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Helium-Monolayer Completion on Graphite

C. E. Campbell*
Institute of Theoretical Physics, Department of Physics, Stanford University, Stanford, California 94305

and

F. J. Milford
Battelle Memorial Institute, Columbus, Ohio 43201

and

A. D. Novaco†
Brookhaven National Laboratory, Upton, New York 11973

and

M. Schick‡
Department of Physics, University of Washington, Seattle, Washington 98105

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The densities at which monolayers of He^4 and He^3 on graphite are completed are calculated. as are their compressibilities. In addition, the binding energy of the first few atoms on the second layer is obtained.

I. INTRODUCTION

As a result of an intriguing series of experiments performed on monolayer films of helium,[1-5] several calculations of the expected properties of such films have been carried out. Almost without exception, these calculations are applicable to the system either in the limit of vanishing density[6-9] (i.e., calculation of the single-particle bands) or at densities at which fluid behavior is expected. In this paper we examine the system at higher densities at which the monolayer is nearing completion and the second layer begins to form. We calculate the density of a completed monolayer and its compressibility, estimate its Debye temperature, and calculate the binding energy of the first few atoms on the second layer. The particular system treated is that of helium adsorbed on graphite.

The density at which a monolayer is completed is the result of competition among several factors, but the basic physics seems clear. When, at the absolute zero of temperature, an atom is added to an existing monolayer, energy is gained owing to the attractive interactions between the added atom and the substrate as well as between the atoms in the monolayer. Were the atom to be added further from the substrate in an attempt to form a second layer, less energy would be gained from the two interactions. The loss would arise from the weaker substrate interaction at the larger distance. As the density of the monolayer increases, less energy is gained by adding the particle to it, owing to the enhancement of zero-point energy. Finally, at the completion density the energy gained by adding an atom to the monolayer is no longer greater than that obtained by adding it above the monolayer, and the second layer begins to form.

From the above description it is clear that what is needed to calculate the completion density is the ground-state energy of the monolayer as a function of density and the minimum energy of a single atom in the nascent second layer as a function of the density of the monolayer beneath it. These problems are addressed in Secs. II and III, respectively.

II. GROUND-STATE ENERGY OF MONOLAYER

The densities of completed monolayers of He^4 and He^3 adsorbed on graphite, calculated from experimental data, are 0.115 and 0.107 $Å^{-2}$, respectively.[10] The corresponding average particle separations are comparable to those found in bulk solid helium. It might be expected that the atoms are well localized in a close-packed triangular array which, at these densities, is out of registry with the periodic array of substrate adsorption sites.[11] While the method of correlated basis functions[12] is well suited for inclusion of the resulting correlation, we chose a simpler approach to the calculation of the ground-state energy of the system.

We assume that the atoms are, in fact, well localized laterally in a triangular close-packed array and are characterized by a probability distribution in the z direction, perpendicular to the substrate. This distribution is approximated by that appropriate to the lowest-energy single-particle state. The potential energy of this configuration arises from the helium-helium and helium-substrate interactions. The former contribution is obtained by introducing an effective potential which is a function only of the lateral distance ρ between

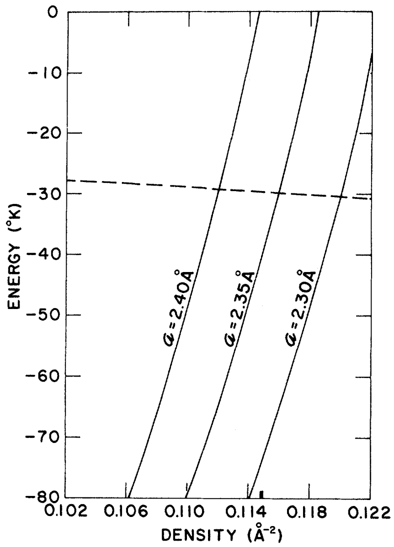

FIG. 1. Chemical potential of monolayer He^4 shown as a function of density for three values of the hard-core parameter. The dashed line is the energy of a particle in the nascent second layer. Marker on abscissa indicates experimental completion density.

atoms:

$$V_{\text{eff}}(\rho)=\int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dz'\ V(\rho, z-z')P(z)P(z') ,$$

where $V(\rho, z-z')$ is the bare helium-helium potential, and

$$P(z)=\int dx\,dy\, |\psi(x,y,z)|^2 ,$$

where $\psi(x,y,z)$ is the single-particle wave function of lowest energy obtained by Hagen, Novaco, and Milford[8] and the integration is over the normalization area.

