

Review

Physical Properties and Molecular Interactions Applied to Food Processing and Formulation

Tiago Carregari Polachini ^{1,*}, Sergio Andres Villalba Morales ², Luís Roberto Peixoto Filho ³,
Elisa Franco Ribeiro ¹, Larissa Santos Saraiva ² and Rodrigo Corrêa Basso ^{3,*}

¹ Institute of Biosciences, Humanities and Exact Sciences (Ibilce), São Paulo State University (Unesp), Campus São José do Rio Preto, Cristóvão Colombo Street, 2265, São José do Rio Preto 15054-000, Brazil

² Graduate Program in Food Science and Technology, Federal University of Tocantins, Campus Palmas, Palmas 77001-090, Brazil

³ Institute of Science and Technology, Federal University of Alfenas, Campus Poços de Caldas, Poços de Caldas 37715-400, Brazil

* Correspondence: tiago.polachini@unesp.br (T.C.P.); rodrigo.basso@unifal-mg.edu.br (R.C.B.); Tel.: +55-173-221-2221 (T.C.P.); +55-353-697-4710 (R.C.B.)

Abstract: Food processes have been requiring increasingly more accurately designed operations. Successful design results in products with high quality, in addition to offering energy and cost savings. To these ends, fundamental knowledge regarding the physical properties and thermodynamic mechanisms of the material is essential. The aim of this review was to highlight important concepts and applications of some thermophysical properties (density, specific heat, thermal conductivity and thermal diffusivity), as well as recent methods for their determination. The rheology of fluids and solids is widely discussed according to the concepts, classification, modeling and applications involved in food and equipment design. Herein, we report destructive and non-destructive assays for the evaluation of food properties. Due to the complexity of food systems, the effects of modifications of the structure and physicochemical reactions on the quality of the resulting food are addressed based on thermodynamic aspects. This analytical perspective was adopted in food systems rich in fats, proteins, polysaccharides and simple sugars. Using the information reported in this study, formulations and unit operations can be better designed. In addition, process failures become more predictable when fundamental knowledge is available. Therefore, food losses can be avoided, quality can be maintained and operations can be effectively resumed when deviations from ideal conditions are evidenced.

Keywords: physical properties; food rheology; molecular interactions; thermodynamic transitions; physical behavior



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1. Introduction

Foods are usually complex systems in which different classes of compounds are present, including water, polysaccharides, fats and proteins. Their characteristics are determined both by the properties of these components and by the various forms of interaction among them. These products, in turn, are subjected to different processing operations that, whether intentionally or not, result in structural modifications. At the same time, the correct dimensioning of these operations is based on knowledge of the properties of the processed food matrices.

The behavior of density, thermal conductivity, specific heat and thermal diffusivity is directly dependent on the temperature and composition of the materials. Thus, processes that involve changes in those properties are designed based on the knowledge of their behavior according to those parameters. This behavior is determined by the correct measurement of their physical properties using different methods according to the physical characteristics of the systems.

Due to their structural complexity, foods exhibit different behaviors when subjected to mechanical stress and/or temperature changes. They can deform, either reversibly or irreversibly, when they are solid, and they can flow when they are liquid under the application of tensile forces. The way in which and the intensity with which they react to applied stresses, changing their physical structure, can be measured by experimental tests and/or mathematically described by rheological models.

Food components undergo changes in state or phase transitions that can be accelerated and/or modified according to the operating conditions to which they are subjected. Molecular interactions among food constituents are the result of composition, temperature and, for systems containing at least one vapor phase, pressure. The description of the behavior of these constituents, as well as the interactions among them, can be determined by studying the thermodynamic parameters of these systems.

In the discussed context, in this manuscript, we present different methods for determining the physical properties of foods, perform a brief analysis of the rheological behavior of food systems, as well as the experimental assays used in their determination, and study the thermodynamic aspects of systems containing the major constituents of foods.

2. Physical Property Measurements

The determination and evaluation of the physical properties (also known as thermo-physical properties) of raw material and processed food products are essential for the correct design of any food process. Accurate information regarding such properties allows for the suitable design of unit operations involving heat, mass and/or momentum transfer processes. Unsuitable methods for estimating those properties have direct effects in over- or under-designed equipment and processes, which lead to unnecessary costs and even failures on production lines.

In the past, the design of unit operations used to be conducted based on the practical knowledge acquired over the years. However, it has been noted that the accuracy of the specificity of each processing condition can lead to significant economic and technical differences, which may be beneficial or prevent any associated losses. As a consequence, the dependence of mathematical models on the accurate determination of physical properties has been highlighted [1]. Figure 1 confirms this growing trend, presenting specific information regarding physical property data of food products. This Figure represents the number of publications indexed in Web of Science between 2000 and 2022 that contained the expressions “physical properties” and “food” as key terms. The value increases from 300 publications in 2000 up to more than 4500 in 2022. Whereas new food processing technologies have assumed an important role in recent publications, important fundamental research has accompanied this trend.

In this context, knowledge of methods for measuring the main physical properties of foods with different characteristics is necessary to correctly obtain data to be used in food processing operations, as well as to describe their behavior using empirical or semiempirical models. In this section, the main methods used to determine density, specific heat, thermal conductivity and thermal diffusivity in foods are presented, as well as some of their applications.

2.1. Density (ρ)

Density (ρ), or specific volume (γ) in the inverse form, is one of the main physical properties used in food processing of both fluid and solid products. Even though it is commonly used to describe the amount of a given product occupying a certain volume, density can often be interpreted as a concentration parameter in mass transfer processes of fluids [2].

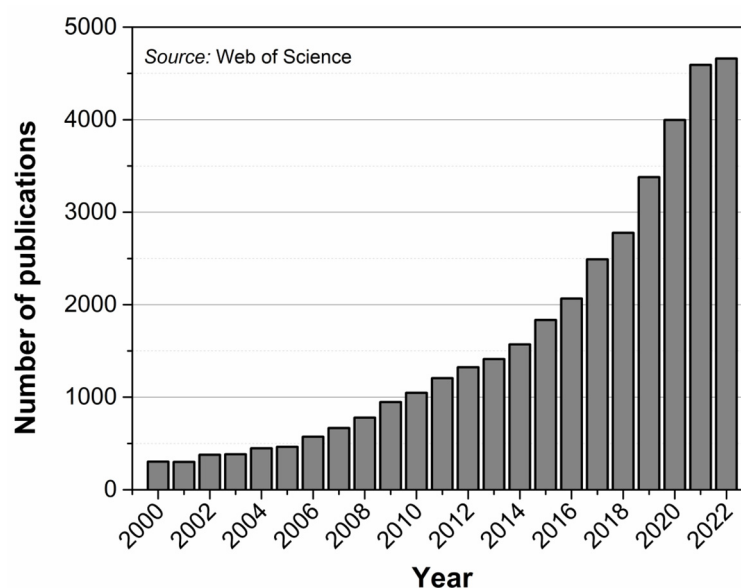


Figure 1. Number of publications reported in Web of Science between 2000 and 2022 that contained the terms “physical properties” and “food”.

Concerning solid materials, density can be determined as the bulk density, considering the porosity of a bed; as the apparent density of solids, considering the capillaries and intrinsic porosity of the material itself; and as the true density, considering only the compact solid fraction of the material without considering the pores [3,4]. These parameters are traditionally determined by the correlation of gravimetric and volume measurements. The volume of food products was originally measured by solvent displacement (mostly using toluene) [5]. In spite of the efficiency of some solvents, their use has been associated with toxic practices and destructive assays. In this sense, current techniques have aimed to determine the volume of food products by 3D imaging using techniques such as digital imaging, laser scanning, computed tomography and resonance imaging [6–8].

In the case of liquids, pycnometers are the most used equipment to obtain adequate measurements of liquid products [9]. On the other hand, there is some difficulty in changing samples with successive cleaning of the apparatus and in controlling the temperature of the sample and the overall calibration. For these reasons, electronic techniques involving the use of density meters have demonstrated accurate results, in addition to being easy to handle, even when dealing with suspensions [10,11]. More advanced techniques involve the collection of ultrasonic measurements using electrostatic transducers and signal processing to detect density variations in foods [12].

