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Structure of liquid carbon tetrachloride up to the subcritical point measured by wide *Q*-range neutron diffraction

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Structure of liquid and gaseous CCl_4 at elevated temperatures from 195 °C to the subcritical point 275 °C ($T_c=285.15$ °C) along the liquid–vapor coexistence curve have been studied by means of pulsed neutron diffraction. Structure factor in a wide range of momentum transfer Q from 0.03 to 20 Å^{-1}, covering from the small angle scattering region to atomic-scale structure region, has been obtained. Long-range density fluctuation and atomic scale structure have been analyzed: (1) molecular orientational correlation still exists in liquid CCl_4 at 275 °C while it disappears in its saturated vapor; (2) correlation lengths of density fluctuation are 10–13 Å for the liquid at 275 °C and 13–17 Å for its saturated vapor; and (3) molecular-density fluctuation $(\langle N_m^2 \rangle - \langle N_m \rangle^2)/\langle N_m \rangle$ is estimated to be 2.4 for the liquid at 275 °C and 9.3 for its saturated vapor. © *1997 American Institute of Physics.* [S0021-9606(97)50932-1]

I. INTRODUCTION

The structure of liquid carbon tetrachloride (CCl_4) has been widely studied both experimentally[1–12] and theoretically.[13–18] Most experimental studies were made on the liquid at room temperature. One of the authors (MM) measured[12] the structure factors of liquid CCl_4 from the triple point (−22 °C) to 160 °C along the liquid–vapor coexistence curve by means of pulsed neutron diffraction. It was shown[12] that an effective diameter, a packing fraction, and orientational correlation of CCl_4 molecules were important factors to characterize the temperature dependence of the structure of liquid CCl_4 and, furthermore, that the preferred orientation between molecules exists, even at 160 °C. These findings may be characteristic for liquids of relatively high density, where a repulsive interaction between molecules is dominant factor of determining the fluid structure.

On the contrary, as the density of liquid decreases or the fluid state approaches the liquid–vapor critical point, an attractive interaction begins to play an important role in the fluid structure. One of the most significant structural changes raised from the attractive interaction is density fluctuation correlated in a long distance. Measurement of structure factors in a wide range of momentum transfer Q including small angle scattering region is, therefore, essential to study the structure of low-density fluids. From this viewpoint we intend to measure the structure factors of liquid and gaseous CCl_4 at a low-density state in a wide range of Q from 0.03 to 20 Å^{-1} by means of pulsed neutron diffraction aiming to examine the structural change due to the attractive interaction in detail.

II. EXPERIMENT

The critical temperature (T_c), critical pressure (P_c), and critical density (d_c) of the CCl_4 fluid are 283.15 °C, 45 atm, and 0.5576 g/cm^3, respectively.[19] Because in a previous experiment[12] a Ti–Zr null-alloy cell was used satisfactorily for structural measurements of liquid CCl_4 up to 160 °C, we attempted to use it for the present experiment, but it turned out that the alloy was chemically attacked by liquid CCl_4 above 200 °C. Therefore, a silica-glass tube of thick wall (5.7 mm in inner diameter, 2.0 mm in wall thickness, and 82 mm in height) was chosen as a new sample cell. A suitable amount of liquid CCl_4 of 27 mm in height at room temperature was sealed in the silica-glass tube in vacuum after solidifying the liquid CCl_4 at the liquid nitrogen temperature. During the diffraction experiment the sample was heated by a pair of infrared lamps and, in addition, by two electronic subheaters, each of which was located at the top or bottom of the cell to improve a uniformity of sample temperature. The cell was wrapped with a thin vanadium foil of 0.025 mm thick so as to be heated efficiently by the infrared radiation. The temperature was monitored by thermocouples at three positions of the cell, i.e., the bottom, the center, and the top, and was kept within 2 °C over the whole cell. The meniscus between liquid CCl_4 and its vapor did not change largely in the present experiment; it was 27 mm in height at 20 °C, increased slightly with increasing temperature, and was about 32 mm at 275 °C. A slit made of sintered[10] B_4C with a vertical opening of 20 mm was, therefore, placed below the meniscus during the measurements of liquid CCl_4, while the cell was moved downward against the slit for the measurement of gaseous CCl_4 so that the vapor was exposed to the neutron beam.

