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 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.

Keywords: Sulfur hexafluoride, Carbon dioxide, Water, Critical properties, Wang-Landau

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 intermediated 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

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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, 17, 18, 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 method is consistently used to generate the data for all systems and contours, (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, 23, 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, 17, 18, 19]. This approach takes advantage of a flat histogram sampling technique, the Wang-Landau scheme [27, 28, 29, 30, 31, 32], combined with an expanded ensemble approach [33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 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, 17, 18, 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

SF_6 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/deletion 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.

CO_2 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 SF_6 .

Finally, we use the SPC/E force field [15] to model H_2O . 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 SF_6 and CO_2 .

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 H_2O , Ewald sums are used to calculate the electrostatic part of the potential energy (with the same parameters as in ref. [18]).

4. Results and Discussion

4.1. SF_6

We start by discussing the results obtained for SF_6 . The left panel of Fig. 1 shows the grand-canonical partition function $\Theta(\mu, V, T)$ (top left of Fig. 1) as well as the associated $Q(N, V, T)$ functions (bottom left). The plot of $\log \Theta(\mu, V, T)$ against the chemical potential μ provides a direct insight into the nature of the fluid (subcritical or supercritical) as a function of the thermodynamic conditions. At low temperature (below 293 K), the plots for $\log \Theta$ exhibit a sharp change beyond a threshold value for μ , corresponding to the vapor→liquid transition. As temperature increases, $\log \Theta$ displays a smoother increase with μ , showing that the fluid is now supercritical. As shown in Eq. 1, the grand-canonical partition function is a sum of the $Q(N, V, T)$ functions (weighted by the $\exp(\mu N)$). The differences observed for Θ as a function of T are therefore directly connected to those seen, for different T , on $Q(N, V, T)$ as a function of N , since the slope of the $\log Q$ plot against N is related to μ . This means that, at low temperature, when the slope for $\log Q$ is very large, the transition towards the high density phase (or equivalently the sharp increase in $\log \Theta$) will occur for larger values of μ . Moreover, for ($T > 400$ K), the curves for $\log Q$ are flatter, confirming that the fluid is supercritical.

Knowing $\Theta(\mu, V, T)$ and $Q(N, V, T)$ allows us to determine the loci for the thermodynamic contours. We define the number distribution $p(N)$ as

$$p(N) = \frac{Q(N, V, T) \exp(\beta \mu N)}{\Theta(\mu, V, T)} \quad (5)$$

This yields the conditions of coexistence, obtained by numerically solving the following equation:

$$\sum_{N=0}^{N_b} p(N) = \sum_{N_b}^{\infty} p(N) \quad (6)$$

where N_b is the point at which the function $p(N)$ reaches its minimum, and the left hand side and the right hand side of the equation correspond to the

Figure 1: EWL results for SF_6 . (Top left) $\log \Theta(\mu, V, T)$ against μ for 243 K (black), 243 K (black), 263 K (red), 293 K (green), 400 K (blue), 600 K (indigo), 800 K (brown), 1000 K (magenta) and 1200 K (cyan). (Bottom left) $\log Q(N, V, T)$ against N (same legend as for $\log \Theta$). (Top right) $p(N)$ at coexistence for 293 K. (Bottom right) $p(N)$ along the S_0 line (indigo), Z line (blue), H_{min} line (green) and H line (red) at 600 K.

