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REVIEW ARTICLE

Molecular Dynamics and Structure in Physical Properties and Stability of Food Systems

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Abstract Physical properties and stability are critical for delivering safe and healthy food to the consumers and thus is a theme that attracts food scientists for a long time. Recently, literature suggests that stability can be fully grasped only if food molecular dynamics and structure are taken into consideration, i.e. an appropriate understanding of the behaviour of food products requires knowledge of its composition, structure and molecular dynamics, through the three-dimensional arrangement of the various structural elements and their interactions. Food systems behaviour is strongly dependent on the water molecular dynamics. Understanding changes in location and mobility of water represents a significant step in food stability knowledge, since water "availability" profoundly influences the chemical, physical and microbiological quality of foods. Nuclear magnetic resonance has been presented as a powerful technique to investigate water dynamics and physical structures of foods through analysis of nuclear magnetisation relaxation times, because it provides information on molecular dynamics of different components in dense complex systems. The application of this technique may be very useful in predicting food systems physicochemical changes, namely texture, viscosity or water migration. This paper aims at reviewing some of the main aspects related to food physical properties and stability, and the role of water in these properties. More specifically, this paper intends to contribute to a deeper understanding of the relationship of molecular constituents–structure–function of food systems, contributing to the development of foods with improved functionality.

Keywords Food systems · Water · Molecular dynamics · Structure–function · Stability · Physical properties

Overall Molecular Dynamics Concept

Molecular dynamics has been pointed as the actual most promising parameter for characterising multicomponent systems. Analysis of systems at a molecular scale has been demonstrated to be a useful methodology for investigating complex geometries and molecules, as well as studying structural and dynamic properties [71].

Molecular dynamics involves, at a microscopic level, the displacement of reactants, which promote chemical reactions. Macroscopically, molecular dynamics can be related to the viscosity of the material, which in turn controls the flow properties, structure collapse, mechanical properties and thus the product texture [57].

It is generally accepted that the knowledge of molecular dynamics is determinant for assessing physicochemical and microbiological stability of food systems [38, 57] and is quite dependent on composition and matrices microstructure.

Food stability is a critical parameter for different stakeholders. Concerning consumers, stability assures safety, nutritional and sensorial quality of food products and answers to the increasing demand for a diversity of ready-to-eat food with fresh appearance and health-promoting properties [46]. For industry, stability allows maximising shelf-life: minimising waste along the distribution chain, increasing profit and reducing the environmental impact [32, 53, 54, 67].

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Food physical stability is assessed by shelf-life changes of mechanical, thermal or surface properties, which are often related to food product's quality, processing behaviour or development of novel food products and processes [8, 36]. Physical state is directly affected and responsible for the molecular dynamics of a matrix [40, 51].

It is possible to observe in Fig. 1 a simplified scheme of how molecular dynamics covers several concepts related to food properties and stability, being a key and linking factor between all aspects involved in food systems assessment, including food structure/microstructure. The better understanding of these factors and relationship between them is essential for controlling degradation reactions rates and maintaining food integrity [53].

Food systems are complex mixtures of water, biopolymers (proteins and polysaccharides), low molecular weight ingredients (minerals, sugars, surfactants, etc.) and colloid particles (oil droplets or air bubbles). The molecular dynamics between these different components reflects on the stability of such systems, determining the physical state, microstructure and composition, which impacts on food characteristics [55]. Water, as one of the most important food constituents and its interactions with other food ingredients, controls both thermodynamic and dynamic properties of all aqueous elements [57]. These interactions affect mainly appearance and sensory attributes (texture/firmness) [47, 64, 72], nutrient quality [72] and the microbiological load [30]. The extensions of the reactions between food constituents, usually associated with metabolic processes, are responsible for the degradation of quality, safety and nutritional attributes.

Although molecular dynamics has been considered an useful methodology for investigating complex systems (geometries and molecules) [71] and the degradation reactions extension, a large number of studies have been focused on chemically pure or homogeneous materials, such as proteins or polysaccharides, instead of food systems. The data for "pure and simple" systems cannot be extrapolated when considering food systems, since it is necessary to take into account the heterogeneity of the systems, as well as their interactions with water [57]. Moreover, it is important to consider the system's microstructure to understand the spatial and molecular distribution of water within its food matrix environment and determine whether water is already accessible for metabolic reactions.

