

Dynamics of Density Fluctuation of Supercritical Fluid Mapped on Phase Diagram

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The increasing use of supercritical fluids in a wide range of practical applications has motivated a number of recent attempts to understand the fundamental aspects of fluid structure. Supercritical fluid structures are known to be very inhomogeneous,^{1–3} and this inhomogeneity is related to the efficiencies of chemical reactions and extraction processes. In our previous studies, we evaluated the inhomogeneity of several fluids according to density fluctuations and correlation lengths from measurements of small-angle X-ray scattering (SAXS) and thermodynamic calculations.⁴ From the results, we learned that when a contour map of density fluctuation is drawn on a phase diagram, a ridge is formed on the map.

This ridge does not correspond to the critical isochore but rather accords with only a locus of maximum or minimum points of each of the second-order derivatives of the Gibbs or Helmholtz free energy, for example, specific heat capacity, isothermal compressibility, and sound velocity. These physical meanings are characterized by the use of the van der Waals theory and by the use of thermodynamics.^{4b} As for experimental aspects, rate constants or product yields for photochemical reactions, solubility and relaxation times show an inflection, a minimum, or a maximum around the ridge. In another aspect, the experimental results of vibrational Raman and terahertz absorption spectroscopies show that a local structure in the vicinity of a molecule changes from gaslike to liquidlike around the ridge.⁵ In this communication, we investigate how to characterize a ridge of dynamics in the time domain and where to locate the ridge on the phase diagram by measuring the dynamic light scattering (DLS) of fluoroform (CHF₃).

The details of DLS experiments for supercritical fluids have been described elsewhere.⁶ From a light intensity auto-correlation function measured by DLS, an electric field autocorrelation function $g^{(1)}(t)$ is obtained. In the case of neat media consisting of small molecules, the time profile of the electric field correlation function is characterized by the dynamics of density fluctuation, which is caused by the thermal fluctuation of dielectric medium via diffusive and/or Brownian motions of molecules.⁷ In the present study, all data are measured at the wave vector of $k \cong 1.0 \times 10^{-2} \text{ nm}^{-1}$, whose scale corresponds to a mesoscopic region in real space. As a result, the electric field autocorrelation function here is ascribed to the time correlation of density fluctuation. This function indicates time evolution in mesoscopic volume, where numerous molecules are inhomogeneously dispersed. We collected numerous data to generate a map of dynamics around the critical point, i.e., ranges of reduced density $0.3 \leq \rho_r = \rho/\rho_c \leq 1.7$ and reduced temperature $0.96 \leq T_r = T/T_c \leq 1.06$. The critical constants of CHF₃ are reported to be $T_c = 299.06 \text{ K}$, $P_c = 4.836 \text{ MPa}$ and $\rho_c = 0.525 \text{ g cm}^{-3}$.⁸ Temperature and pressure during a measurement were carefully

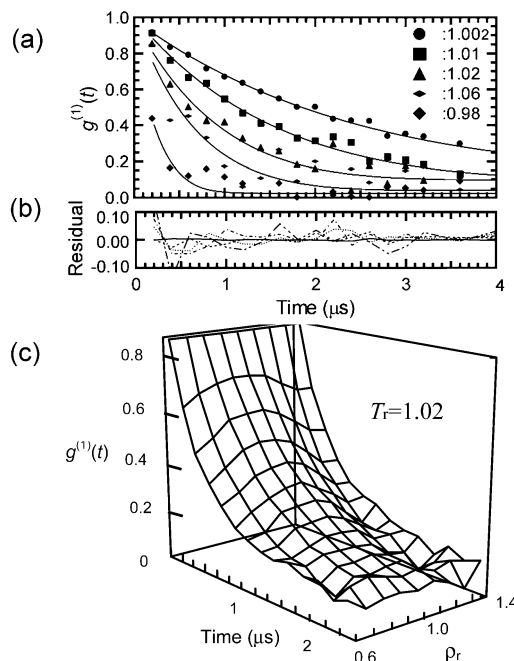


Figure 1. (a) Temperature ($T_r = T/T_c$) dependence of correlation functions at density $\rho_r = \rho/\rho_c = 1.0$. The exception is for $T_r = 0.98$ as $\rho_r = 1.6$. (b) Residuals between data and fitting functions. (c) Density dependence of correlation functions at $T_r = 1.02$.

adjusted to within a deviation of $\pm 0.03\%$, because the structure of a fluid is very sensitive to those changes.

