# Thermal Shear Waves in Mesoscopic Liquids

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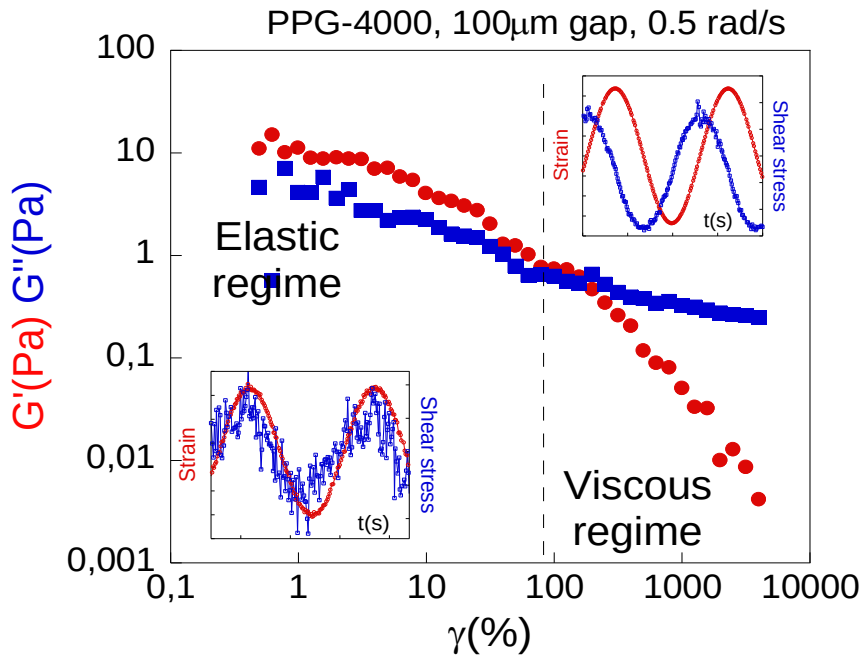
Abstract: A thermal response is identified upon applying oscillatory shear excitation in the conventional viscous regime (frequency range within 0.08 to 0.8 Hz) of ordinary liquid (polypropylene glycol) at room temperature. The liquid confined between surfaces with high energy to reinforce the wetting contact and of low thermal conductivity generate almost instantaneous and reversible (hot and cold) thermal waves upon applying the oscillatory shear strain. The amplitude of thermal waves that can reach + 0.04 °C and -0.04 °C in amplitude, depends on the scale in the same way as the liquid elasticity which is hardly accessible for a thickness scale of the order of a millimeter. The observed thermal effects indicate that mesoscopic liquids are able to convert (partly) mechanical shear energy in local thermodynamic states, therefore exhibit local thermoelastic waves. A transition from a linear, thermo-elastic behavior, to a non-linear behavior, similar in strain behavior to an elastic to plastic regime is identified from low to very large deformation.

Keywords: confined liquids, dynamic analysis, thermoelasticity.

## 1. Introduction

From large length scales (geological and even astrophysical scales) down to nanoscale confinement, fluids play crucial roles definitively at all length scales. But how to differentiate liquids from solids and does this difference depend on the scale at which the observation is done? It is conventionally accepted that the rapid molecular dynamics of (ordinary) liquids do not allow the propagation of low frequency shear waves, and thus that the (static) shear modulus is a solid-like characteristic. However, the properties of the confined material can be very different from that of the three-dimensional bulk phase. Recent experimental and theoretical developments based on scale dependent analysis challenge the rapid dynamics hypothesis and point to the possible existence of a mesoscopic liquid shear elasticity at low frequency (Fig.1a). Under the assumption of elastically correlated liquid molecules, a new thermal approach was set up to analyze the behavior of the liquid to a mechanical shear strain.


a)




b)

**Fig.1:** a) We examine the low frequency shear strain domain (~1Hz) of liquids where recent developments have pointed out the existence of liquid shear elasticity at mesoscale. b) Confined liquids exhibit a shear elastic dynamic behavior of the polypropylene glycol (PPG-4000) at low strain amplitude (visible here below $\gamma < 100\%$ where $\gamma = \delta l/e$ with $\delta l$ being the displacement and $e$ the gap thickness). The elastic response is identifiable by a shear modulus G' higher than then viscous modulus G" (and confirmed by nearly in-phase shear stress-shear strain waves on the left insert). At large strain amplitude, shear stress and strain waves are $\pi/2$-phase shifted indicating a viscous behavior. The measurements are carried out in total wetting conditions (Alumina substrate), at 100µm thickness, room temperature and far away from the glass transition (Tg = -75°C). The applied frequency $\omega = 0.5$ rad/s rules out any coupling with molecular relaxation time ($\tau_{relax} \approx 10^{-9}$s).