probability of the vapor and of the liquid phase, respectively. We provide in the top right corner of Fig. 1 the curve for $p(N)$ obtained at coexistence for $T = 293$ K. From there, the densities at coexistence can be readily calculated to obtain the binodal curve. $p(N)$ is also used to locate the Zeno line by solving the $Z = 1$ equation

$$P\bar{V}/RT = \log \Theta(\mu, V, T)/\bar{N} = 1 \quad (7)$$

where $\bar{V}$ is the reciprocal density and $\bar{N} = \sum Np(N)$ is the average number of particles in the system. The corresponding point of the Zeno line at $T = 600$ K is shown in bottom right corner of Fig. 1. For the H line and H_{min} contour, we evaluate the enthalpy from $p(N)$ as

$$H = U + PV = \frac{\sum (E_{pot}(N) + \frac{3}{2}k_B T) p(N)}{\sum p(N)} + k_B T \log \Theta(\mu, V, T) \quad (8)$$

where $E_{pot}(N)$ is the potential energy per molecule for a system of N molecules. The H line is then obtained by solving $\bar{H} = 4RT$ and the H_{min} contour by minimizing H reaches at fixed T . Examples of $p(N)$ for the H and H_{min}

Figure 2: (a) EWL results for the coexistence curve of SF_6 (open circles), critical point (filled circle), S_0 line (indigo), Z line (blue), H_{min} line (green) and H line (red). (b) Thermodynamic functions along the Z line (top) and the H line (bottom), with $-G$ (circles), $-H$ (squares) and TS (triangles).

points at $T = 600\text{ K}$ are also provided in Fig. 1. The S_0 contour is obtained by differentiating numerically P twice with respect to the number density and finding μ such that $(\partial^2 P / \partial \rho^2)_T = 0$, with the corresponding $p(N)$ at $T = 600\text{ K}$ shown in Fig. 1.

We show in Fig. 2(a) the binodal as well as the critical point obtained from the EWL results for the newly parameterized force field. We use a scaling law, with a critical exponent of 0.326, to determine the critical temperature and the law of rectilinear diameter for the critical density (see Table 1). The results are in good agreement with the experimental results [44] ($T_c = 318.7\text{ K}$ and $\rho_c = 0.737\text{ g/cm}^3$). Also shown in Fig. 2(a) are the EWL contours for SF_6 . As for the LJ fluid [13], the straightness of the Z line and of the H line is conserved throughout the phase diagram, both in the subcritical and in the supercritical regimes. Specifically, linear fits to the EWL results lead to an Average Absolute Relative Deviation ($AARD$) error ($AARD(\%) = \frac{1}{N} \sum_i \left| \frac{T_{Fit} - T_{sim}}{T_{sim}} \right|$) of 1.0 % for the Z line and to an error of 1.1 % for the H line. The fits yield the Boyle parameters, i.e. the Boyle temperature T_B and Boyle density ρ_B (intercepts for the Z line), as well as the H parameters, T_H and ρ_H (intercepts for the H line), given in Table 1. The $T_B : T_H$ ratio for SF_6 (0.54) is in good agreement with that obtained

for the LJ fluid (0.53). Similarly, the $\rho_B : \rho_H$ ratio for SF_6 (0.99) is close to that of LJ (0.92) and the shapes for the H_{min} and S_0 contours are similar to the LJ contours. We then model the H_{min} line with a quadratic law, $T_{H_{min}(\rho)} = T_H (1 - \rho/\rho_H)^2$, which is exact for vdW [13]. The simulation results are accurately modeled by this law (see Fig. 2(a)), with an error of 6.8 %. Similarly, we model the results for the S_0 line with a cubic law $T_{S_0}(\rho) = T_B (1 - \rho/\rho_B)^3$ and obtain an overall fair agreement, with an AARD of 21%, which is reasonable given the numerical uncertainties arising from the successive differentiations involved to obtain the S_0 line and the fact that this law does not allow for any adjustable parameter. The similarity between SF_6 and the LJ/vdW systems can be attributed to the type of intermolecular interaction that exists in SF_6 , specifically, to the nonpolar nature of SF_6 and the absence of long-range interactions.

Table 1: Boyle, H and critical parameters for SF_6 , CO_2 and H_2O (T are given in K , and ρ in g/cm^3).

