A corresponding-state framework for the structural transition of supercritical fluids across the Widom delta

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Thermodynamic anomalies of near-critical fluid are deeply related to its inhomogeneous structure. The inhomogeneous structure of monatomic fluid can be analyzed based on the simple Voronoi tessellation methods. Here we provide a classification algorithm based on the radical Voronoi tessellation to define the Widom delta, supercritical gas-liquid coexistence region, of polyatomic molecules. In specific, we use a weighted mean-field classification method to classify a molecule into either gas-like or liquid-like. Classical percolation theory methods are adopted to understand the generality of the structural transition and to locate the Widom delta. From the pressure-temperature relation, we demonstrate that a three-parameter corresponding state theorem is valid for the structural transition, which states that the fraction of gas-like molecules of a substance is equal to that of another if their reduced pressure, reduced temperature and the critical compressibility factor are the same.

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I. INTRODUCTION

Supercritical fluid, a state of matter beyond the liquid-gas critical point, is regarded as one of the most promising alternatives to conventional liquid solvents used in chemical processes. One of the useful physical characteristics for the industrial application is its great tunability; small changes in the thermodynamic conditions result in the continuous yet substantial adjustment of thermophysical properties and thermodynamic response functions. It is currently believed that this tunability is deeply related to the inhomogeneous nature of supercritical fluids, refuting the conventional point of view which sees it as a monotonic and homogeneous state of matter.

Thus, a considerable amount of theoretical and experimental works were devoted to understanding the anomalous behavior of supercritical fluids. In scattering and spectroscopic measurements, a large density fluctuation was observed, which imply the existence of the structural inhomogeneities. Anomalous behaviors of the response functions and transport properties in the vicinity of the critical point also supported the existence of two different states in the supercritical region. As a result, the following thermodynamic methods were suggested to understand the inhomogeneous structure of supercritical fluids. First, thermodynamic response functions and the correlation length were used to locate the thermodynamic states where the supercritical gas-liquid transition occurs. Simeoni et al. proposed that the Widom line, loci of the maximum correlation length, is a supercritical gas-liquid boundary. Banuti et al. suggested that the line of heat capacity maxima, one of the pseudo-boiling lines, follows the three-parameter corresponding state principle. However, the response-function based separation of the supercritical region has shown its limits in the following aspects. First, the magnitude of the correlation length and response function maxima rapidly decays and disappears when far from the critical temperature. Second, the Widom line and the pseudo-boiling lines only overlap near the critical point. They diverge from each other departing from the critical point. Third, the location of the response function maxima shows a path-dependence: The lines of the response function maxima on isobars and isotherms do not overlap with each other. From these remarks, Schienbein and Marx recently addressed that no unique separating line can be deduced from the response functions.

Independent from these response-function based methods, the structural characteristics
of the supercritical fluid have also been studied, which can be dated back to the works of Bernal\textsuperscript{14,15}. In the spirit of the Bernal’s work, Finney\textsuperscript{16}, Woodcock, and Heyes\textsuperscript{17} located the percolation transition loci based on the rigidity calculation of the monatomic fluid. The pair correlation function integrals were also used to understand the nature of the inhomogeneous structure of near-critical fluids\textsuperscript{7,18–20}. Several molecular-level classification schemes have also been proposed to define the gas-like and the liquid-like structures in supercritical fluids. Traditionally, the fixed-distance cutoff methods\textsuperscript{21–24} were used to analyze the inhomogeneous structure of supercritical fluids based on the cluster analysis, but the fixed cutoff methods were susceptible to the selection of the cutoff radius\textsuperscript{24}. Hence, a series of recent works have used the Voronoi tessellation as a tool to define the local structure of supercritical fluids\textsuperscript{25–27}. For instance, Ovcharov et al. proposed a method for phase identification (MPI) based on the Voronoi tessellation to define liquid, gas, and surface atoms in the two-dimensional system\textsuperscript{28}.