A new experimental protocol has shown that it is possible to improve the viscoelastic response of fluids and access a nearly static mesoscopic shear elasticity by taking into account the fluid/substrate interfacial forces and using high energy surfaces like the Alumina ($Al_2O_3$) that provides a total macroscopic wetting [1,2]. A strong liquid/substrate interaction amplifies the transmission of the shear strain to the fluid. In such conditions, the dynamic response exhibits at mesoscopic scale, a liquid shear elasticity in the low frequency range (0.1-10Hz) (Fig.1b). Fig.1b points out how the elastic-like regime, identifiable by a shear modulus G' higher than the viscous modulus G" at low strain amplitude, is progressively replaced by a viscous regime by increasing the strain amplitudes. Fig.1b illustrates the

behavior of a 100 µm layer of polypropylene glycol (PPG-4000)). At macroscopic scale, the liquid exhibit only a viscous response whatever the applied shear strain.

As a result, the viscoelastic response is not universal but is a function of the scale at which the fluid response is measured [1, 3-12]. The mesoscopic shear elasticity concerns both simple liquids (Van der Waals and H-bond liquids), complex fluids (polymer melts, molecular glass formers, ionic liquids) and physiological fluids [1-12].

Because of the shear elasticity, fluids resist to a shear strain and their resistance depends on the considered scale, being reinforced when the scale decreases [1, 5, 6-7, 12]. Therefore, when a fluid is submitted to a shear strain, its elasticity might be actioned, inducing either its expansion or its compression. Indeed when an elastic material expands, its thermal energy is changed. The immediate consequence is that a thermo-elastic coupling becomes possible, challenging the assumption of an instant dissipation via thermal fluctuations and justifying the search of a thermal approach.

Here we use the experimental conditions that have enabled the identification of the low frequency shear elasticity (low frequency oscillatory shear strain, sub-millimeter scale and total wetting substrate/fluid conditions). A simultaneous measurement of the liquid temperature in the gap is recorded to explore the stability of the thermal liquid equilibrium using nearly insolating surfaces to focus the analysis on the liquid behavior only.

## 2. Experimental:

Important instrumental progresses in infrared detection enable now an accurate determination of the temperature in a wavelength range of 7-14µm. We record the *in-situ* temperature of confined viscous fluids submitted to a controlled external mechanical shear strain at room temperature (300 K), away from any critical point and without external heat sources.

The infra-red emissivity measurements are carried out in real-time conditions with a microbolometer array of 382 x 288 pixels working at 27 Hz in the range of long wave Infrared bands (LWIR), i.e. wavelengths ranging between 7 to 14 µm. The thermal emissivity is measured by radiation transfer using the Stefan-Boltzmann law: $E= e_m.\sigma.A\ (T^4 - T_c^4)$ where $E$ the radiated energy, $e_m$ the emissivity coefficient, $A$ the radiating area, $T$ the temperature of the sample and $T_c$ the temperature of the surroundings. $\sigma$ is the Stefan's constant. The microbolometer array focusses with a depth field of 0.1mm, the liquid confined between two surfaces, one animated with an oscillatory motion of frequency $\omega$ and the other one fixed. The thermal pictures are corrected from the static thermal environment by subtracting the median value measured at rest prior the dynamic measurements.