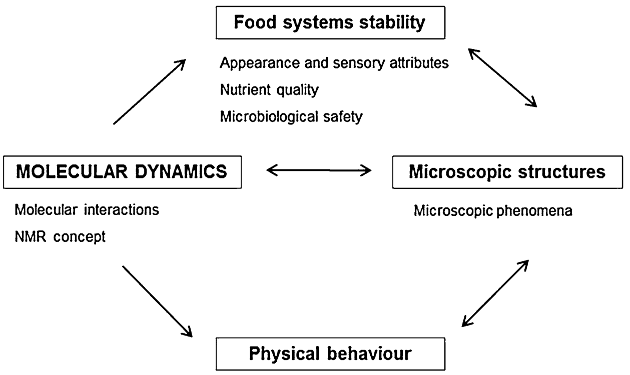

Fig. 1 Schematic representation of molecular dynamics as a key factor for food physical properties and stability assessment

Aspects of Water Molecular Dynamics

Water is the most important solvent, dispersion medium and plasticiser in biological and food systems [45]. It affects reactions, can be a substrate and a product of reactions and is involved in nutrient transport and dissolution of salts and other solutes. It establishes pH, acts as a polymer plasticiser and modulates viscosity, osmotic pressure, etc. [69]. Specifically, the state of water in food influences physical properties, such as rheological, electrical, optical, thermal or mass transfer [36].

For long, water has been recognised as one of the most important food components in impacting food physicochemical and microbiological attributes, shelf-life and deteriorative changes [24, 31, 32, 36, 44, 50, 54, 59, 61]. Therefore, determination of water content is one of the most frequent analyses in the food industry laboratories [44]. Water content of food systems normally ranges from 80 to 95 %, for high-moisture foods, to a percentage close to zero in semi-dry and dry foods [5, 50]. However, various foods with the same water content differ in stability [30], which demonstrates that the sole value of "water content" in a food does not inform about the nature of water [18, 30, 44]. In fact, in a food matrix, water molecules can be accessible or not to participate in degradation reactions [44].

The knowledge of each of these fractions is important, specifically because available water, its location and the interactions with the other food components (like proteins and polysaccharides) are responsible for the physicochemical and microbiological properties and stability of foods [45, 59].

As such, besides water content in a food material, it is important to understand the water state and dynamics for a proper comprehension of properties and stability of food products.

Water mobility/dynamics can thus be described as a manifestation how "freely" water molecules can participate in reactions or how easily water molecules diffuse to the reaction sites to participate in reactions [58]. Presence of molecules of different molecular weight and solubility in water can have a profound influence on water mobility/

dynamics, as this is dependent on the physicochemical properties of other nonaqueous food constituents and their interactions with water and among themselves [58, 70].

Different parameters have been used in the literature to describe water dynamics in the food systems and its repercussion in stability: water activity, glass transition temperature or water relaxation time. These concepts are detailed in the next sub-sections.

Water Activity Concept and Shortcomings

Water activity (a_w) concept was introduced in the mid-twentieth century as a critical parameter for estimating food stability [54] and has been one of the most widely used concepts to evaluate food's water accessibility [30]. For a long time, a_w was regarded as the most important parameter controlling the behaviour of food during processing and storage, with particular emphasis on its effects on reaction degradation rates [5, 31, 41, 59]. This parameter has been used thoroughly as the indicator for microbial growth and microbial stability of a food system [68]. Also, with respect to most of degradation reactions of a chemical, enzymatic, or physical nature, such as lipid oxidation, non-enzymatic and enzymatic activities, and the texture/mouthfeel of foods following production, water activity is currently used as an important parameter [41, 59, 61].

Despite the irrefutable significance of a_w for food science and engineering, the limitations of this analysis are, actually, evident. Water activity is a thermodynamic measure of the chemical potential of water in the system, assuming that food is in equilibrium with the surrounding atmosphere [36]. However, it is well known that most foods are not in the state of equilibrium [24, 53]. Water activity measurements may not provide, for example, the relationship of the evolution of the structural changes of the food material with the changes of the water–macromolecules and water–water interactions that occur during food shelf-life [71], and studies have stressed that under many common circumstances, the thermodynamics activity of water is far less relevant to processing and storage than structure-related properties, which can restrict the mobility and diffusion of the reactants [5, 61].

