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FAST TRACK COMMUNICATION

Identification of a low-frequency elastic behaviour in liquid water

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Online at stacks.iop.org/JPhysCM/24/372101**Abstract**

This article deals with the identification of solid-like properties measured at room temperature at a sub-millimetre length scale in liquid water. At a macroscopic scale, normal liquids (i.e. above melting temperature), and in particular water, are typically and empirically defined by the absence of shear elasticity, in contrast to solids or plastic fluids that require a stress threshold for flowing. A novel method optimizing the transmission of the shear stress to the sample enables a more complete probe of the mechanical response of liquids. It reveals that glass formers and viscous alkanes actually exhibit finite macroscopic shear elasticity away from any phase transition. This protocol is here applied for the first time to liquid water at room temperature, revealing, at the sub-millimetre scale, a low-frequency solid-like property.

(Some figures may appear in colour only in the online journal)

1. Introduction

On the basis of a Maxwell gas model (1867), it has long been suspected that liquids exhibit shear elasticity only at sufficiently high solicitation frequencies (MHz or GHz). Recent experimental improvements show that actually it is possible to measure also shear elasticity at low-frequency (0.01–16 Hz) and at the sub-millimetre scale [1–4]. In other words, liquids exhibit long-range solid-like correlations at a macroscopic scale away from any phase transition.

We probe here for the first time the low-frequency dynamic response of liquid water and show an elastic response at a sub-millimetre thickness. This result has been enabled by applying a weak mechanical stress efficiently transmitted to the liquid by improving the boundary conditions between liquid and the substrate. These conditions preserve the liquid as close as possible to its equilibrium state. This protocol, established since 2005, has enabled the measurement of several decades higher mechanical response independent of the frequency in melts of standard polymers [1, 2]. The thus far neglected shear elasticity (i.e. solid-like component) was highlighted far away from the glass transition and at a

macroscopic scale. Later, the observation of a low-frequency shear elasticity above the melting point in glass formers such as glycerol [3] or o-terphenyl [4], and more recently in a viscous liquid heptadecane [5], invalidated an interpretation in terms of dynamic heterogeneities (clusters) reminiscent of the glass transition [6, 7]. The low-frequency shear elasticity has the characteristics of a generic condensed matter property (i.e. at thermodynamical equilibrium).

Here, we describe the first experiments carried out on liquid water with this method.

Several decades of physical, chemical, biological, thermodynamical, and interfacial studies has certainly made water the most studied liquid [8]. It has been in particular established that the confined geometry (capillaries, at the interface, in thin layers, or in interactions with biological systems) leads to a slowing down of dynamics with respect to the ‘bulk’ properties [8–11]. Mechanical measurements reveal scale-dependent interactions at the molecular scale or at a multiple of that, as reported for example in surface force apparatus experiments [9, 10]. These studies are restricted to layers several molecules thick, i.e. typically layers of much less than the micron scale. Several authors report on

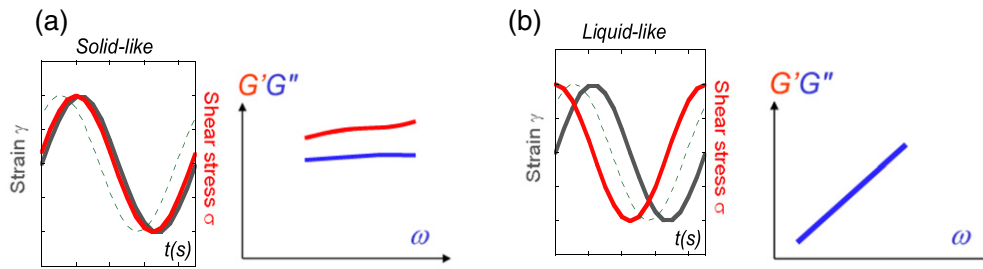


Figure 1. Schemes of the sine strain input wave (grey line) and shear stress output response (red line) (the dotted line represents the $\pi/4$ phase shift output wave (---)), and corresponding low-frequency dynamic spectra (logarithmic representation). (a) Solid-like behaviour: input and output waves are close in phase: $G' > G''$ with G' and G'' weakly dependent on the frequency. (b) Viscous behaviour: input and output waves are out of phase with $\Delta\phi > \pi/4$ (here $\Delta\phi = \pi/2$) with G' negligible compared with G and G'' vanishing with the frequency.

an increased viscosity at the 1000–10000 Å length scale away from the surface. These results were interpreted by surface-induced effects or interfacial phenomena [9, 10] and some by intrinsic properties [12]. The mechanical approaches (SFA, flow measurements) were mainly carried out without specific optimization of the interactions of the liquid to the substrate. By improving these boundary interactions, the present results on liquid water report on elastic properties at several hundreds of microns length scale (figure 4) and invite us to rethink how the liquid state should be considered.

