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Rheological approaches to food systems

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Abstract

Foods, consumer products and cosmetics belong to a wide range of colloidal and non-colloidal materials. Often, they are composite materials comprising several classes of fluid and solid constituents, including biopolymer gels, particulate suspensions, emulsions and foams. Length scales relevant for such materials may be anywhere between those associated with the molecular conformation of the ingredients up to long-scale dimensions of processing flows. The corresponding time scales may be in the sub-millisecond regime during aggregation of the ingredients or up to years during the shelf life of the final product. Rheological research of food material focuses on both the interaction between its ingredients, which might exhibit a complex rheological response function themselves and the influence of processing on the food structure and its properties. This brief overview summarizes suitable food rheology approaches and is grouped by the degree of abstraction of length scales and interactions. *To cite this article: P. Fischer et al., C. R. Physique 10 (2009).*

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Résumé

Rhéologie et aliments. Les aliments, produits de consommation et cosmétiques font partie d'un large éventail de matériaux colloïdaux ou non. Ce sont souvent des matériaux composites comprenant plusieurs classes de constituants fluides et solides, notamment des gels de biopolymères, des suspensions de particules, des émulsions et des mousses. Les longueurs importantes dans ces matériaux peuvent être n'importe quoi entre celles qui caractérisent la conformation des molécules et les dimensions des écoulements de fabrication. L'échelle de temps peut être inférieure à la milliseconde lors de la combinaison des ingrédients, et plusieurs années quand le produit fini a rejoint son étagère. La recherche rhéologique sur les aliments se concentre à la fois sur l'interaction entre les ingrédients, qui pourraient eux-même présenter une fonction de réponse complexe, et l'influence du procédé de fabrication sur la structure de l'aliment et ses propriétés. Le bref panorama qui suit résume les méthodes rhéologiques appropriées que l'on classe selon l'échelle de longueur les interactions. *Pour citer cet article : P. Fischer et al., C. R. Physique 10 (2009).*

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1. Introduction

The food products we encounter every day may be simple liquids (some clear soft drinks are aqueous solutions of sugar and water-soluble flavors), or solids (sugar or salt crystals) - but the vast majority of food materials belong to the category of soft condensed matter [1-5]. From the agricultural production of the raw materials, to the physiology of flavor perception and nutrient uptake [6,7], food materials often involve physicochemical phenomena occurring on a wide variety of length and time scales. The length scales range from those associated with the molecular conformation of food proteins, to the convective mixing length scales of the order of meters in industrial scale food processing [8–12]. Time scales may be in the sub-millisecond regime during the generation of foam bubbles or emulsion drops in an industrial dispersing device, up to months or even years associated with the long-term shelf life of canned food products. Many food raw materials are synthesized and assembled by plants and animals and depend on external factors such as soil quality, climate and farming standards. It is therefore not surprising that common analytical and synthetic approaches to colloid and polymer science are often difficult to apply for food materials. However, characterizing and, ideally, understanding the rheology of food materials is essential for numerous aspects of food science and technology, such as the standardized characterization of raw materials and innovative products, or for optimized conservation and industrial processing. A major challenge in food rheology is to identify the main component, i.e., to classify the material to be tested as a suspension (e.g. chocolate [13–17]), emulsion and interfaces [18–23], foam (e.g. ice cream [24–26] or wet foams [27–29]), gel (e.g. dairy [30–32] or biopolymer mixtures [33–37]), melt (e.g. dough [38–43]), etc., and in a second step to estimate or measure the concentration and size of the constituent elements (dispersed phase, effective polymer concentration, etc.) and their relevant interactions leading to particulated suspensions, gels, emulsions, or phase-separated aggregates [8,9]. Because a 'food material' can be a slice of meat, a strawberry suspended in yoghurt, or a gelled biopolymer mixture, the field is defined by its application rather than by a straightforward physical classification of materials, such as, for example, in polymer rheology (melt, blend, solution and composite rheology). Whereas in classic polymer or colloid rheology the tested material can often be probed on a specific length scale, food is a multi-scale material composed of materials that have distinguished rheological signatures themselves. Foods as composite materials combine the rheological responses of its individual components with additional effects originating from the interaction between all ingredients. Therefore, studies in food rheology often focus on one of three very different levels of complexity: (i) phenomenological approaches; (ii) flow behavior of non-colloidal systems; and (iii) physics of food colloids (see Fig. 1(a)). To elucidate structural aspects prior to rheological experiments, literature on food materials is essential [1-3,44-47], but it is advisable to check for non-food literature when dealing with rheological problems of food [4,48,49] and colloidal aspects [50–53], always keeping in mind that food is not a model system.

