Equilibrium Properties of Dense Hydrogen Isotope Gases Based on the Theory of Simple Fluids

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We present a new method for the prediction of the equilibrium properties of dense gases containing hydrogen isotopes. The proposed approach combines the Feynman−Hibbs effective potential method and a deconvolution scheme introduced by Weeks et al. The resulting equations of state and the chemical potentials as functions of pressure for each of the hydrogen isotope gases depend on a single set of Lennard-Jones parameters. In addition to its simplicity, the proposed method with optimized Lennard-Jones potential parameters accurately describes the equilibrium properties of hydrogen isotope fluids in the regime of moderate temperatures and pressures. The present approach should find applications in the nonlocal density functional theory of inhomogeneous quantum fluids and should also be of particular relevance to hydrogen (clean energy) storage and to the separation of quantum isotopes by novel nanomaterials.

I. Introduction

Johnson et al.[1,2] and Tanaka et al.[3] found that carbon nanotubes and carbon nanohorns might serve as "quantum sieves" to separate common hydrogen from its radioactive isotope, tritium. To explain this novel phenomenon, both of these research groups employed basic quantum mechanical principles. Hydrogen isotopes are characterized by the same physical size and shape; however, tritium is more massive than both deuterium and hydrogen. Furthermore, it is well-known that the thermal de Broglie wavelength increases as the temperature and molecular mass are lowered. As a result, the interactions between hydrogen isotopes are different in the both the bulk phase and in confinement. Also, the interaction energies of the lighter hydrogen isotopes are weaker than the heavier isotopes because of the higher energies of the quantum states.[4] In confinement, these quantum effects are enhanced in comparison with the bulk phase because of the very large potential gradients that exist within objects of nanoscale dimensions, and, as a consequence, the motion of quantum molecules is restricted in some directions. A quasi-one-dimensional system such as a single-walled carbon nanotube would appear to be a very good illustration of this effect.[5,6] In the radial direction, the movement of light molecules at low temperatures is quantized, whereas, in the longitudinal direction, the molecules can move freely.[7]

It is clear that an accurate description of the properties (most notably, pressure−volume−temperature behavior and chemical potential) of hydrogen isotopes in the bulk phase is necessary for the proper modeling of "quantum filters" by computer simulations or density functional theories of inhomogeneous quantum fluids. Computer simulations have been successfully applied to the prediction of the equilibrium properties of hydrogen isotopes.[8,9] On the other hand, Evans et al.,[10] Tarazona et al.,[11,12] Henderson et al.[13] and others[14−16] have developed theoretical methods appropriate for classical fluids. These theories have several advantages over direct computer simulations. First, they are less computationally demanding. Second, they provide deep insight into the microscopic properties of fluids such as the role of repulsive forces in freezing phenomena and so forth. Third, they are as accurate as direct computer simulations; although a significant problem is in the correlation of the potential parameters to experimental measurements or other reference data.[15]

A key feature connected with the behavior of simple classical fluids was remarked upon by Weeks et al.[17] thirty five years ago: *"At intermediate and large wave vectors, the repulsive forces dominate the quantitative behavior of the liquid structure factor. The attractions are manifested primarily in the small wave vector part of the structure factor; but this effect decreases as the density increases and is almost negligible at reduced densities higher than 0.65."* Indeed, short-range repulsive forces are primarily responsible for the ordering of nematic liquid crystals.[18,19] For such stiff molecules, the simple hard-rod model introduced by Onsager can explain the nematic−isotropic liquid transition without the need to include the influence of the attractive forces.[20,21] In the same spirit, as has been shown by Sese and others, for moderate temperatures and pressures, the effective potential method introduced by Feynman and Hibbs (FH) may be employed to incorporate quantum effects into the analysis of the behavior of fluids.[22−26]

In the work reported here, we combine the FH effective potential method[4,27] with the treatment of attractive and repulsive forces according to the scheme introduced by Weeks et al.[17] As others have done, we select the two-parameter Lennard-Jones (LJ) spherical potential as the reference potential.[3,24,26] Furthermore, in view of the mean field approximation involved in our modeling, the LJ parameters were optimized with reference to both the equation of state and the dependence of

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the chemical potential on pressure for hydrogen, deuterium, and tritium, as obtained from Monte Carlo simulations. The present results do not support the equation of state for hydrogen at 77 K suggested by Jagiello et al.[28,29] Our approach can also be easily adopted for isotopes of any other element to obtain their equilibrium properties.

