Measurement of Pressure of Gaseous H↓: Adsorption Energies and Surface Recombination Rates on Helium

A. P. M. Matthey, J. T. M. Walraven, and Isaac F. Silvera

Natuurkundig Laboratorium, Universiteit van Amsterdam, 1018-XE Amsterdam, The Netherlands

Pressure decay measurements are used to study adsorption and recombination of atomic hydrogen on liquid helium surfaces below 1 K. Recombination is suppressed by five orders of magnitude by applying a 10-T magnetic field. The surface–recombination–rate constant (K_s) and the adsorption energy (ϵ_a) of H↓ on ^{4}He are $K_s B^2/T^{1/2} = (2.6 \pm 0.8) \times 10^{-7}$ cm^2 T^2 K$^{-1/2}$ sec^{-1} and $\epsilon_a/k_B = 0.89 \pm 0.07$ K. An estimate of $\epsilon_a/k_B = 0.59$ K is obtained for H↓ on a dilute ^{3}He-^{4}He mixture.

We have recently shown that atomic hydrogen can be stabilized for periods of hours in a low-temperature cell when all surfaces are covered with a superfluid film of ^{4}He.[1,2] It has subsequently been created in three other laboratories.[3-5] In a magnetic field B the hydrogen is spin polarized and referred to as H↓. H↓ is predicted to undergo Bose-Einstein condensation (BEC) if sufficiently high densities can be achieved.[6] However, processes which limit the highest densities[2,3] of H↓ have not been identified. In this Letter, we provide the first experimental proof that magnetic fields stabilize H↓ against recombination to H$_2$. We show surface recombination to be the dominant recombination process in our system. We also measure the adsorption energy of H↓ on ^{4}He finding $\epsilon_a/K_B = 0.89 \pm 0.07$ K. This is consistent with the theoretical estimate of Mantz and Edwards[7] and with very recent zero-field measurements of Morrow *et al.*[8]

The large value of ϵ_a combined with surface recombination rates create a serious barrier against achieving conditions for BEC. Measurements with a very dilute ^{3}He-^{4}He surface coverage yield a significant and promising reduction of ϵ_a. Although H↓ is predicted to be the only elemental material that remains a gas[6] at $T = 0$ K, there have only been indirect determinations of its state. We have directly measured the pressure, p, of H↓ using a sensitive capacitance manometer providing the most direct evidence that H↓ is a gas for $T \gtrsim 0.27$ K, our lowest accessible temperature. For densities studied, $n_g \lesssim 1 \times 10^{16}$ atoms/ cm^3, we have shown that H↓ behaves as a perfect gas, i.e., $p = n_g k_B T$.

The experimental techniques have been described in some detail elsewhere.[1,2] Here we shall give a brief description with detail of new developments. Atomic hydrogen from a microwave discharge flows via a tube into a cell at

temperatures as low as 0.27 K in which all surfaces are covered with superfluid ^{4}He. The cell is in the center of a solenoidal magnetic field of maximum value 11 T which serves to polarize the hydrogen and confine it in the cell by magnetic compression. The H↓ is further confined by a helium vapor compressor (HEVAC) located in the fill tube. In earlier experiments the H↓ was detected by a bolometric technique: simple and extremely sensitive but with the disadvantage that it destroys the sample, resulting in tedious time-consuming measurements. We have now developed a sensitive capacitance manometer which measures the pressure of H↓ and is nondestructive. The gauge, which is an integral part of the sample cell, is shown in Fig. 1(a). The flexible membrane is a 12.5-μm-thick gold-plated Kapton sheet attached with Stycast-1266 epoxy. The capacitance was measured with an ac bridge and calibrated at low temperature against a Barocell pressure gauge with use of ^{4}He gas. The manometer would normally measure the pressure due to H↓ and ^{4}He in the chamber. A superleak connecting the vacuum side of the membrane to the H↓ side equalized the ^{4}He pressure, so only the H↓ pressure was measured. This could also serve as a detector of superfluidity in H↓ if it occurs. The sensitivity of the manometer was measured to be 11.1 pF/Torr with a minimum detectable pressure of 10^{-6} Torr corresponding to a resolution $\Delta c/c = 1.7 \times 10^{-7}$. A bolometer detector is also built into the cell to destroy the H↓ in establishing the capacitance base line. The cell has a volume $V = 1.7$ cm^3 and an area $A = 32$ cm^2.

