From firm to fluid - Structure-texture relations of filled gels probed under Large Amplitude Oscillatory Shear

T.J. Faber\textsuperscript{a,b,1,*}, L.C.A. van Breemen\textsuperscript{b}, G.H. McKinley\textsuperscript{c}

\textsuperscript{a}FrieslandCampina, PO box 1551, 3800 BN Amersfoort, The Netherlands
\textsuperscript{b}Polymer Technology, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands
\textsuperscript{c}Department of Mechanical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge - MA 02139, USA

Abstract

Soft-solid foods show a progressive transition from a viscoelastic solid state to a flowing fluid state when subjected to a large load. The engineering properties and sensory texture of soft-solid foods depend strongly on the rheological properties that characterize this fluidization. In this paper we use Large Amplitude Oscillatory Shear (LAOS) rheometry to quantify the texture of emulsion-filled food gels in terms of measurable material properties. We provide unambiguous rheological definitions for the firmness, rubberiness, softening and fluidization of soft-solid food gels. We propose a new measure for the load-induced solid-fluid transition, the fluidizing ratio, which quantifies the progression of damage and the degree of plastic flow in the soft-solid gel. We use another dimensionless measure, the thickening ratio, to reveal and characterize the resulting sequence of flow regimes. We use our rheological definitions to quantify the texture of zero-fat, low-fat and full-fat semi-hard cheese respectively. Our data provides evidence that the rate of two physical processes, microcrack nucleation and microcrack propagation, are controlled by the amount of fat emulsion in the gel and govern the rubberiness and brittleness of semi-hard cheese. By translating texture terminology into quantitative material properties measured using Large Amplitude Oscillatory Shear, we augment the capabilities of LAOS as an analytical tool for structure-texture engineering of soft-solid food gels.

Keywords: emulsion-filled gels, fluidization, food texture engineering, microstructure, LAOS

1. Introduction

Product reformulation, the replacement or removal of ingredients from a product in order to reduce caloric content, raw material costs, or carbon footprint, is a major theme in the structured processed-food industry [Norton et al. 2006, Almeida-Rivera et al. 2007]. Radical reformulation often leads to deficits in the sensory texture profile of the food product...
but numerous alternative structuring routes are available that potentially over-come this trade-off (Van der Sman and Van der Goot, 2009; Mezzenga et al., 2005; Dickinson, 2012; Stokes and Frith, 2008). Due to constraints of time and money, a systematic and effective approach is needed to choose between these structuring alternatives. Such a rational approach requires models that relate the food microstructure to its sensory texture profile (Aguilera, 2005).

Panel tests provide detailed and quantitative information on how formulation influences the sensory texture profile (Drake, 2007), however the datasets obtained do not give any clues to the relation between microstructure and texture. On the contrary, rheological measurements, such as the creep-recovery experiment for example, do provide information on the material microstructure, as well as quantitative measures for the ‘firmness’ and ‘rubberiness’ of soft-solid gels, which are measures quantifying the resistance of the gel to deform and flow respectively (Fig. 1a,b, Faber et al., 2016a). Hutchings and Lillford (1988) argue that narrowing down a texture attribute to a point on a curve of an instrumented texture measurement, is an over-simplification of the concept of sensory texture. They point out that the perceived texture is a measure of the process of breaking down structure, rather then the measurement of an equilibrium state. In previous work, we have treated the firmness of cheese, a soft-solid emulsion-filled gel, as a time-dependent, linear viscoelastic property (Faber et al., 2016b). The time-dependency of firmness reflects the dynamic aspect of the perception of this texture attribute (Scott Blair and Coppen, 1940). We developed an equation of state for the firmness containing two intrinsic material properties: the first is a scale factor or “quasi-property” denoted $G$, which sets the scale of the stress in the material, and the magnitude of this scale factor is determined by the extent to which the structural elements form a space-spanning network, the level of ‘crowding’ in the material and the stiffness of the structural elements (Palierne, 1990; 1991; Mellema et al., 2002; Pal, 2008; Stokes and Frith, 2008; Bot et al., 2014) The second material property in our equation of state, the fractional exponent $\beta$, quantifies the frequency and temporal response of the cheese and its magnitude is determined by the rate of rearrangements of protein colloids and aggregates (Mellema et al., 2002; Van Vliet et al., 1991; Van Vliet and Walstra, 1994).

Thus for food materials belonging to the class of soft-solid, emulsion-filled gels, a structure-texture engineering model is in place to keep the firmness on a constant level while changing the food’s composition. Developing structure-texture relations for the rubberiness of these types of food products is a more challenging task though. In Faber et al. (2016a) we defined rubberiness as the amount of strain recovered at the end of the creep / recovery experiment and, as in our expression for the firmness, we quantified rubberiness from the magnitude of
G, β and the time of duration of the experiment. Our equation predicts approximately equal
rubberiness for all cheese compositions in the linear viscoelastic regime, whereas panel tests
have shown that reduced fat cheese is perceived as more rubbery than full fat cheese [Yates and
Drake, 2007; Childs and Drake, 2009]. Our creep recovery tests showed that distinctions in
the rubberiness were only revealed when the material response became amplitude-dependent,
implying that rubberiness is a textural attribute that reflects the non-linear response of the
material. This is in line with the antonym for rubbery, which is ‘moldable’, and which has
connotations to the plastic nature of cheese [Davis, 1937]. This suggests that a rheological
measure for the rubberiness of cheese, should be based on a test that probes the yielding and
plastic response of the material [Barnes, 1999].

Large Amplitude Oscillatory Shear (LAOS) experiments are very suitable for simulta-
neously probing the time-dependent and amplitude-dependent response of materials in one
test protocol [Hyun et al., 2011]. Furthermore, data obtained in LAOS provides informa-
tion on the underpinning physical processes responsible for the collapse of microstructure
[Rogers et al., 2011b], which is a prerequisite for structure-texture modeling. In recent years,
a number of non-linear material functions have been proposed to facilitate physical interpre-
tation of the large datasets that are generated by modern rheometers in LAOS experiments
[Cho et al., 2005; Ewoldt et al., 2008; Rogers et al., 2011b; Dimitriou et al., 2013; Ewoldt
2013a]. Cho et al. (2005) were the first to consider strain- and strain-rate as two independent
orthogonal inputs in a controlled-strain LAOS experiment (henceforth denoted LAOStrain,
(Dimitriou et al., 2013)), and they additively decomposed the resulting stress into an elastic
and a viscous contribution. Ewoldt et al. (2008) elaborated on the concept of stress decom-
position, and used Chebyshev polynomials of the first kind to quantify the inter-cycle and
intra-cycle evolution of the elastic and viscous stresses. They showed that the coefficients
of the Chebyshev polynomials are physically relevant non-linear material functions. They
developed an ontological framework that characterizes and quantifies the evolution of the
shape of the Bowditch-Lissajous curves that visualize the response of a material to Large
Amplitude Oscillatory Shear. Their framework consists of appropriately-defined orthogonal
higher order dynamic moduli and viscosities, and descriptions of elastic and viscous non-
linearities in terms of physical mechanisms such as strain hardening and softening, or shear
thinning and thickening. This ontological framework was recently extended to incorporate
definitions for Large Amplitude Oscillatory Shear experiments performed in controlled stress
mode (LAOStress, Laeuger and Stettin, 2010; Dimitriou et al., 2013; Ewoldt, 2013a).

Rogers et al. (2011b) interpret the shape of the Bowditch-Lissajous curve of yield stress
fluids undergoing large amplitude oscillatory shear, in terms of a sequence of physical pro-
cesses (SPP) that describe the transition of these type of materials from a “solid” to a “soft” state. The dynamic aspect of this transition was denoted by active terms like “yielding”, ‘shear melting” and “fluidization” (Helgeson et al., 2007). The underpinning physical processes were described from the perspective of microstructural elements being trapped and escaping from surrounding cages, while the cages are themselves stretching and transitioning in anisotropic flows of clusters (Laurati et al., 2014, Rogers et al., 2011b, Min Kim et al., 2014). In this paper we also interpret the LAOS response of our soft-solid gels in terms of physical processes that lead to the progressive collapse of the underlying microstructure. However, the onset and progression of flow occurs not just because of particle and cluster rearrangement but also because of nucleation and propagation of cracks in the gel phase. This has recently been shown by Leocmach et al. (2014) to be the governing physical process that drives the collapse of brittle protein gels like cheese (the material under investigation in the present study).

Charalambides et al. (1995) use measures from solid mechanics such as energy release rate, fracture toughness and Young’s modulus to derive structure-function relations for Cheddar cheese. Their focus is thus on either the ultimate failure point or the initial stress-strain response of the compression curve. We find this approach to deriving structure-function relations somewhat limited, as both the time-dependency of the response, as well as the transition from viscoelastic to a elastoviscoelastic response remains uncharacterized. Both aspects are crucial in describing firmness and the transition of a soft-solid to a flowing fluid. Similar arguments hold against the use of fracture strain and fracture stress measured in torsion gelometry to derive structure-function relations of cheese. In this technique capstan shaped cylinders are twisted until fracture (Tunick and Van Hekken, 2002). Furthermore, both techniques require samples with a minimum level of firmness in order to be cut into a cylindrical shape that can hold its own weight. Shear rheometry does not have this constraints and can therefore also be applied to soft, spreadable foodstuffs.

Tariq et al. (1998) where the first to apply Large Amplitude Oscillatory Shear measurements on a soft-solid food material, being Mozzarella Cheese. They used spectral analysis, a viscoelastic constitutive model and a visual inspection of the Lissajous curve to quantify departure from linearity. Numerous studies now exist in which the Large Amplitude Oscillatory Shear protocol is used to characterize food materials, here we briefly discuss some typical examples and approaches to derive structure-texture relations from LAOS data. Van der Vaart et al. (2013) systematically changed the microstructure of dark chocolate melt suspensions to study the effect on the flow properties of the melts. These properties are a predictor for both the processability as well as the final sensory texture of the chocolate. Ng et al. (2011) analyzed the rheological properties of the gluten gel phase of wheat-flour dough. It is widely
believed that these properties have a strong influence on the breadmaking qualities. They used a constitutive model that describes the observed power-law relaxation, finite extensibility and progressive transition to a softer network. Sun et al. (2014) related the strain-stiffening of gelatin gels measured in LAOStrain to the molecular and network architecture using a constitutive model that accounted for the fractal nature of the network. Ptaszek et al. (2016) used LAOS to characterize the nonlinear rheological properties of fresh wet foams, prepared with egg white protein and stabilized using hydrocolloids. Melito et al. (2013) used statistical techniques to correlate panel test data to the magnitude of the non-linear material functions of Cheddar cheese. They compared the response to that of Mozzarella, in which the protein strands are more anisotropic and American cheese, which has a less compact and fused structure. Rogers et al. (2009) also correlated large strain experiments to the sensory profile of Cheddar cheese differing in age and fat content. These correlations pointed towards the extent of strain weakening as the critical measure to differentiate in texture attributes.

All of these previous studies contain elements required for building a structure-texture engineering model. However they don’t provide unambiguous rheological measures for “texture”, which are ultimately required to make an explicit connection between the sensory texture profile and the microstructure of soft-solid foods. In this paper, we use LAOStress and LAOStrain to quantify and characterize the solid-fluid transition of semi-hard cheese, a canonical example of a soft-solid, emulsion-filled, gel. We define quantitative measures for the firmness, rubberiness, brittleness and fluidization of cheese. First we show how firmness and rubberiness are quantified from the first-harmonic moduli and compliances. Then we demonstrate how the progression of damage and onset of flow are quantified from the evolution in the shape of the elastic Bowditch-Lissajous curve. We quantify the extent of solid-fluid transition with a new measure, the fluidization ratio, and characterize the resulting fluid with a modified thickening ratio. We show that the presence of a minimum amount of emulsion in the gel, gives rise to a highly non-linear elastoviscoplastic response and that fat content and water-protein ratio are the critical control parameters for achieving the correct level of firmness, rubberiness, brittleness and fluidization. We conclude by interpreting the magnitude of our quantitative rheological measures for the texture of soft-solid gels in terms of the microscopic physical processes that lead to the collapse of the cheese microstructure.