2. Rheological approaches for material characterization

'Rheology is the study of the deformation and flow behavior of matter': Rheological properties vary from viscous fluids and elastic solids, defining the spectrum of possible material responses to applied stress σ , strain γ , or shear rate $\dot{\gamma}$. The aim of rheological fluid characterization is to quantify the functional relationships between deformation, rate of deformation, and the resulting stresses acting in rheometric flow conditions. The obtained flow properties are described in constitutive equations that establish a correlation between stress and kinematics. For macroscopic phenomenological description of a flow phenomenon (e.g. power law, Bingham, Herschel–Bulkley model) it is not necessary to include information on the microstructure under flow. More advanced constitutive equations, such as the Giesekus or the Phan–Thien–Tanner models consider microscopic descriptions of the flow properties and local microstructure, i.e., morphology, conformation, and flow-induced orientation and structural changes, which deliver contributions to the stress tensor [4]. The correlation of stress, deformation, flow properties, and consecutive approaches of description by phenomenological and constitutive models is depicted in Fig. 1(b). Besides the linear flow response of the material (viscosity, elasticity, viscoelasticity, viscoplasticity), non-linear flow properties also must be accounted for [4,48].



Fig. 1. (a) Length scales relevant for food structures and associated levels of abstraction in food rheology. The shaded areas in the 'phenomenological' and 'non-colloidal' models are generally not considered in these approaches even though transport processes occurring on those length scales may influence the measured rheological properties. (b) Correlation of stress, deformation, and the measurable flow properties (Newtonian and non-Newtonian responses). Consecutive description of the measured flow properties of complex materials can be divided in phenomenological models and constitutive equations.

2.1. Phenomenological modeling of Newtonian and non-Newtonian flow functions

In the most common rheological experiment a shear rate or shear stress is applied to the sample and a flow curve (viscosity as a function of shear rate $\eta(\dot{\gamma})$) is recorded. In food one can expect Newtonian flow properties mostly for 'pure' liquids (such as oils or salt solutions), for dilute polymeric solutions, or for dilute suspensions and emulsions. In these cases, the intrinsic viscosity $[\eta]$, i.e. the viscosity of a single aggregate suspended in a solvent is the most important parameter for characterization. More concentrated dispersed systems, colloidal and non-colloidal, show various non-Newtonian flow properties such as shear-thinning, shear thickening as well as transient changes of the viscosity. Fig. 2(a) shows that different total solids volume concentrations c_v of the same aggregates, in this case TiO₂ in polyethylene glycol, will already lead to completely different flow responses. The obtained viscosity function $\eta(\dot{\gamma}, t)$ can be described by models following the Newtonian Ansatz:

Newtonian law:
$$\tau = \eta \dot{\gamma}$$
 (1)

Power law model:
$$\tau = \kappa \dot{\gamma}^n$$
 (2)

where η is the viscosity, τ the shear stress, $\dot{\gamma}$ the shear rate, κ the flow coefficient, and *n* the flow index. The flow index *n* may vary from n = 1 (leading to the Newtonian law) to n < 1 or n > 1 to describe shear-thinning or shear-thickening flow behavior. Additionally, most complex food materials are often yield stress fluids, may exhibit wall slip, and may undergo shear-induced phase transitions [54–56,13,57,58,4]. Therefore, many additions to the Newtonian or power



