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From Hidden Shear-Elasticity to Opto- and Thermo-Elastic properties in Confined Polymer Melts and Viscous Liquids

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Abstract: The newly identified low frequency elasticity of mesoscopic liquids opens the route to the identification of novel dynamic liquid properties. We present two experimental examples illustrating the impact of the liquid elasticity in optics and thermodynamics. We reveal that at mesoscopic scale, liquids are able to convert the mechanical energy in optical and thermal effects. The fluids are submitted to a low frequency (\sim Hz) mechanical shear strain (external stress), thus excluding a coupling with molecular time scales. The dynamic response is probed using two *in situ* methods accessing in real time optical response of the isotropic phase of liquid crystals and probing the thermal response upon shear deformation. In both cases, a dynamic response is identified: the isotropic phase of liquid crystals exhibits a low frequency dynamic birefringence while ordinary liquids exhibit cold and hot thermal waves synchronous to the low frequency excitation.

Introduction:

Due to the diffusive nature of liquid molecules, shear waves are not supposed to propagate in a liquid medium for excitations slower than the molecular dynamics [1, 2]. As a result, it has long been considered that liquids require no significant force to displace individual molecules. The resistance to shear forces indicates a solid body. The shear elasticity G' measures its resistance. It is defined as the ratio of the applied shear stress (σ) to the shear deformation γ : $\sigma = G' \cdot \gamma$. According to the previously announced principle, no shear elasticity is expected in the liquid state. However, recent experimental improvements and theoretical considerations indicate that the situation is not so simple and that liquids present actually shear elasticity accessible in the confined state. The measurement of the mesoscopic liquid shear elasticity has been made possible applying very careful experimental conditions in particular by improving the wetting boundary conditions between the fluid and the substrate. This protocol has enabled to reveal a “static” mesoscopic shear elasticity in various fluids at the sub-millimeter scale (Fig.1)[3-7]. Shear elasticity of about few Pascal up to thousand Pascal was identified both on simple liquids and complex fluids (entangled and unentangled polymer melts, molecular glass formers, Van der Waals liquids, ionic liquids, H-bond liquids including liquid water) pointing out a probable generic character. The pioneering works of Derjaguin et al carried out at the micron-scale [8, 9] and of Reiter et al [10], have been thus confirmed and extended to scales up to the sub-millimeter. Furthermore, recent theoretical works revisited the Frenkel model and elaborated a new model explaining the existence of finite shear elasticity of confined liquids and its scale dependence. Based on non-affine lattice dynamics, they concluded to the following dependence: $G' = \beta' L^{-3}$, where β' is a constant and L is the scale of the system [11-12]. The model is consistent with low scale experimental observations and confirms shear elasticity as an intrinsic property of the liquid state.

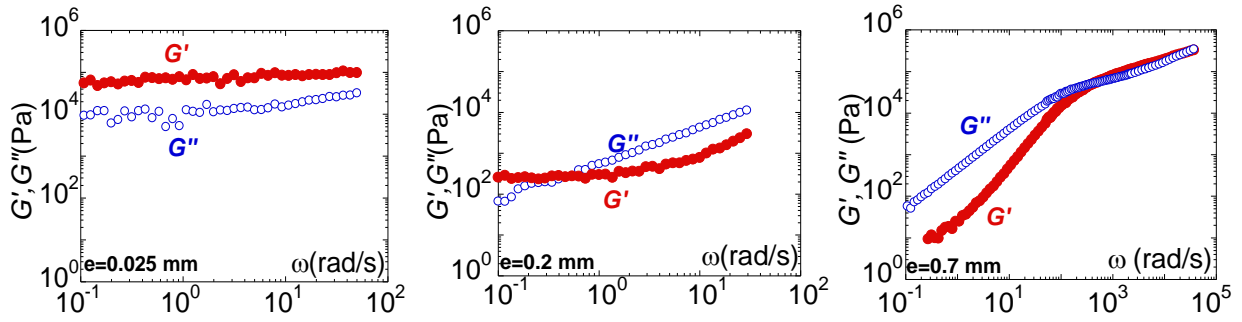


Fig.1: By improving the wetting between the surface and the polymer melt, it has been shown that viscoelastic moduli of ordinary liquids do not vanish at low frequency but exhibit a solid-like response observable at the sub-millimeter scale (room temperature measurements carried on Alumina surface (in total wetting conditions, sample: PBuA melt, $M_w = 47500$, $T = T + 90^\circ\text{C}$ [5]). The low frequency shear elasticity has been recently explained in the frame of new theoretical liquid models. The low frequency shear elasticity is understood as a residual elasticity varying as L^{-3} , L being the gap thickness [11, 12].

