



Molecular dynamics simulation on the local density distribution and solvation structure of supercritical CO₂ around naphthalene



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ABSTRACT

Molecular Dynamics (MD) simulations were performed to understand the solvation structure and the mechanistic nature of the divergence of partial molar volume (\bar{v}_2^∞) near the critical point. Isothermal-isobaric (NpT) simulations were carried out at $T_r = 1.03$ from $p_r = 0.87$ to $p_r = 3.72$ with the truncated and shifted Lennard-Jones and the Weeks-Chandler-Andersen (WCA) potentials. A statistical analysis on the structural characters was carried out to investigate the origin of the divergent \bar{v}_2^∞ near the critical point. The result suggested that no distinct cluster structure exists. Rather, a solute enters the pre-existent high-density and/or low-density domain and its preference depends on the magnitude of the solute/solvent attractive interaction. The influence of the attractive forces is propagated via the density fluctuation throughout the entire system. Thus, the interplay between the solute/solvent attraction and the pre-existent density fluctuation is the mechanistic origin of the divergence of \bar{v}_2^∞ near the critical point.

1. Introduction

Near-critical and supercritical fluids are actively used for a wide range of applications such as extraction, precipitation, impregnation, polymer synthesis and reaction [1–4]. This versatility of supercritical fluids originates from their unique characteristic, an instant tunability of solvation power by adjusting the operating pressure; the solubility of solutes in supercritical fluids can largely change in the vicinity of critical point [5]. This tunability is believed to originate from the structural characteristics of a near-critical mixture. One of the interesting structural features of the supercritical fluid (1)/solute (2) mixture would be the divergence of partial molar volume of solutes (\bar{v}_2^∞) near the critical point of the solvent. \bar{v}_2^∞ becomes either largely positive or negative in the vicinity of the critical point. This indicates that a solute greatly reduces or increases the total dimension of the system when added to a neat supercritical medium. Debenedetti et al. proposed that the sign of \bar{v}_2^∞ largely depends on the solute/solvent interaction energy (ϵ_{12}) and the solutes can be classified into three categories: attractive, weakly attractive and repulsive solutes [6,7].

In order to interpret the divergence of \bar{v}_2^∞ , a distinct solute/solvent cluster formation was first assumed. For instance, Guggenheim quasi-chemical approach has been used to correlate the solubility and the solvation structure by regarding the cluster of n CO₂ molecules and a solute molecule as a complex [8]. Noroozi et al. used Molecular

Dynamics simulation to calculate the solvation free energy of ibuprofen and acetaminophen in supercritical CO₂. They estimated \bar{v}_2^∞ from the pressure derivative of the solvation free energy, regarding \bar{v}_2^∞ as a measure of the cluster formation around the solute [9]. From the late 1980s, however, many studies maintained that the density fluctuation in near-critical fluids, not a solute/solvent interaction, should be considered to understand the steep change of \bar{v}_2^∞ near the critical point [10]. From the Ornstein-Zernike relation, McGuigan and Monson stated that a long-range correlation is mainly responsible for the divergence of \bar{v}_2^∞ [11]. Chialvo and Cummings decomposed \bar{v}_2^∞ into short-range [$\bar{v}_2^\infty(\text{SR})$] and long-range [$\bar{v}_2^\infty(\text{LR})$] contributions based on the direct correlation function, which are represented as: $\bar{v}_2^\infty(\text{SR}) = \rho^{-1}(1 + C_{11}^0 - C_{12}^\infty)$ and $\bar{v}_2^\infty(\text{LR}) = \kappa k_B T C_{11}^0 (C_{11}^0 - C_{12}^\infty)$ where C_{11}^0 and C_{12}^∞ are the solvent/solvent and solvent/solute direct correlation functions at infinite dilution, κ is the isothermal compressibility and k_B is the Boltzmann constant [12]. Stubbs et al. performed Monte Carlo (MC) simulations of naphthalene/CO₂ system. They calculated and compared the radial distribution functions of CO₂ molecules around a CO₂ molecule to those of CO₂ molecules around a naphthalene molecule. From the results, they stated that approximately 60% of the volume decrease occurred in the vicinity of the solute and 40% of the shrinkage came from the uniform condensation from a distance [13]. Thus, both studies by Stubbs et al. and Chialvo and Cummings supported that both short-range and long-range contributions should be