2. Experimental details

The dynamic probe uses a soft mechanical stress, as non-disturbing as possible, to keep intact the material properties (linear conditions). The study is focused on the low-frequency response (10^{-1} – 10^2 rad s^{-1}), applying therefore low shear strain stresses (0.1%–2%). This dynamic mechanical analysis belongs to the rare methods that give access to slow relaxation times.

This method consists in applying a small shear stress/strain to the fluid via surface contact. A strong interaction between the liquid and the substrate is obtained by using a zero-porosity alumina substrate [13]. It optimizes the liquid/substrate interaction by promoting the full wetting of the liquid on the surfaces and expelling the eventual interfacial gas layer between the liquid and the substrate (total wetting conditions [14]).

The sample (distilled water), free of dissolved gas, placed in the gap of two wetting surfaces is submitted to a small shear solicitation of constant shear strain γ_0 (imposed strain mode). Its response is measured via the shear stress transmitted by the sample to the second surface (immobile and coupled to a sensor). Reported data correspond to macroscopic measurements carried at room temperature and 0.125 mm gap thickness.

The oscillatory motion and the shear stress measurement are provided by a conventional rheometer (ARES2) equipped with alumina plates of 40 mm diameter. This device has been equipped with a 7-digits voltmeter (Keithley—Rate: 300 data/s) that simultaneously measures the voltage of the motor imposing the oscillation (input wave), while another 7-digits voltmeter measures the voltage associated with the

sensor (output wave). This setup enables simultaneous access to the strain/stress signals and to the dynamic profile using the conventional formalism following the relationship: $\sigma(\omega) = \gamma_0 \sin(\omega t + \Delta\phi)$, with $\sigma(\omega)$ the shear stress and $\Delta\phi$ the phase shift between the input and the output waves, or in terms of shear elastic (G') and viscous (G'') moduli: $\sigma(\omega) = \gamma_0(G'(\omega) \sin(\omega t) + G''(\omega) \cos(\omega t))$, with G' the component in phase with the strain and G'' the out-of-phase component.

A perfect solid-like response displays no phase shift in the output response. Experimentally, solid-like materials always exhibit a short delay due to internal freedom degrees. As long as the phase shift remains lower than $\Delta\phi < \pi/4$, the elastic component G' dominates the viscous component G'' (figure 1(a)).

If the output response of the material presents a phase shift larger than $\pi/4$, then the viscous component G'' dominates the elastic component G' (figure 1(b)). The sample exhibits a liquid-like behaviour. If the phase shift reaches $\pi/2$ (G' vanishes), the sample is defined as purely viscous.

The sample response can be scanned as a function of the frequency (ω), typically from 10^{-1} up to 10^2 rad s^{-1} (i.e. probing timescales from 0.01 up to 10 s) giving the frequency range over which the sample responds elastically or in a dissipative way (viscous behaviour).

The solid-like behaviour is independent of the frequency whereas a (Maxwell) liquid-like behaviour typically displays a vanishing response characterized by a ω -scaling of the viscous modulus and a ω^2 -scaling dependence of the elastic modulus. A purely viscous sample does not display any elastic component.

Finally, it should be stressed that the formalism in terms of G' and G'' imposes that the resulting stress wave keeps the shape of the imposed strain wave (sinusoidal-like). The study of the signal will show that this condition is actually valid in two extreme situations only, corresponding to the very weak and to the high strain fields respectively.

3. Results

3.1. Dynamic relaxation measurements

Figure 2(a) illustrates the input sinusoidal wave and the output shear stress transmitted by a layer of 0.125 mm of liquid water