Moreover, the water activity analysis does not consider microstructure or the possibility that there may be local regions differing in water content and presumably of water availability [24], fact that could be important for microbiological stability, since some authors [25, 27, 69] demonstrated that microorganisms are sensitive to the local properties of the system, i.e. local water activity, translational motions and microstructure, and not to the bulk water activity. Some authors also showed that microbial response in a solution is more dependent on the solute used to control a_w values than on a_w itself [12, 68], showing the importance of solute interaction.

Therefore, water activity, defined as a relative vapour pressure, reflects only the surface properties of a system and not necessarily the molecular dynamics that takes place in its interior [69].

Furthermore, it has been reported that solutions with the same water activity can present dramatic differences in the system's "kinetics" (here assessed by viscosity) (see Fig. 2) [5, 41].

Glass Transition Temperature

The glass transition temperature (T_g) was often used, since the early 1980s, as a parameter that would be able to assess food stability and overcome the limitations of water activity. This concept has been extensively applied, giving way to a new important area of research and application: food material science [6, 53, 55, 62]. Essentially, this approach "simplifies" the foods as partially crystalline partially amorphous materials. The amorphous part is in a metastable state, which is very sensitive to changes in moisture content and temperature. Such amorphous matrix may exist either as a very viscous glass or as a more liquid-like "rubbery" amorphous structure. The characteristic temperature, T_g, at which the glass–rubber transition occurs, is the physicochemical parameter that is a basis for product properties, stability and safety of foods [13, 56, 61] (Fig. 3).

The transition observed at T_g resembles a second-order thermodynamical transition, at which the material undergoes a change of state but not a phase change [53], and the temperature at which it occurs is dependent on both composition and solid content of a material [19]. T_g greatly influences food stability, as the water in the concentrated phase becomes less mobile and therefore less accessible to support or participate in reactions [53, 61]. Below T_g, the food is expected to be physically stable, and above this temperature, the difference (T–T_g) between T_g and the

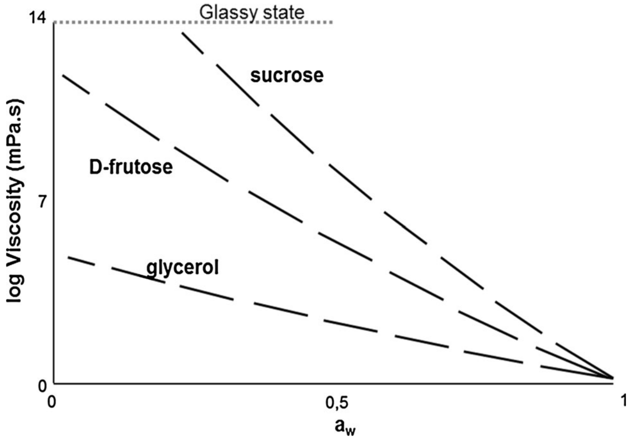

Fig. 2 Viscosity versus water activity of model solutions produced with different solutes (adapted from [5])

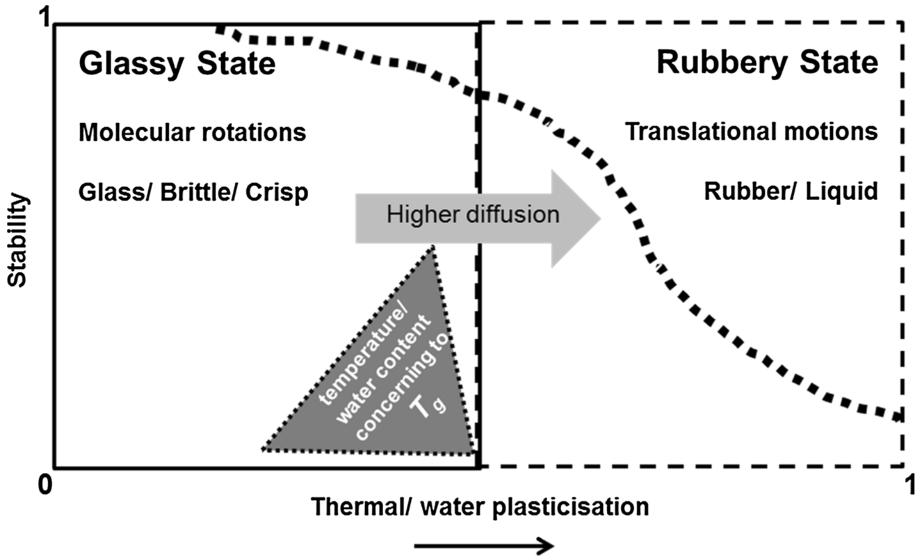

Fig. 3 Representation of T_g effects on structural transformation and diffusion-controlled changes in biological food systems (adapted from [56])

storage temperature T is assumed to control the rate of physical, chemical and biological changes. As discussed already, these physical and chemical reactions, which are dependent on the diffusion of reactant molecules, would be quite slow in the supercooled liquid or rubber, in the vicinity of the T_g, and kinetically controlled by mobility or viscosity [10].

