Electronic supplementary information - Characterising the mechanical properties of soft solids through acoustics and rheology, exemplified by anhydrous milk fat.

Acoustic emission

Acoustic emission (AE) is a phenomenon that occurs when a material undergoes deformation and/or fracture. It is caused by the rapid release of elastic energy that is stored in the material due to mechanical loading. The elastic energy release is linked to the onset and propagation of cracks in soft solids and can be described by various fracture mechanics models.

Acoustic emission (AE) has shown great potential in providing insights into the mechanical behaviour of soft solids undergoing deformation and/or rupture. However, there are several challenges associated with linking AE to friction and rupture in these materials.

One of the primary challenges is accurately interpreting the AE signals and distinguishing between different types of events - and mathematical models attempting linkage are scarce. AE signals can arise from a variety of sources, including microcracking, plastic deformation, and frictional sliding. The challenge lies in differentiating between these sources and identifying the underlying physical processes that give rise to the signals. This is further complicated by the highly heterogeneous nature of many soft solids, with variations in material properties and microstructure across different regions of the material.

Another challenge is the attenuation of AE signals as they propagate through the material. Soft solids have lower acoustic velocities and higher attenuation coefficients than more rigid materials, which can make it difficult to detect signals from deep within the material.

Selecting an appropriate fracture mechanics model to relate AE to friction and rupture is also challenging. Different models have different assumptions and limitations and may be more or less appropriate depending on the specific material and loading conditions. Careful experimental validation is required to ensure that the selected model accurately represents the underlying physics.

One such model is the Kaiser effect model, which assumes that the AE signal is proportional to the cumulative release of elastic energy during the deformation process. The Kaiser effect states that the AE signal is independent of the loading history up to the point of AE detection, and that it only depends on the amount of energy released during that specific deformation event [14–16]. Mathematically, the Kaiser effect can be expressed as:

$$\Delta AE = f(G)$$

Equation 1

where ΔAE is the change in AE signal, and G is the elastic energy release rate associated with the fracture or deformation event. The function $f(G)$ is dependent on the specific material properties and the type of deformation or fracture being considered.

Another model that links AE to elastic energy release and fracture in soft solids is the Continuum Damage Mechanics (CDM) model. This model describes the evolution of damage in the material as a scalar variable (D), which represents the degree of loss of material integrity due to microcracking or other forms of deformation. The elastic energy release rate in the CDM model can be expressed as:

$$G = \frac{E\,a}{\pi W}[(1 - D)\Delta\sigma]^2$$

Equation 2

where E is the elastic modulus of the material, a is the crack length, W is the width of the crack, $\Delta\sigma$ is the stress intensity factor, and $1 - D$ represents the remaining intact material. This equation relates the amount of elastic energy released during deformation or fracture to the degree of damage in the material.

"Soft Solids" from an elastic perspective

Soft solids, also known as visco-elastic materials, represent an intriguing class of substances to the scientific community as their mechanical properties lie between those of traditional rigid solids and viscous fluids. These materials exhibit both solid-like characteristics, such as maintaining their overall shape, and liquid-like behaviour, allowing for significant deformations under applied stress [17].

The deformation behaviour of soft solids is typically quantified by the stress-strain relationship, which describes how the material responds to external mechanical forces. In the case of linearly elastic materials, Hooke's law relates stress, σ, and strain, ε, through a constant called the elastic modulus, E:

$$\sigma = E \cdot \varepsilon$$

Equation 3

The elastic modulus signifies the material's stiffness and how resistant it is to deformation.

However, for soft solids, this relationship can become non-linear at larger strains due to the rearrangement and interactions of their microstructures. Non-linear models, such as the Ogden or neo-Hookean models, are employed to describe their stress-strain behaviour more accurately.

The Ogden model [18] is based on the strain energy density function, W, which describes the energy stored in a material due to deformation. For soft solids, the Ogden model is given by:

$$W = \Sigma\left[\left(\frac{2\mu_i}{\alpha_i}\right)\cdot\left(\lambda_1^{\alpha_i} + \lambda_2^{\alpha_i} + \lambda_3^{\alpha_i} - 3\right)\right]$$

Equation 4

Where μ_i and α_i are material-specific parameters and λ_1, λ_2, and λ_3 are the principal stretches of the material.

