

Adsorption Energy and Nuclear Relaxation of H \downarrow on ^3He - ^4He Mixtures

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We have determined the adsorption energy of H \downarrow on ^3He - ^4He mixtures to be $\epsilon_a/k = 0.34 \pm 0.03$ K, essentially independent of ^3He - ^4He concentration. We observe a pure second-order decay of the density due to surface recombination with rate constant $K_s/T^{1/2} = 1.4 \times 10^{-9}$ cm 2 K $^{-1/2}$ s $^{-1}$ at $B = 8$ T. The nuclear relaxation time T_1 , predicted to be of order hours, is found to be of order seconds by an indirect measurement. H \downarrow remained gaseous down to $T = 0.085$ K, the lowest temperature measured.

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It has recently been shown that atomic hydrogen (deuterium) can be made in a long-lived gaseous state by polarizing the electron spins (H \downarrow , D \downarrow) at low temperatures in high magnetic fields and coating all walls of the confining chamber with liquid helium to suppress adsorption and subsequent recombination on the surfaces.¹ Efforts to achieve gaseous densities greater than $\sim 10^{18}$ cm $^{-3}$ in H \downarrow , required to bring the Bose-Einstein condensation (BEC) temperature into an accessible temperature range, have not been successful. It was shown that adsorption of D \downarrow and H \downarrow on ^4He surfaces^{3,4} was responsible for the limited densities: in steady state, atoms condense on the ^4He surfaces and recombine as fast as they are fed into the hydrogen stabilization cell (HSC). The adsorption energy of H \downarrow on ^4He was found to be $\epsilon_a/k = 0.9$ K.^{3,4} Silvera and Goldman⁵ and Edwards and Mantz⁶ have also shown that to achieve BEC in the gas phase in the presence of ^4He surfaces, the surface coverage n_s must be saturated to a level $n_s^{\text{sat}} \approx (5-10) \times 10^{13}$ cm $^{-2}$, a value proportional to ϵ_a . Experimentally the maximum coverages that can be achieved, as limited by filling flux and heating, are of order 5×10^{11} cm $^{-2}$.^{4,7} Thus, using current techniques it is necessary to find surfaces with a substantially lower value of ϵ_a . ^3He was expected to provide such a surface with a smaller adsorption energy and efforts concentrated on this system to achieve higher densities required for BEC. Matthey, Walraven, and Silvera⁴ studied ^3He - ^4He mixtures with a few parts per thousand ^3He concentration and found a reduction of ϵ_a of about $\frac{1}{3}$; however they were unable to study the effect of larger ^3He concentrations due to a restricted temperature range. In this Letter we describe measurements for unrestricted concentrations, x , of $^3\text{He}_{1-x}\text{He}_x$ and find $\epsilon_a/k = 0.34 \pm 0.03$ K, essentially independent of x as long as there is enough ^4He to provide

several monolayers of coverage. We observe a pure second-order decay of the density due to recombination with rate constant $K_s/T^{1/2} = 1.4 \times 10^{-9}$ K $^{-1/2}$ sec $^{-1}$ at $B = 8$ T. All told this means that ^3He surfaces will not suffice for BEC and another path must be found. The most obvious is to reduce the rate constant K_s .

A gas of H consists of two states $|a\rangle = -|\uparrow\downarrow\rangle + \epsilon|\uparrow\uparrow\rangle$ and $|b\rangle = |\downarrow\downarrow\rangle$, where $\epsilon \approx a/4\mu_B B$ is the mixing coefficient of electron spin (\uparrow) and nuclear spin (\downarrow) due to the hyperfine interaction, a . Calculations^{8,9} of the relaxation rate T_1 between the two states in the gas phase yield $T_1 \geq 16000$ sec for $B = 10$ T, $n_g = 10^{16}$ atoms/cm 3 , and $T \leq 0.5$ K. Matthey, Walraven, and Silvera⁴ have shown that recombination rates are proportional to B^{-2} , confirming a model in which recombination takes place due to collisions of atoms in $|a\rangle$ states with atoms in $|a\rangle$ or $|b\rangle$ states, but not between $|b\rangle$ state atoms, only. Thus if T_1 is long, only a gas of H \downarrow in the $|b\rangle$ state would also be metastable with a value of K_s orders of magnitude smaller. We have developed a technique to measure T_1 indirectly with a pressure gauge. We found $T_1 \leq 10$ sec! Thus T_1 is not bottlenecked and the suggestion of Statt and Berlinsky⁸ will not work. A more positive observation, that H \downarrow exerts a pressure at temperatures down to 85 mK (our lowest temperature), lends more evidence that this extreme quantum system will remain gaseous to $T = 0$ K.