Mesoscopic shear elasticity means that liquids are able to resist to flow below their elastic threshold. What happens when the elastic threshold is exceeded? We can suspect that mesoscopic elasticity has profound implications on microfluidics, surface instabilities, local thermodynamics, fluidic transport mechanisms and that it makes possible the identification of new liquid properties usually associated to solid-like characteristics [13] such as low-frequency optical birefringence or spectacular strain-driven thermoelastic effects that we illustrate in this paper. Low frequency shear elasticity challenges also molecular theories since long range elastic correlations imply collective dynamics that are not taken into account in conventional molecular models. It is thus important to search for other solid-like properties that can be identified in mesoscopic liquids.

We show here experimental examples that point out the importance of considering long range elastic correlations in mesoscopic liquids.

The first example comes from a revisited study of the dynamic behavior of the liquid (isotropic) phase of liquid crystals. In LC-displays the tunable optical properties are exclusively studied and expected in the mesophases, typically below the first order isotropic-nematic phase transition. The mechanism is based on the reorientation of the liquid crystalline (nematic) domains. This reorientation is usually achieved by applying external fields as electric, magnetic or mechanical fields [14]. No tunable properties are expected at temperatures above the liquid crystal phases; i.e. in the isotropic phase. This phase is considered as an ordinary liquid [14-16] and thus is little studied.

But, the existence of “static” shear elasticity of various fluids at the sub-millimeter scale [3-7, 13] allows us to revisit the mesoscopic dynamic properties of the isotropic phase on new assumptions. By assuming a coupling between pretransitional orientational fluctuations existing in the isotropic phase and long range elastic interactions recently identified, we revealed that a strong and reversible dynamic optical response is generated in the isotropic phase upon applying a low frequency low strain mechanical excitation (Fig.2) [17-19].

Fig.2 illustrates the emergence of optical birefringence in the isotropic phase of a low molecular weight liquid crystal polymer (LCP95) in use for LC-displays in its liquid crystal phase. This molecule exhibits a particularly strong optical signal in the isotropic phase.