As an example of typical obtained data, Figure 1a shows the time correlation functions of density fluctuation at different reduced temperatures. It is seen that the time correlation decays in the range of a few μs . The values in Figure 1b indicate residuals between the experimental data and the fitting functions. Small residuals show that the data are well analyzed by a single-exponential function, whose decay is responsible for the dynamics characterized by hydrodynamic theory.⁹ The density dependence of time correlations at $T_r = 1.02$ is summarized in Figure 1c. As the density approaches $\rho_r = 1.0$, the decay becomes slower. This corresponds to the observation of a “critical slowing down” in the time domain. The critical slowing down here indicates that the time evolution of numerous molecules diffusing in mesoscale slows as the thermodynamic state approaches the critical point. In a study of the time domain, the critical slowing down has been observed by a molecular dynamics simulation of neat Lennard-Jones fluid in the supercritical region.¹⁰ In the simulation, the local density dynamics of inhomogeneously dispersed solvent particles slows as the density approaches $\rho_r = 1.0$. The present experimental results tend to agree with the theoretical ones.

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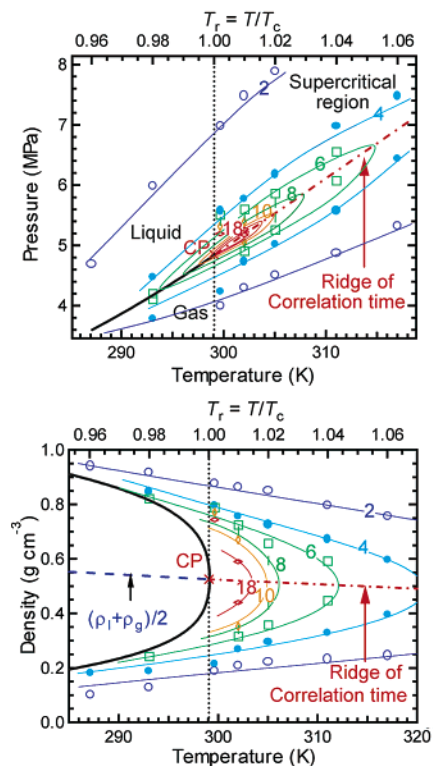


Figure 2. Correlation times (10^{-7} s) of density fluctuation mapped on the (a) P – T phase diagram and the (b) ρ – T one. Symbols and curves indicate obtained results and contour curves, respectively. Thick solid curve and dashed lines in (b) are liquid–vapor coexistence curve and rectilinear diameter, respectively.

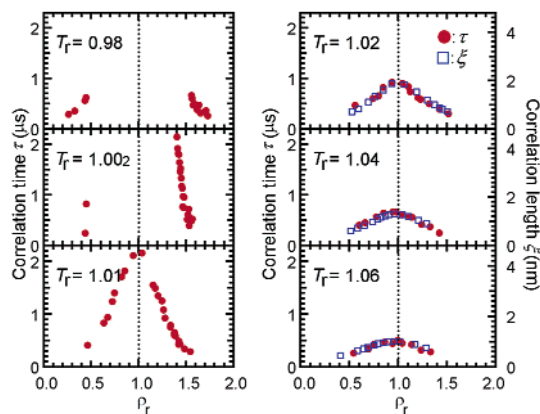


Figure 3. Correspondence between correlation time (●) and correlation length (□) at $T_r = 1.02, 1.04,$ and 1.06 .

Using obtained correlation functions of gas, liquid, and supercritical states, the correlation times of density fluctuation are mapped on the pressure–temperature (P – T) and density–temperature (ρ – T) phase diagrams shown in Figure 2. The dynamics is described by contour curves of correlation times around the critical point, and the time axis appears in the phase diagrams. To the best of our knowledge, this is the first time that the dynamics of supercritical fluid has been mapped onto phase diagrams. In Figure 2a, a ridge of correlation time is seen along an extension of the vapor–liquid coexistence curve. In the case of the ρ – T phase diagram, the ridge is located along an extension of the rectilinear diameter, where the density equals $(\rho_l + \rho_g)/2$ with ρ_l and ρ_g of liquid and gas densities. In both diagrams, the time evolution of density fluctuation becomes slowest along the ridge. It is noted that the ridge of correlation time exists along an extension of the *intermediate* lines between

gas and liquid states; these lines are the liquid–vapor coexistence curve in Figure 2a and the rectilinear diameter in Figure 2b. On the basis of these results, the ridge of dynamics seems to behave as a trace of the intermediate between the gas and liquid states. Similar tendencies around ridges have been observed by rotational and vibrational dynamics in the supercritical region,⁵ i.e. by a change from rotational to damped rotational motions or by a significant enhancement of local density.

