

## Effects of crystalline substrate potentials on quasi-two-dimensional liquid helium\*

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The effects of a finite substrate-helium interaction and of the crystalline structure of a substrate potential on the liquid phase of a monolayer of helium are explored for models of three systems: helium physisorbed on a basal-plane surface of graphite;  $^4\text{He}$  adsorbed on graphite preplated by a close-packed layer of neon; and  $^4\text{He}$  adsorbed on graphite preplated by a close-packed layer of argon. The ground-state energy as a function of the areal density is calculated for each of these models by introducing a class of trial wave functions which have finite extent orthogonal to the substrate, possess the same translational symmetry as the substrate, and include short-range correlations between the helium atoms. The results for  $^4\text{He}$  on bare graphite are virtually identical with previous results for the model of  $^4\text{He}$  atoms in a two-dimensional structureless box, with very small quantitative differences. The indications for  $^3\text{He}$  on bare graphite are that the liquid is not self-bound. In contrast to the bare-graphite substrate, the other two substrates exert a strong influence on the liquid, substantially increasing the equilibrium density.

### I. INTRODUCTION

The physics of quasi-two-dimensional quantum fluids has recently been explored experimentally in the form of single layers (monolayers) of helium physisorbed on the basal plane of graphite.<sup>1</sup> The remarkable property of this graphite substrate is that, with the exception of a few discrete densities, the experimental results can be understood in terms of the helium alone<sup>2</sup>; i. e., the only role of the graphite is to confine the helium to a two-dimensional layer. The periodic structure of the graphite surface provides no qualitative effect except at the discrete densities where the helium settles into a lattice-gas phase. This situation is in marked contrast to other substrates which appear to dominate the properties of the adsorbed quantum fluids.<sup>3</sup>

While the theoretical understanding of many of the properties of helium adsorbed on graphite can be obtained qualitatively and semiquantitatively from the model of helium in two dimensions, an analysis of the role of a structured substrate and the finite extent of the monolayer in the third dimension (perpendicular to the adsorbing surface) is useful on several grounds. First, it should be shown explicitly that the graphite substrate does not play an important qualitative role. Second, there may be some weak quantitative effects of the substrate. Third, it is of interest to study the effects of substrates other than graphite on adsorbed quantum fluids. With regard to this last point, physisorption of quantum fluids should play an important role in the characterization of surfaces.

In this paper we focus on the ground-state energy of the adsorbed helium as a function of its structure. The structure of the ground state will be closely related to the structure of the adsorbed system at very low temperatures. We view our calculation as a determination of the  $T=0$  °K isotherm of the phase diagram. The effects of finite temperature require a more detailed study including an analysis of the excited states of the system.

In Sec. II we develop a theory which is capable of describing the ground state of an inhomogeneous quantum fluid. This is accomplished by introducing a class of trial wave functions which include the correlations between helium adatoms as well as structure of the substrate potential as seen by the helium atoms. The Schrödinger equation is replaced by Euler-Lagrange equations for the wave function by using the variational principle. The equations then are solved approximately.

The operational aspects of the problem are described in Sec. III, where we specify the helium-helium interaction and the interaction of the helium adatoms with the various substrates under consideration. Uncertainty concerning the latter interactions as well as dynamic effects of the substrate require us to classify our results as preliminary. Section IV contains the numerical results for  $^4\text{He}$  adsorbed on the basal plane of graphite with a brief discussion about  $^3\text{He}$  on the same substrate. Section IV B contains somewhat cruder numerical results for  $^4\text{He}$  adsorbed on neon-plated graphite and on argon-plated graphite. Though we plan to return to a more detailed consideration of these latter substrates at a later time, the results shown here are adequate to exhibit the sensitive

dependence of an adsorbed quantum fluid on the nature of the substrate, and by contrast the utility of the graphite substrate as an extremely smooth, nearly two-dimensional adsorbing surface.

We conclude in Sec. V with a brief discussion.

## II. THEORY

The helium adatoms are confined to a plane near the planar substrate surface by the substrate-adatom interaction. It is assumed that the zero-point motion of the adatoms perpendicular to the substrate surface is small compared to their average interatomic spacing, in which case they form a quasi-two-dimensional system. The interaction of the adatoms with the substrate is described by a time-independent single-body potential  $U(\vec{r}, z)$ , where  $\vec{r}$  is a two-dimensional vector which locates the adatom in a plane parallel to the surface, and  $z$  locates the adatom in the direction perpendicular to the surface. Adopting the convention that  $z$  is positive outside the substrate and negative inside, the potential  $U$  is attractive for large positive  $z$ , repulsive as  $z$  tends to zero, and has a periodic dependence upon  $\vec{r}$  which reflects the crystalline structure of the substrate surface. The adatom-adatom interaction is given by a two-body potential  $v(\rho)$ , where  $\rho$  is the distance between the adatom pair. Then the Hamiltonian for this system is

$$\hat{H} = \sum_{j=1}^N \left[ -\frac{\hbar^2}{2m} \left( \nabla_j^2 + \frac{\partial^2}{\partial z_j^2} \right) + U(\vec{r}_j, z_j) \right] + \sum_{i < j} v(\rho_{ij}), \quad (1)$$

where  $N$  is the number of adatoms,  $\rho_{ij}^2 = r_{ij}^2 + z_{ij}^2$ ,  $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$ ,  $z_{ij} = z_i - z_j$ ,  $m$  is the mass of the adatom, and  $\nabla_j^2$  is the two-dimensional Laplacian.

