



Research paper

Ideality contours and thermodynamic regularities in supercritical molecular fluids



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ABSTRACT

Using Expanded Wang-Landau simulations, we calculate the ideality contours for 3 molecular fluids (SF_6 , CO_2 and H_2O). We analyze how the increase in polarity, and thus, in the strength of the intermolecular interactions, impacts the contours and thermodynamic regularities. This effect results in the increase in the Boyle and H parameters, that underlie the Zeno line and the curve of ideal enthalpy. Furthermore, a detailed analysis reveals that dipole-dipole interactions lead to much larger enthalpic contributions to the Gibbs free energy. This accounts for the much higher temperatures and pressures that are necessary for supercritical H_2O to achieve ideal-like thermodynamic properties.

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1. Introduction

Supercritical fluids [1] have become increasingly important in environmentally benign separations and reactions [2,3], and for new ways of processing materials [4]. This is because of their unusual physical properties including their high compressibility, their transport properties intermediate between gas and liquid and their high dissolving power [5]. Among the supercritical fluids used in these applications, carbon dioxide stands out as one of the most versatile [6]. Recent work has also highlighted the role played by supercritical water in nature, e.g. in the Earth crust and mantle [7], and as a green solvent for the catalytic conversion of biomass into fuel [8]. Processes aiming to capture and store SF_6 , a potent greenhouse gas that is supercritical under ambient conditions, are also currently being developed [9]. However, there are still significant gaps in our understanding of the thermophysical properties of supercritical fluids [10,11].

Recent work has shown the emergence of several remarkable thermodynamic contours [12,13] that could help bridge this gap in knowledge. The existence and similarity of such contours, which span the supercritical domain, would allow to build a correspondence between the supercritical fluids of different compounds, in the spirit of the law of corresponding states that connects the binodal and critical point for a wide range of substances. The aim of this work is to study supercritical fluids that are found in a number of technological and environmental applications and to provide a

full picture of their thermodynamics in the supercritical domain of their phase diagram. We focus specifically on three molecular fluids: SF_6 , for which we parametrize a new force field, carbon dioxide modeled with the TraPPE force field [14] and water modeled with the SPC/E potential [15]. We study the behavior of these molecular fluids along a number of remarkable contours, known as the Zeno line (where the compressibility factor is equal to 1), the H line (where the enthalpy is the same of that of an ideal gas), the S_0 line (where the isothermal compressibility, or, equivalently, the structure factor at zero wave vector S_0 is equal to zero) and the H_{\min} line (the line of minima for the enthalpy isotherms). Recent work has shown the peculiar behavior of supercritical fluids along these lines (most notably the straightness of the Zeno line and of the H line for the Lennard-Jones (LJ) fluid [13]). However, the behavior of molecular fluids along these contours is still largely unknown. To elucidate this point, we determine the thermodynamics properties of supercritical SF_6 , CO_2 and H_2O , analyze the impact of the type of intermolecular interactions and of their strength on the thermodynamic contours and regularities, and interpret the results in terms of their enthalpic and entropic contributions to the Gibbs free energy.

The paper is organized as follows. In the next section, we briefly define the thermodynamic contours and regularities studied in this work. Then, in the next section, we present the simulation method, molecular models and technical details. In particular, we discuss how the recently developed Expanded Wang-Landau simulations [16–19] are applied to determine the loci for the thermodynamic contours in the supercritical region of the phase diagram. The advantage of using EWL simulations is twofold: (i) the same

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method is consistently used to generate the data for all systems and contours and (ii) the conditions needed to achieve ideal-like behavior often involve very high temperatures/pressures, with few, if any, experimental data or equations of state covering that region of the phase diagram. We determine the properties of supercritical fluids and compare the behavior of the different fluids to characterize the effect of the intermolecular interactions on the thermodynamic contours before drawing the main conclusion of this work in the last section.

2. Contours and regularities

Recent work has shown that several thermodynamic regularities established on the van der Waals (vdW) equation can be extended to real substances [13]. First, the contour $Z = P/\rho T = 1$ (where Z is the compressibility factor, P the pressure, ρ the number density and T the temperature) follows a straight line in the density-temperature plane for the vdW equation, for model systems [20], water [21] and several other compounds [22–24]. Second, the H contour (curve of ideal enthalpy) is a straight line for the vdW equation [12] and for the LJ fluid [13]. However, the shape of the H line has yet to be established for molecular systems. We also consider two other contours, the S_0 and H_{min} lines. The S_0 line is the curve of maxima for the isothermal compressibility where $(\partial^2 P/\partial \rho^2)_T = 0$, and extends from the critical point into the supercritical region of the phase diagram. It corresponds to the line of density fluctuation maxima, that delimits the ridges in the supercritical region [11,25,26], and, as such, is connected with the possible separation of the supercritical region into gas-like and liquid-like phases [26]. The H_{min} line is defined as the line of minima for the enthalpy isotherms. As discussed in [13], the H_{min} line underlies the line of ideal enthalpy, as its limiting values, both at zero density and at zero temperature, coincide with that of the H line. The impact of the intermolecular interactions on the shape of these contours is unknown. Elucidating the thermodynamics of molecular fluids along these 4 contours will be a first step towards establishing a correspondence between supercritical fluids, as these contours span the supercritical region of the phase diagram.