Although the main application of food density results is the characterization of physical properties, they can also provide insights about important changes in the quality of the product. For example, density measurements of food solids subjected to drying directly reflect the magnitude of the shrinkage that occurred during water removal [13]. Water content, size, maturity and uniformity of the peel of fruits can also be estimated according to density measurements [14]. Density also reflects the capacity for thorough homogenization of powder mixtures [15], which is crucial when dealing with milk powder [16], for example. Determining the correlation between density and viscosity can provide ready-to-use data, as well as important information that can be used to assess the quality of vegetable oils [17,18]. When dealing with foams, density is also indicative of air incorporation and, thus, foam stability with the aim of drying, but it can also be used for various other food and culinary applications [19].

2.2. Specific Heat (c_p)

Specific heat capacity refers to the capacity of a given material to be heated by one unit of temperature when an amount of energy is provided. Also called the thermal property, the

study on the specific heat of food materials is essential to predict and control heat transfer processes and energy balances. Notwithstanding the quantification of heat conduction in food products, the measurement of thermal properties such as specific heat is essential for optimizing food quality degradation and/or microbial inactivation using well-designed thermal processes [20].

The differences between the thermal responses of two materials when the same amount of energy is provided are attributed to their specific heat values. This parameter is commonly represented by c_p when measured at a constant pressure. Otherwise, the abbreviation c_v is used when the volume is considered constant.

In general, the specific heat values of food products can be well-estimated according to the specific heat capacity of their components using predictive equations [21]. The limitation of this method is associated with the lack of consideration of the intermolecular interactions among the components of the food product, even in the same group, i.e., by differentiating simple sugars from starch [22]. Experimentally, specific heat has been traditionally measured using calorimeters made of a vacuum thermos bottle. They consist of a specific apparatus that enables energy balancing when heat is provided to the sample inside the bottle [23]. In order to provide more accurate and rapid data, the use of a differential scanning calorimeter (DSC) has become increasingly popular [24], currently representing the most used method for estimation of specific values and their temperature dependence in different applications [11,25,26].

It is clear that knowing the specific heat directly affects food safety with respect to the adequate design of pasteurization and sterilization processes, comprising situations both under atmospheric pressure and high-pressure processing conditions [20]. Nevertheless, the performance of other thermal processes is influenced by correctly determining specific heat, which includes the determination of the specific heat of oils using in deep fat frying of food products [27]. Furthermore, using modulated differential scanning calorimetry, the influence of temperature, the average carbon number and the average number of double bonds on the specific heat of oils to be used in food applications can be evaluated [22]. In solids such as cumin seeds, specific heat capacity can vary according to particle size and bulk density—important information to be analyzed [28]. As observed, since specific heat is strongly influenced by the water content of food products, its estimation for retort processed vegetables provides insights about deterioration and water loss during storage [29]. An analogous behavior is commonly observed with respect to other thermal properties, as described below.

2.3. Thermal Conductivity (λ)

Similarly to specific heat, thermal conductivity (λ) is also associated with the energy balances and the ease of heat transfer through molecule-to-molecule contact. This parameter composes the Nusselt number and provides the magnitude of the ease of heat transfer, even in comparison with transport properties by the calculation of the Prandtl number [30]. It is the factor proportional to the steady state for heat flow conduction and represents the rate of heat flow that crosses a sectional area between two surfaces under a temperature gradient [31].

Although the use of a thermal conductivity probe is considered the most common method for estimating thermal conductivity, the measurement itself is still challenging due to many potential error sources [1]. Most of the difficulties are related to the heterogeneity of the food structure, in addition to variations in temperature and even in the phase distribution. In fact, the estimation of thermal conductivity is not an issue strictly attributed to foods but also to the packaging material. The addition of nanocomposites to plastic films and sheeting may alter the thermal conductivity of the packaging, influencing the stabilization of the food product throughout the supply chain [32]. For these reasons, the use of differential scanning calorimeters (DSCs) has increasingly been considered as a viable solution for the determination of the thermal conductivity of small and more homogeneous samples [33].

Even though thermophysical properties such as thermal conductivity can be estimated through predictive models using secondary parameters, e.g., water content and solid and fat contents, they do not consider the real variations along the food structure as the experimental determinations [34,35]. The adequate determination of the thermal conductivity values is not only related to the design of equipment and unit operations. It provides information on the efficiency and performance of novel processing technologies, such as ohmic heating and dielectric processing [36]. Moreover, because it varies with the material compositions, it plays an important role in measuring the efficiency of complexation and emulsification [33].

2.4. Thermal Diffusivity (α)

Thermal diffusivity (α) is also attributed to thermal processes, resulting from the combination of the three aforementioned properties (density, specific heat and thermal conductivity) ($\alpha = \lambda / \rho c_p$). Heat exchange by conduction mechanisms is affected by thermal diffusivity and by the influencing variables that play an important role in the three previously mentioned parameters.

This property represents the correlation between the rate of heat conducted through the material and the rate of stored heat [11]. The most common techniques used to estimate thermal diffusivity of foods are based on food composition [21] or experimentally obtained values of specific heat capacity, thermal conductivity and density [37]. Regarding the direct experimental determination, the use of diffusivity cells can still be highlighted in thermal diffusivity determination to obtain time–temperature measurements in transient thermal processes [38,39]. Most recently, thermal lenses have been used with the same final purpose [40,41]. Additionally, effective or apparent thermal diffusivity can be estimated using analytical solutions of Fourier's equation during the heat process [42,43].

Similarly to thermal conductivity, thermal diffusivity is affected not only by the composition but also by the state of the food components and the phase distribution. For example, Carciofi et al. [42] observed differences in the α values of mortadella before and after protein denaturation. Differences are also attributed to granular and porous food according to the phase distribution of the alveoli and capillaries, tending to result in higher α values as the porosity and/or dispersed air increase [44].

The use of thermal diffusivity has been improved not only in terms of optimization of pasteurization processes [45] but also for the evaluation of ultrasound propagation in ultrasound-assisted processes [46], for the characterization of protein structure [47], as an indicative parameter for the detection of adulteration in coconut oil [41], for the estimation of the concentration of *Moringa oleifera* used to produce antioxidant and antimicrobial extracts [40] and even for the estimation of the biodiesel fraction in fuel blends [48].

3. Rheological Behavior of Foods

The rheological behavior of a substance indicates how it deforms with the application of an external stress [49]. The type and degree of deformation depend on the nature of the substance, its composition and variables such as temperature and intensity, as well as the time of stress application [50,51].

In food processing, it is possible to work with solids, liquids, gases and complex mixtures thereof, such as emulsions and suspensions. Food industries are also based on the processing of a wide variety of raw materials that undergo physical and chemical transformations as they are submitted to numerous unit operations and chemical reactions aiming to obtain a final product. Throughout such processes, the raw materials, intermediates and products show specific rheological properties that need to be determined and predicted with the aim of guaranteeing an adequate design of processing equipment and setting of operational parameters, such as stirring velocity, pumping power and temperature. This information has a significant effect on plant design criteria, such as the requirement of power and production costs [52–54].

In this section, a description of the rheological behavior of foods (solids and fluids) and its application for the characterization and processing of foods is presented, as well as the main instruments used to determine rheological properties.

3.1. Rheology of Solid Foods

The main rheological properties of solid foods are the elastic modulus, viscous modulus and viscoelasticity, in addition to the texture profile, which can contribute to a better rheological characterization by analyzing parameters such as hardness, elasticity, chewability, cohesiveness and resilience [55]. For example, Salunke and Metzger [55] produced pasteurized processed cheese and reported the extent to which these parameters were affected when milk protein concentrate and micellar casein concentrate were added. The authors of Ref. [56] determined the rheological properties of “Minas Frescal” cheese using a texture analyzer and reported the hardness, elasticity, firmness and deformation of the product using the modulus of elasticity, instantaneous tension and viscoelasticity.