Our current experimental objectives are to study the properties of H↓ in contact with helium surfaces and in high magnetic fields to understand the limitations and conditions for achieving the higher densities required for BEC and superfluidity of this Bose gas. The highest densities
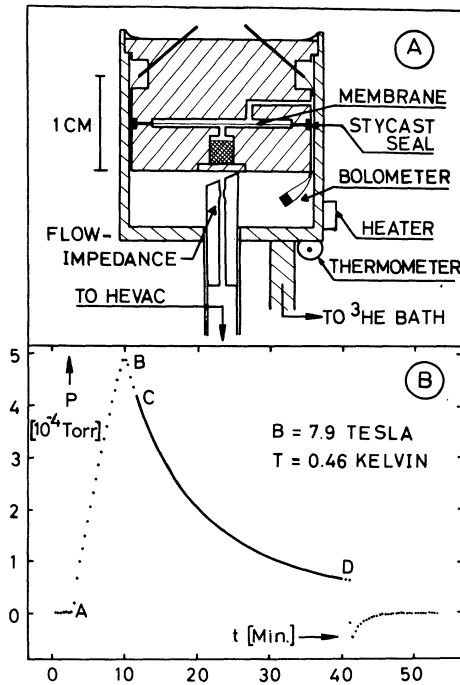
FIG. 1. (a) Schematic drawing of pressure gauge in stabilization cell. (b) Typical experimental run showing buildup and decay of pressure; for discussion, see text.

currently achieved are $10^{16}-10^{17}$ atoms/cm^3.[2,3] The critical temperature for BEC in a noninteracting Bose gas is $T_c = 3.31\hbar^2(n_g/g)^{2/3}/mk_B$ where g is the spin degeneracy. For $g=1$ and $n_g=10^{17}$ atoms/cm^3, $T_c = 3.5$ mK. Densities one to two orders of magnitude higher will be required to observe BEC in the more easily accessible 50-mK range. Limitations on the buildup of density can be determined by studying the decay of the density. An isothermal study of the temporal decay of pressure provides the decay of the density which obeys the approximate rate equation[9]

$$dn_g/dt = -(n_g/\tau) - K_v n_g^3$$
$$-(A/V)K_s n_s^2 + \varphi/V. \qquad (1)$$

Here the first term represents the loss due to thermal escape of atoms out of an open ended cell with time constant[2,3,10] τ; the second and third are volume and surface recombination loss, with rate constants K_v and K_s, respectively. n_s is the surface density and φ is the incoming flux. We assume $N = N_g + N_s \simeq N_g$. A careful study of the pressure decay will provide the rate constants and allow an estimate of the maximum attainable densities. Recently two of us[9] have shown that the

density of D↓ which also obeys Eq. (1) is limited by surface recombination. For low densities the surface adsorption isotherm[11,12] is $n_s = n_g \lambda \exp(\epsilon_a/k_B T)$, where $\lambda = (2\pi\hbar^2/mk_B T)^{1/2}$ is the thermal de Broglie wavelength. After substituting this n_s into Eq. (1), the third term becomes $K_s^{\text{eff}} n_g^2$, with $K_s^{\text{eff}} \equiv K_s(A/V)\lambda^2 \exp(2\epsilon_a/k_B T)$.[13] A measurement of K_s^{eff} as a function of temperature was used to determine ϵ_a for D↓ on ^{4}He. The density limiting processes in H↓ could not be identified in a similar manner, since the bolometric detection technique, used earlier in Ref. 9, is not well suited to study the slow decay processes observed in this system. The development of the capacitance pressure gauge has allowed such a study. By choosing A/V large, T sufficiently small, and B sufficiently high, the volume recombination term can be rendered negligible at moderate densities.