Our recent works have focused on the application of the Voronoi tessellation to analyze the structural transition of monatomic supercritical fluids. Machine learning\textsuperscript{29} and probabilistic classification strategy\textsuperscript{30} successfully pinpointed the location of the supercritical gas-liquid coexistence region. This geometric definition of the supercritical gas-liquid coexistence region, called the Widom delta, has shown the following advantages compared to the conventional approaches. First, the boundaries of the Widom delta agree with those obtained from the rigidity calculation\textsuperscript{17}. They are also similar to the coexistence lines detected from the MPI algorithm\textsuperscript{28}. Second, neither path-dependence nor termination of the coexistence region was observed. Thus, a contradiction which comes from the path-dependence of the response functions does not occur. As the temperature increases, supercritical gas-liquid coexistence region of the LJ fluid converges to that of the Weeks-Chandler-Andersen (WCA) fluid\textsuperscript{30}; it does not disappear in the deep supercritical region. Third, the algorithm depends only on the critical density as a classification criterion, which is an intrinsic property of a fluid. Since selecting a proper cutoff distance comes with a certain degree of arbitrariness, a classification scheme without the cutoff distance is meritorious. Lastly, defining a coexistence “region” instead of a single line for the demarcation of the supercritical fluid phase is adequate to describe the continuous structural variation of supercritical fluids; no discontinuous (first-order) phase transition occurs above the critical point.

This work aims to extend the classification method, originally demonstrated in the simple monatomic Lennard-Jones fluid system\textsuperscript{30}, to examine the structural transition of polyatomic
supercritical fluids and to discover their general structural characteristics. We first compute
the fraction of gas-like molecules by classifying molecules into gas-like and liquid-like applying
the geometric procedure based on the radical Voronoi (Laggerre) tessellation. Structural
characteristics of the gas-like and liquid-like clusters are examined based on the percolation
theory. The classical percolation theory enables us to shed light on the generality of the
structural evolution based on the fraction of gas-like molecules. Specifically, we locate the
supercritical gas-liquid coexistence region including the supercritical gas-liquid boundary
and the percolation transition lines from the finite-size scaling analysis. We further demon-
strate the generality of the supercritical gas-liquid coexistence region on the phase diagrams.
The density-temperature diagram shows that the supercritical gas-liquid coexistence region
is quasi-universal; the coexistence regions of non-polar and polar substances almost overlap
with each other except strongly hydrogen-bonded substances. The pressure-temperature
relation shows that supercritical gas-liquid transition of various substances follows the ex-
tended corresponding state principle.

II. COMPUTATIONAL DETAILS

A. Molecular Dynamics (MD) simulations

Ten substances are selected to investigate the general characteristics of the Widom delta.
The interaction parameters for methane, ethane, carbon dioxide, nitrogen, oxygen, and
ethylene oxide are modeled using the Transferable Potentials for Phase Equilibria (TraPPE)
forcefields. For water and methanol, the potential parameters are adopted from the
TIP4P/2005 and OPLS/2016 forcefields, respectively. The interaction parameters for
ammonia are obtained from work by Eckl et al. The critical points of these substances
are estimated based on the flat top proposal. According to the flat top proposal, the
rigidity and its first derivative of a system become zero at the critical point ($d\rho/dp = 0$ and
$d\rho^2/dp^2 = 0$).

To calculate the rigidity and its first derivative, we perform NVT simulations in the
vicinity of the critical points reported in the earlier works. The number of molecules is 1,000.
The timestep is 1 fs. The interatomic potentials are truncated at the cutoff radius of 16.0 Å
and the analytic tail correction term is added. For polyatomic species, the Lorentz-Berthelot
TABLE I. Critical constants estimated based on the flat top proposal.

| Substances | $T_c$ [K] | $p_c$ [bar] | $\rho_c$ [kg/m$^3$] |
|------------|-----------|-------------|----------------------|
| Ar         | 164.31    | 63.93       | 471.30               |
| $N_2$      | 129.97    | 38.61       | 291.91               |
| $O_2$      | 158.02    | 58.39       | 398.78               |
| $CH_4$     | 199.52    | 56.55       | 147.21               |
| $C_2H_6$   | 312.08    | 60.09       | 195.52               |
| $CH_2OCH_2$| 470.68    | 97.16       | 358.11               |
| $CO_2$     | 311.99    | 86.50       | 452.35               |
| $NH_3$     | 414.60    | 132.42      | 215.09               |
| $H_2O$     | 654.10    | 178.90      | 284.23               |
| $CH_3OH$   | 537.07    | 89.14       | 247.32               |

mixing rules are used to model the interaction between different atoms:

