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Diffusion of hydrogen atoms in helium gas and helium atoms in hydrogen gas

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The potential of Meyer and Frommhold describing the interaction between hydrogen and helium atoms is used to calculate the diffusion coefficients of hydrogen atoms in helium gas and helium atoms in hydrogen gas as functions of temperature, taking into account higher-order corrections of transport theory. Comparison with experiment suggests that the interaction potential should be steepened at small nuclear separations. Calculations of the diffusion coefficients for temperatures between zero and 1000 K with the modified potential are reported. The corresponding H-He scattering length resulting from the zero-temperature value of the diffusion coefficients has the magnitude $0.359a_0$. Direct calculation shows it to be negative.

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I. INTRODUCTION

Considerable attention has been given to the construction of the interaction potential of hydrogen and helium atoms. The most sophisticated *ab initio* calculation is that of Meyer and Frommhold [1] who conducted a study of the resulting hyperfine pressure shift and collision-induced infrared absorption. Meyer and Frommhold obtained good agreement with experiment except at very low temperatures. A measurement of the diffusion coefficient D of hydrogen atoms in helium gas at 1 K was made by Hardy *et al.* [2]. It was interpreted by Jochemsen, Berlinsky, and Hardy [3] who explored the accuracy of several interaction potentials by calculating the corresponding diffusion coefficients in the temperature range between 0.5 K and 2.5 K.

There have been several measurements of D for hydrogen atoms in helium gas at higher temperatures [4–6] that can also be used to assess the accuracy of the potentials [6].

The values of D are useful in a variety of contexts [2,6,7]. We calculate the diffusion coefficients of H in He and He in H as functions of temperature. We find that after a slight modification the interatomic potential of Meyer and Frommhold [1] yields diffusion coefficients of H in He that are consistent with measurements at 1 K [2], 273 K [5], and 333 K [6]. We include higher-order corrections in the expression for the diffusion coefficient and we present results over the temperature range from zero temperature to 1000 K. We discuss the zero-temperature limit and derive the magnitude of the scattering length for H-He collisions from the diffusion coefficient as $0.359a_0$.

II. THEORY

According to the Chapman-Enskog theory [7], if n_1 and n_2 are the number densities of particles 1 and 2, respectively, and M_1 and M_2 are their masses, the diffusion coefficient D can be written in terms of the collision integral $\Omega_{(1,1)}$ in the form

$$D=\frac{3kT}{16\mu(n_1+n_2)}\,\frac{1+\varepsilon_0}{\Omega_{(1,1)}},$$

where μ is the reduced mass $M_1M_2/(M_1+M_2)$ and ε_0 is a correction factor which is usually neglected. Collision integrals $\Omega_{(l,s)}$ are defined by

$$\Omega_{(l,s)}=\left(\frac{kT}{2\pi\mu}\right)^{1/2}\int_0^\infty \exp(-\gamma^2)\,\gamma^{2s+3}Q_l(v)\,d\gamma,$$

where v is the relative velocity, $\gamma^2=\mu v^2/2kT$ and $Q_l(v)$ are elastic collision cross sections. To evaluate D, we need $Q_1(v)$ and $Q_2(v)$. They may be expressed in terms of the elastic scattering phase shifts η_l corresponding to orbital angular-momentum quantum number l as

$$Q_1=\frac{4\pi}{k^2}\sum_{l=0}^{\infty}(l+1)\sin^2(\eta_{l+1}-\eta_l)$$

and

$$Q_2=\frac{4\pi}{k^2}\sum_{l=0}^{\infty}\frac{(l+1)(l+2)}{(2l+3)}\sin^2(\eta_{l+2}-\eta_l),$$

where $k=\mu v/\hbar$ is the wave number. For the case $n_1\gg n_2$, the correction factor ε_0 is given by Chapman and Cowling [8] as

$$\varepsilon_0=5(C-1)^2\{5-4B+6(M_1/M_2)^2+8A(M_1/M_2)\}^{-1},$$

where A, B, and C are the ratios

$$A=\Omega_{(2,2)}/5\Omega_{(1,1)},$$
$$B=(5\Omega_{(1,2)})-\Omega_{(1,3)})/5\Omega_{(1,1)},$$
$$C=2\Omega_{(1,2)}/5\Omega_{(1,1)}.$$

The phase shifts are determined from the asymptotic solutions of the partial-wave equations

$$\frac{d^2}{dR^2}f_l(R)+\left(k^2-2\mu V-\frac{l(l+1)}{R^2}\right)f_l(R)=0,$$

where $V(R)$ is the interaction potential, $f_l(R)$ behaves asymptotically as

TABLE I. Diffusion coefficient of H in ^{4}He gas.