The Ogden model can accommodate the complex stress-strain behaviour observed in soft solids, making it suitable for a wide range of applications in biomedical engineering, soft robotics, and material design.

However, for practical reasons, the neo-Hookean model is often used as it is a simpler representation of the non-linear behaviour of soft solids [19]. It is particularly useful for materials that exhibit nearly incompressible behaviour. The neo-Hookean model is expressed as:

$$W = \left(\frac{\mu}{2}\right)\cdot\left(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3\right)$$

Equation 5

Where μ is the shear modulus.

The neo-Hookean model provides a good approximation for small to moderate deformations in soft solids and has been widely used in engineering towards certain microstructure properties.

One of the distinctive characteristics of soft solids is their visco-elastic behaviour, which combines features of viscosity and elasticity. When subjected to stress, soft solids exhibit time-dependent responses. The relaxation modulus, $G(t)$, is a fundamental parameter in characterizing visco-elasticity. It quantifies the material's ability to relax and dissipate stress over time, indicating the gradual return to its original state after deformation.

Mathematically, the relaxation modulus is related to the stress relaxation function, $R(t)$, representing the stress decay with time, through the Laplace transform:

$$G(t) = \int R(t)\,dt$$

Equation 6

The stress relaxation function relies on the material's internal dynamics, which are often influenced by the arrangement and interactions of its constituents, such as polymer chains, colloidal particles, or biological fibres.

Soft solids also exhibit creep behaviour, which refers to their time-dependent deformation under a constant applied stress. The creep compliance, $J(t)$, characterises the material's strain response over time when subjected to constant stress.

Like the relaxation modulus, the creep compliance is related to the creep compliance function, $C(t)$, representing the strain development with time under constant stress, through the Laplace transform:

$$J(t) = \int C(t)\, dt$$

Equation 7

Creep can have significant implications in engineering applications where materials must withstand prolonged loads, as in building foundations or visco-elastic damping materials [20]. Rheology is a crucial aspect of soft solids, dealing with their flow and deformation behaviour. Soft solids' visco-elastic nature leads to complex flow responses, particularly under oscillatory stress. The complex viscosity, η^*, is a key parameter in rheology, representing the material's resistance to flow [21]

The complex viscosity comprises two components: the storage modulus, η', characterising the elastic response of the material, and the loss modulus, η'', representing the viscous response.

$$\eta^* = \eta' + i\eta''$$

Equation 8

The storage modulus represents the material's ability to store and recover elastic energy, while the loss modulus accounts for the dissipation of energy as heat during deformation.

Ultrasound and "Soft Solids"

Ultrasound waves are mechanical waves that propagate through a medium, including soft matter foods, by transferring energy through particle oscillations. These waves exhibit longitudinal compressional behaviour, where particles vibrate parallel to the direction of wave propagation. In the case of soft matter foods, these particles represent the constituents of the material, such as water, oil, or protein molecules.

The behaviour of mechanical waves, including ultrasound, is governed by the wave equation, which describes how the wave's amplitude evolves over both time and space. For one-dimensional wave propagation, the wave equation can be expressed as:

$$\frac{\partial^2 u}{\partial t^2} - \frac{c^2 \partial^2 u}{\partial x^2} = 0$$

Equation 9

In this equation, $\xi(x,t)$ represents the displacement of particles at position x and time t. The first term, $\frac{\partial^2 \xi}{\partial t^2}$, represents the acceleration of particles over time, and the second term, $\frac{c^2 \partial^2 \xi}{\partial x^2}$, represents the curvature of the wavefront in space. The constant c is the speed of sound in the medium, which depends on the material's properties, such as density and compressibility.

For soft matter foods, which are typically visco-elastic, the wave equation can be modified to incorporate the effects of visco-elasticity. The generalised wave equation becomes:

$$\frac{\partial^2 \xi}{\partial t^2} - \frac{c^2 \partial^2 \xi}{\partial x^2} = \eta \frac{\partial \xi}{\partial t} + \frac{\eta' \partial^2 \xi}{\partial t^2}$$

Equation 10

In this modified equation, η and η' represent the damping coefficients that characterise the visco-elastic behaviour of the material. These coefficients account for the energy dissipation and the delayed response of the material to mechanical perturbations.