The differences from the work of Tariq et al. (1998) and the present work are threefold. First, the authors used the generalized Maxwell model with discrete relaxation spectrum to fit stress-strain responses. This required eight to eighteen parameters for a reasonable fit. We use a two-parameter fractional constitutive model not only to fit the response at a given strain amplitude and frequency, but also to predict the response at alternate strain amplitudes and
frequencies. I.e. our model is more compact and more effective. Second, we not only visualize the onset of a non-elliptical shape, we also quantify the shape evolution using geometrically defined moduli. Third, we quantify and characterize the onset of non-linearity using concepts of rubberiness, softening, fluidization, rate thickening and rate thinning.

2. Materials and methods

2.1. Cheese composition

Foil ripened Gouda rectangular cheeses (500 × 300 × 100 mm) were acquired at an age of 3-14 days and kept at 5°C to minimise compositional changes due to protein breakdown or (de-)solubilization of minerals [Lucey et al., 2005; O’Mahony et al., 2006]. Fat content was varied by using cheese from three fat classes: zero-fat (≈ 0% fat in dry matter, fidm), low fat (≈ 20% fidm) and full-fat (≈ 48% fidm). The cheese was analyzed for composition according to international standards (standard in brackets): pH (NEN 3775, Netherlands Normalisation Institute), l-lactic acid (ISO 8069, International Standard Organisation), protein (through total nitrogen / soluble nitrogen / anhydrous nitrogen fractions [Visser [1977]]), ash (Association of Official Analytical Chemists AOAC 930.30), calcium (insoluble calcium phosphate, AOAC 984.27), lactose (ISO 5762-2), water (=100-total solids (ISO 5534)), fat (ISO 1735) and chloride (ISO 5943). Weight fractions of protein, water and fat were converted to volume fractions according to the procedure outlined by Yang et al. (2011) taking the temperature-dependent densities of these main cheese constituents from Sahin and Sumnu (2006).

2.2. Cheese hydration

Cheese slices of approximately 60 × 60 × 4.5 mm were cut from a block coming from the core of the cheese using a wire cutter with a wire thickness of 0.3 mm. To provide cheese with different water / protein ratios (w/w%, denoted as w/p), the hydration procedure developed by Luyten (1988) was followed, with slight adaptations for shear rheometry. Part of the slices were hydrated in a salt solution, which had equal concentration of calcium (Ca²⁺) and chloride (Cl⁻) as in the moisture of the non-hydrated cheeses on a molar basis. For the fraction of soluble calcium (out of total calcium) a value of 20% was assumed (McMahon et al., 2005). Hydration was performed by submersing a single cheese slice for 1, 2, 4, 8, 16 or 24 hours in 250 ml of the salt solution. After this period, slices were taken from the liquid and excessive moisture was carefully removed with tissue paper. Just before and after hydration the slices were weighed. From the weight increase the new water/protein ratio was calculated, assuming that the concentration of soluble components in the cheese moisture remained the same and
that there was no net transfer of material from the cheese to the liquid. Slices were wrapped in aluminum foil and kept in the refrigerator for 2-3 days to allow for moisture equilibration (Luyten, 1988). From each cheese slice, three discs of 25 mm diameter and approximately 4.5 mm thickness were punched for parallel plate shear rheometry. The punch was designed such that contact area with the disc was minimized. Exact thickness of the disc was recorded using the gap width measurement of the rheometer. Samples that were tested at temperatures of $T = 25^\circ$C were allowed to equilibrate to room temperature ($T = 20^\circ$C) in aluminum foil for at least 30 minutes prior to further preparation.

2.3. Large amplitude oscillatory shear rheology

Measurements were performed with a Physica MCR501 Rheometer (Anton Paar, Austria) with a parallel plate geometry. To prevent slip, serrated upper and lower plates were used. The temperature of the lower plate was controlled with a Peltier stage, and the upper plate and cheese environment were thermally controlled with a cap hood. The upper plate was lowered with a speed of 25 $\mu$m/min until a normal force of 2 N (8 kPa) was reached. The gap width was recorded at that point and decreased by an extra 2% while keeping the normal force constant at 2 N to ensure full contact with the cheese, resulting in an initial gap width range of 4.2 - 4.4 mm. While conducting LAOStrain and LAOStress measurements, the gap distance was controlled by keeping the normal force at a fixed level of 2 N. After loading the sample between the two parallel plates it was heated at a heating rate of 0.5 $^\circ$C per minute until the desired temperature of either $T = 10^\circ$C or $T = 25^\circ$C was reached. The exposed surface area of the sample was covered with sunflower oil to minimise sample drying during the experiment. A maximum weight loss of 0.5 w/w% was recorded. Measurements were started 100 seconds after the equilibrium temperature was reached. Automatic adjusting time and averaging settings were used to avoid inter-cycle transient effects at constant stress or strain amplitudes.

To test if slip was eliminated the stress-strain response of a cycle was analyzed on the presence of one of the following indicators for slip: 1) irregular fluctuations in the stress-strain response of the Lissajous curves; 2) broadband noise in the Fourier Transform stress-strain response; 3) a-symmetry and unclosed loops in the Lissajous curve; 4) a magnitude of the ratio of the first and second harmonic of the Fourier Transform of the stress-strain response $n_1/n_2 > 0.1$ (Tariq et al., 1998); 5) Secondary loops in the Lissajous curve plotted from the viscous perspective (Tariq et al., 1998). In addition marker tests were performed on a selection of samples (Chakrabarti, 2006). From these analyses we conclude that we have minor slip in our measurements, that only occurs at strains well in the non-linear regime. The
marker tests also showed the absence of edge fractures. Strain amplitudes at which minor slip occurs are indicated with filled symbols in Fig. 5(a), Fig. 5(b), Fig. 7(a), and Fig. 7(b). Size independence of the material response was confirmed with measurements on a selected set of samples using an alternate plate diameter of 50 mm and a sample with a thickness of 2.3 mm respectively.

LAOStrain. Strain sweeps were conducted at a frequency $\omega = 5$ rad/s and a logarithmical increase of the strain amplitude $\gamma_0$ from 0.01 to 100 %, at temperatures of $T = 10 \, ^\circ C$ and $T = 25 \, ^\circ C$.

LAOSTress. Stress sweeps were conducted at a frequency $\omega = 5$ rad/s and a logarithmical increase of the stress amplitude $\sigma_0$ from 10 to $10^5$ Pa, at temperatures of $T = 10 \, ^\circ C$ and $T = 25 \, ^\circ C$.

Frequency sweep. To probe the time-dependency of the LAOStrain and LAOSTress response, strain sweeps and stress sweeps were repeated on different samples of the same test material, at a frequency $\omega = 0.2, 0.5, 1, \text{and} \, 2$ rad s$^{-1}$ and a temperature of $T = 25 \, ^\circ C$.

Creep compliance. A large step stress $\sigma_0$ was imposed on the test specimen of amplitude $\sigma_0 = 1000$ Pa and held at this value for $t = 100$ s at fixed measuring temperatures of either $T = 10 \, ^\circ C$ or $T = 25 \, ^\circ C$, while measuring the resulting strain $\gamma(t; \sigma_0)$. Subsequently the imposed stress was released and the resulting strain recovery or recoil was measured for $t = 100$ s.

2.4. Confocal Scanning Laser Microscopy (CSLM)

A Leica inverted CSLM (TCS SP2, DM IRE2) was used. The water/protein phase was stained with fluorescent isothiocyanate (FITC) and the fat phase with Nile red (0.1%/0.01%). Staining occurred by placing a sample of approximately $1 \times 5 \times 5$ mm$^3$ in a solution of the dyes in a glycerol / water / polyethylene glycol (PEG) (45/5/50 %) mixture for 30 minutes. All cheese manipulations (cutting and staining) were done at 8 °C in the cold room to prevent fat melting. Stained cheese was transported to the confocal microscope in a Petri dish placed in a polystyrene foam box containing frozen ice pack isolated by rubber foam. Image acquisition was done below 15 °C using a conditioned air flow. Single 2D images were obtained from the internal structure, by imaging at a depth of about 10 µm below the surface generated with a razor blade. The frame size of all images was 119.05 ×119.05 µm (1024 × 1024 pixels) obtained with a water immersion objective (63×, NA = 1.2). Baseline adjustment and auto-dye-finding were applied to all images acquired using LEICA Confocal Software (LCS).
3. Results and discussion

3.1. Firmness and Rubberiness

3.1.1. Firmness

In previous work we have demonstrated that the firmness $F$ of a food gel, is a time-dependent, linear viscoelastic property, which can best be measured in a controlled-stress experiment (Faber et al., 2016a). In Fig. 2(c) we show the result of measuring the firmness of cheese in a creep/recovery experiment at a time $t_f = 100$ s (circles), where the firmness is defined as the inverse of the creep compliance at the end of the creep phase,

$$F = 1/J(t_f)$$

which has units of Pa. Note that the time of $t_f = 100$ s is a user-defined choice. In (Faber et al., 2016b) we provide an extensive analysis of the effect of the loading conditions on the response of cheese in the creep-recovery test, and show that the creep response of cheese is well described by a power-law in time. A well-defined ‘equilibrium time’ therefore does not exist. However we also show that the effect of $t_f$ on the magnitude of the firmness $F$ is easily quantified once the intrinsic linear viscoelastic material properties of cheese are extracted from the creep response. The measurements presented in Fig. 2(c) are performed on zero-fat cheese (blue symbols), which is an unfilled gel (micrograph in Fig. 2(a)), and full-fat cheese (red symbols), which is an emulsion-filled gel (micrograph in Fig. 2(b)) and at two temperatures of $T = 10^\circ$C (filled symbols) and $T = 25^\circ$C (hollow symbols). Fig. 2(c) shows two effects of dispersing fat in the gel phase. First, at $T = 10^\circ$C, the fat acts as a strong firmness enhancer: the compliance $J(t)$ of zero-fat cheese (blue filled circle) decreases by a factor of seven compared to full-fat cheese (red filled circle), and the firmness $F$ thus increases by the same factor. Second, at $T = 25^\circ$C, the full-fat curve shows a clear inflection point, marked with a cross, whereas the slope of the creep curve for zero-fat cheese at $T = 25^\circ$C continuously declines. We have shown in previous work that this inflection point, marks a transition from primary creep to tertiary creep and ultimately fracture, caused by the formation and propagation of microcracks in the gel phase (Faber et al., 2016b; Leocmach et al., 2014). This signature of a non-linear response, should be avoided when measuring the firmness $F$, since this textural attribute is defined in the linear viscoelastic regime. This implies that when comparing firmness of several materials a suitable combination of stress amplitude $\sigma_0$ and creep time $t_f$ must be chosen (the ‘stress-time’ (Davis, 1937; Faber et al., 2016b)), such that none of the materials display a non-linear response. This requires either an iterative testing procedure, or very small stress amplitudes and times. Both are inconvenient, especially when a large
number of formulations, varying over a wide range of firmness, need to be measured. A Large Amplitude Oscillatory Shear-experiment in controlled-stress mode (LAOStress, Dimitriou et al., 2013), does not have the limitation of imposing a single loading condition per test run. Instead, a range of stress amplitudes $\sigma_0$ can be imposed, where the lower limit of $\sigma_0$ can be set such that for all the materials tested the material response within the linear viscoelastic regime is probed, regardless of their firmness. In the same test run, the non-linear properties can be probed as well, by choosing the appropriate upper-limit of the stress amplitude range.

In the LAOStress experiment, a cosinusoidal oscillating stress $\sigma(t)$ is imposed (Ewoldt, 2013a), defined by:

$$\sigma(t) = \sigma_0 \cos \omega t$$

where the time-scale of the oscillation is set by the frequency $\omega$. We define the firmness $\hat{F}$, measured using a LAOStress experiment at a frequency $\omega_f$, as the inverse of the magnitude of the complex creep compliance,

$$\hat{F} \equiv \frac{1}{|J^*(\omega_f)|}$$

which has units of Pa, like the definition for the firmness $F$ presented in Eq. (1). In the LAOStrain experiment, a sinusoidal oscillating strain $\gamma(t)$ is imposed, defined by (Ewoldt, 2013a):

$$\gamma(t) = \gamma_0 \sin \omega t$$

where the maximum strain is set by the strain amplitude $\gamma_0$, and the time-scale by the frequency $\omega$. When the imposed strain is in the linear viscoelastic range, we can define a linear viscoelastic complex shear modulus $G^*(\omega)$. Substituting the relation (Ferry, 1980)

$$|J^*(\omega)| |G^*(\omega)| = 1$$

in the oscillatory-stress based definition of the firmness $\hat{F}$, Eq. (3), we obtain

$$\hat{F} \equiv |G^*(\omega_f)| = \tilde{F},$$

i.e. at a test frequency $\omega_f$ and temperature $T$ the magnitude of the firmness $\hat{F}$ of a material measured using LAOStrain is equal to the magnitude of the material’s firmness $\tilde{F}$ measured using LAOStress. In appendix A we show that this is indeed the case.