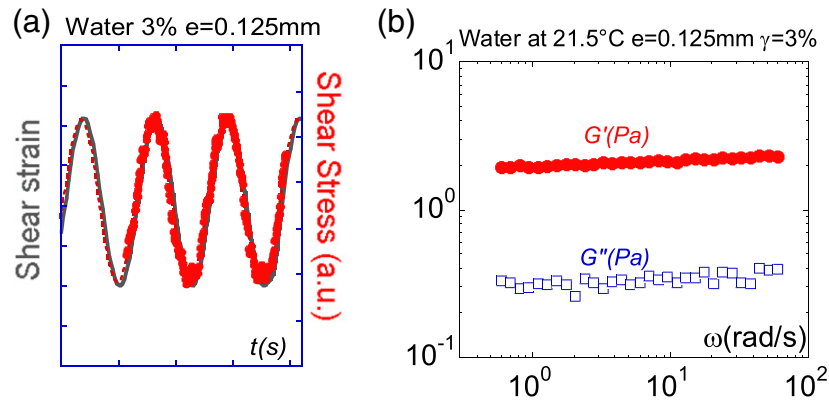


Figure 2. (a) Signals corresponding to the input sine strain wave (data points: grey squares) and output shear stress (data points: red circles) wave measured on liquid water at low strain ($\gamma_0 = 3\%$) and at $\omega = 1 \text{ rad s}^{-1}$. The continuous and dashed lines correspond to a sine modelling of the input (—) and the output waves (--- (red)) (phase shift $\Delta\phi = 9 \pm 1^\circ$). (b) Low strain frequency viscoelastic moduli of liquid water measured at room temperature (21.5°C), at 0.125 mm gap thickness and $\gamma_0 = 3\%$. The shear modulus G' (red circles) is independent of the frequency and higher than G'' (blue squares).

over four oscillation periods. The liquid water is solicited at 24°C at low strain amplitude ($\gamma_0 = 3\%$) using total wetting boundary conditions. Figure 2(a) shows that both input and output waves are almost superposed, indicating a nearly instantaneous sample response ($\Delta\phi < 8^\circ$), i.e. a solid-like response. This result indicates that when the liquid is firmly anchored on the surfaces, its response to a weak mechanical solicitation is solid-like. A similar in-phase signal is observed over the wide range of frequency tested in figure 2(b). Since the output shear stress is sinusoidal, a description in terms of elastic G' and viscous G'' moduli (linear regime) is justified. Figure 2(b) gathers the evolution of G' and G'' versus frequency at low strain amplitude versus frequency. The shear modulus G' dominates the viscous component. Both moduli are weakly dependent on the frequency, which is characteristic of a (linear) solid-like response, in agreement with the in-phase wave displayed in figure 2(a).

This result highlights the efficiency of the protocol associating a total wetting with a weak mechanical stress, enabling, for the first time, one to measure shear elasticity in water at a hundred microns length scale and at such low frequencies.

3.2. From solid-like to conventional viscous behaviour: strain dependence of the mechanical response

The solid-like wave is delicate and can easily shear-melt by increasing the strain amplitude. The evolution of the mechanical response on increasing the strain amplitude is presented on figure 3(a). At low strain amplitude, both input and output waves are close in phase ($\Delta\phi < 8^\circ$), indicating a major elastic component (G'). The elastic regime corresponds to the 'red' zone. In this regime, the elastic modulus $G'(\omega)$ is higher than the viscous modulus $G''(\omega)$ (the viscous component (G'') contributes to about 1% of the total modulus $G = \sqrt{G'^2 + G''^2}$).

At higher strain amplitudes, both elastic and viscous moduli collapse, with a more pronounced fall for the elastic modulus and leading to a crossover from a solid-like to a viscous-like behaviour. At high strain amplitude, the viscous

modulus dominates (blue zone) and the elastic component becomes negligible with respect to the total modulus (less than 1% of G at 30 rad s^{-1}).

As a result, the usual viscous behaviour of water is recovered on wetting substrates, by applying high strain amplitudes, thus away from mechanical equilibrium conditions. It shows that a linear solid-like regime exists prior to the conventional flow regime. A similar strain dependence scheme has been reported for other liquids and melts and by different authors [1–6], confirming that the shear elasticity in the liquid state can be easily lost in favour of the usual flow behaviour.

Figure 3(b) details the mechanism of transition from solid-like to viscous behaviour. At low shear strain, both input (shear strain) and output (shear stress) waves are nearly superimposable (figure 3(b) left). At intermediate strain rates ($\gamma_0 = 10\%$, middle figure of figure 3(c)), the output wave is no longer sinusoidal but distorted with apparent harmonics. The occurrence of the distorted signal coincides with the entrance into the non-linear regime, where the values of G' and G'' are strongly dependent on the strain rate. Since the signal is no longer sinusoidal, a modelling in simple terms of G' and G'' is not strictly meaningful. The wave distortion shows harmonics that can be interpreted as the result from a truncation/recombination of the primitive wave. This effect has to be typically related to a release process of the elastic energy stored in the sample.