	T_B	ρ_B	T_H	ρ_H	T_c	ρ_c
SF_6	680 ± 6	2.95 ± 0.07	1255 ± 15	2.97 ± 0.15	323 ± 3	0.75 ± 0.01
CO_2	683 ± 3	1.84 ± 0.03	1255 ± 7	1.89 ± 0.04	306 ± 3	0.47 ± 0.01
H_2O	1599 ± 19	1.34 ± 0.05	2722 ± 17	1.84 ± 0.08	641 ± 5	0.31 ± 0.01

We now turn to the variations of the properties along the Z line and the H line. Let us consider first the case when SF_6 behaves as an ideal gas from a Zeno standpoint. The top of Fig. 2(b) shows that the entropic contribution to the G is predominant throughout the temperature range. However, we observe a crossover between the $-G$ curve and the TS curve as the fluid goes from the subcritical to the supercritical regime. This crossover occurs with a changing sign of H when going from subcritical temperatures (where H is negative as a result of the strong attractive intermolecular interactions) to supercritical temperatures (where, as a result of the decrease in density, the contribution from the attractive intermolecular interactions becomes negligible). Considering now the case where SF_6 exhibits the same enthalpy as an ideal gas, we do not observe any crossover between TS and G since H always remains positive.

4.2. CO_2

The results for the phase diagram and contours for CO_2 are shown in Fig. 3(a). The results are in good agreement with the experimental data [44]

Figure 3: (a) EWL results for the coexistence curve of CO_2 (open circles), critical point (filled circle), S_0 line (indigo), Z line (blue), H_{min} line (green) and H line (red). (b) Thermodynamic functions along the Z line (top) and the H line (bottom), with $-G$ (circles), $-H$ (squares) and TS (triangles).

at coexistence and for the critical properties ($T_c = 304.2\text{ K}$ and $\rho_c = 0.47\text{ g/cm}^3$). We fit the Z and H lines for CO_2 to a straight line. This shows that the quadrupolar interactions do not impact the features of the contours. The straightness of the lines, in particular of the Z line holds well with an $AARD$ of 0.5 %. The EWL results for CO_2 are in very good agreement with those extrapolated from the experimental data on low temperature liquids [24]. The EWL $T_c : T_B$ ratio (0.44) and $\rho_c : \rho_B$ ratio (0.26) are close to those (0.42 and 0.26) from [24]. We also observe that the straightness of the H line also holds, with a very low $AARD$ for the H line of 0.8 %. The $T_B : T_H$ ratio (0.54) is similar to SF_6 (0.54) and the $\rho_B : \rho_H$ ratio (0.97) is close to the value found for SF_6 (0.99). This shows the limited impact of the quadrupolar interactions on the straightness of the ideality contours. We then use the H and Boyle parameters to model the EWL results for the H_{min} line and for the S_0 line. We find that both the two quadratic (for H_{min}) and cubic (for S_0) laws adequately account for the behavior of CO_2 , as shown in Fig. 3(a). We find an $AARD$ of 3.6% for the H_{min} line and of 24 % for the S_0 line with the two laws proposed on the basis of the vdW equation and with no adjustable parameter. This further establishes that CO_2 , like SF_6 , has a behavior close to a vdW/LJ system in the supercritical region.

We finally calculate the ratios $\rho_c(CO_2) : \rho_c(SF_6)$, $\rho_B(CO_2) : \rho_B(SF_6)$ and $\rho_H(CO_2) : \rho_H(SF_6)$ and find that these are all roughly of 0.62. Similarly, the ratios for the critical, Boyle and H temperatures for the two compounds are all close to 1. These results show that a correspondence between the supercritical properties of nonpolar molecular fluids can be established.

