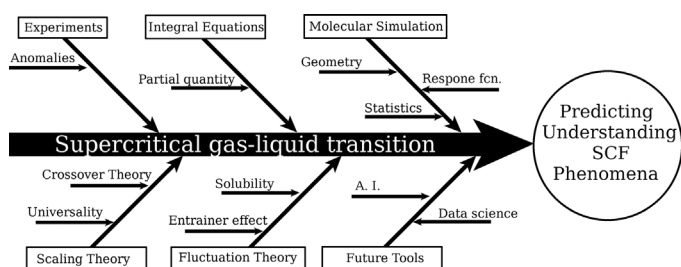# Current theoretical opinions and perspectives on the fundamental description of supercritical fluids

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GRAPHICAL ABSTRACT

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ABSTRACT

We briefly overview the theoretical advances for the fundamental description on the supercritical fluids since the late 1980s. The concept of supercritical gas-liquid boundary and its importance are introduced. The current state of the state-of-art theories about supercritical gas-liquid boundary (Integral Equation Approximation, Fluctuation Theory of Solutions, and molecular simulations) are examined. Based on these principles and the remarkable progresses in the field of supercritical fluids, the direction of future research and promising methodologies are given. The future researches on the fundamental descriptions of supercritical fluids are expected to play a crucial role in extending the knowledges and utilizing supercritical fluid technologies.

1. Introduction

In recent 40 years, supercritical fluid science and technology have bloomed. Supercritical fluids have been widely utilized in the physical and/or chemical processes such as extraction, impregnation, precipitation, extrusion, drying, chromatography, leaching, power generation, and hydrothermal synthesis [1–8]. This versatility of supercritical fluids stems from their duality. they can have both gas-like and liquid-like properties depending on the thermodynamic conditions, and these thermophysical and transport properties are instantaneously tunable.

The idea that supercritical fluid is not a single homogeneous fluid, but an inhomogeneous fluid at molecular level where gas-like and liquid-like structure coexists starts from the Bernal's metal ball experiments [9,10]. From his experiments, Bernal classified fluids into four categories including gas, associated gas, expanded liquid and liquid and defined a hypercritical line between associated gas and expanded liquid. This idea was firstly verified by the experimental measurements of the critical anomalies around the critical point by Sengers and Voronel [11]. These behaviors cannot be understood from the viewpoint of mean-field theory. Thus, the theory of critical phenomena and fluid polyamorphism theory were employed and supported by spectroscopic measurements, which showed that large density fluctuation becomes maximum at a certain set of thermodynamic states [12–18]. This set of thermodynamic states, called hypercritical line by Bernal, is later defined the supercritical gas-liquid boundary, Widom

line [19–21], or pseudo-boiling line [8,22–24], which is under active investigation by physicists, chemists and chemical engineers.

Supercritical gas-liquid boundary is of great importance in the fundamental aspect and the application of supercritical fluid technologies. In the fundamental viewpoint, the existence of the supercritical gas-liquid boundary leads to the following fundamental questions. How do we define liquid-like and/or gas-like properties of supercritical fluids? Seeking answers for these questions will result in a revised phase diagram. From the aspects of application, this revised phase diagram is used to reduce operating costs and maximize the efficiency of processes because the supercritical gas-liquid boundary could be a reference state for tuning the thermodynamic properties. Ultimately, theoretical understanding of supercritical fluids will lead to the rational design of global equation of state for the prediction/correlation of thermophysical properties of supercritical fluids [25,26]. For example, an addition of kernel term to traditional (i.e., van der Waals type) and molecular-based (i.e., Statistical Associating Fluid Theory (SAFT), perturbed hard chain theory) EoS leads to more accurate description of supercritical fluids for a wide range of thermodynamic condition. Thus, theoretical advances on the fundamental properties of supercritical fluids are expected to give physical insights and solid backgrounds for building this type of EoS in rational and efficient ways. This direction of researches is reviewed in the article written by Vega in this special issue.

So far, theoretical researches for understanding the supercritical gas-liquid boundary have extensively exploited the statistical mechanical theories (the Integral Equation Approximation (IEA) and the Fluctuation Theory of Solutions (FST)) and molecular simulations since late 1980s. Initially, these studies have been heavily contributed to purely fundamental journals related to chemical physics and physical chemistry, but number of relevant publications has increased continuously in The Journal of Supercritical Fluids (Fig. 1). This increase substantiates that understanding the fundamental aspects of supercritical fluids would enable us to provide an optimal solution for the process design and analysis.