At large shear strain ($\gamma_0 > 5000\%$), the wave recovers a nearly sinusoidal shape with a phase advance of about $\Delta\phi = \pi/2$ (figure 3(b) at right). This output sine wave can be modelled in terms G'' . The associated spectrum displays a viscous behaviour, as indicated in the dynamic spectrum measured at $\gamma_0 = 5000\%$. The curve obeys an ω -scaling with a slope $\eta = 10^{-3} \text{ Pa s}$, of the order of the tabulated dynamic viscosity value [16]. It is interesting to note that the evolution from the low strain amplitude sinusoidal wave to the large strain amplitude sinusoidal-like wave does not correspond to a simple shift of the phase but to a strong modification of the signal.

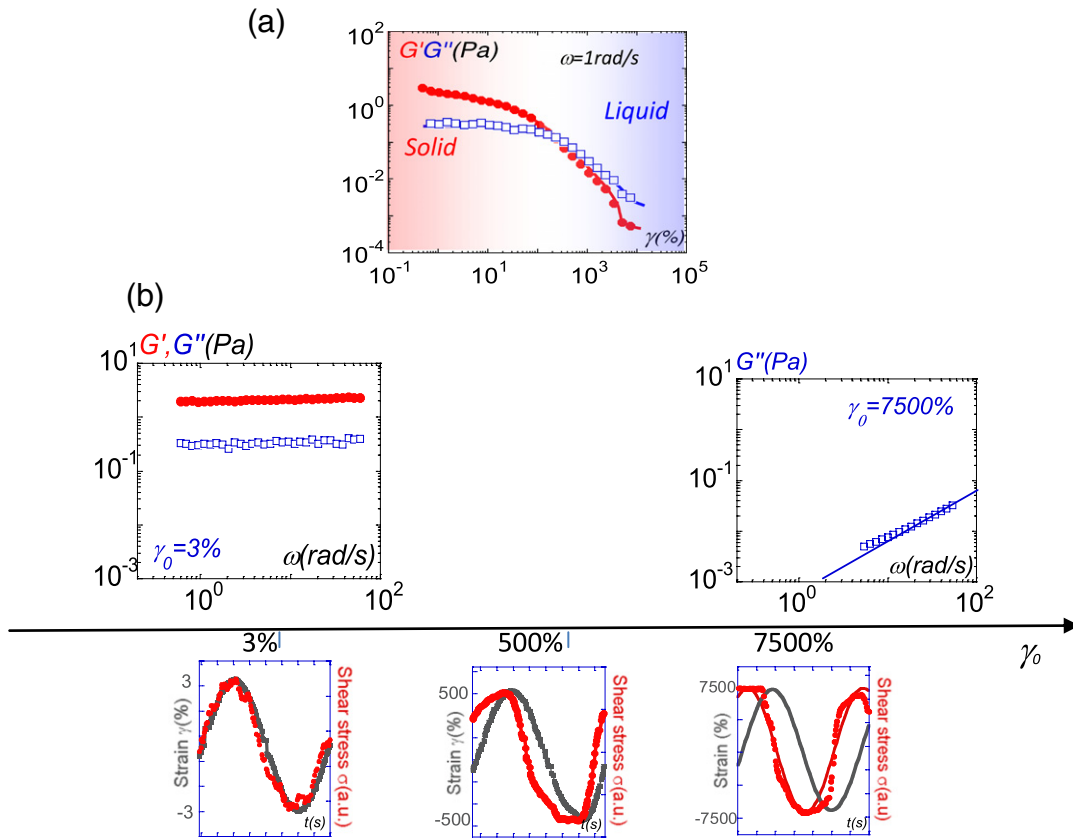


Figure 3. (a) Strain dependence of the viscoelastic moduli (G' : red circles; G'' : blue squares) of liquid water at $\omega = 1 \text{ rad s}^{-1}$ and at 0.125 mm gap thickness at room temperature (γ_0 evolves from 2.5% up to 7500%). The lines are guides to the eye. (b) Details of the frequency dependence at weak and at large strain amplitudes ($\gamma_0 = 3\%$ and at $\gamma_0 = 7500\%$ respectively) and corresponding input sine wave (grey squares) and output shear stress (red circles) waves. The red line is a sinusoidal fit of the data points. The frequency dependence at intermediate strain amplitude (500%) is not displayed since the wave is no longer a sine wave. The blue straight line shows the ω -scale of G'' , indicating a dynamic viscosity $\eta = 10^{-3} \text{ Pa s}$, in agreement with conventional experiments [16].

