

## Helium on Graphite: Low-Temperature Desorption Kinetics and Sticking Coefficient

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We have used a graphite fiber as a substrate to study the kinetics of desorption and sticking of  $^4\text{He}$  for temperatures between 15 and 1.6 K. The sticking coefficient on the clean surface is 0.026, and is independent of coverage from 0 to 1 layer. A simple phenomenological model is used to show that the desorption rates and sticking coefficient we observe are consistent with previous thermodynamic measurements.

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Helium on graphite is one of the most well studied and best understood physisorption systems. The thermodynamic properties are accurately known over a wide range of temperature and coverage.<sup>1</sup> Scattering experiments have provided a detailed understanding of the helium-graphite interaction potential<sup>2</sup> which in turn has been used to refine the microscopic theories of the thermodynamic properties. Despite the wealth of thermodynamic and scattering data, there is very little information on the kinetics of adsorption and desorption for helium on graphite or any other well-characterized substrate at low temperatures.<sup>3</sup> This is unfortunate because theories of helium desorption and sticking are conceptually simple and have received considerable attention recently.<sup>4-11</sup> Because of the weak binding to the substrate and the low temperatures involved, energy exchange between helium and a solid surface is thought to involve processes in which an adatom absorbs or emits a single substrate phonon. Theories which utilize the one-phonon assumption predict an activated form for the desorption time  $\tau$ , with  $\tau = \tau_0 \exp(Q/T_s)$ , where  $T_s$  is the substrate temperature and  $Q$  is related to the binding energy, which may depend on coverage. The value of  $\tau_0$  is sensitive to details of the model and ranges from  $10^{-3}$  to  $10^{-8}$  sec. Similar theories applied to the problem of sticking yield a sticking coefficient  $\alpha$  on a bare surface of a few percent, with only a weak temperature dependence. The coverage dependence of sticking has not been investigated in detail.

We present here the first low-temperature measurements of  $\alpha$ ,  $\tau_0$ , and  $Q$  of helium on a well-characterized surface. We find a value of  $Q = 137$  K, in good agreement with previous measurements of the binding energy on graphite, and  $\tau_0 = 3 \times 10^{-10}$  sec. The sticking coefficient on the clean graphite surface is 0.026, which is approximately equal to the theoretically expected value, but much smaller than the sticking coefficient recently observed on metal films.<sup>12</sup>

Both the sticking coefficient and the desorption time can be determined by monitoring of the response of the coverage to a perturbation of the substrate temperature. The principal experimental difficulty in ap-

plying traditional flash-desorption techniques to the case of helium is the measurement and control of the substrate temperature on short time scales. We have overcome this problem by using a graphite fiber 10  $\mu\text{m}$  in diameter as a substrate.<sup>13</sup> The fiber can be electrically heated to a temperature slightly above ambient, and, because of its small size, it comes into internal thermal equilibrium is less than a microsecond. Since the electrical resistance of the fiber depends on its temperature, the fiber also serves as an excellent thermometer of the substrate temperature. An additional advantage is that the surface of the fiber can be cleaned by heating it *in situ* to 1500 K, which requires dissipation of only a fraction of a watt. The crystallographic orientation of the graphite *c* axis is predominantly normal to the axis of the fiber.<sup>14</sup> The homogeneity of the surface is sufficiently good that steps are observed in adsorption isotherms<sup>15</sup> and features corresponding to desorption from the first and second layers of helium are also observed.<sup>16</sup> As in previous studies,<sup>17-19</sup> we have used a superconducting bolometer to detect the atoms desorbed from the heated substrate.

The inset of Fig. 1 shows a schematic diagram of the apparatus. A thin-film superconducting bolometer  $0.2 \times 0.2$  mm<sup>2</sup> in area on a sapphire substrate is used to detect the atoms desorbed from a fiber which is suspended between two sapphire supports. The fiber is 6 mm long and the distance between the fiber and the bolometer is 0.7 mm. The cell is also equipped with a thin-film Constantan heater and bolometer which were used to monitor the cell pressure and as a reference in the sticking-coefficient measurements. The background gas pressure, and therefore its chemical potential, are deduced from the time required for a monolayer film to adsorb on the heater.<sup>18</sup> The chemical potential and the temperature are sufficient to determine the coverage by use of the thermodynamic data of Ref. 1. In order to use the fiber as a thermometer, its resistance  $R(T)$  was measured in the range 1.6-40 K with  $R(T) = R_0(1 - 5.80 \times 10^{-4}T - 2.04 \times 10^{-5}T^2)$  and  $R_0 = 342 \Omega$ . The transient temperature rise due to a current pulse through the fiber was