Focusing now on the properties along the Z line, we find a similar behavior for CO_2 similar to SF_6 . Over the same temperature interval (240 K -600 K), G undergoes an almost three-fold decrease for both fluids (2.7 for CO_2 , compared to 2.9 for SF_6), resulting from a combined decrease in the enthalpic contribution, with a change in sign in the top of the temperature range, ($\times 2.1$ for CO_2 and $\times 2.6$ for SF_6) and an increase in the TS ($\times 4.1$ for CO_2 and $\times 4.0$ for SF_6). The results for the H line show similar trends for both compounds. Considering the same temperature interval for the two fluids (600 K -1200 K), we find a decrease in the G by a factor of 3.4 for CO_2 (as compared to 2.9 for SF_6), resulting from a decrease in enthalpy by a factor of 2 for CO_2 (same as for SF_6) and an increase in the entropic term by a factor of 3.1 for CO_2 (compared to 2.7 for SF_6). These similarities further show the quadrupolar interactions in CO_2 have a moderate effect on the thermodynamics of the supercritical fluid.

4.3. H_2O

We show in Fig. 4(a) the EWL results for the binodal and contours for H_2O , with a critical temperature $T_c = 641$ K in good agreement with the experimental value of 647 K [44] and previous work [45], and a critical density $\rho_c = 0.31$ g/cm^3 close to the experiment [44] (0.322 g/cm^3). The EWL results reveal that the polar nature of H_2O impacts significantly the fluid properties along the Z line. Specifically, we find an *AARD* error of 3.7 %, greater than for the nonpolar fluid SF_6 and for the quadrupolar fluid CO_2 . However, the linear fit still describes well the Z line and allows us to determine the Boyle parameters for H_2O (see Table 1). We then fit the H line. Given that low temperature results for the H line are not accessible (since they lie within the domain of stability of the solid), the linear fit relies on points obtained at high temperatures and yields the H parameters shown in Table 1, with an *AARD* of 0.3 %. While the $T_B : T_H$ ratio for H_2O is reasonably close to that obtained for other fluids (0.59 for H_2O compared to 0.54 for the SF_6), the Boyle and H densities are markedly different, with a decrease in $\rho_B : \rho_H$ ratio which decreases down to 0.73 for H_2O from 0.97 (CO_2) and 0.99 (SF_6). This suggests that the dipolar interactions become predominant at

Figure 4: (a) EWL results for the coexistence curve of H_2O (open circles), critical point (filled circle), S_0 line (indigo), Z line (blue), H_{min} line (green) and H line (red). (b) Thermodynamic functions along the Z line (top) and the H line (bottom), with $-G$ (circles), $-H$ (squares) and TS (triangles).

low temperatures and that very large pressures/densities are required for the enthalpy of H_2O to become equivalent to that of an ideal gas. The behaviors of the H_{min} and S_0 lines strongly depart from that found for SF_6 and CO_2 , with large deviations from the quadratic law for H_{min} (AARD of 21%) and from the cubic law for S_0 (AARD of 35%). The two laws completely miss the qualitative features of these two lines in the low temperatures/large densities regime. For the H_{min} line, the quadratic law only models well the behavior of the $SPCE/E$ model for temperatures above 1500 K, while the cubic law never really captures the S_0 line and the critical point. Furthermore, the correspondence seen in the case of SF_6 and CO_2 does not apply to H_2O , as e.g. the ratio of the H densities of H_2O and CO_2 is 0.97, while the ratio of the Boyle densities for the two compounds is 0.73.

Fig. 4(b) shows the variations of the properties along the Z line. A notable difference with SF_6 and CO_2 is the relative importance of the two contributions (enthalpic and entropic) to G . The enthalpic contribution amounts to up to 70 % of the G for H_2O at the beginning of the Z line, while it is only of 17 % in the case of SF_6 and of 22 % for CO_2 . The stronger intermolecular interactions in H_2O imply that larger temperatures need to be applied to reach ideality as shown by the larger value for T_B for H_2O (1599.4 K). Simi-

lar conclusions hold for the H line, with the dipolar interactions in resulting in a larger T_H .