II. Theory

Following Sese,[23,24] we assume that the hydrogen isotopes interact via the quadratic FH quantum effective potential,

$$V_{FH}(r) = V_{LJ}(r) + \frac{\beta\hbar^2}{24\mu_m}\left[\frac{d^2}{dr^2}V_{LJ}(r) + \frac{2}{r}\frac{d}{dr}V_{LJ}(r)\right] \quad (1)$$

where the classical potential is represented by the one-center LJ equation,

$$V_{ff}(r) = 4\epsilon_{ff}\left[\left(\frac{\sigma_{ff}}{r}\right)^{12} - \left(\frac{\sigma_{ff}}{r}\right)^{6}\right] \quad (2)$$

Here, $\beta = (k_B T)^{-1}$, $\hbar = h/2\pi$, $\mu_m = m/2$ is the reduced mass of a pair of interacting fluid molecules, h denotes Planck's constant, k_B is Boltzmann's constant, σ_{ff} denotes the LJ collision diameter, and ϵ_{ff} is the LJ potential well. We want to stress that, for hydrogen, deuterium, and tritium, the LJ parameters have the same numerical value. The second term in eq 1 accounts for quantum corrections to the statistical properties generated by the classical LJ potential. The FH variation approach is expected to be reliable for de Broglie wavelengths in the range $\lambda_B^* = h/(2\pi m k_B T \sigma_{ff}^2)^{1/2} \leq 0.7$. This boundary value was established by Sese by direct comparison of the structural properties of quantum fluids computed from FH and path integral Monte Carlo simulations.[23,24,30,31] Obviously, for $\lambda_B^* > 0.7$, eq 1 cannot capture the quantum spreading resulting from Heisenberg's uncertainty principle. The approximation of the diatomic hydrogen isotope molecule by an effective LJ sphere is justified by the high temperature and low-density region investigated in the current study.

Substituting eq 2 into eq 1 yields

$$V_{FH}(r) = 4\epsilon_{ff}\left[\left(\frac{\sigma_{ff}}{r}\right)^{12} - \left(\frac{\sigma_{ff}}{r}\right)^{6}\right] + \frac{\zeta}{r^2}\left[\left(\frac{\sigma_{ff}}{r}\right)^{12} - \chi\left(\frac{\sigma_{ff}}{r}\right)^{6}\right] \quad (3)$$

where

$$\zeta = 22\cdot\epsilon_{ff}\left(\frac{\beta\hbar^2}{\mu_m}\right), \chi = 1.0/4.4$$

Weeks et al.[17] demonstrated that the correlations in classical fluids are primarily determined by the repulsive forces. In accord with this fundamental observation, we assume a deconvolution of attractive and repulsive forces in quantum fluids according to a similar scheme. This is considered to be reasonable since the quantum correction enlarges the effective diameter of the molecule in comparison to its classical counterpart. However, the general form of the potential function is characterized by a similar deconstruction (see Figure 1). Following Weeks et al.,[17] we represent the attractive part of the FH effective potential by the following scheme (see Figure 1):
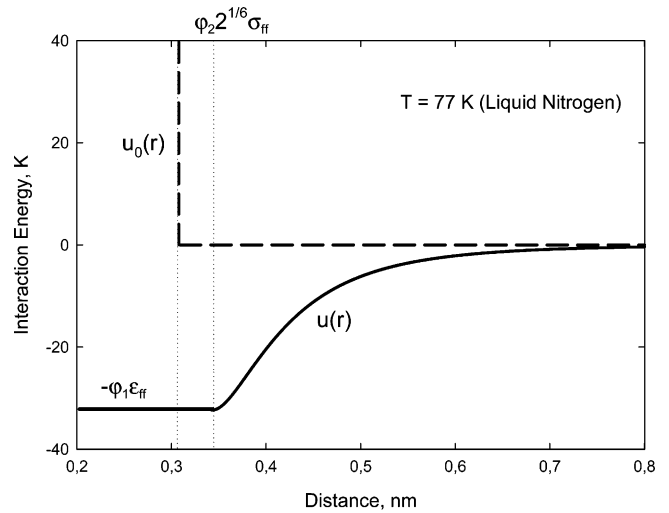

