PHYSICAL REVIEW A VOLUME 3, NUMBER 2 FEBRUARY 1971

Ground State of ^{4}He Monolayers Adsorbed on Inert Substrate*

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(Received 5 October 1970)

We investigate the properties of a system of ^{4}He atoms at the absolute zero of temperature interacting via a Lennard-Jones potential, and constrained to motion in two dimensions by an otherwise inert substrate. Results of a semiclassical calculation indicate that the ground state is that of a self-bound liquid. It further indicates that a close-packed-solid configuration is not self-bound. A quantum-mechanical variational calculation is performed to obtain an upper bound on the energy of the system. A result of -0.61 °K per particle is obtained at a density of 0.035 Å^{-2}. The relationship between this calculation and recent experiments on ^{4}He monolayers is briefly discussed.

I. INTRODUCTION

Recent experimental investigations of adsorbed helium monolayers have been interpreted as indicating that the system consists of a condensed phase in equilibrium with both an adsorbed and a bulk vapor.[1] Several models of such a system have been investigated in order to illuminate both the static[2] and dynamic[3] effects of the substrate on the adsorbed atoms. However, in order to extract from the experimental results the effects of the substrate, one must know those properties of the monolayer which are due to the interaction between helium atoms alone. In this paper, we study the ground state of a monolayer system of helium atoms which are constrained to motion in two dimensions by an otherwise inert substrate.

It might be expected that the zero-point motion of the helium atoms would be of great importance in determining the properties of the two-dimensional system just as these motions prevent solidification of the bulk system except under pressure. To determine whether the ground-state configuration of the system is representative of a liquid or a solid, a semiclassical approach due to London is employed in Sec. II. It is found that the lowest energy of the system is obtained for a rather open configuration of particles which is taken to represent a liquid. In addition, it is found that the close-packed solid is not self-bound owing to the effects of the large zero-point motions.

In Sec. III, the ground-state energy of the liquid is estimated by means of a quantum-mechanical variational calculation. An upper bound on the ground-state energy per particle of -0.61 °K at a density of 0.035 Å^{-2} is obtained, in substantial agreement with a previous result of Hyman.[4] Possible improvements to this calculation are discussed.

II. SEMICLASSICAL CALCULATION

We consider a system of N helium atoms constrained to motion in two dimensions and interacting via the Lennard-Jones 6-12 potential

$$V(r)=4k_B\epsilon\left[(\sigma/r)^{12}-(\sigma/r)^{6}\right]\ , \tag{2.1}$$

where ϵ and σ are the de Boer–Michels parameters,[5] $\epsilon=10.22$ °K, $\sigma=2.556$ Å, and k_B is Boltzmann's constant. At the absolute zero of temperature, a classical system interacting via the above potential would condense to a two-dimensional solid with particle separation very near the minimum of this potential. Because of the small mass of the helium atom, however, the quantum-mechanical zero-point motion will be important producing an appreciable kinetic energy and changing the potential energy from its classical value. In order to estimate the magnitude of the kinetic energy, we follow London[6] and observe that the zero-point motion arises from the restriction on the particle motion due to the strong repulsive core of the interaction. Therefore, as a first approximation, one can replace the particles by impenetrable disks of diameter a and assume that the zero-point energy depends only on the density of particles. Under this assumption, analytic expressions for the kinetic energy per particle can be obtained in the region of very low and very high densities. The energy per particle of a hard-disk gas at low densities has been shown by one of us[7] to be given by

$$\text{K.E.}/N\rightarrow(-2\pi\hbar^2/ma^2)\,\xi/\ln\xi,\quad \xi\rightarrow 0 \tag{2.2}$$

where ξ is the dimensionless density defined by $\xi=na^2$. In the high-density limit, each disk can be viewed as trapped in a cage formed by its nearest neighbors. The kinetic energy is then approximately given by the energy of the lowest state of a point mass confined to a circle of radius $d-a$, where d is the nearest-neighbor separation. This energy is $\text{K.E.}/N=\hbar^2k^2/2m$, where $k=\alpha/d-a$, and $\alpha=2.40$ is the first zero of the cylindrical Bessel function of order zero. The distance d may be expressed in terms of ξ by noting that at high densities the system will attain a close-packed triangular structure. This observation leads to the relation

$$d = ac\xi^{-1/2} ,$$

where

$$c^2 = 2/\sqrt{3} ,$$

so that

$$\mathrm{K.E.}/N \to (\hbar^2/2ma^2)\alpha^2\xi/(c - \xi^{1/2})^2, \quad \xi \to c^2 . \tag{2.3}$$

