

Structural relaxation by digital-correlation spectroscopy

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The utility of digital-correlation spectroscopy for investigating structural relaxation in liquids on time scales from 1 μ sec to 1 sec is established. A digital correlator was used to analyze the Rayleigh scattering of light from undercooled glycerol. The correlation function obtained is related to the isothermal structural relaxation dynamics of the liquid. The data were found to join smoothly with those obtained ultrasonically at higher temperatures.

In the spectrum of light scattered by a viscoelastic liquid, the shape and intensity of the polarized Rayleigh line are governed by the combined effect of thermal diffusion and longitudinal stress relaxation on the fluctuations in density responsible for the scattering.^{1,2} The important parameters characterizing the line are the frequency shift of the Brillouin lines ω_B , the stress relaxation time τ , and the thermal diffusion rate $\lambda\kappa^2/\rho C_p$. (Here λ is the thermal conductivity, ρ is the density, and C_p is the specific heat at constant pressure of the liquid; κ is the magnitude of the wave vector of the density fluctuation under examination.) In terms of these we distinguish three limiting cases:

Case I: $1/\tau \gg \omega_B \gg \lambda\kappa^2/\rho C_p$. Here the Rayleigh line arises entirely from the isobaric portion of the density fluctuations associated with energy transport via thermal diffusion. The line is a Lorentzian of half-width $\lambda\kappa^2/\rho C_p$ reflecting a correlation function for these fluctuations of the form

$$\Phi(t) = (\text{const.}) \exp(-\lambda\kappa^2 t / \rho C_p). \quad (1)$$

Because the relaxation time τ is short compared with $1/\omega_B$, the adiabatic portion of the density fluctuations associated with "internal" or structural relaxation processes remains in equilibrium with the phonon modes and thus contributes only to the Brillouin lines in the spectrum.

Case II: $\omega_B \gg 1/\tau \gg \lambda\kappa^2/\rho C_p$. Because of the slow rate of thermal diffusion the adiabatic and isobaric fluctuations may be uncoupled (as in Case I.) Consequently the Rayleigh line contains the Lorentzian contribution noted above. However, in this case the relaxational part of the adiabatic density fluctuations equilibrate slowly and thus cannot contribute to the phonon modes. Rather they constitute the so-called Mountain component of the Rayleigh line. If, for example, the relaxation process is described by a correlation function $\psi(t)$ —normalized such that $\psi(0) = 1$ —then the Mountain component consists of a line centered at the incident-light

frequency of a halfwidth given approximately by $\Gamma \approx 1/\tau_{ps} = [\int_0^\infty dt \psi(t)]^{-1}$. Since $\Gamma \gg \lambda\kappa^2/\rho C_p$, the Rayleigh line consists of a rather broad Mountain component on which is superimposed the narrower "normal" component. The appropriate correlation function is here of the form

$$\Phi_2(t) = A\psi(t) + B e^{-\lambda\kappa^2 t / \rho C_p}, \quad (2)$$

where A and B are constants.

Case III: $\omega_B \gg \lambda\kappa^2/\rho C_p \gg 1/\tau$. The Rayleigh line again consists of two components, but now it is the Mountain component that forms the narrow line, while the normal Lorentzian component associated with heat transport appears as a relatively broader background. Moreover, because the viscoelastic relaxation process occurs quite slowly compared with the thermal diffusion rate, the relaxational behavior responsible for the Mountain line shape is *isothermal* rather than adiabatic. In addition, the thermal diffusion must proceed without changes in the liquid structure; consequently it must be the "unrelaxed" values of such parameters as the specific heat, C_p^∞ , that govern the thermal diffusion rate. We expect the correlation function to be of the form

$$\Phi_3(t) = A\phi(t) + B e^{-\lambda\kappa^2 t / \rho C_p^\infty}. \quad (3)$$

The structural relaxation function $\phi(t)$ characterizes the isothermal viscoelastic relaxation at constant stress; the average relaxation time is given by $\tau_{pT} = \int_0^\infty dt \phi(t)$.

The measurement of the scattered-light spectrum corresponding to the structural relaxation term is, in this case, very difficult by ordinary spectroscopic (or ultrasonic techniques) since the Mountain linewidth $\leq 10^5 \text{ sec}^{-1}$. We have used a digital autocorrelator to measure the time-correlation function of the scattered-light intensity, and from this obtained the correlation function $\phi(t)$. Our principal interest in this work is to establish the utility of digital-correlation spectroscopy in

studying structural relaxation in viscous liquids on a time scale of approximately 10^{-8} to 1 sec.

In this paper we report measurements in liquid glycerol, corresponding to the conditions appropriate to Case III above. Since measurements were made only for times such that $\lambda\kappa^2t/\rho C_p \gg 1$, the correlation function (3) can be simplified to

$$\Phi_3(t) \approx A \phi(t). \quad (4)$$

The correlator was operated in the "single-clipped" mode so that the measured correlation function $G(t)$ is given by³

$$G(t) = \langle n_k(0)n(t) \rangle, \quad (5)$$

where $n(t)$ is the number of photopulses during the time interval t to $t+\theta$, where θ is the bin size; $n_k(0)=0$ if $n(0) \leq k$, and $n_k(0)=1$ if $n(0) > k$, where k is the clipping level. This is related to $\phi(t)$ through^{3,4}

$$G(t) = a + b\phi(t)^2, \quad (6)$$

where a and b are constants determined by the experimental conditions.