With the assumption of lateral localization, the potential energy arising from helium-helium interactions can now be calculated by performing a planar lattice sum of V_{eff}, which yields a quantity denoted V_{sum}. The bare helium-helium potential is taken to be the Lennard-Jones 6-12 potential

$$V=4\epsilon\left[\left(\frac{\sigma}{r}\right)^6-\left(\frac{\sigma}{r}\right)^{12}\right]$$

with de Boer-Michels parameters:

$$\epsilon/k_B=10.22\ ^\circ\text{K}, \quad \sigma=2.56\ \text{Å}.$$

The kinetic energy of the configuration is divided into that arising from lateral correlations of the atoms and a contribution from motion perpendicular to the substrate. The former contribution is approximated by using London's method[13] as adapted by Campbell and Schick[14] to a two-dimensional system. The kinetic energy is equated to that arising from the zero-point energy of a system of hard disks with the same number density as the helium atoms under consideration. The hard-disk diameter a is chosen to represent the effect of the strong short-range repulsion present in V_{eff}. The particular choice of a will be discussed in Sec. III. The expression which results for this contribution to the kinetic energy per particle is given by

$$T/N=-2\pi\hbar^2\xi/\{ma^2(c-\xi^{1/2})[\ln\xi/c^2-b(c-\xi^{1/2}]\} ,$$

where ξ ($=na^2$) is equal to the areal density n in units of a^{-2}, and b and c are constants equal to 0.483 and 1.07, respectively.

The remaining contribution of the energy per particle of the monolayer comes from the potential energy of the helium-substrate interaction and the kinetic energy owing to motion in the z direction. An estimate of the sum of these two energies which is consistent with our approximation is simply the single-particle ground-state energy obtained by Hagen, Novaco, and Milford,[8] which we denote by e_{sp}. These values are -188 and -181.4 °K for He^4 and He^3, respectively.

In summary, the energy per particle e_0 of the ground state of an adsorbed monolayer of helium in the high-density limit is approximated by

$$e_0(n)\approx V_{\text{sum}}/N+T/N+e_{\text{sp}}.$$

Note that the first two terms on the right are density dependent.

The final aspect of the approximation is that the periodicity of the substrate is ignored. The validity of this approximation is enhanced at high densities by the fact that the helium atoms cannot be in registry with the substrate. As a consequence, the correlation between atoms will force a nearly uniform sampling of points in the unit cell.

To calculate the density of a completed monolayer, we need only the derivative of the ground-state energy with respect to particle number, i.e., the chemical potential, which may be written

$$\mu(n)=e_0(n)+n\,\frac{de_0(n)}{dn} .$$

This quantity is shown as a function of density for He^4 in Fig. 1 and He^3 in Fig. 2 for three different values of the hard-disk parameter a.

The relation between the ground-state energy and density can also be used to obtain the compressibility. We return to this quantity in Sec. III.

III. MONOLAYER COMPLETION

The density of first monolayer completion, n_1, is that density at which the chemical potential, calculated above, is equal to the energy $e_2(n)$ of a single particle on the second layer:

$$\mu(n_1)=e_2(n_1) .$$

An approximation to $e_2(n)$ is obtained by solving the single-particle Schrödinger equation with the poten-

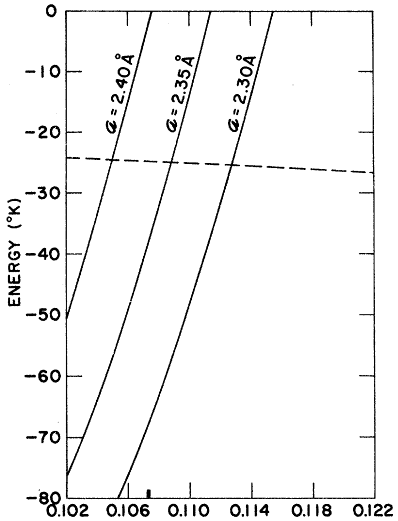

FIG. 2. Chemical potential of monolayer He^3 shown as a function of density for three values of the hard-core parameter. The dashed line is the energy of a particle in the nascent second layer. Marker on abscissa indicates experimental completion density.

tial provided by the monolayer of density n and the substrate. Exchange interactions are therefore ignored, a procedure which is justified *a posteriori* by the small overlap of the wave functions of particles in the first and second layers. In attempting to calculate the potential seen by an atom on the second layer, one must consider how the configuration of the atoms in the monolayer appears to the atom on the second layer, i.e., what are the relative vibrational frequencies in the two parts of the system. If the monolayer appears to be stationary, then the potential arising from it will depend on both the lateral and z coordinates of the second-layer atom and will be given by

$$W(\vec{\rho}, z) = \sum_j \int_{-\infty}^{\infty} dz' \; V(\vec{\rho} - \vec{\rho}_j, \; z - z') P(z') \, ,$$

where j runs over the triangular lattice of the first layer. The uniform substrate potential is then added to this to obtain the total potential seen by an atom in the second layer.