For soft-solid gels that display power-law stress relaxation over a broad range of time-scales (e.g. cheese), the magnitude of the complex shear modulus $G^*(\omega)$ is accurately described by (Jaishankar and McKinley, 2013):

$$|G^*(\omega)| = G_0 \omega^\beta$$
in which \( G \) and \( \beta \) are the material parameters of the Scott Blair model. The ‘quasi-property’ \( G \) is a scale factor that sets the scale of the stress in the material with units of Pa s, the dimensionless fractional exponent \( \beta \) quantifies the temporal and frequency response of the material. The magnitude of linear viscoelastic material functions, such as the creep compliance \( J(t) \) in Eq. (1), the shear complex compliance \( J^*(\omega) \) in Eq. (3), and the complex shear modulus in \( G^*(\omega) \) in Eq. (5) are readily interconverted and can also be expressed in terms of these two intrinsic material properties \( G \) and \( \beta \) (Jaishankar and McKinley 2013; Table A.1 in Faber et al. 2016b). Fitting the Scott Blair model’s expression for the creep compliance (Eq. (A.10) in Faber et al. 2016b) to the data for the creep response of full-fat cheese at \( T = 10 \, ^\circ\text{C} \) (red, filled) and zero-fat cheese at \( T = 10 \, ^\circ\text{C} \) and \( T = 25 \, ^\circ\text{C} \) (blue, filled and hollow) in Fig. 2(c), shows that the response of these three samples is indeed in the linear viscoelastic regime (fit not shown here, Faber et al. 2016a,b).

Fourier transformation of a non-linear viscoelastic stress response, \( \sigma(t; \omega, \gamma_0) \) to an imposed oscillatory strain gives (Ewoldt, 2013a):

\[
\sigma(t; \omega, \gamma_0) = \gamma_0 \sum_{n=odd} \left[ G'_n \sin n \omega t + G''_n \cos n \omega t \right]
\]

where the non-linear material functions \( G'_n(\omega, \gamma_0) \) and \( G''_n(\omega, \gamma_0) \), are the \( n \)th harmonic dynamic elastic and viscous moduli respectively. The first-harmonic dynamic elastic and viscous modulus \( |G'_1(\omega, \gamma_0), G''_1(\omega, \gamma_0)| \), are average measures of the dynamic modulus over one full cycle (Ewoldt et al. 2008). In the linear viscoelastic regime, these moduli are equal to the shear storage modulus \( G'_1(\omega, \gamma_0)=G'(\omega) \), and shear loss modulus \( G''_1(\omega, \gamma_0)=G''(\omega) \) respectively. From \( G'_1(\omega, \gamma_0) \) and \( G''_1(\omega, \gamma_0) \) we calculate the magnitude of the first-harmonic complex modulus, \( G^*_1(\omega, \gamma_0) \), using

\[
|G^*_1(\omega, \gamma_0)| = \sqrt{G'_1^2 + G''_1^2}
\]

The magnitude of the complex modulus \( G^*(\omega) \), and thus the firmness \( \hat{F} \), is equal to the plateau value for the first-harmonic complex modulus \( G^*_1(\omega, \gamma_0) \).

In Fig. 3(a) we show values of the first-harmonic complex modulus \( G^*_1(\omega, \gamma_0) \) determined in a strain sweep at a frequency \( \omega = 5 \, \text{rad s}^{-1} \), for samples of the same test materials as used in Fig. 2(c). We have plotted the magnitude of the firmness \( \hat{F} \) as circles on the vertical axis. The shading on the left ordinate axis, with a gradient from top to bottom indicates schematically the ranking of the samples from firm to soft. As in Fig. 2(c) the response of full-fat cheese at \( T = 10 \, ^\circ\text{C} \) (red, filled circle) and zero-fat cheese at \( T = 10 \, ^\circ\text{C} \) and \( T = 25 \, ^\circ\text{C} \) (blue, filled and hollow circles) is predominantly linear viscoelastic, the order of ranking from firm to soft is identical for these samples to the order in Fig. 3(a). Although firmness is a time-dependent
property and the timescales of the measurements in Fig. 2(c) and Fig. 3(a) vary widely, this does not influence the ranking on firmness. The magnitudes for the fractional exponent $\beta$ of the three samples, which quantify temporal effects on the firmness measurements $F$ and $\hat{F}$, only show a small variation from $0.15 < \beta < 0.19$. In the linear viscoelastic regime the ranking on firmness is thus governed by the difference in magnitude of the quasi-property $G$.

The firmness measurement of full-fat cheese at $T = 25 \, ^\circ\text{C}$ is based on a non-linear response in Fig. 2(c), whereas in Fig. 3(a) the firmness measurement is based on a linear viscoelastic response. As a result the full-fat cheese at $T = 25 \, ^\circ\text{C}$ is ranked firmer than the zero-fat cheese at $T = 10 \, ^\circ\text{C}$ in Fig. 3(a) whereas in Fig. 2(c) the ranking between the two cheeses types is reversed. This demonstrates that the propensity for a soft-solid material to yield has a significant effect on the apparent magnitude of the firmness in a creep / recovery experiment.

3.1.2. Rubberiness

In previous work we have defined ‘moldability’ as the antonym for ‘rubberiness’ (Faber et al., 2016a). Moldability refers to the plastic nature of cheese (Davis, 1937): if the loading of the cheese is severe enough, part of the imposed strain is irrecoverable, and the sample deformation becomes permanent. In the stress-strain curve of a ductile plastic material loaded in tension or compression, the strain beyond which deformation will be permanent is clearly visible as a local maximum in the stress. This maximum is referred to as the ‘yield point’, and the coordinates give the yield stress ($\sigma_y$) and yield strain ($\gamma_y$) respectively. Reiner and Scott Blair (1967) define yielding as an abrupt event, which marks the beginning of ‘flow’ in a material, where ‘flow’ is defined as non-recoverable deformation proceeding in time. These definitions show that the concepts of rubberiness, plasticity, flow and yielding are strongly interrelated.

In the creep phase of the creep / recovery experiment, the yielding event is marked by an inflection point in the compliance-time curve, defined by

$$\min \frac{dJ(t)}{dt} = \sigma_0^{-1} \min \frac{d\gamma(t)}{dt} = \sigma_0^{-1} \dot{\gamma}(t)_{\text{min}}$$

(10)

where $\dot{\gamma}(t)_{\text{min}}$ is the minimum in the instantaneous strain rate profile (computed by differentiating the measured shear strain $\gamma(t)$). The yield point in a non-linear creep / recovery experiment, is thus the point in time where the strain rate in the material reaches a local minimum value. In Fig. 2(c) the yield point for full-fat cheese at $T = 25\, ^\circ\text{C}$ (hollow red squares) is clearly visible, and is denoted with a cross. The time $t$ at which yielding occurs is denoted as the yield-time $t_y$ and has a magnitude of $t_y = 45$ seconds. For times $t < t_y$ the deformation is
predominantly that of a viscoelastic solid, and for materials that display power-law relaxation, such as cheese, the strain-rate decreases exponentially in time so that, \( \dot{\gamma}(t) \propto t^{-\beta} \) for \( t < t_y \), where \( \beta \) is the fractional exponent. This regime is commonly denoted as ‘primary creep’ or ‘Andrade’ creep (Andrade, 1910). The yield-time \( t_y \) marks the transition from ‘primary’ creep to a deformation regime where the strain-rate \( \dot{\gamma}(t) \) diverges as \( (t_y - t)^{-1} \), as a result of rapid growth of fractures in the sample (Leocmach et al., 2014). This regime is denoted as ‘tertiary’ creep. The transition regime of ‘secondary’ creep, is the region of irrecoverable or plastic flow. If the stress is released from the sample during the secondary creep regime, the extent of plastic flow can be measured as the unrecoverable strain \( \gamma_\infty(t) \), or unrecoverable compliance \( J_\infty(t) = \gamma_\infty(t)/\sigma_0 \), in the recovery phase of the creep/recovery experiment. The overall material response is then commonly called elastoviscoplastic.

In Faber et al. (2016a) we have defined rubberiness as the relative amount of recovered compliance,

\[
R = \frac{J(t_f) - J(t_f + \Delta t_r)}{J(t_f)}
\]

where \( t_f \) is the time of observation for measuring firmness (i.e. the elapsed time at the end of the creep phase) and \( \Delta t_r \) is the elapsed time of recovery at which we measure the rubberiness \( R \). In Fig. 2(c) the absolute extent of unrecovered compliance for each of the four samples, is depicted by the last square marker of each creep/recovery curve, at time \( t = \Delta t_r + t_f = 200 \) s. The magnitude of the rubberiness \( R \) of each sample is plotted as a triangle on the right-hand ordinate axis, using a coloring scheme that corresponds to the colors used for the samples of the curves. The three samples that do not yield during the creep phase, full-fat cheese at \( T = 10 \) °C (red, filled triangle) and zero-fat cheese at \( T = 10 \) °C and \( T = 25 \) °C (blue, filled and hollow triangles) show a small variation in the magnitude of the rubberiness \( R \). We have shown previously that in the linear viscoelastic regime the magnitude of \( R \) is governed by the magnitude of the fractional exponent \( \beta \), not by the quasi-property \( G \), and that the recorded values of the unrecovered compliance is merely a finite time-effect (Faber et al., 2016b). For times \( \Delta t_r \gg t_f \), the amount of strain will asymptotically approach zero and the rubberiness \( R \approx 1 \).

Various sources report that reduced-fat cheese is perceived as more rubbery than full-fat cheese (Yates and Drake, 2007; Childs and Drake, 2009), a discrimination we do not find for the three samples discussed above. The measurement of the rubberiness of the full-fat cheese at \( T = 25 \)°C in Fig 2(c) (red hollow triangle) shows that it requires a yielding event to make the discrimination between zero-fat and full-fat cheese. As a result of the yielding and
subsequent plastic flow, the rubberiness of the full-fat cheese at \( T = 25^\circ\text{C} \) is a factor of 2.5 lower than the three non-yielded samples. This suggests that incorporating a measure of ‘the resistance to yield’ will provide a more suitable definition for rubberiness than ‘the extent to which a sample return to its original shape’ proposed by Faber et al. (2016a).

In order to measure the resistance to yield in the creep / recovery experiment, a stress-time loading must be chosen that leads to yielding of all the samples in the creep phase. This requirement for the loading condition is exactly the opposite of what we required for the firmness measurement in the previous section, and implies that firmness and rubberiness cannot easily be measured in a single creep / recovery experiment. Furthermore, if we want to use Eq. (11) to quantify rubberiness, the imposed load must lead to a elastoviscoplastic deformation that is viscometric for the complete duration of the creep phase: wall slip, fracture or inhomogeneous flow of the sample will complicate the analysis. These two constraints on the loading conditions again require an iterative testing procedure, and are nearly impossible to meet when the firmness and yield strains of the samples vary widely. So the same arguments discussed earlier also hold for rubberiness and rationalize why a LAOS experiment is preferred over a series of creep / recovery experiments.

In LAOStrain, the resistance to yield is quantified by the magnitude of the yield strain amplitude \( \gamma_{0,y} \), and therefore we define the rubberiness \( \hat{R} \): \[
\hat{R} \equiv \gamma_{0,y}.
\] (12)

The rubberiness \( \hat{R} \), measured in LAOStrain, is thus a dimensionless quantity, just as the rubberiness \( R \) measured with the creep / recovery experiment (Eq. (11)). The magnitude of the yield strain amplitude \( \gamma_{0,y} \) is determined using the relation

\[
\frac{|G_1(\omega,\gamma_0)| - |G^\prime(\omega)|}{|G^\prime(\omega)|} > y
\] (13)

where we use \( y = 0.01 \) as the measure for yielding. The magnitudes of the rubberiness \( \hat{R} \) of zero-fat (blue) and full-fat cheese (red), at the two temperatures of \( T = 10^\circ\text{C} \) (filled symbols) and \( T = 25^\circ\text{C} \) (filled symbols), are plotted as triangles on the horizontal axis in Fig. 3(a). Note that the full-fat cheese at \( T = 10^\circ\text{C} \) and \( T = 25^\circ\text{C} \), have swapped position in the order of ranking on rubberiness as compared to Fig. 2(b). The same holds for the zero-fat cheese measured at \( T = 10^\circ\text{C} \) and \( T = 25^\circ\text{C} \).

