Fluorescent molecular rotor probes nanosecond viscosity changes

Caporaletti, F.; Bittermann, M.R.; Bonn, D.; Woutersen, S.

DOI
10.1063/5.0092248

Publication date
2022

Document Version
Final published version

Published in
Journal of Chemical Physics

License
Other

Citation for published version (APA):
Fluorescent molecular rotor probes nanosecond viscosity changes

Viscosity is a key property of liquids, but it is difficult to measure in short-lived, metastable samples due to the long measuring times required by conventional rheology. Here, we show how this problem can be solved by using fluorescent molecular rotors. The excited-state fluorescence decay rate of these molecules is sensitive to the viscosity of their local environment, and by combining pulsed laser excitation with time-resolved fluorescence detection, we can measure viscosities with a time resolution of a few ns. We demonstrate this by measuring in real time the viscosity change in glycerol induced by a nanosecond temperature jump. This new approach makes it possible to measure the viscosity of extremely short-lived states of matter.

ABSTRACT

Viscosity is one of the most important properties of condensed-phase systems, as it determines both diffusive and convective transport rates. Viscosity is usually measured using conventional rheology, but it requires comparatively large sample volumes (typically milliliters) and long measuring times (seconds or more). However, there are many liquid samples that exist for only a short period of time: a spectacular case is water in no man’s land, which exists for only a few μs before crystallizing, but there are many other examples, such as super-heated solids and non-equilibrium states during phase separation in liquid mixtures. To understand the physics of such short-lived liquid states, being able to measure their viscosity can form a crucial contribution. Here, we demonstrate that this can, in fact, be done by using molecular rotors as ultrafast viscosity probes. Molecular rotors are fluorescent molecules that upon photo-excitation can return to their ground state through two relaxation channels: fluorescence and a non-radiative relaxation process involving intramolecular twisting. The non-radiative relaxation channel becomes less efficient when the rotor is in a highly viscous environment (where the intramolecular twisting is hindered), causing an increase in the fluorescence lifetime. There is a well-established quantitative relationship between the fluorescence lifetime and the viscosity of the local environment of the molecular rotor, and this makes it possible to use molecular rotors as a local viscosity probe with excellent spatial resolution. Here, we instead use molecular rotors to measure viscosity with high temporal resolution. Since the fluorescence decay occurs with a time constant that is typically ~1 ns, we can accurately measure the viscosity-dependent fluorescence lifetime within a few ns by combining pulsed laser excitation with time-resolved detection of the fluorescence. In this way, we can measure viscosities with unprecedented time resolution. To test this idea, we measure the time-dependent viscosity change induced in a liquid by a short (~4 ns) temperature jump (T-jump). Such T-jump experiments are a valuable tool to probe equilibration kinetics and short-lived states of matter. The basic idea is to rapidly drive a system out of equilibrium and probe its metastable properties along with its relaxation kinetics. Typically, ultrafast (<10 ns) laser pulses are used to generate T-jumps. In particular short mid-infrared pulses can resonantly excite intramolecular vibrations of the liquid that rapidly (<1 ps) convert the vibrational excitation into heat, causing a practically instantaneous temperature increase. Since the timescale of the T-jump is usually shorter than the time for sound waves to propagate through the sample, the heating process is initially isochoric. T-jump experiments are a well-established tool for investigating protein folding, super-heated solids, phase-separation kinetics, aggregation in microemulsion, and metastable liquids.

Our proof-of-concept measurements are carried out on glycerol, a model viscous liquid. To probe the viscosity, we use the water-soluble hemicyanine molecular rotor trans-4-[4-(dimethylamino) styryl]-1-methylpyridinium iodide (4-DASPI). The fluorescence

Cite as: J. Chem. Phys. 156, 201101 (2022); doi: 10.1063/5.0092248
Submitted: 22 March 2022 • Accepted: 6 May 2022 • Published Online: 23 May 2022

Federico Caporaletti, Marius R. Bittermann, Daniel Bonn, and Sander Woutersen

AFFILIATIONS
1 Van der Waals-Zeeman Institute, Institute of Physics, University of Amsterdam, 1098XH Amsterdam, The Netherlands
2 Van ’t Hoff Institute for Molecular Sciences, University of Amsterdam, 1098XH Amsterdam, The Netherlands