The diffraction data were observed for liquid CCl_4 at 20, 195, 215, 235, 255, and 275 °C and gaseous CCl_4 at 275 °C along the liquid–vapor coexistence curve, empty cell, background, and vanadium standard by using HIT and SAN in
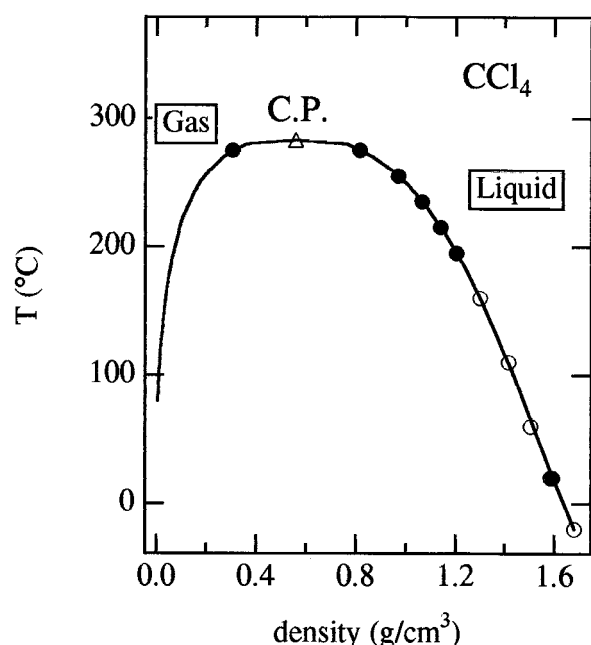
FIG. 1. Temperature–density relation of liquid and gaseous CCl_4 along the liquid–vapor coexistence curve. Solid circles are experimental points studied here, while open circles are those studied previously (Ref. 12).

FIG. 2. Experimental structure factors $S_m(Q)$ of liquid and gaseous CCl_4: a linear plot.

struments at KENS spallation neutron source of KEK, Tsukuba. The fluid states studied in this work are shown by solid circles on a curve of the temperature–density relation along the liquid–vapor coexistence curve[19] in Fig. 1. The highest temperature in this experiment is 0.982 of T_c. The density decreases by a factor of 6 when the state changes from the liquid at 20 °C to the gas at 275 °C. The molecular number densities ρ_m of the fluids studied in this work are summarized in Table I.

The observed intensity was corrected for background, sample cell, attenuation and multiple scattering, and normalized to the absolute one by using the vanadium standard for HIT experiments and the vanadium and water standards for SAN experiments. The coherent differential scattering cross section $I(Q)$ was obtained from the absolute intensity by subtracting the incoherent scattering cross section. The structure factor $S_m(Q)$ is defined as coherent scattering intensity per molecule,[4] i.e.,

$$S_m(Q) = \frac{I(Q)}{N_m(\Sigma_i b_i)^2}, \tag{1}$$

where N_m is the number of CCl_4 molecules, b_i is a coherent scattering length of element i, the sum of i is over all atoms in a molecule, and $Q = 4\pi \sin\theta/\lambda$ with a neutron wavelength λ and a scattering angle 2θ. The values of b_i are $b_C = 0.6646 \times 10^{-12}$ cm and $b_{Cl} = 0.9577 \times 10^{-12}$ cm (Ref. 20). Since $S_m(Q)$ tends to $\Sigma b_i^2/(\Sigma b_i)^2$ as Q goes to infinity, $S_m(Q)$ approaches 0.2034 at high Q. $S_m(Q)$ in a Q range of 0.2 Å$^{-1} < Q < 20$ Å^{-1} was obtained by using the HIT instrument and that in a lower Q range of 0.03 Å$^{-1} < Q < 1$ Å^{-1} was obtained by using the SAN instrument. Both $S_m(Q)$'s were joined around $Q = 0.5$ Å^{-1}.