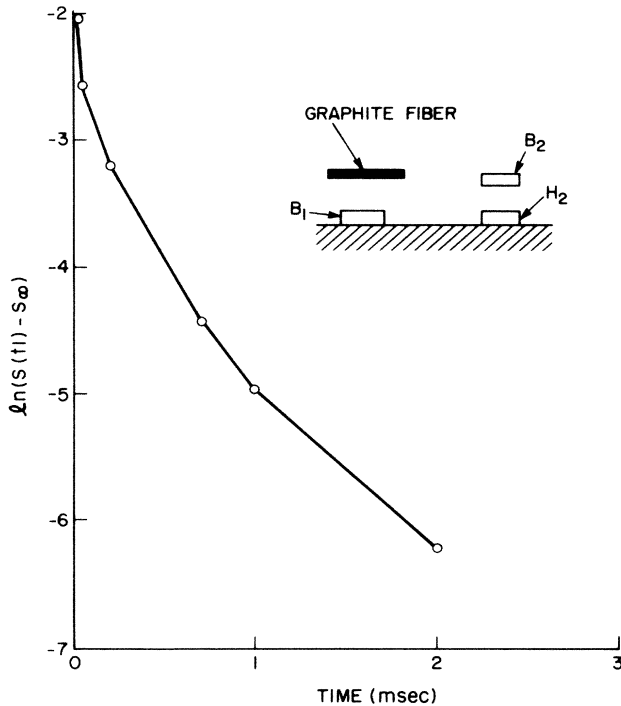


FIG. 1.  $\ln[S(t_1) - S_\infty]$  as a function of time. Inset shows a schematic diagram of the apparatus. B1 is bolometer for fiber, B2 is bolometer for Constantan heater H2.

measured by using it as one arm of an ac bridge operating at 2 kHz. With the bridge in balance at the ambient temperature, a current pulse injected into the fiber causes an exponentially decaying off-balance signal which is proportional to the Joule heating and inversely proportional to the heat capacity of the fiber. The temperature can be determined to within  $\pm 0.1$  K. The heat capacity which we deduce from our measurements corresponds closely to previous measurements on polycrystalline graphite.<sup>20</sup> The decay time of the off-balance signal is related to the thermal diffusivity of the fiber. The thermal relaxation time is 20 msec and is independent of temperature, which implies a phonon scattering length of 300 Å.

The experiments described here involve application of a sequence of two electrical pulses to the fiber. The first pulse raises the temperature from the ambient (typically 2.5 K) to the desorption temperature  $T_s$ . The helium coverage on the fiber decreases in response to the increase of the substrate temperature. At a later time,  $t_1$  after the first pulse, a second pulse heats the fiber to 30 K and rapidly desorbs any helium that remains. The atoms desorbed by the second pulse are detected by the bolometer. If the temperature of the fiber has not relaxed, i.e. if  $t_1 < 2$  msec, the bolometer signal is proportional to the coverage  $n(t_1, T_s)$  at time  $t_1$  and temperature  $T_s$ . In the opposite limit of  $t_1 > 20$  msec, the temperature of the fiber

is the ambient temperature  $T_{\text{amb}}$  and the coverage increases to the equilibrium coverage at a rate determined by the background gas pressure and the sticking coefficient on the substrate.

The desorption rate at temperature  $T$  is determined from the bolometer signal  $S(t_1)$  as a function of delay time  $t_1$ . The assumption of first-order kinetics leads us to expect an exponential decay of the signal  $S(t_1) = S_0 \exp(-t_1/\tau) + S_\infty$ , where  $S_\infty$  is the asymptotic value for large  $t_1$ ;  $\tau$  is determined from a plot of  $\ln[S(t_1) - S_\infty]$  vs  $t_1$ , as shown in Fig. 1. Although the background gas conducts a negligible amount of heat from the fiber, the cooling due to the desorption itself can be significant; for desorption of a full layer the temperature drop is approximately 1 K. To minimize this effect, we selected a pulse-sequence repetition period which is five times shorter than the coverage relaxation time. Even though the equilibrium coverage at the ambient temperature for the data of Fig. 1 is approximately one layer, no more than 0.2 layer is allowed to readsorb before another heat pulse flashes the fiber clean. All of the desorption-rate data were taken in this low-coverage limit. Despite these precautions, the relaxation of the coverage was not a perfect exponential. The curvature of the plot in Fig. 1 may be due to a distribution of binding sites or to an intrinsic nonlinearity in the desorption kinetics. In order to parametrize our data we have used a least-squares fit of the simple exponential model to define an average relaxation time for each value of the fiber temperature. With this experimental technique it is possible to measure time constants in the range  $10^{-6} < \tau < 10^{-3}$  sec, which corresponds to substrate temperatures between 15 and 8 K. A plot of  $\ln\tau$  vs  $1/T$  is shown in Fig. 2. A best fit to the data gives