The experimental techniques for stabilization¹ and the use of a pressure gauge⁴ have been described elsewhere. We have now built our hydrogen stabilization cell (HSC) into a high-cooling-power dilution refrigerator (Oxford Instruments) with bottom access. The heart of the system is shown in Fig. 1. The hydrogen atoms are created in a room-temperature microwave discharge, flow through teflon tubing, are cooled to 4.2 K at the accommodator, and flow into the HSC, which

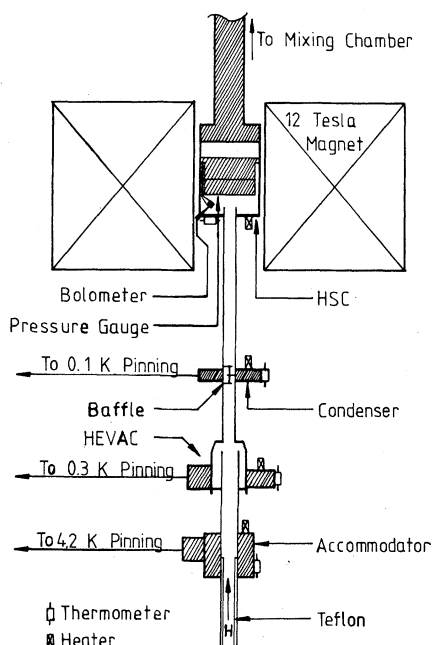


FIG. 1. Low-temperature section of cryostat.

when filled with helium to coat the surfaces, operates at $T \geq 30$ mK. The helium vapor compressor (HEVAC) and condenser provide thermal isolation of the HSC by condensing the fluxing helium vapors and enable very low temperatures to be reached by taking this heat load off of the mixing chamber. A bolometer is used to destroy the $\text{H}\uparrow$ to establish the pressure baseline. The HSC has a volume of $V = 1.7 \text{ cm}^3$ and an area of $A = 32 \text{ cm}^2$.

It is useful to review our thermometry. Our main measurement thermometer on the HSC is a 200- Ω Matsushita carbon resistor. On the copper pole leading to the mixing chamber we have a National Bureau of Standards superconducting fixed-points device (SRM 768), a cobalt crystal for nuclear-orientation thermometry, and two germanium thermometers. The Matsushita resistor and the germanium thermometers were calibrated *in situ* against the other two devices and against the ^3He vapor-pressure scale down to 200 mK using our low-temperature manometer. At points of overlap mutual agreement was within 2 mK. The magnetic field dependence at 8 T of the Matsushita resistor was determined with the field-independent ^3He vapor scale. A very weak dependence was found and for lower temperatures we used a field-cycling technique. The germanium thermometers served to check the stability of the Matsushita resistor. We judge our thermometry to have an accuracy of ± 3 mK

in the range of our experiments. Although such a careful calibration required about two months' work, it was important to achieve reliable results.

As shown earlier² the adsorption energy can be determined by measuring the decay of the gas density n_g as a function of temperature. With no thermal leakage out of the fill tube, n_g decays according to

$$dn_g/dt = K_v n_g^3 - K_s^{\text{eff}} n_g^2 + \varphi/V, \quad (1)$$

where K_v is the three-body volume recombination rate constant, φ is the filling flux, and $K_s^{\text{eff}} \equiv K_s(A/V)\lambda^2 \exp(2\epsilon_a/kT)$ is the effective surface recombination rate constant.^{2,4} Here, K_s is the intrinsic surface rate constant and $\lambda = (2\pi\hbar^2/mkT)^{1/2}$ is the thermal de Broglie wavelength. Since at constant temperature the pressure $p \sim n_g$, we can monitor the density decay with the pressure gauge. For our density ranges ($n_g \lesssim 5 \times 10^{15} \text{ cm}^{-3}$) decay curves were found to be due to second-order rates to within experimental error.