A typical pressure fill-decay plot is shown in Fig. 1(b). The cell is filled for a period of 5–10 min with H↓ starting at point A. At point B the discharge is turned off and the cell cools to point C where it is then stabilized in temperature to within 1 mK. The pressure decay is then observed for periods up to 1 h to point D where the remaining H↓ is destroyed with the bolometer. The data are sampled with a Nicolet-1174 transient recorder and transmitted to a PDP/11 computer. It is fitted to a combined first- and second-order decay process using a nonlinear least-squares fitting procedure to a function of the form

$$p(t) = \frac{p(0)\exp(C_1 t)}{1 + [1 - \exp(C_1 t)]p(0)C_2/C_1},$$

where C_1 and C_2 are the first- and second-order rate constants. With use of $p = n_g k_B T$, the density decay constants $1/\tau$ and K_s^{eff} are calculated. No evidence was found for the presence of a significant third-order term. Separate measurements were made to establish that $p \propto N$, by using the bolometric technique to measure N, and that $p \propto T$. The latter relationship was less accurately established, because of uncertainties in the temperature dependence of the density in our system.[10] The constants were determined as a function of temperature for $0.34 < T < 0.54$ K at $B = 7.9$ T and magnetic field for $5 < B < 10$ T at $T = 0.385$ K.

To determine ϵ_a for H↓ on ^{4}He we plot $K_s^{\text{eff}} T^{1/2}$ vs $1/T$ as shown in Fig. 2(a). The factor $T^{1/2}$ arises from the T^{-1} dependence of λ^2 and the $T^{1/2}$ dependence expected for K_s.[9] This has been established by Morrow et al.,[8] who measured ϵ_a by two independent techniques: decay of the density,
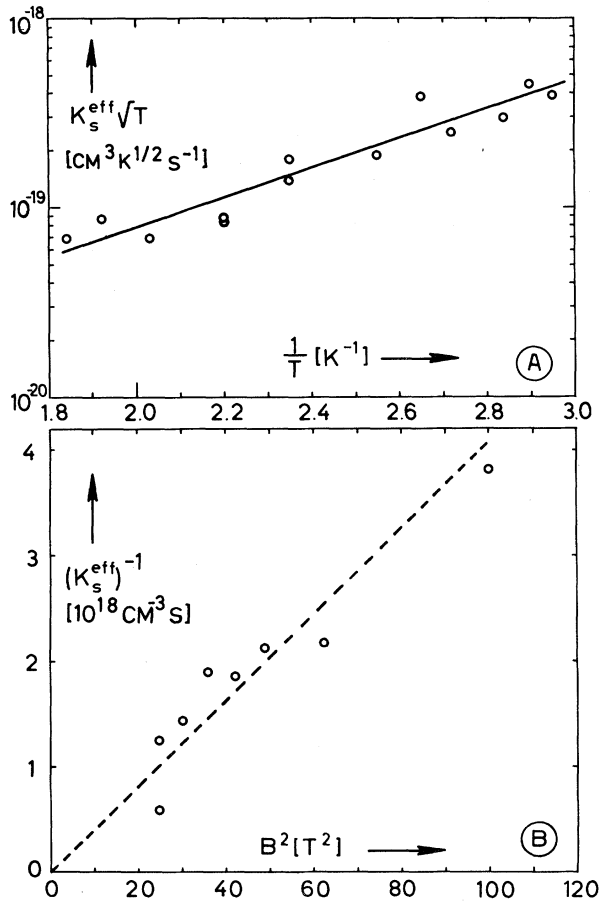
FIG. 2. (a) Logarithmic plot of $K_s^{eff} T^{1/2}$ vs $1/T$. The adsorption energy is determined from the slope. (b) Field dependence of the rate of surface recombination plotted as $(K_s^{eff})^{-1}$ vs B^2 for $T = 0.385$ K.

as is done here, and shift of the zero-field hyperfine resonance transition as a function of temperature. From the slope of the plot in Fig. 2(a), we find $\epsilon_a/k_B = 0.89 \pm 0.07$ K. Morrow et al. found 0.95 ± 0.02 K by the decay technique and 0.92 ± 0.04 K from the hyperfine shift. This may be compared with $D_\downarrow$ on ^{4}He which has a value of $\epsilon_a/k_B = 2.6 \pm 0.4$ K when we use the $T^{1/2}$ temperature dependence of K_s of Ref. 9.