Fig. 2. (a) Viscosity as a function of shear rate for different total volume concentrations c_v of TiO₂ aggregates in polyethylene glycol. Depending on the aggregate concentration Newtonian, shear thinning and shear thickening can be observed; (b) Illustration of various phenomenological models to describe the flow curves of non-Newtonian liquids. The simplest descriptions of non-Newtonian liquid behavior is the power law model that in combination with the Bingham model will lead to the Herschel–Bulkley model. Double logarithmic plots are commonly used.

law model covering complex flow phenomena have been introduced and some of them are presented in the following list [59]:

Bingham model:
$$\tau = \tau_0 + \eta_P \dot{\gamma}$$
 (3)

Herschel–Bulkley model: $\tau = \tau_0 + \kappa \dot{\gamma}^n$ (4)

Sisko model:
$$\eta = \kappa \dot{\gamma}^{n-1} + \eta_{\infty}$$
 (5)

Cross model:
$$\eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + (\kappa \dot{\gamma})^{1-n}}$$
 (6)

where η_0 , η_∞ , η_P and τ_0 are zero-shear viscosity, viscosity at infinite shear rate, Bingham viscosity, and yield stress, respectively. The range of applicability of the different models is depicted in Fig. 2(b). It should be noted that the sample is usually considered as one-phase fluid developing a well-defined laminar flow profile in the shear gap of the rheometer and that structural or morphological information on the μm and nm level to describe the flow behavior are not needed (therefore all equations can also be used to model e.g. a nation's gross income as a function of increasing raw material prices, etc.).

Fig. 3 demonstrates that these models can often fail to describe the flow properties of complex food systems over a wide range of shear rates. The flow curve of chocolate melts with different fat/emulsifiers additions exhibit shear-thinning behavior (Fig. 3(a)) is fitted to the Herschel–Bulkley, Windhab, Casson, and Tscheuschner models suitable for chocolate melts [59]. All models are not able to describe the entire flow curve correctly (Fig. 3(b)) since they cannot reflect flow-induced changes of the structure at either the non-colloidal and colloidal level. The figures also demonstrate that the applicability of the models varies from one sample to the other and even between different ranges of shear rates.

But why is such an empiricism widely used not only in food rheology? There are three good reasons for it: (i) Due to the complex composition of food and resulting non-ideal rheometrical flow situation (e.g. yielding, heterogeneous material composition) it is the most economical way to describe the flow curve without considering complex hydrody-namical solutions as well as colloidal and non-colloidal interactions. (ii) Linked to this, most rheological investigations performed on this level of sophistication are addressing quality control issues or aim to provide viscosity information for food processing or formulation and product development [60,13]. Therefore, the models provide a possibility of predicting how a particular liquid will behave in different or more complex flow situations. A simple example would be the description of the flow curve of a non-Newtonian liquid measured in a cone-and-plate geometry, and then the prediction – using appropriate mathematical equations – of its behavior in pipe or drainage flows. (iii) Finally, computational fluid dynamics (CFD) simulations are used to design and to scale processing equipment; most, if not



Fig. 3. (a) Flow curves of chocolate masses containing 4% of fat/emulsifier additive to modify the yield value. (b) Fitting quality for the Windhab, Herschel–Bulkley, Casson, and Tscheuschner model represented by the relative error between the experimentally obtained flow curve and the fitted flow curve.



Fig. 4. Interactions in intrinsic, diluted and concentrated dispersions. Depending on the concentration and size of the aggregates different features such as rheological and structural properties change.

all available commercial codes have restrictions in the rheological constitutive equation that is implemented in the equation of motion (often reducing the model set to the Newtonian, power-law, or Herschel–Bulkley equation).

2.2. Brownian versus non-Brownian motion

Human perception senses aggregate sizes from several micrometer upwards while many food emulsions and food suspensions also have droplet sizes and particle sizes of several micrometers. As a consequence, food manufacturing operations (e.g. in dispersion processes), aim at changing the microstructure on the micrometer length scale. In the colloidal and non-colloidal approach therefore two important features have to be considered to interpret a flow curve (or any other rheological response function): (i) concentration; and (ii) size of the primary aggregate. Both parameters influence the aggregate–aggregate (inter-particle forces) and aggregate–matrix fluid (shear forces, thermal energy) interaction on the colloidal and non-colloidal level as depicted in Fig. 4. The time scale

