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Local density enhancement in neat supercritical fluid due to attractive intermolecular interactions

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Abstract

Short-range structure in the neat supercritical fluid consisting of polar molecules is investigated by measuring Raman spectrum of fluoroform (CHF_3) at reduced temperature $T_r = T/T_c = 1.02$. The spectra are analyzed by the Schweizer–Chandler model, and the spectral shift is decomposed into attractive and repulsive components as a function of density varied by a factor of 50. The attractive component shows larger shift than the one anticipated from the uniform molecular distribution. A local density enhancement due to the attractive intermolecular interactions is definitely observed in the neat supercritical fluid and evaluated against bulk density.
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1. Introduction

Supercritical fluids have been well known as very inhomogeneous mediums in molecular distribution [1,2]. As very long-range inhomogeneity, several kinds of neat fluids were investigated by static Rayleigh light scattering in the past a few decades [3]. From the results, it is shown that correlation lengths reach up to a few micrometer at very close to the critical temperature, e.g., reduced temperature $T_r = T/T_c \approx 1.0001$. The inhomogeneity ranging over mesoscopic scale has been studied by small-angle X-ray scattering (SAXS) at temperature relatively far from the critical one ($T_r \geqslant 1.02$), and the inhomogeneous behaviors are characterized by the density fluctuation as well as the correlation length with a few nanometer [4–8]. From the results, the same behaviors in the long-range inhomogeneity among supercritical CO_2 [4,5], CHF_3 [5,6], and C_2H_4 [7] have been observed, and the principle of corresponding state is ensured except for supercritical H_2O [8]. The time evolution of density fluctuation in neat supercritical fluids has been evaluated by dynamic light scattering, and the correspondence between dynamic and static density fluctuations is observed [9,10]. Also the critical slowing down has been mapped onto P–T and ρ–T phase diagrams, and the contour curves of slowing down have been observed at the top of critical point [10].

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As *short-range inhomogeneity* in the vicinity of a solute molecule, static and dynamic structures of *supercritical solutions* have been extensively investigated by various experimental and theoretical methods [1,2,11,12]. On the contrary, there have been not so much studies on the short-range inhomogeneity of *neat supercritical fluids* so far. Whether or not the local density is enhanced in neat systems has been recently discussed from theoretical and experimental approaches [13–18]. A study of the Lennard-Jones (L-J) fluid by two-dimensional molecular dynamics (MD) simulation first evaluates the local density enhancement in the neat fluid [13]. According to tetraherz absorption spectra of neat supercritical CHF_3 affected by short-range structure, a nonlinear spectral shift as a function of density are interpreted as an enhanced local density [14]. On the contrary, the study for a neat L-J fluid combined Monte Carlo simulation with integral equations shows almost linear correlation between local coordination number and bulk number density in the supercritical region [15]. A linear vibrational-frequency shift of Raman spectrum as a function of density has been recognized as the lack of local density enhancement in neat supercritical ethane [16,17].

As mentioned above, the short-range inhomogeneity in neat supercritical fluids shows different features depending on the kinds of molecules, although the long-range one in almost all neat systems gives the same behaviors in the inhomogeneity, followed by the principle of corresponding state [5,19]. Our research interest in this Letter is how short-range inhomogeneity is affected by molecular interactions. In order to elucidate the short-range inhomogeneity in the neat system of a polar molecule, we select fluoroform (CHF_3) with the large dipole moment (1.65 D) [20] and measure the symmetric C–F stretching (v_2) mode as a function of density varied by a factor of 50.

2. Experimental

A light source was an argon-ion laser operated at a single line of 514.5 nm with power of 200 mW in front of an optical cell. The scattering light was collected by lenses and entered into a monochro-

mator (TRIAX 550, JovinYbon-Spex) equipped with a charge coupled device (CCD) camera after passing through a supernotch filter (Kaiser) in order to remove Rayleigh scattering. An optical configuration between the light source and the detection was set to be ss-polarization by using a half-wave plate and a polarizer. It was confirmed that the measured v_2 band consists of a Q-branch with negligible P- and R-branches.