In this section we have argued that one can interchangeably use the LAOStress- or LAOStrain-method to measure the firmness of a food gel. However the two shearing protocols result in different magnitudes for the rubberiness both in a relative and absolute sense, as we demonstrate in Appendix A. There we prove that that the magnitude of the material rubberiness \( \hat{R} \)
measured using LAOStrain, is equal to the magnitude of the rubberiness $\tilde{R}$ measured using LAOStress, normalized by the firmness of the material, $\tilde{R} = \tilde{R}/\tilde{F}$. We thus have to select between the two methods for quantifying rubberiness. We prefer the LAOStrain-measure for the rubberiness $\tilde{R}$ over the LAOStress-measure $\tilde{R}$ for three reasons. Firstly, LAOStrain provides a measure for the rubberiness that is independent of the firmness of the material, whereas the LAOStress method does not. The second argument is that $\tilde{R}$ has the (dimensionless) unit of accumulated material strain, just as in the definition of the rubberiness $R$ measured in the creep / recovery experiment, whereas $\tilde{R}$ has units of stress. In food rheology, it is common practice to reserve units of Pa for quantifying the stiffness, hardness or firmness of food materials (Davis [1937], Sherman [1970], Duizer et al. [2011]). A final practical argument in favour of LAOStrain measurements, is that they more readily allow probing the material response deeper into the fluid regime, which we demonstrate in Fig. 3(b,c). We have plotted the intra-cycle maximum of the stress during LAOStrain measurement, $\sigma_{\text{max}}$ (unfilled squares), as a function of the imposed strain amplitude, $\gamma_0$, for zero-fat (blue, Fig. 3(b)) and full-fat cheese (red, Fig. 3(c)). The intra-cycle maxima are calculated using Eq. (8). In Fig. 3(b,c) we have also plotted the intra-cycle maxima of the measured strain $\gamma_{\text{max}}$ (filled squares), as a function of the imposed stress amplitude $\sigma_0$, using Eq. (A.2). The combination of the stress-induced rise in the compliance $J_1'(\omega, \sigma_0)$, and the simultaneous increase in the stress amplitude $\sigma_0$ in LAOStress, results in a self-catalyzed, abrupt failure of the material which is absent in LAOStrain. As a result, the range of stress amplitude $\sigma_0$ over which deformations can be controlled in LAOStress, is smaller than the range of intra-cycle maxima that can be measured in the stress $\sigma_{\text{max}}$ during LAOStrain deformation.

3.2. Softening vs. Fluidization

Fig. 3(a) shows three routes towards a decrease in the first harmonic complex modulus $G_1'(\omega, \gamma_0)$ of a full-fat cheese at $T = 10^\circ$C (red squares): 1) reformulation by removing all the fat (from filled red circle to filled blue circle); 2) increasing the temperature $T$ (indicated by the white arrow from red filled square to red unfilled square), and 3) increasing the imposed strain amplitude $\gamma_0$ (indicated by the red dashed arrow alongside the red filled squares). A popular descriptive term for a material with low modulus (or high compliance) is ‘soft’ (Ewoldt [2013b]). Hence a rheological definition of ‘softening’ measured using LAOStrain could be ‘a decrease in the first harmonic complex modulus $G_1'(\omega, \gamma_0)$’. ‘Soft’ has connotations with ‘pleasant touch’ (Essick et al. [2010]). This suggests that the ‘softening’ of cheese always increases the user affinity and that any of the three routes towards a decrease in $G_1'(\omega, \gamma_0)$ are suitable. Below we show that this is not the case and that the term “softening” requires further
specification.

Route 1, reformulation of the cheese by removing fat, makes the cheese less caloric, and
less firm, but also more rubbery. Calorie reduction is an incentive for cheese reformulation,
however an increase in rubberiness is undesired (Yates and Drake [2007]). Furthermore, we
have shown in previous work (Faber et al. [2016b]) that the reduced firmness of the zero-fat
cheese will lead to sagging of the cheese blocks during storage, which is a second undesired
side-effect of the cheese reformulation. Route 2, increasing the temperature $T$, decreases
the firmness (indicated by the white arrow in Fig. 3[a]) and has only a minor effect on the
rubberiness. By storing the cheese at $T = 10^\circ C$ sagging will not be an issue. Increase of the
cheese temperature in the mouth will induce the transition from firm to soft as indicated by
the white arrow in Fig. 3[a]). Route 3, increasing the strain amplitude $\gamma_0$, does not affect the
caloric content, nor the firmness, nor the rubberiness of the cheese, but transitions the full-fat
cheese from a more solid to a more fluid state, as indicated by the dashed arrow in Fig. 3[a].

The example above demonstrates that ‘softening’ of a soft-solid gel can have very different
origins from a rheological perspective, and is not always favorable from a user affinity or ma-
terial processing perspective. It is therefore too generic a measure to build structure-property
relations on, and we propose to use two separate terms to describe the reduction in the mod-
ulus $G_1^*(\omega, \gamma_0)$ of soft-solid food gels such as cheese. We define ‘softening’ as a decrease in
the firmness, i.e. by changing the composition or the temperature of the material. We thus
reserve the term ‘softening’ for modifications of the intrinsic, linear viscoelastic properties of
the food gel. In Fig. 3[a], softening is depicted by the vertical gradient in the shaded area to
the left.

For strain-induced softening, a process which does not change the intrinsic material prop-
erties of the cheese, we use the term ‘fluidizing’. This term is commonly used in the study of
granular materials (Kunii and Levenspiel [1991]), to indicate the transition from a static solid-
like to a dynamic fluid-like state. Recently the term has gained a foothold in LAOS studies
on yield stress fluids, to separate the event that marks yielding, from the subsequent process,
i.e. the progression of irreversible flow (Rogers et al. [2011a] Laurati et al. [2014] Min Kim
et al. 2014). In Fig. 3[a] we have marked yielding by a point on the abscissa (triangles) and
use it to quantify rubberiness. Fluidization of the full-fat cheese at $T = 10^\circ C$, is indicated
by the dashed arrow to demonstrate it is a process rather than an event. Fluidization covers
a range of strain amplitudes that is either broad, such as for the full-fat cheese in Fig. 3[a]
(red squares), or small, like for the zero-fat cheese (blue squares). Fig. 3[a] shows that the
broadness of the fluidizing regime, is inversely correlated to the yield strain amplitude $\gamma_0$,y,
and thus rubberiness $\tilde{R}$. In Fig. 3[a], the increase the rubberiness is depicted by the horizontal
gradient in the shaded area at the bottom of the figure.

Our measurements show that the addition of fat to zero-fat cheese increases the propensity of semi-hard cheese to soften when temperature is increased, as well as the propensity of the cheese to fluidize under an increasing load. Both temperature-induced softening, as well as load-induced fluidization occur during oral processing and have connotations to the in-mouth “melting” of soft-solid food gels. Our distinct rheological definitions for ‘softening’ and ‘fluidization’ allow for separation of these two contributions to ‘meltability’ and to identify the structure parameters that drive the melting sensation of soft-solid food gels such as semi-hard cheese.

3.3. Damage progression and failure

To visualize the deformation-induced fluidization of cheese, we plot the material response to the imposed sinusoidal oscillating strain as ‘Bowditch-Lissajous’ curves of the material response, henceforth referred to compactly as Lissajous plots. In Fig. 4(a)-(c) we show Lissajous plots for a selection of strain amplitudes $\gamma_0$ from oscillatory strain sweeps performed on zero-fat cheese (blue lines) at $T = 10^°C$, and at frequencies of (a) $\omega = 1$ rad s$^{-1}$ and (b) $\omega = 5$ rad s$^{-1}$. The elliptical shapes of the curves in Fig. 4(a) and (b) indicate that the material response is linearly viscoelastic for strain amplitudes $\gamma_0 \leq 0.2$. The trajectory of the ellipse $\{\gamma(t), \sigma(t)\}$ is described by (Ng et al., 2011)

$$\sigma^2 - 2\sigma \gamma G' + \gamma^2 (G'^2 + G''^2) = G''^2 \gamma_0^2$$

We have shown previously that within the range of $1 \text{ rad } s^{-1} < \omega < 5 \text{ rad } s^{-1}$, zero-fat cheese displays power-law relaxation, and the magnitude of the storage and loss moduli $[G'(\omega), G''(\omega)]$ that enter Eq. (14) are described by the power-law equation of state or ‘Scott Blair element’ (Faber et al., 2016b; Jaishankar and McKinley, 2013) such that:

$$G'(\omega) = G \omega^\beta \cos (\pi \beta / 2)$$

$$G''(\omega) = G \omega^\beta \sin (\pi \beta / 2)$$

To compare this model with the data we need to determine the two material parameters $G$ and $\beta$. By performing a strain-sweep of the first-harmonic dynamic moduli $G'_1(\omega, \gamma_0)$ and $G''_1(\omega, \gamma_0)$ at $\omega = 1$ rad s$^{-1}$, reading out the magnitude of the phase angle $\delta$ reported by the rheometer software in the linear viscoelastic regime, and using the relation $\tan(\delta) = G''(\omega)/G'(\omega) = \tan (\pi \beta / 2)$, we obtain the magnitude of $\beta = 0.19$. The magnitude of the quasi-property $G = 1.4 \times 10^4$ Pa $s^\beta$ is readily obtained by reading out the magnitude of the
first-harmonic complex modulus \( G^*(\omega, \gamma_0) \) in the linear viscoelastic regime, and using the relation \( |G^*(\omega)| = G_0 \beta \) \cite{Jaishankar and McKinley, 2013}.

Fig. 4(a) and (b) show that the model described by Eq. (14) and Eq. (15) (circles), correctly predicts the shape of the ellipses as a function of strain amplitude \( \gamma_0 \) and frequency \( \omega \) in the linear viscoelastic regime. In Fig. 4(c), the strain amplitude exceeds the yield strain amplitude of zero-fat cheese \( \gamma_0 > \gamma_{0,y} \approx 0.3 \) and the material response becomes elastoviscoplastic (EVP). The curvature of the Lissajous plot changes from the elliptical shape predicted by the model (dashed blue line), to a ‘banana-shaped’ curve (blue continuous line), which indicates a non-linear material response and is typical for damaged elastomers \cite{Merabia et al., 2010}. The ‘banana-shape’ is also encountered when loading rubbery food materials like dough \cite{Ng and McKinley, 2008} and Mozzarella cheese \cite{Melito et al., 2013} in LAOStrain mode.

In order to quantify the intra-cycle non-linearities such as those shown in Fig. 4(c), Cho et al. \cite{Cho et al., 2005} proposed additively decomposing the total stress into an elastic (') and a viscous ("') part:

\[
\sigma_{TOTAL} = \sigma^\prime(x) + \sigma''(y)
\]  

(16)

where the arguments \( x \) and \( y \) are the normalized strain and normalized strain-rate respectively

\[
x \equiv \gamma(t)/\gamma_0 = \sin \omega t \tag{17}
\]

\[
y \equiv \dot{\gamma}(t)/\dot{\gamma}_0 = \cos \omega t
\]

The magnitude of the elastic stress \( \sigma' \) and viscous stress \( \sigma'' \) are related to the Fourier decomposition of the stress-signal in Eq. (8) by \cite{Cho et al., 2005, Ewoldt et al., 2008}

\[
\sigma' = \frac{\sigma(\gamma, \dot{\gamma}) - \sigma(-\gamma, -\dot{\gamma})}{2} = \gamma_0 \sum_{n \text{odd}} G'_n(\omega, \gamma_0) \sin n \omega t
\]

\[
\sigma'' = \frac{\sigma(\gamma, \dot{\gamma}) - \sigma(-\gamma, -\dot{\gamma})}{2} = \gamma_0 \sum_{n \text{odd}} G''_n(\omega, \gamma_0) \cos n \omega t
\]  

(18)

The dashed red line in Fig. 4(c) shows the model prediction of the intra-cycle evolution of the elastic stress \( \sigma' \), which is described by the linear relation \( \sigma'(\omega, \gamma) = G_0 \beta \cos(\pi \beta/2) \gamma \). The actual measured response of \( \sigma'(\gamma) \) (solid red line) shows positive curvature, a signature of non-linearity \cite{Ewoldt and Bharadwaj, 2013}. The predicted maximum in the elastic stress of the linear viscoelastic model is given by \( \sigma'_{max}(\omega, \gamma_0) = G_0 \beta \cos(\pi \beta/2) \gamma_0 \) (hollow square) and deviates from the measured magnitude of \( \sigma'_{max} \) (filled square). This deviation is a second signature of non-linearity in the material response. The same two features of non-linearity are observed in Fig. 4(d) where we have plotted the measured stress against the imposed strain rate, to provide a ‘viscous perspective’ of the three-dimensional space curve \( \sigma(\gamma, \dot{\gamma}) \) \cite{Ewoldt et al., 2008}. The predicted evolution of the viscous stress as a function of strain...
rate is given by $\sigma''(\omega, \dot{\gamma}) = G''(\omega)\dot{\gamma}/\omega = G\omega^{\beta-1} \sin (\pi\beta/2) \dot{\gamma}$ and is plotted as a red dashed line. The predicted maximum in the viscous stress is given by $\sigma''_{\text{max}}(\omega, \gamma_0) = G''(\omega)\gamma_0 = G\omega^\beta \sin (\pi\beta/2) \gamma_0$ and is plotted as an unfilled circle in Fig. 4(c) and (d). The actual value of the stress at a strain of $\gamma = 0$ (corresponding to the viscous stress in the cheese) is shown by the filled circle.

