Atomic and molecular hydrogen isotopes in liquid helium

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We present a theoretical analysis of the properties of atoms and molecules of hydrogen and its isotopes in liquid ^{4}He. Numerical results on the chemical potentials and on the volume coefficients of these admixtures as functions of the bulk helium density are reported and discussed in detail. The *ab initio* calculations are based on optimized wave functions of Jastrow type and employ realistic hydrogen-helium potentials. The optimization is performed within a standard paired-phonon analysis in conjunction with the hypernetted-chain approximation. The results on chemical potentials and volume coefficients are given from the hypernetted-chain approximation and are supplemented by the results of a variational Monte Carlo procedure. In contrast to the atomic states, diatomic hydrogen, deuterium, and tritium molecules penetrate the helium surface and dissolve into the bulk interior.

I. INTRODUCTION

Recent exciting experiments on spin-polarized gases of atomic hydrogen and deuterium at low temperatures and densities, being higher by several orders of magnitude than those which hitherto could be achieved, have opened a door to the exploration of many new or poorly understood phenomena of interest in diverse areas of physics.[1,2] It is now known experimentally that the interaction of hydrogen with the surface of a confining helium chamber dominates the most important properties of such spin-aligned systems. At present, experimental and theoretical interest is therefore focused on detailed studies of the fate of H, D, and T atoms during and after the recombination process at the helium surface. In particular, we would like to know if hydrogen or one of its isotopes is clustered together with itself, is bound to the helium surface, or if it dissolves into the bulk liquid helium.[3]

In this contribution we address the latter problem, exploring the properties of isotopic hydrogen atoms and molecules sufficiently below the ^{4}He surface where they depend mainly on the local density of the interior liquid. The behavior of the foreign particle in this region is governed by the properties of the chemical potential, replacing one ^{4}He atom in the liquid by one hydrogen atom or molecule. These studies are not only of interest in their own right but also provide valuable information and input data which will be necessary for a more sophisticated treatment of the bound-state problem of one foreign particle at or above the helium surface.[4-7]

Our *ab initio* study is based on a microscopic approach by invoking the variational principle for the expectation value of the ground-state energy with respect to a spatially correlated wave function. The optimization procedure adopted here employs the paired-phonon analysis of homogeneous boson mixtures developed and described in Refs. 8–10. This method improves systematically upon an earlier approach[5,11] where constraint variations with simple parametrized wave functions have been performed. Expectation values are calculated within the hypernetted-chain (HNC) approximation and—in the most interesting cases—by employing an appropriate Monte Carlo algorithm.[12]

The following section summarizes the formal theoretical concept and provides explicit expressions for the chemical potential and the volume coefficient, which are the central quantities of interest. Numerical results on these functions are reported and discussed in the subsequent sections. The behavior of the hydrogen atoms H, D, and T in liquid ^{4}He is described in Sec. III. Section IV is reserved for a detailed report on the results characterizing the properties of the isotopic hydrogen molecules in the ^{4}He liquid interior.

II. FORMALISM

On a microscopic level the behavior of a foreign particle in the presence of a many-body medium such as liquid helium is determined by a Hamiltonian

$$H = H_{11} + H_{12} , \tag{1}$$

where

$$H_{11} = -\frac{\hbar^2}{2m_1} \sum_{i=1}^{N-1} \nabla_i^2 + \sum_{i<j}^{N-1} v_{11}(r_{ij}) \tag{2}$$

is the Hamiltonian of $(N-1)$ ^{4}He atoms with atomic mass $m_1 \equiv m_{He}$ interacting via a pair potential v_{11}. The operator

$$H_{12} = -\frac{\hbar^2}{2m_2} \nabla_N^2 + \sum_{i=1}^{N-1} v_{12}(r_{iN}) \tag{3}$$

represents the kinetic energy of the foreign atom or molecule with mass m_2 and the potential energy of the foreign

particle admixed to $N-1$ helium atoms.