An optical cell for high pressure conditions was used as specially constructed one [21]. Fluctuations of pressure and temperature were suppressed to be less than $\pm 0.1\%$ during a measurement. Chemical purity of CHF_3 was commercially guaranteed to
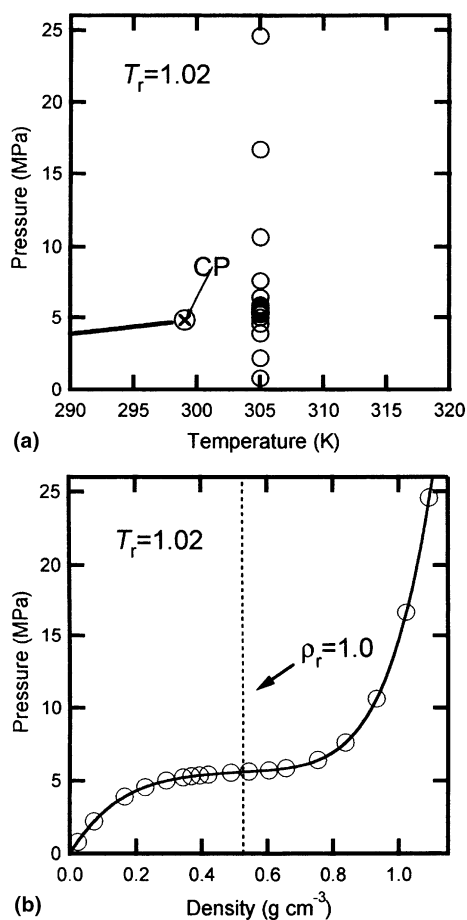

Fig. 1. Measured thermodynamic states for Raman spectra of supercritical CHF_3 along isotherm of reduced temperature $T_r = T/T_c = 1.02$ plotted on P–T (a) and ρ–P phase diagrams (b).

be 99.99%. Critical constants of CHF_3 are reported to be $T_c = 299.06$ K, $P_c = 4.836$ MPa, and $\rho_c = 0.525$ g cm^{-3} [22]. Thermodynamic states of the present measurements are plotted on the P–T phase diagram in Fig. 1a. Corresponding densities are also shown in Fig. 1b, which are calculated from the empirical state equation [22] by use of measured P and T values.

3. Results

Fig. 2 shows the spectra which have been assigned as a symmetric C–F stretching (ν_2) mode [23]. The data are collected along isotherm of
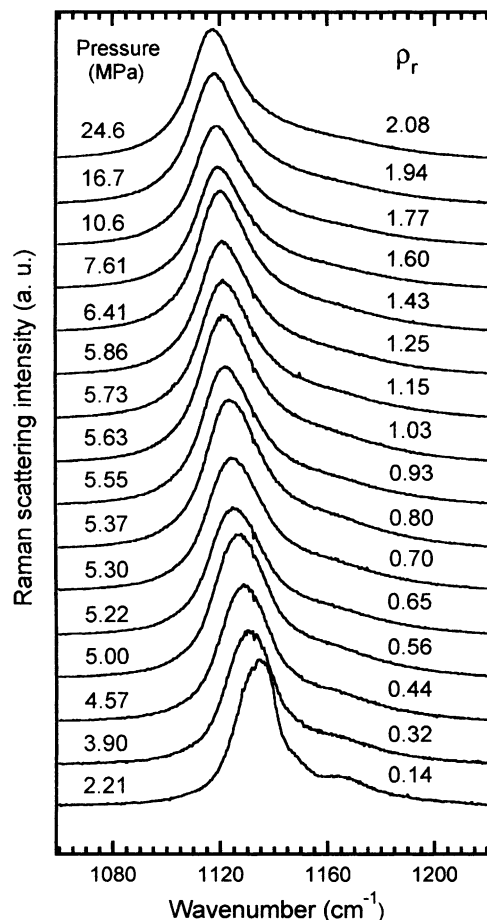
Fig. 2. Vibrational Raman spectra of ν_2 mode of CHF_3 at supercritical states.
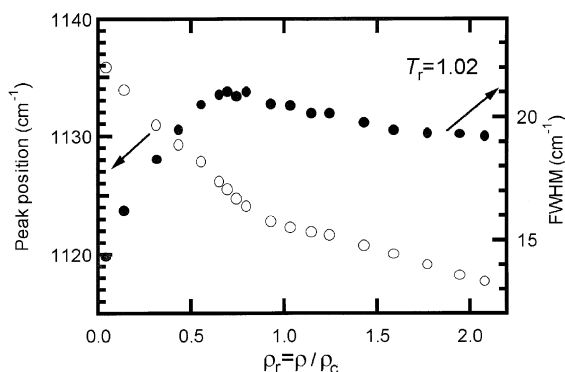
Fig. 3. Density dependence of peak positions (○) of spectra and width (●).