Author to whom correspondence should be addressed: f.caporaletti@uva.nl
properties of 4-DASPI have been very well characterized, in particular the relationship between its fluorescence decay and the viscosity.\textsuperscript{6–9,14,30,31} We study solutions of 4-DASPI in glycerol with a concentration of \( \approx 40 \, \mu M \), which is sufficient to detect the fluorescence, while excluding potential inner filter effects and possible interactions between fluorophores while in the excited state. In fact, at the concentrations used in our experiments, the average distance between the 4-DASPI molecules is about 20 nm,\textsuperscript{32} which is several orders of magnitude larger than the average displacement by diffusion while in the excited state (\( \sim 1 \) ns).

A simplified sketch of the experimental setup is shown in Fig. 1(a). The sample is kept in a quartz cell with a thickness of 1 mm. A near-infrared (NIR) pulse (8 mJ/pulse) with a duration of \( \approx 4 \) ns [Fig. 1(b)], a bandwidth of 2 nm, and a focal beam diameter of 700 \( \mu m \) is used to generate the temperature jump. Its wavelength is resonant with the overtone of the OH-stretching mode of glycerol [Fig. 1(d)], and since the excited vibrational modes relax to the ground state within a few ps, the temperature increases nearly instantaneously. At the selected wavelength, roughly 70% of the NIR pulse is absorbed, meaning that the heat is deposited throughout the optical path through the liquid and not only at its surface. The peak temperature \( (\Delta T) \) and pressure jump \( (\Delta p) \), achieved at the center of the pump beam, can be easily estimated, assuming a Gaussian profile for the NIR laser, using the relations:\textsuperscript{31}

\[
\Delta T = \frac{E_p \alpha}{\pi \Delta \lambda \rho \kappa_T}, \quad \Delta p \approx \frac{\beta}{\kappa_T} \Delta T, \tag{1}
\]