A simple interpolation formula between Eqs. (2.2) and (2.3) is

$$\mathrm{K.E.}/N = - 2\pi c\hbar^2\xi/ma^2(c - \xi^{1/2})[\ln\xi/c^2 - b(c - \xi^{1/2})] , \tag{2.4}$$

where $b = - 2c^{-1} + 4\pi c\alpha^{-2}$. Figure 1 shows this kinetic energy as a function of ξ. The value of the hard-core diameter was taken to be 2.3 Å, the value chosen by London.[6] The potential energy is calculated classically by performing appropriate lattice sums. A two-dimensional solid is represented by a close-packed lattice. A two-dimensional liquid cannot, of course, be represented by a perfectly regular array. However, in the spirit of the Keesom-Taconis model for bulk liquid helium,[8] we investigate a series of more open lattices which can be taken to represent instantaneously the structure of the short-range order which essentially determines the potential energy per particle. Presumably these open lattices are unstable with respect to rotational modes which, while breaking the long-range order, preserve the short-range order and lower the energy only slightly.

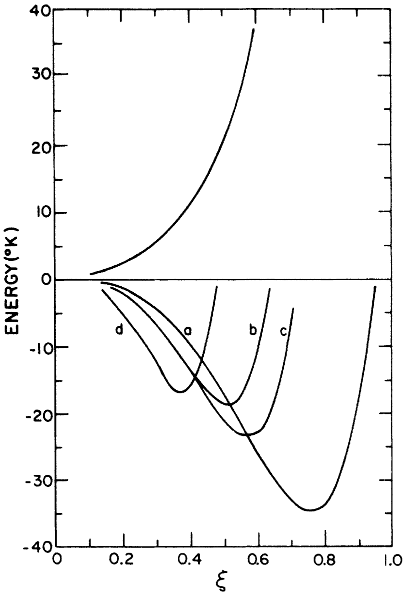

FIG. 1. Kinetic energy per particle of hard disks of radius 2.3 Å and classical potential energy per particle of the four lattices of Fig. 2, as functions of the dimensionless density ξ.

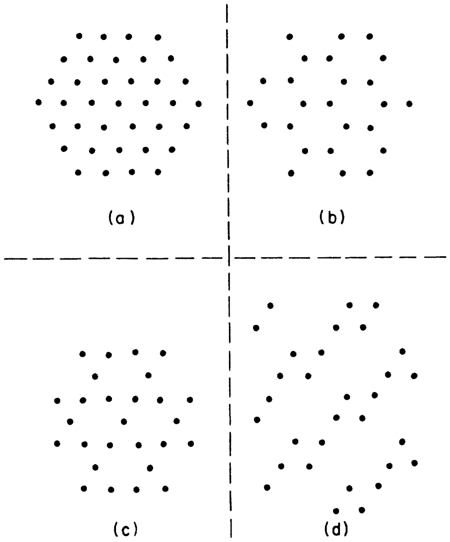

FIG. 2. Four lattices investigated in the semi-classical calculation.

Figure 2 shows four of the lattices investigated. The two-dimensional solid is represented by the triangular lattice of Fig. 2(a). The remaining three lattices are obtained by removing particles from the close-packed structure. Lattice (b) is a honeycomb structure in which each particle has three nearest neighbors, as compared to six in the close-packed structure. Lattice (c) is one of the trigonal planes of the Keesom-Taconis lattice. (In the other trigonal plane, the particles are close-packed.) Each occupied site has four nearest neighbors. Lattice (d) is a more open lattice in which each particle has three neighbor particles and holes, as does each hole. This lattice has one-half the density of the close-packed structure of equal nearest-neighbor spacing. Although there appear to be two inequivalent occupied sites, they are in fact energetically equivalent for two-body interactions.