Figure 1. Deconvolution of the FH interaction potential into a part containing all the repulsive forces (dashed line), $u_0(r)$, and a part containing the attractive forces (solid line), $u(r)$.

$$\Phi_{att}(r) =$$
$$\begin{cases} -\varphi_1\epsilon_{ff} & r \leq r_m \\ 4\epsilon_{ff}\left[\left(\frac{\sigma_{ff}}{r}\right)^{12} - \left(\frac{\sigma_{ff}}{r}\right)^{6}\right] + \frac{\zeta}{r^2}\left[\left(\frac{\sigma_{ff}}{r}\right)^{12} - \chi\left(\frac{\sigma_{ff}}{r}\right)^{6}\right] & r_m < r \leq r_c \\ 0 & r > r_c \end{cases}$$
$$(4)$$

where $r_m = \varphi_2 2^{1/6}\sigma_{ff}$, $r_c = 5\sigma_{ff}$, and the two temperature-dependent parameters φ_1 and φ_2 are obtained from an analysis of the position of the minimum in the FH potential. Also note that $\varphi_1 \leq 1$ and $\varphi_2 \geq 1$, and, as one may observe from Figure 1, φ_1 and φ_2 are responsible for scaling both the position and magnitude of the minimum of the FH potential for all hydrogen isotopes. Reducing the influence of quantum effects by increasing the temperature reproduces the deconvolution scheme introduced by Weeks et al.[17] since $\varphi_1 \rightarrow \varphi_2 \rightarrow 1$. At any given temperature of interest, φ_1 and φ_2 can be simply determined by standard numerical methods.

According to the van der Waals approximation, the pressure and chemical potential of a homogeneous quantum fluid can be determined from[10]

$$P(\rho_b) = P_{hs}(\rho_b) + \frac{1}{2}\rho_b^2\int\Phi_{att}(|\vec{r} - \vec{r}'|)d\vec{r} \quad (5)$$

$$\mu(\rho_b) = \mu_{hs}(\rho_b) + \rho_b\int\Phi_{att}(|\vec{r} - \vec{r}'|)d\vec{r} \quad (6)$$

The integral in each of these expressions may be determined using eq 4, which can be solved analytically to give

$$\int\Phi_{att}(|\vec{r} - \vec{r}'|)d\vec{r} = \sum_{i=1}^{5}I_i \quad (7)$$

where the coefficients are defined as follows:

$$I_1 = -\frac{4}{3}\pi\sqrt{2}\varphi_1\epsilon_{ff}\sigma_{ff}^3\varphi_2^3 \quad (8)$$

$$I_2 = \frac{16}{9}\epsilon_{ff}\pi\sigma_{ff}^3\left[3\left(\frac{\sigma_{ff}}{r_c}\right)^3 - \left(\frac{\sigma_{ff}}{r_c}\right)^9\right] \quad (9)$$

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$$I_3 = \frac{16}{9}\epsilon_{ff}\pi\sigma_{ff}^3\varphi_2^{-9}\left[\frac{1 - 6\varphi_2^6}{2\sqrt{2}}\right] \qquad (10)$$

$$I_4 = 4\pi\zeta\sigma_{ff}\left[\frac{1}{5}\chi\left(\frac{\sigma_{ff}}{r_c}\right)^5 - \frac{1}{11}\left(\frac{\sigma_{ff}}{r_c}\right)^{11}\right] \qquad (11)$$

$$I_5 = 4\pi\zeta\sigma_{ff}\varphi_2^{-11}\left[\frac{1}{11}\frac{1}{2^{11/6}} - \frac{\varphi_2^6}{5}\chi\frac{1}{2^{5/6}}\right] \qquad (12)$$