When ultrasound waves propagate through a soft matter (food), they interact with its microstructure, leading to changes in wave behaviour. As the ultrasound waves encounter interfaces between different phases within the food, such as solid-gel or liquid-air interfaces, reflections and refractions occur due to acoustic impedance mismatches. This acoustic impedance, Z, at an interface between two media is defined as the product of the material's density, ρ, and the speed of sound, c,:

$$Z = \rho \cdot c$$

Equation 11

The variation in acoustic impedance at interfaces causes echoes and can be utilised for ultrasound imaging techniques like tomography, allowing the visualisation of the soft matter food's internal microstructure.

In addition to impedance mismatches, ultrasound waves experience attenuation as they traverse through the soft matter food. This attenuation is due to various phenomena, including scattering, absorption, and visco-elasticity.

Scattering occurs when the waves encounter in-homogeneities or microstructural elements within the soft matter food, causing changes in the direction of wave propagation. Scattering of (ultra)sound in soft matter involves the superposition of the incident and scattered waves, where the scattered wave's amplitude is determined by the scattering potential and the wave vector.

In the below we consider the case of one-dimensional wave propagation through soft matter:

The incident ultrasound wave can be represented as:

$$P_{incident(x,t)} = P_0 \cdot e^{[i(kx - \omega t)]}$$

Equation 12

Where P_0 is the initial amplitude of the incident wave, k is the wave vector, x is the spatial position, t is time, and ω is the angular frequency.

Upon interacting with inhomogeneities or microstructural elements, the incident wave undergoes scattering, resulting in the generation of scattered waves. The scattered ultrasound wave can be expressed as:

$$P_{scattered}(x,t) = A \cdot e^{i(kx - \omega t + \varphi)}$$

Equation 13

Where A is the amplitude of the scattered wave, and φ is the phase shift introduced during scattering.
The total ultrasound wave at a specific point in space and time, considering both the incident and scattered waves, can be expressed as the superposition of these waves:

$$P_{total}(x,t) = P_{inciden}(x,t) + P_{scattered}(x,t)$$

Equation 14

Considering now the scattering cross-section, σ, of the inhomogeneity or microstructural element. The scattering cross-section represents the measure of the probability of scattering and is related to the scattering amplitude, A, as follows:

$$\sigma_s = |A|^2$$

Equation 15

The scattering amplitude can be further expressed in terms of the scattering potential, V, and the wave vector, k, as:

$$A = -\left(\frac{2\pi}{k}\right)\cdot V$$

Where the wave vector is defined as a function of wavelength λ as

$$k = \frac{2\pi}{\lambda}$$

Equation 16

Incorporating the scattering amplitude into the total ultrasound wave expression we arrive at:

$$P_{total}(x,t) = P_0 \cdot e^{[i(kx - \omega t)]} - \left(\frac{2\pi}{k}\right)\cdot V \cdot e^{[i(kx - \omega t + \varphi)]}$$

Equation 17

Absorption involves the conversion of ultrasound energy into heat as it interacts with the constituents of the material. Visco-elastic properties of soft matter foods also contribute to attenuation, with energy being dissipated as the waves interact with the material's structure.
Absorption of ultrasound in soft matter occurs when the ultrasound waves interact with the constituents of the material, leading to the conversion of ultrasound energy into heat. Continuing with a one-dimensional wave propagation of ultrasound through soft matter, the incident ultrasound wave can be represented as:

$$P_{incident}(x,t) = P_0 \cdot e^{i[(kx - \omega t)]}$$

Equation 18

During propagation, the ultrasound wave interacts with the constituents of the soft matter, such as water molecules, proteins, and other molecules. This interaction leads to the dissipation of ultrasound energy. The rate of absorption of ultrasound energy can be quantified using the absorption coefficient, α, which represents the fraction of ultrasound energy absorbed per unit distance travelled in the soft matter.
The change in acoustic pressure, ΔP, due to absorption as the ultrasound wave travels through a small distance dx in the soft matter can be described as:

$$\Delta P = -\alpha \cdot P_{incident}(x,t) \cdot dx$$

Equation 19

where $\alpha \cdot P_{incident}(x,t)$ represents the energy absorbed per unit distance traveled.
The total absorption effect along the entire propagation path is determined by the integration of the change in acoustic pressure over the distance, Δx, through the soft matter:

$$\int \Delta P = \int -\alpha \cdot P_{incident}(x,t) \cdot dx$$

Equation 20

Integrating from the initial position, x_0, to the current position, x, we arrive at:

$$P_{total}(x,t) = P_{incident}(x_0,t) - \alpha \cdot (P_0/(i \cdot k)) \cdot \left[e^{i(kx - \omega t)}\right.$$

