

Liquid-like and gas-like dynamics in supercritical fluids

It is common knowledge that, in most systems, the liquid-gas transition terminates at a critical point with a specific temperature, T_c , and pressure, P_c . In the region beyond this point ($T > T_c$, $P > P_c$), a first-order phase transition no longer exists. This region is usually referred to as the supercritical fluid state and thought of as a single featureless continuum. However, it is known that the properties of the fluid can undergo dramatic changes within the supercritical region, especially near the critical point, and many applications take advantage of precisely this aspect [1]. A detailed description of the supercritical fluid state is thus important from both a fundamental physics point of view and a practical perspective.

Thanks to years of research and a vast amount of available data, the thermodynamics of supercritical fluids has become well understood. It is found that the line of maxima of a given response function (e.g., the isobaric heat capacity, C_P) indicates the location of a rapid crossover between liquid-like and gas-like properties, especially in the near-critical region. This line is referred to as the "Widom line" [2] and it serves as a natural extension of the liquid-gas binodal beyond the critical point.

However, it remains unclear what happens on the microscopic level. Particularly, a systematic study of the molecular-scale dynamics in supercritical fluids is lacking. To investigate this, we used a combination of inelastic X-ray scattering (IXS) measurements and molecular dynamics (MD) simulations. The sample of choice was water, with a critical point at $P_c = 221$ bar and T_c = 647 K. The IXS measurements were carried out at SPring-8 BL43LXU, using the Si(999) reflection with 17.8 keV incident X-rays. The resolution function was measured with plexiglass and had a full width at half maximum around 3 meV for all 20 analyzers used in the experiment. A pressure cell with diamond windows was used to reach supercritical conditions. The MD simulations were performed using LAMMPS. We chose the TIP4P/2005 potential [3], which has been shown to well reproduce various properties of water particularly in the sub- to supercritical region, with simply a 75 bar shift in pressure (i.e., 300 bar in experiment corresponds to 225 bar with TIP4P/2005) [4].

We focus on the *P* = 300 bar isobar and examine the longitudinal current correlation function, $J_l(Q,\omega)$, where *Q* is the momentum transfer and $\hbar\omega$ the energy loss of the X-ray photon. It bears a simple relation with the dynamic structure factor, $S(Q,\omega)$: $J_l(Q,\omega)$ = $(\omega^2/Q^2) S(Q,\omega)$, and the latter can be measured with IXS. In MD, $J_l(Q,\omega)$ can be calculated directly. Details of data treatment can be found in [4]. Note that J_l can be conveniently normalized by a factor M/k_BT , where M is the molecular mass, after which the spectra under different temperatures can be compared.

Figure 1 presents the normalized $J_l(Q,\omega)$ spectra along P = 300 bar with temperatures from 400 K to 800 K. Results from MD and IXS agree well. It is known that various physical properties undergo a liquid-like to gas-like transition in this temperature range, and here the microscopic picture becomes clear. Notably, J_l appears to contain two components, one peaked at lower ω and one higher. With increasing temperature, the former (referred to as the G component) grows and the latter (L component) diminishes, as indicated by the arrows, leading to a liquid-like to gas-like dynamical transition.

To quantify this transition, we decompose the spectra and extract the L and G components using non-negative matrix factorization (NMF) [4]. The results are shown in Fig. 2(a,b). We can then define a parameter *f* representing the spectral weight of the L component and study its temperature evolution. As shown in Fig. 2(c), *f* decreases with temperature as expected, and with a rapid crossover near the Widom line indicated by the maximum in C_P or κ_T .

It is natural to ask whether these phenomena are specific to water, whose liquid-like dynamics are closely related to hydrogen bonding [4]. Thus, we performed MD simulations of three other systems



Fig. 1. Normalized $J_l(Q,\omega)$ along P = 300 bar obtained from (a) MD and (b) IXS at three different Q values, as annotated in the plots. The spectra from blue to red are from 400 K to 800 K at 100 K steps. MD spectra are multiplied by the detailed balance factor. An offset is applied between different Q values. Arrows indicate the trend with increasing temperature.



Fig. 2. (a) L (dashed) and G (solid) components of the MD spectra; (b) the same for IXS spectra; colors and Q values correspond to Fig. 1. (c) Circles: MD; crosses: IXS. Black solid lines: fraction of the L component, f; dotted lines: its temperature derivative; these lines are a guide to the eye. Also shown are C_P (red) and κ_T (blue) scaled to match the derivative of f. Solid vertical line indicates the approximate position of the Widom line.

represented by diverse potentials—Si, Te, and Lennard-Jones (LJ) fluid (see [5] for details). Figure 3 shows, for each system, three representative J_l spectra taken at low, intermediate, and high temperatures along an



Fig. 3. Two-component behavior in other fluids. Each row shows a system in low- (blue), intermediate- (gray), and high- (red) temperature states. Left column: MD data (symbols) and NMF fit (solid lines). Right column: extracted L (dash-dotted) and G (dashed) components; the peak positions are marked by symbols. σ and ε are LJ units.

isobar $P \approx 1.6P_c$. It can be seen that, as in the case of water, these spectra consist of two components. In particular, the intermediate spectrum clearly contains the characteristics of both the low-*T* and the high-*T* spectra. Using the NMF method, the components can be extracted as shown in Fig. 3, allowing further quantitative analysis.

In conclusion, with a combination of IXS measurements and MD simulations, we find a twocomponent behavior in the molecular-scale dynamics of water near its critical point. The change in the ratio between the components leads to a liquid-like to gaslike transition, which happens most rapidly near the thermodynamic Widom line. Further MD simulations indicate that the two-component behavior is common among diverse supercritical fluid systems and may be a universal phenomenon.

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