Energy accommodation coefficient for square well and Morse potentials

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(Received 10 June 1974)

In a previous paper one of the authors has developed a model for the energy accommodation coefficient which uses a step potential to characterize the average interaction between the gas particles and the surface.[1] We wish to extend the results of that work by including an attractive surface interaction in the potential and by carrying out unitary calculations (using the CCGM theory[2-4]) which include the effects of bound states on the single phonon scattering process.[5] Calculations are carried out for the accommodation of helium at a tungsten surface in the usual limit of gas and surface temperatures approaching the same value.[6,7] Reasonable agreement with experimental data is obtained, as well as qualitative agreement for the ratio of ^{3}He accommodation to that of ^{4}He. The unitary calculations seem to place definite limits on the validity of single phonon calculations carried out in the distorted wave Born approximation.

For the calculations presented below we have represented the attractive interaction near the surface by both the square well and Morse potentials. The square well potential is given by $V = (V_0 + D) S(-z + u_z) - DS(-z + w + u_z)$, where V_0 is the height of the repulsive barrier, D is the well depth, w is the well width, and u_z is the small perpendicular deviation of the surface from its equilibrium position; $S(x) = 0$ if $x < 0$ and equals unity if $x > 0$. As in I u_z is calculated for a semi-infinite isotropic continuum whose surface can undergo small perpendicular vibrations. This model includes all three types of acoustic phonons found near a surface, Rayleigh waves, mixed waves, and bulk waves. The Morse potential is given by $V = D \{\exp[-2q(z - u_z)] - 2\exp[-q(z - u_z)]\}$, where D is the well depth and q is the range parameter.

Figure 1 shows the results of DWBA calculations for the accommodation of helium on tungsten for two different Morse potentials and the square well potential. The Debye cutoff temperature was adjusted to obtain a fit with the data[8,9] in the neighborhood of 100 K. For the square well the results are virtually independent of the barrier height V_0 as long as it is chosen to be larger than the highest energy particles contributing to the accommodation. All other parameters are the same as those used in I. The Debye temperatures for these curves fall in the lower range of reported values (270 K[10] to 379 K[11]) but this is to be expected since the Debye temperature of the surface should be about half that of the bulk.[12] Comparison of the two Morse potential results shows that an effect of increasing the depth of the attractive well is to cause a dropoff of α at large temperatures,[13] in agreement with the results of Gilbey.[14] Further calculations with both the square well and Morse potentials show that α decreases with the range

of the well and increases with Debye temperature. As a function of well depth α increases at lower temperatures but decreases at higher temperatures as mentioned above.

We have also calculated the Rayleigh mode contribution to α for both potentials using the unitary T-matrix in Eq. (5) of II. Since the Rayleigh mode contribution makes up approximately half of the total value of α this gives a good indication of the applicability of the Born approximation. We find that for temperatures less than 100 K the agreement with DWBA is quite good, but for temperatures over 200 K the single phonon DWBA is too large and is no longer valid.

It is shown in I that the low temperature behavior of α varies as T^3. This behavior is in marked disagreement with the experimental data which seems to indicate that the accommodation is increasing at lower temperatures. The low temperature discrepancy remains even when resonance effects with the bound states are included as in Eq. (5) of II or when scattering in and out of the bound states by two phonon processes is taken into account.[15] Although there are numerous classical theoretical treatments[16] which agree reasonably well with the data one would not expect these to be valid for helium since the interaction of a light gas with the surface should be quantum mechanical especially at low temperatures. It has been suggested that the low temperature discrepancy could be due to some resonance or diffraction effects which have not been included in the theory.[1,15] However, it also seems quite likely that the in-
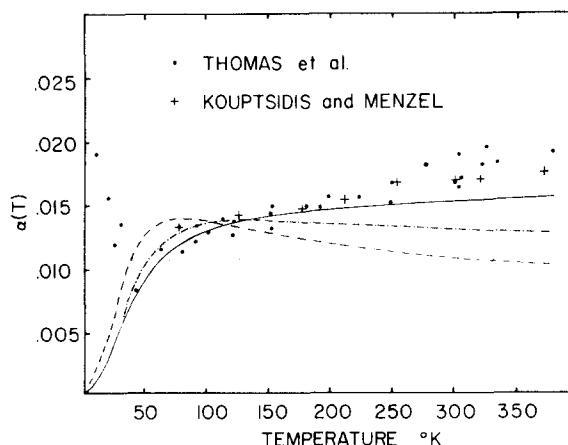