Because the cell wall was rather thick, the signal from the liquid sample was roughly one-third of the total intensity for the HIT experiment. In order to see whether the corrections described above were made reasonably well, $S_m(Q)$ of liquid CCl_4 at 20 °C obtained in the present experiment was compared with that measured previously.[12] We confirmed that the present result was in good agreement with the previous one[14] within an experimental error, which was estimated to be a few percent typically, and the corrections were made satisfactorily.

III. RESULTS

$S_m(Q)$'s for liquid CCl_4 at 20, 195, 215, 235, 255, and 275 °C and for gaseous CCl_4 at 275 °C are shown in Fig. 2 in a range of Q up to 12 Å^{-1} in a linear scale. Figure 3 shows a log $S_m(Q)$–log Q plot in order to emphasize the wide-Q range behavior of $S_m(Q)$. The characteristic feature of $S_m(Q)$ in a range of Q less than 4 Å^{-1}, which is related to

TABLE I. Correlation length ξ and molecular-density fluctuation $(\langle N_m^2\rangle - \langle N_m\rangle^2)/\langle N_m\rangle$ obtained for liquid and gaseous CCl_4 at elevated temperatures T along the liquid–vapor coexistence curve. ρ_m is a molecular-number density taken from Ref. 19. See the text for ξ_1 and ξ_2.

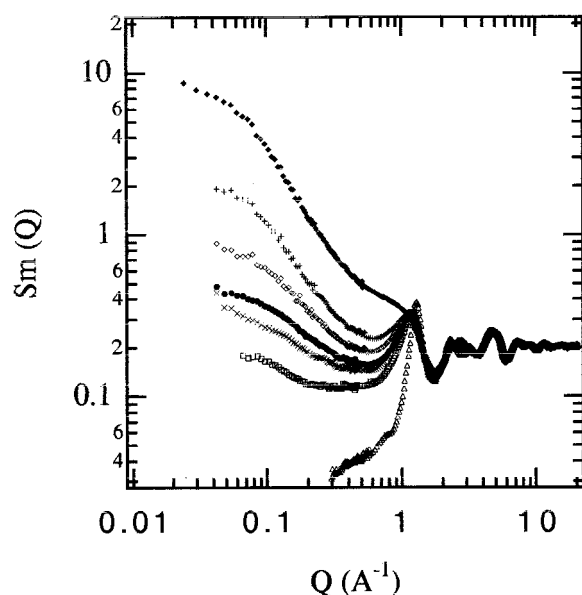| State	T (°C)	ρ_m (molecules/Å³)	ξ (Å) ξ_1	ξ_2	$\frac{\langle N_m^2\rangle - \langle N_m\rangle^2}{\langle N_m\rangle}$
Liquid	20	0.006 20	⋯	⋯	0.03
Liquid	195	0.004 71	4.7	⋯	0.20
Liquid	215	0.004 46	5.3	7.7	0.35
Liquid	235	0.004 17	5.4	7.9	0.47
Liquid	255	0.003 80	6.8	8.6	0.90
Liquid	275	0.003 19	10.0	13.0	2.4
Vapor	275	0.001 09	13.0	17.0	9.3

FIG. 3. Experimental structure factors $S_m(Q)$ of liquid and gaseous CCl$_4$: a log–log plot. From bottom to top, liquid CCl$_4$ at 20 (triangles), 195 (squares), 215 (crosses), 235 (solid circles), 255 (diamonds), 275 °C (pulses), and gaseous CCl$_4$ at 275 °C (solid diamonds).

FIG. 4. Reduced radial distribution functions $4\pi r\rho_m[g(r)-1]$ of liquid and gaseous CCl$_4$.

the intermolecular structure,[12] depends strongly on the fluid state or density. The main peak located around 1.2 A^{-1} shifts to the lower-Q region and becomes broader with decreasing density, but is still clearly observed in the liquid at subcritical point 275 °C. While in the gaseous CCl$_4$ at 275 °C, a hump is observed in the same Q region instead of a clear peak. The feature of $S_m(Q)$ in a range of Q larger than 4 A^{-1} is basically independent of density studied in this work, indicating that the intramolecular structure does not change much in these thermodynamic states. The small angle scattering is observed above 195 °C and increases rapidly with decreasing density, as shown in Fig. 3, which indicates a marked increase of the density fluctuation as the state approaches the critical point.