$T_r = 1.02$ in various pressure and/or density. The spectra show slightly antisymmetric shapes, because the right wing of ν_2 band partially overlaps with the weak band of antisymmetric C–F stretching mode (ν_5) around 1160 cm^{-1}. By fitting the observed spectra with Gaussian functions, density dependences for the peak position and the width of ν_2 are obtained as a function of the reduced density $\rho_r = \rho/\rho_c$ and plotted in Fig. 3. From the results, two characteristic features are seen. First, the spectra shift toward lower energy side with increase of density, and the amount of shift becomes smaller from higher density than $\rho_r \approx 0.8$. Second, the width broadens with increase of density, and it gradually becomes constant in the higher density region. As similar features in the shift and the width, their density dependences change around $\rho_r \approx 0.8$. This implies that the local structure around a vibrating molecule changes near there.

4. Analysis of spectral shift on the basis of the Schweizer–Chandler model

As the density increases, average forces along a vibrational coordinate exerted by surrounding molecules causes the shift of vibrational frequency. On the basis of the Schweizer–Chandler (SC) model [24], the density dependence of a vibrational Raman spectrum was analyzed for liquids and solutions at high pressures of GPa [24–27] and supercritical fluids at MPa with medium density

[16,28]. In the model, the frequency shift Δv is partitioned into contributions from the repulsive and the attractive force components as follows:

$$\Delta v = \Delta v_R + \Delta v_A, \tag{1}$$

where Δv, Δv_R, and Δv_A, are net, repulsive, and attractive frequency shifts, respectively. The repulsive contribution is calculated using a hard-sphere approximation and pseudo-diatomic model [24]. The attractive one is derived by subtracting the repulsive shift from the net shift. The repulsive shift as a function of density is expressed as follows [24]:

$$\frac{\Delta v_R}{v_0} = c_1 \exp(m_1\rho*) + c_2 \exp(m_2\rho*) - c_3 \exp(m_3\rho*), \tag{2}$$

where v_0 is the vibrational frequency in the isolated condition. The coefficients c_i are related to values of harmonic and anharmonic force constants of a molecule. From the result of detailed ab initio calculation of a CHF_3 molecule, their values are reported to be 8.36 aJÅ^{-2} and −30.9 aJÅ^{-3}, respectively [30]. The coefficients m_i are reported as empirical parameters [25], depending on molecular size. The density in Eq. (2) is represented as $\rho* = \rho\sigma_s^3$, where σ_s is diameter of hard sphere (0.43 nm) obtained from van der Waals volume of CHF_3 [29].

