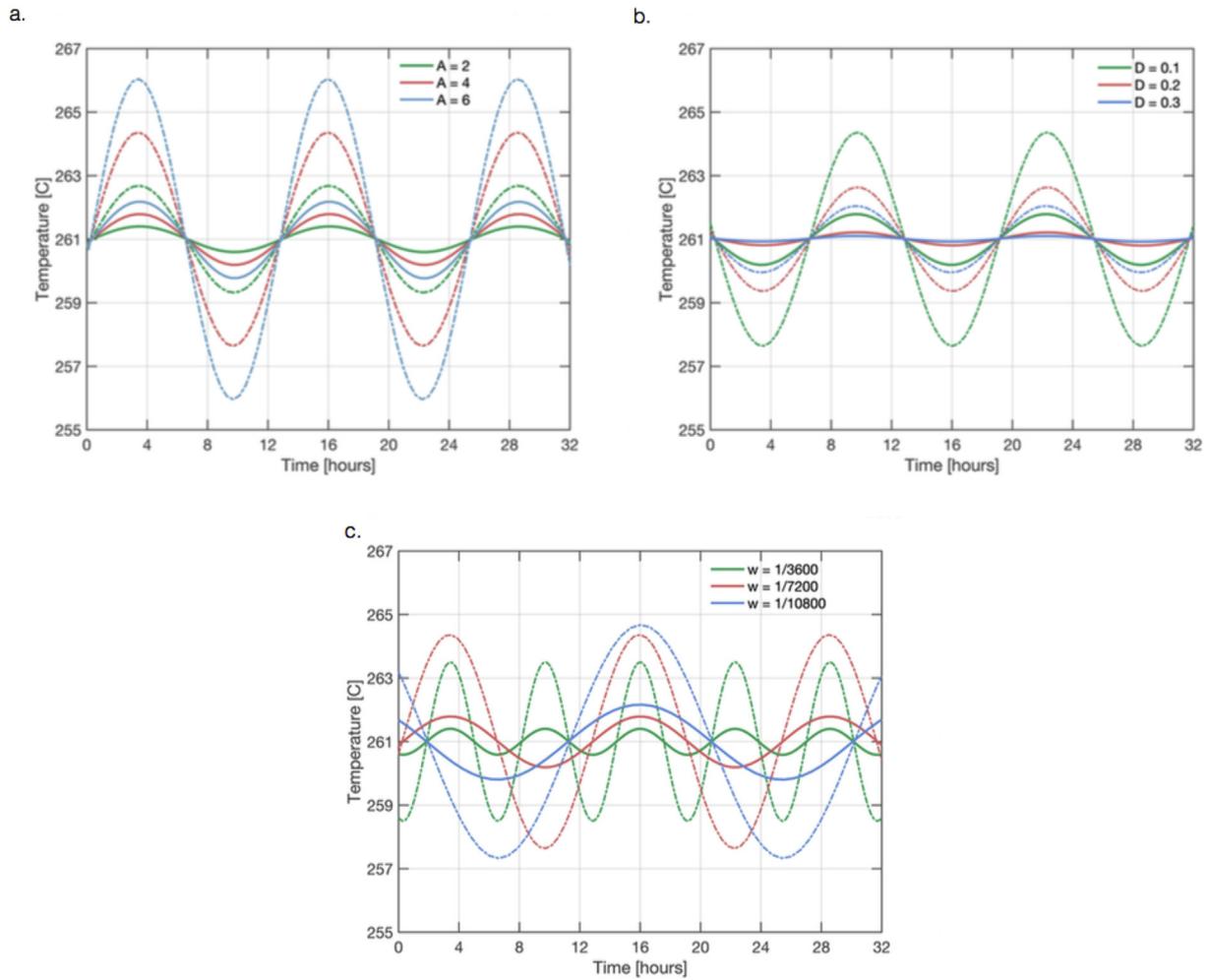
Fig. 6. Internal temperature fluctuations experienced under isochoric (solid line) and isobaric (dashed line) conditions for various input parameters: **a**, Amplitude is varied. D = 0.1 m; w = 1/7200 s, T_D = −12C. **b**, Characteristic system length is varied; w = 1/7200 s, A = 4C, T_D = −12C. **c**, Frequency is varied; D = 0.1 m; A = 4C, T_D = −12C. *Note: all curves have been phase-shifted in time for ease of comparison.*
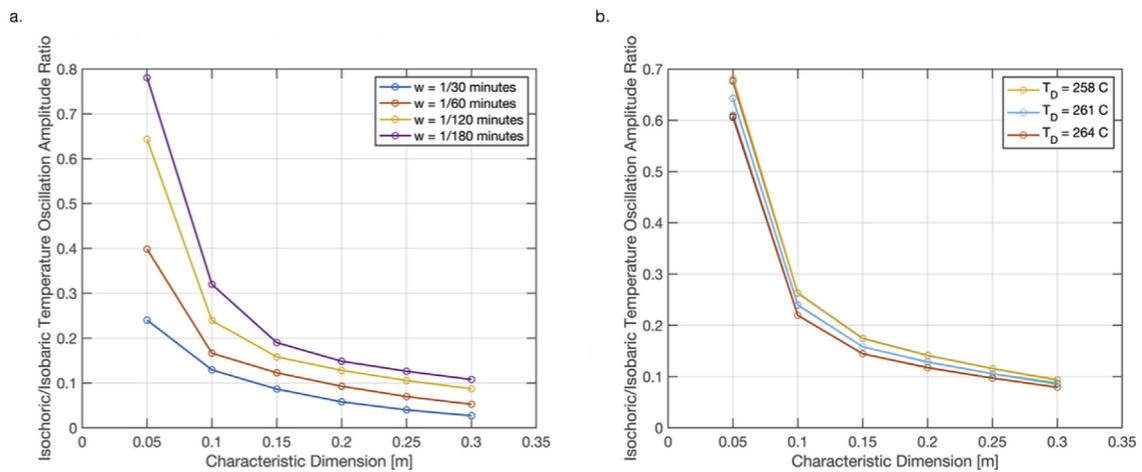
Fig. 7. Ratios of the amplitude of temperature fluctuation experienced within identical systems under isochoric and isobaric conditions (isochoric/isobaric). **a**, Ratios for an applied amplitude of A = 4C and design temperature T_D = −12C, with varying frequency and characteristic length. **b**, Ratios for frequency w = 1/7200 s, with varying applied amplitude A, design temperature T_D, and characteristic length. Note that curves for varying values of A at a given design temperature appear indistinguishable.

