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Identification of Strain-Induced Thermal Response in Polymer melts and Liquid glass formers

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Abstract: We are working on improving the way to characterize liquids and viscoelastic fluids by reinforcing the fluid/substrate interfacial forces (total wetting) and building the temperature cartography upon applying an oscillatory mechanical shear field. Three fluids are studied: a low molecular weight polybutylacrylate (PBuA), the polypropyleneglycol (PPG) and the glycerol. We demonstrate that the fluids do not dissipate the injected strain energy but transforms it in shear bands of opposite temperature variations synchronous with the applied shear field. This thermodynamic change suggests a coupling to shear elastic modes in agreement with the identification of low frequency shear elasticity theoretically foreseen and experimentally demonstrated.

Keywords: liquid state, polymer melt, glass former, shear strain, shear elasticity, adiabatic transformation, thermo-elasticity.

1. Introduction:

The empirical study of fluids is a very ancient discipline; the first tools proving the will of humans to control the liquid flow dates back from the irrigation methods. Fluid mechanics is the discipline that studies the fluid behavior and its associated internal forces. The viscoelasticity theory is one of the modern descendant branches of this long history. The theoretical works of Y. Frenkel have considerably influenced the understanding of the dynamic of the liquids [1]. The "Kinetic theory of liquids" was later adopted and generalized for viscoelastic fluids like polymers and polymer solutions on the same assumptions. Frenkel established that liquids exhibit elastic shear waves at high frequency only (GHz). Consequently, liquids contrast with solids by a lack of low frequency shear elasticity (Maxwell-type viscoelastic behavior).

A low frequency elasticity (0.1-10Hz) has been recently identified in mesoscopic fluids by different authors using different techniques [2-8]. These experimental observations converge implying that fluids flow above a weak elastic threshold. The "static" 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 [2-9]. Low frequency shear elasticity has profound implications for the microfluidic mechanisms and the thermodynamics, and more generally for the understanding of the fluidic transport, of the instabilities thus with possible interest for the industrial and biological sectors. In parallel, the Frenkel calculation has been revised revealing now the pertinence of considering the low frequency shear elasticity in liquids [10-12] and an alternative way to understand the liquid state based on long range elastic intermolecular interactions [13-16].

The existence of a finite shear elasticity in fluids at low frequency justifies the search of other solid properties. In particular, shear elasticity and bulk elasticity are linked in solid (isotropic) materials:

$G = E/2(1 + \nu)$ where G is the shear elasticity, E the bulk elasticity and ν a parameter of elasticity depending on the nature of the material (Poisson coefficient). On the other hand, the bulk elasticity is directly related to the compressibility variation via: $E = -V.dP/dV$ where V is the volume and dP/dV the derivative of the pressure with respect to the volume. G and E are thermodynamic quantities those values depend on how the temperature varies during the shear or pressure variation.

We here explore the thermal properties that might be correlated to the probe of shear elastic properties of the liquid state. For this, the fluid is submitted to an oscillatory shear strain of finite amplitude in accordance with the conventional method of viscoelastic measurements. The thermal behavior of three ordinary fluids (a polymer melt, a polymer glass former and a molecular glass former) is considered upon applying a low frequency oscillatory shear strain:

Challenging the assumption of an instant dissipation via the fast lifetime of the thermal fluctuations [17], we show on the three examples that the deformation energy of usual viscous or viscoelastic liquids can be converted into temperature changes generating non-uniform and complementary thermal shear bands. We demonstrate that the internal energy of the liquid changes upon applying a low frequency shear strain, thus demonstrating a necessary coupling with a shear elastic modulus.

Experimental:

The infra-red emissivity measurements are carried out in real-time conditions. 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. σ is the Stefan's constant. The camera focusses the liquid confined between two surfaces, one animated with an oscillatory motion of frequency ω 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 shear strain γ is defined by the amplitude of the displacement divided by the gap thickness: $\gamma = \delta/l$ where δ is the displacement and l 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 [6, 18]. The excellent wetting procured by the alumina substrate strengthens the interaction of the liquid molecules to the surface. The high affinity to the substrate eliminates the interfacial gas layer between the liquid and the substrate (pancake effect) and lowers its propensity to slip on the surface (total wetting conditions).