T_g is a very promising and innovative concept for food science and is considered as a future challenge when associated with other food mechanisms [53]. Despite this, experimental evidences demonstrate some fragility [12, 26, 38, 70]. Glass transition temperature considers mobility at a macromolecular level and, therefore, is a parameter descriptive of the physical state and overall mobility of macromolecules, which differs from the molecular mobility of smaller molecules such as water [38, 69].

Moreover, some experimental evidence does not support a clear correlation between T_g and microbial activity [12, 70]. Similarly, many investigations demonstrate that glass transition alone cannot explain enzymatic and nonenzymatic activities below T_g. In some cases, reactions occur slower in the rubbery state than in the glassy state (e.g. ascorbic acid oxidation, because the structural collapse in the rubbery state impeded O_2 diffusion through the system, which resulted in slower ascorbic acid degradation rates) [38].

Moreover, T_g is not as easy to measure as, for example, water activity and may not be a representative parameter in multicomponent, multidomain complex foods [41].

Water Proton Relaxation Time and NMR as a Powerful Technique for Assessing Proton Relaxation Time

Biological systems, and particularly foods, consist largely of water and macromolecules, both rich in protons. Proton relaxation time is a characteristic of proton dynamics/mobility [10] and is a function of physical and chemical characteristics of individual chemical compounds as well as interactions among them [42, 58]. Water protons are one of the most important contributors to the proton relaxation in biological systems, and the interaction between water and macromolecules is the most important factor affecting proton relaxation process [58].

Nuclear magnetic resonance (NMR) spectroscopy is one of the most common investigative techniques used to evaluate systems molecular dynamics, by identifying molecular structures and evaluating the progress of chemical reactions [42]. This technique provides information on different food components that are considered as dense complex systems [16, 23, 58], both in solution and in solid state [15, 29, 74]. It also allows to study independently the dynamics of water and food solids [30].

Water dynamics/mobility can be analysed by NMR, through proton (^{1}H), deuterium (^{2}H) and oxygen-17 (^{17}O) [70]. ^{1}H NMR, as the most used NMR technique, has been used to investigate water dynamics and physical structures thought analysis of proton nuclear magnetisation relaxation times [20, 37]. Many researchers have found that the mobility of water, as measured by NMR, is related to the dynamics and "availability" of water in complex systems [23, 58], i.e. the higher the mobility of water, the higher the availability of water, very mobile water molecules take a long time to reach their equilibrium state, or relax very slowly, thus having a small relaxation rate or long relaxation time [58].

In these measurements, the samples are submitted to a static magnetic field and the protons are excited by means of a radiofrequency pulse. The analysis of the signal emitted while the samples return to equilibrium (*FID*) allows determining the spin–lattice (T_1) and spin–spin (T_2) relaxation. This later variable is related to the mobility of the protons in the sample matrix [20].

For example, in plant tissues different compartments can be discriminated, where water molecules or protons are in exchange. These exchange rates between compartments are controlled by the proton permeability of the membranes separating the compartments and/or by the diffusion process by which water molecules reach the membranes [63].

NMR can be applied in complex food systems [1, 7, 14] to do quantitative and conformational analysis (nutritional or functional aspects), quality control of packaging materials, process control [42] and also to evaluate food quality during storage period [11]. In the last case, the degradation changes that occur along the storage promote changes both in water and in solutes bounding and structure, which results in differences in NMR properties of the food [40, 58].

Literature reports diverse studies applying this technique to different foods and with different purposes. Some examples are discussed below (Practical application of NMR to assess molecular dynamics and structure).

Food Structure/Microstructure

Food "matrices" (systems) physical behaviour and stability depend strongly on its molecular mobility, but also on its microstructure. Food microstructure recognises that foods are highly structured and heterogeneous materials, composed of architectural elements. The types of such structural units and their interactions are decisive for the food physical behaviour and functional properties, such as texture or sensorial attributes, and also physical and chemical stability during storage. They influence the water/solute interactions and hence the water availability to participate in microbial growth and degradation reactions [2]. In fact, these intermolecular interactions in which the water molecules play a very important role can determine the structure of the food material at the beginning of a given process and during processing [71].