The opposite extreme occurs if the characteristic frequencies of the atoms in the monolayer are much greater than that of the second-layer atom. In this case, the first layer of helium atoms may be replaced by a layer which is uniform laterally and which has density n. The potential arising from such a layer is independent of ρ and is given by

$$W'(z) = n \int d\vec{\rho}' \int_{-\infty}^{\infty} dz' \; V(\vec{\rho} - \vec{\rho}', \; z - z') P(z') \, .$$

As above, this potential is added to that arising from the substrate to obtain the total potential. The result is shown in Fig. 3 for a density of 0.12 Å^{-2}.

In order to determine the sensitivity of the monolayer completion density to the choice between the two potentials above, the calculation of $e_2(n)$ was carried out for several densities using each potential. The use of $W(\rho, z)$ necessitates methods previously used to find the eigenstates and eigenvalues of a helium atom adsorbed on a rare-gas-plated substrate.[7] For the ground-state energy, this involves expanding the true ground state in plane waves in the lateral coordinates and Morse functions in z. A 1% accuracy was obtained by using seven plane waves and five Morse functions. The calculation employing the potential $W'(z)$ is much simpler as it only involves solving a one-dimensional Schrödinger equation. The values of $e_1(n)$ obtained via this latter method are shown by the dashed line in Figs. 1 and 2 for He^4 and He^3, respectively. The values of $e_1(n)$ which result from the former method differ from those shown by an amount between 1% and 10% for densities in the range from 0.10 to 0.12 Å^{-2}. An examination of Fig. 1 or Fig. 2 shows that such a difference makes only a very small (less than 2%) change in the density of monolayer completion, owing to the large derivative of the chemical potential with respect to density. In fact, this large derivative makes the monolayer completion density practically insensitive to a quantum-mechanical calculation of $e_2(n)$. The completion density is bounded from above by that density at which the chemical potential becomes positive and from below by that density at

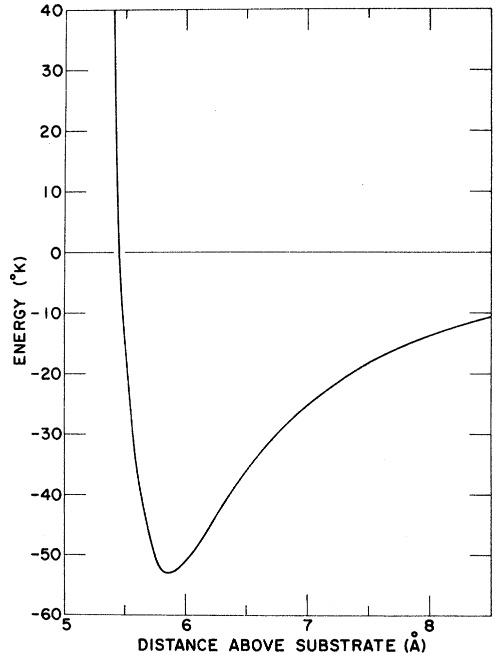

FIG. 3. Potential caused by graphite substrate and layer of helium atoms at a density of 0.12 Å^{-2}.

which the chemical potential is equal to the classical value of $e_2(n)$, the minimum of the potential energy which varies with density. This simple argument provides the following bounds for He^4 completion density n, for a choice of hard-core diameter equal to 2.35 Å: $0.1125\ \text{Å}^{-2} < n_1 < 0.1185\ \text{Å}^{-2}$.

From Figs. 1 and 2 it can be seen that a choice of hard-core diameter of 2.35 Å gives monolayer completion densities which are quite close to the experimentally determined values of 0.115 Å^{-2} for He^4 and 0.107 Å^{-2} for He^3. In fact, a choice of $a = 2.36$ Å for the former and $a = 2.37$ Å for the latter gives agreement with experiment. The close agreement between these two values of a is gratifying. Moreover, they are somewhat less than the value of σ (2.56 Å) at which distances the Lennard-Jones potential is zero. Thus they are consistent with the interpretation of their representing hard-core diameters.

From the calculated ground-state energy of the monolayer as a function of density, we can immediately obtain the compressibility K:

$$K = -\frac{1}{A}\frac{dA}{d\phi} = \left(2n^2\frac{de_0(n)}{dn} + n^3\frac{d^2e_0(n)}{dn^2}\right)^{-1},$$

where ϕ is the spreading pressure. Taking $a = 2.35$ Å we obtain for K at the completion density the value of 0.53×10^{-2} cm^2/erg for He^4 and 0.73×10^{-2} cm^2/erg for He^3. Lastly, the predicted binding energy of the first few atoms on the second layer is 30 °K for He^4 and 25 °K for He^3.