The classical potential energy for each of these lattices has the form

$$V(\xi)/N = \epsilon_{12}\xi^6 - \epsilon_6\xi^3 ,$$

where ϵ_{12} and ϵ_6 are positive and are obtained for each lattice from the appropriate lattice sum. Figure 1 shows the classical potential energy for the four lattices as a function of ξ.

The semiclassical estimate for the energy of each configuration is obtained by adding the hard-disk estimate of the zero-point energy, Eq. (2.4), to each classical potential energy. The results are shown in Fig. 3. It is seen that the lowest energy per particle is obtained for the most open lattice

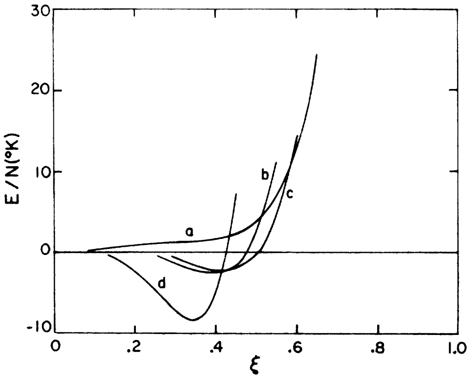

FIG. 3. Total energy per particle of the four lattices calculated semiclassically, as a function of the dimensionless density ξ.

(d). This indicates that for the two-dimensional system, the ground-state configuration represents a liquid rather than a solid just as in the bulk system and for the same reason that applies to the bulk; that is, the effect of the zero-point motion. This effect is even more pronounced in the two-dimensional system, however, for it is seen in Fig. 3 that contrary to the bulk result, the close-packed solid is not self-bound; i.e., its energy is positive for all densities.[9] The same result is obtained for a square lattice. The increased importance of the zero-point motion in the two-dimensional system is easily understood when one considers that the potential energy of the two-dimensional close-packed solid is approximately one-half that of the bulk (six instead of twelve nearest neighbors), while the zero-point energy of the solid is approximately two-thirds that of the bulk.

The particular value of the ground-state energy per particle of the liquid as obtained from Fig. 3, − 8.26 °K, cannot be taken too seriously for several reasons. First, at liquid densities, it cannot be expected that the particles are very well localized so that the classical calculation of the potential energy is not very reliable at such densities. Second, the value of the total energy at liquid densities is quite sensitive to the estimate of the kinetic energy, that is, both to the hard-core radius chosen and to the particular expression taken to interpolate between the analytic forms of the kinetic energy appropriate at low and high densities. For example, using the form for the kinetic energy given in Eq. (2.4), but changing the hard-core radius to 2.5 Å, one finds that only lattice (d) is self-bound and its ground-state energy is decreased several degrees.

The above remarks do not, however, affect the primary result of this section, that the energy of the liquid state is lower than that of the solid. Further, it is to be expected that they will not change the conclusion that the solid is not self-bound, for at the high densities characteristic of the solid, the particles are highly localized, thus decreasing the error in the classical estimate of the potential energy. In addition, at these densities the zero-point energy should be well described by the analytic expression of Eq. (2.3).

With the knowledge that the ground state of the two-dimensional system represents a liquid, we now turn to a quantum-mechanical calculation to obtain the energy of this state.

III. VARIATIONAL CALCULATION

An alternative procedure for calculating the binding energy of the liquid is one employed in calculations of the properties of bulk liquid ^{4}He. This is the quantum-mechanical variational calculation of the ground-state energy in the Jastrow function space. The technique, described below, when applied to the bulk system has produced lower bounds on the binding energy of 85% of the experimental result, with a calculated equilibrium density within 10% of experiment.[10–12] Although *a priori* claims of this accuracy in the two-dimensional system cannot be made, a rigorous lower bound on the binding energy can be obtained and ultimately corrected for contributions from outside the Jastrow function space.

A Jastrow function (often called a Bijl-Dingle-Jastrow function[13]) is a trial function of the form

$$\psi_0(r_1, \cdots, r_n) = \exp\tfrac{1}{2} \sum_{i\neq j}^{N} -u(r_{ij}), \qquad (3.1)$$

where $u(r)$ is any real function. This wave function has the correct symmetry to serve as a trial function for the ground state of the N-body boson system. It is also of the simplest form to give a finite expectation value of a Hamiltonian which contains a singular two-body potential such as that of Eq. (2.1). For the expectation value to be finite, $u(r)$ must increase without limit as r approaches zero.