Schreuders et al. [57] quantified the non-linear rheological similarity of animal meat and synthetic meat, and with the results of shear stress and deformation determined according to the linear viscoelastic regime, classified the texture in terms of its resistance and elasticity, concluding that heating animal meat results in a more resistant and elastic product. Paredes et al. [58] mechanically characterized cultured meat products, using texture profile analysis with double resistance test and rheological analysis of viscoelastic properties as complementary techniques, characterizing these products based on the following parameters: hardness, cohesion, chewiness, resilience, elasticity and shear modulus.

Many other types of equipment are used to determine specific rheological properties of foods, such as meats or fruits. Some of them are listed in Table 1.

Table 1. Equipment used for the analysis of deformation in foods.

Analysis	Equipment	Properties	Estimated Values	Reference
Flow length of ketchup	Bostwick consistometer	Viscosity	80 Pa·s	[59]
Characterization of the flow properties of superconcentrated paste	Ring shear test	Cohesiveness and flowability	Ffc < 1	[60]
Determination of the consistency of fermented milk	Adam’s consistometer	Consistency	6–9 cm	[61]
Bread dough mixing properties	Farinograph	Water absorption	51–55%	[62]
Test to measure meat texture	Warner–Bratzler shear test	Shear force	23.25–72.59 N	[63]
Characterization of gelatine based on gel strength	Bloom gelometer	Gel strength	250 N	[64]
Extensional properties of noodles	Brabender extensograph	Extensibility	60–120 cm ²	[65]
Texture properties of butter	Penetrometer	Texture	40.67–74.67 °p	[66]
Firmness of fruits and vegetables	Magness–Taylor pressure test	Force	5.53 N	[67]

3.2. Rheological Classification of Fluid Foods

Fluid rheology has been widely studied and applied to food science and engineering. Its application started with the definition of ideal fluids, which are those that show irreversible deformation when submitted to a stress, i.e., fluids that flow and do not recover their initial forms. In this process, part of the energy received by the fluid is dissipated as heat and is not recovered after removing the strain [68]. In general, fluids submitted to a stress can flow due to several types of reorganizations of their particles, such as a new orientation or stretching, dropped deformation or the destruction of aggregates [69].

The dependence of viscosity on the time of stress is the first criterion used for the classification of fluids [49,70]. Therefore, fluids can be dependent on or independent of stress time and viscoelasticity. In turn, time-dependent fluids can be classified as thixotropic when their viscosity decreases over time when submitted to a constant strain stress or rheopectic when their viscosity increases over time.

Fluids whose rheology is not dependent on time are then classified according to their deformation as a function of shear stress as Newtonian, dilatant, pseudoplastic or Bingham plastic [49]. Newtonian fluids are those whose viscosity is independent of the shear rate; this means they present a constant viscosity. The viscosity of pseudoplastic fluids decreases as the shear rate increases, whereas dilatant fluids show higher viscosity at higher shear rates. Bingham plastic fluids show a similar response to that of pseudoplastic fluids, but they also require a minimal stress strain to deform. Finally, viscoelastic fluids are show mixed rheological properties of ideal fluids and elastic solids, since they show partial elastic recovery after deformation. The viscosity of non-Newtonian fluids is usually referred to as apparent viscosity, since it depends on shear rate and time [49,70]. Table 2 shows the rheological behavior and apparent viscosity of some fluids used in the food industry.

Table 2. Rheological behavior and apparent viscosity of foods.

Fluid	Rheological Behavior	Apparent Viscosity (Pa·s)	Temperature (°C)	Reference
Juice	pseudoplastic	0–30	25	[71]
Yogurt	pseudoplastic	100–1000	25	[72]
White wine 0%	Newtonian	0.00353	20	[73]
Sunflower oil	Newtonian	0.0619	25	[74]
Jelly	pseudoplastic	13.222	25	[75]
Honey	Newtonian	05–50	25	[76]
Skimmed milk concentrate	pseudoplastic	0–4	55	[77]
Olive oil	Newtonian	0.074	25	[74]
Ketchup	pseudoplastic	80–166	23	[59]
Ice cream	pseudoplastic/thixotropic	0.1–0.5	25	[78]
Salad dressing	pseudoplastic	2.6	30	[79]
Bread dough	pseudoplastic/viscoelastic	3939	25	[80]
Barley flour suspension	pseudoplastic	0.1–1	30	[81]
Corn starch suspension	dilatant	1–1000	25	[82]
Potato starch soups	dilatant	0.01–0.05	60	[83]
Waxy potato starch	rheopectic	0.2–0.8	20	[84]

3.3. Analytical Determination of the Rheological Properties of Fluids

Rheometry measures the response of a fluid to controlled flow variables that produce inelastic deformation of its initial form, such as geometry, strain stress and temperature [85]. Rheological analyses have become ordinary tests for characterizing raw materials, intermediates and final products in the food industry. Such analyses are essential for quality control and safety; solution and prevention of problems in non-Newtonian fluids; and correct sizing and operation of equipment for transportation, mixing, separation and storage. Therefore, it is essential to select and correctly interpret the type of rheological analysis and further applications for each type of fluid.

The rheological behavior and several rheological properties of liquids can be determined using a rheometer. This device allows for the measurement of the strain used during the deformation of a fluid sample under a controlled shear rate and temperature. The sample is set between two plates. The inferior plate is static, and the superior plate rotates according to the desired shear rate or strain. Rheometers can perform several types of tests under a wide range of shear rates, producing complete rheograms of the deformation of the sample. Additionally, it may be necessary to perform more than one analysis according to the rheological parameters. A flow curve is commonly used as an initial rheological test of a fluid, aiming to determine its rheological behavior and to determine the stress–shear rate

dependency [86]. To obtain a complete flow curve, the device measures the stress it applies to produce a specified shear rate in the superior plate, usually in a shear range from 10 s^{-1} to 1000 s^{-1} . Nevertheless, this range can be modified according to the fluid or shear-rate range of interest. Figure 2 shows the flow curves of example fluids whose rheology is not dependent on time [87].

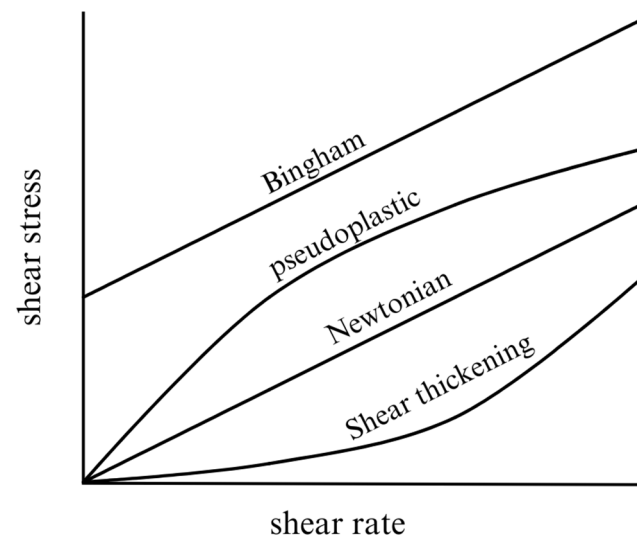


Figure 2. Flow curves for the rheological classification of fluids.

Some other usual rheological analyses consist of the determination of the dependence of viscosity on temperature and analyses to determine thixotropic or viscoelastic behavior. Thixotropic or rheopectic fluids can be identified by a hysteresis in the stress–shear rate curves [88]. Furthermore, the area of thixotropy can be calculated according to differences in the areas under the ascending and descending flow curves. If the curves are similar, the fluid is considered non-thixotropic [78]. Viscoelastic behavior is principally described by shear viscoelasticity $G(\omega)$, which depends on elastic modulus ($G'(\omega)$), and viscous modulus ($G''(\omega)$) according to the following equation [89].

$$G(\omega) = G'(\omega) - G''(\omega)$$

Viscosity is the main rheological property of the fluids tested in the food industry, since it represents their resistance to flow. For Newtonian and low-viscosity fluids, the measurement of dynamic or cinematic viscosity is usually performed in viscometers. The simplest and lowest-priced viscometers consist of vertical U-type glasses and are based on the measurement of the time for a fluid to flow between two points under the force of gravity [43,90]. In these systems, the hydrostatic pressure changes with fluid height; therefore, it cannot be used for non-Newtonian fluids. Some configurations of these viscometers are known as Cannon–Fenske, Ostwald and Ubbelohde configurations [91–94]. Rotational viscometers are more accurate, since they use a similar working principle to that of rheometers and maintain a constant deformation of the fluid between several types of solid pieces, such as concentric cylinders, a superior cone and inferior plate or parallel plates [86,95]. In addition, Stokes viscometers have been widely used in quality control. This last type of equipment is based on the measurement of the time a sphere submerged in fluid takes to pass through two points under the action of gravity at terminal velocity [96,97].