Although the chief goal of this study is to mathematically demonstrate the existence of these unique thermodynamic features, it is also valuable to view the presented findings in a greater industrial context: ICS presents a method by which global cold storage might be improved without replacing the world's current 1.6 billion food refrigeration and freezing units. From a discrete technological perspective, ICS systems are simply rigid containers filled entirely with a given solution (containing less than 1% air) and capable of withstanding a design pressure based on the desired final temperature; these devices contain no moving parts or electronics and are easily constructed (Lyu et al., 2017a; Năstase et al., 2017a; Rubinsky et al., 2005; Wan et al., 2018). Thus, ICS capabilities could potentially be added to any existing freezer—a means of increasing the efficiency and quality of frozen food storage without generating significant appliance waste or requiring major infrastructural changes. ICS is distinct from most emergent refrigeration technologies in this way— it aims to increase efficiency by altering the fundamental thermodynamics at play *within the contents* of the freezer, as opposed to altering the freezer itself.

3. Conclusion

In this work we present thermodynamic analyses and a heat transfer phase change model to demonstrate mathematically that preserving food matter in an isochoric container can significantly reduce the energy requirements of frozen food storage. This is accomplished by two newly discovered thermodynamic phenomena that arise in isochoric systems: the prevention of total freezing of a liquid volume at temperatures between $0\,°C$ and $-20\,°C$ and the marriage of latent and sensible heat effects. The energy required to completely freeze a mass of water is nearly 100 times that required to simply cool it to a subfreezing temperature—thus by preventing a large percentage of the water content of stored food matter from freezing in an isochoric system, the energy expenditure of the cold storage process is reduced. Furthermore, we show that within an isochoric container, the internal temperature cannot change without some amount of ice also forming or melting. Thus the contents stored within an isochoric container, which can include liquid food products (such as milk or juice) or solid food products of high water content (such as meat, fish, vegetables, or fruits) immersed in solution, behave like optimized phase change materials, maximizing their effective thermal mass. This increase in thermal mass dramatically increases the temperature stability of the system as a whole, not only improving the storage quality of the products by combatting fluctuation-dependent effects like moisture migration, but also enhancing the efficiency of the freezer in which the isochoric container is stored.

In light of growing food storage demands and increasing global temperatures, new solutions for improving frozen food storage are keenly needed. The unique fundamental thermodynamics of isochoric freezing present a potential pathway toward both more efficient and higher quality food preservation, and warrant significant further research.

4. Methods

4.1. Isochoric ice percentage correlations

The function employed to relate ice percentage to equilibrium temperature in the thermodynamic model of isochoric freezing, $mp_{ice}(T)$, was calculated using the method of Rubsinky et al. This method incorporates known pressure-temperature relations for pure water (as available in the phase diagram of water, Fig. 2A) alongside standard compressibility and thermal expansion data in order to estimate the percentage of ice that will exist in an isochoric system at a given equilibrium temperature (and thus pressure) between 0C and the triple point of water, ice I, and ice III. With the addition of solutes the freezing point depression caused by increasing concentration is also

incorporated, and the model has been experimentally validated for both pure water and multiple solutions. For easy reproduction, the ice percentage correlation for pure water is provided here:

$$mp_{ice}(T) = -0.0002T^4 - 0.0107T^3 - 0.3088T^2 - 5.8734T$$

The same method is used to produce the function $T_f(\bar{S})$ relating phase transition temperature to freezing front position in the phase change model of isochoric freezing, with slight differences. For the 1D formulation employed, the mass percentage should be converted to a volume percentage in order for $\bar{S} = S(t)/B$ to be equivalent, and the ice volume-temperature data should then be correlated to produce $T_f(\bar{S})$. Note that the temperature values used in this correlation can only be interpreted as phase change temperatures in an isochoric system, in which the equilibrium temperature of the system will always equal its phase change temperature in the temperature domain from $0\,°C$ to $-21.985\,°C$.

4.2. Adaptation of thermodynamic approach for aqueous solutions

In order to apply the thermodynamic approach described in the text to aqueous solutions, the thermal mass of the solutes must also be considered. The presence of solutes will adjust the ice percentage correlation due to the freezing point depression effect associated with increased concentrations, as shown in Fig. 2B. The method detailed by Rubinsky (Rubinsky et al., 2005) includes the capability to account for this effect. Furthermore, the mass considered in eqn. (1–3) must be amended to reflect only the mass of water, and an additional integrated sensible heat term should be added to account for the thermal mass of the solute. For example, for a solution of 21.5% sucrose by mass, initially chilled to $0\,°C$, eqn. (3) will be adjusted to:

$$E = \int_{T_0}^{T_1} L(T) m_{water} mp'_{ice}(T)dT + \int_{T_0}^{T_1} c_{p_{water}}(T) \times m_{water}(1 - mp_{ice}(T))dT$$
$$+ \int_{T_0}^{T_1} c_{p_{ice}}(T) \times m_{water} mp_{ice}(T)dT + \int_{T_0}^{T_1} c_{p_{sucrose}}(T) \times m_{sucrose}dT$$

Here, the mass of the water plus the mass of the sucrose is equal to the total mass of the system.

It should be noted that this method assumes the thermal mass of water and a given solute to be linearly additive. While this is often not strictly the case, small variation in the magnitude of the sensible heat terms will not significantly affect the outcome, as the process of ice 1 freezing in water-based systems is dominated by latent heat effects (ste ~ 0.1).