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}; \quad \epsilon_{ij} = \sqrt{\epsilon_{ii} \epsilon_{jj}}.$$  \hspace{1cm} (1)

The systems are equilibrated for 100,000 steps, and the system pressures are collected every step during 1,000,000 steps. By fitting the cubic equations, the inflection points at different isotherms were obtained. The critical temperature is then calculated as the temperature where $d\rho/dp$ at the inflection point becomes zero. Then, the critical density and pressure are computed. Table I shows the critical points of the substances calculated in this manner. After the critical point of each substance is estimated, we perform NVT simulations at $T_r = T/T_c = 1.05 - 3.70$ and $\rho_r = \rho/\rho_c = 0.2 - 2.4$ with the same cutoff radius and the number of molecules. The systems are equilibrated for 100,000 steps, and the system configurations are collected every 10,000 steps during the production run (1,000,000 steps). The pressure data are sampled every step.

Besides, we simulate supercritical argon at $T_r = 3.70$ and $\rho_r = 0.75 - 1.17$ to examine the system size effect and to carry out the finite-size scaling analysis. The numbers of molecules are $N = 1,000, 2,000, 4,000, 8,000$, and 16,000. The simulations for the finite-size scaling analysis include 100,000 steps of equilibration run followed by 500,000 steps of data production. The trajectories are collected every 1,000 steps.
B. Classification strategy

A probabilistic classification algorithm on the LJ monatomic fluid is extended to the polyatomic substances as follows. Since the atomic radii of polyatomic molecules are different, we adopt the radical Voronoi tessellation (Laguerre tessellation) to partition the space into per-atom cells and define the local density of a molecule. In the radical Voronoi tessellation, a configuration of \( N \) polydisperse spheres is partitioned into \( N \) cells based on the power distance between each other. The power distance of a point with respect to a sphere is defined as the squared length of the tangential line from the point to the sphere, hence is dependent on the radius of the sphere (Fig. 1b). The Laguerre cell of a sphere \( S \) is then defined as the set of points that are ‘closer’ to the \( S \) than any other spheres, in terms of the power distance metric. Note that the radical Voronoi tessellation is identical to conventional Voronoi tessellation when the spheres in the system are monodisperse (Fig. 1a).

Thus, a system with \( N \) molecules which has \( n_a \) atoms each has \( n_a N \) Laguerre cells obtained from radical Voronoi tessellation. We adopt the atomic radii as the LJ distance parameter, \( \sigma_{jj} \) for atom type \( j \). Furthermore, defining the local volume of \( i^{th} \) molecule as the sum of Laguerre cells of its constituting atoms, its local density can be defined as the reciprocal of its local volume:

\[
\rho_i = \frac{1}{\sum_{j=1}^{n_a} v'_{ji}}
\]

The neighbors of the \( i^{th} \) molecule is defined as the molecules of which atomic Laguerre cells share faces with those of the \( i^{th} \) molecule, and the second neighbors are defined as the neighbors of neighbors.

After the local density data of the molecules are obtained, the following weighted mean-field strategy is used to determine whether a molecule is gas-like or liquid-like. When the \( i^{th} \) molecule should be classified, the mean local densities of the molecule and its nearest neighbors are first obtained. Consecutively, the mean local densities of the neighbors and the nearest neighbors of the nearest neighbors, which include the \( i^{th} \) molecule and the second nearest neighbors of the \( i^{th} \) molecule, are calculated. These mean local densities of the \( i^{th} \) molecule and its nearest neighbors are averaged to obtain the mean local density of a central molecule (\( \bar{\rho}_i \)) weighted based on the chemical distance from the central molecule. Hence, it
FIG. 1. Two-dimensional representation of (a) simple Voronoi tessellation and (b) radical Voronoi (Laguerre) tessellation of the particles at the same positions. In the Laguerre tessellation, the power distance is used to partition the space into per-atom cells: Note that spheres with larger radii claim larger area in the space. The color scheme denotes the weighted mean-field strategy to classify a monatomic molecule based on the Voronoi network. To classify a central molecule (dark cell), local densities of molecules up to its second neighbors are averaged with a weight based on the chemical distance.