3.4. Rheology of Emulsions

Emulsions are thermodynamically unstable heterogeneous mixed systems composed of immiscible liquids such as water and oil, where the dispersed liquid phase is distributed in a continuous phase [98]. These emulsions have a wide application range in the food

industry and can be easily identified in products such as ice cream, sauces, butter, margarine, milk and yogurt, presenting different physicochemical, sensory and nutritional parameters [99].

The study of the rheological properties of food emulsions is necessary to attain knowledge of product stability and quality, as well as in industrial applications in pipes and equipment, since the characterization of the flow contributes to the definition of the structure of the food during production and its behavior in different processes and may also help in consumer perception and acceptability [100,101].

The rheological behavior of emulsions is influenced by their composition, microstructure and interactions of molecules [102]. When there is a small amount of oil, the fluid behaves like a Newtonian liquid, and the apparent viscosity does not depend on the shear rate, presenting a constant value and lower viscosity [102,103]. When the volume of oil is greater compared to the amount of water, these emulsions behave as non-Newtonian flows, where the apparent viscosity depends on the shear rate; therefore, the fluid has a higher viscosity [82,102].

The size of droplets in the emulsion varies according to the apparent viscosity because when a thicker mixture is formed, the size of droplets decreases, requiring greater shear force and increasing the surface area between the polar and nonpolar phases, resulting in a more solid emulsion [104]. However, when the droplets reach a certain size range in the emulsion, the mixture no longer shows significant variation; thus, the application of a force for a longer period does not decrease the viscosity, presenting the behavior of solid spheres in suspension [104]. Other important parameters to be verified in the rheology of emulsions are the storage modulus, which defines the elasticity of the emulsion regarding the solid properties, and the loss modulus, which results in data related to the viscosity of the liquid properties, making it possible to determine the emulsion stability [105].

3.5. Food Rheology Applied to Equipment Design

Foods are exposed to stresses of different kinds and magnitudes during their processing, with the use of equipment in unit operations such as pumping, stirring, extrusion and pulverization. Table 3 shows the shear rate range presented by foods when submitted to stresses from diverse unit operations. This information is significantly useful to understand and predict the rheological responses that foods can present in several processes.

Table 3. Processing–shear rate equivalence in food processing.

Process	Shear Rate (s^{-1})	Application	Product	References
Extrusion	1–1000	Mixture of biopolymers	Pea flour and pea starch	[106]
Extrusion	20–1200	Mixture of polymers	Extruded corn and wheat	[83]
Mixture and agitation	0.1–100	Former nanocomposite solutions	Cassava starch and laponite	[107]
Tube flow	4–430	Pumping	Ice cream	[108]
Extrusion	1–200	Mixture of polymers	Rice flour	[109]
Mixture and agitation	0.798–150	Homogenization of liquids	Lily nut drink	[84]
Spraying	10–200	Drying technique	Durian seed gum	[110]
Gelatinization	0.01–1000	Folder separation	Tuber meal starch	[111]

For all fluids, the correct determination of viscosity is fundamental, since this property is used in calculations of mass and heat transport, reaction kinetics and tank design, especially for the determination of dimensionless values such as Reynolds, Schmidt and Nusselt numbers [49]. Therefore, it is necessary to recalculate viscosity according to the change in parameters such as temperature and pressure. For liquids, the exponential decrease in viscosity with increasing temperature can usually be predicted by the Andrade equation described below, where A and B are adjustment factors [112,113]. Nonetheless, it is worth mentioning that gas viscosity increases with temperature, and it can be estimated using the Sutherland Equation (2), where C and S are adjustment factors [114,115]. Furthermore, for

some materials, the dependence of viscosity on pressure becomes significant in processes such as extrusion and high-power pumping, in which high pressures are applied to foods. The dependence of viscosity on pressure can be modeled by Equation (3).

$$\mu = Ae^{-B/T} \quad (1)$$

$$\mu = \frac{CT^{3/2}}{T+S} \quad (2)$$

$$\mu = \mu_0 e^{\alpha(P-P_0)} \quad (3)$$

where μ_0 is the viscosity at a reference pressure, P is pressure, P_0 is a reference pressure and α is an adjustment factor known as the viscosity growth coefficient [116].

Additionally, for the correct tube sizing and pumping calculations, especially for non-Newtonian fluids, specific equations and selection criteria must be used according to the rheological behavior of the fluid [49]. For instance, pseudoplastic fluids must be pumped by centrifugal or fast displacement pumps, since high strain rates decrease their viscosity [51,117]. Conversely, slow displacement pumps must be used to pump dilatant fluids. Similarly, the stress applied to mix dilatant fluids cannot be too high, since it would increase the fluid viscosity and, thus, power consumption. The opposite behavior is observed in pseudoplastic fluids, which must be submitted to higher stress with the aim of reducing their viscosity. Additionally, it is worth mentioning that in agitation and mixing operations, the calculation of the power of the agitator depends on the Reynolds number, which, in turn, depends on the viscosity of the fluid. Since many foods exhibit a pseudoplastic behavior, Reynolds number correction must be performed in mixing tanks for these fluids, since near the blades, the velocity gradient is large, and the apparent viscosity is low. Therefore, as the liquid moves away from the paddles, the velocity decreases and apparent viscosity increases [118].

Furthermore, in agitation systems, the selection of the impeller depends on the desired flow profile (axial or radial) and the fluid rheology. Patil et al. [60] used a paddle stirrer for the crystallization of superconcentrated dairy products with an initial viscosity of up to 1 Pa.s, then used a four-blade knife stirrer for the agitation of the superconcentrated product, whose viscosity was about 10 Pa.s. A paddle stirrer was also used at by Kieserling et al. [119] a low shear rate for the preparation of a yogurt that showed a linear viscoelastic deformation of 0.7%. Gomez-Arellano et al. [120] used a helical stirrer to produce sesame protein dispersions with an apparent viscosity between 0.003 and 0.009 Pa.s. Kurt and Atalar [78] used an Ultra-Turrax® disperser, an instrument usually employed to homogenize suspensions and emulsions, for the production of ice creams that showed pseudoplastic and thixotropic behaviors and apparent viscosities from 0.1 Pa.s up to 0.5 Pa.s at 4 °C.

4. Thermodynamic Aspects in Foods

Thermodynamic properties are directly related to the characteristics of foods, which, in turn, are considered complex systems formed by different classes of molecules, such as volatile compounds, proteins, carbohydrates, lipids, organic acids and minerals. These constituents can exist in the free form or linked to other molecules [121]. The characteristics of these systems are more determined by the interaction among the components than by their properties in the pure form. Thus, despite knowledge of the properties of food compounds, the control of the properties and behavior of food matrices under different conditions is often performed empirically.

Food formulations are prepared based on characteristics desired by consumers. The sensory properties of foods are affected by the behavior of the ingredients at the microstructural level. The solidification and fusion of the resulting structures are a consequence of the phase transition and phase equilibrium of the constituents and their interactions, thereby determining the quality of the food. Knowledge of those phenomena is crucial in several stages of food processing, such as recovery, solubilization or encapsulation of compounds

of interest, removal of undesirable components, design formulation and even analysis and quality control [121].

Stability, texture and appearance, among other food characteristics, are also dependent on the phase transitions and interactions of the compounds in the systems. In turn, until phase equilibrium is reached, mass transfer is the driving force behind the migration of the components within the food matrix and their release into the external environment. This set of phenomena is affected by processes such as heating, cooling, evaporation and homogenization and is also related to the physical properties of the product.

In this context, understanding thermodynamics related to phase transition and equilibrium is necessary for the modulation and preservation of food characteristics, as well as for the creation and improvement of formulations. The descriptive thermodynamic parameters of the equilibrium behavior also determine the operational conditions of the processing of many foods, since they are directly related to the phenomena of mass transfer (and even heat transfer) in food systems.