Does a hydrogen atom or molecule dissolve into liquid helium? To answer this question we must construct the spatially correlated ground state which is associated with the Hamiltonians (1)—(3). For a finite number N of particles we may try to do this by employing a Green's-function Monte Carlo algorithm. At present, our calculations will be based on an approximate ground-state wave function of suitable form:

$$\psi = \exp\left[-\frac{1}{2}\sum_{i<j}^{N-1} u_{11}(r_{ij}) - \frac{1}{2}\sum_{i=1}^{N-1} u_{12}(r_{iN})\right] . \qquad (4)$$

We may choose N to be finite or take the thermodynamic limit $N \to \infty$ where the density ρ of the bulk liquid is held constant. In case ansatz (4) is not flexible enough to answer our question with sufficient accuracy we can go one step further and include triple correlation factors in Eq. (4), etc. These additional pieces describe effects caused by backflow ignored in ansatz (4).

The wave function (4) permits differing spatial correlations between like and unlike particles. To determine the optimal functions $u_{11}(r)$ and $u_{12}(r)$ we follow Refs. 8—10. This procedure rests on the variational principle for the ground-state energy $\langle \psi | H | \psi \rangle / \langle \psi | \psi \rangle$ and leads in the thermodynamic limit to a set of two Euler-Lagrange equations for the radial distribution functions $g_{11}(r)$ and $g_{12}(r)$ for like and unlike particles, respectively. Adopting the hypernetted-chain approximation which relates functions $u_{11}(r)$ and $u_{12}(r)$ to $g_{11}(r)$ and $g_{12}(r)$ the Euler-Lagrange equations may be cast into a simple form and solved by standard methods invoking the paired-phonon analysis.

The behavior of hydrogen atoms or molecules in the interior of the ^{4}He liquid is determined by the chemical potential

$$\mu = N(E_i - E_p) . \qquad (5)$$

The quantity NE_p is the energy of N ^{4}He atoms, NE_i is the energy of $(N-1)$ ^{4}He atoms plus one foreign particle. Thus, μ represents the change in energy by replacing one ^{4}He atom of the liquid by one impurity. The energy portions are evaluated as expectation values of the appropriate Hamiltonian (1) with respect to the corresponding optimal wave function of type (4).

In the thermodynamic limit Eq. (5) may be cast into the form[9,10]

$$\mu = \frac{\partial E(\rho,x)}{\partial x}\bigg|_{x=0} = 2(E_{12}-E_{11}) + \frac{\partial E_{11}}{\partial x} . \qquad (6)$$

Here, $E(\rho,x)$ is the expectation value of the energy per particle of the mixture being at density ρ and concentration x of the admixed component. The derivative may be broken down into the energy contributions $(i,j=1, 1$ or $1,2)$

$$E_{ij} = \frac{1}{2}\rho \int v_{ij}^*(r)g_{ij}(r)d\vec{r} ,$$

$$v_{ij}^*(r) = v_{ij}(r) - \frac{\hbar^2}{8}(m_i^{-1}+m_j^{-1})\nabla^2 u_{ij}(r) , \qquad (7)$$

and a term $\partial E_{11}/\partial x$ which represents the energy change

of the background liquid induced by the admixed particle. In terms of the optimal structure functions generated by the paired-phonon procedure[8] in conjunction with the hypernetted-chain approximation the derivative is given by the integral

$$\frac{\partial E_{11}}{\partial x} = \frac{\hbar^2}{8m_1} \frac{1}{(2\pi)^3\rho}$$

$$\times \int (S_{11}-1)[(S_{11}-1)^2 - S_{12}^2]S_{11}^{-2}k^2 d\vec{k} . \qquad (8)$$