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considered. The decomposition of \tilde{v}_2^∞ , however, does not provide whether the density inhomogeneities around a solute comes from the solute-induced local density augmentation or not. Ruckenstein and Shulgin proposed that the density enhancement around naphthalene and pyrene would come from the density fluctuation. They calculated the excess number of CO₂ molecules around another CO₂ molecules by means of the Fluctuation Solution Theory (FST) and compared the CO₂/CO₂ radial distribution function to CO₂/naphthalene radial distribution function. Based on the calculation, they stated that a solute prefers to locate in high density region [14,15].

Thus, the origin of the high-density and/or low-density domain near the solute is not clear. It could come from the solute-induced density enhancement or the large density fluctuation of a neat near-critical fluid. Furthermore, the hypothesis proposed by Ruckenstein and Shulgin is not established clearly. If a solute only preferred the high-density domain regardless of their interactions, the categories of solutes proposed by Debenedetti et al. would not affect the divergence of \tilde{v}_2^∞ , which is, of course, not consistent with theoretical and experimental results. Hence, an interplay between solute/solvent interactions and the density fluctuation observed in neat near-critical fluids should be considered for the mechanistic understanding of the divergence of \tilde{v}_2^∞ .

Therefore, the aim of this work was to propose an integrated explanation on the divergence of \tilde{v}_2^∞ and the origin of the heterogeneous structure of near-critical fluids around the solute. To study the structural characteristics of supercritical mixture, Molecular Dynamics (MD) simulations were performed. The model solute and solvent were naphthalene and CO₂, respectively. First, the critical point of the CO₂ model was obtained by using the *NVT* simulations. Then, isothermal-isobaric (*NpT*) MD simulations of dilute naphthalene/CO₂ mixtures were performed at the reduced temperature of $T_r = 1.03$. From the simulations, \tilde{v}_2^∞ of naphthalene was calculated and compared to the experimental results. To understand the role of attractive forces between solute and solvent, two kinds of potentials were used for solute/solute and solute/solvent interactions; the truncated and shifted Lennard-Jones (LJ) potential and the Weeks-Chandler-Anderson (WCA) potential [16]. For both potentials, several aspects of the simulation results were interpreted by using Voronoi tessellation and an Inverse Gamma-Normal mixture model [17].

2. Methods

2.1. Models

Lennard-Jones (LJ) type potential is frequently used to model the intermolecular potentials. If the Lennard-Jones particles have partial charges, the potential can be expressed by Eq. (1).

$$\varphi_{LJ}(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (1)$$

In Eq. (1), q_i is the charge of the atomic species i , and ϵ_0 is the permittivity of free space. σ_{ij} and ϵ_{ij} are the distance and energy constants between species i and j . σ_{ij} describes the finite distance at which $\varphi_{LJ}(r)$ becomes zero, and ϵ_{ij} indicates the depth of the potential well. r_{ij} is the distance between species i and j . As seen in Eq. (1), the Lennard-Jones potential asymptotically approaches to zero as r_{ij} increases. Thus, the tail contribution of the potential could be dealt with by either adding a tail correction and/or truncating the potential. In this work, $\varphi_{LJ}(r)$ was truncated and shifted instead of adding the tail correction term to compare it with the Weeks-Chandler-Anderson (WCA) potential. The truncated and shifted LJ potential (φ_{tr}) is represented as:

$$\varphi_{tr}(r_{ij}) = \begin{cases} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] - \varphi_{LJ}(r_c) + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} & (r \leq r_c) \\ 0 & (r > r_c) \end{cases} \quad (2)$$

Table 1
Forcefield parameters for CO₂ and naphthalene.