FIG. 1. The energy accommodation coefficient for helium on tungsten using the Morse and square well potentials. ———, Morse potential with Debye temperature $\theta_D = 320$ K, $D = 50$ K, and $q = 1.3 \times 10^8$ cm^{-1}; – – – –, Morse potential with $\theta_D = 240$ K, $D = 160$ K, and $q = 1.3 \times 10^8$ cm^{-1}; —·—·— square well potential with $\theta_D = 270$ K, $D = 50$ K, and $w = 2 \times 10^{-8}$ cm.

creased accommodation observed experimentally could be due to enhanced energy exchange caused by adsorbed helium on the surface. It is easily shown that α is inversely proportional to the mass density of the surface. A fractional layer of helium on the surface could greatly enhance the accommodation coefficient over the affected temperature range. The work of Dash and co-workers[17] has shown that helium monolayers can be readily formed on various substrates at low temperatures so it appears that more experimental data are necessary in order to resolve the question.

As explained in I these calculations have been carried out for a gas which is perpendicularly incident on the surface and then allowed to scatter in accordance with the conservation of momentum and energy. Goodman has reported calculations for a three dimensional gas incident on the surface,[18] but in order to carry out the two additional integrals that this involves he found it necessary to use a repulsive exponential potential and the phonon spectrum of a bulk Debye continuum. In order to test the effects of the dimensionality we have applied the present model to the same potential and parameters used by Goodman. Although the overall agreement with the experimental data is not good, the two different calculations compare very favorably. The slight differences appear to be caused less by the dimensionality than by differences in phonon distributions. For example, at lower temperatures our calculations are somewhat larger due to the proportionately stronger contribution of the Rayleigh modes which are not present in Goodman's model.

There exist several experimental investigations of the relative accommodation coefficient values of ^{4}He to ^{3}He, and all of these indicate that the ratio α^4/α^3 is greater than unity, varying from 1.03 at 77 K to 1.1 at 298 K.[8,9,19] Using the same parameters as in the calculations of Fig. 1 we have determined the accommodation coefficient values for ^{3}He. (There is no reason to suspect that any property other than the isotopic mass should affect the surface interaction.) For the step potential of I α is proportional to the mass of the scattered particles giving a ratio $\alpha^4/\alpha^3 = \frac{4}{3}$, independent of tem-

perature. For the square well potential the ratio is slightly less than $\frac{4}{3}$ while the Morse potential gives a value of 1.2. Although these values are large in comparison with experiment, the theory does correctly predict the mass dependence ratio to be greater than unity for all temperatures, and it also shows that inclusion of a more realistic type of attractive well near the surface considerably improves the agreement.

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NMR in the solid isomers twistane and adamantane

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(Received 8 November 1974)

Adamantane, which possesses a sharp heat capacity transition[1] accompanied by a crystal–crystal transition[2,3] at 208.62 °K, is a well studied example of a molecular crystal composed of globular-shaped molecules which reorient and diffuse. Temperature dependent NMR[4-7] and infrared[8] measurements for adamantane have been reported as well as the synthesis and characterization of its twist boat isomer, twistane (tricyclo [4.4.0.0.^{3,8}] decane).[9,10]

We have measured the temperature dependent NMR linewidths and second moments for adamantane and linewidths, second moments, and spin–lattice relaxation times for twistane and interpreted the results in terms of the structure and dynamics of these crystals.

All PMR experiments were performed on vacuum-sublimed polycrystalline samples at 60 MHz employing a slightly modified Varian DP-60 spectrometer and a high