A conventional rheometer (ARES2 from TA-Instruments) is used to impose a sin shape oscillatory shear strain following the conventional formalism: $\gamma(t) = \gamma_0 \sin(\omega t)$ with γ_0 the imposed shear strain [6]. In the present study, only the low frequency regime (1 rad/s) is studied where the three chosen fluids exhibit a viscous-like behavior. All the measurements are carried out at room temperature.

The three samples are the following ones:

- The ordinary polymer sample is an amorphous polymer: a polybutylacrylate (PBuA) of $M_n = 40\,000$ molecular weight and 1.19 polydispersity (Polymer Source manufacturer). This molecular weight corresponds to the onset of entanglement state ($M_w \cong 2.M_e$ where $M_e = 22000$) [19]. The melt is here studied at room temperature, i.e. at about 100°C above the glass transition temperature ($T_g = -64^\circ\text{C}$) at 0.285mm gap thickness. Its room temperature terminal viscoelastic time deduced from conventional viscoelastic measurements is of $\tau_{\text{relax}} = 0.03\text{s}$ [6]. At low frequency (Hz), the PBuA behaves as a viscous liquid ($\eta = 380\text{ Pa.s}$, [6]).
- The polymer glass former is the polypropyleneglycol-4000 (Sigma-Aldrich manufacturer). The molecular weight is given 3500-4500 g/mol which corresponds to about 55 repetition units. It is a viscous liquid at room temperature ($\eta = 100\text{ mPa.s}$) and its relaxation time is out of the dynamic range of conventional mechanical tools [20].
- The glycerol is a very studied liquid due its extremely wide range of uses and its biocompatibility. It is a glass former which exhibits at room temperature of viscosity ($\eta = 1.41\text{ Pa.s}$). The molecular relaxation time is far away from the dynamic range of mechanical tools, being accessible by Brillouin scattering at 7 GHz [21].

We restrict the liquid study to the low frequency response (Hz). In this range and according to Deborah number ($\tau \cdot \omega > 1$), no coupling with viscoelastic (or molecular) relaxation time is possible. The dynamics of the fluids is examined in a regime where they exhibit a viscous behaviour (flow regime).

2. Results:

We probe and compare the thermal response of these three liquids upon applying a low frequency (1 rad/s) oscillatory shear strain in small gap conditions ($e \sim 300\mu\text{m}$). We first focus on the polymer melt (PBuA) which is a van der Waals fluid and then present the thermal responses exhibited by the polymer and molecular H-Bond glass formers (PPG and glycerol).