Also, the effective water diffusivity in foods, as well as free water content, highly depends on pore structure or particle size distribution [49, 50, 73].

In addition to water, other structural elements can be identified in foods, such as oil droplets, gas cells, fat crystals, strands, granules, micelles and interfaces [2]. These structural elements, composed of proteins, carbohydrates and lipids (in various combinations and proportions), can exist in different states (glassy/rubbery/crystalline/liquid and solubilised) even at uniform temperatures and water activity. This structural heterogeneity will necessarily affect the molecular dynamics in the system and consequently the macroscopic food quality attributes [40] and their behaviour along storage.

Designing the food structure during processing can also affect the behaviour during shelf-life. For example, physically separating the reactants in microstructural locations can control the biochemical activity by avoiding the reactants to be in contact, thus minimising the development of off-flavours and browning reactions [2].

Food microstructure can also be altered by controlling various intermolecular and inter-particle interactions among the different ingredients during processing and storage [35]. Engineering structures requires knowledge on the molecular organisation of the ingredients (short- and long-range molecule assemblies) and physical properties, such as charge density, hydrophobicity, molecular size and conformation under different environmental conditions [60]. The expression "structure–function", nowadays widely used, describes basically the way in which physicochemical and functional properties of foods are related to their structure [3].

Practical Application of NMR to Assess Molecular Dynamics and Structure

As previously described, molecular mobility/dynamics has been identified as one of the actual most promising parameters for assessing physicochemical properties in multicomponent systems. This fact justifies the significant number and type of experimental works performed in food systems. This section briefly discusses examples of ^{1}H NMR practical applications on food systems, considering matrices of different complexities.

Edible Films as Food Systems Models

Edible films have been studied for a long time for their potential to improve shelf-life and safety of food products [4, 17]. The literature is extensive in characterisation of such materials and particularly in reporting the thermomechanical behaviour and barrier properties of glassy biopolymers and polymers [9, 33]. These systems are partially crystalline/partially amorphous and easily reproducible materials. From a fundamental perspective, foods are mainly edible and digestible biopolymers that are partially crystalline/partially amorphous [71], and thus, edible films can be very interesting food model systems for mobility and microstructure studies. Also, in these films, water is one of the most important components, i.e. is used significantly as a plasticiser, creating hydrogen bonds with the polymeric chains present in the system and influencing its physical properties, e.g. relaxation [21].

However, the lack of systematic information about the relationship between the effect of films composition on the microstructure and molecular dynamics of polymeric systems behaviour is evident. A few published papers take advantage of these techniques.

^{1}H NMR has been used to characterise starch–chitosan films with different levels of glycerol [39]. This technique proved to be useful in clarifying the interactions between films components. It was showed that the addition of glycerol promoted the interactions among chitosan, starch and glycerol through hydrogen bonding. The stronger glycerol/starch/chitosan interactions in samples containing higher glycerol concentration were confirmed by an observed decrease of glycerol mobility.

Another research work was developed with the purpose of investigating the effect of polysaccharide/plasticiser (chitosan/glycerol and water) concentration on the molecular dynamics and microstructure of the film [20]. In this case, results of molecular mobility contributed to the understanding of the films molecular rearrangement. NMR measurements showed two different populations with mobility in the matrix: water and glycerol. It was possible to conclude that, while glycerol is mainly bounded to the chitosan chain network, the water present in the system is predominantly free from the polymeric chain. However, it was observed that for lower glycerol concentrations, free chitosan binding sites can also be occupied by water molecules (Fig. 4a). Water content and water activity measurements also allowed concluding that not only the water content affects the water mobility, but also structural differences in the film may influence the water relaxation time. Water mobility relates to the water in the bulk and thus complements information on water activity of a system (Fig. 4b, c).

^{1}H NMR experiments have also allowed understanding the differences on ascorbic acid stability observed in different films [34]. This study proved that the water dynamics influences the ascorbic acid stability and recognises which of the compounds added to film-forming solutions (e.g. calcium) interacted with this dynamics.