The calculation proceeds by choosing a suitable $u(r)$ which depends on several parameters, and then extremizing the expectation value of the Hamiltonian with respect to these parameters. The usual choice in three dimensions has been

$$u(r) = A(d/r)^p, \qquad (3.2)$$

where the variational parameters are p and A. The minimum is found at $p = 5$ and is not very much affected by taking $p = 4$ or $p = 6$. That p falls in this range is probably related to the fact that, for a r^{-12} repulsive potential, the two-particle wave function behaves like e^{-B/r^5} for small r, where B is a constant.

For the two-dimensional calculation, we also take the form given in Eq. (3.2) for $u(r)$. The effort in the variational calculation is considerably reduced by taking $p = 5$ at the outset, leaving only one parameter to be varied. This choice seems reasonable since the two-body wave function in two dimensions has the same form for small r as that given above.

With the wave function of Eq. (3.1), the expectation value of the kinetic energy per particle can be put in the form

$$\frac{\text{K. E.}}{N} = \pi n \int_0^\infty g(r) r \frac{\hbar^2}{4m}\left(\frac{u'(r)}{r} + u''(r)\right) dr, \tag{3.3}$$

and the potential energy per particle is given by

$$\frac{\text{P. E.}}{N} = \pi n \int_0^\infty g(r) r V(r)\, dr, \tag{3.4}$$

where $g(r)$ is the radial distribution function defined by

$$g(r) = \frac{N(N-1)}{n^2} \int \psi_0^2 \, d\bar{r}_3 \cdots d\bar{r}_N \Big/ \int \psi_0^2 \, d\bar{r}_1 \cdots d\bar{r}_N \,. \tag{3.5}$$

There are two common integration techniques which enable $g(r)$ to be calculated from Eq. (3.5) with great accuracy for very small values of N, say in the range of 30–1000 particles. The system can be extended without limit by means of periodic-boundary conditions. The first of these techniques is the well-known Monte Carlo procedure.[10] The second method, recently employed by the Orsay group,[11] takes advantage of the mathematical equivalence of the probability density ψ_0^2 to the Boltzman factor of classical statistical mechanics. Thus, the radial distribution function of a fictitious classical system interacting via the two-body potential $\phi(r)$ at temperature T is identical to the desired $g(r)$ of Eq. (3.5) provided that

$$u(r) = \phi(r)/k_B T.$$

The function $g(r)$ for the quantum-mechanical system of interest is generated by numerically solving the classical equations of motion for the fictitious system of particles interacting via the potential $\phi(r)$ and characterized by the velocity distribution corresponding to temperature T. This technique is commonly referred to as the method of molecular dynamics.[14] In calculations of the properties of bulk liquid ^{4}He, it gives results in close agreement with those of McMillan[10] obtained by Monte Carlo methods, and of Massey and Woo[12] who obtain $g(r)$ by methods other than those described above.

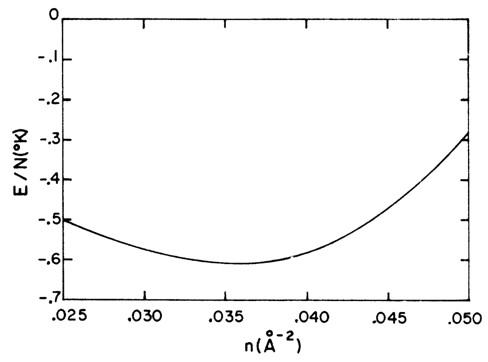

FIG. 4. Total energy per particle obtained from the variational calculation, as a function of density.

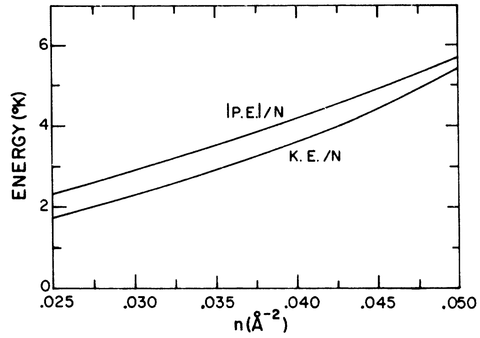

FIG. 5. The magnitude of the potential and kinetic energy per particle as obtained from the variational calculation, as a function of density.