2.1 Thermal response of the polymer melt: PBuA under oscillatory shear strain:

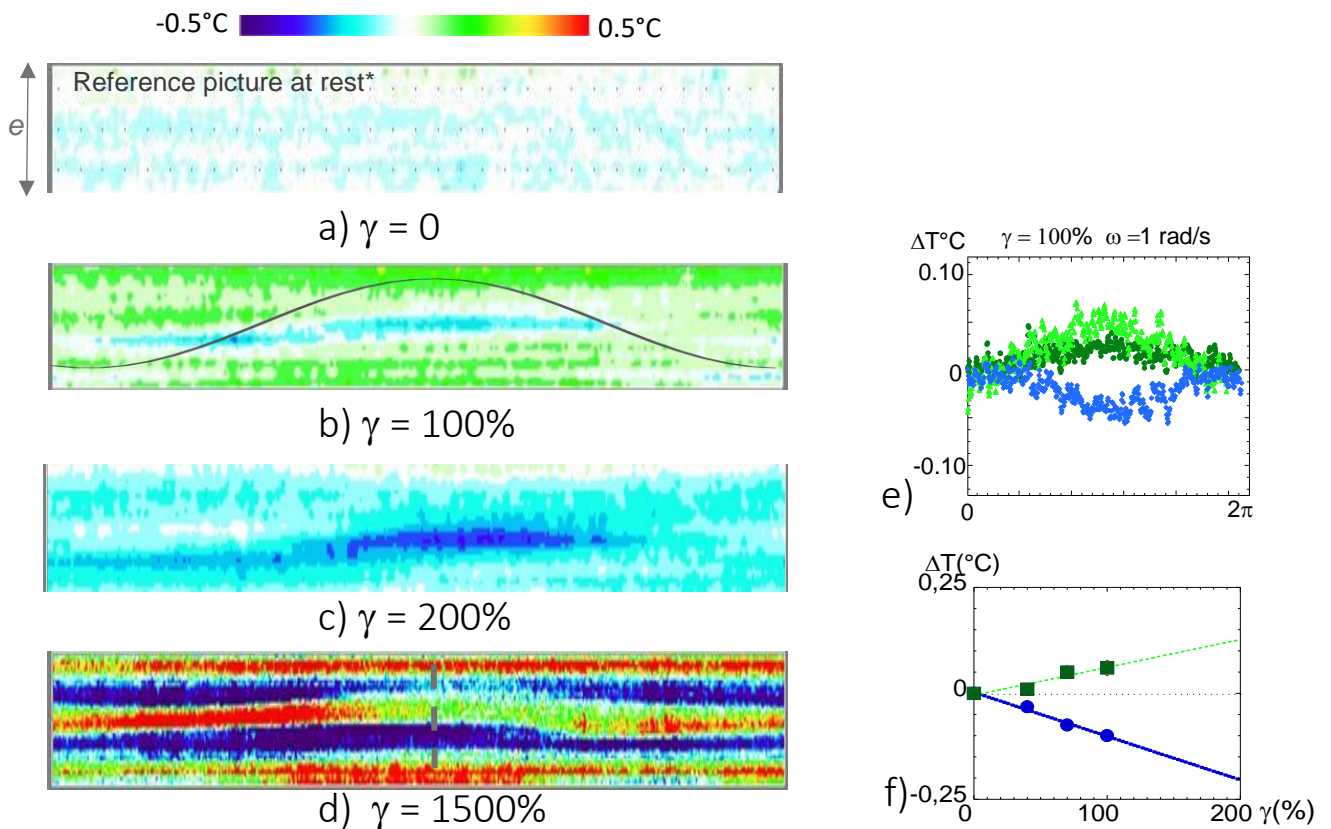


Fig.1a: Time evolution of temperature cartography of a polymer melt (PBuA) recorded every 0.04s at rest (a) and along one oscillatory period (b-d) submitted to an oscillatory shear strain at 1 rad/s frequency (280 μm gap, alumina surfaces, room temperature measurements). The upper plane is fixed while the bottom one oscillates at $\omega = 1$ rad/s. The continuous line of (b) is an eye-guide of the sin strain function and the dotted line points out the maximum strain. a) $\gamma = 0\%$, b) $\gamma = 100\%$, c) $\gamma = 200\%$, d) $\gamma = 1500\%$. e) Temperature profiles over one period of the temperature recorded on the central part (blue points) and on each side of the gap (bottom (light green) and upper (dark green) bands) at 100% shear strain and 1 rad/s). f) Evolution of the temperature variation ($\Delta T = T - T_{\gamma=0}$) of the cold (●) and of the hot zones (■).

Fig.1 gathers the 2D reconstructed picture of the thermal evolution obtained on increasing the shear strain amplitude. At rest prior the strain application (Fig.1a), the temperature of the melt is at equilibrium. Upon increasing the shear strain, the polymer melt emits a thermal signal that is particularly visible at high strain rate (Fig.1 b-d). The thermal signal splits in cold and hot shear bands that oscillate with the applied strain excitation. At low strain amplitude ($\gamma < 200\%$), the medium band of the gap

exhibits a cooling while the fluid band in contact with the surface produce a heating. The quantitative analysis indicates that both cold and hot thermal waves oscillate oppositely, are approximately in phase with the strain (Fig.1e) and local cold and hot thermal shear bands that reinforce upon increasing the shear strain (Fig.1f). At high shear strain amplitude ($\gamma > 500\%$), the thermal contrast is in some places larger than 1°C . The shear bands are very visible but are also more complex superposing several thermal waves of different temperatures elongated along the strain direction.

2.2 Identification of a thermal response of H-bond glass formers under oscillatory shear strain:

Viscosity ratios of about 10^3 and of 10^5 respectively separate the polymer melt (PBuA) from the polypropylene glycol (PPG-4000) and the glycerol. Therefore, eventual thermal effects on these glass formers are expected at high shear strain amplitudes with respect to the polymer melt. Fig.2 illustrates the thermal response of the PPG-4000 in similar conditions as for the polymer melt (Fig.1c) displayed at 1500% and 1 rad/s. Qualitatively similar thermal properties are found with the emission of a thermal signal identified for PPG-4000. The liquid splits in cold and hot shear waves oscillating nearly in phase with the low frequency strain excitation $\Delta T(t) = \Delta T_A \cdot \sin(\omega \cdot t + \Delta\phi)$ where ΔT_A is the amplitude of the thermal wave and $\Delta\phi$ the phase shift with respect to the shear strain wave is about $37^\circ \pm 2^\circ$. The central zone corresponds to the induction of cold while the liquid in contact with the surfaces correspond to the hot zones. In contrast to the polymer melt, the thermal signal keeps the shape of the excitation over a wide strain range.