is calculated as:

\[ \bar{\rho}_i = \frac{1}{N_i + 1} \sum_{j \in NN(i)} \left( \frac{1}{N_j + 1} \sum_{k \in NN(j)} \rho_k \right) \]

where \( N_m \) is the number of neighbors of the \( m^{th} \) molecule, and \( \text{NN}(m) \) is the set of neighbors of the \( m^{th} \) molecule. For instance, in the two-dimensional systems shown in Fig. 1, the local density of the central atom (dark blue cell) which has \( N_c \) nearest neighbors is counted \((N_c + 1)\) times. The local densities of the nearest neighbors are counted four times. The second nearest neighbors are counted either once or twice. If the second nearest neighbor shares two faces with two first nearest neighbors, it is counted twice; otherwise, it is counted once. Finally, if this averaged local density is higher than the critical density, the \( i^{th} \) molecule is classified as liquid-like. Otherwise, it is gas-like.

After the weighted mean-field classification is carried out, the gas-like fraction of a system is calculated as:

\[ \Pi_{\text{gas}} = \frac{N_{\text{gas}}}{N_{\text{gas}} + N_{\text{liq}}}; \Pi_{\text{liq}} = 1 - \Pi_{\text{gas}} \]

where \( N_{\text{gas}} \) and \( N_{\text{liq}} \) mean the numbers of gas-like and liquid-like molecules, respectively.
C. Percolation analysis

In our last work, we estimated the percolation transition densities $\rho_{pa}$ and $\rho_{pb}$ of the monatomic LJ fluid from the gas-like fraction curve. They were defined as the densities where $\Pi_{gas}$ starts to change steeply.

$$\rho_{pa} = \frac{\log(a) + 2}{b}; \rho_{pb} = \frac{\log(a) - 2}{b}$$

Here, $\rho_{pa}$ is called the percolation transition density of the available volume and $\rho_{pb}$ is the percolation transition density of the bonded clusters. This work estimates $\rho_{pa}$ and $\rho_{pb}$ in a more elaborate manner based on the classical percolation theory. Percolation theory states that a spanning (infinite) cluster connected across the periodic boundary emerge as the occupation probability of a particle increases. The occupation probability at which an infinite cluster appears is called the percolation threshold. To examine the percolation behavior, we apply the clustering algorithm proposed by Stoll to the Voronoi network. In this algorithm, two molecules are regarded to be connected if their classification results are identical and they are the nearest neighbors to each other. Hence, two molecules distant from each other are included in the same cluster if there exists a string of molecules of the same type linking them. The algorithm first counts the independent clusters without regard for the periodic boundary conditions. Second, it tests whether a cluster is infinite or not. The algorithm deems a cluster as an infinite one if one of its molecules at the periphery of the simulation box is connected to another one at the opposite side. After the infinity test, the independent clusters obtained in the first step are connected if they are linked across the periodic boundary conditions.

After the infinity test, we obtain the percolation probability ($p_{inf}$), the probability to find an infinite cluster at an instantaneous time step. A finite-size scaling analysis is then carried out to determine $\Pi_{thr}^\infty$ in the following manner. We first fit the following sigmoidal equation to $p_{inf}$ data.

$$p_{inf}^i = [1 + \exp(a\Pi_t + b)]^c$$

where $i$ is the type of the molecule ($i = \text{gas, liq}$). Then, the average percolation threshold
(\Pi_{i}^{av}) and the transition region width (\Delta) are computed as:

\[
\Pi_{i}^{av} = \int \Pi_{i} \left( \frac{dp_{inf}^{i}}{d \Pi_{i}} \right) d \Pi_{i} \quad (7)
\]

\[
\Delta_{i}^{2} = \int (\Pi_{i} - \Pi_{i}^{av})^{2} \left( \frac{dp_{inf}^{i}}{d \Pi_{i}} \right) d \Pi_{i} \quad (8)
\]

