

Improved Data Analysis on Atomic Dynamics in Liquid CCl₄

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About two decades ago, we measured inelastic x-ray scattering (IXS) on liquid CCl₄ [1] to investigate longitudinal acoustic (LA) phonon dynamics in this molecular liquid. CCl₄ is considered as the simplest molecular liquid because the molecular species are almost isotropic and connected with a van der Waals interaction with each other like liquid rare gas. Thus, we analyzed the IXS spectra by using a damped harmonic oscillator (DHO) model [2] to obtain the excitation energies of LA phonons, and found that the microscopic sound velocity in the molecular level highly exceeds the ultrasonic one by about 37%.

Recently, we measured IXS on liquid acetone [3] and the obtained data were analyzed by using generalized Langevin formalism [4]. The generalized Langevin equation used in this study is described by a damped oscillation equation for the intermediate scattering function $F(Q,t)$, the time-Fourier transforms of the measurable dynamic structure factor, $S(Q,\omega)$, with a memory function. Here, the memory function was assumed to be composed of one thermal and two viscoelastic decay channels, where the fast and slow viscoelastic are called as microscopic μ -relaxation and structural α -relaxation processes, respectively. To avoid any interferences of parameters, we employed a simple idea of sparse modeling so that the parameters exhibit smooth changes with Q . For liquid acetone, we found that the $Q \rightarrow 0$ limit of the fast μ -relaxation rate is about 60 fs, which is highly related to the vibrational dynamics of the dipoles of liquid acetone, and that of α -relaxation rate of 0.5-1.0 ps, being similar to the reorientation correlation time of 0.75 ps.

Based on this sophisticated analytical method for the IXS spectra, we revisit liquid CCl₄ to examine the feasibility of the generalized Langevin formalism and a sparse modeling. The left panel of Fig. 1 shows logarithmic plots of IXS spectra (circles) and their fitting results (solid curves) of liquid CCl₄ at selected Q values. Broad LA excitation modes are observed as shoulders at the both sides of the central quasielastic peaks. The mode energy of the LA excitations, ω_Q , is calculated as the maxima of the current-current correlation function, $J(Q,\omega) = \omega^2/Q^2 \cdot S(Q,\omega)$. The model coincides well with the experimental data.

The middle upper panel of Fig. 1 shows the dispersion relation, and the dashed line indicates the hydrodynamic relation predicted by adiabatic sound velocity of $v_s = 923.4$ m/s [5]. As clearly seen in the figure, the mode excitation energies highly exceed the hydrodynamic prediction. The middle lower panel of Fig. 1 shows the dynamical sound velocity calculated as $v_Q = \omega_Q/Q$. The adiabatic sound velocity is also given as the dashed line. The v_Q value reaches about 1450 m/s, exceeding the v_s value by about 57%, which is much larger than the previous result of 37% [1] obtained from the DHO model.

The right panel of Fig. 1 shows the Q dependence of the fast μ - (upper) and slow α -relaxation rates obtained from the present generalized Langevin analysis. Although the data are rather scattered, both the values look to gradually decrease with increasing Q . The $Q \rightarrow 0$ limit of are about 0.2 and 1.5 ps for the τ_μ and τ_α values, respectively. These values are larger than those of liquid acetone of 0.06 and 0.5-1.0 ps for τ_μ and τ_α values, respectively. These differences may be owing to the bonding origins between molecules, a van der Waals liquid for CCl₄ and a dipolar liquid for acetone.

Further analyses are now in progress to reduce the ambiguities of parameters in the generalized Langevin formalism. Detailed comparisons with macroscopic dynamic properties of liquid CCl₄, such as Raman data and rotational motions, are also just getting underway.

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FIGURES

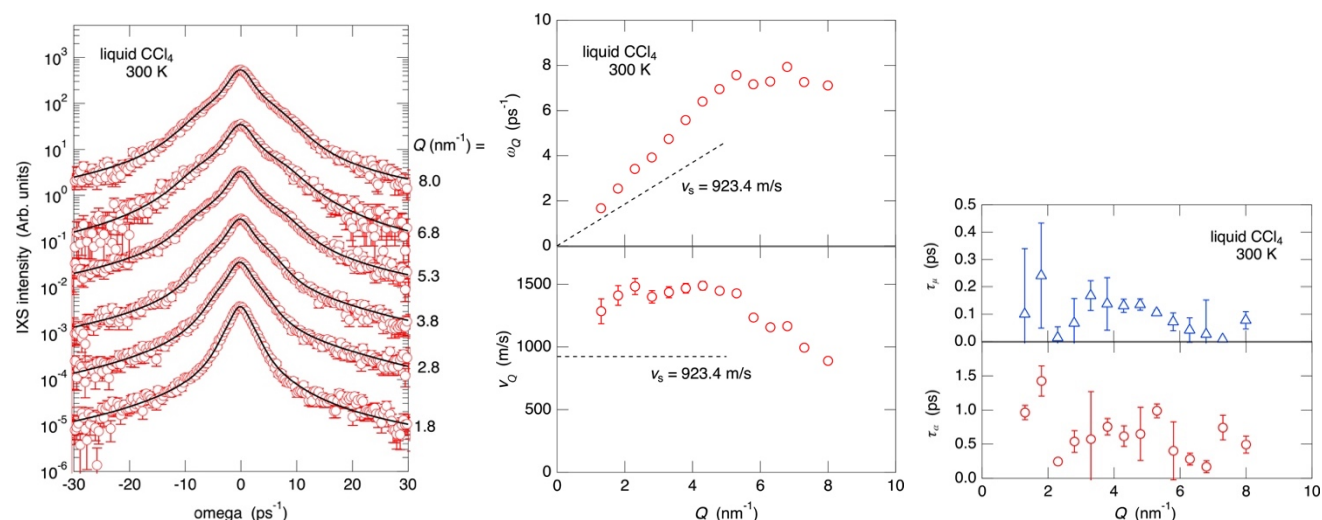


Figure 1: (Left) Logarithmic plots of IXS spectra of liquid CCl_4 at selected Q values. The solid curves represent the generalized Langevin fits. (Middle) The dispersion relation (upper) and dynamical sound velocities (lower) with Q . (Right) The fast (upper) and slow (lower) viscoelastic relaxation rates of the memory function in the generalized Langevin formalism.