Real Food Matrices: Fruits

Fruits are high water content products, with a complex cellular structure where water can be present in both intra- and extra-cellular spaces. The general fruit constitution may be described as a watery solution of low molecular weight species, mainly sugars, salts and organic acids, and high molecular weight hydrocolloids, contained in a water-insoluble cellular matrix of macromolecules, mostly carbohydrates including insoluble pectic substances, hemicelluloses, proteins and, sometimes, lignins. Intracellular air spaces are present in parenchymous tissue, and these may be considered as true structural elements, having a very characteristic influence on the perceived texture. This complexity makes these systems of special interest for mobility studies.

Many studies have been performed on the application of ^{1}H NMR techniques for evolution of quality in fruits. This technique allows using the changes in the distribution of water proton transverse relaxation times to monitor the subcellular compartmentation of water.

^{1}H NMR has been a tool used for purposes as diverse as studying the effect of preservation processes [28, 48, 66], monitoring food quality changes during storage [75], analysing food quality characteristics [22, 43, 65] or just monitoring ripening [52].

The work of Hills and co-workers was an important milestone on the use of this technique. The group first identified the signals of water in the cellular wall, cytoplasm and vacuole [23, 24, 26] and applied the methodology for

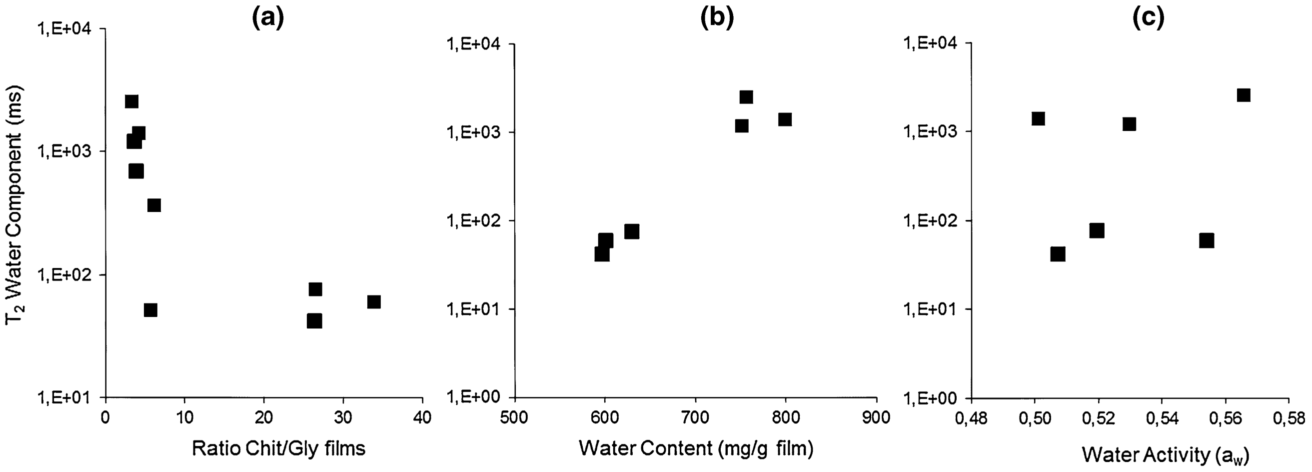

Fig. 4 Films water proton transverse relaxation time (T_2) as function of films. **a** Polysaccharide/plasticiser ratio. **b** Water content. **c** Water activity (adapted from [20])

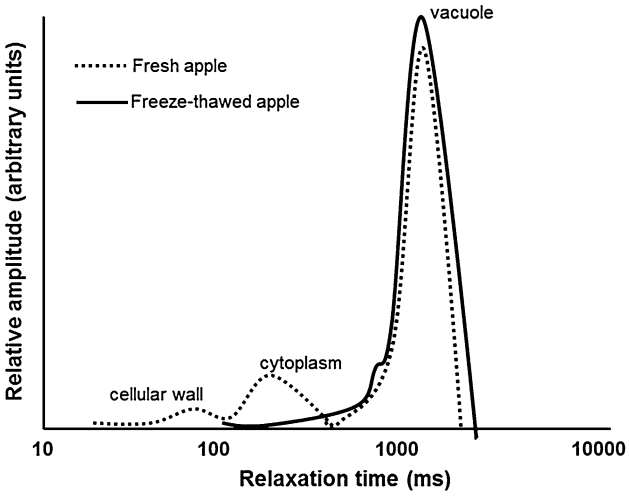

Fig. 5 Distribution of transverse water proton relaxation times in fresh and freeze-thawed apple tissues (adapted from [28]