The percolation threshold for an infinite system (\Pi_{i}^{\infty}) is then obtained as an intercept of the following linear equation.

\[
\Pi_{i}^{av} = a \Delta_{i} + \Pi_{i}^{\infty} \quad (9)
\]

where \(a\) and \(\Pi_{i}^{\infty}\) are fitting parameters.

III. RESULTS AND DISCUSSION

A. Molecular-level classification

Fig. 2 shows the fraction of gas-like molecules at \(T_{r} = 1.05\) and \(T_{r} = 3.50\). As observed in our earlier work on the monatomic LJ fluid, the dependence of gas-like fraction on the bulk density could be expressed by an inverse sigmoid function based on the fluid polyamorphism formulation. In the theory of fluid polyamorphism, the structural transition between two different amorphous structures is regarded as a reaction.

\[
A(\text{gas}) \rightleftharpoons A(\text{liquid}) \quad (10)
\]

The equilibrium constant \(K_{eq}\) is then calculated as \(K_{eq} = \Pi_{\text{liquid}}/\Pi_{\text{gas}} = \exp(-\beta \Delta G^{\ddagger})\) where \(\beta\) is the thermodynamic beta \((1/k_{B}T)\) and \(\Delta G^{\ddagger}\) is the Gibbs energy difference between the amorphous structures. By assuming that \(\Delta G^{\ddagger}\) is proportional to the bulk density, the following equation can be derived.

\[
\Pi_{\text{gas}} = 1 - \frac{1}{1 + a \exp(-b \rho_{r})} \quad (11)
\]

In the vicinity of the critical temperature \((T_{r} = 1.05)\), the gas-like fraction curves of CH₃OCH₃ and hydrogen-bonded substances (ammonia, water, and methanol) do not agree with those of non-polar/weakly polar substances (Fig. 2a). \(\Pi_{\text{gas}}\) of polar substances start to decrease at lower densities than those of non-polar ones. When the temperature increases,
FIG. 2. Dependence of the gas-like fraction ($\Pi_{\text{gas}}$) on the bulk density at (a) $T_r = 1.05$ and $T_r = 3.50$. The fraction of gas-like molecules decreases from one to zero as the density increases. At $T_r = 1.05$, the gas-like fractions of hydrogen-bonded and strongly polar substances start to decrease at lower densities than non-polar substances. As the temperature increases, the gas-like fraction curves of hydrogen-bonded molecules collapse to those of non-polar ones. The inconsistency of $\Pi_{\text{gas}}$ curves of different substances diminishes (Fig. 2b). This temperature dependence substantiates that the supercritical gas-liquid transition across the Widom delta is largely influenced by the competition between the attractive force and the diffusive motion of the particles. Near the critical point, the magnitude of the kinetic energy is comparable to the attraction due to its neighbors. Hence, the magnitude of the intermolecular attraction matters. As the temperature increases, a significant proportion of molecules possess kinetic energy much higher than the attractive interactions. As a result, the supercritical gas-liquid transition density increases, and the discrepancy of the gas-like fraction curves among the substances decreases. It should also be noted that the $\Pi_{\text{gas}}$ curves of different species at $T \sim T_c$ only overlap with each other when the density increases. This result
FIG. 3. Local density distributions of carbon dioxide (a-c) and water (d-f) at $T_r = 1.05$. The fraction of liquid-like molecules of water is always greater than that of carbon dioxide in the supercritical gas-liquid coexistence region, which substantiates the strong local density augmentation induced by the attractive interactions.

indicates that the Weeks-Chandler-Andersen (WCA) liquid perturbation theory\textsuperscript{43} cannot be used to analyze the structural characteristics of the near-critical fluid\textsuperscript{14}. As Toxvaerd stated\textsuperscript{45}, the equilibrium structure of the gas and the near-critical fluid is strongly affected by the presence of the attractive interaction.