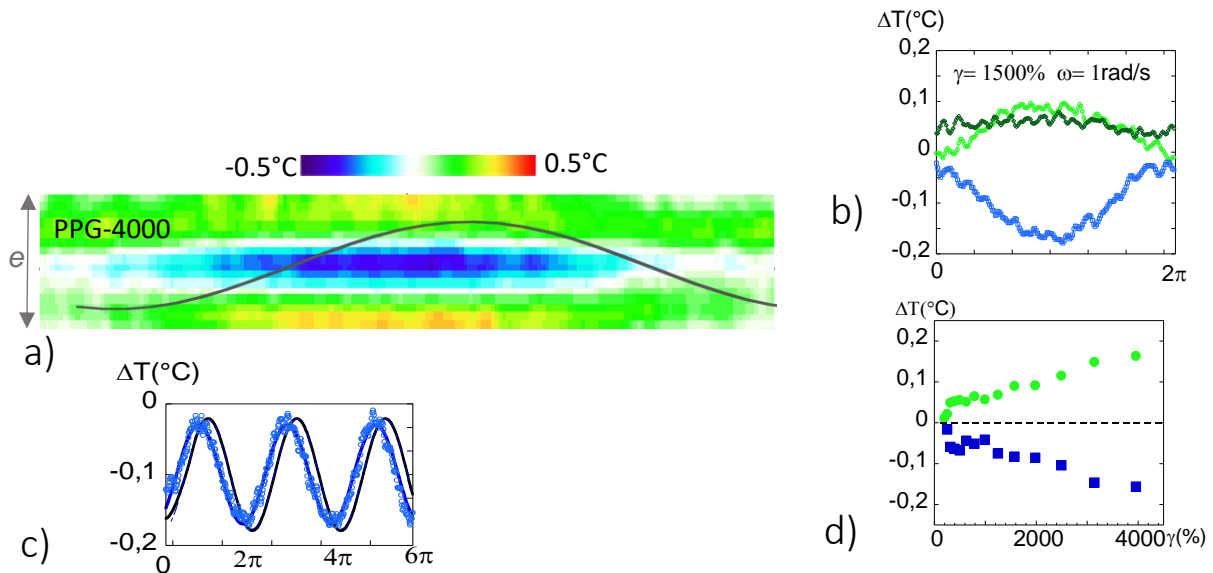


Fig.2: a) Time evolution of temperature cartography of the PPG-4000 upon low frequency oscillatory shear strain ($\omega = 1 \text{ rad/s}$, $\gamma = 1500\%$ and $e = 340\mu\text{m}$ gap thickness, room temperature measurements) along one oscillatory period. The upper plane is fixed while the bottom one oscillates at $\omega = 1 \text{ rad/s}$. The continuous line is an eye-guide for the sin strain function – the phase shift is $\Delta\phi = 34 \pm 2^\circ$. b) Temperature profiles over one period of the temperature recorded on the central part (blue points) and on each side of the gap (bottom (light green) and upper (dark green) bands) at 1500% shear strain and 1 rad/s. c) Detail of the temperature oscillation of the medium part (black line: strain wave, blue points: temperature at ($\omega = 1 \text{ rad/s}$, $\gamma = 1500\%$ and $e = 340\mu\text{m}$ gap thickness). d) Evolution of the temperature variation ($\Delta T = T - T_{\gamma=0}$) of the cold (■) and of the hot zones (●) at low strain amplitude at $e = 240\mu\text{m}$.