We have also determined the magnetic field dependence of the surface rate: $K_s(B) = \gamma(B)K_s'$. A simple model for this dependence proposes $\gamma \sim 1/B^2$.[14,15] The stabilized H↓ consists of atoms in two hyperfine states $|a\rangle \simeq -|\downarrow\uparrow\rangle + \epsilon|\uparrow\downarrow\rangle$ and $|b\rangle = |\downarrow\uparrow\rangle$ (↓, electron spin; ↑, proton spin), where $\epsilon \simeq a/4\mu_B B$ is the admixture of the electron spin-up state into the ground state (a is the zero-field hyperfine splitting). By assuming that only atomic collisions in which at least one atom is in the $|a\rangle$

state can lead to recombination, we[14] find a probability $\gamma = \frac{1}{4}$ at zero field and $\gamma = \frac{1}{2}\epsilon^2$ for our present high-field regime. This corresponds to a reduction of the zero-field rate by $2\epsilon^2 = 1.3 \times 10^{-5}$ at 10 T. A confirmation of this model is found in Fig. 2(b), where we plot $(K_s^{eff})^{-1}$ vs B^2. The dotted line relates to our best value for K_s: $K_s B^2/T^{1/2} = (2.6 \pm 0.8) \times 10^{-7}$ cm^2 T^2 K$^{-1/2}$ sec^{-1}. Morrow et al. observed $K_s^{eff} = 4.5 \times 10^{-16}$ cm^3/sec in zero field at $T = 0.5$ K. Comparison with our results may be made by scaling[16] A/V and using $\gamma = \frac{1}{4}$. We calculate $K_s^{eff} = 1.2 \times 10^{-15}$ cm^3/sec, in reasonable agreement with the observed value.

These results have serious implications for observing BEC in current geometries. It has been shown[11,12] that to attain BEC the surface must be saturated to a value $n_s^{sat} = \epsilon_a/2\alpha_2 = 6 \times 10^{13}$ cm^{-2}, where α_2 is taken from a linear expansion for the two-dimensional interaction energy in terms of the density. There are two conditions for stability: static and dynamic. Silvera and Goldman have shown[11] that coverages up to 1.8×10^{14} cm^{-2} will have static stability. The limitations which we have measured have again shown[9] that only dynamic stability is important. For example, with use of the high-flux results of Cline et al.[3] with $n_g = 7.5 \times 10^{16}$ cm^{-3} obtained at 0.3 K, the adsorption isotherm yields $n_s = 4.6 \times 10^{11}$ cm^{-2}. This is much lower than the static stability value or n_s^{sat}.

More promising are some preliminary measurements on a 0.2% ^{3}He-^{4}He mixture, where we observed a reduction of K_s^{eff} by a factor of 6.1. If we attribute this completely to a change in adsorption energy, we find $\epsilon_a/k_B \simeq 0.59$ K. Unfortunately, in our temperature range we were unable to do a useful measurement with a saturated mixture because of fluctuations in the background pressure of ^{3}He which are not compensated by the superleak. A possibility exists that the surface of the mixture is saturated with ^{3}He and little additional reduction of ϵ_a will be found with increasing ^{3}He concentration, although a reduction of the bulk density will also reduce ϵ_a.

We also note that the presence of the first-order loss of atoms from our cell prevented us from establishing evidence for the interesting relaxation-limited recombination process proposed by Statt and Berlinsky,[15] which may also allow achievement of higher surface densities in high fields.

We acknowledge useful discussions with V. V. Goldman and R. Sprik. We thank W. S. Truscott for his advice in designing the pressure gauge,

R. Scheltema for its construction, and the Sticht-
ing voor Fundamenteel Onderzoek der Materie
for financial support.

[1]I. F. Silvera and J. T. M. Walraven, Phys. Rev.
Lett. 44, 164 (1980).

[2]I. F. Silvera and J. T. M. Walraven, J. Phys. (Paris),
Colloq. 41, C7-137 (1980); J. T. M. Walraven, I. F.
Silvera, and A. P. M. Matthey, Phys. Rev. Lett. 45,
449 (1980).

[3]R. W. Cline, T. J. Greytak, D. Kleppner, and D. A.
Smith, J. Phys. (Paris), Colloq. 41, C7-151 (1980).

[4]W. N. Hardy, M. Morrow, R. Jochemsen, B. W.
Statt, P. R. Kubik, R. M. Marsolais, A. J. Berlinsky,
and A. Lendesman, J. Phys. (Paris), Colloq. 41, C7-
157 (1980), and Phys. Rev. Lett. 45, 453 (1980).