Figure 4 shows reduced radial distribution functions $4\pi r\rho_m[g(r)-1]$ obtained from the Fourier transform of $S_m(Q)$ truncated at around 19 Å^{-1} by the following equation:

$$4\pi r\rho_m[g(r)-1]=\frac{2}{\pi}\int Q\left(s_m(Q)-\frac{\Sigma b_i^2}{(\Sigma b_i)^2}\right)$$
$$\times \sin Qr \, dQ, \tag{2}$$

where $g(r)$ is a composite distribution function involving a weighted sum over the partial functions. The two sharp peaks are clearly observed below 3 Å for each curve, although there are many other fine ripples. We think these ripples are caused by the noise in $S_m(Q)$ inevitably introduced due to the experimental difficulties of the low density of samples and of using the thick cell. The least-squares fitting of $S_m(Q)$ to the intramolecular form factor[12] $F_1(Q)$ reveals that the first peak is located at 1.76–1.79 Å and as-
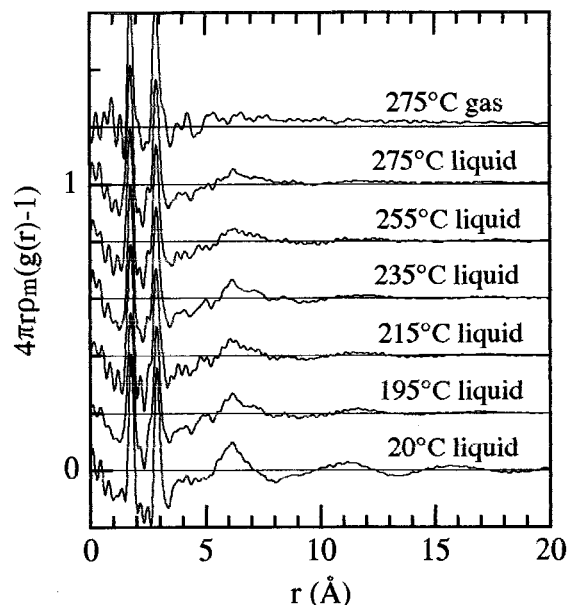
signed to an intramolecular C–Cl bond length. The second one is located at 2.88–2.90 Å and assigned to an intramolecular Cl–Cl atomic spacing. The next two peaks observed around 4 and 6 Å for the liquid at 20 °C have been attributed[12] to the intermolecular atomic distribution between molecules correlated in the orientation. Figure 4 shows that the latter two peaks become broader with decreasing density and almost disappear for the gas at 275 °C, indicating a gradual loss of the orientational correlation with decreasing density.

It is noted that the $4\pi r\rho_m[g(r)-1]$ curve of gaseous CCl$_4$ at 275 °C has a unique feature due to the density fluctuation; a positive value extends far beyond 20 Å only with a slow decay, in comparison with an oscillatory behavior around a baseline for the typical liquid at 20 °C. This behavior is characteristic for a long-range density fluctuation and is discussed in detail in the next section.

IV. DISCUSSION

In a previous experiment[12] it was found that the preferred orientation exists in the liquid CCl$_4$, even at 160 °C. Figure 5 plots the experimental $S_m(Q)$ compared with an intramolecular form factor $F_1(Q)$ and an intermolecular form factor for uncorrelated molecules $F_u(Q)$ for the liquid CCl$_4$ at 20 °C (a), at 275 °C (b), and the gaseous CCl$_4$ at 275 °C (c). The discrepancy between $S_m(Q)$ and $F_1(Q)$ in a Q range from 2 to 3.5 Å^{-1}, where $F_u(Q)$ is negligibly small, is a clear evidence of the existence of the orientation correlation, because if there is no orientational correlation, $S_m(Q)$ is given[4] by