Fig. 4(c) shows that in the elastoviscoplastic regime, the linear viscoelastic constitutive model over predicts the maximum in the elastic stress; the damage accumulating in the gel causes a loss of strength in the elastic network (Mari et al., 2014). In Fig. 5(a) we visualize the inter-cycle progression of damage in zero-fat cheese, by plotting the measured response $\sigma'_{\text{max}}(\gamma_0)$ (squares), and compare these to the prediction of the linear viscoelastic constitutive model (solid line). The cycles denoted with roman numbers correspond to the cycles highlighted in Fig. 3(b) and depicted in Fig. 5(a). Up to the yield point at cycle I, the maximum elastic stress grows with strain amplitude at a rate predicted by the fractional constitutive model: $G\omega^\beta \cos (\pi\beta/2) = \hat{F} \cos (\pi\beta/2)$ (Eq. (15),(6)), where $\hat{F}$ is the frequency-dependent firmness measured in LAOStrain. For strain amplitudes below the yield strain amplitude $\gamma_0 < \gamma_{0,y}$ (with $\gamma_{0,y} \equiv \hat{R}$, the magnitude of the rubberiness measured in LAOStrain), all of the strain is recoverable, even though there is viscous dissipation as denoted by the circles. The rate of recovery is governed by the magnitude of the fractional exponent $\beta$, and the time-scale of the deformation $\omega$ (Faber et al., 2016a). Between cycle I and II, at strain amplitudes $\gamma_0 > \gamma_{0,y}$, the formation of microcracks result in an elastoviscoplastic response (Faber et al., 2016b; Leocmach et al., 2014), which leads to a decrease in the inter-cycle growth rate of the maximum elastic stress $\sigma'_{\text{max}}(\gamma_0)$ and an increase in the amount of irrecoverable strain. At cycle II a global maximum in $\sigma'_{\text{max}}(\gamma_0)$ is reached, which we denote as the elastic failure stress $\sigma'_{f}$ of the material. The failure strain at this point has a value of $\gamma_{0,f} \approx 0.7$. Beyond the failure point, the elastic stress declines. The most probable cause is microcracks in the protein network percolating into larger fractures (Leocmach et al., 2014).

The response of the maximum elastic stress $\sigma'(\gamma)$ in the full-fat cheese, an emulsion-filled gel, is remarkably different from the zero-fat cheese, an unfilled gel. Fig. 5(b) shows that the initial growth-rate of $\sigma'_{\text{max}}(\gamma_0)$ is larger for the full-fat cheese than for zero-fat cheese, as a result of the higher firmness. However, since the magnitude of the rubberiness of full fat cheese is smaller, the material displays an elastoviscoplastic response prior to cycle I. The probable cause for the shift of the plastic response towards lower strain amplitudes is localisation of strains in the gel phase, caused by the presence of the micron-sized spherical fat globules, which plasticize the matrix (Hall, 1991; Smit et al., 1999). Both zero-fat and full-fat cheese fail at similar strain amplitudes of $\gamma_{0,f} \approx 0.7$. (Note that we have indicated the strain...
amplitudes $\gamma_0$ at which mild slip is observed with filled symbols, both in Fig. 5(a) and both in Fig. 5(b). However, full-fat cheese displays a broad plateau in the elastic stress prior to failure, and, as a result, the amount of plastic deformation accumulated prior to failure is significantly larger than in zero-fat cheese. According to Reiner and Scott Blair (1967), the amount of plastic deformation prior to failure is inversely correlated with brittleness, as they define ‘brittle’ as “tending to break under the condition of minimal previous plastic deformation”. Shah et al. (1995) base their definition of ‘brittle’ on the stress-response to a deformation after the peak stress. In a brittle material, the stress suddenly drops to zero whereas in ‘ductile’ materials the stress is maintained at a constant level. In ‘quasi-brittle’ materials, like rock, concrete and clay, the stress gradually decreases after the peak stress is reached. Van den Berg et al. (2008) also correlated the extent of brittle failure of uniaxially compressed food gels to the rate of stress decrease after the peak stress. Using the definitions for ‘brittleness’ from Reiner and Scott Blair (1967) and Shah et al. (1995), the mode of failure in zero-fat cheese may be viewed as more brittle then in full-fat cheese. Fig. 5(a) and Fig. 5(b) show a correlation between the magnitude of the elastic failure stress $\sigma'_f$, or peak stress, and the rate of decline of the intracycle maximum in the elastic stress $\sigma'_\text{max}(\gamma_0)$ after the peak stress is reached. This suggests that the magnitude of $\sigma'_f$ is a strong indicator for the brittleness of soft-solid gels.

3.4. Quantifying and characterizing fluidization

An alternative approach to characterizing the evolution of damage and the onset of flow in soft-solid gels, is through geometrically-defined dynamic moduli that quantify the non-linearity of the material’s response (Ewoldt et al., 2008). In Fig. 6(a) we have plotted the evolution in the elastic stress $\sigma'(\gamma)$ for the cycles denoted I, II and III for-zero fat cheese at $T = 25 \, ^\circ\text{C}$ (blue lines). The endpoint of each curve represents the maximum elastic stress $\sigma'_\text{max}(\gamma_0)$ (squares, plotted for all cycles in Fig. 5(a)). The dashed lines represent the dynamic tangent modulus $G'_K$ at conditions corresponding to maximum strain ($\gamma = \gamma_0$) and zero strain rate ($\dot{\gamma} = 0$). In the linear viscoelastic regime, (cycle I in Fig. 6(a)), the magnitude of this tangent modulus is equal to the magnitude of the storage modulus i.e. $G'_K \equiv G'(\omega)$, and the dashed line coincides with the (linear) blue curve for the elastic stress. In the non-linear regime, the tangent curves rotate clock-wise, indicating that the magnitude of $G'_K$ decreases. Both for zero-fat cheese, Fig. 6(a), and full-fat cheese, Fig. 6(b), we interpret the decline in $G'_K$ as a measure of damage accumulating in the gel phase, leading to a loss of strength in the gel at large strains.

A major benefit of decomposing the oscillating stress response into elastic and viscous stress contributions, is that these two curves are single-valued functions of the strain or strain...
rate respectively. This facilitates the quantification of non-linearity of the material response, e.g. by fitting a polynomial function to the curve (Cho et al., 2005). Ewoldt et al. (2008) show that the Chebyshev polynomials of the first kind (Abramowitz and Stegun, 1964) are the most suitable choice of functions. These polynomials satisfy the criteria of orthogonality over a finite domain, rotational symmetry, rapid convergence, and a direct one-to-one correspondence to techniques of time-domain Fourier Transform rheology (Ewoldt et al., 2008). The Chebyshev basis functions $T_n(x)$ are defined by the recurrence relation

$$T_0(x) = 1$$
$$T_1(x) = x$$
$$T_{n+1}(x) = 2xT_n(x) - T_{n-1}(x)$$

Expressions for the elastic stress $\sigma'$ and the viscous stress $\sigma''$ are given in terms of these basis functions by

$$\sigma' = \gamma_0 \sum_{n: odd} e_n(\omega, \gamma_0) T_n(x)$$
$$\sigma'' = \dot{\gamma}_0 \sum_{n: odd} v_n(\omega, \gamma_0) T_n(y)$$

where $e_n$ and $v_n$ are the n-th order material coefficients, that quantify the elastic and viscous stress response to the normalized strain $x$ and strain rate $y$ respectively. The relationship between the Chebyshev coefficients and the Fourier coefficients for odd values of $n$ from Eq. (8) are (Ewoldt et al., 2008)

$$e_n = G'_n(-1)^{(n-1)/2}$$
$$v_n = \frac{G''}{\omega}$$

The maximum strain elastic tangent modulus $G'_K$ is readily calculated from the magnitude of the individual elastic Chebyshev harmonic coefficients $e_n$:

$$G'_K = \left. \frac{d\sigma'}{dy} \right|_{y=\gamma_0} = e_1 + 9e_3 + 25e_5 + ...$$

Equations (22) and (21) show us that for cycle I in Fig. 6(a), for which the response is fully described by the first-harmonic $n = 1$, we have, $G'_K = e_1 = G'_1 = G'(\omega)$. We use the elastic coefficients obtained by fitting the data in Fig. 6(a) and (b) to quantify the differences in the non-linear response of the zero-fat and full-fat cheese respectively.

In Fig. 6(c) and (d) we also depict the full elastic Lissajous curves for cycle I, II and III for zero-fat cheese ((c), blue) and full-fat cheese ((d), red). The dynamic elastic tangent moduli $G'_M$ at minimum strain $\gamma = 0$, and maximum strain rate $\max\{\dot{\gamma}(t)\} = \dot{\gamma}_0 = \omega\gamma_0$ (dashed lines) are plotted through the maxima of the viscous stress $\sigma''_{max}$ (shown by open circles). Again we
see a clockwise rotation of the tangents, indicating an inter-cycle decrease of the minimum strain modulus. This modulus $G'_M$ is calculated from the elastic Chebyshev coefficients $e_n$ by

$$G'_M = \left. \frac{d\sigma'}{dy} \right|_{\gamma=0} = e_1 - 3e_3 + 5e_5 + ... \quad (23)$$

Dimitriou et al. (2013) suggest that for yielding materials, like cheese, the decrease in the material function $G'_M$ is a measure for the onset of plastic flow in the material, as it probes the elastoplastic material response at maximum strain rate. In combination with $G'_K$, which we interpret as a measure of the accumulation of damage in the elastic network, we thus have two material functions that together quantify the solid-fluid transition of soft-solid gels under dynamic loading. We quantify the level of fluidization, i.e. the extent to which the elastic solid gel has transitioned into a flowing fluid by a dimensionless fluidizing ratio

$$\Phi \equiv \frac{G'_K - G'_M}{G'_K} = \frac{12e_3 + 20e_5 + ...}{e_1 + 9e_3 + 25e_5 + ...} \quad (24)$$

This ratio is defined in analogy to the hardening ratio $H$ introduced by Ewoldt et al. (2008), however we use the tangent modulus $G'_K$ instead of the secant modulus $G'_L$ to characterise the material response at maximum strain. A secant modulus averages the contribution of both large straining and rate of shearing to the material response, by contrast the tangent modulus at large strains (and zero strain rate) provides a more local measure of the residual elastic properties of the damaged gel.

Visual inspection of Fig. 6(a)-(d) shows that the rate of decrease of the modulus $G'_M$ at maximum strain rate is larger than for $G'_K$, which results in positive values of the fluidizing ratio $\Phi$. In Fig. 7(a) we have plotted the evolution of $\Phi$ for zero-fat cheese (blue) and full-fat cheese (red) measured in a LAOStrain sweep at a temperature of $T = 25 ^\circ C$. The strain at which fluidization sets in is a measure for the rubberiness $\hat{R}$ of the cheese, the plot thus shows at a glance that zero-fat cheese is an order of magnitude more rubbery than full-fat cheese. The ultimate magnitude of $\Phi$ for both cheese types is comparable at large strains $\gamma_0 \approx 1$, suggesting that in full-fat cheese fluidization is ultimately dominated by structural changes in the gel phase (which is common to both materials).