[5]B. Yurke, D. Igner, E. Smith, B. Johnson, J. Den-
ker, C. Hammel, D. Lee, and J. Freed, J. Phys.
(Paris), Colloq. 41, C7-177 (1980).

[6]C. E. Hecht, Physica (Utrecht) 25, 1159 (1959);
W. C. Stwalley and L. H. Nosanow, Phys. Rev. Lett.
36, 910 (1976); L. H. Nosanow, J. Phys. (Paris), Colloq.
41, C7-1 (1980).

[7]I. B. Mantz and D. O. Edwards, Phys. Rev. B 20,
4518 (1979).

[8]M. Morrow, R. Jochemsen, A. J. Berlinsky, and
W. N. Hardy, Phys. Rev. Lett. 46, 195 (1981).

[9]I. F. Silvera and J. T. M. Walraven, Phys. Rev.
Lett. 45, 1268 (1980).

[10]J. T. M. Walraven and I. F. Silvera, Phys. Rev. Lett.
44, 168 (1980), and J. Phys. (Paris), Colloq. 41, C7-
147 (1980).

[11]I. F. Silvera and V. V. Goldman, Phys. Rev. Lett.
45, 915 (1980).

[12]D. O. Edwards and I. B. Mantz, J. Phys. (Paris),
Colloq. 41, C7-257 (1980).

[13]Note that this definition of $K_s{}^{eff}$ differs by a factor
V^{-1} from that in Ref. 9.

[14]I. F. Silvera, in Proceedings of the Winter School,
Lammi, Finland, January 1979 (unpublished); I. F.
Silvera and J. T. M. Walraven, in Proceedings of the
European Physical Society Conference on Condensed
Matter, Antwerp, Belgium, January 1980 (to be pub-
lished).

[15]B. W. Statt and A. J. Berlinsky, Phys. Rev. Lett.
45, 2105 (1980).

[16]We calculate $A/V = 4$ from Ref. 8.

Lattice-Location Experiment of the Ni-Si Interface by Thin-Crystal Channeling of Helium Ions

N. W. Cheung[a] and J. W. Mayer[b]

California Institute of Technology, Pasadena, California 91125

A thin-crystal channeling experiment has been devised to locate preferential sites of
monolayers of Ni atoms deposited onto Si crystalline substrates. The Ni scattering yield
shows dips or peaks in the angular scan measurements when channeled along the major
crystallographic axes and planes of Si. The results can be explained by a dispersed Ni-
Si interface with 2.1×10^{15} Ni atoms/cm^2 occupying the tetrahedral interstitial voids of Si.

PACS numbers: 61.16.-d, 61.80.Mk

Numerous techniques such as low-energy elec-
tron diffraction, Auger-electron spectroscopy,
X-ray photoemission (XPS), ultraviolet photoelec-
tron spectroscopy, and ion channeling have been
applied to the study of metal-semiconductor inter-
faces.[1-6] Recently, such studies have revealed
that interfaces between metals and semiconduc-
tors such as Si, GaSb, InP, and GaAs are chem-
ically reactive even at room temperatures and
that the interfaces are far from being abrupt as
modeled by various theoretical studies. For the
Ni-Si system, the existence of an intermixed in-
terface between as-deposited Ni atoms and the
crystalline substrate has been observed by ion
channeling for clean Si surfaces prepared under
ultrahigh-vacuum conditions as well as chemical-
ly cleaned Si surfaces.[6] With a coverage of 1
$\times 10^{16}$ Ni atoms/cm^2, approximately 6×10^{15} Si at-
oms/cm^2 are nonregistered with respect to the
crystalline (111) substrate. An XPS study has al-
so confirmed the room-temperature reactivity be-
tween Ni and Si and the Ni atoms were found to be
in a Si-rich environment.[5,7]

In the present study, a thin-crystal channeling
experiment has been devised to locate the lattice
sites of monolayers of Ni atoms deposited onto Si
crystalline substrates. Ion-beam channeling has
been applied to locate preferential sites of impur-
ities in bulk crystals.[8] By making use of the
"flux-peaking" effect of ion channeling, the rela-
tive position of the impurity atoms with respect
to the host's crystalline matrix can be determined