5. Conclusions

In this work, we determine the ideality contours and the Boyle, critical and H parameters of SF_6 , CO_2 and H_2O . For SF_6 , we parametrize a 6-site force field that yields critical properties in excellent agreement with the experiment. We find the straightness of the Z and H lines also holds for a nonpolar molecular fluid like SF_6 . Then, for CO_2 , we find that quadrupolar interactions have a moderate impact on the thermodynamic properties of the supercritical fluid, and that the straightness of the Z and H lines remains valid across the phase diagram. Similarly, the behavior of the H_{min} line and of the S_0 line is accurately modeled by the simple polynomial laws that hold for the vdW equation. The results also show that a correspondence between the supercritical properties of nonpolar molecular fluids can be established since two nonpolar compounds exhibit the same ratio for their respective Boyle and H properties. The case of H_2O exhibit departures from this behavior, with large deviations in the Z and H lines from linear fits. The same conclusions apply for the H_{min} and S_0 lines, which exhibit strong departures from a vdW-like behavior, and show that the correspondence found between the supercritical properties of nonpolar fluids does not apply to H_2O . This change in behavior can be attributed to the strong dipole-dipole interactions in H_2O , which lead to a larger contribution of the enthalpic term to the Gibbs free energy and to higher temperatures/densities to achieve ideality. Further work, using water models developed for very high temperature/pressure conditions [46], would help refine these findings.

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References

- [1] E. Kiran, P. G. Debenedetti, C. J. Peters, Supercritical Fluids: Fundamentals and Applications, volume 366, Springer Science & Business Media, 2012.
- [2] P. G. Jessop, T. Ikariya, R. Noyori, Chem. Rev. 99 (1999) 475–494.
- [3] A. Baiker, Chem. Rev. 99 (1999) 453–474.

- [4] C. A. Eckert, *Nature* 383 (1996) 313–318.
- [5] J. W. Tom, P. G. Debenedetti, *J. Aerosol Sci.* 22 (1991) 555–584.
- [6] X. Han, M. Poliakoff, *Chem. Soc. Rev.* 41 (2012) 1428–1436.
- [7] R. Kessel, P. Ulmer, T. Pettke, M. Schmidt, A. Thompson, *Earth Planet. Sci. Lett.* 237 (2005) 873–892.
- [8] A. A. Peterson, F. Vogel, R. P. Lachance, M. Fröling, M. J. Antal Jr, J. W. Tester, *Energy Environ. Sci.* 1 (2008) 32–65.
- [9] I. Senkovska, E. Barea, J. A. R. Navarro, S. Kaskel, *Micropor. Mesopor. Mat.* 156 (2012) 115–120.
- [10] V. Brazhkin, Y. D. Fomin, A. Lyapin, V. Ryzhov, E. Tsiok, K. Trachenko, *Phys. Rev. Lett.* 111 (2013) 145901.
- [11] V. Brazhkin, V. Ryzhov, *J. Chem. Phys.* 135 (2011) 084503.
- [12] V. Nedostup, *High Temperature* 51 (2013) 72–78.
- [13] E. Apfelbaum, V. Vorob’ev, *J. Phys. Chem. B* 117 (2013) 7750–7755.
- [14] J. J. Potoff, J. I. Siepmann, *AIChE Journal* 47 (2001) 1676–1682.
- [15] H. Berendsen, J. Grigera, T. Straatsma, *Journal of Physical Chemistry* 91 (1987) 6269–6271.
- [16] C. Desgranges, J. Delhommelle, *J. Chem. Phys.* 136 (2012) 184107.
- [17] C. Desgranges, J. Delhommelle, *J. Chem. Phys.* 136 (2012) 184108.
- [18] C. Desgranges, J. Delhommelle, *J. Chem. Phys.* 140 (2014) 104109.
- [19] C. Desgranges, J. Delhommelle, *J. Chem. Phys.* 144 (2016) 124510.
- [20] E. Apfelbaum, V. Vorob’ev, *J. Chem. Phys.* 130 (2009) 214111.
- [21] M. C. Kutney, M. T. Reagan, K. A. Smith, J. W. Tester, D. R. Herschbach, *J. Phys. Chem. B* 104 (2000) 9513–9525.
- [22] E. Apfelbaum, V. Vorob’ev, *J. Phys. Chem. B* 112 (2008) 13064–13069.