B. Structural analysis

We further characterize the structural characteristics based on the local density distributions and the percolation theory. Fig. 3 shows the local density distributions of carbon dioxide and water at $T_r = 1.05$. The local density distributions of liquid-like molecules are more symmetric than those of gas-like ones. Compared to the local density distributions of carbon dioxide, those of water at the same reduced conditions (Fig. 3d-f) show stronger local density augmentation. Moreover, the distributions of water are broader, which means that more high-density molecules exist as a result of the strong intermolecular interactions. This result indicates that the classification method proposed in this work also detects the effect of the strong polar forces on the local density augmentation as the integration of the pair
FIG. 4. (a) The probability of finding an infinite liquid-like cluster in a configuration and the number of independent (b) gas-like and (c) liquid-like clusters at \( T_r = 1.05 \). (d) The probability of finding an infinite liquid-like cluster in a configuration and the number of independent (e) gas-like and (f) liquid-like clusters at \( T_r \sim 3.50 \). As the temperature increases, the absolute slope of \( p_{\text{inf}} \) curves increases. The maximum number of independent clusters also increases due to thermal agitation.

correlation function did. Fig. 4a-c shows the dependence of \( p_{\text{inf}} \) and \( \langle n_c \rangle \) on the bulk density at \( T_r = 1.05 \). Here, \( \langle n_c \rangle \) is the number of independent gas-like or liquid-like clusters. At \( T_r = 1.05 \), \( p_{\text{inf}}^{\text{liq}} \) of the substances except strongly polar molecules collapse to a single line. \( p_{\text{inf}}^{\text{liq}} \) of water and methanol starts to increase at lower densities than the other fluids. The \( p_{\text{inf}}^{\text{gas}} \) curves show an opposite dependence on the bulk density (see the supplementary material). At high temperatures (\( T_r \sim 3.50 \)), \( p_{\text{inf}}^{\text{liq}} \) and \( p_{\text{inf}}^{\text{gas}} \) of all substances collapse to single lines (Fig. 4d). This temperature dependence agrees with the behavior of \( \Pi_{\text{gas}} \) shown in Fig. 2. The steepness of \( p_{\text{inf}} \) curves became high like the WCA fluids.

The narrower and higher peaks of \( \langle n_c \rangle \) at high temperatures (Fig. 4e and f) reflect that the thermal agitation prevents the formation of large clusters far from the critical point. In near-critical fluids, the inhomogeneous fluid structure fluctuates slowly. As the temperature increases, the thermal fluctuation becomes so vigorous that the inhomogeneous fluid structure cannot remain stable. As a result, the mean cluster size decreases and the maximum number of liquid-like (gas-like) clusters increases. It can also be observed that
FIG. 5. (a) Effect of the system size on the classification results and the finite-size scaling results of (b) gas-like and (c) liquid-like clusters of supercritical argon. No significant system size effect was observed for the classification results. The dotted lines denote the percolation thresholds for infinite systems obtained from the finite-size scaling analysis.

The maximum of \( \langle n_c^{\text{gas}} \rangle \) is always lower than that of \( \langle n_c^{\text{liq}} \rangle \). This comes from the fact that the mean local density of liquid-like molecules is higher than that of gas-like ones. Due to the large volume, an infinite gas-like clusters can be easily formed compared to liquid-like clusters.