A calculation of the chemical potential (6) employing the expressions (7) and (8) neglects the contributions of the so-called elementary diagrams. A standard variational Monte Carlo approach based on ansatz (4) with the optimally determined functions $u_{11}(r)$ and $u_{12}(r)$ as input data permits the avoidance of the above (hypernetted-chain) approximation.[12] With the help of Eq. (5) we may calculate the expectation values E_i, E_p, and μ accurately with an absolute statistical error $\delta\mu = N \times [(\delta E_i)^2 + (\delta E_p)^2]^{1/2}$. As found in an analogous Monte Carlo treatment of the pure ^{4}He system the size effects are very small. There are only insignificant differences between our results for 32 and 64 particle systems.[12]

Ansatz (4) ignores the presence of triple, quadruple, ... spatial correlation factors in the true ground state. To learn something about their importance and influence on the chemical potential we study the properties of the volume coefficient α. This thermodynamic quantity describes the relative increase in volume if we replace one ^{4}He atom in the liquid by one impurity. It may be directly extracted from the optimal structure function via $-\alpha = 1 + S_{12}$ ($k=0$). The exact chemical potential μ and volume coefficient α associated with the true ground-state wave function are related by[13]

$$\frac{\partial\mu}{\partial\rho} = \alpha\dot{X}(0)\rho^{-1} \equiv D(\rho) , \qquad (9)$$

where

$$\dot{X}(0) = \lim_{k\to 0} \hbar^2 k^2/4m_1 S_{11}^2(k) = m_1 c^2 \qquad (10)$$

determines the velocity c of first sound in liquid helium.[9] In general, the expressions on the left- and right-hand sides of Eq. (9) differ from each other if we insert the quantities $\mu(\rho)$ and $D(\rho)$ associated with an approximate ground-state wave function such as ansatz (4). The magnitude and behavior of this deviation may thus provide some indications about the influence of multiparticle correlation factors on the density dependence of the chemical potential μ.

III. RESULTS ON H, D, AND T

An early theoretical discussion of binary mixtures of atomic hydrogen, deuterium, and tritium with helium has been given in Refs. 5, 7, and 11. It was found that the boson systems H-^{4}He and T-^{4}He completely phase separate at zero temperature and H, D, and T atoms do not penetrate the surface of liquid ^{4}He since their chemical potentials are positive.[6]

We study these systems within the improved theoretical

approach summarized in the preceding section. We are particularly interested in studying the density dependence and the sensitivity due to the hydrogen-helium interaction. This interaction is described by a potential of Lennard-Jones form:

$$v_{12}(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] \tag{11}$$

with the parameters $\epsilon = 6.6$ K and $\sigma = 3.2$ Å which has been employed before.[6,10] To represent the He-He interaction we adopt the HFDHE-2 potential of Aziz et al.[14]

Our numerical results on the chemical potential for replacing one ^{4}He atom in the bulk by one H or T atom as a function of density are plotted in Fig. 1. They are derived from Eqs. (6)—(8) with the optimal structure functions as input. These functions are calculated by an iterative paired-phonon procedure yielding results on functions $\mu(\rho)$—within the adopted approximation—with a numerical accuracy of about 2%. The results will only marginally shift if potential (11) with $\epsilon = 6.6$ K and $\sigma = 3.2$ Å is replaced by the more refined hydrogen-helium potential of Ref. 15. To explore the consequences of a rather drastic change in the interaction we have increased the strength of potential (11) from $\epsilon = 6.6$ K to $\epsilon = 8.1$ K. This strength has been recently advocated by Silvera.[3] At a density $\rho = 0.0172$ Å^{-3} we find in this case that the chemical potentials (shown in Fig. 1) are lowered by about 6 to 8 K.