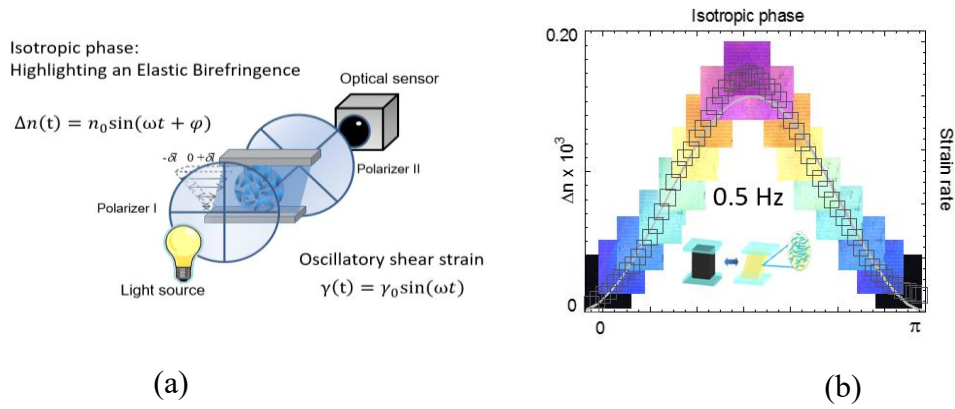


Fig.2: By applying a low frequency shear strain, an optical birefringence is induced in the isotropic phase of a liquid crystal (sample: LCP95 made of 12 liquid-crystal units - Merck manufacturer). a) Scheme of the optical oscillatory shear strain setup. b) Optical behaviour: the different (Newton) colors indicate different values of birefringence depending on the shear strain amplitude (recorded between crossed polarizers with an incident white light during $\frac{1}{2}$ a period, the liquid is confined between optical transparent glasses of extremely low birefringence index). The continuous line is the motion (gray sine line \rightarrow) while the black open squares (\square) presents the experimental data of the induced birefringence measured at a wavelength of 614 nm for a sample thickness of $250\mu\text{m}$, at 0.5Hz and 10% strain amplitude. The phase shift between the imposed motion (shear rate) and the induced birefringence modelled by a sine wave is about $\phi = 7^\circ$ at 0.5 Hz for a strain amplitude $\gamma = 10\%$ at 1°C above the isotropic transition from [19].

The low-frequency optical birefringence, synchronous with the excitation, has been measured up to 15°C into the isotropic phase with the advantage of producing a true black phase between crossed polarizers in the unexcited state (while it is impossible to obtain a deep extinction with random nematic domains). The isotropic liquid works as an optically active material when excited by a low frequency mechanical shear strain. Such spectacular observation demonstrates a low frequency dynamic coupling that exists between the pretransitional fluctuations (clusters of molecules with identical directions coexisting within the isotropic phase) and necessary elastic properties of the liquid. The liquid phase of liquid crystals can thus behave as a low frequency optical oscillator in response to a low frequency mechanical excitation. The birefringence is produced by the mechanical deformation of the isotropic phase at low frequency. This means that the mechanical energy brought by the shear strain does not increase the entropy as it should be the case for an entropic system (and as a liquid is supposed to be) but that it lowers its entropy since the birefringence highlights an ordering and thus internal correlations. The low frequency elastic birefringence has been identified in the isotropic phase of several liquid crystalline fluids, including the isotropic phase of Liquid Crystal Polymers. It indicates a likely generic property probably connected to other spectacular optical properties very early reported by different authors for the isotropic phase [20, 21].

The second approach uses the thermal radiation, thus probing larger scale compared to the optical birefringence, of the order of $\sim 10\mu\text{m}$ against 500 nm for optical measurements. Few physical studies exploit the property that a thermal radiation is naturally emitted, produced by the molecular agitation (equilibrium thermal noise). The thermal emissivity is thus a tool to characterize the thermodynamic state. Due to the mesoscopic shear elasticity, it is relevant to examine a possible interplay of the liquid dynamics and shear deformation. For that, we use a dynamic approach similar to dynamic mechanical analysis, applying an oscillatory shear stress but probing a thermal signal. It is a thermo-mechanical analysis.

We illustrate micro-thermal results obtained on applying a low frequency shear deformation to polypropylene glycol (PPG-4000 – manufacturer Merck) confined at sub-millimeter scale (Fig.3). PPG is an ordinary fluid whose glass transition temperature is -73°C . Therefore, the thermal observations are carried out at about 100°C over the glass transition temperature without external heating source.

