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

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Abstract: From the newly identified low frequency liquid elasticity, it turns out the possibility to reveal novel dynamic properties of liquids at mesoscopic scale. We present two examples illustrating the impact of the mesoscopic liquid elasticity in optics and thermodynamics. We show strain induced optical effects and thermo-induced effects that occur in the liquid state and reveal the need to take into consideration the elastic character of fluids at small scale. The fluids are submitted to a low frequency (~ Hz) mechanical shear strain (external stress). We probe the dynamic response by two methods, either accessing instant optical response of the liquid phase of liquid crystals and or probing the thermal response upon mechanical deformation. It is shown that the isotropic phase of liquid crystals can exhibit a dynamic birefringence in the isotropic phase while ordinary liquids exhibit cold and cold thermal waves upon low frequency excitation.

Introduction:
On the basis of a Maxwell gas model, it has long been suspected that liquids and polymer melts exhibit (shear) elasticity at high solicitation frequencies (MHz or GHz) only [1, 2]. Recent experimental improvements seem to indicate that liquids present also shear elasticity at very low frequency (0.1 to 10Hz); i.e. a nearly “static” shear elasticity. We developed an experimental protocol to reveal a “static” mesoscopic shear elasticity of polymer melts and liquids up to sub-millimeter scale (Fig.1)[3-7]. A 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 and extending the pioneering micron-scale works of Derjaguin et al [8, 9] and later of Reiter et al [10] up to the sub-millimeter scale. Finite low frequency shear elasticity means that liquids are not viscous at all scales but that below an elastic threshold, they exhibit a solid-like behavior.

Fig.1: 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 response of PBuA melt, Mw = 47500, T = T + 90°C - L. Noirez et al, Polymer Int. 58 962 (2009)).
Mesoscopic shear elasticity has profound implications on flow, surface instabilities, thermodynamics, fluidic transport mechanisms and make possible the identification of new liquid properties [11] such as the low-frequency birefringence or spectacular strain-driven thermoelastic effects that we illustrate in this paper and that were known in solids only. 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.

We show here on two representative examples 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 [12]. No tunable properties are expected at temperatures above the liquid crystal phases; i.e. in the isotropic phase. This phase is usually considered as an ordinary liquid [12-14]. But, the recent identification of “static” shear elasticity in polymer melts and viscous liquids at the sub-millimeter scale [3-7, 11] allows us to revisit the mesoscopic dynamic properties of the isotropic phase on new assumptions. By assuming a coupling between orientational pretransitional 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 a low frequency low strain mechanical excitation (Fig.2) [15-17]. A 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. The isotropic liquid works as an optically active material when it is excited at low frequency; this means that the mechanical energy brought by the shear strain is not used for increasing the entropy as it should be the case for an entropic system (and as a liquid is supposed to be) but it lowers its entropy (the birefringence highlights an ordering), implying internal correlations. The low frequency elastic birefringence is identified in the isotropic phase of several liquid crystalline fluids, and including the isotropic phase of LC-polymers, indicating a likely generic property and is probably connected to spectacular optical properties very early reported by different authors for the isotropic phase [18, 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: Low frequency induced birefringence. a) Setup of the oscillatory shear strain experiment. b) The different (Newton) colors indicate different values of birefringence depending on the shear strain amplitude (photographs 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 \( \Downarrow \)) while the black squares (□) presents the experimental data of the induced birefringence. The phase shift between the imposed motion and the induced birefringence modelled by a sin wave is about \( \varphi = 7° \) at 0.5 Hz and strain amplitude \( \gamma = 10 \% \), at 1°C above the isotropic transition (sample LC95 from Merck manufacturer) from [Kahl P, Baroni P, Noirez L (2016) Bringing to Light Hidden Elasticity in the Liquid State Using In-Situ Pretransitional Liquid Crystal Swarms. PLoS ONE 11(2): e0147914. https://doi.org/10.1371/journal.pone.0147914].

The second approach uses the thermal radiation, thus probing larger scale effect with respect to the optical birefringence, of the order of the infrared wavelength (~ 10 \( \mu \)m against 500 nm). Few physical studies exploit the fundamental property that a thermal radiation is naturally emitted by the condensed matter above zero degree Kelvin. The thermal emissivity is also a tool to access the thermodynamic state. We illustrate micro-thermal results obtained on applying a low frequency shear deformation to polypropylene glycol (PPG-4000) confined at sub-millimeter scale (Fig. 3).