In the following section some of the thermodynamic phenomena related to state transitions, phase equilibria and molecular interactions in systems containing mostly fats, sugars, polysaccharides and proteins are presented. Those are the main constituents of foods that, as previously discussed, determine their physical, chemical and sensory properties.

4.1. Systems Containing Triacylglycerols

Among several properties of lipid-rich food formulations, consistency, solid content and viscosity are determined by the crystallization process, which, in turn, depends on the equilibrium transitions of triacylglycerols between two thermodynamic states. Fats are composed of 95% or more of triacylglycerols. They start to solidify when they are cooled below the highest melting point of their constituents. At temperatures below this point, the system is subcooled or supersaturated, and the chemical potential of the constituents in the liquid phase becomes greater than their chemical potential in the solid phase. In order to reduce the free energy of the system, triacylglycerols from the liquid phase crystallize in the solid phase [122,123]. However, in this process, the same triacylglycerol can be present in different crystalline forms or polymorphs, which are responsible for determining the characteristics of the lipid-based product [124].

Crystallization is normally divided into two stages. The first stage, nucleation, can occur either by primary or secondary mechanisms. Primary nucleation consists of the transition of molecules from a supersaturated liquid phase to a solid phase considered stable: the crystalline nucleus [125]. On the other hand, secondary nucleation occurs when fragments of a developing crystal break off and act as a nucleus for the formation of another crystal [124,126,127]. The second stage of crystallization consists of crystalline growth when molecules from the supersaturated liquid phase are incorporated into the formed solid phase, leading to the growth of fat crystals [122].

The three crystalline forms in fats are denoted as α , β' and β , with the first and last forms corresponding to the least and the most stable forms, respectively, according to the classification defined based on the molecular arrangement during the crystal formation process. The three polymorphic forms can crystallize directly from the liquid phase or undergo transition from one form to another in the solid phase. In the monotropic polymorphism, the transition between crystalline forms always occurs irreversibly from the least thermodynamically stable form to the most stable form [124].

Due to its monotropic characteristic, the Gibbs energy is highest for the α -type crystalline form (less dense crystalline packing), intermediate for the β' -type form and lowest for the β -type form (dense crystalline packing). Each polymorphic form has a specific melting temperature at higher values [124].

The polymorphic form of fat crystals determines their microstructure, which, in turn, directly affects the mechanical and sensory properties of foods. Polymorphic α -type crystals are rarely found in fat-based foods because of their low stability. Polymorphic

β' -type crystals allow for the generation of fatty systems with good mechanical and sensory properties for food production, while the β -type form results in products with large crystals that lead to a sandy sensory perception, impairing the mechanical and sensory properties of the food [128].

The melting and crystallization properties of triacylglycerols in their individual forms are necessary to understand the behavior of systems in the medium where they are inserted. Nevertheless, the food lipid bases are constituted of mixtures of different triacylglycerols. Thus, understanding of the behavior of the solid–liquid equilibrium of mixtures is required for proper formulation of foods containing lipid systems. In this sense, the equilibrium can be studied using diagrams that present important empirical information about the behavior of molecular interactions in mixtures of triacylglycerols with different degrees of saturation and molecular symmetry/asymmetry [129].

Due to the complex behavior of triacylglycerol mixtures, mainly due to the formation of polymorphs, the study of these systems based on the concept of a “quasi-equilibrium” state is considered acceptable. In this state, it is assumed that no significant changes will occur in the crystallized solid phase for a given time period, even if the system has not reached a real state of equilibrium. Thus, when performing adequate heat treatments, the desired polymorphic form for the system can be obtained, and the concentration of solid material in the system can be evaluated [130].

Conventionally, four ideal types of systems are reported for binary mixtures of triacylglycerols with respect to their behavior at the solid–liquid equilibrium: monotectic with the formation of true solid solutions, monotectic with the formation of partial solid solutions, eutectic and peritectic [131] (Figure 3).

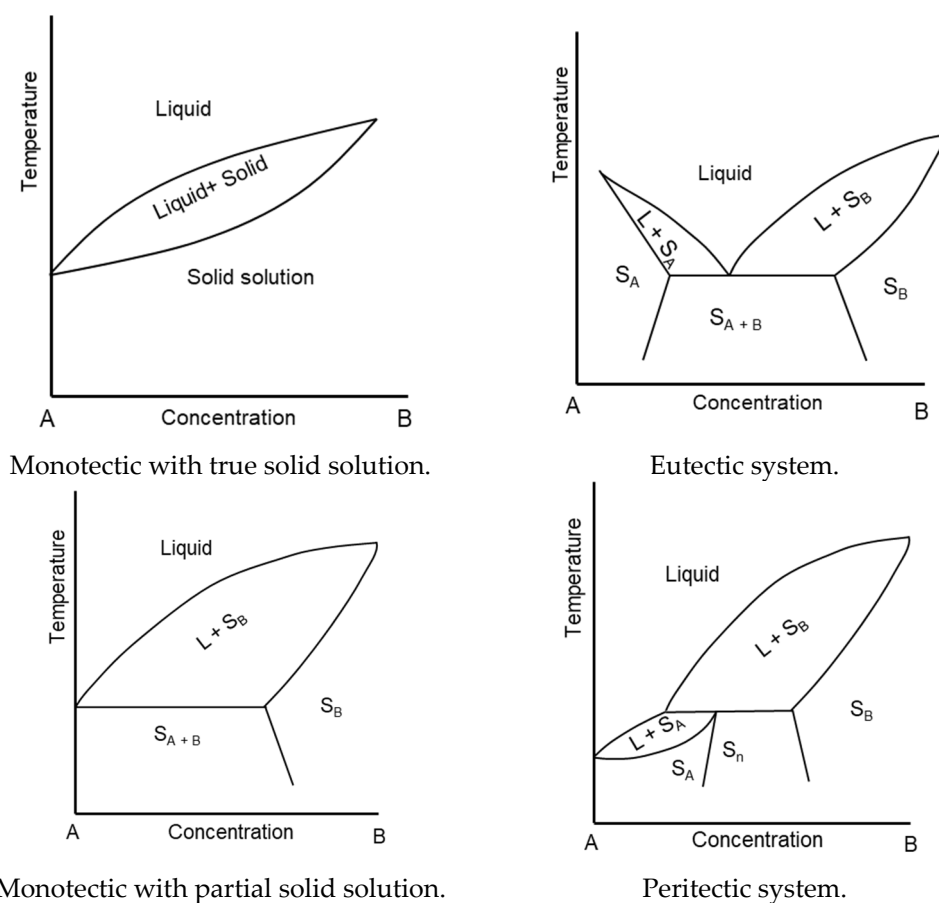


Figure 3. Common phase diagrams of triacylglycerol binary mixtures: components of the systems (A, B); homogeneous liquid phase (L); pure component in the solid state (S_A , S_B); solid solution containing both components in the crystal (SS); a third component in the solid phase (S_n).

Monotectic systems are those formed by mixtures of triacylglycerols with similar melting points, molar volumes and polymorphic structures. In these systems, continuous or true solid solutions and partial solid solutions may be formed. In the first type, the components in the mixture behave similarly in terms of the transition between the liquid and solid states throughout the entire concentration range. The middle region of the diagram describes the range of compositions and temperatures within which the incorporation of the two components in the crystals forms a true solid solution coexisting with a homogeneous liquid phase. On the other hand, the bottom of the diagram is only composed of the solid phase, without the presence of liquid, in which the two components are present. The second type occurs with an increase in the melting point difference between the triacylglycerols. In these systems, the lower region of the diagram represents the simultaneous presence of both components in the solid phase. However, in contrast to observations in the first system, the latter shows a differentiation in terms of composition in the solid phases instead of only presenting the formation of a single solid structure throughout the entire concentration range. The intermediate region of these diagrams describes the mixture of a homogeneous liquid phase associated with a pure solid or a solid consisting of crystals of both triacylglycerols [132,133].