3. Simulation methods

3.1. Expanded Wang-Landau simulations

We use the Expanded Wang-Landau (EWL) simulation method [16–19]. This approach takes advantage of a flat histogram sampling technique, the Wang-Landau scheme [27–32], combined with an expanded ensemble approach [33–43], in which the difficult insertion/deletion of entire molecules is achieved by varying the size of a fractional molecule (more details are given in [16–19]). The advantage of the EWL method is that it only requires the temperature and volume as input parameters, and that a single EWL run is required, for a given temperature, to obtain the properties for all densities. The simulation consists in evaluating the partition function $\Theta(\mu, V, T)$ in the grand-canonical ensemble:

$$\Theta(\mu, V, T) = \sum_{N=0}^{\infty} Q(N, V, T) \exp(\beta \mu N) \quad (1)$$

with

$$Q(N, V, T) = \frac{V^N}{N! \Lambda^{3N}} \int \exp(-\beta U(\Gamma)) d\Gamma \quad (2)$$

Having an accurate estimate for the grand-canonical partition function allows, in turn, for the calculation of all thermodynamic

properties of the system, particularly those difficult to compute such as, e.g. the Gibbs free energy and the entropy.

3.2. Molecular models

SF₆ is modeled with a set of six LJ sites, each site standing for a F atom. Interactions between two LJ sites (i, j) are given by

$$\phi(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad (3)$$

where r_{ij} is the distance between the two atoms, and ϵ and σ are the energy and size parameters for the potential. We use a distance between the center of the molecule (S atom) and each of the F atom of 1.62 Å. Optimizing the values for the LJ parameters to best reproduce the vapor–liquid densities at coexistence leads to the following set of parameters: $\epsilon/k_B = 78$ and $\sigma = 2.75$ Å. The interaction between the F atoms of the fractional molecule and of a full (regular) molecule is obtained by scaling the energy and size parameters by $(l/M)^{1/3}$ and $(l/M)^{1/4}$, respectively, where M is the number of stages in which the insertion/delition steps are divided and l is the current value for the stage number of the fractional molecule [16]. In addition, the size of the fractional molecule (i.e. the bond length between S and F) is scaled by $(l/M)^{1/4}$ to ensure that the fractional molecule is smaller than a full molecule.

CO₂ is modeled with the TraPPE potential [14]. Each molecule is described as a distribution of three LJ sites and three point charges (one on each atom) with the interaction between atoms (i, j) as

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

To model the interaction between an atom of the fractional molecule with an atom of a full molecule we scale the interaction parameters $\epsilon_{ij}, \sigma_{ij}$ and the product $q_i q_j$ by $(l/M)^{1/3}, (l/M)^{1/4}$ and $(l/M)^{1/3}$, respectively. We scale the size of the fractional molecule (i.e. the bond length between C and O) as above, in the case of SF₆.

Finally, we use the SPC/E force field [15] to model H₂O. It relies on the same functional form for the interaction potential as Eq. (4). We add that we also use the same scaling both for the interaction between the fractional molecule and a full molecule and for the size of the fractional molecule as for SF₆ and CO₂.

3.3. Technical details

EWL simulations consist of the following Monte Carlo (MC) steps for all molecules: 37.5% of the attempted MC moves are translations of a single molecule (full or fractional), 37.5% are rotations of a single molecule (full or fractional) and the 25% remaining moves are changes in (N, l) values. The number of stages M is set to 100, the starting value for the convergence factor f in the iterative Wang-Landau scheme to e , its final value to 10^{-8} , with each (N, l) value being visited at least 1000 times for a given value of f . Simulations are carried out on cubic cells for all systems, with periodic boundary conditions, and a box length of 30 Å. LJ and quadrupolar interactions are calculated using a spherical cutoff set to half the box length. The usual tail corrections are applied beyond that cutoff distance for the LJ part of the potential. In the case of H₂O, Ewald sums are used to calculate the electrostatic part of the potential energy (with the same parameters as in Ref. [18]).

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