The similar dependence of \( p_{\text{inf}} \) and \( \Pi_{\text{gas}} \) on the temperature indicates that \( \Pi_{\text{gas}} \) can work as an order parameter to describe the supercritical gas-liquid coexistence region; \( p_{\text{inf}}^{\text{liq}} \) and \( p_{\text{inf}}^{\text{gas}} \) curves of all substances at all temperatures collapse to single lines when \( \Pi_{\text{gas}} \) is used as an order parameter (see the supplementary material). Therefore, we conduct the finite-size scaling analysis to calculate the percolation threshold \( (\Pi_f^\infty) \). Fig. 5b demonstrates that no significant finite-size effect exists for \( \Pi_{\text{gas}} \). This result again supports our idea that the
fraction of gas-like molecules can be used as a robust parameter to define the supercritical gas-liquid coexistence region. Fig. 5b shows the dependence of \( p_{\text{inf}}^{\text{gas}} \) on \( \Pi_{\text{gas}} \). Unlike \( \Pi_{\text{gas}} \), \( p_{\text{inf}}^{\text{gas}} \) largely depends on the system size. As the number of molecules in a system increases, the \( p_{\text{inf}}^{\text{gas}} \) curve becomes like a step function. \( p_{\text{inf}}^{\text{liq}} \) shows a similar behavior as a function of \( \Pi_{\text{liq}} \) (Fig. 5c). By applying Eqn. (8) and Eqn. (9), we can obtain \( \Pi_{\text{gas}}^{\infty} \) and \( \Pi_{\text{liq}}^{\infty} \) as

\[
\Pi_{\text{gas}}^{\infty} = 0.09163 \pm 0.0014; \quad \Pi_{\text{liq}}^{\infty} = 0.1489 \pm 0.0088
\]

The percolation thresholds are comparable to the bond percolation and site percolation thresholds of a pruned Voronoi network. The percolation threshold of liquid-like clusters is larger than that of gas-like clusters. Again, this result indicates that the percolation of gas-like cluster can occur at lower concentration of gas-like molecules since the gas-like molecules have large local Voronoi volumes which enable them to be easily connected with each other throughout the entire system.

C. Location of the supercritical gas-liquid coexistence region

Since we obtain the percolation thresholds of gas-like and liquid-like clusters for an infinite system, we can calculate the percolation transition densities \( \rho_{pa} \) and \( \rho_{pb} \) by solving Eqn. (11) for \( \rho \). In addition, we can calculate the supercritical gas-liquid boundary as a set of densities where the gas-like fraction becomes 0.5 (\( \rho_{sgl} = \log(a)/b \)). Hence, the Widom delta, the supercritical gas-liquid coexistence region which is enclosed with two percolation transition loci and bisected by the supercritical gas-liquid boundary, is completely defined from the gas-like fraction data.

Fig. 6 shows the supercritical gas-liquid coexistence region on \( \rho_r-T_r \) diagram. As expected from the \( \Pi_{\text{gas}} \) curves, the crossover densities (\( \rho_{sgl}, \rho_{pa} \) and \( \rho_{pb} \)) of different substances mostly agree with each other except for strongly polar molecules including water, ethylene oxide, ammonia, and methanol. In the case of methanol and water, \( \rho_{pb} \) is lower than that of non-polar substances, whereas \( \rho_{pa} \) lines agree with the others. This discrepancy would reflect the asymmetry of the influence of the attractive force on the structure of supercritical fluid. In contrast to dilute gas, the structural characteristics of dense supercritical fluids are mainly determined by the repulsive forces. Since the steepness of the repulsive part of the LJ potential is not relevant to the magnitude of the attractive interaction, \( \rho_{pa} \) does not show
FIG. 6. Supercritical gas-liquid coexistence regions on the $\rho_r-T_r$ diagram. From top to bottom, the three branches correspond to $\rho_{pa}$, $\rho_{sgl}$, and $\rho_{pb}$, respectively. The percolation transition loci and supercritical gas-liquid boundary of non-polar substances obtained from the gas-like fraction curves coincide with each other. Hydrogen-bonded substances and strongly polar ones deviate from the power law equations of non-polar species near the critical temperature. As the temperature increases, they collapse to those of non-polar species.

A significant dependence on the type of the substances. In other words, $\rho_{pa}$ determines the boundary where the structure of supercritical fluid can be interpreted without consideration of the attractive force. On the other hand, $\rho_{pb}$ shows a substance-dependence because the influence of the attractive force becomes significant in the low-density region.