$$S_m^u(Q)=F_1(Q)+F_u(Q)[S_c(Q)-1], \tag{3}$$

where $S_c(Q)$ is a molecular center structure factor, and from Eq. (3) it is evident that $S_m(Q)=F_1(Q)$, where $F_u(Q)=0$.
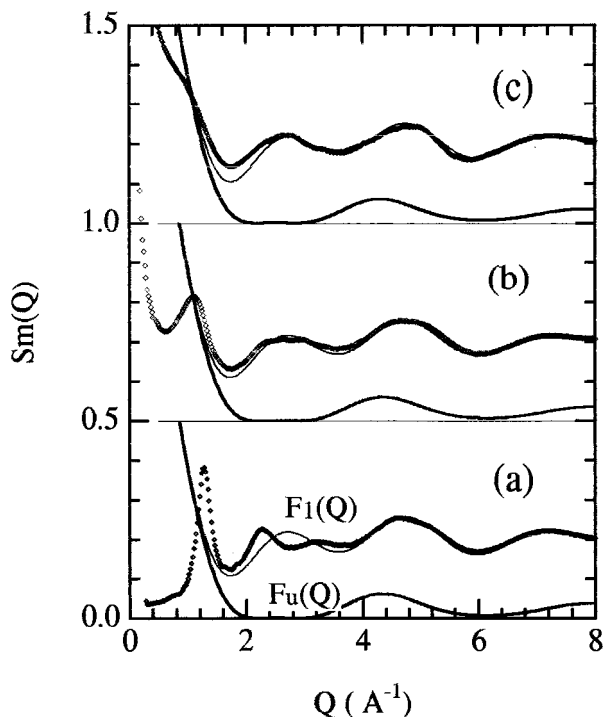
FIG. 5. Comparison of experimental structure factor $S_m(q)$ (open circles), intramolecular form factor $F_1(Q)$ (thin solid lines), and uncorrelated intermolecular form factor $F_u(Q)$ (thick solid lines) for liquid CCl$_4$ at 20 °C (a), at 275 °C (b), and gaseous CCl$_4$ at 275 °C (c).
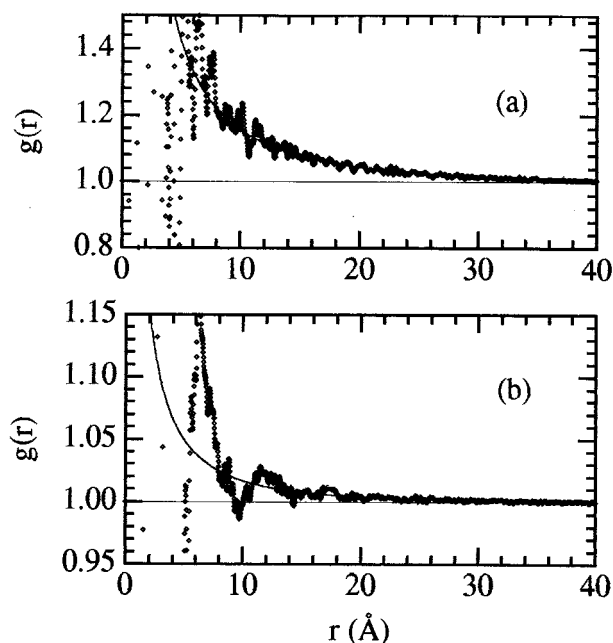

FIG. 6. Long-distance behavior of experimental $g(r)$ (dots) in comparison with density fluctuation $[\alpha g_f(r)+1]$ (solid line) calculated by Eq. (5) with $\xi=13$ Å for gaseous CCl$_4$ at 275 °C (a) and $\xi=10$ Å for liquid CCl$_4$ at 275 °C (b).

This discrepancy is clearly recognized for the liquid at 20 °C, as shown in Fig. 4(a). The similar discrepancy is clearly seen for the liquid at 275 °C, as shown in Fig. 4(b), although it is much smaller than that observed in Fig. 4(a). On the other hand, $S_m(Q)$ for gaseous CCl$_4$ at 275 °C seems to coincide with $F_1(Q)$, as shown in Fig. 4(c). We may conclude that some orientational correlation still exists in the liquid CCl$_4$ at the subcritical temperature while it disappears in its saturated vapor. This result agrees qualitatively with the MD simulation,[15] which suggests that much of the structure persists when the temperature is raised to near-critical values.