The liquid, here the polypropyleneglycol-4000 (Sigma-Aldrich manufacturer, molecular weight: 3500-4500 g/mol, glass transition: Tg = -75°C) is viscous at room temperature ($\eta$ = 100 mPa.s). The low frequency range probed in this study rules out any coupling with molecular relaxation times [13]. The liquid is submitted to an oscillatory shear strain using the conventional dynamic analysis imposing a sin shape oscillatory shear strain following the conventional formalism: $\gamma(t) = \gamma_0.\ sin(\omega.t)$ where $\omega$ is the frequency and $\gamma_0$ the imposed shear strain [8, 9]. All the measurements are carried out at room temperature. The shear strain $\gamma$ is defined by the amplitude of the displacement divided by the gap thickness: $\gamma = \delta l/e$ where $\delta l$ is the displacement and $e$ the gap thickness. The transmission of the stress from the surface to the sample is reinforced by using high energy alumina fixtures of 45 mm diameter [1,2]. The excellent wetting procured by the alumina substrate strengthens the interaction of the liquid molecules to the surface. The high affinity to the substrate reduces the interfacial gas layer trapped between the liquid and the substrate ("pancake" effect) enabling total wetting conditions and the low

thermal conductivity of Alumina surfaces (~30W/mK) enables to consider the dynamic measurements as adiabatic with respect to the experimental time scales.

# 3. Results:

## 3.1 Revealing a thermo-mechanical coupling in mesoscopic liquids and its elastic nature:

To examine the thermal properties, the liquid is probed in conditions as close as possible to equilibrium conditions. A low frequency shear wave (0.5 rad/s) is applied. The lowest shear strain providing an exploitable thermal image is 200% (microbolometer limitations). Following Fig.1b, these conditions correspond to the entrance in the viscous regime.

In agreement with previous studies, it is observed that the liquid temperature is no more homogeneous upon applying an oscillatory shear strain but exhibits local variations of temperature. These thermal variations are positive and negative, localized in space and time. They divide the fluid in nearly three zones called the upper and the bottom zones, and the middle zone (Fig.2a).

The first remarkable result is that a thermal wave is recorded in the so called viscous regime upon applying a low frequency (nearly static) shear strain (Fig.2a). Fig.2b shows the evolution of the temperature (full amplitude value from maximum to minimum temperature) in three bands selected to represent the three main different thermal behaviors as the function of the strain amplitude. The average temperature in the gap is also represented.

The thermal wave reproduces the mechanical waveform of the shear strain input (left insert of Fig.2b); it can be modeled as: $\Delta T(t) = \Delta T_A \cdot sin(\omega \cdot t + \Delta\varphi)$ where $\Delta T_A$ is the amplitude of the thermal wave and $\Delta\varphi$ is the phase shift with respect to the shear strain wave and $\omega$ the frequency of the mechanical excitation. The thermal wave is reversible and stable over time. We see the hot and the cold parts of the thermal response are symmetric for different strain values, meaning that the sin waveform holds true as the deformation is increased, showing the linearity of the phenomenon. Thus, we may propose that the temperature oscillates symmetrically around a temperature which is the equilibrium temperature, meaning that for a thermal variation of 0.08 K, hot and cold parts have the same value of 0.04 K.

In the regime of linear thermal response, the thermal signal can be modeled by a sin wave of same period as the oscillatory strain. All the thermal bands exhibit a nearly linear dependence to the shear strain amplitude (Fig.2b), indicating a possible thermoelastic behavior [14 and references therein].

The study of the phase shift between the imposed shear strain and the thermal waves is also instructive. Both hot and cold, and average bulk phase shift of the thermal waves are reported in Fig.3.

- At low strain amplitude ($\gamma < 1000\%$), the phase shift is negligible $\Delta\varphi < 10\%$, indicating a nearly instant response, in agreement with a “pure” elastic behavior.

- At moderate strain amplitude ($1000\% < \gamma < 2000\%$), the phase shift increases nearly linearly up to a plateau while being always less than $\pi/4$,

- At large strain amplitude ($\gamma$ > 2000%), the phase shift reaches a value around 42°. It does not evolve anymore meaning that the thermal response remains mainly in phase with the imposed shear strain.