Under the various conditions adopted the chemical potentials (6) are positive and increase rapidly with increasing density. The latter property indicates that it becomes
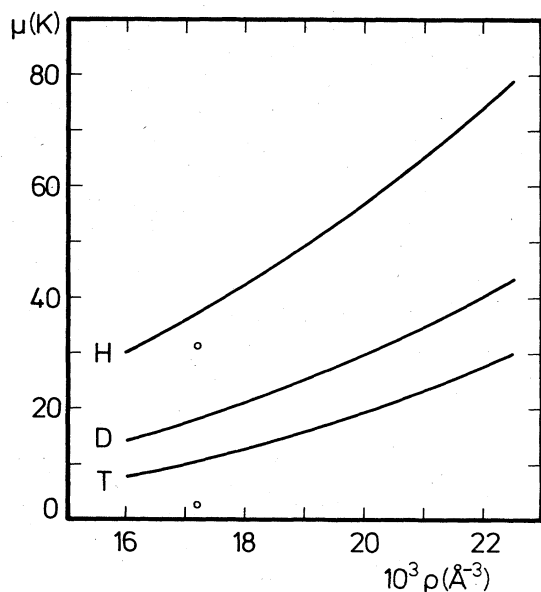
energetically favorable for the hydrogen atoms to reside in regions of low densities. We learn from Fig. 1 that the chemical potentials for H and D atoms are positive and so large that they cannot penetrate the helium surface. The situation might be somewhat more subtle for T atoms if we follow Silvera[3] and assume the hydrogen-helium potential to be strongly attractive $(\epsilon = 8.1$ K). In this case we find a rather weak chemical potential, $\mu \simeq 2.9$ K, at density $\rho = 0.0172$ Å^{-3}. We therefore expect that under these conditions a tritium atom would very much behave like a ^{3}He atom in liquid helium.[16]

Our numerical results on the volume coefficients α as a function of density are depicted in Fig. 2. This quantity is positive at all densities considered, it increases if the density is lowered and becomes singular at about $\rho \simeq 0.016$ Å^{-3}. At this density the optimal ground state (4) of the ^{4}He liquid is unstable against density fluctuations, i.e., quantity $\ddot{X}(0) = m_1 c^2$ vanishes. Calculating function $D(\rho) = \alpha \ddot{X}(0)\rho^{-1}$ from these results we find, for example, in the case of tritium, $D \sim 1000$ K Å^3 at $\rho \simeq 0.017$ Å^{-3} and $D \sim 2000$ K Å^3 at $\rho \simeq 0.021$ Å^{-3}. Evidently, quantity $D(\rho)$ is positive and increases with increasing density. This behavior is consistent with our results on

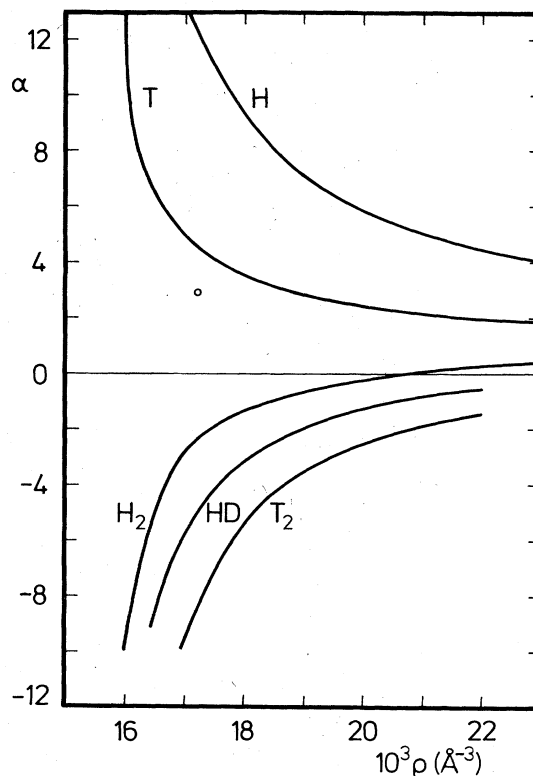FIG. 2. Theoretical volume coefficients α of H and T atoms and H_2, HD, T_2 molecules in liquid helium as a function of ^{4}He density ρ. Results are extracted from the optimal structure functions $S_{12}(k)$ at $k = 0$ associated with ansatz (4) and potentials of form (11) with (i) $\epsilon = 6.6$ K, $\sigma = 3.2$ Å for H, T atoms, (ii) $\epsilon = 15.56$ K, $\sigma = 3.01$ Å for H_2, HD, and T_2 molecules in liquid ^{4}He. The open circle represents the result on coefficient α for T atoms at $\rho = 0.0172$ Å^{-3} if the strength of the T-^{4}He interaction is increased to $\epsilon = 8.1$ K.