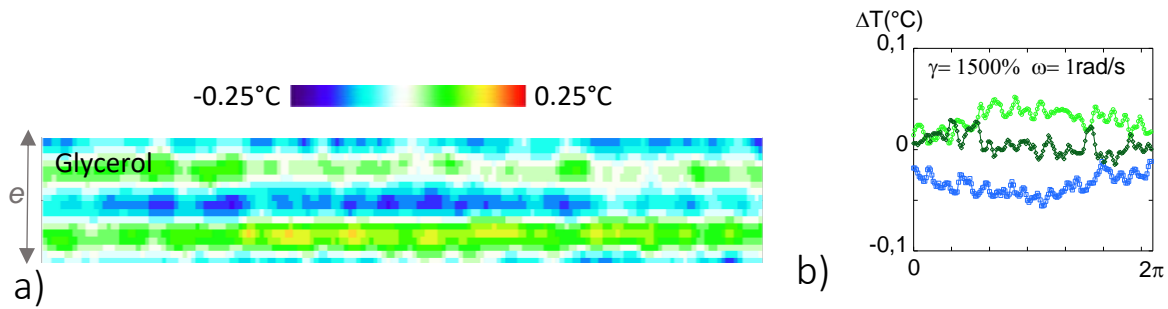


Fig.3: a) Time evolution of temperature cartography of the Glycerol upon low frequency oscillatory shear strain ($\gamma = 1500\%$ and $e = 350\mu\text{m}$ gap thickness, alumina surfaces, room temperature measurements) along one oscillatory period. The upper plane is fixed while the bottom one oscillates at $\omega = 1 \text{ rad/s}$. b) Temperature profiles over one period of the temperature recorded on the central part (blue points) and on each side of the gap (bottom (light green) and upper (dark green) bands) at 1500% shear strain and 1 rad/s.

Compared to the PPG-4000, the glycerol exhibits a weaker thermal variation synchronous with the oscillatory strain. This weaker response might be interpreted by a lower global entropy (intermolecular, conformational). Glycerol is a molecular liquid with symmetrical geometry whereas the low molecular weight PPG-4000 is an oligomer, meaning increased conformational entropy and multiple intermolecular interactions per molecule.

3. Discussions -Conclusions:

A prerequisite for the understanding of the flow properties which are essential in many industrial and biological processes is a complete characterization of the fluid properties prior entering the flow regime. This is the aim of this study that points out, on the basis of three ordinary liquids, an unknown liquid property: the ability to convert the shear strain injected energy by a thermal dynamic signal. These observations are carried out away from any phase transition and thus, might indicate a generic liquid property so far neglected.

At low frequency, a low molecular weight polybutylacrylate, a polypropyleneglycol and the glycerol exhibit strain induced non-uniform temperatures of opposite temperature variations and varying synchronously with the applied shear field. The remarkable thermal compensation indicates a bulk rearrangement keeping a globally constant temperature; i.e. an adiabatic process. The in-phase and linear-like dependence of the amplitude of the negative and positive temperatures generated versus strain amplitude highlights an instant thermodynamic response is evidenced (in the low strain regime) on both the polybutylacrylate and the polypropylene glycol (PPG-4000). Both thermal compensation, linear-like and in-phase thermal response exclude time-dependent processes as conduction, diffusivity or convection effects. The nearly instant thermal response is characteristic of the excitation of an elastic property: the liquid is mechanically compressed and stretched such that no heat exchange enters or leaves the system (in the low strain regime).

The strain-induced cold and hot zones can exhibit a thermal amplitude of $\pm 0.5^\circ\text{C}$ in the case of the unentangled polymer melt. This adiabatic process, the generation of cold zones and the low molecular weight of the tested samples exclude an interpretation in terms of viscous friction heating as it is conventionally expected in highly viscous liquids like high molecular weight (entangled) polymer and at high (steady state) shear rates [22]. The production of cold and hot zones indicates that the injected shear strain energy is not dissipated but transformed as local stretched and compressed states giving rise to different temperatures. For such a thermo-mechanical coupling to exist in shear geometry, it is necessary to suppose that liquids support shear stress and thus assume a coupling-like of shear elastic modes with the bulk elasticity of the liquid similarly as for solid materials. The thermal waves reveal a collective liquid response. This is in agreement with the assumption of long range intermolecular interactions [13-15], with the identification of low frequency shear elasticity theoretically anticipated

[13] and experimentally identified in various simple and complex fluids [2-9]. Low frequency shear elasticity measures the strength of the intermolecular interactions. Liquid shear elasticity makes possible the identification of new properties like the present thermal property or spectacular strain-driven harmonic thermoelastic effects [23]. Shear elasticity opens the route to these alternative models revisiting the zero-frequency shear elasticity assumption [10-12], predicting a length-scale dependence of viscoelastic parameters [10, 13] or inspired from the nonaffine stresses in disordered solids [16]. This experiment shows also that moving apart from standard mechanical measurements by improving the liquid/substrate interactions (total wetting) and probing sub-millimeter scales can provide detailed information on hidden links that couples the liquid (thermo)-dynamics to the mechanical shear strain.

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