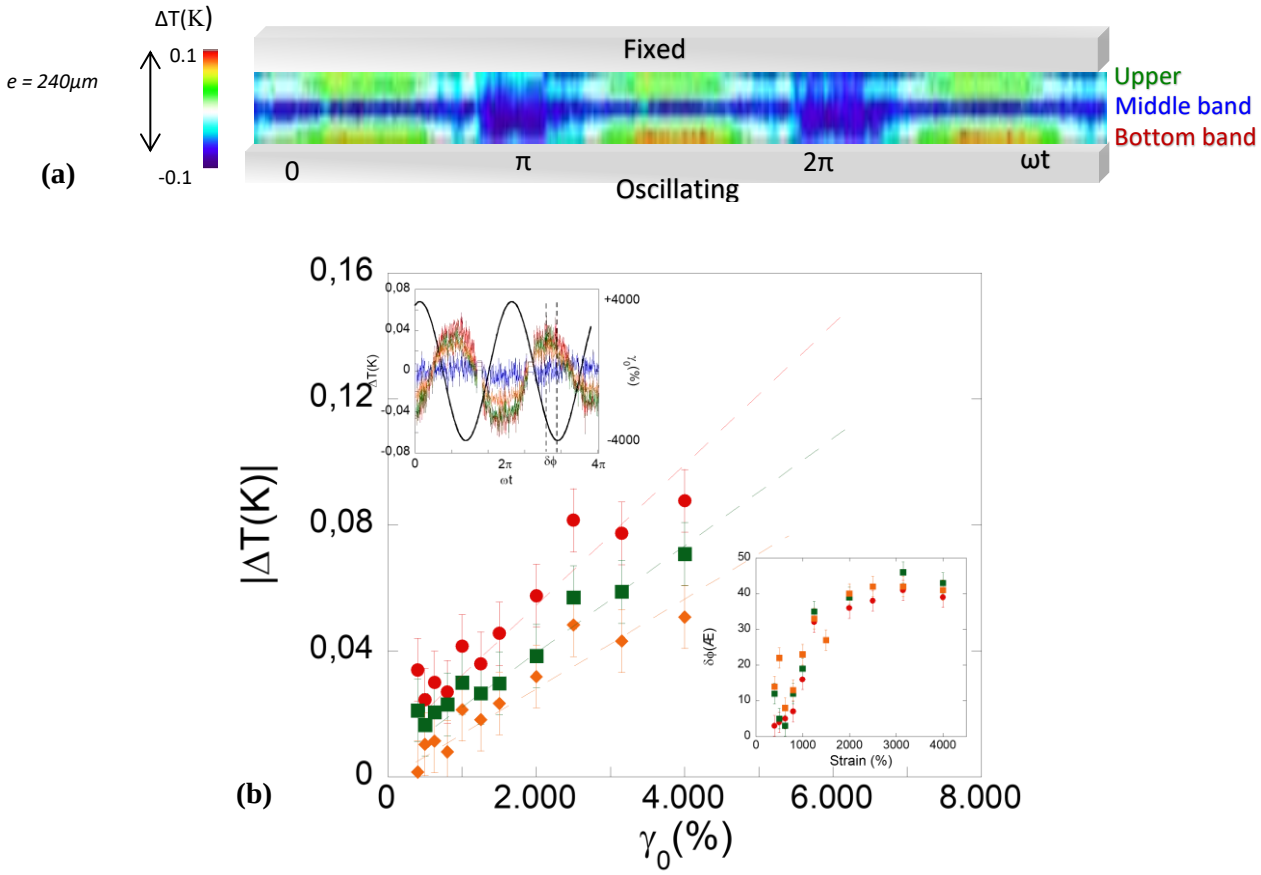



**Fig.2: a)** Thermal response of the liquid PPG-4000 recorded along three oscillatory period (ω = 0.5 rad/s, γ = 2000%, and e = 240 µm gap thickness, room temperature measurements carried out on alumina plates, the upper plane was fixed while the bottom one oscillated). **b)** Strain dependence of the maximum of the temperature variation amplitude (Peak-to-peak amplitude) $|\Delta T(K)|$. Sample: PPG-4000 at gap thickness 0.240mm, ω=0.5 rad/s, as extracted from the sin harmonic fit - measurements below 400% are below the accuracy. The left insert details the thermal waves recorded at γ = 4000%, at the same gap thickness (240µm) and frequency (ω=0.5rad/s). The right insert illustrates The color code is the same for the three figures: Bottom band: (●), upper band: (■) and total gap: (◆).

The linearity of the dependence of the thermal effect on the amplitude of strain is a strong indication of a mechanism occurring from the smallest values of shear strain, also compatible with a thermo-elastic behavior. Let's describe the frame of a classical thermoelastic behavior.