$$t_D \approx \frac{a^2}{D_0} = \frac{6\pi \eta a^3}{k_B T} \tag{7}$$

indicates the time for a particle to diffuse a distance equal to its radius a. Here, η is the matrix phase (solvent) viscosity and D_0 is the particle diffusivity,

$$D_0 = \frac{k_B T}{6\pi \eta_s a} \tag{8}$$

To distinguish Brownian and non-Brownian systems, both the primary aggregate size, the thermal energy $k_B T$, and the imposed external stress matter. A dimensionless group can be defined as the ratio of a characteristic diffusion time t_d to the characteristic shearing time $t_{\text{shear}} = \dot{\gamma}^{-1}$; this ratio is the Péclet number *Pe*. Hence the typical timescales for Brownian motion and for the flow process are compared and it is possible to estimate the shear stress at which the structure of the suspension is influenced by the flow:

$$Pe = \frac{\sigma a^3}{k_B T} \propto \dot{\gamma} t_d \tag{9}$$

where σ is the shear stress and $\dot{\gamma}$ the shear rate. At *Pe* much smaller than unity, Brownian motion dominates while at higher *Pe* structure distortions by shear flow are more pronounced: Brownian motion can no longer restore the structure of the suspension to its equilibrium state and shear thinning and shear thickening will occur. Orientation effects of the aggregates may become important if $Pe \ge 10$ [4].

2.3. Non-colloidal food rheology

A famous example for the influence of non-colloidal aggregates suspended in a matrix fluid on the rheology of the final food product is chocolate [13,16]. Chocolate consists mainly of cocoa fat, cocoa particles, sugar, milk powder, and emulsifiers which influences quality (stability, taste, perception, etc.), processing behavior, and rheological properties (viscosity and yield value) of the molten chocolate. A recent society-driven trend in food science is the replacement or the reduction of fat. This would be the creation of low calorie chocolates with the same perceived properties as the full fat product. The easiest way to achieve this goal is the reduction of the fat content (cocoa and milk fat) but this would lead to an increase of the chocolate melt viscosity resulting in problems during processing and in consumer acceptance. A more sophisticated approach would be to optimize the particle size distribution, i.e. increasing the packing fraction of the dispersed phase to keep the chocolate melt viscosity acceptable for processing. There are two ways of doing so: Optimizing the size distribution and/or shape of the dispersed solid particles. In the first case not only monodispersed aggregates but bi- to multi-modal aggregate size distribution will lead to reduction of the viscosity while keeping the solid volume fraction constant or to an increase of the solid volume fraction while keeping the viscosity constant [61]. The same effect can be achieved when modifying the shape of the aggregates from spheres to cylinders, rods or any other elongated structure [62-66]. The viscosity of mono-, bi-, and multi-modal spheres suspensions and fiber can be calculated according the Krieger–Dougerty equation $(\eta \simeq \eta_{solvent}(1 - \frac{c_v}{c_{v,max}})^{-[\eta]c_{v,max}})$ where $c_{v,\text{max}}$ is the maximum packaging that can be achieved for the aggregates [4]) and is presented in Fig. 5: A monotonic increase of the viscosity as a function of solids volume concentration, c_v , can be seen, with a strong increase as the total solid volume concentration approaches $c_{v,\max} \approx 0.6$ for sphere suspensions and $c_{v,\max} \approx 0.4$ for fiber suspensions.

The viscosity of concentrated suspensions is a function of shear rate and the slope in the shear-thinning domain depends on concentration (see Fig. 2(a)) and on particle characteristics, such as size distribution and shape. Fig. 6(a) shows the viscosity as a function of shear rate for these suspensions with total solid volume concentration of $c_v = 0.5$ and fiber fractions ranging from $0 \le c_{v,f} \le 0.33$. They are characterized by shear thinning at low shear rates and an upper Newtonian viscosity plateau η_{∞} . The suspension of spheres ($c_{v,f} = 0$) exhibits the least pronounced shear thinning and lowest viscosity. Both characteristics get more pronounced as the fiber fraction increases ($0.125 \le c_{v,f} \le 0.33$. The flow behavior of suspensions mixtures of fibers and spheres is similar to the properties of suspensions made up of fractions of fine and coarse spherical particles where the coarse particles are suspended in a fluid made up of the suspension of fine spheres. The upper Newtonian viscosities η_{∞} of such suspensions can be modeled using the Farris model [67,68]. The results indicate the extended applicability of the model for suspensions with shape polydispersity and propose a mixing rule for such systems as shown in Fig. 6(b).