Neither the compressibility nor the binding energies have been measured experimentally, although the Debye temperature has.[4] This latter quantity cannot be obtained directly from our calculation as it depends on the speed of transverse waves in addition to the compressibility. However, by the following argument we may obtain an estimate of the order of magnitude of the Debye temperature to be expected from the above compressibility.[15] We estimate the velocity of longitudinal waves from the density and compressibility according to[16] $C_L^2 = 5/(9n_{\text{bulk}}K_{\text{bulk}})$, which is appropriate for the bulk solid. For the ratio of transverse to longitudinal sound velocities averaged over angles, we take the similar quantity from the bulk. This latter can be obtained from values of the bulk Debye temperature and longitudinal speed of sound measured at the same density and yields a ratio[17] of 0.52. With these two estimates one can immediately obtain a value of 67 °K for the Debye temperature of the monolayer at completion, which is to be compared to the experimental value[4] of 58 °K. A similar calculation predicts a Debye temperature of 72 °K for completed He^3 monolayers.

In summary, we have calculated the completion densities for monolayers of He^4 and He^3 as well as their compressibilities and the binding energy of the initial atoms on the second layer. We have also shown that the completion density is almost entirely determined by the chemical potential of the first layer. Improvements upon these results may therefore be expected from those calculations which include more carefully the correlations among atoms in the first layer.[18]

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Experimental Electron Energy Distributions for Townsend Discharges in Argon Gas

Jon R. Losee and David S. Burch
Department of Physics, Oregon State University, Corvallis, Oregon 97331

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In this work the electron energy distribution functions and the anisotropic drift term of the velocity distribution functions in non-self-sustaining (Townsend) discharges in argon were determined by direct measurement for a range of E/N (electric field strength per gas-atom concentration) from 70 to 407 townsends (Td) (1 Td $=10^{-17}$ V cm^2). Some structure in the form of the distribution functions is observed, but the prediction of Heylen and Lewis for argon is not fully supported. The experimental method employed is to energy analyze electrons effusing from apertures in the anode of a discharge cell with a spherical retarding electric field. The experimental energy distributions were used along with cross-section data from the literature to compute the electron mobilities, diffusion constants, mean energies, and Townsend's first-ionization coefficients. Combination of the data with results from kinetic theory permitted evaluation of the anisotropic part of the velocity-distribution function.

INTRODUCTION

Gaseous discharges of the non-self-sustaining, or Townsend, type have a long history of service for investigation of the fundamental processes which occur when electrons pass through a gas of low concentration N. The electrons are driven by a uniform electric field E, and, over a wide range of the parameters, the behavior of the discharge is found to be governed by the quotient E/N. A complete description of Townsend discharges is afforded by a knowledge of the electron velocity distribution, which is also a function of E/N, and the cross sections for the various collisional processes available to the constituents of the discharge. In most cases, the electron-energy-distribution function serves as well as the velocity distribution for computation of the transport parameters.

Direct measurement of the important cross sections has been made for many gases, and transport parameters have been the object of most investigations which employed Townsend discharges. However, there has been but one prior report[1] of a direct measurement of the distribution functions. In this paper we present the results of further efforts, these to determine energy-distribution functions for Townsend discharges in argon.

EQUIPMENT AND DETAILS

The experimental method used in the present work is a modification of the retarding-field method employed by Roberts and Burch.[1] The procedure will be discussed with reference to Fig. 1. Electrons effusing from apertures in the anode of the discharge cell are energy analyzed with a retarding electric field maintained between the anode and the collector. The anode of the discharge is a gold foil, 4.9 μm thick. It is perforated at its center with about 200 apertures of 13 μm diam and spaced 160 μm center to center in a circular area 2.5 mm in diam. A pattern of apertures is used rather than the large single aperture indicated in Fig. 1 so that adequate electron current to the collector can be realized along with satisfaction of the criterion for effusive flow. A guard ring,

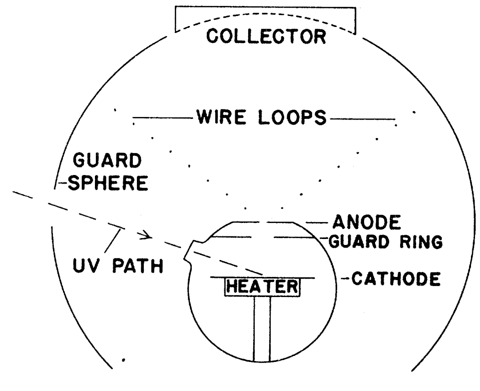

FIG. 1. Simplified schematic of the discharge cell and the energy analyzer.