Experiment $T(k)$	1	273	333
[1]	$3.2(2)\times10^{-4}$		
[5]		1.86(19)	
[4]		2.38	
[6]			2.42(7)
Theory			
a	3.47×10^{-4}	1.97	2.78
b	3.1×10^{-4}	1.97	2.75
c	3.21×10^{-4}	1.78	2.50

[a] Meyer-Frommhold potential [1].
[b] Jochemsen *et al.* [3].
[c] Modified potential.

$$f_l(R)\sim\sin\left(kR-\frac{1}{2}l\pi+\eta_l\right)$$

and all quantities are expressed in atomic units.

III. CALCULATIONS

We initially adopted the interaction potential of Meyer and Frommhold [1] and we computed the diffusion coefficient of H atoms in helium gas at temperatures of 1 K, 273 K, and 333 K at which measurements have been made [2,4–6]. Hardy *et al.* [2] gave their measurement in the form of an effective diffusion cross section of (20 ± 1)Å^2 at 1 K which translates to a diffusion coefficient of $(3.2\pm0.2)\times10^{-4}$ cm^2 s^{-1}. A comparison of the experimental and theoretical values of D at standard pressure is presented in Table I. We include in Table I the values derived from the semiempirical potential recommended by Jochemsen *et al.* [3] in their discussion of diffusion at very low temperatures. Their potential reproduces the value measured at 1 K [2] but according to Redsun and Knize [6] it yields a value of 2.75 at 333 K, significantly larger than the measured value of 2.42. A similar discrepancy occurs with the Meyer-Frommhold potential. Some modification of the potentials appears to be required. Considerable care was exercised in the construction of the potential-energy curves at large separations [1] and the dispersion component that dominates asymptotically is of high precision [8–10]. We explored the effects of changes in the repulsive wall of the potential. A steepening of the potential at small separations led to the third set of theoretical values of D given in Table I. The agreement between theory and experiment at the three temperatures is now satisfactory apart from the early measurement of Khouw *et al.* [4] at 273 K which appears to be too large. In Fig. 1 we compare the three potentials. The differences are not large. The empirical potential that we have constructed is not unique but it does lead to much better agreement between theory and experiment for the diffusion coefficients. Meyer and Frommhold [1] calculated the hyperfine pressure shift of H atoms in a buffer gas of helium and obtained good agreement with experiment except at temperatures near 1 K. It would be instructive to repeat their calculations with our modification of their potential. The original Meyer-Frommhold potential and the modified potential are listed in Table II. For $R\geqslant6a_0$, we made no changes.

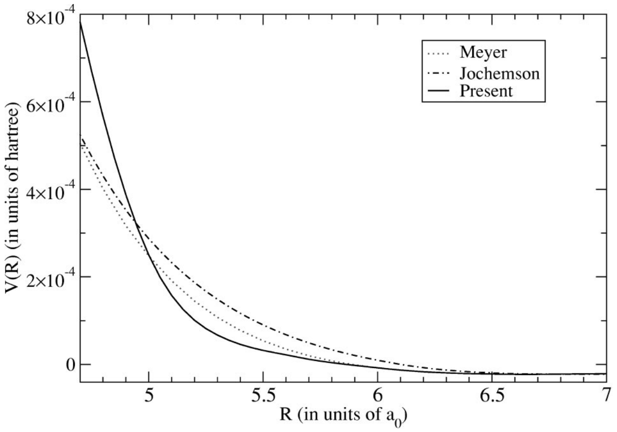

FIG. 1. Energy showing comparisons of repulsive parts of potentials, by Meyer and Frommhold [1], by Jochemsen *et al.* [3], and present work.

IV. CORRECTIONS TO THE DIFFUSION COEFFICIENT

The values of D given in Table I include the correction ε_0 in expression (1). The values of the correction factors ε_0 for H in He and for He in H calculated with the modified potential are presented in Table III together with the corresponding values of D for temperatures ranging from zero to 1000 K. The tabulated diffusion coefficients for both H and He and He in H can be reproduced to within an error of 2% for $T>273$ K by the expression

$$D=1.032\times10^{-4}T^{1.74}\ \text{cm}^2\ \text{s}^{-1}.$$

The correction factor ε_0 for H in He equals 0.054 at zero temperature, passes through a maximum of 0.53 at 0.1 K and decreases to 0.009 at 1000 K. The correction factor for helium atoms in hydrogen gas is 1.8×10^{-3} at zero temperature and at no temperature does it exceed 0.05. The correction factors depend on the ratios of elastic cross sections and are relatively insensitive to the interaction potential. At temperatures near 1 K, our values of ε_0 for H in He gas are similar

TABLE II. Meyer-Frommhold (MF) and modified potentials (the two potentials are identical for $R\geqslant6a_0$) in microhartrees.