Eutectic systems are commonly formed by components that differ in molar volume, molecular shape and polymorphism but with similar melting points. During cooling, the crystallization of their constituents occurs independently. Two regions composed of a liquid phase are observed in their diagrams, each of which contains a solid phase composed of a pure triacylglycerol, a region containing a homogeneous liquid phase, a region with the presence of two pure solid triacylglycerols and two regions with individual pure solid components [132,134].

Peritectic systems are commonly formed by mixtures of unsaturated triacylglycerols containing, at least of which contains two unsaturated fatty acids. In this type of system, the formation of crystals in the solid phase occurs by the association of the two triacylglycerols, leading to the formation of a new crystalline structure that behaves as a new component. The lower central region of the diagram represents the formation of this new component [132,134].

In this sense, the description of solid–liquid equilibrium is important for understanding and predicting phase separation behavior. It is usually modeled based on a set of theoretical simplifications using descriptive or predictive thermodynamic models in the representation of solid–liquid equilibrium diagrams. Comparing the use of the Margules model with the UNIFAC models and a predictive UNIQUAC model in the description of the behavior of the solid–liquid equilibrium of binary systems composed of triacylglycerols, deviations were observed. For the purposes of temperature calculations, deviations between 0.46 and 6.30% for the descriptive model and between 0.70 and 6.0% for the predictive models were noticed. These results highlight the use of thermodynamic models as important tools in the elaboration of diagrams for this type of system [133].

4.2. Sugar-Rich Systems

In many food formulations, particularly in confectionery, controlling the characteristics of sweeteners is crucial to obtaining products with adequate properties, ranging from appearance to texture. In foods, sugars can be found dissolved in water, dispersed as a crystalline phase, immobilized in amorphous or glassy form or in combinations of these states. As observed, since phase transitions in a given characteristic of a food item may occur during processing, undesirable transitions may also occur during storage [135].

The solubility, glass transition, boiling point and freezing point of solutions, as a function of concentration, are some determining parameters used to evaluate the equilibrium and state transition behaviors of sugar-rich foods during processing [135].

Although glass transition is very important in food systems due to its stable state, it should be considered a state transition instead of an equilibrium condition. In this second-order transition, the material changes state but not phase [135]. Glass transition

occurs in the presence of amorphous regions in the food matrix and is characterized by the discontinuity point in the physical properties when altering temperature [136].

Studying the melting behavior of sugars is a complex task. For example, sucrose contains impurities, water and a small amount of non-crystalline material (amorphous). Additionally, at temperatures close to the melting point, reactions such as decomposition and caramelization also occur [137]. The heating rate has a direct influence on kinetic decomposition processes. For the determination of the melting temperatures, decomposition temperatures and fusion enthalpies of sucrose, glucose and fructose, variabilities were verified in these parameters among the samples and when a different heating rate was applied. Initial decomposition temperatures were found to be lower than the melting point at low heating rates for sucrose and fructose. On the contrary, at heating rates greater than 10 °C/min, the decomposition temperatures were higher than the melting temperatures of the same components [138]. Despite these difficulties, values reported for the melting parameters of sugars were obtained by differential scanning calorimetry. The melting onset temperature, melting peak temperature and melting enthalpy were determined to be 186.19 °C, 190.55 °C and 127.10 J/g for sucrose; 158.4 °C, 162.27 °C and 208.71 J/g for glucose; and 113.59 °C, 126.31 °C and 188.59 J/g for fructose, respectively [139].

State diagrams were reported and are used for the study of the behavior of glucose, fructose and sucrose solutions, as well as their mixtures [140]. The freezing temperature and glass transition temperature values were calculated using the Chen and Gordon—Taylor equations, respectively [141], and the data obtained by calorimetric analysis. In Figure 4, a decrease in the glass transition temperature as a result of the plasticizing effect of the presence of water can be observed. Similarly, the decrease in the freezing temperature of water as a function of the increase in the solids concentration for each sugar was verified. The maximum glass transition value was observed for pure sucrose, while the minimum value was observed for pure fructose. Despite the difference between sucrose molecules, a disaccharide, and fructose and glucose, monosaccharides, the behavior of the glass transition temperature is very similar among the three components. On the other hand, the dependence of the freezing point on the sugar concentration follows the following sequence: sucrose > glucose > fructose [140].

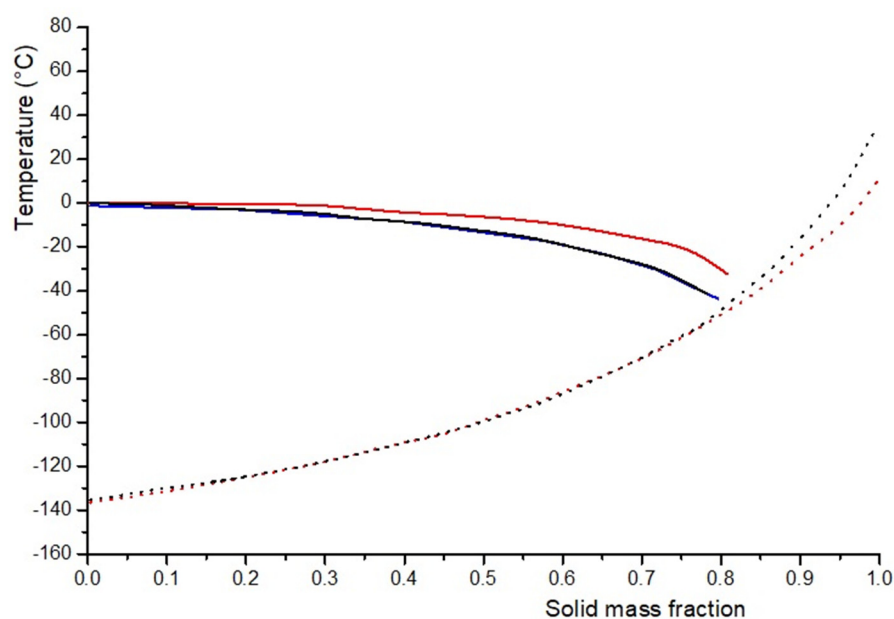


Figure 4. State diagrams for sugar solutions in water. The blue, red and black lines represent fructose, sucrose and glucose melting (solid lines) and glass transition (dashed lines) temperatures, respectively, with the lines for fructose and sucrose overlapping each other.

The solid–liquid equilibria of the aqueous solutions of glucose, sucrose and fructose were thermodynamically modeled by calculating the activity coefficients of the liquid phase using the UNIQUAC model. The solubility of fructose was greater than that of the other sugars for the entire range of temperatures studied, while the solubility of sucrose was greater than that of glucose for temperatures below 74 °C and lower at higher temperatures [142].

The behavior of the boiling temperatures of glucose, fructose [143] and sucrose [144] solutions as a function of sugar concentration are reported at different pressures in Figure 5. Calculation of the liquid phase activity coefficients for glucose and fructose was performed using the UNIFAC–Lyngby thermodynamic model. A negative deviation from ideality was reported, the activity coefficient behavior of which moves away from unity with increasing sugar concentrations in water. Additionally, it shows lower solvent vapor pressure. Comparing the behavior of glucose and fructose, slightly higher boiling temperatures were observed for fructose in the entire concentration range, showing greater deviations from ideality. This behavior is related to the difference between the isomer ratios in fructose solutions in relation to those in glucose solutions, especially at high temperatures [143].