In earlier experiments we had found that we could not load a cell with $\text{H}\uparrow$ when using a pure ^3He coating. Evidently the $\text{H}\uparrow$ atoms vaporize the ^3He from the surface between the accommodator and HSC, condense and recombine. Superfluid ^4He is driven to warmer regions and suppresses such processes. In the present experiment mixtures of $^3\text{He}_{1-x}^4\text{He}_x$, with $2 \leq (1-x)/x \leq 6$, were studied in which there was enough ^4He to provide a saturated film in the absence of ^3He . To within experimental error we found the same decay constant for n_g independent of x . Data for $(1-x)/x = 2$ are shown in Fig. 2. Here we show the filling of the cell at $T = 200$ mK from point A to point B and, after stabilizing the temperature with $\varphi = 0$ at $T = 133$ mK, the decay of the density from point C to point D. The sample is destroyed at point D to establish the zero baseline. All measurements were made for $T < 200$ mK so that the background vapor pressure of ^3He made a negligible contribution to the pressure. Figure 2(b) shows a plot of $K_s^{\text{eff}}\sqrt{T}$ vs $1/T$: the slope of this curve is $2\epsilon_a/k$. A value $\epsilon_a/k = 0.34 \pm 0.03$ K was found for the adsorption energy and $K_s/T^{1/2} = 1.4 \times 10^{-9} \text{ cm}^2 \text{ K}^{-1/2} \text{ sec}^{-1}$ for the rate constant at 8 T. This is about three times slower than what we found for $\text{H}\uparrow$ on ^4He and may be due to a more extended spatial surface state on ^3He , although we should probably repeat these measurements in the same cell to remove doubt of possible systematic errors.

The attractive part of the adsorption potential

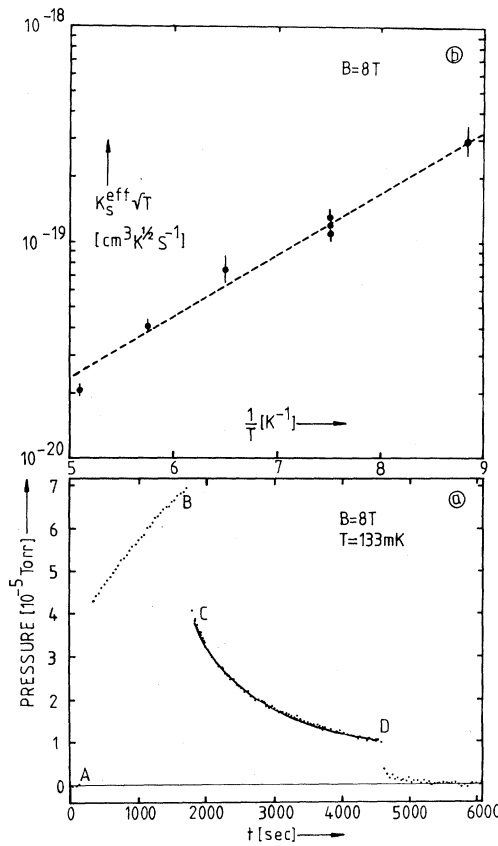


FIG. 2. Decay of pressure of H^\dagger on a ${}^3\text{He}_{0.66}{}^4\text{He}_{0.33}$ surface: (a) Pressure as a function of time; (b) $K_s^{\text{eff}} \times \sqrt{T}$ vs T^{-1} ; the slope is $2\epsilon_a/k$.

arises from a sum over the long-range part of the H-He pair potentials. This is sensitive to the bulk helium density and the surface density profile.¹⁰ ${}^3\text{He}$ is expected to have a lower adsorption energy for H^\dagger than ${}^4\text{He}$ for two reasons: (1) the bulk density is substantially smaller, and (2) the surface density profile is more extended. At low temperatures a ${}^3\text{He}$ - ${}^4\text{He}$ mixture phase separates; the superfluid ${}^4\text{He}$ -rich phase is diluted with about 6.4% ${}^3\text{He}$. The ${}^3\text{He}$ -rich phase is almost pure ${}^3\text{He}$ and, because it is lighter, when dealing with bulk quantities it will reside on top of the ${}^4\text{He}$ phase. The ${}^3\text{He}$ phase will reside principally in the coldest region, the HSC; the ${}^4\text{He}$ phase will be spread out, driven to warmer regions. We initially fill the HSC with pure ${}^4\text{He}$ which covers all surfaces. As ${}^3\text{He}$ is added (at $T=0\text{K}$) it will first form a monolayer of ${}^3\text{He}$ on the surface and then saturate the ${}^4\text{He}$ film to around 6.4%. Additional ${}^3\text{He}$ will build up on the surface to a certain equilibrium thickness and all further ${}^3\text{He}$ will re-

side in the reservoir of the HSC. This model has received some confirmation by recent measurements of Ellis *et al.*¹¹ By simply balancing gravity against the long-range forces due to the substrate we find $d_3/d_4 = (m_4/m_3)^{1/3} - 1 \approx 0.1$, where d_3 and d_4 represent the thickness of the ${}^3\text{He}$ and ${}^4\text{He}$ layers and m_4/m_3 is the isotopic mass ratio.¹² Thus we estimate the ${}^3\text{He}$ film to be 3-4 layers thick, and our measurements of adsorption energy are probably representative of the value for bulk ${}^3\text{He}$.¹³