In analogy to this dimensionless function $\Phi$ that quantifies fluidization from an elastic perspective, we define a thickening ratio $\Theta$, which tracks the evolution of the solid-fluid transition from the viscous perspective:

$$\Theta \equiv \frac{\eta'_K - \eta'_M}{\eta'_K} = \frac{12v_3 + 20v_5 + ...}{v_1 + 9v_3 + 25v_5 + ...} \quad (25)$$

where $\eta'_K$ and $\eta'_M$ are the dynamic tangent viscosities at maximum strain rate, and zero strain rate (maximum strain) respectively. These viscosities are calculated from the Chebyshev harmonics $v_n$ by
\[ \eta'_K = \left. \frac{d\sigma}{d\gamma} \right|_{\gamma=\gamma_0} = v_1 + 9v_3 + 25v_5 + \ldots \]

\[ \eta'_M = \left. \frac{d\sigma}{d\gamma} \right|_{\gamma=0} = v_1 - 3v_3 + 5v_5 + \ldots \]  

(26)

Also here we have taken the original definition of the thickening ratio \( T \) from Ewoldt et al. (2008) and replaced the dynamic secant viscosity by a tangent viscosity. We retain the term ‘Thickening’ ratio however, and the use of the antonyms ‘thick’ and ‘thin’ to describe the resistance and propensity to flow respectively, as this terminology is common in the texture profiling of fluid food materials (Jowitt, 1974). By using the symbol \( \Theta \) instead of \( T \) we indicate that this measure is calculated using only tangent viscosities.

In Fig. 6(e) and (f) we show the Lissajous curves for cycle II for zero-fat cheese (blue) and full-fat cheese (red) from the viscous perspective. The black solid lines represent the viscous stress \( \sigma''(\dot{\gamma}) \). For full-fat cheese we need to retain information up to (at least) the fifth harmonic to describe the evolution in viscous stress with strain rate. By contrast, for zero-fat cheese, the leading order non-linearity is third-order and addition of the fifth harmonic which is very small (\( v_5 \approx v_3/10 \)) does not have a significant impact on the magnitude of \( \eta'_K \) or \( \Phi \).

In Fig. 7(b) we show the evolution of the Thickening ratio \( \Theta \) of zero-fat cheese (blue) and full-fat cheese (red) at a frequency of \( \omega = 5 \text{ rad s}^{-1} \). From the data in Fig. 7 it is possible to clearly differentiate between the responses of the different cheeses, and from the characteristics of the three regimes (denoted A, B and C), we can infer the sequence of physical processes (Rogers et al. (2011b)) by which the microstructure collapses in each case. To augment our physical interpretation of the mechanical response of the zero-fat cheese curve (blue), we can make use of the microrheological studies on unfilled, brittle protein gels from Leocmach et al. (2014); the three regimes A, B, C are analogues of the primary, secondary and tertiary creep identified in their controlled stress experiments. In regime A, the response of zero-fat cheese is predominantly linear viscoelastic and \( \Theta \approx 0 \). In this regime all deformations are recoverable and there is no plastic flow. In regime B, fluidization sets in as microcracks nucleate and propagate in the gel matrix. The progressive collapse of the microstructure results in strain softening and a shear thinning response. In regime C, the percolating cracks form sample-spanning fractures, which results in the ultimate failure of the gel. Again note that we have indicated the strain amplitudes \( \gamma_0 \) at which mild slip is observed with filled symbols, both in Fig. 7(a) and both in Fig. 7(b).

The response of the full-fat cheese (red curve) in Fig. 7(b) is remarkably different. First we observe mild inter-cycle shear thinning, starting at low strain amplitudes in regime A. We attribute this response to an increased rate of strain localization in the gel, induced by
the present emulsion. In regime B, the softening is arrested, and the response changes to a
local inter-cycle shear thickening analogous to the rubber toughening observed in brittle ther-
moplastic composites \cite{Hall1991, Wu1985}. As the strain amplitude increases further, the
process of crack propagation continues, which ultimately leads to the extreme shear thinning
observed in regime C. Beyond cycle II the sample deformation becomes inhomogeneous and
therefore we have connected the three points in this interval with a dashed line in Fig. 7(a)
and Fig. 7(b).

The comparison of the breakdown path of zero-fat and full-fat cheese demonstrates that
the addition of the fat emulsion to the gel, also adds one level of complexity to the breakdown
pathway for the cheese microstructure.

3.5. Comparing formulations on the basis of the evolution of $\Phi$ and $\Theta$

In this final section, we demonstrate that evaluating the fluidization ratio $\Phi$, alongside our
re-defined thickening ratio $\Theta$, augments the capabilities of LAOS as an analytical tool for
structure-texture engineering of soft-solid gels, thereby making reformulation studies more
effective. In Fig. 8(a,b) we have plotted the magnitudes of (a) $\Phi$, and (b) $\Theta$, of zero-fat (blue),
low-fat (green), and full-fat (red) cheese, at $T = 10^\circ$C. These cheese types contain a fat
volume fraction of $\phi_f = 0\%$, $\phi_f = 12\%$, and $\phi_f = 30\%$ respectively. The plots with
the filled symbols represent a decrease of $\Delta T = 15^\circ$C with respect to the measurements from
Fig. 7 (which we have replotted in Fig. 8 for quantitative comparison using shaded and hollow
symbols). All of the data in Fig. 8 are truncated such that only two of the three flow regimes
discussed in the previous section are visible; regime A characterized by mild fluidization as
a result of microcrack nucleation and propagation, and regime B corresponding to strong
fluidization arising from flowing gel fragments.

We define a critical strain amplitude $\gamma_c$ as the strain amplitude for which the fluidizing
ratio $\Phi > 0.1$. The magnitude of the critical strain for full-fat cheese $\gamma_c \approx 0.01$ is a factor
of 12 lower then for low-fat cheese ($\gamma_c \approx 0.12$), whereas the filler volume fraction of full-fat
cheese is a factor of 2.5 higher. This data is consistent with a previously suggested relationship
between the critical strain and the filler volume fraction $\gamma_c \propto 1/\phi_f^3$, motivated by arguments
that the fluidization scales linearly with surface to surface inter-particle distance of the filler
\cite{Wu1985}.

The critical strain $\gamma_c$ of full-fat cheese at $T = 25^\circ$C (red hollow symbols, $\gamma_c \approx 0.04$)
is a factor of 4 higher then at $T = 10^\circ$C (red filled symbols). This is only partly explained
by the temperature-induced increase in $\gamma_c$ of the gel phase, which is only a factor of 1.25
for the same temperature increase of $\Delta T = 15^\circ$C (blue filled vs hollow symbols, $\gamma_c \approx 0.20$
and $\gamma_c \cong 0.25$ respectively). The remaining increase in the critical strain for full-fat cheese, must come from the melting of the fat particles. Using composite models, Yang et al. (2011) estimate that over the temperature range of $T = 10 \degree C$ to $T = 25 \degree C$ the melting of fat leads to a decrease in shear modulus of the fat particles by a factor of $\sim 200$. This softening results in a significant fraction of the imposed macroscopic strain accumulating in the fat globules at $T = 25 \degree C$, whereas for the rigid particles at $T = 10 \degree C$ this strain localization in the fat phase is negligible.

In Fig. 8(c,d) the water content of the gel, expressed as the water / protein ratio $w/p$ with units of g/g, is raised by 33% from $w/p = 1.8$ to $w/p = 2.4$. Fig. 8(c) shows that the hydration of cheese does not affect the rate of sample softening or microcrack formation. However Fig. 8(d) demonstrates that hydration has a significant effect on the resulting fluid-like characteristics of the fluid properties of full-fat cheese (red) in non-linear regime B. The response of $\Theta$ changes from shear thickening (hollow symbols) to shear thinning (filled symbols). A probable cause is that in the hydrated samples the voided regions following crack formation, are rapidly invaded with water (as shown for diluted casein gels by Leocmach et al. (2014)), which acts as a low viscosity lubricant in the void spaces between the viscous fat droplets and the gel matrix. A second important factor is that hydration makes the protein gel matrix softer and therefore more pliable, which reduces frictional forces between two neighboring gel fragments. Additional evidence for the hypothesis that the gel firmness affects friction, comes from the change in the response of zero-fat cheese from thickening to thinning when increasing the temperature from $T = 10 \degree C$ to $T = 25 \degree C$, which reduces the firmness $\hat{F}$ by a factor of 2.4.

The plots of the thickening ratio $\Theta$ in Fig. 8(b,d), show that the emulsified fat phase plays a pivotal role in modulating the solid-fluid transition of cheese also. Full-fat cheese shows strong responses to an increase in shear (b,d), temperature (b), and degree of hydration (d), respectively, the three most important processes occurring in the mouth. Reduction of fat content significantly reduces the magnitude of these response functions. Our microrheological interpretation, supported by the strain sweeps of the fluidizing ratio $\Phi$ and thickening ratio $\Theta$, show that alternative structuring routes for low fat cheeses with limited volumes of the fat filler, should be aimed at reducing the surface to surface average inter-particle distance, and enhancing the temperature-induced softening of the filled gel.
4. Conclusions

In this paper, we have used Large Amplitude Oscillatory Shear (LAOS) both in controlled-stress and controlled-strain mode (LAOSTress and LAOStrain, respectively), to quantify and characterize the solid-fluid transition of semi-hard cheese, a soft-solid, emulsion-filled, gel. We defined quantitative measures for the firmness, rubberiness, softening, and fluidization of cheese and interpreted the magnitudes and evolution of these measured parameters in terms of physical processes that lead to the progressive collapse of the cheese microstructure.

We defined firmness $\hat{F}$ as a resistance to deformation and quantified this texture attribute as the inverse of the magnitude of the complex creep compliance in LAOSTress, $1/|J^*(\omega)|$, or the magnitude of the complex shear modulus in LAOStrain $|G^*(\omega)|$, which are interchangeable measures. We defined rubberiness $\hat{R}$ as a resistance to flow, which is quantified as either the magnitude of the yield stress amplitude $\sigma_{0,y}$ in LAOSTress, or the yield strain amplitude $\gamma_{0,y}$ in LAOStrain. The yield point is the point where the complex creep compliance, or complex shear modulus, departs measurably from its plateau value, and the material response changes from that of a linear viscoelastic solid to a non-linear elastoviscoplastic material. The LAOStrain protocol for measuring the firmness $\hat{F}$ and rubberiness $\hat{R}$ is preferred over the corresponding LAOSTress measures ($\tilde{F}$ and $\tilde{R}$), since it results in rubberiness and firmness being two independent quantities. Furthermore LAOStrain allows for larger controlled loadings in the non-linear, fluidized, regime, while still retaining a homogeneous viscometric flow field.

We proposed a set of definitions to distinguish between alternative routes for ‘softening’ a cheese. We defined ‘softening’ as decreasing the firmness, by changing the intrinsic, linear viscoelastic material properties. ‘Fluidization’ is clearly demonstrated to be the load-induced transition of the cheese from a more solid-like to a more fluid-like state.

Fluidization of a soft-solid gel can be abrupt or gradual, which we have visualized by plotting the magnitude of the intra-cycle maximum in the elastic stress $\sigma'_{\text{max}}(\gamma_0)$ as a function of strain amplitude. We identified the peak in the elastic stress as the failure stress $\sigma'_f$ of the gel, and argued that the magnitude of $\sigma'_f$ is an indicator of the ‘brittleness’ of the sample.

We augmented the ontological framework for LAOS developed by Ewoldt et al. (2008) to quantify the progression of damage and onset of flow in soft-solid gels. We have defined two ratios based on local tangency conditions to the elastic and viscous Lissajous curves, that highlight the changes in the materials modulus and viscosity at zero and maximum strain / strain-rate respectively. The first is the fluidization ratio $\Phi$ which quantifies the extent and rate of fluidization in the material’s elastic properties. The second is the redefined thickening ratio $\Theta$ that characterizes the non-linearities in the viscous response of the resulting fluid.

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Our LAOS-based measures for firmness, rubberiness, softening, fluidization and rate thickening unambiguously quantify the texture profile of soft-solid food gels in multiple dimensions. These rheological measures also provide insight into the structure parameters that need to be controlled for an optimal texture profile. Our measurements on semi-hard cheese show that the fat particles emulsified in the water/protein gel phase, have a pivotal role in increasing the sensitivity of the appropriate material response functions of cheese to temperature and shear, i.e. in increasing the propensity of the food material to soften and fluidize. From our data we inferred that the inter-particle surface to surface distance and the temperature sensitivity of the emulsified filler, as well as the water-protein ratio of the gel, are the key structure parameters that largely control the softening and fluidizing properties of semi-hard cheese.