Fig. 3: By applying a low frequency mechanical stimulus (~ Hz), the liquid (here polypropylene glycol – PPG-4000) emits a modulated thermal signal synchronous with the stimulus at 1rad/s. a) Real-time mapping of the temperature confined in a 340\( \mu \)m gap (gap view at room temperature measurements at \( \gamma = 4000\% \) gathering about ~800 frames, alumina substrate). b) Temperature variations of the bottom, middle and upper bands displayed in red, blue and green. The average bulk temperature is in orange. The continuous line is an eye guide for the applied shear strain. The zero \( \Delta T \) is defined relative to the equilibrium temperature. c) Strain dependence of the maximum of the temperature variation (absolute value: \(|\Delta T(K)|\)). Thermal waves recorded for the bottom (●), middle (■), upper (▲) bands and total liquid volume (●) respectively at \( \gamma = 2500\% \), \( \omega = 1 \) rad/s and \( e = 340\mu m \). (d) Amplitude of the thermal variation of the hot (bottom) wave versus shear strain at 1 rad/s and 340\( \mu \)m.

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 much below every known relaxation times (molecular relaxation times are of the order of \( 10^{-6} \)s [20]). 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 hot and cold thermal bands of about 20µm width 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 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 [21]. It reveals a collective behaviour of the liquid that is not described by conventional theoretical approaches. The adiabatic mechanism rules out convection or conduction effects. 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: 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 [22, 23]:

$$\Delta T = -T_0 \cdot \alpha / (\rho \cdot c_p) \cdot \sigma$$

where $\alpha$ is the linear expansion coefficient, $\rho$ the density of the material, $c_p$ the specific heat at constant pressure, $T_0$ is a reference temperature and $\sigma$ the stress. We have seen that the thermal change $\Delta T$ is linear in respect with the applied shear strain $\gamma$ which is here the only external field. Therefore the slope of $\Delta T$ versus strain could give access to a shear elastic component supposing $\sigma = G' \cdot \gamma$. The equivalent shear elasticity is about 70 kPa for a band of about 20µm, which is of the order of values reported for 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, that the density change is negligible, which is also an assumption in the case of a mechanism involving compressive and extensive waves. Finally, positive or negative $\Delta T$ 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: The Hooke law illustrated by a balance between restoring energy and kinetic energy for a suspended spring evolving following a sin wave of its compressive state (extended or compressed).

Furukawa and Tanaka [24] suggested that liquids can be compressible by shear flow in order to explain the cavitation creation problem. 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 high shear rates or high shear strain, other effects are expected due to slippage and viscous friction in particular near the walls [25].

Fig.3 shows that the liquid thermal waves behave like harmonic oscillators; their response is synchronous with the applied strain. It cannot be coupled with relaxation times \((1/\omega >> \tau_{\text{relaxation}})\), implying that the shear deformation is solely responsible for the creation of the bands. Consequently, the liquid integrates and converts (at least partly) the shear wave energy to organize in local temperature bands. Frenkel [1] was one of the first to propose the existence of transverse modes in liquids above \(\omega > \omega_F\). At high frequency, liquids are supposed to propagate both longitudinal and transverse waves. However, the applied mechanical excitations are from far away to the Frenkel frequency. Several authors using different theoretical approaches suggest that long range intermolecular interactions play a key-role in the dynamic liquid and melt behaviour [26-29] and thus that collective responses are possible at smaller frequency. In particular, Trachenko et al. revisited the Frenkel theory [30-35]. They use a generalized viscosity that contains short-term elasticity and predict a new frequency \(\omega = \sqrt{c^2k^2 - 1/4c^2}\), 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 \(c\tau\) corresponding to the maximum propagation length of the shear waves. This implies a scale-dependence of the propagation of the shear elastic waves that is now taken into account with new developments [34-37] in agreement with the present thermal observations that are restricted to low scale measurements.

Conclusions:

We have shown on two examples of fluids probed 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 not easily accessible by conventional shear stress measurements and only access an apparent viscous behaviour. New approaches such as dynamic optical measurements or the very recent thermal approach have to be employed to reveal the elastic response of liquids, and describing as completely as possible hidden scale-dependent liquid properties that dominate the dynamic behavior at mesoscopic scale. Thanks to elastic correlations, we are confident that many new features and related applications remain to be discovered together with the development of new theoretical models [34-37] in link with the experimental evidences.

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