According to the Ornstein–Zernike theory,[21] the structure factor for density fluctuation in a low-Q region is characterized by a Lorentzian,

$$S_m(Q) \propto \frac{1}{1+\xi^2 Q^2}, \tag{4}$$

or a corresponding distribution function $g_f(r)$, Fourier transform of Eq. (4), is given by an exponential function,

$$g_f(r) \propto \frac{1}{r}\exp\left(-\frac{r}{\xi}\right), \tag{5}$$

where ξ is a correlation length of fluctuation. In Fig. 6 we plot the experimental $g(r)$ for both the liquid and gaseous CCl$_4$ at 275 °C in an enlarged vertical scale, in comparison with that calculated by Eq. (5) with $\xi=10$ Å for the liquid at 275 °C and $\xi=13$ Å for its saturated vapor, where we plot $[\alpha g_f(r)+1]$ with a scaling factor α instead of $g_f(r)$ itself. One may clearly see that an asymptotic behavior of experi-

mental $g(r)$ is characterized well by Eq. (5) at large r. In order to see the Q dependence of $S_m(Q)$ in a low-Q region, we plot $1/S_m(Q)$ against Q^2 in Fig. 7. A good linear relation is obtained in a sufficiently low-Q region less than 2×10^{-2} Å^{-2} for each curve, especially for the liquid and gaseous CCl$_4$ at 275 °C, as suggested from the large-r behavior of $g(r)$ described above. It should be noted that Q
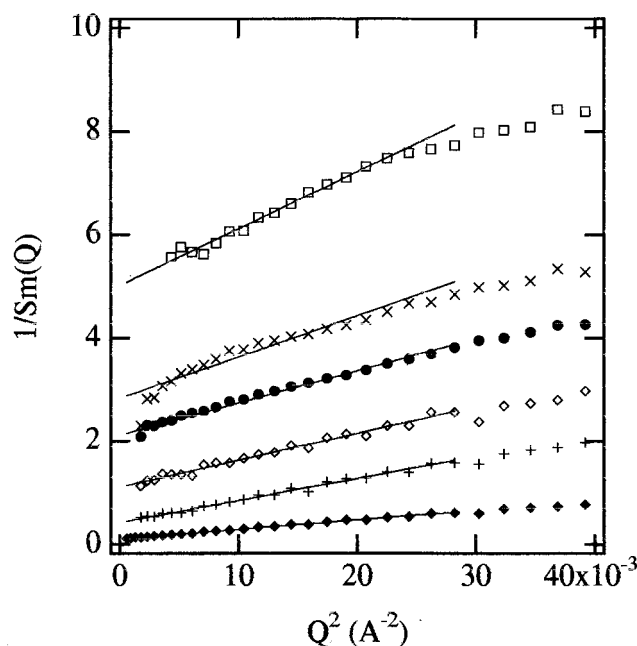

FIG. 7. Plots of $1/S_m(Q)$ vs Q^2: liquid CCl$_4$ at 195 (squares), 215 (crosses), 235 (solid circles), 255 (diamonds), and 275 °C (pluses), and gaseous CCl$_4$ at 275 °C (solid diamonds).

dependence of $F_1(Q)$ and $F_u(Q)$ does not affect this linear relation because the values of $F_1(Q)$ and $F_u(Q)$ are almost unity in this Q^2 range. The values of ξ estimated from this linear relation are listed as ξ_1 in Table I.