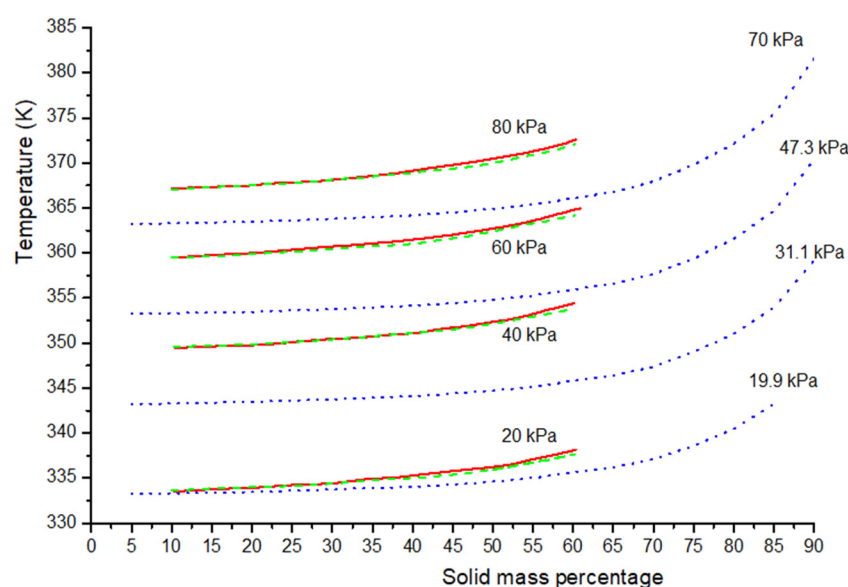


Figure 5. Boiling point diagrams for sugar solutions in water: the blue, green and red lines represent sucrose, glucose and fructose, respectively.

4.3. Protein and Polysaccharide-Rich Systems

The most important parameters for determining thermodynamic behaviors among different foods are determined by characteristics of their structure-composing macromolecules. The incompatibility and compatibility among the existing macromolecules, as well as the formation of complexes, are direct results of attraction and repulsion forces. Attractive forces leading to the formation of soluble or insoluble complexes are predominant in systems composed of macromolecules with opposite charges, with biopolymer concentrations greater than 0.001% (m/m) and lower than 2 to 12% (m/m) and ionic strength lower than 0.3% [145].

Gelation is a phenomenon of interest for food formulation that occurs, among other factors, due to protein–protein interactions. This phenomenon is dependent on the properties of the proteins, which, in turn, can be altered due to the aggregation of these macromolecules during gelation. They also suffer from interference from other types of proteins in the medium, causing changes in the properties of the resulting gels [146]. The exposure of functional groups to proteins through their denaturation results in aggregates [146]. These aggregates are formed by hydrophobic interactions, electrostatic interactions, hydrogen bonds and covalent bonds, depending on the availability of functional groups [147].

The aggregates of protein–polysaccharides present a set of properties of interest for food production. Their ability to increase viscosity and to gelify food systems can confer specific properties to food formulations without any heat treatment. They also have interfacial properties that contribute to the stability of emulsions. These complexes can also be used to encapsulate components, acting as modulators in the delivery of sensitive compounds. The interaction between these macromolecules also contributes to the practice of structuring food matrices, modifying their structure and increasing their stability.

The formation of complexes between proteins and polysaccharides is the main result of non-covalent bonds. The electrical charges of proteins depend directly on their amino acid composition. Although electrostatic interactions are the main driving force for the formation of these complexes, hydrophobic interactions and hydrogen bonds also contribute to these phenomena [148]. Polysaccharides containing carboxylic groups become deprotonated at a pH higher than their pKa. Thus, the presence of electrical charges results in electrostatic attraction or repulsion between molecules. In turn, carboxylic groups in both polysaccharides and proteins, as well as amine groups, give rise to hydrogen bonds. The binding strength of these linkages depends on parameters such as pH, ionic strength and temperature, among others. Unfolded proteins have their sites exposed to the solvent, favoring interaction with polysaccharides.

Linkages between anionic polysaccharides and cationic proteins can result in soluble or insoluble complexes [149]. The initial interaction between anionic polysaccharides and cationic proteins causes charge neutralization, resulting in insoluble aggregates [150]. Additional linkages of anionic polysaccharides to neutral aggregates make them anionic, with the formation of soluble complexes. In turn, the association between proteins and anionic polysaccharides is governed by the interaction between the anionic sites of the polysaccharides and the cationic sites of the proteins. The linkages between anionic polysaccharides and the cationic region of proteins lead to the formation of soluble anionic complexes [151].

The compaction of protein and polysaccharide molecules due to the formation of complexes results in entropy loss from the system. This may also be seen as a consequence of the increase in the order of the system due to the organization of water molecules at the interface of the resulting complexes. On the other hand, the decrease in the total electrostatic free energy of a mixture is responsible for the formation of complexes between proteins and polysaccharides. This trend results in a positive enthalpic contribution as a consequence of the electrostatic interaction between the biopolymers. This favorable enthalpic contribution to the formation of complexes has been reported as predominant in most of the investigated systems and is considered the driving force for their formation [152–156].

Phase behavior in systems containing protein + water + polysaccharides can be studied using phase diagrams. In such systems, the compatibility between soy globulin and branched polysaccharides has been reported. This compatibility decreases in the following sequence: polysaccharides with carboxylic groups (gum arabic) > neutral polysaccharides > polysaccharides containing sulfate groups (dextran–sulfate). On the other hand, a great similarity was reported regarding phase behavior for systems containing water + proteins + polysaccharides with linear chains (sodium alginate, carboxymethylcellulose and pectin), even though great differences were observed in monomer composition, primary structure and molar mass [157].

A specific type of polysaccharide, i.e., starch, is formed by amylose and amylopectin chains, and is among the main components of the human diet. Gelation occurs when heating a mixture of water and starch, as the water molecules penetrate starch granules, swelling them, expanding the entire structure. As the temperature increases and starch gelatinization takes place, the hydrogen bonds break, causing the release of amylose molecules into the medium [158]. In turn, retrogradation takes place as the system cools down and amylose and amylopectin molecules reassociate themselves into new ordered structures, resulting in increased starch crystallinity, increased gel hardness and loss of water molecules. This rearrangement process between amylose and amylopectin is affected, among several factors, by the presence of other compounds in the medium, such as proteins [159].

Starch interacts with proteins through different types of binding. Electrically charged groups form dipole–dipole interactions with phosphate groups and proteins. Hydrophobic groups hinder the release and recombination of amylose, while hydrophilic groups interfere with the mobility between water molecules. Covalent bonds between proteins can accelerate starch retrogradation, while glycosidic bonds between starch and proteins in operations at high temperatures can slow down this process. Thus, the influence of proteins on starch retrogradation is related to four main mechanisms: water mobility, hydrogen bonds, electrostatic interactions, hydrophobic interactions and covalent bonds [147].

During extrusion operations, high shear and temperature cause starch fragmentation and protein denaturation. Proteins affect the properties of starches at micro- and macro-molecular levels. The behavior of starch–protein complexes depends on factors such as starch and protein concentrations, the types of proteins and the thermal and mechanical conditions during processing. Three general hypotheses are highlighted for the formation of some types of starch–protein complexes during thermomechanical operations: penetration and adsorption of proteins on the surface of starch granules, aggregation of proteins in a continuous phase, and covalent and non-covalent bonds between protein and starch molecules [160].

5. Overall Discussion

A discussion of the physical properties of foods, as presented in Section 2, must take in account that foods are among the most complex types of materials in terms of determining their physical properties. Owing to its biological and natural origin, the same food from the same plant or animal species may have a different chemical compositions. In addition, the resulting properties are dependent on processing conditions to which the material is exposed during its development. Furthermore, the distribution of its components is not homogeneous, commonly presenting discontinuous physical structure. These characteristics result not only in significant variations in properties measured for the same type of food but also often in important issues when carrying out analytical measurements. Considering the points raised above, it is important to obtain well-stated information regarding the concepts of each physical property to elect the most suitable determination method for a given property.

The density, thermal conductivity, specific heat and, consequently, thermal diffusivity of the same food of vegetable origin, type of meat and even processed food can change depending on the conditions to which it is exposed. In raw materials, the distribution of physical structures can vary according to the section analyzed. In plant stems, for example, it is possible to obtain different heat transfer rates when analyzing the xylems and phloem tissues. In meat products, mass transfer can occur differently depending on whether it occurs perpendicular or parallel to the fibers. When dealing with processing conditions, it becomes even harder. Processes can, either voluntarily or involuntarily, lead to modification of food subjected to, e.g., drying or dehydration, freezing, heating or cooling, breaking or crushing, or stirring or mixing, which may cause alterations from shrinkage, cell disruption, phase breakdown and particle size alterations up to irreversible chemical reactions, certainly resulting in different values of physical properties.