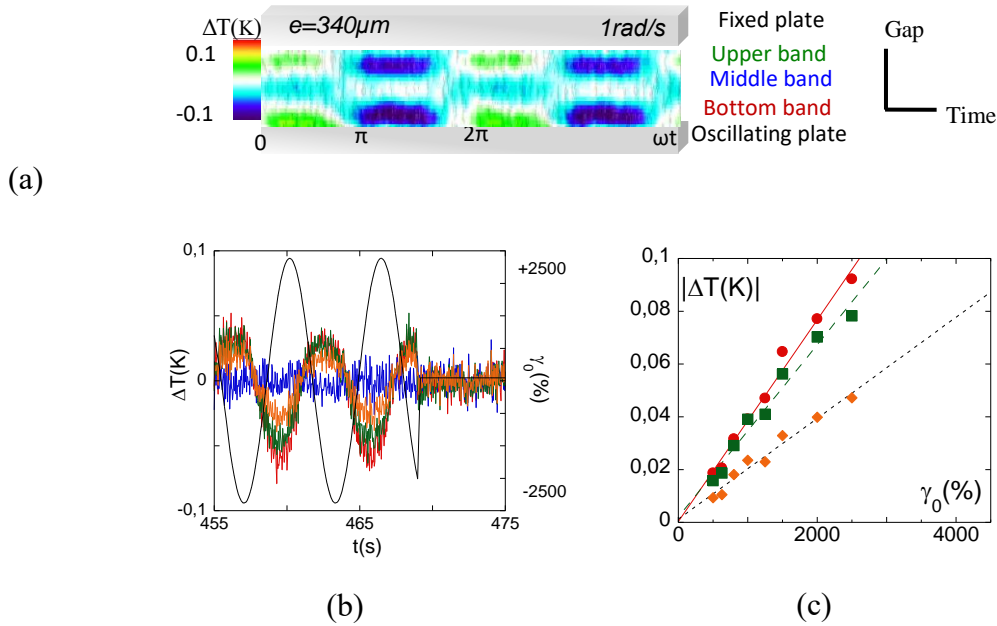


Fig.3: By applying a low frequency mechanical stimulus ($\omega = 1\text{ rad/s}$), the liquid (here polypropylene glycol – PPG-4000) emits a modulated thermal signal synchronous with the stimulus. a) Real-time mapping of the temperature confined in a $340\mu\text{m}$ gap (gap view at room temperature measurements at $\gamma = 4000\%$ gathering about ~ 800 frames, alumina substrate). b) Thermal waves recorded for the bottom (●), middle (■), upper (■) bands and total liquid volume (♦) respectively at $\gamma = 2500\%$, and $e = 340\mu\text{m}$. The zero ΔT is defined relative to the equilibrium temperature. (c) Strain dependence of the amplitude of the thermal variation of the hot (bottom) wave versus shear strain at 1 rad/s and $340\mu\text{m}$ (absolute value: $|\Delta T(\text{K})|$).

Fig.3 reveals that a low frequency mechanical shear strain impacts the liquid thermal equilibrium in such a way that a thermal wave propagates through the liquid at low frequency; i.e. at time scales well below all known relaxation times (molecular relaxation times are of the order of 10^{-6}s [22]). The figure evidences that the thermal variation $\Delta T(\text{K})$ of the liquid oscillates compared to the thermal equilibrium ($\Delta T(\text{K}) = T - T_{\text{equil}}$). The thermal waves are multiple, synchronous with the excitation, harmonic at low strain amplitude (Fig.3b). The study of the amplitude of the thermal wave indicates a linear behavior with respect to the strain rate (Fig.3c). The thermal bands of about $60\mu\text{m}$ width alternate between a hot and a cold state over time and relax simultaneously when the excitation is stopped (Fig.2b). It confirms the adiabatic nature of the thermal effect indicating that the temperature changes are only local and works without exchanges with the environment. These enounced non-dissipative properties are characteristics of an elastic response. The local thermal changes correspond to dynamic compressed and dilated states; i.e. to slightly different densities and thus to slight shift in a non-equilibrium pressure-temperature phase diagram.

The identification of thermal bands in ordinary viscous liquids at the sub-millimeter scale under the action of a low frequency mechanical shear is a recent observation of utmost importance [23]. It reveals a collective behaviour of the liquid that is not described by conventional theoretical approaches. The adiabatic mechanism and the absence of any

external heat sources rule out convection or conduction as the origin of the seen thermal effect. The existence of cold and hot bands thus indicates that the alternation of “stretched” states of the liquid coexisting with compressed ones. These two states compensate dynamically over one period: i.e. the system does not exchange energy with the environment; in agreement with an adiabatic-like process. No heat is added ($dQ = 0$). (Strain) work offered to the fluid is transformed into internal energy by organizing liquid in temperature bands. An analogy is the thermoelastic stress analysis in solids. The basic equation of the thermoelasticity in solids can be written as [24, 25]:

$$\Delta T = -T_0 \cdot \alpha / (\rho \cdot C_p) \cdot \sigma = G' \cdot \gamma_{loc} \quad (1)$$