Equation 21

Integrating from the initial position, x_0, to the current position, x, we arrive at:

$$P_{total}(x,t) = P_{incident}(x_0,t) - \alpha \cdot (P_0/(i \cdot k)) \cdot \left[e^{i(kx - \omega t)}\right.$$

Equation 22

Applied to the incident wave over the specified distance:

$$\int_{x_0}^{x} P_{incident(x,t)} \cdot dx = P_0 \cdot \int_{x_0}^{x} e^{i[(kx - \omega t)]} \cdot dx$$

Equation 23

This integral evaluates to:

$$\int_{x_0}^{x} P_{incident(x,t)} \cdot dx = (P_0/(i \cdot k)) \cdot \left[e^{i(kx - \omega t)}\right] \mid [x_0 to\ x]$$

Equation 24

$$\int_{x_0}^{x} P_{incident(x,t)} \cdot dx = (P_0/(i \cdot k)) \cdot \left[e^{i(kx - \omega t)} - e^{i(kx_0 - \omega t)}\right.$$

Equation 25

Substituting this expression back into the previous equation, we receive:

$$P_{total}(x,t) - P_{incident}(x_0,t) = -\alpha \cdot (P_0/(i \cdot k)) \cdot \left[e^{i(kx - \omega\right.$$

Equation 26

Rearranging the equation to solve for the total acoustic pressure $P_{total}(x,t)$:

$$P_{total}(x,t) = P_{incident}(x_0,t) - \alpha \cdot (P_0/(i \cdot k)) \cdot \left[e^{i(kx - \omega t)}\right.$$

Equation 27

With this, we have described the absorption of ultrasound energy within the context of soft matter using the absorption coefficient (α). The attenuation of ultrasound waves can be modelled by the attenuation equation:

$$\frac{\partial P}{\partial x} + \alpha \cdot P = 0$$

Equation 28

In this equation, $\frac{\partial P}{\partial x}$ represents the spatial gradient of the acoustic pressure, and α is the attenuation coefficient, quantifying the rate of ultrasound intensity reduction as it propagates through the soft matter food. The detailed nature of the ultrasound attenuation coefficient is addressed in the next section.

We conclude that the behaviour of mechanical waves, particularly ultrasound, is governed by the wave equation. This fundamental equation accounts for the propagation of waves in both time and space, incorporating terms related to acceleration and wave-front curvature. To address visco-elastic behaviour, modifications are made to the wave equation, including the inclusion of damping coefficients. When ultrasound waves traverse through soft matter foods, they interact with the intricate microstructure, leading to phenomena such as reflections, refractions, and echoes due to impedance mismatches. However, these waves also experience attenuation due to several factors, including scattering, absorption, and the visco-elastic properties of the material itself. Scattering arises as waves encounter in-homogeneities or microstructural elements, causing directional changes in wave propagation. Mathematically, the incident and scattered ultrasound waves can be precisely represented through expressions involving amplitudes, phase shifts, and wave vectors. The scattering cross-section and amplitude play a significant role, connected to the scattering potential and wave vector. As ultrasound energy interacts with the material's constituents, it undergoes absorption, converting into heat. The absorption coefficient, a crucial parameter, quantifies the fraction of energy absorbed per unit distance travelled in the soft matter. To model the total acoustic pressure accounting for absorption, the attenuation equation comes into play, featuring the attenuation coefficient to describe the ultrasound intensity reduction during propagation.

We now derive a mathematical relationship appropriate for the elastic behaviour of soft solid in which retardation plays a central role and then show that this general relationship contains the appropriate behaviour in the limits of an elastic solid and a Newtonian fluid. We stress the importance of the generally ignored bulk viscosity and discuss its measurement. We then illustrate the use of these relationships. Other approaches to this problem involve empirical or semi-empirical descriptions of viscosity and yield stress [22] which are not discussed further in this paper.