For the discussion of the flow properties in the non-colloidal regime no information on the length scale relevant for colloidal interaction and aggregation was needed. However, one is able to optimize the final food product, in this



Fig. 5. Viscosity of suspensions of spheres and fibers as a function of the total solids volume concentration c_v . Enhancing particle packing while simultaneously reducing the liquid phase volume is an economically attractive alternative to fat substitution by other fluids: Increasing the modality leads to a higher solid volume fraction at constant viscosity ($\eta = const$. line) or lower viscosity at the same total solid volume faction ($c_v = const$. line).



Fig. 6. (a) Viscosity as a function of shear rate for suspensions with mixture of spheres and fibers and solids volume concentrations of $c_v = 0.5$. (b) Effect of polydispersed or structured particles on the rheology of concentrated non-Brownian suspensions: Viscosity for mixtures of fiber-shaped and sphere-shaped particles according to the Farris model for bidispersed spherical suspensions [62]. Independent of their chemical composition, fibers may serve as a structure enhancer of the composite system, providing an alternative to bulk polymer thickeners (c_v : total volume fraction of disperse phase; $c_{v,f}$: fraction of particles with fiber morphology).

case chocolate, by understanding the role of concentration, size and shape of the relevant ingredients, i.e. cocoa fat as matrix fluid and cocoa particles, sugar, and milk aggregates as dispersed phase. Such knowledge provides formulation scientists with additional freedom to control and manipulate the macroscopic rheology of suspensions [62,37,61,66] and emulsions [69,23].

2.4. Colloidal and macromolecular food rheology – polysaccharides and proteins

On the colloidal level, food research focuses on the understanding and utilization of the self-assembly of food ingredients. Molecular dispersions of single non-aggregated nano-particles, proteins, and biopolymers are normally studied in the dilute case and expressed by the intrinsic viscosity $[\eta]$. For the semidiluted and concentrated regimes



Fig. 7. (a) Progressive increase of the viscosity of locust bean gum powders, as revealed by steady shear rheometry. The flow curves illustrate the high sensitivity of Newtonian viscosity to both intrinsic viscosity [η] and concentration *c*. Since the concentration is kept constant (~ 1% w/w) the curves show the influence of [η], i.e. the influence of the molecular weight *M* that is increased by better extraction of the polysaccharides from the seeds. (b)–(d) By sectioning of carob endosperms (images show different cuttings) it can be shown that the relative proportion of galactomannan polysaccharides as well as molar mass is not uniformly distributed within the endosperm. The highest achievable viscosity based on this optimization was obtained in a lateral endosperm section (image (c), middle section) as depicted in (a).

different routes of description have to be taken for the individual material classes and mixtures of material classes. In the following we give two examples to illustrate the structure of colloidal systems and its feedback to rheological signatures: Biopolymer solutions (interaction biopolymer–biopolymer and biopolymer–solvent on the colloidal level) and protein stabilized emulsions (interaction on the colloidal level and link to micrometer level where engineering happens). Both cases illustrate the multistage approach taken in food science and map a way to establish the link between molecular structure and rheology that is common in colloid and polymer rheology.