FIG. 1. Chemical potential μ for replacing one ^{4}He atom in the liquid at density ρ by one H, D, or T atom. The calculation is based on a hydrogen-helium potential (11) with parameters $\epsilon = 6.6$ K and $\sigma = 3.2$ Å employing ansatz (4) and Eqs. (6)—(8) with optimally determined structure functions as input. Open circles at $\rho = 0.0172$ Å^{-3} indicate the shift in energy for H and T atoms if the well depth of the hydrogen-helium potential is increased to $\epsilon = 8.1$ K.

the slope of the chemical potential $\mu(\rho)$ which may be taken from Fig. 1. A crude numerical estimate of the derivative $\partial\mu/\partial\rho$ yields, indeed, positive values of the same order of magnitude but they are roughly twice as large as the corresponding results on quantity $D(\rho)$. As discussed in Sec. II this quantitative discrepancy must be caused by neglecting the elementary contributions to the expectation values in question and, in particular, by omitting the multiparticle correlation factors in ansatz (4). We expect that these effects will presumably shift the above numerical results on the chemical potentials to somewhat smaller values. However, we do not believe that such more refined (but rather elaborate) calculations will lead to a substantial or qualitative change of the picture drawn above. Since H, D, and T atoms do not dissolve into the liquid interior it is—in a next step of exploration—much more warranted to study the surface bound states of these atoms within a version of the present theory which is adapted to treat inhomogeneous mixtures.

IV. NUMERICAL RESULTS ON MOLECULES

Recently, Silvera reported on results of an experiment which provides direct evidence that hydrogen after recombination to the molecular state penetrates the surface of liquid ^{4}He either in the form of single molecules or molecular clusters.[3] Before attacking the more complex problem of an H_2 molecular surface state we concentrate on a theoretical study of diatomic molecules such as H_2, D_2, T_2 and HD, HT, DT in the helium liquid interior.

The exploration is based on the formalism of Sec. II. The interaction between one ^{4}He atom and one hydrogen molecule is described by the Lennard-Jones potential (11) adopting the parameters[17] $\epsilon=15.56$ K and $\sigma=3.01$ Å. The optimal structure functions needed for expressions (6)—(10) are generated by an iterative paired-phonon procedure.[8] They are employed for calculating the associated chemical potential μ, the volume coefficient α and quantity D at various densities ρ and isotopic masses m_2. Figure 3 depicts an isochore of the energy μ as a function of the mass ratio m_2/m_{He}. Except at very small hypothetical masses $(2m_2 < m_{He})$ the chemical potential is negative at experimental saturation density, $\rho=0.021\,85$ Å^{-3}, and decreases monotonically with increasing molecular mass. Consequently, hydrogen molecules penetrate—in contrast to the atoms—the surface of liquid ^{4}He and tend to dissolve into the interior.