We have chosen the molecular-dynamics technique to perform the integrals in Eq. (3.5). A computer code developed by Rahman[15] for calculating the properties of a classical bulk system was modified to apply to a two-dimensional system. This is composed of 108 particles (a number chosen somewhat arbitrarily), at some density n_0. The energy-expectation value is calculated for a set of values of the variational parameter A at a fixed value of $d = d_0$ in Eq. (3.2). The scaling law of McMillan[10] can be used to obtain the energy at density n for the same set of values of A with d given by $d_0(n_0/n)^{1/2}$. The minimum value of the energy at each density is plotted in Fig. 4. It is seen that the ground-state energy per particle is

$$E/N = (-0.61 \pm 0.1)\,^\circ\text{K},$$

which is attained at a density of $n = 0.035$ Å^{-2}. The kinetic and potential energies which add to give the result shown in Fig. 4 are displayed in Fig. 5. It is to be noted that the total energy is the result of a large cancellation between the potential and kinetic energies. A small error in either of these terms becomes a large relative error in their sum. It was necessary in the 108-particle system to go approximately 2500 steps in time after equilibrium was established to produce energies within the error given above. Furthermore, the effect of the periodic-boundary conditions in such a small box is magnified by the large cancellation. Earlier calculations with 27 particles showed large fluctuations due to the small number of particles and an apparent tendency to settle down to ground-state energies several tenths of a degree smaller in magnitude than those displayed in Fig. 4.

A Monte Carlo calculation for a system of 32 particles with the same ground-state wave function has been carried out by Hyman.[4] The ground-state energy per particle obtained, -0.62 °K, occurs at a somewhat higher density, 0.042 Å^{-2}, than obtained above. The discrepancy must be attributed to the difference in the number of particles.

The radial distribution function $g(r)$ which characterizes the two-dimensional system at the density at which it attains its minimum energy is shown in Fig. 6. Also shown for comparison is the radial distribution function obtained by Schiff and Verlet[11] for bulk liquid ^{4}He at equilibrium density 0.0218 Å^{-3} using the same technique and trial function we have used. From the observations that the peak in $g(r)$ occurs at a greater distance and is of greater width in the two-dimensional system than in the bulk, it can be concluded that the mean separation of the particles is larger and they are less well localized in the former system than in the latter.

The upper bound on the ground-state energy provided by the variational calculation described in this section can be decreased somewhat by the application of several other techniques. One of these is the paired phonon analysis,[16,17] which determines the wave function and expectation value which satisfies the extremum condition

$$\frac{\delta}{\delta u(r)} \frac{(\psi_0, H\psi_0)}{(\psi_0, \psi_0)} = 0 \qquad (3.6)$$

in the complete space of Jastrow functions ψ_0. This removes the restriction to the subspace of Jastrow function defined by the parametrization of Eq. (3.2). This technique has been applied to the bulk ^{4}He system by Campbell and Feenberg.[17] An additional correction can be obtained by introducing wave functions which are not in the Jastrow space. Davison and Feenberg,[18] for example, have calculated the contribution of the states

$$\rho_{\vec{k}}\, \rho_{\vec{l}}\, \rho_{-\vec{k}-\vec{l}}\, \psi_0$$

in second order of perturbation theory to the ground-state energy where ψ_0 is the wave function satisfying Eq. (3.6) and where $\rho_{\vec{k}}$ is the usual density fluctuation operator. The total of these two contributions is about a 1 °K lowering of the ground-state energy of the bulk system bringing the theoretical results into very close agreement with experiment. The magnitudes of these corrections in the two-dimensional system must, of course, be calculated independently.