This new suite of material measures, tested on a wide range of formulations of semi-hard cheese, have illustrated how to augment the capabilities of LAOS, so that it can serve as an analytical tool for structure-texture engineering of soft-solid food gels.

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References


1. (a) Semi-hard cheese belongs to the material class of soft solids. It is predominantly solid at rest and shows a transition to a fluid when manipulated or masticated. 'Firmness', 'rubberiness' and 'smoothness' are the typical textual terms used to assess the solidity and (lack of) fluidity of the cheese by hand or in-mouth. (b) In previous work (Faber et al., 2016a,b), we have defined linear viscoelastic rheological measures quantifying firmness and rubberiness that can be determined from creep / recovery experiments in shear. Firmness is a linear viscoelastic property, whereas rubberiness is a measure of the non-linear elastoviscoplasticity of the material. (c) For the simultaneous measurement of firmness and rubberiness in one test run, the Large Amplitude Oscillatory Shear protocol is more suitable than the creep / recovery experiment. Experiments may be performed with either a sinusoidal strain input (of amplitude $\gamma_0$) or a stress input (of amplitude $\sigma_0$).

2. Stress-controlled texture measurement of zero-fat (blue) and full-fat (red) soft-solid gel. The microstructure of full-fat cheese can be characterized as emulsion-filled gel. CSLM images of (a) zero-fat cheese and (b) full-fat cheese. (c) Creep / recovery curves of zero-fat (blue) and full-fat cheese (red) at a stress amplitude $\sigma_0 = 1000$ Pa and two temperatures of $T = 10^\circ$C (filled squares) and $T = 25^\circ$C (hollow squares). Firmness is defined as the inverse of the maximum compliance $F \equiv 1/J(t_f)$ at $t_f = 100$ s. Rubberiness is defined as the extent to which the material recovers from the strain at the end of the experiment $R \equiv 1 - J(t_r)/J(t_f)$ at $t_r = 200$ s. (triangles on the right-hand ordinate axis). However, the LAOSstrain measurements more readily allow probing the material response deeper into the fluid regime. The roman numerals along the curves in (b) and (c) correspond to the specific LAOSstrain cycles examined in more detail in Fig. 6.
4 (a,b) Measurements (blue line) and model prediction (circles) of the oscillatory stress response of zero fat cheese subjected to LAOStrain loading. Our model is based on a fractional constitutive framework, with only two material properties: a fractional exponent of $\beta = 0.19$, quantifying the frequency dependency of the response and a ‘quasi-property’ $G = 1.4 \times 10^5$ Pa $\times$, which quantifies the scale of the stress in the material. Our model correctly predicts the shape of the ellipse as a function of the strain amplitude $\gamma_0$ and frequency $\omega$.

(c) In the non-linear regime, the Bowditch-Lissajous curve becomes increasingly ‘banana-shaped’ (solid blue line) and the elastic stress contribution (solid red line) becomes curved, a characteristic typical for damaged elastomers. The linear viscoelastic model (dashed line, hollow symbols) cannot predict this curvature and over predicts both the maximum of the elastic stress (squares) and viscous stress (circles).

(d) Same data as in (c), plotted from a ‘viscous’ perspective.

5 (a,b) Evolution of the intra-cycle maxima of the elastic stress $\sigma_{max}^\prime(\gamma_0)$ ( hollow squares) and viscous stress $\sigma_{max}^{\prime\prime}(\gamma_0)$ (hollow circles) as a function of the strain amplitude $\gamma_0$ for zero-fat (blue) and full-fat (red) cheese measured at $T = 25^\circ$C and a frequency $\omega = 5$ rad s$^{-1}$. The continuous and dashed line represent the predictions of the linear viscoelastic constitutive model. Both zero-fat and full-fat cheese display an inter-cycle maximum of the elastic stress $\sigma_f^\prime$, (indicated by the numeral II) at a failure strain amplitude $\gamma_f \approx 0.1$. We define this inter-cycle maximum as the failure criterion for the food gel. The full-fat cheese curve (b) displays a broad plateau in the maximum elastic stress $\sigma_{max}^\prime$ and a small decrease beyond the failure point. By contrast, the zero-fat cheese shown in (a), displays a more clearly pronounced peak in the $\sigma_{max}^\prime$ curve.

(e) Magnitude of the elastic stress of zero-fat cheese, at a frequency of $\omega = 5$ rad s$^{-1}$ (hollow) and $\omega = 0.2$ rad s$^{-1}$ (filled). The magnitude of $\sigma_{max}^\prime(\gamma_0)$ is normalized by the factor $\omega^2 \cos(\pi \beta/2)$.

(f) The solid-fluid transition of zero-fat (blue) and full-fat (red) cheese at $T = 25^\circ$C and $\omega = 5$ rad s$^{-1}$ depicted using the Lissajous representation. (a,b).

The continuous lines represent the intra-cycle evolution of the elastic stress $\sigma^\prime$. The hollow squares are the intra-cycle maxima $\sigma_{max}^\prime$ of the elastic stress as a function of strain amplitude $\gamma_0$. The dashed lines indicate the tangent modulus $G_k^\prime$ to the curve of the elastic stress at $\gamma = \gamma_0$ and provide a measure of the loss of strength of the elastic network. (c,d) Lissajous curves of the total stress response at three strain amplitudes $\gamma_0 = 0.2, 0.6, 1.0$. The hollow circles show the intra-cycle maxima in the viscous stress $\sigma_{max}^{\prime\prime}$. The dashed lines through these points are the tangent modulus $G_M^\prime$ at maximum strain rate $\dot{\gamma} = \gamma_0$. The slope of these tangents represent the resistance of the material to plastic flow. (e,f) Lissajous plots of cycle II from the viscous perspective (blue and red curves) with the viscous stress $\sigma^{\prime\prime}(\omega)$ plotted as black continuous lines. The dashed lines represent the minimum and maximum strain rate dynamic viscosity $\eta_M^\prime$ and $\eta_k^\prime$ respectively. (f) Full-fat cheese displays a more pronounced (fifth-order) non-linearity. Truncating the description of $\eta_k^\prime$ at third-order over-predicts its magnitude as shown by the dot-dashed line.
Strain sweeps showing the evolution in (a) the Fluidizing ratio $\Phi$, and (b) the Thickening ratio $\Theta$, of zero-fat cheese (blue) and full-fat cheese (red) measured at a temperature $T = 25\, {^\circ}C$ and $\omega = 5\, \text{rad s}^{-1}$. (a) Both cheese formulations show comparable ultimate magnitudes of the Fluidizing ratio, however the rise of $\Phi$ of full-fat cheese is more gradual and sets in at lower strains. (b) The non-Newtonian fluid properties of full-fat and zero-fat cheese are characterized by the evolution of the Thickening ratio, which reveals three flow-regimes A, B and C. Zero-fat cheese displays continuous inter-cycle thinning, whereas full-fat cheese shows some initial thinning, followed by thickening and thinning. Beyond cycle II the sample of full-fat cheese is no longer homogeneous, indicated with a dotted line in (a) and (b). The strain-rate amplitudes at which mild slip is observed are indicated using filled symbols.

Evolution in the Fluidizing ratio $\Phi$ (a,c) and Thickening ratio $\Theta$ (b,d) of cheese varying with temperature (a,b) and degree of hydration (c,d). Three different cheeses are depicted: 0 v/v% (blue), 12 v/v% (green), 30 v/v% (red). For comparison, the measurements from Fig. 7 are replotted using shaded and hollow symbols. (a,b) Temperature decrease from $T = 25\, {^\circ}C$ (hollow) to $T = 10\, {^\circ}C$ (filled). (a) Both a temperature reduction and increase of fat content increase the rate of fluidization with increasing strain. (b) Temperature reduction changes the response of zero-fat cheese from shear thinning to weakly shear thickening, and closer to that of full-fat cheese. (c) Increasing the water/ protein ratio from $w/p = 1.8$ (hollow) to $w/p = 2.4$ (filled) does not have a significant effect on the rate of fluidization in regime A. (d) However it changes the fluid characteristics of full-fat cheese from shear thickening to shear thinning.

A.9 Values for the first-harmonic creep compliance $J_1^c(\omega, \sigma_0)$ in a stress-sweep of samples of the same test material as used for Fig. 2(c). The firmness is defined as the inverse of the magnitude of the complex creep compliance $\tilde{F} \equiv 1/|\tilde{J}^c(\omega)|$, and are plotted as circles. In a LAOStress measurement the appropriate measure of rubberiness is the amplitude of the yield stress $R \equiv \sigma_{Y}^{\alpha,\gamma}$, and is indicated here for each material by the triangles. The gradient of the shaded area to the left denotes schematically the transition from firm to soft, which we define as ‘softening’. The white arrow indicates a temperature-induced softening. The gradient of the shaded area at the bottom indicates schematically the transition from rubbery to moldable, which we define as ‘plasticizing’. The dashed arrow indicates a stress-induced transition from solid to fluid-like behaviour, which we denote as ‘fluidizing’.

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Figure 1: (a) Semi-hard cheese belongs to the material class of soft solids. It is predominantly solid at rest and shows a transition to a fluid when manipulated or masticated. ‘Firmness’, ‘rubberiness’ and ‘smoothness’ are the typical textural terms used to assess the solidity and (lack of) fluidity of the cheese by hand or in-mouth. (b) In previous work (Faber et al., 2016a,b), we have defined linear viscoelastic rheological measures quantifying firmness and rubberiness that can be determined from creep/recovery experiments in shear. Firmness is a linear viscoelastic property, whereas rubberiness is a measure of the non-linear elastoviscoplasticity of the material. (c) For the simultaneous measurement of firmness and rubberiness in one test run, the Large Amplitude Oscillatory Shear protocol is more suitable than the creep/recovery experiment. Experiments may be performed with either a sinusoidal strain input (of amplitude $\gamma_0$) or a stress input (of amplitude $\sigma_0$).
Figure 2: Stress-controlled texture measurement of zero-fat (blue) and full-fat (red) soft-solid gel. The microstructure of full-fat cheese can be characterized as emulsion-filled gel. CSLM images of (a) zero-fat cheese and (b) full-fat cheese. (c) Creep/recovery curves of zero-fat (blue) and full-fat cheese (red) at a stress amplitude $\sigma_0 = 1000$ Pa and two temperatures of $T = 10\, ^\circ C$ (filled squares) and $T = 25\, ^\circ C$ (hollow squares). Firmness is defined as the inverse of the maximum compliance $F \equiv 1/J(t_f)$ (circles) at $t_f=100$ s. Rubberiness is defined as the extent to which the material recovers from the strain at the end of the experiment $R \equiv 1 - J(t_r)/J(t_f)$ at $t_r=200$ s. (triangles on the right-hand ordinate axis).
Figure 3: (a) Strain-sweep of the first-harmonic complex shear modulus $G_1^*(\omega, \gamma_0)$ measured using LAOStrain, of samples from the same zero-fat cheese (blue) and full-fat cheese (red) as in Fig. 2(c), and measured at the same temperatures of $T = 10 \degree C$ (filled symbols) and $T = 25 \degree C$ (open symbols) at $\omega = 5 \text{ rad s}^{-1}$. The magnitudes of the firmness $\hat{F}$ of the samples are equal to the plateau values of the magnitude of the first-harmonic complex shear moduli and are plotted as circles on the ordinate axis. The rubberiness $\hat{R}$ is defined as the magnitude of the yield strain amplitude $\gamma_0$ and plotted as triangles on the abscissa. (b,c) The LAOStrain and LAOStress experiments measure the same ratios of maxima in the stress and maxima in strain, defined by $\sigma_{\text{max}}/\gamma_0$ and $\sigma_0/\gamma_{\text{max}}$ respectively. However the LAOStrain measurements more readily allow probing the material response deeper into the fluid regime. The roman numerals along the curves in (b) and (c) correspond to the specific LAOStrain cycles examined in more detail in Fig. 6.
Figure 4: (a,b) Measurements (blue line) and model prediction (circles) of the oscillatory stress response of zero fat cheese subjected to LAOS (strain) loading. Our model is based on a fractional constitutive framework, with only two material properties: a fractional exponent of $\beta = 0.19$, quantifying the frequency dependency of the response and a ‘quasi-property’ $G = 1.4 \times 10^4 \text{ Pa } \beta$, which quantifies the scale of the stress in the material. Our model correctly predicts the shape of the ellipse as a function of the strain amplitude $\gamma_0$ and frequency $\omega$. (c) In the non-linear regime, the Bowditch-Lissajous curve becomes increasingly ‘banana-shaped’ (solid blue line) and the elastic stress contribution (solid red line) becomes curved, a characteristic typical for damaged elastomers. The linear viscoelastic model (dashed line, hollow symbols) cannot predict this curvature and over predicts both the maximum of the elastic stress (squares) and viscous stress (circles). (d) Same data as in (c), plotted from a ‘viscous’ perspective.
Figure 5: (a,b) Evolution of the intra-cycle maxima of the elastic stress $\sigma'_{\text{max}}(\gamma_0)$ (hollow squares) and viscous stress $\sigma''_{\text{max}}(\gamma_0)$ (hollow circles) as a function of the strain amplitude $\gamma_0$ for zero-fat (blue) and full-fat (red) cheese measured at $T = 25$ °C and a frequency $\omega = 5$ rad s$^{-1}$. The continuous and dashed line represent the predictions of the linear viscoelastic constitutive model. Both zero-fat and full-fat cheese display an inter-cycle maximum of the elastic stress $\sigma'_f$ (indicated by the numeral II) at a failure strain amplitude $\gamma_f \approx 0.7$. We define this inter-cycle maximum as the failure criterion for the food gel. The full-fat cheese curve (b) displays a broad plateau in the maximum elastic stress $\sigma'_{\text{max}}$ and a small decrease beyond the failure point. By contrast, the zero-fat cheese shown in (a), displays a more clearly pronounced peak in the $\sigma'_{\text{max}}$ curve. (c) Magnitude of the elastic stress of zero-fat cheese, at a frequency of $\omega = 5$ rad s$^{-1}$ (hollow) and $\omega = 0.2$ rad s$^{-1}$ (filled). The magnitude of $\sigma'_{\text{max}}(\gamma_0)$ is normalized by the factor $\omega^\beta \cos(\pi \beta/2)$. 