2.4.1. Biopolymer solutions

As an illustration of how rheometric methods have had a useful impact on real biopolymer systems, consider the galactomannan polysaccharides as the major component of seed gums such as guar gum or locust bean gum. Powders obtained from such endosperms are widely used as water-soluble thickeners and stabilizers in food formulations. The flow curves in Fig. 7(a) illustrate typical shear-thinning behavior of semidilute locust bean gum solutions (ca 1% w/w), with a clearly defined Newtonian response at very low shear rates. For many nonionic polysaccharides above their entanglement concentration, the Newtonian viscosity scales as the third to fourth power of dimensionless concentration, $\eta_0 \sim (c[\eta])^{3-4}$, defined as the product of intrinsic viscosity [η] and polymer concentration c [70,71]. If the zero-shear viscosity can be determined in a rheometer under the appropriate conditions, then it provides a very sensitive means to assess changes in either [η] or c. For example, degradation occurring by any number of means (e.g. acid hydrolysis, shear degradation) or changes in solubility can be monitored efficiently through η_0 . For galactomannan polysaccharides in solution [η] $\sim M^{0.72}$, and thus it is possible to correlate viscosity reduction with molar mass M [72,73]. We

have previously used such methods to optimize the extraction and milling steps necessary to produce locust bean gum powders from the native biological tissues [74]. Progressive optimization led to powders with far higher viscosities than typical industrial products, a result of both preventing chain degradation and improving solubility. It was even found by sectioning the endosperm (see Fig. 7(b)–(d)) that the polysaccharides were not uniformly distributed within the endosperm even though their molar masses as determined by size exclusion chromatography were effectively identical. The highest achievable viscosity based on this optimization was obtained in a lateral endosperm section, which has 2–3 times higher achievable Newtonian viscosity than a corresponding industrial product (dark squares in Fig. 7(a)).

2.4.2. Protein stabilized emulsions

Proteins adsorbed at fluid/fluid interfaces are relevant to a number of phenomena in colloidal systems, such as the stability and flow behavior of food foams and emulsions [75,76]. Unlike small molecular weight surfactants, proteins such as β -casein [77], β -lactoglobulin [78,79], bovine serum albumin [80–82], or lysozyme [81] do not only decrease the interfacial tension of a lipid/water or air/water interface, but they strongly modify the rheological properties of the interface [83–85]. For example, emulsions develop flow-induced morphologies if the stresses due to the applied flow field can overcome the interfacial forces that favor the spherical drop morphology at rest [23,75,86]. Shape anisotropy of emulsion drops can be studied when the ratio of interfacial to hydrodynamic stresses is in a range in which drop sizes, time scales and shear stresses are experimentally accessible for rheological and optical measurements. The flow and interfacial properties of the system can be combined into a dimensionless group, the Capillary number $Ca = \sigma a/\Gamma$, i.e. the ratio of hydrodynamic stresses, σ , to interfacial stresses, Γ/a , where Γ is the interfacial tension and *a* the radius of the undeformed drop. Drop breakup occurs if *Ca* exceeds a critical Capillary number Ca_{crit} ; values for Ca_{crit} as a function of the drop to continuous phase viscosity ratio have been collected for various flow types and materials [87,88]. In particular, the deformation and breakup behavior of protein-covered emulsion drops is influenced by the rheological properties of the adsorption layer [89,90].

3. Summary and perspectives

Food products are made from natural materials, and therefore the ingredients possess innate structural and textural properties with tremendous impact on the flow behavior of the final food, which is a multi-scale material from the colloidal domain to the millimeter, from colloidal interaction to pure hydrodynamics. Figs. 3(a), 6(a) and 7(a) show flow curves for typical food materials such as chocolate melts and biopolymer solutions: The rheological measurement (rotational rheometer equipped with a Couette cell) is in all cases the same but the results can be discussed and interpreted using different approaches. The phenomenological approach can be successfully used to optimize and understand food process operation, the non-colloidal approach provides information on the role of different ingredients to eventually provide a full picture of the aggregation in complex food material compositions: Knowing the influence of specific ingredients on the flow behavior of complex fluids enables the design of manufacturing processes for materials with tailored properties. It is important to keep in mind that food materials are among the most challenging systems to study in experimental rheology. The 'simple' shear flow curves shown above are only the tip of the iceberg. Besides the more obvious challenges (time-dependence, nonlinearity, wall slip, etc.), many characteristics of food materials often need to be addressed using specialized measurement techniques, such as squeeze flow [91], extensional rheometry [92], vane or impeller rheometry [93,94], interfacial rheometry [85,90], or rheo-optics [44].

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