To determine the contributions of elementary diagrams neglected in the hypernetted-chain results the same quantity is calculated from Eq. (5) within the variational Monte Carlo (VMC) approach. With the optimal functions $u_{11}(r)$ and $u_{12}(r)$ as input data the standard Monte Carlo procedure yields a chemical potential fitted by curve VMC in Fig. 3. It represents the results of a least-mean-square fit to the Monte Carlo data which are calculated with an absolute statistical accuracy of $\delta\mu\simeq0.9$ K. It is very gratifying that the elementary contributions (difference between curve HNC and curve VMC) yield only small corrections to the hypernetted-chain results. They are negative thus supporting the tendency of the molecules to dissolve into the liquid.
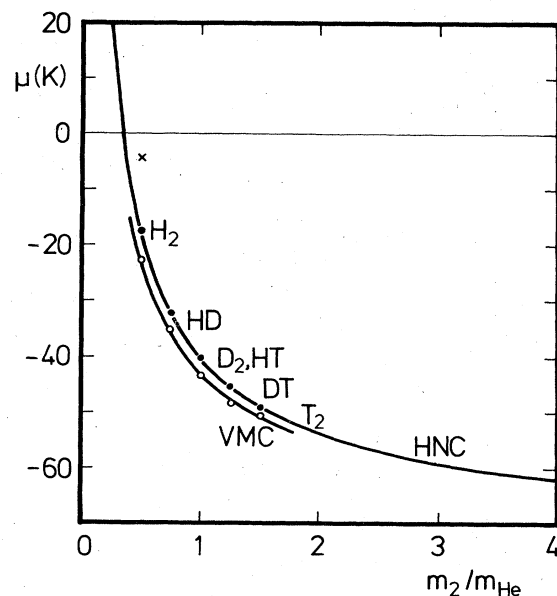

FIG. 3. Chemical potential μ for replacing one ^{4}He atom in liquid helium at density $\rho=0.021\,85$ Å^{-3} by one diatomic hydrogen molecule as a function of the isotopic mass ratio m_2/m_{He}. Curve HNC represents the optimized hypernetted-chain results and curve VMC depicts a least-mean-square fit of the associated variational Monte Carlo results (open circles). The interaction between a molecule and an ^{4}He atom is described by Eq. (11) with $\epsilon=15.56$ K and $\sigma=3.01$ Å. The cross indicates the energy shift for a H_2 molecule if the parameters are changed to $\epsilon=13.34$ K and $\sigma=3.03$ Å.

To study the penetration process of the various molecules in more detail we plot our numerical results on the chemical potentials for H_2, HD, and T_2 versus density ρ (Fig. 4). The energies μ, in hypernetted-chain approximation, are negative at all densities considered and the heavier molecules are more strongly bound to the liquid than the lighter ones. With increasing density the chemical potential of H_2 increases slightly, that of HD has an extremely flat minimum and the T_2 chemical potential decreases monotonically. Obviously, T_2 is tightly bound and dissolves into the liquid interior. The results on H_2 and HD seem to indicate that these molecules prefer to reside at liquid densities below saturation. However, the energy variation over the range of densities considered is relatively small and comparable in size with the magnitude of the elementary contributions to the chemical potentials of H_2 and HD found above at saturation density (see Fig. 3 and open circles in Fig. 4 at $\rho=0.021\,85$ Å^{-3}). For this reason we extend the Monte Carlo calculation on H_2 from saturation density to lower densities. These Monte Carlo data are also shown by open circles in Fig. 4. Curve VMC represents a least-mean-square fit to these data. As expected the magnitude of the elementary contributions is small everywhere and decreases by lowering the density. We believe that the elementary portions to the HD and T_2 potentials have a similar dependence. The Monte Carlo result at $\rho=0.021\,85$ Å^{-3} then indicates that the T_2 chemical potential is very well approximated by the hypernetted-chain result. In the case of HD molecules we

expect that the flat minimum in the hypernetted-chain result on quantiy μ disappears if the elementary pieces are included. We are therefore convinced that HD as well as all heavier molecules dissolve entirely into the liquid interior. The H_2 molecule is the most interesting system. The Monte Carlo results on its chemical potential μ show a shallow minimum at density $\rho \simeq 0.018$ Å^{-3}. Provided ansatz (4) is sufficiently accurate the behavior suggests that H_2 molecules penetrate the surface of the liquid but might tend to reside in regions of densities below saturation.