We shall now describe our nuclear relaxation measurements. If relaxation is bottlenecked ($T_1 \gg$ recombination time), then when starting with equal amounts of $|a\rangle$ and $|b\rangle$ states ($n_{g0} = n_a + n_b$) the H^\dagger should decay to $n_g = n_b/2 = n_{g0}/4$, according to the rate equations of Ref. 7. If this is so and the model holds for both gas-phase and surface atoms, then we can measure T_1 with our pressure gauge. With a high-purity ${}^3\text{He}$ coating the surface (so that the theory is not complicated by the ${}^3\text{He}$ spin), we load the HSC to a density $n_g = 5 \times 10^{15} \text{ cm}^{-3}$ at a high temperature $T_i = 400\text{ mK}$ where the recombination decay time is long. We then lower the temperature to $T_f = 200\text{ mK}$ where the decay time is fast (initial halving time 5 sec). After waiting long enough for the density to decay to a steady state we can return to T_i and see if $n_g = n_{g0}/4$. If so the further decay rate at T_i should be a measure of T_1 , the nuclear relaxation rate. We found that the density at T_f rapidly decays to zero with no bottlenecking for either ${}^4\text{He}$ or ${}^3\text{He}$ - ${}^4\text{He}$ mixtures. Surface T_1 's have been calculated to be of the order of seconds for our conditions.¹⁴ If this T_1 were the only important process, then the measured decay rate should be increased by the ratio of atoms in the gas phase to those in the surface phase, about 10^3 . Surface relaxation alone cannot account for our observations. Direct recombination of atoms in the b state by dipole-dipole interaction may be important.¹⁵

Although we can now estimate that higher densities of order 10^{18} cm^{-3} can be achieved with $\varphi = 10^{16}/\text{sec}$ by use of a ${}^3\text{He}$ - ${}^4\text{He}$ surface, consequences for achieving critical densities for BEC are serious. First, with $\epsilon_a/k = 0.34\text{ K}$, saturation densities n_s^{sat} at BEC will be of order $3 \times 10^{13} \text{ cm}^{-2}$. Rates, K_s , can be reduced by brute force by about a factor of 10 with larger static fields ($B=25\text{ T}$); however, this is inadequate to sustain such high coverages. We have just shown that purification by rapid recombination does not work because of rapid T_1 's. One might also at-

tempt to pump $|a\rangle$ -state atoms to electron spin-flipped states which would then be ejected from the HSC by the field gradients, leaving a gas enriched in $|b\rangle$ -state atoms. If T_1 is fast, however, this technique is also frustrated. Although this unique system, H^\dagger , presents a number of exciting new phenomena and areas of research, it seems that one of the most fascinating, the weakly interacting Bose-Einstein condensed gas, will not be easily achieved.

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Longitudinal Acoustic Impedance and the Squashing Mode in Superfluid $^3\text{He-B}$

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We have observed an unexpectedly strong effect of the squashing mode in $^3\text{He-B}$ on the longitudinal acoustic impedance Z . Most peculiar is the behavior of the reactive part Z'' which displays both large positive and negative excursions. Our analysis illustrates the role of the boundary conditions on the superfluid order parameter and of the crossover with temperature of the squashing mode from a propagating wave with velocity c_{sq} (which is measured) to a nonpropagating surface wave (whose imaginary velocity accounts for the anomalies of Z'').

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The squashing mode in superfluid $^3\text{He-B}$ is an eigenmode of the complex tensorial order parameter which couples strongly to density fluctuations.¹ In weak-coupling theory its eigenfrequen-

cy is proportional to the gap function: $\omega_{sq} = (\frac{12}{5})^{1/2} \Delta_{BCS}(T)$. This distinctive mode was identified first in the vicinity of the transition temperature T_c .¹ In more recent sound-propagation ex-