Approximately 800 mW of optical power from a Coherent Radiation Laboratories Ar⁺ laser (488.0 nm) was focused into a high-purity water-free sample of liquid glycerol from which dust particles had been removed by filtration. The glycerol samples used for the runs were specified to contain less than 0.02% water by weight. The vessel containing the sample was built in the form of an optical cross fused into a Dewar and has been described by Pinnow *et al.*⁵ The temperature was stable to within $\pm 0.1^\circ\text{C}$. The light scattered through 90° was spatially filtered, focused on a 300- μm -diam pinhole and then detected by a photomultiplier tube. The photopulses output by the phototube are amplified, discriminated, and then fed to the 100-channel digital correlator.⁶

The isothermal structural relaxation function

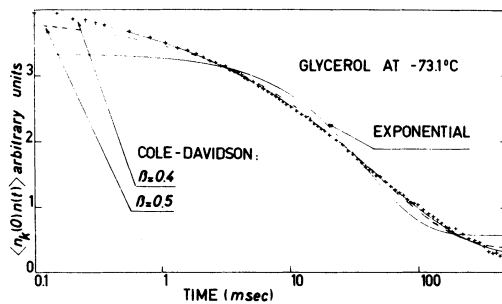


FIG. 1. Measured correlation function $G(t)$ at -73.1°C . The best fits to the data have been computed assuming that $\phi(t)$ is given by Eqs. (7) and (8) for $\beta=0.4$ ($\tau_0=435$ msec); $\beta=0.5$ ($\tau_0=590$ msec); and $\beta=1$ ($\tau_0=76$ msec).

was obtained at 11 temperatures in the range -80 to -48°C , over which range the average relaxation time τ_{pT} was found to vary by a factor of nearly 10^5 . The experimental data for a given temperature consist of a set of between 10 and 15 measurements of $G(t)$ taken for different values of the sampling time θ ranging from $\theta \sim \tau_{pT}/5000$ to $\theta \sim \tau_{pT}/5$. By fitting together these curves, the correlation function $G(t)$ was obtained over a large time domain. It was clear that $\phi(t)$ could not be described by a simple exponential decay, and in view of previous work on structural relaxation⁷ it was decided to analyze the data by assuming

$$\phi(t) = \int_0^\infty d\tau g(\tau) e^{-t/\tau}, \quad (7)$$

where $g(\tau)$ is the Cole-Davidson distribution⁸

$$g(\tau) = \frac{\sin\beta\pi}{\pi\tau} \left(\frac{\tau/\tau_0}{1-\tau/\tau_0} \right)^\beta \quad (0 \leq \tau/\tau_0 < 1) \quad (8)$$

and vanishes for $\tau/\tau_0 \geq 1$. In this, τ_0 represents a cutoff for the distribution, and β is a parameter in the range $0 < \beta \leq 1$, which measures the width of the distribution, the case $\beta=1$ corresponding to a single relaxation time. In terms of these two parameters, it is easy to show that τ_{pT} is given by

$$\tau_{pT} = \bar{\tau} = \int_0^\infty d\tau \tau g(\tau) = \beta\tau_0. \quad (9)$$

A typical set of experimental data is presented in Fig. 1. At all temperatures measured, best fits were found for $\beta=0.40 \pm 0.05$; using Eq. (9) the values of τ_{pT} were deduced. These are presented

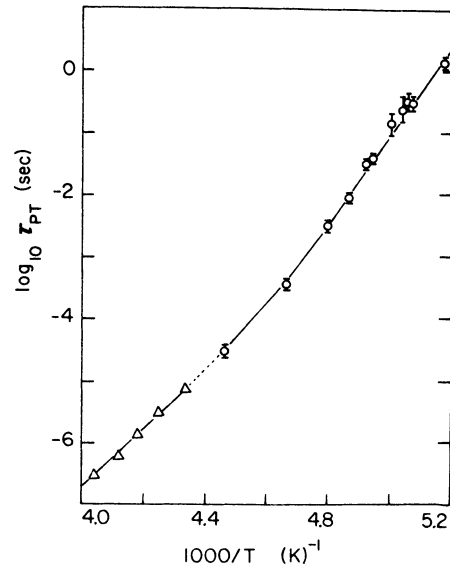


FIG. 2. Average relaxation times τ_{pT} plotted vs reciprocal temperature. The data measured here are indicated by O; those calculated from ultrasonic results are indicated by Δ .

in Fig. 2. In passing we note that these data obey an Arrhenius law of the form $\tau_{pT} \propto e^{E^*/RT}$ with an activation energy $E^* = 32.4$ kcal/mole.

A brief comparison of these results with earlier ultrasonic structural relaxation studies⁹ in glycerol is appropriate. From these data we can obtain the complex, frequency-dependent, adiabatic, longitudinal compliance, which is related to the relaxation function $\psi(t)$ through a Fourier transform. These data can be described by a Cole-Davidson distribution of width parameter 0.44 ± 0.03 independent of temperature over the range -40 to 0°C . The values of τ_{ps} obtained by fitting the ultrasonic results were used to compute values for τ_{pT} by the relation $\tau_{pT} = \tau_{ps}(C_p/C_p^\infty)$.⁷ From the measurements of specific heat for glycerol above and below the glass transformation temperature,¹⁰ we estimate that $C_p/C_p^\infty \approx 1.6$. The computed values of τ_{pT} are shown in Fig. 2. As is apparent, the agreement with the results obtained here is quite

good.

We have shown that the use of digital-correlation spectroscopy in measuring the Mountain component of light scattered by a liquid is a viable tool for investigating structural relaxation phenomena on a time scale of 10^{-6} to 1 sec., a range inaccessible to other more conventional experimental techniques. For the specific system—glycerol—studied here, the measurements indicate that there is little difference in the form of the isothermal and adiabatic structural relaxation functions. The measured relaxation times join smoothly with those measured at higher temperatures using ultrasonic techniques.

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