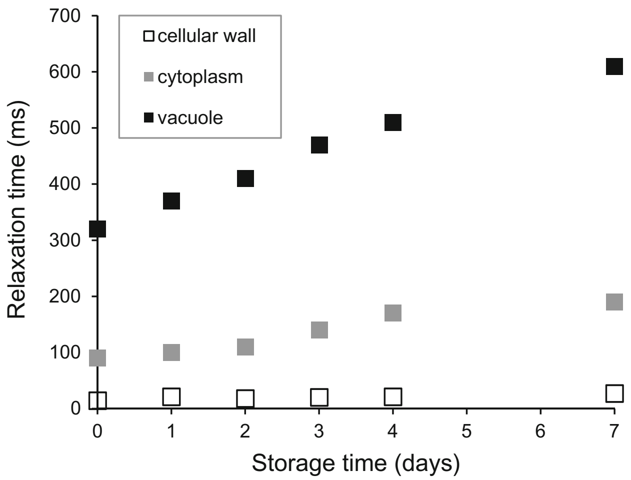

Fig. 6 Banana proton transverse relaxation time, during 7 days of storage (adapted from [52])

studying the effect of preservation processes in foods. An example is the study on changes in subcellular water compartmentation in parenchyma apple tissues during freezing/thawing [28]. Figure 5 shows the differences in water proton transverse relaxation time profile for fresh and freezing/thawing apple tissues. For the fresh apple, tissue behaviour presents a proton distribution following three peaks that can be assigned to water located in the vacuolar, cytoplasm and cell wall compartments. After thawing, the absence of the three peaks indicates membrane rupture and loss of turgor in the tissue, the cellular structure was broken and the vacuole, cytoplasm and cellular wall lost their integrity and become just one compartment.

As discussed, another example of the use of NMR is to understand the response of fruit quality parameters to different storage conditions, such as on pomegranate fruit [75]. In this case, NMR measurements allow analysing the microscopic structure changes during storage and confirm the water environment in each component. The authors found that water was redistributed between subcellular compartments of the pomegranate aril tissues during controlled atmosphere storage.

Another study has addressed the water proton relaxation times in different pear varieties with two different levels of internal damage (sound tissue and disordered tissue) and tried to find a relationship with the internal browning process and complement the observations with image techniques [22]. It was possible to conclude that, at least for one pear variety, internal browning (postharvest disorder) may be identified and correlated with the NMR parameters. Moreover, it was also possible to infer that the cell decompartmentation facilitates the accessibility of enzymes and subtracts (responsible for browning reactions). The analysis of firmness and soluble solids content was performed, and no correlation between internal browning was found, evidencing once again the relevance of NMR to support the internal inspection of the fruit.

One last example is a study aiming to understand the banana ripening phenomenon [52], showing the relationship between changes in water dynamics with variations in chemical composition. Results from NMR allow explaining the ripening process that happen for a period of 7 days, and where membrane-bound starch granules are almost converted to soluble sugars. Shortly, three components were determined, attributed to vacuole, cytoplasm and cell wall. T_2 values attributed to cytoplasmatic and vacuolar water show a gradual increase, correlated with the disappearance of starch that acts as a relaxation sink (Fig. 6). The disappearance of these granules during ripening increases the cytoplasm and vacuolar water fractions that can be influenced by the chemical diffusive exchange effect, increasing cytoplasm and vacuole T_2.

Conclusions

This paper reviews some critical issues and highlights works in food systems molecular dynamics assessment. Molecular dynamics together with structure/microstructure is an important approach to study food systems properties and stability. Water is one of the most important food components and is a key factor in biological systems performance. Water activity, glass transition temperature and water proton relaxation time are three concepts that have been used to determine the water performance. Water proton relaxation time, assessed by NMR techniques, is one of the broadest methods to understand dynamics even in complex biological systems like foods. Dynamic properties play an important role in complementing the information provided by methods based on systems equilibrium and global kinetics. However, the lack of systematic information, even in straightforward model food matrices is evident.

Further work on relationships between water and solids mobility and glass transition or water activity in food systems is a fundamental and necessary approach to fully attain food physical properties and stability. The absence of studies on the relationship between degradation of quality factors and molecular mobility along shelf-life is also evident.

These studies may be extremely useful for food product and process design, safety and sensorial attributes and also for better understanding and predicting, for example, food storage stability conditions.

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