The strain tensor (strain is change in dimension divided by the original dimension resulting from a stress defined as force on the point of strain resulting from the surrounding material) is:

$$S'_{ij} = \frac{1}{2}\left(\frac{\partial \xi_i}{\partial x_j} + \frac{\partial \xi_j}{\partial x_i}\right)$$

Equation 29

Where ξ is the displacement of a volume element. $\dot{S}'_{ij}$ is the time derivative of the strain tensor (The strain rate tensor):

$$\dot{S}'_{ij} = \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right)$$

whose velocity components are the time derivative of displacement:

$$v_i = \frac{\partial \xi_i}{\partial t}$$

And the velocity vector v is defined in terms of the unit vectors *i, j*
and *k*:

$$v = iv_x + jv_y + kv_z$$

Equation 30

The stress tensor, *P*, can be related to the strain tensor in a way which connects current stresses to the deformation history [23]. This is also called 'retardation' because there is a time lag (*t'*) arising from the deformation history.

$$\mathrm{P} = p\delta_{ij} - \int_{-\infty}^{t}\left[\breve{B}(t-t') - \frac{2}{3}G(t-t')\right]\dot{S}(t')\delta_{ij}dt' - 2\int_{-\infty}^{t} G(t -$$

Equation 31

Here $\breve{B}(t)$ is the time dependent bulk modulus from which the reciprocal of the adiabatic compressibility, *B,* is absent, and *G(t)* is the time-dependent shear modulus. d_{ij} is the Kronecker delta symbol, which has the value $\delta_{ij} = 1$ when i=j and $\delta_{ij} = 0$ when $i \neq j$.

To obtain solid-like behaviour, we set

$$\breve{B}(t) = \left(\lambda + \frac{2}{3}\mu\right)h(t)$$

Equation 32

$$(t) = \mu h(t)$$

Equation 33

where *h(t)* is the Heavyside step function, λ and μ are the Lamé constants.
We can now write the individual components of the stress tensor, P, in terms of the Lamé constants:

$$P_{ij} = -\left(\lambda + \frac{2}{3}\mu\right)Tr\left(S'_{ij}\right)\delta_{ij} - 2\mu S_{ij}$$

$$= \left(\lambda + \frac{2}{3}\mu\right)S\delta_{ij} - 2\mu S'_{ij} + \frac{2}{3}\mu S\delta_{ij}$$

$$= \lambda S\delta_{ij} - 2\mu S'_{ij}$$

Equation 34

here *S* is the trace of the strain tensor S', the traceless strain tensor S_{ij} is:

$$S_{ij} = S'_{ij} - \frac{1}{3}S\delta_{ij}$$

Equation 35

Allegra and Hawley (1972)[24] use the transformation $G = \mu \rightarrow -i\omega\eta$ to obtain the behaviour of the liquid from the stress tensor for the solid using the shear viscosity h_s . This ignores the bulk viscosity, h_B, and is not general enough to apply to many visco-elastic (soft solid) liquids such as polymers which exhibit relaxation effects. Equation 33 on the other hand, is general enough to account for relaxation effects as well as more complex behaviours.
For the case of a Newtonian liquid, we choose:

$$\breve{B}(t) = \eta_B\delta(T)$$

$$G(t) = \eta_s\delta(T)$$

Equation 36

we then obtain the stress tensor for liquid-like behaviour:

$$\mathrm{P} = -p\delta_{ij} + \left(\eta_B - \frac{2}{3}\eta_s\right)\dot{S}\delta_{ij} + 2\eta_s\dot{S}'$$

Equation 37

which is written in terms of the strain-rate tensor and agrees with the stress tensor in Epstein and Carhart (1953), Batchelor (1967) and Morse and Ingard (1968).

Ignoring relaxation effects (the $\breve{B}(t-t')$ in Equation 31) which may be important in polymers, gives the principal stress as:

$$p = \frac{1}{3}Tr(P) = -\left(\lambda + \frac{2}{3}\mu\right)S = -BS$$

Equation 38

The principal stress *p* is simply the hydrostatic pressure, and the equation relates pressure to the fractional change in volume, *S*, through the bulk modulus, *B*. This equation also relates the Lamé constants to the bulk modulus in the case of a solid.

Note here once again the importance of the bulk viscosity (also called the longitudinal viscosity [25]) which is measured either using ultrasound spectroscopy [26] or Brillouin scattering [25]. This mathematical treatment raises the prospect of a unified experimental measurement approach which combines acoustical, textural, and rheological methods to provide a more complete description of the behaviour of soft solid foods.

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