The pressure and chemical potential of a reference system characterized by pure repulsive forces, that is, a hard-sphere fluid, can be computed from the Carnahan−Starling equation of state,[32]

$$P_{hs}(\rho_b) = \rho_b k_B T \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \qquad (13)$$

$$\mu_{hs}(\rho_b) = k_B T\left[\ln(\lambda_B^3\rho_b) + \frac{8\eta - 9\eta^2 + 3\eta^3}{(1 - \eta)^3}\right] \qquad (14)$$

In eqs 13 and 14, $\eta = \pi\rho_b\sigma_{ff}^3/6$ denotes the packing fraction of hard-spheres of size σ_{ff}, and $\lambda_B = h/(2\pi m k_B T)^{1/2}$ is the thermal de Broglie wavelength.

In summary, the present approach, being a combination of the methods of Feynman−Hibbs and Weeks et al. allows the simultaneous description of the equations of state and the variation of chemical potential with pressure for isotopes of any element at moderate pressures and temperatures. For high temperatures, the quantum effects disappear, and the proposed method reproduces the known results provided by the theory of simple fluids.

III. Results and Discussion

A. Simulation Details. According to Gubbins and Quirke,[33] computer simulations are an alternative tool for the estimation of the equation of state for fluids. When the underlying physical situation and the intermolecular potentials are known, computer simulations are a convenient vehicle for extrapolating experimental results to conditions that are difficult to access experimentally. Tritium would appear to be a good example because of its reactivity.[20] In the current work, we used Monte Carlo simulations in the canonical ensemble to obtain the equation of state and the dependence of the chemical potential on pressure for hydrogen, deuterium, and tritium at selected temperatures.[34] Because of their technological importance, we chose five temperatures: 77 K (temperature of liquid nitrogen), 195 K (temperature of dry ice), 273 K (melting point of water), 293 K (room temperature), and 303 K (temperature used in experimental measurements). In the canonical Monte Carlo ensemble simulations, we model the interactions of hydrogen isotopes according to eq 3 with $\sigma_{ff} = 0.2958$ nm and $\epsilon_{ff}/k_B = 36.7$ K. To simulate the bulk properties of hydrogen isotopes, we adopted a cubic simulation box of unit length with periodic boundary conditions in all directions. The number of molecules in all of the MC simulations was 108. In the canonical ensemble, 6×10^4 configurations were generated. We discarded the first 1×10^4 configurations to guarantee equilibration, whereas the latter 3×10^4 configurations were used to obtain the desired thermodynamic properties. For arbitrary selected points, we stored the fluctuations in the total energy. Next, we analyzed the variation of the internal energy to ensure that thermodynamic equilibrium was achieved. During the Monte Carlo simulation,

TABLE 1: Optimized Parameters for the Calculation of the Equations of State for Hydrogen, Deuterium, and Tritium (Eqs 5 and 6)

temperature (K)	pressure range (MPa)	parameter	
		σ_{ff} (Å)	ϵ_{ff}/k_b (K)
77 (liquid nitrogen)	$P < 6$	2.398195	36.688746
194.6 (dry ice)	$P < 10$	2.823009	36.701448
	$P < 20$	2.779135	36.703918
	$P < 40$	2.753677	36.69396
273 (melting point of water)	$P < 10$	2.724697	36.700465
	$P < 20$	2.71788	36.701516
	$P < 40$	2.703775	36.703621
293 (room temperature)	$P < 10$	2.716061	36.700227
	$P < 20$	2.700121	36.701722
	$P < 40$	2.692514	36.703336
303 (measurements)	$P < 10$	2.699777	36.700482
	$P < 20$	2.697533	36.701175
	$P < 40$	2.686159	36.703273

we computed the pressure from the virial theorem corresponding to eq 3. We estimated the excess part of the chemical potential of an isotope according to Widom's particle insertion method,[35] and, using methods described by Frenkel and Smit, we added the tail corrections for the energy and pressure.[36]

