Temperature and Density Dependences of the Dynamics of Liquid *n*-Pentane Studied by Molecular Dynamics Simulation

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In order to elucidate the temperature and density dependences of the power spectra of the velocity autocorrelation functions, molecular dynamics simulation of liquid *n*-pentane has been carried out. Strong temperature dependence is observed in the frequencies lower than ~20 cm^{-1}, while the variation of the density makes significant effect in the whole spectral region where low-frequency phonon modes of liquids are expected to appear.

Due to the recent development of the femtosecond spectroscopic techniques, molecular motion in liquids, which is closely related to chemical reactions in solution, has been extensively investigated. In order to elucidate the microscopic dynamics of the low-frequency modes of liquids, the frequency response functions of the optical Kerr effect (OKE) are analyzed in various manners.[1–3] Kinoshita et al.[1] reported that the frequency response functions of organic liquids showed drastic temperature dependence in the frequency range below ~80 cm^{-1}. Not only the temperature variation expressed by a change in the width of the Lorentzian component but also the extra temperature-varying component around 30–80 cm^{-1} was observed for cumene.

The observed temperature dependence was explained as an appearance of the anharmonic couplings among numerous microscopic oscillators. Assuming the temperature independent frequency distribution of the harmonic oscillators, the frequency response functions in the middle frequency region were reproduced at various temperatures.[1] The distribution of the low-frequency phonon modes should depend on a density of the liquid because the size of the solvent cage decreases with increasing density. Therefore it is necessary to consider further details of the temperature effect of the liquid dynamics.

Using molecular dynamics (MD) simulation, Ji et al. investigated the OKE signal of liquid CS_2.[2] They changed the density and the temperature simultaneously to reproduce the state points of the real liquid. Although we cannot change experimentally the temperature of the liquid without affecting the density, both the temperature and density dependence of the low-frequency modes can be investigated by using MD simulation. In various liquids which do not show specific interactions such as hydrogen bonding, the low-frequency phonon modes appear in the similar spectral region.[1,3] In oder to avoid difficulties caused by the molecular dipole and quadrapole, we performed the MD simulation of liquid *n*-pentane.

The dynamics of 128 *n*-pentane molecules in a cubic cell was simulated with periodic boundary conditions. The united atom model was used.[4] The interaction between the united atoms consists of the bonded and nonbonded forces. The nonbonded interaction is described by a Lennard-Jones (LJ) 6–12 potential, while the bonded interaction consists of an angle bending[5] and a torsional term,[6] The SHAKE algorithm was used to hold the bond lengths at 1.54 Å.[7] The cut off distance of the LJ interaction was taken to be 9.83 Å. The size of the simulation cell was varied with the density of the liquid. The equation of motion was integrated with the velocity Verlet algorithm with a time step of about 0.5 fs. The system was thermostated by using velocity rescaling algorithm.[8] After the thermalization of the system for more than 50 ps, the coordinates and the velocities of atoms were stored every 5 fs for 30 ps. Vibrational analysis of *n*-pentane was carried out on the basis of the ab initio molecular orbital calculation. Gamess[9] was used for this purpose.

From the simulation, translational diffusion coefficients were estimated to be $(6.3 \pm 0.4) \times 10^{-5}$ and $(2.4 \pm 0.3) \times 10^{-5}$ $\mathrm{cm}^2\ \mathrm{s}^{-1}$ at 303 (0.627) and 213 K (0.697 g cm^{-3}), respectively, which were slightly larger than the measured values in literature 5.65×10^{-5} and 1.92×10^{-5} $\mathrm{cm}^2\ \mathrm{s}^{-1}$.[10]

Nuclear dynamics of the molecular system can be discussed by using the power spectrum (PS) of the velocity autocorrelation functions (ACF). The atomic and the molecular PSs ($C_V(\omega)$) are calculated as a Fourier-cos transformation of the velocity ACFs ($C_V(\tau)$) of the atoms and the centers of mass of the molecules, respectively.

$$C_V(\omega) = \int_0^\infty C_V(\tau) \cos \omega\tau \mathrm{d}\tau$$

The PS of the angular velocity ACF is also calculated from the sum of the atomic angular velocities around the centers of mass of the molecules. Although the atomic PS is different from either the frequency response function of the OKE signal or the Raman spectrum, it can be a reasonable representative of the density of the states.

Figure 1 shows the temperature dependence of the atomic and molecular PSs. In these simulations, the density of the liquids was kept at constant of 0.627 g cm^{-3}. For the normaliza-

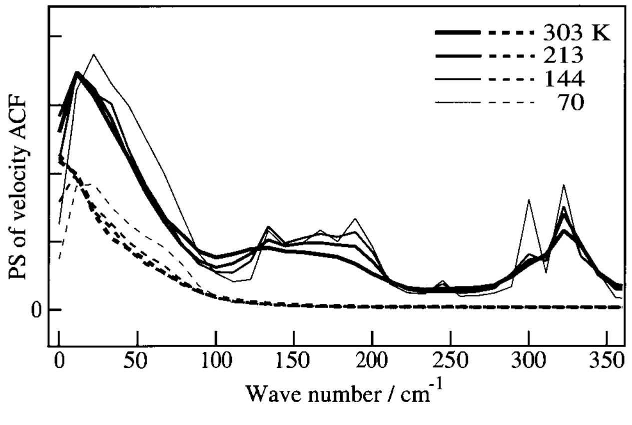

Figure 1. Temperature dependence of the power spectra (PS) of the atomic (solid lines) and molecular (broken lines) velocity autocorrelation functions.

tion, the spectral intensity was divided by the temperature. The constraints of the bond length does not show significant effects of the spectra below 300 cm^{-1}.