In shear geometry, γ is the shear strain where $\gamma(z) = \delta l(z)/e$ with $\delta l$, the displacement of one surface, e the distance between the two surfaces (the gap) and $z$ the considered height in the gap. For simple unidimensional case, initially at the temperature $T_0$, a uniaxial stretching gives rise to

$\gamma(z) = \alpha . (T-T_0)$ / where $T$ is the temperature, $T_0$ the reference temperature (here $T_0$ is the room temperature) and α the thermal expansion coefficient. In the linear region of the thermal response, $(T - T_0) / \gamma(z)$ is indeed constant in hot and cold thermal bands and of nearly similar absolute value (0.18 $10^{-2}$K). It represents the thermal analogue of the shear stress reported to the shear strain, $\sigma/\gamma$ which defines the shear elastic modulus following Hooke's law. Therefore the thermal study might visualize the elastic response of the liquid; i.e. its capability to change its pressure upon mechanical excitation

(the corresponding pressure variation for a temperature variation of $10^{-2}$K is of the order of MPa). The thermal approach reveals at large strain amplitudes, an elastic-like behavior that is not identifiable via a viscoelastic dynamic analysis (Fig.2b).

### 3.2 The scale dependence:

Since we have understood that hot and cold thermal waves exhibit similar characteristic and are both sides of the same elastic-like mechanism that is observable when the liquid is confined, we examine how this dynamic effect evolves with the sample size. The peak-to-peak (pk-pk) value is an interesting parameter since it corresponds to the difference between its positive (hot) peak and its negative (cold) peak refers to the maximum change occurring during one cycle. Fig.3 shows the evolution of the thermal response as a function of the strain at different sample thicknesses from 340µm down to 100µm.

Up to shear strain values $\gamma < 2000\%$, a similar sine-like variation of the temperature is observed in each band. The amplitude of the thermal waves and thus the average temperature exhibit a linear relation with increasing strain up to around $\gamma = 2000\%$. A deviation from the linearity is clearly observed at higher strain values for the smallest gaps, reaching a constant thermal value at 150µm (Fig.3c), and a lowering thermal variation at lower gap thickness (Fig.3d).

The large strain thermal regime at low scale (100µm) corresponds to the regime where the shear elasticity is reinforced (in Figure 5 of [15], the shear elasticity reaches 200 Pa). The low thickness behavior is particularly interesting since a phenomenological analogy could be done with the strain behavior of solids under strain, showing an elastic behavior and at larger strain values, a plastic-like regime in analogy with a plastic deformation observable in most solid materials [16]. In this regime, the thermal modulation is distorted and exhibits harmonics [14]. However, no specific interfacial effects like interfacial surface slip is visible on the basis of the thermal analysis, thus indicating that the thermal bands are related to a bulk mechanism; a variation of the liquid density within the limit of the liquid compressibility. This mechanism is likely precursor of shear banding instabilities optically identified in various complex fluids generally interpreted as concentration changes [17].