Therefore, the measurement of the density of a solid must take into account its external volume and porosity and even the mass transfer process of the liquid or gas in its pores in order to guarantee that they are completely filled. In turn, when measuring the density of a solution, it must be ensured that bubbles do not form and, depending on the method, that it does not contain particulate matter. In the case of foods, which are complex mixtures of components, the partial volume of the components may contribute differently to the overall density of the resulting food—another reason why it is important to accurately measure the density of a given material.

Thermal conductivity and specific heat should also be measured carefully. One precaution to be taken is the use of very small amounts of sample in order to avoid thermal inertia. In the case of solid material, it must be ensured that it is adequately compacted in

order to avoid uneven heating or cooling of the entire sample. Compounds that volatilize under the conditions of analysis require pressure-resistant capsules. The enthalpies of crystallization, melting and vaporization of compounds present in the samples must also be carefully taken into account. In some cases, the structure of the material should not be altered during sample preparation and measurement. In such cases, it is necessary to use non-destructive techniques that preserve the original format of the food during measurement. As a consequence of all of these issues, equipment must periodically be calibrated and data must be revised to avoid significant variations.

In this context, measurements of physical properties of food matrices require careful prior study of their composition and structure, as well as the techniques available for measurement. The performance of multiple measurements and, in the case of material with structural discontinuity, in different parts of it, must also be carefully evaluated.

According to the information shown in Section 3, there is a wide variety of rheological tests and behaviors that need to be understood with the aim of correctly determining the rheological behavior of foods, which is crucial for their efficient processing and further acceptability. In general, foods have characteristics of both solids (linked to energy storage) and of fluids (linked to energy dissipation) when a given force is applied. This makes the application of several rheological tests necessary to achieve complete rheological characterization of a food sample. For example, an emulsion can be submitted to flow curve analysis and to tests for the determination of the modulus of elasticity, which measures energy storage, and the viscous modulus, which is related to energy dissipation. Specifically, in solid foods, parameters related to texture are decisive for their acceptability, since they are linked to the sensation in the mouth or of touch and chewiness. Texture parameters are also used in calculations of processes such as milling. In turn, the rheological properties of fluid foods are decisive in their acceptability by the consumer and in the calculation of transportation parameters and heating and cooling operations, among others.

It is worth mentioning that the rheological properties of foods depend on its composition and structural conformation. For example, the amount, arrangement and length of biopolymer fibers are related to the deformation characteristics of meat and vegetables. The profile of triacylglycerols, their crystal polymorphism and crystal size determine the consistency and spreadability of lipid formulations. The amount of water and gluten, as well as their interactions with the carbohydrates in flours, determine the elasticity of dough. Moreover, the rheological behavior of fluid foods depends principally on their chemical composition, temperature and intermolecular interactions. It must also be considered that weak interactions between molecules or particles in suspension, as well as their tendency to be oriented in parallel direction to the applied force, result in low resistance to flow and consequently reduced viscosity. Hence, in food formulations using emulsions, larger droplet sizes are characterized by lower apparent viscosity. In this context, it becomes clear that the rheological behavior of foods must be analyzed by taking into account their most diverse chemical and morphological characteristics, as well as further processing parameters and sensory acceptance.

Section 4 focuses on interactions and transition or equilibrium in food systems that can be described by thermodynamic models representing the state change or phase change in the most diverse types of food. The boiling point of a solvent in a solution, the melting or solidification of a given component and the polymorphic transitions that occur between the crystals of a solid are all thermodynamic phenomena. Solute-solvent or solute-solute interactions in food systems also are described by thermodynamics, and they determine the structural characteristics of a given food formulation, as well as the correct dimensioning of the operations to which they are subjected.

The tendency to form protein-carbohydrate complexes is supported by the energy released or absorbed as a result of breakage or bond formation between molecules, respectively, which is calculated according to enthalpy changes and the availability of groups for molecular bonds, as evaluated by entropy changes. In turn, the transition of triacylglycerol molecules between polymorphic forms α , β' and β or the passage of sugar crystals from an

amorphous to a crystalline form can be determined by the variation in the Gibbs energy (G) between the two situations.

The most stable food systems have the lowest G values and negative variation ($\Delta G < 0$). Under such conditions, this parameter describes a spontaneous change when a given system passes from a less stable to the most stable condition. On the other hand, a positive change in Gibbs energy ($\Delta G > 0$) results in a non-spontaneous transition change. In equilibrium systems, no changes in Gibbs energy occur ($\Delta G = 0$).

Thermodynamic equilibrium occurs when each component in each phase of a system has an equal chemical potential. Thus, the compositions of the phases in a given system in equilibrium can be obtained by calculations of activity coefficients, which are mathematically related to the chemical potential.

Solid–liquid equilibrium can occur when a solid phase coexists with a liquid phase of the same component in a lipid matrix or when the solubility of a given type of sugar is defined in a given solvent. Activity coefficients, which are necessary for calculation of compositions at equilibrium, are calculated based on experimental studies that support the mathematical adjustment of the parameters of thermodynamic models. The description of the equilibrium compositions depends on the quality of experimentally obtained data, the thermodynamic model used and the quality of the mathematical adjustment.

In foods, the components interact with each other at micro- and/or macromolecular levels, and they can be in different phase transitions and/or physical states. Each type of constituent, as well as their interactions, can differently affect the physical and thermodynamic properties of a food matrix. The mathematical modeling of these properties must consider this complexity and be able, through its parameters, to describe the target behavior of interest. This description is directly related to the quality of the experimentally obtained data, the identification and representation of the main factors responsible for each characteristic and the mathematical adjustment performed. This set of requirements can only be achieved using different statistical tools available and suitable for each specified situation. An adequate experimental design reflects the correct number of experimental assays and the parameter value to be studied. A principal component analysis allows for the identification of the main components and the most significant interactions for each physical property. The identification of the parameters, as well as of their value in descriptive mathematical models of a given property, must be performed based on the numerical method most suitable for each situation. In this context, statistical and mathematical tools must be directly associated with each property studied in foods, under penalty of obtaining results that are not significant or that inadequately represent the desired behavior.

6. Conclusions

This review addressed important issues that are fundamental for the correct design of food processes. We reported how important it is to obtain physical properties with accuracy in order to design momentum, heat and mass transfer processes. Density, specific heat, thermal conductivity and thermal diffusivity were discussed separately regarding concepts, determination methods (from the most traditional to the most recently reported) and recent practical applications in food processes.

The main rheological concepts and classifications were presented in this review in order to highlight the importance of such parameters for food process design and for evaluation the overall quality of food products. This article includes not only the methods used for rheological determinations and data modeling but also the different aspects needed to interpret the results in both solid and liquid foods. Destructive (steady state) and non-destructive (oscillatory) approaches were discussed to provide useful information about techniques of process analysis.

Finally, knowledge of the mechanisms by which physical and chemical changes occur is fundamental, although often neglected. For this reason, important aspects of thermodynamics were indicated for several examples of unit operations. Thermodynamics related to phase transition and equilibrium are necessary to modulate food characteristics and im-

prove shelf life, as well as the formulation itself. This application is more clearly presented using phase transition in lipid-rich systems, which are susceptible to crystallization and melting, thus directly affecting food perception and overall quality. Applications of phase diagrams and basic thermodynamic aspects were also assessed to evaluate the structure and chemical changes in other food products with high contents of proteins, polyacrylamides and sugar. We confirmed that, due to the complex composition of food products, the need for solid knowledge about food properties and the mechanisms underlying processes is essential for further evaluations.

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Nomenclature

ρ	Density
c_p	Specific heat at constant pressure
c_v	Specific heat at constant volume
DSC	Differential scanning calorimetry
λ	Thermal conductivity
α	Thermal diffusivity
τ	Stress-strain
η	Apparent fluid viscosity
γ	Shear rate
k	Coefficient of consistency
n	Characteristic flow index
τ_0	Yield stress
μ_p	Plastic viscosity
μ_0	Viscosity at a reference pressure
P	Pressure
P_0	Reference pressure
α	Adjustment factor known as the viscosity growth coefficient
G	Gibbs energy
H	Enthalpy
T	Temperature
S	Entropy
γ	Activity coefficient
x	Molar fraction of a component
R	Universal gas constant

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