Dynamics of specific heat and other relaxation processes in supercooled liquids by impulsive stimulated scattering

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Abstract. Laser based impulsive stimulated scattering or transient grating excitation in a heterodyne diffraction scheme is a powerful method to extract information about different relaxing properties from different signal contributions. Longitudinal acoustic waves are detected simultaneously with thermal expansion and thermal diffusion. Careful fitting of the time-domain density response at different temperatures makes it possible to obtain the various relaxing physical parameters, and to construct Arrhenius plots for the respective relaxation processes. In this work we focus on the influence of the specific heat capacity $C$ on the slower part of the density response function $S_{\rho}(t)$, and, inversely, on the possibility to extract from experimental $S_{\rho}(t)$ data the relaxation behaviour $C(\omega)$. The specific heat capacity is relevant for both the initially rising part of the impulsive stimulated scattering signal (together with the time and frequency dependent thermal expansion $\gamma(t)$), and for the thermal diffusion dominated decrease of the signal at later times after the excitation. By simulating $S_{\rho}(t)$ data in different scenarios, we address the feasibility of unravelling the impulse response functions $C(t)$ and $\gamma(t)$ (and via Fourier transform also $C(\omega)$ and $\gamma(\omega)$) by careful fitting of the signal. This approach offers a unique possibility to extend the 100 kHz bandwidth of current dynamic calorimetric techniques determining $C(\omega)$ (photopyroelectric spectroscopy) to the sub-GHz range.

1. Introduction

Laser based impulsive stimulated scattering (ISS) or transient grating excitation in a heterodyne diffraction scheme is a powerful method to characterize glass forming liquids [1,2]. Via heating by partial optical absorption, followed by thermal expansion (impulsive stimulated thermal scattering or ISTS) and electrostrictive effects (impulsive stimulated Brillouin scattering or ISBS), two crossed pulsed laser beams, forming a pulsed optical interference pattern with a controllable grating spacing, act as an impulsive transient grating source for longitudinal or shear acoustic waves. Besides the acoustic contributions, the density response after laser excitation also contains contributions of thermal expansion (immediately after the deposition of optical energy) and thermal diffusion (which is slowly washing out the laser induced thermal grating). The dynamically changing density grating $\rho(T)$ can be detected via the accompanying refractive index grating $\delta n(x,t)-\rho(T)$ by monitoring the resulting diffraction of probe laser beams crossing the excitation region. By carefully selecting the polarization of the excitation and detection laser beams, it is also possible to extract information about the rotational relaxation that is triggered by the viscosity-driven aligning effect of the launched acoustic waves [3] or of the
electrostrictive effect (ISBS [1,2]). Usually, transient grating experiments on glass forming liquids are performed in a so-called transmission configuration, by crossing laser beams in the bulk of the typically semi-transparent sample. However, by using a reflection configuration, containing an interface with a solid [4] or with air [5], it is also possible to extract information about the relaxation behaviour of the shear velocity.

In the transmission ISTS configuration, careful fitting of the time-domain density response makes it possible to determine the acoustic velocity and damping (related to the oscillatory part of the signal) and the thermal expansion dynamics and thermal diffusivity (related to the slowly varying part of the signal). Performing the experiment at different temperatures for different transient grating wavelengths (and thus for different frequencies) it is then possible to determine the Debye-like behaviour of the longitudinal acoustic velocity and of the thermal expansion dynamics, and to get the temperature dependence of the thermal diffusivity. From that, the temperature dependence of the relaxation time or frequency of the longitudinal acoustic velocity and of the structural relaxation time can be assessed and analysed in an Arrhenius plot.

In this work we focus on the influence of the relaxation of the specific heat capacity $C$ on the slower parts of the density response function $S_q(t)$, and, inversely, on the possibility to extract from experimental $S_q(t)$ data the relaxation behaviour of the heat capacity, $C(\omega)$. By simulating $\rho(t)$ data in different scenarios for a supercooled material with physical behaviour similar to the one of the well-known glass former glycerol, we address the feasibility of unravelling the relaxing part of $C(t)$ and $\gamma(t)$ (and via Fourier transform also $C(\omega)$ and $\gamma(\omega)$) by careful fitting of the ISS signal.