where α is the linear expansion coefficient, ρ the density of the material, C_p the specific heat at constant pressure, T_0 is a reference temperature and σ the stress. We have seen that the thermal change ΔT is linear in respect with the applied shear strain γ which is here the only external field. The other parameters being relatively constant with respect to the shear stress variation, the slope of ΔT versus strain provides information on a local shear elastic component supposing $\sigma = G' \cdot \gamma_{loc}$. The equivalent local shear elasticity is about $G' \sim 70$ kPa for a band of about $20 \mu\text{m}$, which is of the order of values used in microfluidic systems or of the order of the macroscopic shear elasticity determined using the wetting protocol by stress measurements (Fig.1a)[3, 5]. This equation supposes that we know the local shear strain which is an important assumption. Finally, positive or negative ΔT means that the liquid undergoes opposite stresses and that the strain parameter should be understood similarly as in the Hooke law with a restoring force opposite to that of the displacement (Fig.4).

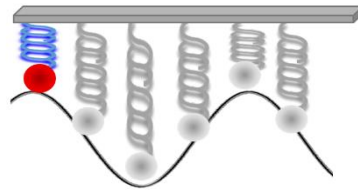


Fig.4: Scheme of the Hooke's law illustrated by a balance between restitution energy and kinetic energy for a suspended spring evolving over time following a sine wave of its state (extended or compressed state).

Furukawa and Tanaka [26] suggested that the compressibility of the liquid can be stressed by shear, which might explain the problem of creating cavitation. They base their study on the existence of density fluctuations inside the liquid. The theory “does not involve any viscoelastic or structural relaxation”. However, the expected shear rate is about 10^6 s^{-1} , much higher than the inverse of the timescales corresponding to the frequency range explored in the present study. At these high shear rates or high shear strain, various effects are expected due to instabilities and slippage in particular near the walls [27].

An analogy can be made between the behaviour of thermal waves and harmonic oscillators, here depicted by a spring ballasted with a weight (Fig.4). The liquid thermal waves is synchronous with the applied strain (same frequency and phase shift lower than $\pi/4$). It cannot be coupled with relaxation times ($1/\omega_{\text{applied}} \gg \tau_{\text{relaxation}}$), implying that the shear deformation is solely responsible for the creation of the bands. Consequently, the liquid integrates and converts (at least partly) the mechanical energy to organize in local temperature bands. Frenkel [1] was one of the first to propose the existence of transverse modes in liquids

above a given frequency ω_F related to the Maxwell relaxation time. If high frequency propagate both longitudinal and transverse waves, the mechanical excitations applied here are several decades below the frequency expected in the original Frenkel model (related to a single particle timescale). Several authors using different theoretical approaches suggest that long range intermolecular interactions play a key-role in the dynamic behaviour of fluids [28-31] and thus that collective responses are possible at smaller frequency. In particular, Trachenko *et al.* revisited the Frenkel theory [11-12, 32-35]. They use a generalized viscosity that contains short-term elasticity and predict a new frequency $\omega = \sqrt{c^2 k^2 - 1/4\tau^2}$, where propagation modes can exist and show the existence of k -gap. The k -gap suggests that the liquid can be considered as collection of dynamical regions of characteristic size $\ell\tau$ where ℓ is the sound velocity and τ the Maxwell timescale. $\ell\tau$ corresponds to the maximum propagation length of the shear waves [11-12, 36-37]. This scale-dependence of the propagation of the shear elastic waves implies the generation of thermal bands of limited widths. The limited length is particularly evidenced at large gaps in oscillatory shear strain [38] and is also illustrated by the multiple band thermal relaxation in step strain measurements [39].

Conclusions:

We have shown on representative examples of fluids probed with different methods, away from phase transitions, that the viscous property describes only a part of the liquid properties. Liquids are not deprived of shear elasticity, but this later is a mesoscale property, thus not easily accessible by usual shear stress measurements conventionally carried out at large thickness (typically around 1mm) and without particular care of the boundary conditions. As a result, the viscous behaviour is only a part of the dynamic spectrum which corresponds to the large scale response of the fluid. New approaches such as dynamic optical measurements or the very recent thermal approach are interesting methods to reveal the elastic properties of liquids that dominate the dynamic behavior at mesoscopic scale. We are confident that many other new features and related applications will be discovered now accompanied new theoretical models [11-12, 36-37] in link with the experimental evidences.

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