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Thermophysical properties of hydrogen along the liquid–vapor coexistence

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ABSTRACT

We present Theoretical Calculations for the Liquid–Vapor Coexistence (LVC) curve of fluid Hydrogen within the first order perturbation theory with a suitable first order quantum correction to the free energy. In the present equation of state, we incorporate the dimerization of H_2 molecule by treating the fluid as a hard convex body fluid. The thermophysical properties of fluid H_2 along the LVC curve, including the pressure–temperature dependence, density–temperature asymmetry, volume expansivity, entropy and enthalpy, are calculated and compared with computer simulation and empirical results.

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1. Introduction

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Hydrogen is the most abundant fluid in the universe as it forms the interiors of stars and giant planets which represent 75 mass% and 90 volume% of all matter [1]. On Earth, H_2 is most found in compounds with almost every other element. Hydrogen gas can be considered an ideal gas over a wide range of temperature. Due to its very low density, Hydrogen gas is positively buoyant and highly diffusive above 22 K. It rapidly mixes with ambient air upon release. The triple point of H_2 is 13.8 K and pressure 0.072 atm [2] while its Liquid–Vapor critical point LVCP was precisely measured by several authors. Table 2 shows the empirical critical parameters of Hydrogen compared with the present work. Hydrogen in both gaseous and liquid phases is essentially an insulator, while it exhibits phase transition to metallic liquid phase at extremely high temperatures ≈ 4400 K and pressures $\approx 2 \times 10^6$ atm. This molecular–atomic transition was firstly predicted in 1935 by Winger and Huntington [3] and eventually proven in 1996 [4,5] in a shock compression experiment. Nowadays metallic H_2 is widely accepted to exist in the interior of Saturn and Jupiter, but it has no practical applications on earth so far.

On the other hand H_2 exists in two different forms [2], either ortho (nuclear spin aligned) or para (nuclear spin anti-aligned). In normal Hydrogen, the ortho–para partition depends mainly on temperature. At 20 K thermal equilibrium partition is 99.821% para: 0.179% ortho. At room temperature it is 25% para; 75% ortho. Most physical properties are differing slightly between para and ortho spin states except the specific heat, thermal conductivity and speed of sound.

Fluid H_2 at very low temperature must be treated quantum mechanically to account for the zero point motion of nuclei. The standard technique for simulating quantum liquids is by using path integral Monte Carlo (PI-MC) [6] and path integral molecular dynamics (PI-MD) [7]. Path integral simulations can also be used to the structure and zero pressure energy of bulk fluid hydrogen at low temperature [8]. At higher temperatures up to T_c, H_2 can be treated within classical statistical Q5 mechanics but with quantum correction contribution, which is temperature dependent function.

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Ceperley [9] derived the expression for the so called degeneracy temperature $T_D = \frac{\rho \hbar^2 \sigma}{m k_B}$ below which quantum effects are important and must be included in theoretical treatment while for $T > T_D$ the fluid can be treated within classical statistical mechanics. Here ρ is the liquid density, σ is the length scale parameter (indicates the position of the zero potential), m is the molecular mass and $\hbar$, k_B refer to Plank's and Boltzmann constants, respectively. $T_D = 5.4$ K for H_2. However T_D is not an accurate parameter to be used in the equation of state (EOS). de Boer [10] was the first to use the quantum parameter

$$\Lambda = \frac{h}{\sigma_o \sqrt{\epsilon_{0\, m}}} \tag{1}$$

which is analogous to reduced de Broglie wavelength, λ_{dB} [11]. The Λ parameter was used to predict the properties of ^{3}He, H_2, deuterium and tritium [2]. The Λ parameter is ranging between 0.064 for Xenon, 2.67 for ^{4}He, 3.08 for ^{3}He while it equals 1.73 for H_2 and 1.22 for Deuterium. This Λ parameter explains the effect of mass as well as the effect of pair potential on the quantum correction in any particular fluid.