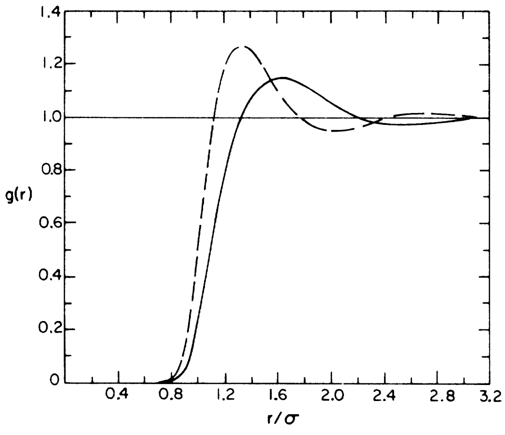

FIG. 6. The radial distribution function obtained from the variational calculation at a density of 0.036 Å^{-2} (solid line) and a similarly obtained radial distribution function for bulk liquid ^{4}He at a density of 0.0218 Å^{-3}.

IV. DISCUSSION

A semiclassical calculation of the properties of a two-dimensional system of bosons at the absolute zero of temperature indicates that the ground-state of the system represents a liquid. It further indicates that the two-dimensional close-packed solid is not self-bound. A variational estimate of the ground-state energy per particle was found to be -0.6 °K.

Stewart and Dash have interpreted their experimental results on the heat capacities of submonolayer helium films adsorbed on argon-plated copper as indicating that the helium is condensed into a two-dimensional solid with a lateral binding of at least 15 °K per particle. If this interpretation is indeed correct then it must be concluded from the results of the calculations of this paper that the presence of a solid state with a large lateral binding cannot be due primarily to the two-particle interaction. It must rather be attributed substantially to the presence of the substrate potential which makes the problem inherently three dimensional and introduces both band-structure and dynamical-interaction effects.

ACKNOWLEDGMENTS

We wish to thank Dr. J. G. Dash for many helpful comments. We are indebted to Dr. A. Rahman for providing us with his computer code for the molecular-dynamics calculation and for useful information. Thanks are also due Dr. D. Hyman for providing us with a copy of Ref. 4.

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*Research supported in part by the Atomic Energy Commission and the National Science Foundation.

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Heat Capacity near the Superfluid Transition in He^4 at Saturated Vapor Pressure

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(Received 24 June 1970)

Apparatus and experimental procedures suitable for a number of high-precision measurements of properties of liquid helium near the superfluid transition temperature T_λ are described. Experimental determinations near T_λ of the heat capacity at saturated vapor pressure are presented. On the basis of these measurements, the asymptotic temperature dependence of the heat capacity at constant pressure C_p is examined and compared with current theories of critical phenomena. Although there is some latitude in the interpretation of the results in terms of the asymptotic behavior of C_p, no interpretation fully in agreement with the original formulations of the scaling laws for critical phenomena, and with a divergent C_p, is consistent with the measurements. It is expected that an extensive discussion of the thermodynamics of the λ line at higher pressure, based on measurements of the heat capacity at constant volume C_v, will be presented in a later publication.

I. INTRODUCTION

In recent years it has been possible to measure rather accurately a number of equilibrium[1-13] and transport[14-20] properties near the superfluid transition temperature T_λ in He^4. Some of these measurements have been used[7,14-16,21] to verify rather accurately predictions based upon the so-called scaling laws[22-27] which relate the temperature dependences of various parameters near critical points. There exist already very detailed measurements of the heat capacity at saturated vapor pressure[1-5] C_s for He^4 near T_λ. However, developments in low-temperature techniques and instrumentation which have occurred since the time of this work make it possible to improve considerably upon these earlier results, and to establish the detailed nature of the divergence of the heat capacity at constant pressure C_p more precisely. It seems particularly desirable to study the divergence of C_p in great detail for the superfluid transition. This system is extremely suitable for high-precision experimental work, and one can hope to put theoretical predictions[22-27] to a more severe test here than is possible near most other critical points. Some of the well-known advantages from an experimental viewpoint of the superfluid transition are the relative ease of attaining thermal equilibrium, even for He I, the high purity of the sample, and the ease with which corrections for the gravitational pressure gradient[28] in the sample can be applied. We therefore have attempted to measure C_s as precisely as can reasonably be done at this time. These new results are in very good agreement with the earlier work.[1-5] Extremely near the transition, where the precision of the measurements is limited by the temperature resolution, the new data are only about a factor of 2 more precise than the older ones. Further away from T_λ, where the precision is limited by other calorimetric techniques, the new results constitute