We stress that the above discussion rests on the assumption (4). We further point out that the chemical potential of H_2 molecules is rather sensitive to changes in the strength of the H_2-^4He interaction. To demonstrate this feature we calculate the chemical potential at $\rho = 0.02185$ Å^{-3} assuming a test potential (11) with $\epsilon = 13.34$ K and $\sigma = 3.03$ Å. This choice has been adopted by Silvera[3] to simulate a more precise H_2-^4He potential.[18] The calculated shift in energy is about $+14$ K. It might be surprising that such an increase is caused by a change of 2 K in the potential well depth. However, expression (7) which determines the energy portion E_{12} involves the potential v_{12} as well as the optimal radial distribution function $g_{12}(r)$. An increase in the strength of the potential generates a larger overshoot in function $g_{12}(r)$ and both effects contribute coherently to the integral (7). The same feature has been observed in the case of an ^3He impurity in liquid helium.[16]

Our numerical results on the volume coefficients of the molecules H_2, HD, and T_2 as functions of density are plotted in Fig. 2. The coefficients for T_2 and HD molecules are negative at all densities considered. Consequently, quantity $D = \alpha \dot{X}(0)\rho^{-1}$ has the same property which is in qualitative agreement with the (Monte Carlo) results on the density dependence of the T_2 (and HD) chemical potentials which have a negative slope, $\partial \mu / \partial \rho < 0$. The volume coefficient for the H_2 molecule is negative at densities $\rho \lesssim 0.021$ Å^{-3} and positive for higher densities. The behavior is in qualitative accord with the existence of a minimum in the variational Monte Carlo results on the chemical potential. This consistency suggests that the minimum is not merely an artifact of approximation (4).

However, deviations from the equality (9) are apparent. Between the densities $\rho = 0.017$ Å^{-3} and $\rho = 0.020$ Å^{-3} the slope of the T_2 curve in Fig. 4 gives roughly $\partial \mu / \partial \rho \sim 1000$ KÅ^3. The value differs from the corresponding result on D in the average by a factor of about 1.9. Similarly, for H_2 molecules function $D(\rho)$ has its zero at density $\rho \sim 0.021$ Å^{-3} whereas the minimum in the chemical potential $\mu(\rho)$ appears at the lower density
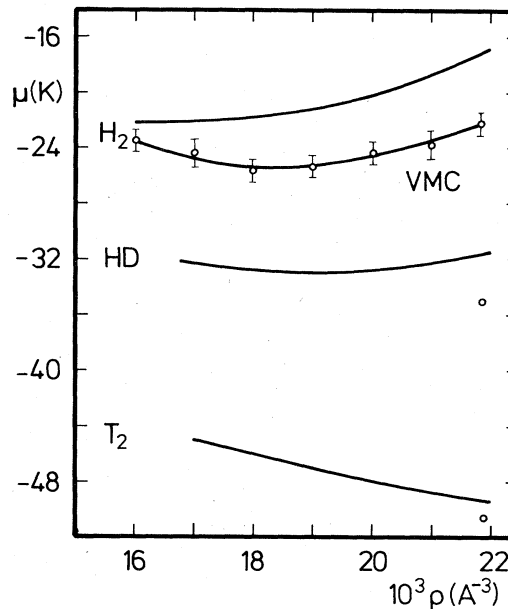

FIG. 4. Chemical potential μ for replacing one ^4He atom in the liquid by one hydrogen molecule plotted versus density ρ. The solid lines represent the optimal hypernetted-chain results on H_2, HD, and T_2, the open circles indicate the corresponding variational Monte Carlo results, and curve VMC depicts the least-mean-square fit to the H_2 Monte Carlo data. The hydrogen-helium potential is described by form (11) with $\epsilon = 15.56$ K and $\sigma = 3.01$ Å.

$\rho \sim 0.018$ Å^{-3}. These quantitative discrepancies are evidently generated by neglecting the triple, quadruple, . . . correlation factors in ansatz (4). Thus, we should be aware that inclusion of these multiparticle correlation factors will correct the detailed dependence of the approximate chemical potentials. However, we strongly believe that these backflow corrections will not lead to significant changes in the magnitude and the gross features of the variational results based on ansatz (4).

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