- [23] E. Apfelbaum, V. Vorob'ev, J. Phys. Chem. B 113 (2009) 3521–3526.
- [24] E. Apfelbaum, V. Vorob'ev, J. Phys. Chem. B 119 (2015) 8419–8424.
- [25] K. Nishikawa, K. Kusano, A. A. Arai, T. Morita, The Journal of chemical physics 118 (2003) 1341–1346.
- [26] V. V. Brazhkin, A. G. Lyapin, V. N. Ryzhov, K. Trachenko, Y. D. Fomin, E. N. Tsiok, Physics-Uspekhi 55 (2012) 1061.
- [27] F. Wang, D. Landau, Phys. Rev. Lett. 86 (2001) 2050–2053.
- [28] M. S. Shell, P. G. Debenedetti, A. Z. Panagiotopoulos, Phys. Rev. E 66 (2002) 056703.
- [29] Q. Yan, R. Faller, J. J. de Pablo, J. Chem. Phys. 116 (2002) 8745–8750.
- [30] G. Gazenmüller, P. J. Camp, J. Chem. Phys. 127 (2007) 154504.
- [31] C. Desgranges, J. Delhommelle, J. Chem. Phys. 130 (2009) 244109.
- [32] T. Aleksandrov, C. Desgranges, J. Delhommelle, Fluid Phase Equil. 287 (2010) 79–83.
- [33] F. Escobedo, J. J. de Pablo, J. Chem. Phys. 105 (1996) 4391.
- [34] A. P. Lyubartsev, A. A. Martsinovski, S. V. Shevkunov, P. N. Vorontsov-Velyaminov, J. Chem. Phys. 96 (1992) 1776–1783.
- [35] M. Muller, W. Paul, J. Chem. Phys. 100 (1994) 719–724.
- [36] W. Shi, E. J. Maginn, J. Chem. Theory Comp. 3 (2007) 1451–1463.
- [37] J. K. Singh, J. R. Errington, J. Phys. Chem. B 110 (2006) 1369–1376.
- [38] F. A. Escobedo, F. J. Martinez-Veracoechea, J. Chem. Phys. 127 (2007) 174103.
- [39] K. S. Rane, S. Murali, J. R. Errington, J. Chem. Theory Comput. 9 (2013) 2552–2566.
- [40] A. R. V. Koenig, C. Desgranges, J. Delhommelle, Molec. Simul. 40 (2014) 71–79.

- 1
2
3
4
5 [41] E. A. Hicks, C. Desgranges, J. Delhommelle, *Molec. Simul.* 40 (2014)
6 656–663.
7
8 [42] A. N. Owen, C. Desgranges, J. Delhommelle, *Fluid Phase Equil.* 402
9 (2015) 69–77.
10
11 [43] C. Desgranges, J. Delhommelle, *J. Chem. Theory Comput.* 11 (2015)
12 5401.
13
14
15 [44] N. B. Vargaftik, Y. K. Vinoradov, V. S. Yargin, *Handbook of Physical*
16 *Properties of Liquids and Gases*, Begell House, New York, 1996.
17
18 [45] G. C. Boulougouris, I. G. Economou, D. N. Theodorou, *J. Phys. Chem.*
19 *B* 102 (1998) 1029–1035.
20
21
22 [46] M. Ceriotti, W. Fang, P. G. Kusalik, R. H. McKenzie, A. Michaelides,
23 M. A. Morales, T. E. Markland, *Chem. Rev.* (2016).
24
25
26
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