Next, we explore the pressure-temperature relation. Fig. 7a shows the supercritical gas-liquid boundaries on the $p_r-T_r$ diagram. Supercritical gas-liquid transition pressures and percolation transition pressures show a linear dependence on the temperature, and their slopes are different from each other. The pressure-temperature relation can be formulated as:

$$p_r v_r = \frac{zT_r}{z_c} \frac{p_r}{T_r} = \frac{\rho_r z}{z_c}$$  \hspace{1cm} (13)

where $z$ is the compressibility factor and $z_c = p_c v_c/RT_c$ is the critical compressibility factor.

By analyzing the limiting behavior of the pressure-temperature relation at high temperature ($T \to \infty$), we can derive a simple expression from Eqn. (13) to understand the pressure-
FIG. 7. (a) Supercritical gas-liquid boundaries of supercritical fluids on the reduced pressure-temperature diagram. (b) The correlation between the slope of the supercritical gas-liquid boundary and the critical compressibility factor ($z_c$). The slope of the supercritical gas-liquid boundary is proportional to the inverse of $z_c$.

temperature relation of supercritical gas-liquid boundary. As shown in Fig. 6, the reduced crossover densities ($\rho_{r,sgl}$) converge to 0.958 at high temperature regardless of the substances. Provided that the linear relation between the pressure and the temperature holds at the temperature limit, we can obtain the following equation.

$$\frac{p_{r,sgl}}{T_{r,sgl}} = \frac{0.958}{z_c} \quad \text{as} \quad T \to \infty \quad (14)$$

Fig. 7b shows that this simple relation can be regarded as a good approximation. The slope of the supercritical gas-liquid boundary is well expressed as a linear function of the compressibility factor ($dp_{r,sgl}/dT_{r,sgl} = 1.633z_c^{-1} + 0.061$). Therefore, the supercritical gas-
liquid boundary can be expressed as:

\[
p_{r,sgl} = (1.633z_c^{-1} + 0.061)(T_{r,sgl} - 1) + 1
\]  

(15)

This linear relation also holds for the percolation transition pressures. Hence, this result shows that the fractions of gas-like molecules (gas-likeness) of two substances are equal to each other at the same reduced pressure and temperature if their compressibility factors are equal. Given that the compressibility factor is a function of the acentric factor \((\omega)\), this result also implies that the supercritical gas-liquid transition follows the three-parameter corresponding state principle, which states that all fluids with the same value of \(\omega\) will have the same fraction of gas-like molecules at the same \(T_r\) and \(p_r\). That is, supercritical gas-liquid coexistence regions of two different substances on the \(p_r-T_r\) diagram agree with each other if their compressibility factors (or acentric factors) are same.

IV. CONCLUSIONS

In conclusion, the classification algorithm based on the radical Voronoi tessellation in conjunction with the percolation theory reveals the generality of the Widom delta among simple molecular fluids. The fraction of gas-like molecules does not show significant substance-dependence except for strongly polar or hydrogen bonding molecules near the critical temperature. At \(T \gg T_c\), the percolation transition lines and the supercritical gas-liquid boundary of all substances including the hydrogen bonded ones collapse to single lines. When the percolation probabilities are expressed as functions of \(\Pi_{gas}\), they collapse into a single line. A finite-size scaling can successfully locate the percolation thresholds of gas-like and liquid-like clusters. The Widom delta on the \(p_r-T_r\) diagram follows the three-parameter corresponding state theorem. Noting that the near-critical heat capacity maxima can be framed into the similarity law\(^{11}\), the generality of the supercritical gas-liquid coexistence region implies that a general two-state model\(^{50}\) would be possibly constructed to link the relation between the response functions and the structural characteristics. Hence, the algorithm designed in this work would be helpful to build a structure-property relation to understand the thermophysical behavior of supercritical fluids.
SUPPLEMENTARY MATERIAL

In supplementary material, we provide the numerical data that can help understand and reproduce the results in the main article. It includes the pressure data of near-critical fluids used for the estimation of the critical point; the fractions of gas-like molecules; the probabilities of finding an infinite cluster; the percolation transition densities (pressures); the number of independent gas-like and liquid-like clusters in \( N = 1,000 \) systems; and the finite-size scaling data.

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