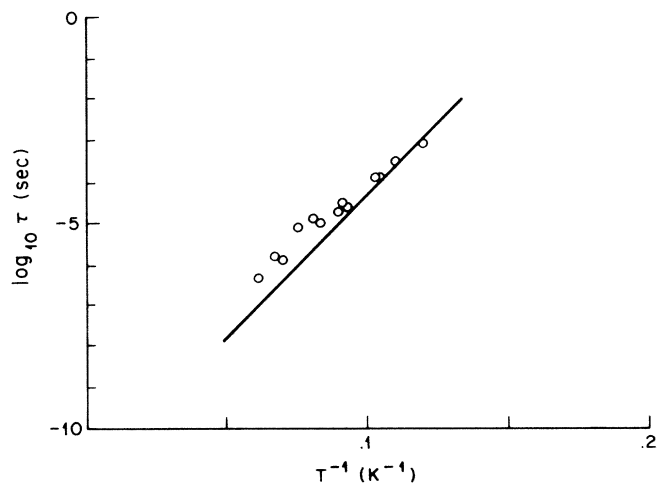


FIG. 2.  $\log(\tau)$  as a function of inverse temperature. Points are experimental data. The line is computed from Eq. (1) using  $\alpha = 0.026$  and the vapor pressure data from Ref. 1.

$Q = 137 \pm 7$  K and  $\tau_0 = (3 \pm 1) \times 10^{-10}$  sec. The value of  $Q$  which we measure is in reasonable agreement with the previously determined binding energy of helium on graphite,<sup>2</sup>  $E_b = 143$  K, and with theoretical calculations.

The sticking coefficient of the background gas on the graphite fiber was measured by comparison of the time required for an equilibrium film to reform on the fiber to the time required to reform the film on a Constantan heater. The sticking coefficient on a similar Constantan film has been previously measured<sup>12</sup> to be  $\alpha \approx 0.66$ . A plot of the normalized bolometer signal  $S/S_{\max}$  as a function of time for delay times  $t_1 \gg 20$  msec is shown in Fig. 3. The rate at which the film recovers is determined by a competition between the rate at which atoms from the gas stick to the fiber and the rate at which atoms are redesorbed from the film. In equilibrium, the two rates must be equal. The vapor pressure of the film is practically negligible, however, until the coverage is very close to its equilibrium value. This accounts for the linear rather than exponential character of the relaxation. We find the recovery time for the helium film on the fiber is 25 times longer than the recovery time on the Constantan heater; this implies a sticking coefficient on graphite of  $\alpha = 0.026$ . The sticking coefficient is very sensitive to surface contamination. An increase of the residual pressure in the cell to  $10^{-6}$  Torr by a cycling of the apparatus to liquid nitrogen temperature causes the sticking coefficient to increase by more than an order of magnitude to  $\alpha(\text{dirty}) \approx 0.4$ . The fact that the sticking coefficients on the contaminated fiber and the metal film are very similar suggests that both surfaces are covered with a layer of condensed gas. The surface of the fiber can be cleaned by momentarily heating it

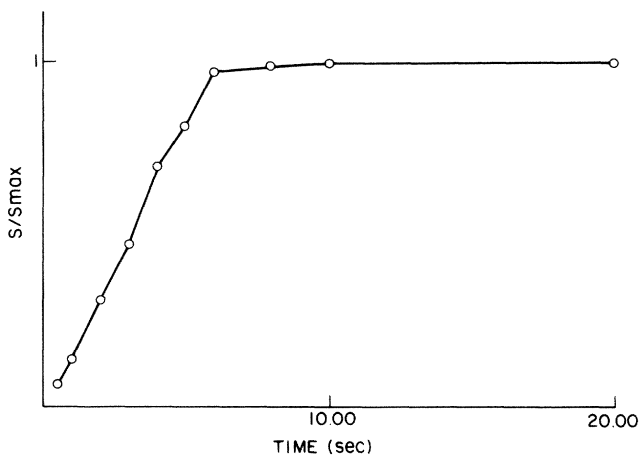


FIG. 3. Normalized bolometer signal as a function of time after a heat pulse which reduced the coverage to zero.  $T_{\text{amb}} = 2.7$ ,  $P_{\text{gas}} = 7 \times 10^{-7}$  Torr, and the asymptotic coverage is 0.9 layer.