The ground-state energy is obtained variationally. A great simplification in the calculation is achieved by ignoring correlations in the  $z$  dependence of the trial ground-state wave function:

$$\Psi(\vec{r}_1, z_1, \dots, \vec{r}_N, z_N) = \left( \prod_{i=1}^N M(z_i) \right) \psi_{2D}(\vec{r}_1, \dots, \vec{r}_N). \quad (2)$$

$M(z)$  describes the "localization" of the adatom near the surface, and its shape should depend upon both adatom-adatom correlations and local (microscopic) density variations caused by the crystalline structure of the substrate surface. The variational estimate for the ground-state energy is  $E = \langle \Psi | \hat{H} | \Psi \rangle / \langle \Psi | \Psi \rangle$  with the variational parameters in  $\Psi$  properly optimized. With correlations in the  $\{z_i\}$  variables absent, it is convenient to define an effective two-dimensional substrate potential  $U_{2D}$  and an effective two-dimensional adatom-adatom potential  $v_{2D}$ :

$$U_{2D}(\vec{r}_j) = \int_{-\infty}^{\infty} dz M(z) \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} + U(\vec{r}_j, z) \right) M(z), \quad (3)$$

$$v_{2D}(r_{ij}) = \int_{-\infty}^{\infty} dz_i \int_{-\infty}^{\infty} dz_j |M(z_i)|^2 v(\rho_{ij}) |M(z_j)|^2. \quad (4)$$

Given a particular form for  $M(z)$ , these integrations define two-dimensional potentials which reduce the three-dimensional problem to a two-dimensional one. The effective two-dimensional Hamiltonian is then

$$\hat{H}_{2D} = \sum_j \left( -\frac{\hbar^2}{2m} \nabla_j^2 + U_{2D}(\vec{r}_j) \right) + \sum_{i < j} v_{2D}(r_{ij}); \quad (5)$$

so the ground-state energy is given by

$$E = \langle \psi_{2D} | \hat{H}_{2D} | \psi_{2D} \rangle / \langle \psi_{2D} | \psi_{2D} \rangle. \quad (6)$$

This procedure is *not* equivalent to separating the substrate potential into a  $z$  and  $\vec{r}$  part, since the effective two-dimensional Hamiltonian depends upon  $M(z)$ . It is, however, a projection of the three-dimensional problem into the two-dimensional plane.

The two-dimensional problem defined by  $\hat{H}_{2D}$  has been considered previously in two limiting cases: (i) the low-density limit, where the effects of the two-body potential can be ignored (i.e., the one-body problem)<sup>4-10</sup> or treated by a low order cluster expansion<sup>11,12</sup>; (ii) the smooth substrate limit, in which the periodic substrate potential is ignored.<sup>2,13,14</sup> Here we include both the effects of the substrate periodicity and the short-range adatom-adatom correlations which should be important at liquid densities. These two effects can be accounted for in the simplest way by choosing the  $\psi_{2D}$  factor in  $\Psi$  to be

$$\psi_{2D} = \prod_{i=1}^N e^{w(\vec{r}_i)/2} \psi_0(\vec{r}_1, \dots, \vec{r}_N), \quad (7)$$

where  $\psi_0$  depends only on the set of interparticle spacings  $|\vec{r}_i - \vec{r}_j|$ .

The statistics of the total trial function  $\Psi$  are contained in  $\psi_0$ , since the remaining factors are symmetric in the coordinates. For boson adatoms (<sup>4</sup>He), the  $\psi_0$  must also be symmetric. The simplest choice for  $\psi_0$  which can account for the short-range correlations between adatoms is the well-known Jastrow function

$$\psi_0(\vec{r}_1, \dots, \vec{r}_N) = \prod_{i < j} e^{u(r_{ij})/2}, \quad (8)$$

where  $u(r)$  becomes large and negative as  $r$  becomes small in order to prevent the overlap of the adatom repulsive cores.

The single-body functions  $\phi_0(\vec{r}_i) = e^{w(\vec{r}_i)/2}$  have the symmetry of the substrate in the liquid or vapor phase, and thus  $w(\vec{r})$  is periodic. In the absence of two-body interactions,  $\phi_0(\vec{r})$  would be the lowest Bloch state for the potential  $U_{2D}(\vec{r})$ .