In the atomic PS, band structure is observed in the higher energy than 200 cm^{-1}, of which the band width decreases with decreasing temperature. Since such peaks are not observed in the molecular PS, it is reasonable to assign these bands to the molecular vibration. Although only a broad band exists around 150 cm^{-1} in the temperatures higher than 200 K, we can see the bands peaked around 130, 170, and 190 cm^{-1} at 70 K. Vibrational analysis on the basis of the ab initio MO calculation of *n*-pentane suggests that the bands are also due to the molecular vibration. The intramolecular vibrational modes of *all-trans-n*-pentane in this energy region are predicted to be 110, 118, and 198 cm^{-1}. The frequencies of the low energy intramolecular vibrational modes show strong dependence on the conformation, which can be a reason of the broad spectra in the high temperatures.

The PS in the region between 0 and 100 cm^{-1} cannot be assigned to the molecular vibration but it should be ascribed to the translation, rotation, and libration. The intensity at 0-frequency, which indicates the contribution of the translational diffusion, decreases with decreasing temperature. The atomic PS of the liquid shows a peak around 20 cm^{-1} and the strong temperature dependence is observed in the lower frequencies. The peak position shows a slight blue shift in the temperatures lower than the freezing point. Above the freezing point the temperature dependence seems to be quite small in the region of 20–100 cm^{-1}.

Figure 2(a) shows the density dependence of the atomic (solid lines) and molecular (broken lines) PSs. The simulations were performed at 303 K. The densities of the real liquid under the atmospheric pressure at 303 and 213 K are 0.627 and 0.697 g cm^{-3}, respectively. Since the density of liquid *n*-pentane near the freezing point was estimated to be about 0.74 g cm^{-3}, 0.80 g cm^{-3} cannot be realized as a density of the liquid. The intensity of the atomic PSs below ~70 cm^{-1} decreases with increasing density, while a little density effect is observed in the higher frequency region. The band maximum of the low-frequency phonon band moves from ~10 cm^{-1} (0.627 g cm^{-3}) to ~20 cm^{-1} (0.74 g cm^{-3}). The strong density dependence is observed near the 0-frequency. The results indicate that the translational diffusion coefficient becomes small in the high densities, which is an appearance of the solvent cage effect.

The density dependence of the molecular PS is significant in the frequencies lower than ~40 cm^{-1} and seems to be different from that of the atomic PS. In order to discuss the details of the nuclear dynamics, the difference spectra between the atomic and molecular PSs were calculated as shown in Figure 2(b). The PS of the angular velocity ACF is also displayed in the figure (broken lines). The band maxima of the difference spectrum and the PS of the angular velocity in the densities ≥ 0.74 g cm^{-3} are very close each other. The rotational libration shows the maximum around 30 cm^{-1} (0.697 g cm^{-3}), while the peak of the molecular PS, which is due to the translational libration appears around 10 cm^{-1}. In the lower densities, PSs of the angular velocity ACF is significantly different from the difference spectra below ~40 cm^{-1}. The the angular velocity PS of 0.627 g cm^{-3} has large intensity in the 0-frequency region, which should be due to the rotational diffusion.

As a conclusion, in the frequencies ≤ 20 cm^{-1}, where the translational motions as well as the diffusive rotation is important, PS shows strong dependence on both the temperature and density. The variation of the temperature seems to affect on the spectral intensity of the experimentally observed Lorentzian component. On the other hand, the density effect appears in both the intensity and the band width. Only the density effect is significant in the frequencies ≥ 20 cm^{-1}, where libration is important. The variation of the density makes significant contribution to the experimentally observed temperature effect of the low frequency phonon modes.

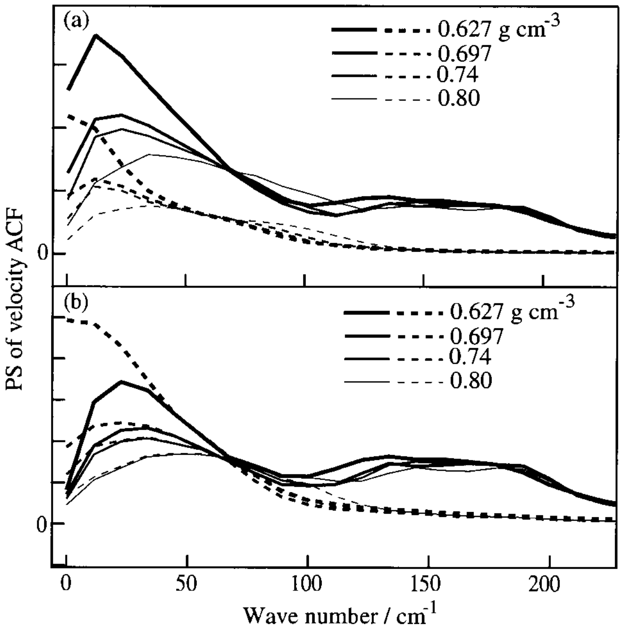

Figure 2. (a) Density dependence of the power spectra (PS) of the atomic (solid lines) and molecular (broken lines) velocity autocorrelation functions. (b) The difference between the atomic and molecular PSs (solid lines) and the PS of the angular velocity autocorrelation function (broken lines).

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