to 1500 K, and at liquid helium temperatures it remains clean for days. The large difference in the sticking coefficients on the clean and contaminated surfaces is analogous to a similar effect observed in the Kapitza resistance at cleaved and imperfect interfaces.<sup>21</sup>

Despite the apparent sensitivity to adsorbed residual gases, the sticking coefficient seems to be independent of helium film coverage in the range of 0 to 1 layer as manifested by the linearity of the plot in Fig. 3. Since the rate at which atoms from the gas approach the surface is constant, a change in the sticking coefficient by even a factor of 2 would result in an easily discernible change in slope of the curve. This result is rather surprising, since kinetic processes at surfaces for other systems typically have a strong dependence on coverage.<sup>22</sup> (See, however, Jacobi and Rotermund.<sup>23</sup>) Also, one expects that for thick films, the sticking coefficient would approach the value for bulk liquid helium which is close to unity.<sup>24</sup> Apparently, the crossover from low to high sticking probability occurs for films thicker than one layer.

The measured clean-surface value of  $\alpha$  is independent of temperature in the range 3.3 to 1.6 K and the magnitude agrees qualitatively with recent quantum mechanical calculations for sticking of helium on tungsten in the zero-coverage limit.<sup>8</sup> This agreement may, however, be fortuitous. According to Ref. 8, the principal channel for sticking is elastic scattering, due to corrugation of the surface potential, from a continuum state to an excited bound state, with subsequent inelastic processes which transfer energy from the adatom to the substrate. The rates for both the elastic and inelastic scattering depend sensitively on the depth of the surface potential and its lateral variation and the phonon spectrum of the substrate. It is difficult to imagine that the rate for these processes would not be affected dramatically by the presence of a partial monolayer of adsorbed gas.<sup>3</sup>

If a desorbing film can be regarded as if it were in equilibrium at its instantaneous value of coverage  $n$ , the desorption-rate and sticking-coefficient measurements described above are not independent. In equilibrium, the two quantities are related by a simple detailed balance argument<sup>25</sup> which yields

$$\frac{dn}{dt} = \frac{-\alpha P_f(n, T_s)}{(2\pi mkT_s)^{1/2}} + \frac{\alpha P_{\text{gas}}}{(2\pi mkT_{\text{amb}})^{1/2}}, \quad (1)$$

where  $P_f(n, T_s)$  is the vapor pressure of the film at temperature  $T_s$  and  $P_{\text{gas}}$  is the background gas pressure. For the temperature range we have investigated, the assumption of equilibrium behavior is plausible because the desorption times are much longer than any characteristic microscopic time scale in the problem. The only input required to predict the desorption rate from Eq. (1) is the sticking coefficient and the vapor

pressure; the data presented here and the thermodynamic data of Ref. 1 provide experimental values for these quantities. The temperature dependence of the desorption rates calculated from Eq. (1) and the vapor-pressure data of Ref. 1 are shown in Fig. 2; for the purposes of this plot we have assumed that the value of  $\alpha$  is constant, with  $\alpha = 0.026$ . Considering the differences in the type of substrate and the experimental techniques used for the vapor-pressure measurements, and the fact that we have used no adjustable parameters, the agreement is remarkably good.

In summary, we have exploited the unique properties of graphite fibers to measure the desorption and sticking kinetics of helium on a clean surface at low temperatures. This experiment provides the first data on a sufficiently well-characterized substrate that quantitative comparison with microscopic theories is possible. Although our results agree qualitatively with one-phonon quantum mechanical calculations, it is difficult to explain the coverage independence of the sticking coefficient with these models. The transition to the high sticking probability observed for the bulk liquid surface is also an intriguing puzzle. For slow desorption, there is a relationship between the desorption rate, the sticking coefficient, and the vapor pressure of the adsorbate which is required to insure detailed balance in equilibrium. We have used this relationship in conjunction with previous thermodynamic measurements to verify the consistency of our data.

that the low-temperature results really are measurements on a surface with an adsorbed helium film of unknown thickness does not seem to have been appreciated by subsequent investigators.

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