B. LJ Parameters for Hydrogen Isotopes. The equations describing the bulk pressure and chemical potential as functions of the density for pure hydrogen isotope fluids should be supplemented with a single set of appropriate parameters, that is, σ_{ff} and ϵ_{ff}.[15] The parameters adopted in the Monte Carlo simulations of hydrogen isotopes, however, cannot be employed in the mean field expressions, eq 5 and 6, because of simplifications introduced into the mean field approach for homogeneous quantum fluids. For proper calibration of the LJ parameters, we define the following functional:

$$\Omega(\rho_b)|_{T=\text{const}} = \frac{1}{3M}\sum_{j=1}^{3}\left[w_1\sum_{i=1}^{M}\sqrt{(P_i^{\text{sim},j} - P_i^{\text{comp},j})^2} + \right.$$
$$\left. (1 - w_1)\sum_{i=1}^{M}\sqrt{(\mu_i^{\text{sim},j} - \mu_i^{\text{comp},j})^2}\right] \quad (15)$$

where $w_1 = 0.5$, M is the number of points, j denotes a given hydrogen isotope (i.e., $j = 1,2,3$ corresponds to H_2, D_2, T_2, respectively), $P_i^{\text{sim},j}$ and $\mu_i^{\text{sim},j}$ are the pressure and chemical potential of the jth isotope in the bulk state computed from Monte Carlo simulations, respectively, and $P_i^{\text{comp},j}$ and $\mu_i^{\text{comp},j}$ are the pressure and chemical potential of the jth isotope in the bulk state computed from eqs 5 and 6, respectively. With the aid of eq 15, our goal is to generate a single pair of LJ parameters σ_{ff} and ϵ_{ff} suitable for use with the mean field equations (eqs 5 and 6), which would provide the same degree of precision in the estimation of both the pressure and the chemical potential as would be obtained if the more rigorous, though computationally demanding, Monte Carlo simulations were employed. The simultaneous description of the pressure and chemical potential of hydrogen isotopes is necessary because of the dependence of the chemical potential upon the thermal de Broglie wavelength (see Table 1S, Supporting Information). As we will show later, the dependences $p = f(\rho_b)$ for hydrogen isotopes at higher temperatures are the same; however, $\mu = f(\rho_b)$ diverges from one hydrogen isotope to another. We have used a real-coded genetic algorithm for solution of the minimization problem given by eq 15.[37]
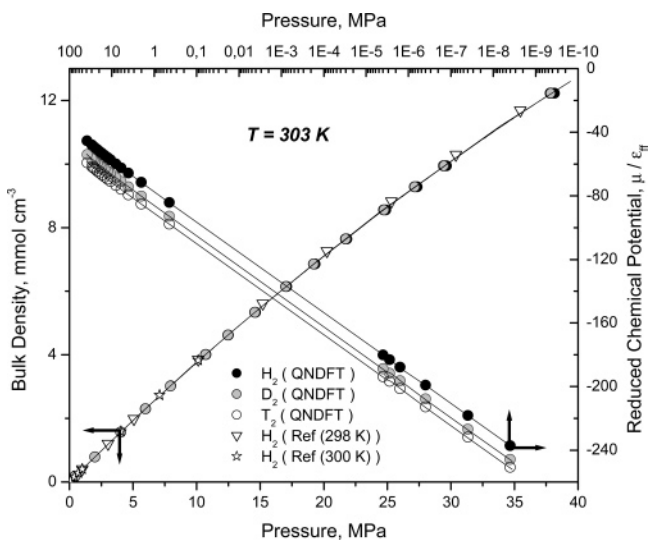
Figure 2. Simultaneous description of the equations of state and the dependence of the chemical potentials on pressure for hydrogen isotopes at 303 K. For comparison, we added experimental equations of state for hydrogen, which are labeled as "Ref".[38]
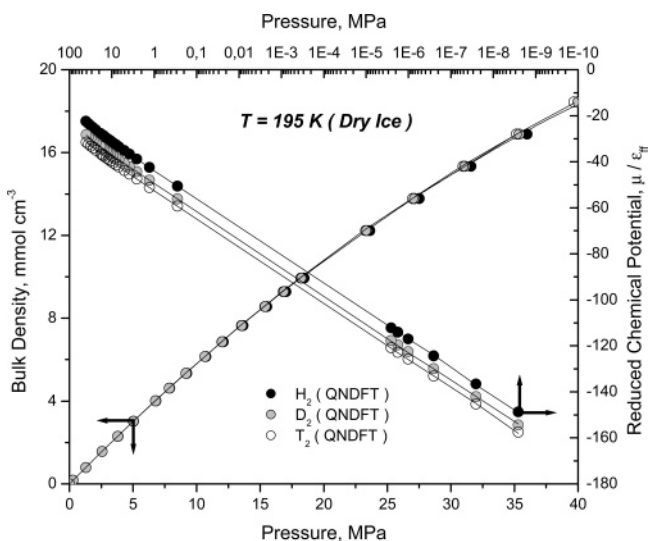