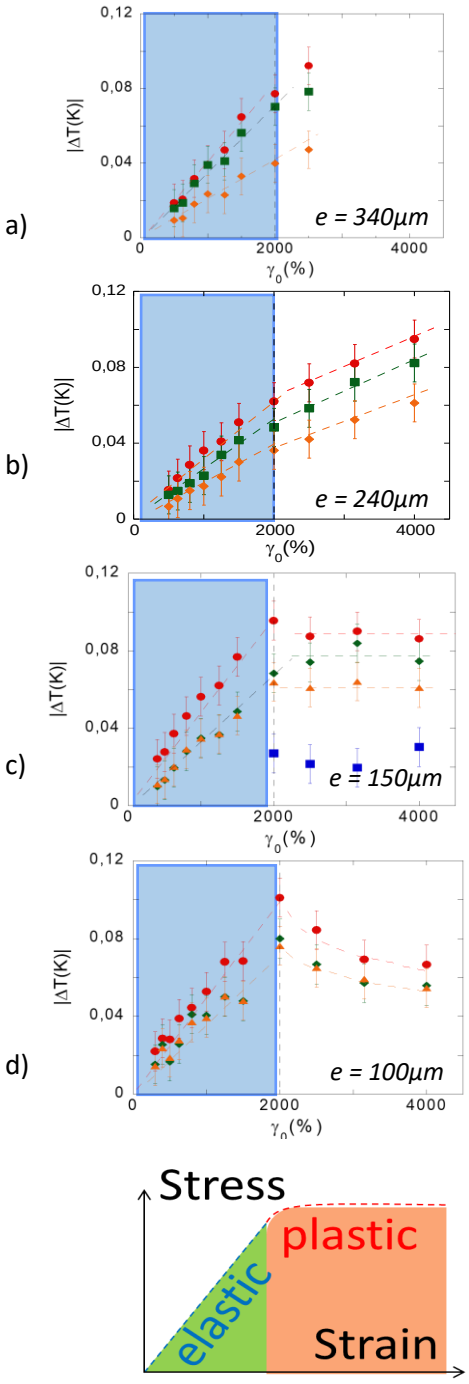



**Fig.3:** Influence of the gap thickness on the thermal response (Peak-to peak value) of the liquid upon increasing oscillatory shear strain at 1 rad/s (PPG-4000, room temperature measurements, total wetting conditions (Alumina)): Bottom band: (●), middle band: (■), upper band: (◆) and total gap: (▲). a) e= 340µm., b) e= 240µm, c) e= 150µm, d) e= 100µm, f) schematic representation of the typical solid-like behavior submitted to an external stress exhibiting elastic behavior at low strain and plastic at large one. The thermal variation of the middle band being much lower than the other bands ("neutral temperature zone"), it is not systematically represented. Large shear strain amplitudes are not experimentally accessible at 340µm.

The thermal changes are observed in the so called viscous regime of the liquid (Fig.1b). The viscous regime is thus more complex than usually accepted; the thermal variation indicates indeed that the liquid has an ability to store dynamically the mechanical energy associate to the shear strain. It proves that shear waves propagate in the liquid, which is a solid-like characteristic. The increase in internal energy due to the mechanical action is also correlated to a slight change of intermolecular distances. This change modifies the entropy of the system with possibly a very slight ordering (in agreement with the existence of a cooling state).

## 4. Conclusions:

The experimental identification of static shear elasticity in confined liquids has paved the way for the search for new small-scale dynamic properties. These scale dependent properties cannot be explained in a continuum model and require unconventional theoretical considerations.

The thermal effects detailed here reinforce the interpretation of the dynamic properties of the confined liquid in terms of elastic correlations. The ability of the liquid to convert the mechanical (shear) wave in local symmetrical hot and cold thermal waves oscillating around the equilibrium temperature while maintaining the waveform and frequency of the mechanical excitation, to exhibit at moderate shear strain a linear dependence of the thermal amplitude with the shear strain, is undoubtedly an elastic characteristic. An instantaneous dissipation of a mechanical action (low frequency) in the noise of thermal fluctuations [18] rules out but indicate that the thermal fluctuations are dynamically correlated.

We have also shown that at very large shear strain amplitude, the thermal effect does not evolve anymore and collapses. This is particularly visible at the smallest gaps (100µm) where the shear elasticity is reinforced. A similar scale dependence has been evidenced for the liquid shear elasticity mainly accessible in confined liquids. The liquid shear elasticity has independently established by both an experimental and theoretical approaches; indeed the scale dependence is in agreement with new theoretical models, foreseeing that liquids can support a limited propagation of shear waves well above nanoscopic scales [19-24]. Liquid elasticity can be also understood in the frame of the non-affine models developed to quantitatively predict elastic and viscoelastic constants in glasses of polymers and colloids (NALD approach [20-21]). In this model, the classical high-frequency elastic modulus $G'_\infty$ (Frenkel model) is completed by a scale dependent low-frequency (static) term :

$$G' = G_\infty - \frac{\alpha}{3} k_{gap}^3 + \frac{\beta}{3}.L^{-3}$$

$\alpha$ and $\beta$ are numerical parameters, $k_{gap}$ is the wave vector over which the transverse wave associated with G' can no longer propagate [21-24]. Beyond this value (i.e. for $k > k_{gap}$), only a residual elastic response remains which must vary as $L^{-3}$, where L is the thickness and that vanishes at large gap.
This $L^{-3}$ law has been experimentally verified on the basis of published data, for a wide range of fluids at the sub-millimeter scale (glycerol, ionic liquids, polymer melt, isotropic liquid crystals) [23]. It is also found to be in line with the moduli of elasticity published by the pioneering Derjaguin at the scale of several microns [6-7] or even at the nanoscopic scale probed by AFM by E. Riedo [3], therefore over a very wide dimensional range.
This new and scale dependent approach combining both thermal and dynamic properties is certainly a promising path for a better understanding of the fluid complexity, in particular in confined geometry, which is typically the microfluidic condition.

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