5. Discussion

Fig. 4 shows the measured net shift, the calculated repulsive one, and the attractive one as a function of reduced density ρ_r and/or packing fraction of molecules at the isothermal condition of $T_r = 1.02$. The repulsive components slightly increase in the present density region, while the attractive ones decrease as molecules are condensed. It has been theoretically described that the attractive component is linearly proportional to the density as given by [24]

$$\Delta v_A = C_a\rho, \tag{3}$$

where C_a is an attractive shift parameter. This equation is based on the SC model, and above linear relationship between the attractive shift and
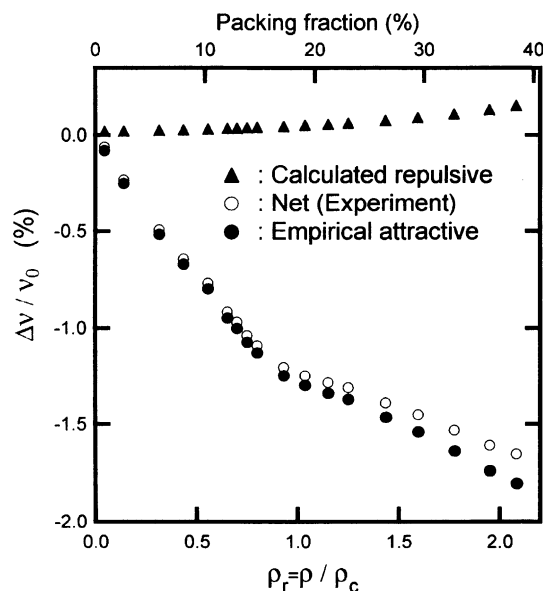
Fig. 4. Net, attractive, and repulsive spectral shifts of v_2 mode as a function of packing fraction and reduced density $\rho_r = \rho/\rho_c$.

density is established on the condition of the homogeneous (uniform) distribution of molecules [23]. As shown in Fig. 4, the attractive shift presents nonlinear density dependence. Therefore, it is considered that the deviation from the linear trend shows the inhomogeneous distribution of molecules in the vicinity of a vibrating CHF_3. Aggregates in the neat fluid can cause further attractive shift than the uniform molecular distribution.

In supercritical solutions, the deviation from the linear trend as a function of bulk density has been frequently observed and interpreted as a local density enhancement around a solute molecule [1,2,11,12]. The enhancement is expressed as follows:

$$\langle\delta\rho_l\rangle = \rho_l - \langle\rho\rangle, \tag{4}$$

where $\delta\rho_l$, ρ_l, and $\langle\rho\rangle$ are local density enhancement, local (effective) density, and bulk (averaged) one, respectively. In the present neat system as well as previous reports for supercritical solutions, a local density is estimated by finding the density on a linear line which gives the same amount of shift on a nonlinear curve [1,2,11–15]. As a result, the local density enhancement is obtained as the dif-

ference between densities on the curve and the linear line as shown in Fig. 5a.

Fig. 5b shows the local density enhancement obtained from the attractive shift of the neat supercritical CHF_3. It is noted that the enhancement exists in the neat fluid in the case of polar molecules. Actually, there are few experimental and theoretical observations on the local density enhancement in neat fluids except for several reports [13,14,18], although it has been well known that long-range inhomogeneity significantly exists in all

of neat fluids [1–10,19]. We observe the enhancement in the neat fluid definitely. It has been also ensured that the enhancement becomes maximum around $\rho_r = 0.8$, where the empirically calculated inhomogeneous width becomes maximum [31]. The enhancement may have possibility to induce further repulsive shift by the increase of local density. However, it has been confirmed that the increased amount by the effect is calculated to be 0.05% as the maximum amount in the present density range. In this situation, the attractive shift by the effect increases from 1.3% to 1.35%, which is so subtle value that it is negligible.