Figure 3. Simultaneous description of the equations of state and the dependence of the chemical potentials on pressure for hydrogen isotopes at 195 K.

TABLE 2: Optimized Parameters for the Calculation of the Equations of State for Hydrogen, Deuterium, and Tritium (Eqs 5 and 6)

			parameter	
temperature (K)	isotope	pressure range (MPa)	σ_{ff} (Å)	ϵ_{ff}/k_b (K)
77 (liquid nitrogen)	hydrogen	< 6	2.074317	36.684471
	deuterium		2.318794	36.686837
	tritium		2.39819	36.688747
	hydrogen	< 10	1.75349	36.651343
	deuterium		2.128009	36.636351
	tritium		2.250168	36.634215

C. The Properties of the Proposed Approach. The key results of the present approach are summarized in Tables 1 and 2. Excluding 77 K, a single set of LJ parameters accurately describes both the equation of state and the variation of the chemical potential with pressure for hydrogen isotopes over a wide range of bulk pressures (see Figures 2 and 3, and
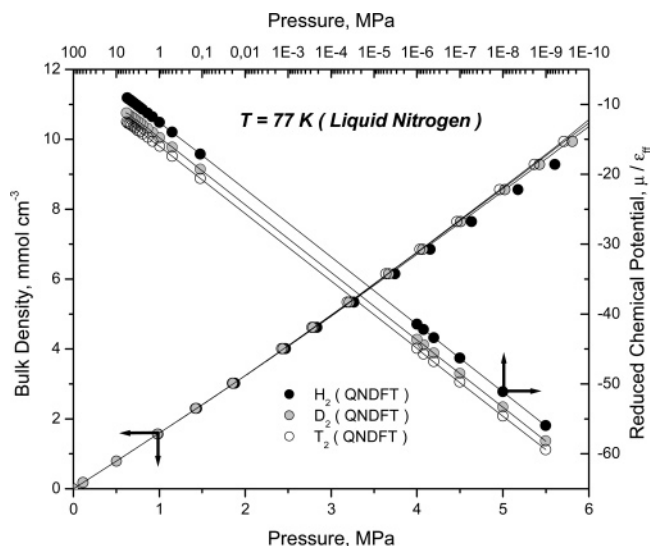