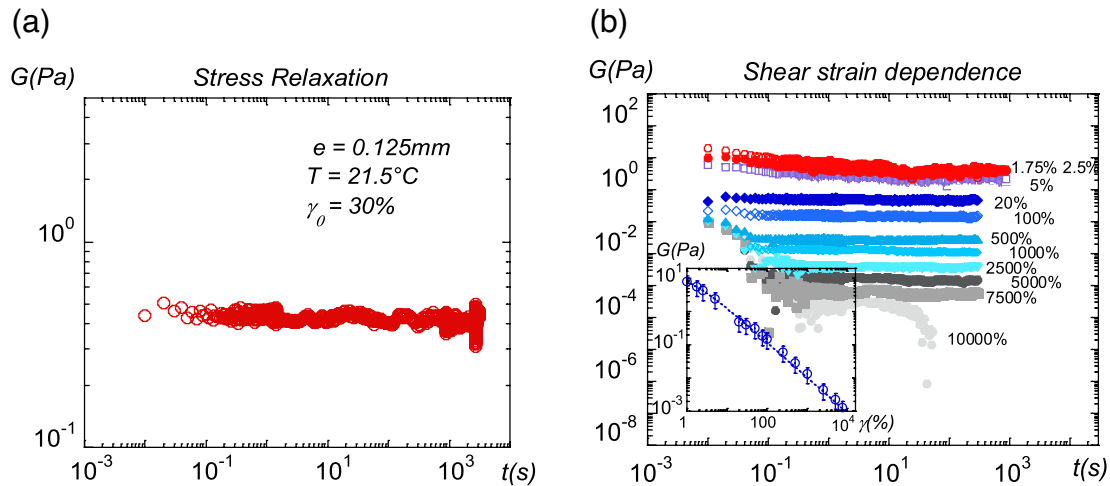


Figure 4. Time dependence of the relaxation of the shear modulus $G(t)$ of liquid water at room temperature ($T = 21.5 \text{ }^\circ\text{C}$) and 0.125 mm gap thickness. (a) Detail of $G(t)$ at $\gamma_0 = 30\%$. (b) Evolution from low ($\gamma_0 = 1.75\%$) up to high strain amplitude ($\gamma_0 = 10000\%$). The inset displays the average value of the stress relaxation modulus versus strain amplitude. The dotted line illustrates the curve fitted by: $G(\gamma) = G_0/(1 + (\gamma/\gamma_0)^b)$.

3.3. Stress relaxation measurements

Another and independent procedure to evidence the solid-like character contained in the liquid water is the relaxation measurement. The sample placed between two surfaces is

submitted to a shear strain γ_0 by moving one surface at the time $t = 0$. The sample transmits the shear stress by contact to the second surface, which is coupled to a sensor. This shear stress $\sigma(t)$ is measured versus time. Figure 4(a) shows the corresponding stress relaxation modulus

$G(t) = \sigma(t)/\gamma_0$ measured on wetting boundary conditions, at room temperature and 0.125 mm gap thickness. As can be seen, the liquid does not flow under strain but displays a weak but non-negligible elasticity. The shear stress does not collapse, even after more than 10^3 s. This is a typical solid-like response, coherent with previous observations [1–5]. Increasing the strain amplitude first induces a rapid modulus drop followed by a stress plateau indicating the subsisting resistance of the liquid (figure 4(b)). At $\gamma_0 = 10\,000\%$, the liquid no longer resists and the stress relaxation falls rapidly, indicating that the liquid flows. The inset displays the average shear stress as a function of the strain amplitude. The shear stress can be modelled by a continuous decreasing function of the shear strain: $G(\gamma) = G_0/(1 + (\gamma/\gamma_0)^b)$ with $b = 1.05 \pm 0.03$ and $\gamma_0 = 0.9 \pm 0.1$. The extrapolation at zero-strain limit gives the intrinsic stress relaxation modulus (of that sample) $G_0 \approx 17 \pm 3$ Pa. G_0 is weak but finite, not negligible and of the same order as the low-frequency dynamic modulus.