(Pseudo)atom	ϵ/k_B [K]	$\sigma[\text{\AA}]$	$q[e]$
C (CO ₂)	27.0	2.800	0.700
O (CO ₂)	79.0	3.050	-0.350
C (Naphthalene)	30.0	3.700	0.000
CH (Naphthalene)	50.5	3.695	0.000

As seen in Eq. (2), the truncated and shifted potential becomes zero at $r = r_c$ so that the continuity of the potential is guaranteed. The role of the solute/solvent attractive interaction could be examined when the WCA potential is adopted [Eq. (3)].

$$\varphi_{WCA}(r_{ij}) = \begin{cases} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \epsilon_{ij} + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} & (r \leq 2^{1/6}\sigma_{ij}) \\ 0 & (r > 2^{1/6}\sigma_{ij}) \end{cases} \quad (3)$$

As seen in Eq. (3), $\varphi_{WCA}(r_{ij})$ is shifted upward by the minimum of the potential (ϵ_{ij}). Therefore, it monotonically decays to zero with negative slope; only the repulsive forces act between species i and j . The intermolecular interactions among CO₂ were always modelled as $\varphi_{tr}(r)$ so that the attractive forces among CO₂ molecules could remain. For σ_{ij} and ϵ_{ij} , the transferable potentials for phase equilibria (TraPPE) force-field parameters was used [18,19] (Table 1). The Lorentz-Berthelot combining rule was used for the interactions between heterogeneous atomic species.

2.2. Molecular dynamics (MD) simulations

Canonical (*NVT*) and Isothermal-isobaric (*NpT*) MD simulations [20] were carried out. For all the simulations, the time step was 1.0 fs. The Nose/Hoover algorithm [21,22] was used to control the temperature and pressure. The number of CO₂ molecules was 2000 and their initial configurations were given as simple cubic structure. The cut-off radius (r_c) was set to be 16 Å. *NVT* simulations were first carried out for the estimation of the critical point because the critical point of a substance largely depends on the system size, the cut-off radius and tail correction functions [23]. The simulation temperatures were from 302 K to 306 K and the densities were from 300 kg/m³ to 620 kg/m³. The system was equilibrated for 100,000 steps and the pressure data were collected for additional 1,000,000 steps. Three sets of simulations were conducted in this manner and the simulation pressures were averaged for the estimation of the critical point.

In *NpT* simulations, the simulation temperature was fixed to be $T_{sim} = 313.15\text{K}$. When $\varphi_{tr}(r)$ was used for all the pairs of molecules, the simulation pressures (p_{sim}) were 70, 82, 93, 120, 181, and 300 bar. At $p_{sim} = 82, 93, 181, \text{ and } 300$ bar, different simulations, in which $\varphi_{WCA}(r)$ was used for solute/solvent and solute/solute pairs and $\varphi_{tr}(r)$ was applied for solvent/solvent interactions, were conducted. In each condition, the number of naphthalene molecules inserted was controlled to be 0, 1, and 2 to determine \tilde{v}_2^∞ of naphthalene. All the systems were equilibrated for 100,000 steps and the data production was run for additional 5,000,000 steps. The total volume was tracked every step and was averaged to get the mean system volume, and the system configuration was collected every 1000 time steps. Three parallel sets of the MD simulations were performed in this manner, then the entire system volumes were averaged to calculate \tilde{v}_2^∞ at the same pressures.

2.3. Structure characterization

Voronoi tessellation was used for the characterization of the structural features. Voronoi tessellation is one of the tessellation methods to divide the space into Voronoi cells. Voronoi cells, as depicted in Fig. 1, are a set of points closest to given seeds, the centers of mass of the molecules. As each of the Voronoi cells contain one molecule, the local

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