Figure 4. Simultaneous description of the equations of state and the dependence of the chemical potentials on pressure for hydrogen isotopes at 77 K.
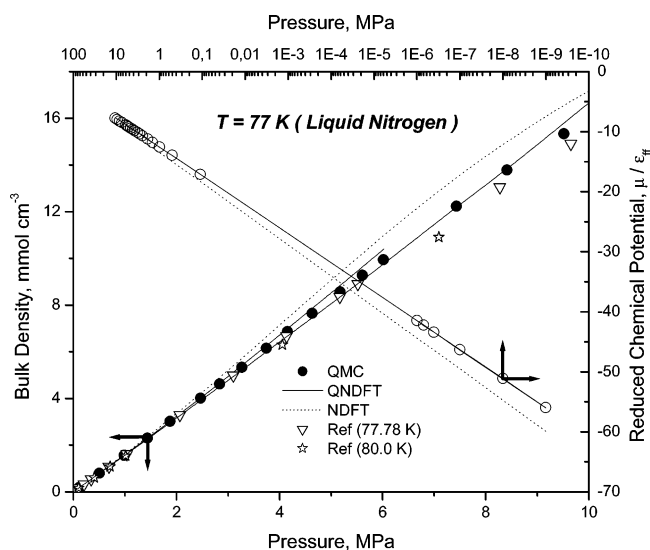

Figure 5. Simultaneous description of the equation of state and the dependence of the chemical potential on pressure for hydrogen at 77 K. Abbreviations: QMC denotes the results of quantum-corrected Monte Carlo simulation; QNDFT denotes the predictions of the proposed method; NDFT denotes the results obtained from the theory of classical simple fluids with parameters suggested by Jagiello et al.;[28,29] and Ref denotes experimental equations of state.[38]

Supporting Information Figures 4S and 5S). Moreover, the LJ parameters slightly depend on the temperature and range of bulk pressure (see Table 1). It is observed that the LJ collision diameter is smaller than the one adopted in the Monte Carlo simulations of hydrogen isotopes, whereas the LJ well depth is almost the same. The slight dependence of the LJ parameters on temperature justifies the deconvolution scheme proposed in the current study. At 77 K, the fitting of both the equation of state and the dependence of chemical potential versus bulk pressure for hydrogen isotopes by a single set of LJ parameters is accurate up to 3 MPa (see Figure 4). For this reason, we have also individually adjusted eqs 5 and 6 for the hydrogen isotopes (see Table 3 and Figure 7S, Supporting Information).

The van der Waals theory of classical fluids adopted by Jagiello et al.[28,29] in their nonlocal density functional theory of inhomogeneous hydrogen cannot describe the equilibrium

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properties of homogeneous hydrogen at 77 K (see Figure 5). At very low pressures of hydrogen (up to 2−3 MPa), the approach described above accurately describes the hydrogen equation of state. However, the dependence of the chemical potential versus bulk pressure of hydrogen is not reproduced. At higher bulk pressures of hydrogen at 77 K, the description of equation of state by the classical scheme is unreliable.

In summary, the proposed method accurately describes the equilibrium properties of hydrogen isotopes. At 77 K and pressures above 3 MPa, we have estimated individual LJ parameters for hydrogen, deuterium, and tritium (see Table 3). Below 3 MPa at 77 K, a single set of LJ parameters can be used for the proper calculation of the equation of state and the dependence of the chemical potential on the density of hydrogen, deuterium, and tritium (see Table 2). For all remaining temperatures investigated in this work, a single set of LJ parameters accurately describes the equilibrium properties of hydrogen isotopes over a wide range of bulk pressures up to 40 MPa (see Table 2). The theory developed here is a starting point for the modeling of inhomogeneous quantum fluids, which is particularly important in the problem of clean energy storage and in the separation of isotopes by quantum sieves.

IV. Conclusion

We present a new method for the prediction of the equilibrium properties of dense gases containing hydrogen isotopes. The proposed approach combines the FH effective potential method and a deconvolution scheme introduced by Weeks et al. Besides its simplicity, the equations developed in this work accurately described both the equation of state and the pressure dependence of the chemical potential for hydrogen, deuterium, and tritium. The present approach should find applications in the nonlocal density functional theory of inhomogeneous quantum fluids and should also be of particular relevance to hydrogen (clean energy) storage and to the separation of quantum isotopes by novel nanomaterials.

Supporting Information Available: The simultaneous description of the equations of state and the dependence of the chemical potentials on pressure for hydrogen isotopes at 273, 293, and 77 K. This information is available free of charge via the Internet at http://pubs.acs.org.

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