In the present work, we suggest an accurate EOS for H_2 based on statistical mechanical perturbation theory in which the short-range repulsive potential is treated as the unperturbed hard sphere reference system with suitable softening correction, while the long-range attraction is included via the double Yukawa potential within the first order perturbation scheme. The dimerization of the H_2 molecule is treated as a Hard Convex Body fluid (HCB) for which an EOS can be derived based on scaled particle theory [12,13]. The quantum correction is included through Wigner–Kirkwood expansion [14,15].

In Section 2, we develop double Yukawa potential for H_2 with suitable parameters fitted to an accurate empirical potential [16]. We introduce the suitable scaling to the hard sphere diameter to account for the shape of dimer H_2. Important functions for the EOS are formulated. In Section 3, the liquid–vapor equilibrium (LVE) curves in both $\rho - T$ and $P - T$ diagrams are given. In Section 4, we provide the numerical procedure for calculating the Liquid–Vapor Coexistence (LVC) curve and present the thermophysical properties of the liquid and vapor H_2 at equilibrium, which we compare with empirical results. Concluding remarks are given in Section 5.

2. Pairwise interaction and scaling of H_2 molecules

The intermolecular interaction of two H_2 molecules has been investigated extensively. A number of theoretical isotropic potentials have been proposed such as Hartree–Fock [17] dispersion type and ab initio type [16]. Several empirical potentials were derived from the equilibrium properties of solid state Hydrogen such as Silvira Golden (SG) [18] potential and Buck et al. [19] potential which was derived from differential scattering cross-section and integral cross-sections of D_2–H_2 collisions. Also Schaefer and Köhler potential [20] based on fitting the empirical second virial coefficients. On the other hand, several semi-empirical models have been developed by assuming simple parametric formula. These have been applied successfully to C_{60} fluid [21–23]. The parameters of these potentials are derived from thermodynamic or structure properties along with knowledge of long ranged spherically symmetric contribution to the dispersion interaction.

Here we consider pairwise potential $u(r)$, which is assumed to consist of soft-sphere repulsion, $u_{ss}(r)$ and a long-range attraction tail, $u_t(r)$,

$$u(r) = u_{ss}(r) + u_t(r) \tag{2}$$

u_{ss} is the modification of hard-sphere potential according to Ross [24] which is treated as the unperturbed reference system of $(\frac{1}{r})^{12}$ potential. The second term of Eq. (2), $u_t(r)$, acts as a perturbation. The long-range attractive forces are introduced through the Double Yukawa (DY) potential function [21–23]

$$u_{DY}(r) = E\epsilon_0 \frac{\sigma_0}{r} \left\{ \exp\left[-\lambda_1 \left(\frac{r}{\sigma_0} - 1 \right) \right] - \exp\left[-\lambda_2 \left(\frac{r}{\sigma_0} - 1 \right) \right] \right\} \tag{3}$$

ϵ_0 and σ_0 represent the potential depth and zero potential position, $u_{DY}(r = \sigma_0) = 0$ while E, λ_1 and λ_2 are the fitting potential parameters. We have used Silvera–Goldman [18] empirical potential, which is one of the exponential-6 potentials for H_2, to obtain the DY parameters, all listed in Table 1. The new semi-empirical potential is found to be satisfactory over a wide range of temperatures and pressures. The advantage of using the DY potential is that the EOS and all relevant thermodynamic functions can be found analytically.

Since H_2 molecule is slightly non-spherical, a suitable non-sphericity parameter, a, and scaling average molecular volume, $\bar{V}$, are required which may improve the performance of the EOS. These parameters are linked together via the Hard Convex Body (HCB) scaling theory [12,13] as

$$a = \frac{1}{3\pi} \frac{V'_{ef} V''_{ef}}{V_{ef}}. \tag{4}$$

The non-spherecity parameter, a, is defined via the effective volume, V_{ef}, and its derivatives as

$$\boldsymbol{V_{ef}} = \frac{\pi}{6} d^3 \bar{V}, \qquad V'_{ef} = \frac{\partial V_{ef}}{\partial d} \quad \text{and} \quad V''_{ef} = \frac{\partial^2 V_{ef}}{\partial d^2}.$$

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