According to reports [16,17], the linear density dependences for spectral shifts of C–H and C–C stretching modes of ethane have been interpreted as the lack of local density enhancement in the neat supercritical fluid at $T_r = 1.02$. From the theoretical point of view, it has been interpreted that almost linear density dependence of local coordination number indicates the weak local density enhancement or its absence in the neat L-J fluid at $T_r = 1.02$ [15]. On the contrary, the Raman spectra of neat supercritical O_2 measured at $T_r = 1.01$ show significant anomalies of spectral width and frequency as a function of bulk density, which is interpreted as the increase of local density [32]. Similar anomalies have been recently observed in vibrational Raman spectra of supercritical N_2 at very close to critical point [33]. From results of Raman measurements [21] and IR absorption [34] of neat supercritical CO_2 at $T_r = 1.02$–1.06, nonlinear density dependences of spectral width and peak shift have been observed near the maximum density fluctuation. By summarizing these results, a molecule with weak quadrupole moment (ethane), the one with strong quadrupole moment (CO_2), and the one with large dipole moment (CHF_3) show linear, nonlinear, significant nonlinear vibrational-spectral shifts against bulk density, respectively. It is likely that the polarity of a molecule, dipole–dipole interaction, and multi-polar electric interactions play an important role in the short-range structure of neat supercritical fluids.

To the best of our knowledge for the latest theoretical investigation [18], the local density enhancement is ensured in the neat fluid by the calculation using inhomogeneous integral equation
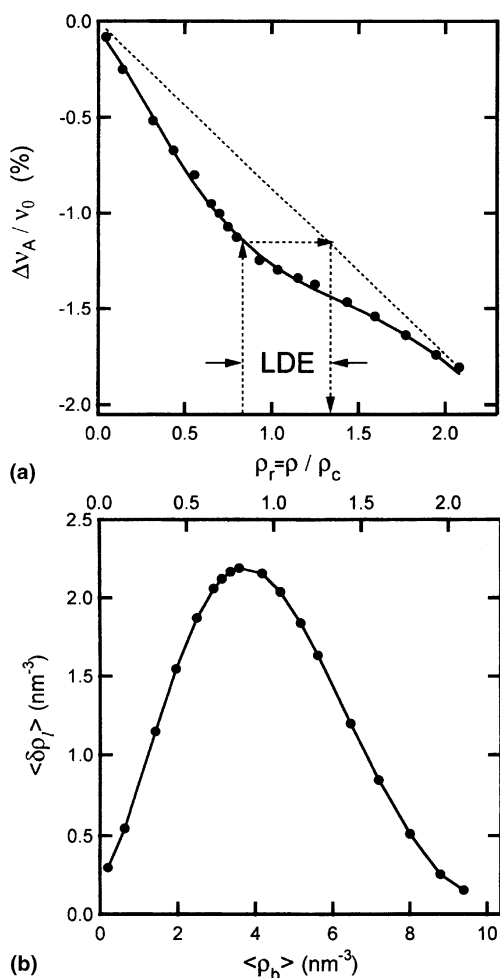

Fig. 5. (a) Attractive shift as a function of reduced density. Dashed line is the attractive shift in the case of uniform molecular distribution. LDE represents the local density enhancement. (b) Local density enhancement of neat supercritical CHF_3 in the volume of 1 nm^3 as a function of bulk density.

theory. It is concluded that the strength of inter-molecular potential and temperature play important roles in the local density enhancement of neat fluids, and the value of enhancement sensitively changes by the kinds of intermolecular potentials. This theoretical result is consistent with the experimental results: nonobserved local density enhancement for neat supercritical ethane and the significant enhancement for neat supercritical CHF_3 at the same reduced temperature. However, it has been clarified that the long-range inhomogeneity exists in all of neat fluids near critical points from a few decades ago [3–10,19], and recently the critical anomaly due to short-range inhomogeneity is also reported in the case of molar polarization of supercritical ethylene [35]. Therefore, the investigation of short-range inhomogeneity in neat systems will be further needed to understand critical phenomena in the nanoscale. In near future, we will report the relationship between short- and long-range inhomogeneities of supercritical CHF_3 [31].

Acknowledgements

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