4. Conclusions

Finite low-frequency shear elasticity is measured by applying a weak mechanical shear stress at room temperature to liquid water at a sub-millimetre thickness. The shear elasticity is unambiguously identified with three different stress measurements presented in figures 2, 3 and 4 respectively. All of them have been carried out by optimizing the motion transfer from the stress source to the sample and from the sample to the sensor. The study of the stress wave shows that a nearly in-phase response to the signal at its source is displayed by water under weak sollicitation in the low-frequency range. The conservation of the input strain sinusoidal shape to the output shear stress wave proves the solid-like character of the response and enables an analysis in terms of (in-phase: G') elastic and (out-of-phase: G'') viscous moduli. The examination of the low-frequency range (10^{-1} – 10^2 rad s^{-1}) indicates in agreement with the shape of the nearly in-phase signal, that the shear modulus G' dominates the mechanical behaviour, with both G' and G'' being weakly dependent on the frequency. The dominance of the shear modulus indicates a major solid-like response.

The solid-like regime ('Solid' red zone of figure 3(a)) is prior in strain to the usual viscous regime ('Liquid' blue zone). Since the lowest strain amplitudes ensure the weakest perturbations of the sample, the elastic response of liquid water is thus the first response of the material. The usual conventional viscous behaviour (carried out without special care of wetting—using generally aluminium substrates), corresponds to a second linear domain and results from a partial transmission of the stress (weak liquid/surface interactions) [2]. On wetting substrates, the viscous response can also be obtained but it requires the application of very high strain amplitudes (right inset of figure 3) once the solid-like response has collapsed (as illustrated in figures 3 and 4, and in [2–5]).

Other measurements (not presented here) carried out at different water thicknesses indicate that the elastic response

persists at least from 0.055 up to 0.500 mm, decreasing with increasing gap and no longer measurable at larger thicknesses. We thus probe a macroscopic property whose strength depends on the length scale. The dimensional character is also found in molten cements or in foam rheology [17, 18]. At 0.125 mm gap thickness, the low-frequency (Hz frequency range) shear modulus water is about 20 Pa (figures 2(b), 3(a)). This value is extremely weak compared to 'conventional' solids characterized by several GPa moduli. It is also weak in comparison to the water moduli measured using the atomic vibration of a piezomembrane by Derjaguin: 30 kPa at a frequency of 73 kHz [15] or by Bund *et al.*: 10 kPa at moderate frequencies (10 MHz) [19]. Finally, compared to the GPa moduli measured by ultra-sonic methods or Brillouin scattering in liquids at GHz frequencies [20], the low-frequency shear elasticity of water also appears extremely weak. These elastic properties are, however, of utmost importance since they show that water resists weakest shear flow.

The water elasticity is in agreement with shear moduli measured with this method on other liquids (heptadecane, glycerol, o-terphenyl, polymer melts) [1–5]. It is also coherent with the gel-like behaviour reported in a non-entangled melt using a piezomembrane in the same frequency range [6], or with x-ray photon correlation results indicating the need to add an elastic term for modelling capillary waves in supercooled polypropylene glycol [20]. Nearly static shear elasticity in the liquid state shows that the intermolecular interactions are actually long range. This claim excludes any interpretation of the macroscopic properties based on individual molecular dynamics. Its measurement on water at room temperature confirms that it is also at variance with the hypothesis of long-lived clusters away from the glass transition [6, 7] or of ill-defined supercooled states [21]. In agreement with Derjaguin's interpretation [15], the low-frequency shear elasticity is an intrinsic condensed matter property and its origin has to be found in the strength and the range of the intermolecular interactions, particularly reinforced by the H-bond interconnectivity in the case of water. The high degree of intermolecular connectivity at the origin of these long-range elastic correlations contributes significantly to the energy of the liquid condensed matter state. Few theoretical approaches consider the condensed matter character of liquids [22, 23]. Even fewer approaches consider the occurrence of multi-scale properties. A phenomenological model introducing power laws in reciprocal space [24] predicts that the intrinsic shear elasticity of a finite volume of liquid is non-zero. It also predicts [25] that the shear modulus measured in a rheology experiment at sufficiently low frequencies is dependent on sample size, decreasing with increasing sample size, a behaviour observed by different authors at the sub-millimetre length scale [1–6, 15]. Quantitative analysis of some of our present data and data at higher frequencies found in the literature in terms of this model is currently under way.

These experimental results have to be extended and the method certainly improved, but they are already rich in perspectives for a better understanding of the multi-scale liquid properties, gelation processes, transport and

flow mechanisms and origin of the capillary forces, and indicate the necessity to provide bridges between disciplines (micromechanics, microtribology, rheology, microrheology, poroelasticity, and surface science).

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