2. Impulsive stimulated scattering in a transient thermal grating configuration for supercooled liquids with relaxing thermo-elastic behaviour: theoretical model and simulation results

A typical ISTS experiment is performed by exciting the sample with an impulsive, quasi-1D light pattern (acting as a heat source via the process of optical absorption) that is very short in time, and quasi-periodic in space. This is achieved by crossing two laser first diffracted and then recombined beams in the $yz$ plane, which results in an interference pattern with wave number $q=2\pi/\lambda$ and spatial period $\lambda$ along the $x$-axis. In order to analyse the density response $\rho(t)$, driven by the temperature response $T(t)$ of the sample, we first solve in frequency domain the thermal diffusion equation and the longitudinal acoustic wave equation with thermal source term, that are given by:

$$\frac{\partial^2 T}{\partial x^2} - \frac{\rho C}{\kappa} \frac{\partial T}{\partial t} = -\frac{Q}{\kappa}$$

$$\frac{\partial^2 u}{\partial x^2} + \frac{1}{c_l^2} \frac{\partial^2 u}{\partial t^2} = \gamma T$$

with $\rho$ [kg.m$^{-3}$] the static part of the density, $C$ [J.kg$^{-1}$.K$^{-1}$] the specific heat capacity, $\kappa$ [W.m$^{-1}$.K$^{-1}$] the thermal conductivity, $\gamma$ [K$^{-1}$] the thermal expansion, $c_l$ [m.s$^{-1}$] the longitudinal acoustic velocity and $Q$ [J.m$^{-3}$] the power density amplitude. For the spatially periodic part of an impulsive grating $Q(x,t)=Q_o \delta(t)\cos(qx)$ the solutions for the temperature $T(x,\omega)$ and the displacement $u(x,\omega)$ then read:

$$T(x,\omega) = \frac{Q_o \cos(qx)}{2\pi(\kappa q^2 + i\omega C)}$$

$$u(x,\omega) = \frac{-q\gamma c_l^2 Q_o \sin(qx)}{2\pi p_C(\alpha q^2 + i\omega)(\omega^2 - q^2 c_l^2)}$$

In the classical case where all physical properties are frequency independent, the displacement response $u(x,t)$ can then be calculated by performing a double Fourier transform, obtaining:

$$u(x,t) = \frac{\gamma Q_o \sin(qx)}{\rho C q \left(1 + \frac{q^2 \alpha^2}{c_l^2}\right)} \left(\exp(-q^2 \alpha t) - \cos(qc_l t) + \frac{\alpha q}{c_l} \sin(qc_l t)\right) \theta(t)$$

The specific heat clearly plays a role in the pre-factor, and, via the thermal diffusivity $\alpha = \kappa(\rho C)$, in the exponentially decaying tail of the signal.

For a supercooled liquid, one can roughly model the frequency dependent dynamics by assuming Debye behaviour for $c_l(\omega)$, $C(\omega)$ and $\gamma(\omega)$:
$c_L(\omega) = c_{L,0} + \frac{c_{L,0} - c_{L,\infty}}{1 + i \frac{\omega}{\omega_c}} \quad C(\omega) = C_{\infty} + \frac{C_{\infty} - C_0}{1 + i \frac{\omega}{\omega_c}} \quad \gamma(\omega) = \gamma_{\infty} + \frac{\gamma_0 - \gamma_{\infty}}{1 + i \frac{\omega}{\omega_c}}$ \hspace{1cm} (4)