Figure 6: The solid-fluid transition of zero-fat (blue) and full-fat (red) cheese at $T = 25 ^\circ C$ and $\omega = 5 \text{ rad s}^{-1}$ depicted using the Lissajous representation. (a,b). The continuous lines represent the intra-cycle evolution of the elastic stress $\sigma'$. The hollow squares are the intra-cycle maxima $\sigma'_{\text{max}}$ of the elastic stress as a function of strain amplitude $\gamma_0$. The dashed lines indicate the tangent modulus $G'_K$ to the curve of the elastic stress at $\gamma = \gamma_0$ and provide a measure of the loss of strength of the elastic network. (c,d). Lissajous curves of the total stress response at three strain amplitudes $\gamma_0 = 0.2, 0.6, 1.0$. The hollow circles show the intra-cycle maxima in the viscous stress $\sigma''_{\text{max}}$. The dashed line through these points are the tangent modulus $G'_M$ at maximum strain rate $\dot{\gamma} = \dot{\gamma}_0$. The slope of these tangents represent the resistance of the material to plastic flow. (e,f). Lissajous plots of cycle II from the viscous perspective (blue and red curves) with the viscous stress $\sigma''(\omega)$ plotted as black continuous lines. The dashed lines represent the minimum and maximum strain rate dynamic viscosity $\eta'_M$ and $\eta'_K$ respectively. (f) Full-fat cheese displays a more pronounced (fifth-order) non-linearity. Truncating the description of $\eta'_K$ at third-order over-predicts its magnitude as shown by the dot-dashed line.
Figure 7: Strain sweeps showing the evolution in (a) the Fluidizing ratio $\Phi \equiv (G'_K - G'_M)/G'_K$ and (b) the Thickening ratio $\Theta \equiv (\eta'_K - \eta'_M)/\eta'_K$. (a) Both cheese formulations show comparable ultimate magnitudes of the Fluidizing ratio, however the rise of $\Phi$ of full-fat cheese is more gradual and sets in at lower strains. (b) The non-Newtonian fluid properties of full-fat and zero-fat cheese are characterized by the evolution of the Thickening ratio, which reveals three flow-regimes A, B and C. Zero-fat cheese displays continuous inter-cycle thinning, whereas full-fat cheese shows some initial thinning, followed by thickening and thinning. Beyond cycle II the sample of full-fat cheese is no longer homogeneous, indicated with a dotted line in (a) and (b). The strain(-rate) amplitudes at which mild slip is observed are indicated using filled symbols.
Figure 8: Evolution in the Fluidizing ratio $\Phi$ (a,c) and Thickening ratio $\Theta$ (b,d) of cheese varying with temperature (a,b) and degree of hydration (c,d). Three different cheeses are depicted: 0 v/v% (blue), 12v/v% (green), 30v/v% (red). For comparison, the measurements from Fig. 7 are replotted using shaded and hollow symbols. (a,b) Temperature decrease from $T = 25^\circ C$ (hollow) to $T = 10^\circ C$ (filled). (a) Both a temperature reduction and increase of fat content increase the rate of fluidization with increasing strain. (b) Temperature reduction changes the response of zero-fat cheese from shear thinning to weakly shear thickening, and closer to that of full-fat cheese. (c) Increasing the water / protein ratio from $w/p = 1.8$ (hollow) to $w/p = 2.4$ (filled) does not have a significant effect on the rate of fluidization in regime A. (d) However it changes the fluid characteristics of full-fat cheese from shear thickening to shear thinning.
Appendix A. LAOStress-based definitions for firmness and rubberiness

In the LAOStress experiment, a cosinusoidal oscillating stress $\sigma(t)$ is imposed (Ewoldt, 2013a), defined by:

$$\sigma(t) = \sigma_0 \cos \omega t \tag{A.1}$$

where the time-scale of the oscillation is set by the frequency $\omega$. Fourier transformation of the strain response in the time domain, $\gamma(t; \omega, \sigma_0)$, results in (Ewoldt, 2013a):

$$\gamma(t; \omega, \sigma_0) = \sigma_0 \sum_{n: \text{odd}} \left\{ J'_n \sin n \omega t + J''_n \cos n \omega t \right\} \tag{A.2}$$

where the $n$-th order Fourier coefficients, $J'_n(\omega, \sigma_0)$ and $J''_n(\omega, \sigma_0)$, are $n$-th harmonic non-linear material functions, called the dynamic elastic compliance and dynamic viscous compliance respectively (Ewoldt, 2013a). The first-harmonic compliances, $J'_1(\omega, \sigma_0)$ and $J''_1(\omega, \sigma_0)$ are averages of the local compliance, over one period of oscillation (Ewoldt et al., 2008):

$$J'_1 = \frac{\omega}{\pi \sigma_0^2} \int_0^{1/\omega} \sigma(t) \gamma(t) dt \quad J''_1 = \frac{1}{\pi \sigma_0^2} \int_0^{1/\omega} \sigma(t) \dot{\gamma}(t) dt \tag{A.3}$$

where $\dot{\gamma}(t)$ is the strain rate. When the material response is linear, then all higher harmonics with $n > 1$ are negligible, and the first-harmonic elastic and viscous compliance are equal to the classical shear storage compliance, $J'_1(\omega, \sigma_0) = J'(\omega)$, and shear loss compliance, $J''_1(\omega, \sigma_0) = J''(\omega)$, respectively. From the first-harmonic compliances, we calculate the magnitude of the first-harmonic complex compliance $J^*_1(\omega, \sigma_0)$, using:

$$|J^*_1(\omega, \gamma_0)| = \sqrt{J'^2_1 + J''^2_1} \tag{A.4}$$

In the linear viscoelastic regime, the first-harmonic complex compliance $J^*_1(\omega, \sigma_0)$, reduces to the complex compliance $J^*(\omega)$. We define the firmness of a gel as the inverse of the magnitude of the complex compliance.

In Fig. A.9 we show values of the first-harmonic complex compliance $J^*_1(\omega, \sigma_0)$ in a stress sweep at a frequency $\omega = 5 \text{ rad s}^{-1}$, for samples of the same test materials as used in Fig. 2(c) and Fig. 3(a). We have plotted the plateau value for the first-harmonic complex creep compliances, $J^*_1(\omega, \sigma_0) = J^*(\omega)$, i.e. the magnitude of the firmness $\hat{F}$ as circles on the ordinate axis. The shading on the left axis, with a gradient from bottom to top indicates schematically the ranking of the samples from firm to soft. The ranking of the samples on the firmness $\hat{F}$ in Fig. A.9 is the same as the ranking on the firmness $\hat{F}$ measured in LAOStrain in Fig. 3(a). Averaging the ratio $\hat{F}/\hat{F}$ of the four samples, results in a mean value of 0.9 and a standard
deviation of 0.1, showing that the LAOSTress and LAOSTrain measure of firmness indeed are
interchangeable as predicted by Eq. (6).

To allow for the quantitative measurement of rubberiness in LAOSTress, we need a mea-
sure for the resistance to yield obtained from the experiment. For the stress sweep of the
first-harmonic complex creep compliance $J^*(\omega,\sigma_0)$ in Fig. A.9 there is no inflection point
from which we can derive an unambiguous definition of the yield point such as in Fig. 2(e).
Instead we use a generic criterion for transition from the linear viscoelastic, to the non-linear
elastoviscoplastic response, which is

$$\left| J_{1}^*(\omega,\sigma_0) - |J^*(\omega)| \right| > y$$

(A.5)

where $y$ is the arbitrarily chosen measure for non-linearity. In this paper we use $y = 0.01$. We
define the maximum of the range of stress amplitudes that satisfies this criterion as the yield
stress amplitude $\sigma_{0,y}$, and define rubberiness as

$$\tilde{R} \equiv \sigma_{0,y}$$

(A.6)

which, like firmness, has units of Pa. Note that the dimensionality of $\tilde{R}$ differs from the units
of rubberiness $R$ measured in the creep recovery experiment and defined in Eq. (11), which are
dimensionless. In Fig. A.9 we have plotted the magnitude of the rubberiness $\tilde{R}$, as triangles
on the stress amplitude axis. This measure of rubberiness clearly discriminates full-fat cheese
from zero-fat cheese, irrespective of measurement temperature; the full-fat cheese (red) and
zero-fat (blue) at $T = 10^\circ C$(filled triangles), differ in rubberiness by over a factor of ten.

Since we use a very small value for $y$, the material response of the material is still almost
linear at the yield point, and the magnitude of the non-linear compliance is approximated
by the magnitude of the complex shear compliance, $J^*(\omega,\sigma_{0,y}) \approx J^*(\omega)$. The magnitude of
the yield strain $\gamma_y$ measured in LAOSTress, is calculated from the yield stress amplitude $\sigma_{0,y}$,
using

$$\gamma_y \approx \frac{\sigma_{0,y}}{|J^*(\omega)|} = \frac{\tilde{R}}{\tilde{F}}$$

(A.7)

Fig. 3(b) and (c) show that at the yield point the magnitude of the yield strain measured
in LAOSTress is approximated by the magnitude of the yield strain amplitude measured in
LAOSTrain, which is equal to the LAOSTrain definition of the rubberiness

$$\gamma_y \approx \gamma_{y,0} = \hat{R}$$

(A.8)

Substituting Eq. (A.8) in Eq. (A.7), gives:

$$\tilde{R} = \frac{\hat{R}}{\tilde{F}}$$

(A.9)
In words this relationships states that the magnitude of the material rubberiness $R$ measured using LAOStrain, is equal to the magnitude of the rubberiness $\tilde{R}$ measured using LAOStress, normalized by the firmness of the material. This is what we predict when we normalize the magnitudes of the rubberiness $\tilde{R}$ (triangles), to the corresponding magnitudes of the firmness $\tilde{F}$ (circles) from Fig. A.9 and compare these normalized values to the magnitude of the rubberiness measured in LAOStrain (triangles in Fig. 3(a)).
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Figure A.9: Values for the first-harmonic creep compliance $J_1^*(\omega,\sigma_0)$ in a stress-sweep of samples of the same test material as used for Fig. 2(e). The firmness is defined as the inverse of the magnitude of the complex creep compliance $\tilde{F} \equiv 1/|J(\omega)|$, and are plotted as circles. In a LAOST stress measurement the appropriate measure of rubberiness is the amplitude of the yield stress $\tilde{R} \equiv \sigma_{0,\gamma}$, and is indicated here for each material by the triangles. The gradient of the shaded area to the left denotes schematically the transition from firm to soft, which we define as 'softening'. The white arrow indicates a temperature-induced softening. The gradient of the shaded area at the bottom indicates schematically the transition from rubbery to moldable, which we define as 'plasticizing'. The dashed arrow indicates a stress-induced transition from solid to fluid-like behaviour, which we denote as 'fluidizing'.