Therefore, in this work, a brief history of the theories relevant to the supercritical gas-liquid boundary since late 1980s will be explored. An extensive review on the hundreds of the publications is avoided. Fundamental descriptions on the thermophysical and transport properties of supercritical fluids so far can be referred in textbooks [27–29], and in-depth extensive reviews on the methodologies mentioned in this work can be found in other literatures [30–32]. Instead, some historical cornerstones and recent important publications are highlighted. Then, a perspective on the future direction and prospective tools for the theoretical exploration of supercritical fluids will be covered.

2. History and current state

2.1. Integral equation approximations

IEA and FST could be regarded as main successful applications of the statistical mechanics on the phase behavior of supercritical fluids.
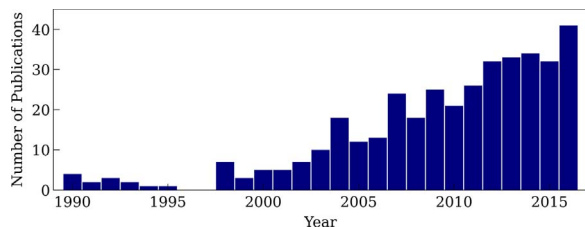

Fig. 1. An increase in the publications dealing with molecular simulations and statistical mechanical theory in The Journal of Supercritical Fluids. The statistical data was obtained from Scopus with the combined search words "molecular simulation" or "fluctuation theory" in the article title, abstract and keywords and "The Journal of Supercritical Fluids" in the source title.

IEA is a numerical procedure for the structural analysis of a system based on correlation functions. Homogeneous IEA has been mainly used to describe liquid structure and solution thermodynamics. It consists of homogeneous Ornstein-Zernike Equation and the closure relations such as the Percus-Yevick (PY) and Hypernetted Chain (HNC) closures. By solving simultaneous equations, the pair correlation functions and the direct correlation functions can be obtained. The correlation function obtained from IEA is used to estimate the thermodynamic properties based on FST [32]. FST provides an expression for the pair correlation function integral, which is also called *Kirkwood-Buff Integral* (KBI). FST can be directly related to the experimental data at any solution composition by the inversion procedure proposed by Ben-Naim and Smith [33,34].

IEA in conjunction with the FST was mainly used in studies dealing with the divergence of partial molar volume of a solute ($\bar{v}_2^\infty$) in dilute supercritical mixtures in the 1990s. The sign of divergence seemed to be related with the extent of intermolecular energy. Hence, Debenedetti proposed to classify solutes into three categories depending on the extent of the interaction energy; attractive, repulsive and weakly attractive solutes [35]. The formation of distinct cluster structure was first proposed as a physical mechanism behind the divergence in the partial molar volume [17]. However, in the early 1990s, IEA yielded that the divergence did not mainly come from the strong attraction and/or repulsive forces between solute and supercritical fluids [36]. Rather, earlier studies from the IEA showed that the large density fluctuation in neat supercritical fluids was mainly responsible for the divergence. To resolve the controversy, Chialvo and Cummings decomposed $\bar{v}_2^\infty$ into short-range and long-range contributions by relating FST with IEA [37]. This approach distinguished the short-range contribution to the divergence from the long-range contribution, but did not provide the origin of high-density domain around an attractive solute. Thus, Ruckenstein and Shulgin modified the definition of excess number of molecules around a solute molecule to describe the density inhomogeneity, and hypothesized that the density inhomogeneity around a solute mainly originates from the pre-existent density fluctuation [38]. The low accuracy of homogeneous IEA made it hard to apply the method for the quantitative analysis of the near-critical system. Hence, Egorov et al. recently improved the accuracy by introducing the inhomogeneous Ornstein-Zernike Equation proposed by Attard [39,40]. These theoretical advances not only provide a physicochemical explanation on the solvation mechanism, but also be readily applied to model the solubility of solute in supercritical fluids. The employment of FST for the prediction of solute solubility was largely endeavored by Ruckenstein and Shulgin [41]. Based on the FST formulations, they developed analytic expressions for the prediction of solute solubility in neat supercritical fluids and their mixtures. Abbott and Schimizu demonstrated how FST methodologies can provide a physical insight to understand the solvation mechanism in supercritical CO_2/co-solvent mixture as well as be easily implemented as an user-friendly application (app) [42]. In summary, statistical mechanical theories and their applications to supercritical fluid systems led us to analyze how this inhomogeneous system works and provided useful tools to predict and/or correlate the experimental results.

2.2. Molecular simulations

Along with the statistical mechanical theories, Monte Carlo (MC) and classical Molecular Dynamics (MD) simulations have been widely utilized for the characterization of the supercritical fluid system. In time-independent MC simulations, the configurations of molecules can be obtained by generating random numbers. Basically, the Metropolis algorithm is the most common method to generate the configurations in MC simulations [43]. In the Metropolis algorithm, new configurations are generated from an old configuration by applying various molecular motions (e. g., translation, vibration, rotation, and switching) to the system. This new configuration can be either accepted or rejected by