where \( E_p \) is the energy of the T-jump pulse, \( \alpha \) is the absorption coefficient, \( D_p \) is the beam diameter, \( \rho \) is the density, \( \beta \) is the coefficient of thermal expansion, and \( \kappa_T \) is the isothermal compressibility. Using Eq. (1) and assuming an initial temperature of 295 K, we estimate \( \Delta T \approx 8 \) K and \( \Delta p \approx 17 \) MPa for our experiment. The NIR laser operates at a frequency of 20 Hz, and to avoid subsequent T-jump pulses hitting the same spot, the sample is scanned through the beam at an average velocity of 25 mm/s, which changes the illuminated spot every shot. During the experiments, the continuous exposure to the 20 Hz pulse train of T-jump pulses causes an overall temperature increase in the sample volume, which, in turn, causes convective heat transfer from the sample cell to its surroundings. As a consequence, during the experiment, the sample cell is at a temperature that is a few degrees above the ambient temperature (this steady-state temperature is reached within a few seconds after switching on the T-jump laser). To probe the viscosity, the fluorescence of 4-DASPI is excited in the center of the T-jump beam profile using a delayed counter-propagating ultra-fast visible pulse (\( \approx 150 \) fs, 4 \( \mu l/pulse \)) with a smaller beam diameter (\( \approx 220 \) \( \mu m \)) and a wavelength of 490 nm, close to the maximum of the excitation spectrum of 4-DASPI [Fig. S1(a)]. The absorption of 4-DASPI in our sample is \( \approx 0.15 \) (Fig. S2), meaning that 75% of the probe beam is transmitted: this ensures that the heated volume is homogeneously probed. The time-evolution of the fluorescence is detected at 90\(^{\circ}\) using a fast photodiode (Thorlabs, DET025A/M-2 GHz). To minimize the amount of detected fluorescence photons, we used only low-pass filters, cutting off all wavelengths below 565 nm: this ensures that most of the 4-DASPI fluorescence is detected, while the scattering
The fluorescence decay can be well fitted by a single exponential decay convoluted with the photodiode response, these two components are not resolved, and we observe the mean value of the two decay constants. This observation is confirmed by the agreement between the lifetime extracted by our fitting procedure \( \tau \approx 1.17(3) \) ns and the amplitude-averaged lifetime (see also the discussion in Ref. 34), expected for the viscosity of glycerol (99%) at ambient conditions (see discussion in Sec. S2 of the supplementary material). This result also confirms that the visible laser pulses used to excite the fluorescence of 4-DASPI do not heat up the sample. Figure 2 shows the evolution of the fluorescence lifetime in response to the T-jump. Figure 2(a) shows the first 150 ns before and after the T-jump. After the arrival of the NIR pump pulse, the fluorescence decay is significantly faster, indicating a reduction of the glycerol viscosity caused by the temperature increase. Note that we can detect the fluorescence decay already 14 ns after the T-jump pulse: our time resolution is limited only by the duration of the T-jump (FWHM \( \approx 4 \) ns) and the lifetime of the 4-DASPI fluorescence (at this viscosity \( \approx 1 \) ns). This unprecedented time resolution makes it possible to detect variations in the viscosity even when occurring at the ns timescale. In this particular experiment, the decrease in viscosity is mostly due to the increase in temperature. At short delay times (<150 ns), there is also a contribution from the increase in the pressure since the T-jump heating is isochoric and the pressure release into a shock wave usually takes about 100 ns.\(^{35}\) The timescale of the decompression can indeed be easily estimated from the radius of impinging T-jump pulse \( (L) \) and the speed of sound of the liquid \( \left( \frac{1}{\tau} = \frac{1}{\tau_{\text{rel}}} \right) \) resulting in a much smaller effect compared to the associated temperature jump \( ( \pm 8 \text{ K}) \). In our experimental conditions \((L = 350 \mu m \text{ and } \nu \approx 2000 \text{ m/s})\), we can expect the shock-wave to dissipate in \( t_{\text{diss}} \approx 150 \text{ ns} \). However, this short-lived contribution is difficult to observe because of the relatively small \( \Delta p \approx 17 \text{ MPa} \) achieved during the T-jump: the increase in pressure increases the viscosity by maximum \( \pm 10\% \),\(^{36,37}\) resulting in a much smaller effect compared to the associated temperature jump \(( \pm 8 \text{ K}) \), which leads to a decrease in viscosity by \( \pm 50\% \) (see, for instance, Refs. 36 and 37 and references therein).

It is also important to stress that the fluorescence of 4-DASPI is not directly sensitive to temperature in the range that is considered here but only to the viscoelastic properties of the sample. Figure 2(b) shows the lifetime at longer delay times. During this time window, the temperature of the sample remains essentially constant. After 0.5 ms, the sample start moving to a new position so that the next T-jump impinges on a fresh spot. The data of Fig. 2 can be directly converted into time-dependent viscosity using the quantitative relationship between the fluorescence lifetime \( \tau_f \) and viscosity \( \eta \) (the Förster–Hoffmann equation)\(^{38}\) as follows:

\[
\tau_f = k \cdot \eta^x,
\] (2)