In the case of liquid CCl$_4$ at 235 °C or less, however, a plot of $1/S_m(Q)$ vs Q^2 deviates from a linear relation with increasing Q^2, as shown in Fig. 7. This means that for these liquids the intensity of small angle scattering is rather weak, so that the scattering intensity from the atomic-scale structure cannot be ignored even at small Q. It is, however, hard to evaluate the latter contribution accurately. Here we evaluate it by using the simplest formula of Eq. (3) with a molecular center structure factor $S_c(Q)$ calculated from a PY hard sphere model,[22] because a repulsive potential alone does not give a significant density fluctuation.[23] The effective diameter of CCl$_4$ molecules estimated previously[12] is used by taking account of the temperature dependence. The net small angle scattering, $S_f(Q)$, is assumed to be given by subtracting $S_m^u(Q)$ from the experimental $S_m(Q)$. The plot of $1/S_f(Q)$ thus estimated versus Q^2 gives again a linear relation below $Q^2 = 2.0 \times 10^{-2}$ Å^{-2} for each sample as before, but with increasing Q^2 the plot deviates from a linear relation in the opposite direction to that shown in Fig. 7. The values of ξ estimated from these plots are listed as ξ_2 in Table I. We believe that the value of ξ_1 is a minimum estimate for the correlation length ξ while ξ_2 is a maximum estimate. Since the effective diameter of CCl$_4$ molecules[12] is about 5 Å, the correlation length ξ estimated for the fluids at 275 °C is a few times the molecular size.

The value of ξ should show critical point behavior with divergence at T_c. However, the thermodynamic state of CCl$_4$ fluid studied in this work is rather far from the critical point and the density is not kept constant, so that it is impracticable to extract the critical exponent from this experiment.

In a monatomic fluid, the density fluctuation is related to the long-wavelength limit of $S(Q)$, $S(0)$, as

$$\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} = S(0). \tag{6}$$

Similarly, the molecular-density fluctuation in a molecular liquid is related to the long-wavelength limit of the molecular-center structure factor $S_c(0)$, hence $S_m(0)$, because in Eq. (3) both $F_1(Q)$ and $F_u(Q)$ tend to unity as $Q \to 0$ so that $S_m(0) = S_c(0)$. Thus,

$$\frac{\langle N_m^2 \rangle - \langle N_m \rangle^2}{\langle N_m \rangle} = S_m(0). \tag{7}$$

Thermodynamically this quantity is related to the isothermal compressibility χ_T as $S_m(0) = \rho_m k T \chi_T$. The values of $S_m(0)$ estimated from an extrapolation of $S_m(Q)$ to $Q \to 0$ are listed in Table I. Because the value of χ_T for liquid CCl$_4$ at a high temperature has not been reported as far as we know, the consistency of the estimated values of $S_m(0)$ with the thermodynamic quantities cannot be determined. In order to se how the molecular density fluctuates, a root-

mean-square density fluctuation defined as $(\langle N_m^2 \rangle - \langle N_m \rangle^2)^{1/2}/\langle N_m \rangle$ is evaluated for a sampling volume of $4\pi\xi_1^3$ arbitrarily chosen here. The value of this fluctuation is given by $[S_m(0)/4\pi\xi_1^3 \rho_m]^{1/2}$ from Eq. (7). The values listed in Table I suggest that the root-mean-square density fluctuation is $\pm 24\%$ for the liquid CCl$_4$ at 275 °C while it is $\pm 55\%$ for its saturated vapor, indicating that the density fluctuation is much pronounced in the gaseous states.

V. CONCLUSION

The structure factors in a wide range of Q from 0.03 to 20 Å^{-1} have been measured on liquid and gaseous CCl$_4$ up to the subcritical point along the liquid–vapor coexistence curve. The following results are obtained. (1) Small angle scattering is clearly seen, even at 195 °C, and evolves significantly as T approaches T_c. (2) The first peak of $S_m(Q)$ of the liquids becomes broader as T approaches T_c, while a hump instead of a clear peak is recognized for the vapor at 275 °C. (3) Orientational correlation still exists in liquid CCl$_4$ at 275 °C but disappears in its saturated vapor. (4) The correlation length ξ of the density fluctuation is 10–13 Å for the liquid at 275 °C and 13–17 Å for its saturated vapor. (5) The molecular-density fluctuations is 2.4 for the liquid at 275 °C and 9.3 for its saturated vapor. (6) The root-mean-square density fluctuation measured in a sampling volume of $4\pi\xi_1^3$ is estimated to be $\pm 24\%$ for liquid CCl$_4$ at 275 °C while it is $\pm 55\%$ for its saturated vapor.

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