This leads to the following exact solution for the transient grating impulse response for temperature and strain $\Delta \rho / \rho$:

$$T(x,t) = \frac{Q \cos(qx)}{\rho C_\infty} \left((\omega^*_L - \omega_L) \exp(-\omega^*_L t) - (\omega^*_L - \omega_L) \exp(-\omega_L t)\right) \theta(t)$$ \hspace{1cm} (5)

In Eq. 5 (details given in Ref. [6]), the damping parameters $\omega_{1,2}^*$ are related to the thermal diffusion damping constant $q^2 \alpha_s = q^2 \kappa / (\rho C_{\infty})$ and to the relaxation parameters of the heat capacity. The angular frequencies $\omega_L$ are related to the sound velocity and damping. $\theta(t)$ is the Heaviside function. In order to calculate simulations of $T(x,t)$ and $u(x,t)$, relaxation parameters were taken from literature for glycerol, and where necessary extrapolated to the frequency and temperature range of interest by using the Debye model fit for the frequency dependence and a Vogel-Fulcher-Tammann (VFT) fit for the temperature dependence. For the sake of conciseness, we only describe the temperature response in words: due to the time- and frequency dependence of the specific heat capacity, the temperature response, which contains an additional exponential function induced by the relaxation of the heat capacity, has an overshooting behaviour, with the overshoot duration increasing with decreasing temperature. This can be explained as follows. At short times, the supercooled liquid is too slow to take up heat in its slow degrees of freedom, so that the heat capacity is low and the temperature rise is high. Only at later times, energy can flow towards the cooperative rearrangements of the amorphous network, so that the heat capacity becomes higher and the temperature lower. The impact of this non-trivial temperature response on the ISTS density response (figure 1) depends on several factors, the main one being the extent to which $\tau_c$, the relaxation time of the heat capacity, is comparable with the thermal diffusion time $\tau_{\text{thermal}} \approx 1 / (q^2 \alpha_s) \approx \rho C_{\infty} / (q^2 \kappa)$. Typically $\tau_c$ is of the order of the acoustic relaxation time $\tau_{\text{ac}}$, and of the structural relaxation time $\tau_s$. This renders it difficult to separately extract the heat capacity dynamics and the thermal expansion dynamics from the initial rise of the signal. As a matter of fact, till now, the effect of both relaxations (exponential functions in equation 5 with decay constants $\omega_{1,2}^*$, $\omega_0^*$, and $\omega_0$), on the density response was modelled in a combined way by assuming a stretched exponential behaviour for the signal [1,2,3,7]. Separating the two effects could be greatly enhanced by exploiting the influence of the specific capacity on the thermal diffusion tail. By choosing a short wavelength $\lambda = 2 \pi q$, the characteristic time of the thermal diffusion tail, which is sensitive to the heat capacity relaxation via the thermal diffusivity, can be brought to timescales similar to $\tau_c$. By combining recorded signals obtained with different wavelengths, the q-dependent effect of the heat capacity relaxation can be untangled from the q-independent thermal expansion contribution to the signal. Details of the calculation and validation of the approach by experimental data [6], as well as a direct fast thermometry approach based on fluorescence spectroscopy [8] will be published elsewhere. Note that also non-Debye behaviour can be simulated by numerically Fourier transforming equations 2, provided a very large number of points are considered in frequency domain, in order to cope with the very large dynamic range of the temporal response (typically from 10 ms for the thermal part of the signal to 1 ns for the acoustic part of the signal).
Figure 1. Simulated transient grating (negative) density response (a.u.) versus log(t), taking into account relaxing behaviour (based on data in literature [detailed description in Ref. [7]]) of the longitudinal acoustic modulus, the specific heat capacity and the thermal expansion coefficient. From left to right: transient grating wavelengths 1, 15, 200 μm. From top to bottom: ωC=10^4,10^5,10^6 s^{-1}. The simulations show the case-dependent effect of varying the relaxation frequency of the heat capacity (ωC=0 (upper red curve), ωC=ωγ (middle green curve), ωC=3ωγ (lower black curve)).

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