FIG. 2. Lifetime of 4-DASPI as a function of the delay with respect to the T-jump pulse. (a) Close-up of the time-zero region. The black solid is a fit to the data with a step function \((x\text{-position of the step kept fixed})\), while the diamonds are the lifetimes of DASPI in glycerol as a function of the pump–probe delay. Inset: fluorescence decay of DASPI at three different delay times, corresponding to the markers with different colors in the main plot: no T-jump (green), \(-100\) ns (blue), and \(+50\) ns (red). The solid curves are fits of an exponential function convoluted with the instrumental response (black dashed line). (b) Semi-logarithmic plot of DASPI lifetime in the long-time region. No thermal relaxation takes place in the probed time-window \( \tau = 0.5 \) ms. After 0.5 ms, the sample is moved to a new spot. Inset: fluorescence decay at two different delay times with respect to the T-jump, as indicated by the markers with different colors in the main plot: \( 10 \) μs (orange) and \( 100 \) μs (brown). The curves are fits of an exponential function convoluted with the instrumental response (black dashed line). The error bars are determined from ten independent measurements, during which each fluorescence decay is averaged over 100 shots.
where \( k \) and \( x \) are parameters depending on the solvent and the fluorescent dye. These parameters can be determined independently from steady-state measurements on water–glycerol solutions with different viscosities (see Sec. S2 of the supplementary material), and using their values, we extract the time-dependent viscosity of glycerol in response to the T-jump. Molecular rotors are sensitive to the viscosity at the microscopic scale, which may differ from the macroscopic viscosity.\(^{14}\) However, in the case of glycerol at ambient conditions, we do not expect such heterogeneity (as is confirmed by the experimentally observed single-exponential fluorescence decay), and the macroscopic and microscopic viscosities are identical. The result is shown in Fig. 3(a). The isochoric heating of glycerol is accompanied by a sudden change in the viscosity, which, probed 10 ns after the T-jump, shows a decrease of \( \approx 40\% \). As a consistency check, we used the known temperature dependence of the viscosity of glycerol\(^{7,17} \) to estimate the magnitude of the T-jump from the observed viscosity jump (see the right y axis of Fig. 3). We find a value of \( \approx 6 \) K, in good agreement with our initial estimate of 8 K.

The results presented here show that fluorescent molecular rotors, combined with ultrafast optical excitation and fluorescence detection, make it possible to measure the viscosity of metastable states in liquids and to directly observe viscosity changes occurring at the ns scale. This unprecedented time-resolution opens up new possibilities to investigate the viscoelastic properties of short-lived systems, in particular of liquid states prepared using temperature jumps. An example is provided by the recent experiments of Kim \textit{et al.}\(^1\) who showed that T-jump experiments can provide access to the liquid–liquid transition of water. By ultrafast heating high-density amorphous ice into the no man’s land,\(^7\) they could observe a liquid–liquid transition in water taking place starting at \( \approx 10 \) ns after the T-jump, while crystallization occurred after a few \( \mu s \). The liquid–liquid transition can be observed only because of the combined temperature (\( \Delta T \approx 100 \) K) and pressure jumps (\( \Delta P \approx 2.5 \) kbar), with the liquid–liquid coexistence line of water located at positive pressure.\(^7\) Our results indicate that molecular rotors can be used to measure the viscosities of these two short-lived liquid phases. In the high-viscosity regime, molecular rotors become progressively less sensitive to viscosity,\(^{19} \) but we expect that in the experimental conditions of Ref. 1, it should be possible to measure the viscosity of supercooled water in no man’s land. In fact, in these experiments, high-density amorphous ice immediately devitrifies after the T-jump, and the resulting liquid state has a relatively high self-diffusion coefficient \( D_{\text{H}_{2}O} \approx 2 \times 10^{-12} \) \( \text{m}^2/\text{s} \). Hence, the conversion between the two liquid phases occurs in a regime of molecular mobility that is even higher than the one investigated here (for comparison, the self-diffusion coefficient of glycerol at ambient conditions is \( D_{\text{gly}} \approx 1.37 \times 10^{-12} \) \( \text{m}^2/\text{s} \).\(^{30} \)

Similarly, molecular rotors can also provide insights into the rheological properties of superheated liquids and solids generated using temperature jumps.\(^3\) Furthermore, since molecular rotors are sensitive to viscosity at the microscopic scale, they can also reveal spatial heterogeneity in short-living states of matter: in the presence of a heterogeneous environment, the fluorescence decay will be characterized by a distribution of lifetimes.\(^{41} \) Thus, the method presented here makes it possible to measure the viscosity in systems and states that are completely inaccessible to conventional rheology.

See the supplementary material for details on the spectral properties of 4-DASPI and the calibration of its lifetime dependence on viscosity.

The authors kindly thank Michiel Hilbers and Wim Roeterdink for technical support and Menno Demmenie for assistance during the experiments. This work was supported by the Netherlands Organization for Scientific Research (NWO) (Grant No. 680-91-13).

**AUTHOR DECLARATIONS**

**Conflict of Interest**

The authors have no conflicts to disclose.

**DATA AVAILABILITY**

The data that support the findings of this study are available from the corresponding author upon reasonable request.
REFERENCES