Let us mention briefly the correlation between dynamic and static density fluctuations of supercritical CHF_3 at the same thermodynamic state. Figure 3 shows the correlation time τ (●) in the present study and the correlation length ξ (□) obtained from a previous SAXS measurement.^{4a} As the time evolution of the density fluctuation slows, the fluctuation grows. Obviously, a good coincidence between τ and ξ is observed in the supercritical region of $T_r = 1.02$ – 1.06 . This coincidence might be brought from the following relations,^{11,12}

$$\frac{1}{\tau k^2} = D_T = \frac{\lambda}{\rho C_p} = \frac{k_B T}{6\pi\eta\xi\lambda_c} \quad (1)$$

where τ is correlation time, k the scattering vector, D_T thermal diffusivity, λ thermal conductivity, ρ density, C_p specific heat capacity at constant pressure, k_B Boltzmann constant, T temperature, η viscosity, ξ correlation length, and λ_c the critical part of thermal conductivity. These expressions were correctly formulated by two groups^{11,12} and were based on the Kawasaki theory⁹ and the Landau–Placzek theory¹³ to combine dynamic and static fluctuations via transport phenomena near the critical point. Since studies on this relation between correlation time (or decay rate: $\Gamma = \tau^{-1}$) and correlation length have been performed at the density $\rho_c = 1.0$ only,^{14,15} it remains unknown as to whether these relations apply to the other thermodynamic states. As shown in Figure 3, however, the present experimental results indicate that the values of τ are linearly related to those of ξ in the ranges as $0.5 \leq \rho_r \leq 1.5$ and $1.02 \leq T_r \leq 1.06$ and that the above theoretical expressions are consistent with the experimental results at the condition of the constant $\lambda/\eta\lambda_c$. In this study, the theoretical relations between dynamics and static fluctuations were confirmed, for the first time, by experiments in the wider ranges.

References

- (1) Kajimoto, O. *Chem. Rev.* **1999**, *99*, 355–389.
- (2) Tucker, S. C. *Chem. Rev.* **1999**, *99*, 391–418.
- (3) Stanley, H. E. *Introduction to Phase Transitions and Critical Phenomena*; Oxford University Press: New York, 1971.
- (4) (a) Nishikawa, K.; Morita, T. *Chem. Phys. Lett.* **2000**, *316*, 238–242. (b) Nishikawa, K.; Kusano, K.; Arai, A. A.; Morita, T. *J. Chem. Phys.* **2003**, *118*, 1341–1346. (c) Nishikawa, K.; Ochiai, H.; Saitow, K.; Morita, T. *Chem. Phys.* **2003**, *286*, 421–430.
- (5) (a) Nakayama, H.; Saitow, K.; Sakashita, K.; Ishii, K.; Nishikawa, K. *Chem. Phys. Lett.* **2000**, *320*, 323–327. (b) Saitow, K.; Otake, K.; Nakayama, H.; Ishii, K.; Nishikawa, K. *Chem. Phys. Lett.* **2003**, *368*, 209–214. (c) Saitow, K.; Ohtake, H.; Sarukura, N.; Nishikawa, K. *Chem. Phys. Lett.* **2001**, *341*, 86–92.
- (6) Saitow, K.; Ochiai, H.; Kato, T.; Nishikawa, K. *J. Chem. Phys.* **2002**, *116*, 4985–4992.
- (7) (a) Berne, B. J.; Pecora, R. *Dynamic light scattering*; Wiley-Interscience: New York, 1976. (b) Chu, B. *Laser Light Scattering*; Academic Press: San Diego, 1991.
- (8) Rubio, R. G.; Zollweg, J. A.; Palance, J. M. G.; Calado, J. C. G.; Miller, J.; Street, W. B. *J. Chem. Eng. Data* **1991**, *36*, 171–184.
- (9) Kawasaki, K. *Ann. Phys.* **1970**, *61*, 1–56.
- (10) Maddox, M. W.; Goodyear, G.; Tucker, S. C. *J. Phys. Chem. B* **2000**, *104*, 6266–6270.
- (11) Sengers, J. V.; Keyes, P. H. *Phys. Rev. Lett.* **1971**, *26*, 70–73.
- (12) Maccabee, B. S.; White, J. A. *Phys. Rev. Lett.* **1971**, *27*, 495–498.
- (13) Landau, L.; Placzek, G. *Phys. Z. Sowjetunion* **1934**, *5*, 172–176.
- (14) Swinney, H. L.; Henry, D. L. *Phys. Rev. A* **1973**, *8*, 2586–2623.
- (15) Letaief, A.; R. Tufeu, R.; Garrabos, Y.; Neindre, B. L. *J. Chem. Phys.* **1986**, *84*, 921–926.

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