	V(R)	
R (units of a_0)	MF	Modified
4.0	2145.88	3258.62
4.5	782.29	1308.02
5.0	247.78	250.00
5.3	107.47	67.09
5.5	53.92	32.00
5.6	34.85	21.84
5.7	19.72	11.72
5.8	7.96	3.96
5.9	−1.02	−2.2
6.0	−7.83	−7.83

TABLE III. Diffusion coefficients and correction factors. Numbers in brackets represent powers of 10.

	H in He gas		He in H gas	
T (K)	D ($\mathrm{cm^2\,s^{-1}}$)	ε_0	D ($\mathrm{cm^2\,s^{-1}}$)	ε_0
0	0	0.054	0	0.002
1×10^{-4}	1.52[−8]	0.053	1.45[−8]	0.002
5×10^{-4}	1.74[−7]	0.049	1.66[−7]	0.002
1×10^{-3}	5.04[−7]	0.043	4.84[−7]	0.001
5×10^{-3}	7.04[−6]	0.009	6.98[−6]	0.000
1×10^{-2}	2.69[−5]	0.002	2.68[−5]	0.000
5×10^{-2}	3.18[−4]	0.502	2.22[−4]	0.049
0.1	2.05[−4]	0.533	1.39[−4]	0.043
0.5	1.95[−4]	0.297	1.52[−4]	0.013
1.0	3.21[−4]	0.163	2.78[−4]	0.006
5	2.71[−3]	0.045	2.60[−3]	0.001
10	7.99[−3]	0.037	7.71[−3]	0.001
50	1.07[−1]	0.029	1.04[−1]	0.001
100	3.35[−1]	0.027	3.27[−1]	0.001
273	1.78	0.021	1.75	0.001
333	2.50	0.019	2.45	0.001
500	5.03	0.014	4.96	0.000
1000	17.2	0.009	17.0	0.000

to those of Jochemsen *et al.* [3] who drew attention to the need to include the ε_0 in evaluating D at low temperatures.

V. LOW TEMPERATURES

The diffusion cross section is illustrated in Fig. 2 as a function of energy. After passing through a minimum near 10^{-5} eV it increases to a maximum at a relative energy $E=4.2\times10^{-4}$ eV. The diffusion coefficients at temperatures between 0.025 K and 0.25 K reflect the rapid change in $Q_1(E)$ around 10^{-5} eV, as do the correction factors ε_0.

In the limit of zero temperatures, only the s wave contributes to the cross sections. Q_1 tends to $4\pi a^2$ and Q_2 to $8\pi a^2/3$, where a is the scattering length defined by

$$\lim_{k\to0}\tan\eta_0=-ka.$$

The parameters A, B, and C are independent of a in the limit of zero temperature and become equal, respectively, to 2/5, 3/5, and 6/5. Thus ε_0 tends to 0.054 for H in He gas and to 0.002 for He in H gas.

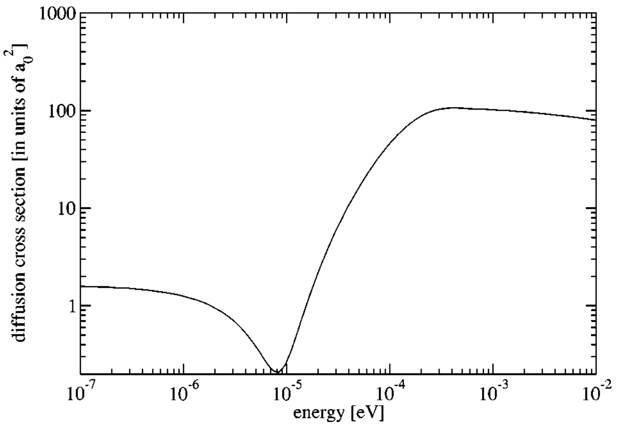

FIG. 2. The diffusion cross section as a function of energy shows that maximum and minimum values occur approximately at $E=4.3\times10^{-4}$ eV and $E=8\times10^{-5}$ eV, respectively.

The diffusion coefficients take the limiting forms

$$D=(1.12\times10^{20}T^{1/2}/n)\ \mathrm{cm^2\,s^{-1}}$$

for H in He gas and

$$D=(1.06\times10^{20}T^{1/2}/n)\ \mathrm{cm^2\,s^{-1}}$$

for He in H gas, where T is in K. The magnitude of the scattering length $a=0.359a_0$ may be derived from either expression. Our calculations of the s phase shift show a to be negative.

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