4.3. Solution of the heat transfer model

The model schematic is featured in Fig. 5. Standard analytical solutions (available in any graduate level heat transfer text) for the temperature distributions in each region are employed, consistent with the governing equations and boundary conditions outlined in eqn. (4–8). For the purposes of evaluating these distributions, S is employed as a discrete dimensional parameter that is not time-dependent, which implicitly implies a quasi-steady assumption—e.g. the assumption that the position of the phase front changes much slower than the sensible temperature distribution. This assumption is valid when the Stefan number is low, as it is in the subfreezing-temperature, water-based isochoric systems considered herein (ste ~ 0.1). The spatial derivatives of these distributions can then be inserted into the energy balance at the phase change interface (eqn. (10)), providing a non-linear first order equation for its position that is solvable using finite differences. An iterative approach was used to solve this equation, in which a guess for the position $S(t)$ was used to evaluate T_f, L, and the requisite spatial derivatives, and the two sides of eqn. (10) were compared. Iteration in S for a given time point t continued until the interface energy balance was

satisfied to within 1%. Standard mesh halving was used to confirm convergence. Considering a mesh of N steps, at an arbitrary point in time $t = N\Delta t$ with $N \geq 3$, the velocity $\frac{dS(t)}{dt}$ of the freezing front was approximated using the following three-point second-order backward difference scheme:

$$\frac{dS(t)}{dt} = \frac{3S_N - 4S_{N-1} + S_{N-2}}{2\Delta t} + O(\Delta t^2)$$

For N = 2, a standard two-point first-order backwards difference was employed. This iterative procedure can be initialized in one of two ways. If investigating the non-steady initial freezing process, in order to avoid singularities, the marching of time is started at $t = 0.01$, and an initial guess of very small S is employed, which can after-the-fact be improved using a four-point forward difference once sufficient marching in time has occurred. Varieties of this approach are commonly employed in similar contexts, including by Savovic (Savović and Caldwell, 2003) and Rizwan-uddin (Rizwan-uddin, 1999a; 1999b). If investigating only the steady-periodic domain however (after all transients have died out), an initial position of S can be determined by setting the $T_f(\bar{S})$ function equal to the final desired temperature T_D and solving for S, a technique unique to isochoric analysis.

In order to generate the temperature curves featured in Fig. 6, the temperature was sampled at the insulated (symmetry) boundary and in the center of the domain, and a spatial average over the entire domain was also taken. In the steady-periodic regime considered, differences of sampling location and averaging yielded differences of less than 1% on the observed amplitude, period, and frequency of the temperature fluctuations, so all of the results presented in this work were measured at a single location, arbitrarily chosen to be the insulated boundary.

Acknowledgements

Nomenclature

Thermodynamic Model

E	Total energy $[J]$
T_0	Initial temperature (the freezing point) $[K]$
T_1	Final storage temperature $[K]$
c_{p_water}	Heat capacity of water $[J/kgK]$
c_{p_ice}	Heat capacity of ice $[J/kgK]$
L	Latent heat of fusion of ice $[J/kg]$
m_{total}	Total mass of the system $[kg]$
m_{water}	Mass of water $[kg]$
$m_{sucrose}$	Mass of sucrose $[kg]$
mp_{ice}	Percentage of the mass of the system that is ice at a given temperature

Phase Change Model

T_s	Temperature of the solid region $[K]$
T_l	Temperature of the liquid region $[K]$
T_D	Target storage temperature $[K]$
T_f	Phase transition temperature $[K]$
$\bar{S}$	Non-dimensional position of the freezing front
k_s	Thermal conductivity of solid phase $[W/mK]$
k_l	Thermal conductivity of liquid phase $[W/mK]$
α_s	Thermal diffusivity of liquid phase $[m^2/s]$
B	Characteristic system length $[m]$
ρ	Density of liquid phase $[kg/m^3]$
L	Latent heat of fusion $[J/kg]$
A	Amplitude of applied temperature fluctuation $[K]$
w	Frequency of applied temperature fluctuation $[1/s]$

Author contributions

M.J.P.P. and B.R. designed the research and analyzed the results. M.J.P.P. performed the research and wrote the manuscript. B.R. revised the manuscript.

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