For adatoms with Fermi statistics (e.g., <sup>3</sup>He), the appropriate symmetry may be inserted by in-

cluding a ground-state Slater determinant of plane waves as a factor in  $\psi_0$ .<sup>15</sup> This has the effect, however, of ignoring the dependence of the periodic part of the Bloch functions on  $\vec{k}$ ; i. e., we use

$$\phi_{\vec{k}} = e^{i\vec{k}\cdot\vec{r}} \phi_0(\vec{r}),$$

which should suffice for a highly mobile band. More generally for Fermi systems, the single-body prefactor multiplying the Jastrow function should be a Slater determinant of Bloch functions.

The primary focus of the remainder of this paper is <sup>4</sup>He, and thus Bose statistics apply. (We return to the <sup>3</sup>He problem in Sec. IV A.) Thus, to obtain  $\psi_{2D}$  and  $E$ , consider a two-dimensional box of area  $A$  containing  $N$  bosons, with Hamiltonian  $\hat{H}_{2D}$ . The expectation value of  $\hat{H}_{2D}$  in  $\psi_{2D}$  requires knowledge of the one- and two-body distribution functions for  $\psi_{2D}$ . The kinetic energy is given by

$$-\frac{\hbar^2}{8m} \int d\vec{r} p_1(\vec{r}) \nabla^2 w(\vec{r}) - \frac{\hbar^2}{8m} \int d\vec{r}_1 d\vec{r}_2 P_2(\vec{r}_1, \vec{r}_2) \nabla_1^2 u(r_{12}), \quad (9)$$

and the potential energy by

$$\int d\vec{r} p_1(\vec{r}) U_{2D}(\vec{r}) + \frac{1}{2} \int d\vec{r}_1 d\vec{r}_2 P_2(\vec{r}_1, \vec{r}_2) v_{2D}(r_{12}), \quad (10)$$

where the  $l$ -body distribution function is given by

$$P_l(\vec{r}_1, \dots, \vec{r}_l) = \frac{N!}{(N-l)!} \frac{\int \psi_{2D}^2(\vec{r}_1, \dots, \vec{r}_N) d\vec{r}_{l+1} \dots d\vec{r}_N}{\int \psi_{2D}^2(\vec{r}_1, \dots, \vec{r}_N) d\vec{r}_1 \dots d\vec{r}_N}. \quad (11)$$

Note that  $p_1(\vec{r})$  is the number density and is a periodic function of  $\vec{r}$  when  $w(\vec{r})$  is periodic. The two-body distribution function  $P_2(\vec{r}_1, \vec{r}_2)$  is likewise a periodic function of the "center-of-mass" variable  $\frac{1}{2}(\vec{r}_1 + \vec{r}_2)$ .

As a convenient first step in the calculation of these quantities, note that setting  $w(\vec{r})=0$  (i. e., using  $\psi_0$  instead of  $\psi_{2D}$ ) provides an upper bound on the total energy. In that case, the single-body distribution function  $P_1^{(0)}(\vec{r}) = N/A = n$  is constant, and the two-body distribution function depends only on the magnitude of the interparticle spacing:

$$P_2^{(0)}(\vec{r}_1, \vec{r}_2) = n^2 g_0(|\vec{r}_1 - \vec{r}_2|),$$

where  $g_0$  is the radial distribution function for  $\psi_0$ . Then the periodic potential  $U_{2D}$  contributes only its average value  $U_0$  to the expectation value:

$$U_0 = \frac{1}{A} \int_A d\vec{r} \int_{-\infty}^{\infty} M(z) \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} + U(\vec{r}, z) \right) M(z), \quad (12)$$

and the remainder of the energy is obtained from a one-dimensional integral over  $r$ :

$$\langle \psi_0 | \hat{H}_{2D} | \psi_0 \rangle / \langle \psi_0 | \psi_0 \rangle = NU_0 + E_0, \quad (13)$$

where

$$E_0 = \langle \psi_0 | \hat{H}_0 | \psi_0 \rangle / \langle \psi_0 | \psi_0 \rangle = N\pi n \int_0^{\infty} dr r g_0(r) \left( v_{2D}(r) - \frac{\hbar^2}{4m} \nabla^2 u(r) \right) \quad (14)$$

and  $\hat{H}_0$  is the "uniform" part of  $\hat{H}_{2D}$ :

$$\hat{H}_0 = \sum_{i=1}^N -\frac{\hbar^2}{2m} \nabla_i^2 + \sum_{i<j}^N v_{2D}(r_{ij}). \quad (15)$$

There is a wide literature on the accurate determination of  $g_0(r)$  from  $u(r)$ . In particular, this procedure has been used to obtain the ground-state energy of <sup>4</sup>He on a smooth substrate,<sup>13,14</sup> using the bare two-body potential  $v(r)$  instead of the effective two-body potential defined above.

To include the effect of periodicity of  $U_{2D}(\vec{r})$  by minimizing  $E$  with respect to  $w(\vec{r})$ ,  $U_{2D}$  and  $w$  are expressed in terms of their Fourier transforms

$$U_{2D}(\vec{r}) = U_0 + \sum_{\vec{G} \neq 0} U_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}, \quad (16)$$

$$w(\vec{r}) = \sum_{\vec{G} \neq 0} w_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}, \quad (17)$$

where

$$U_{\vec{G}} = \frac{1}{A} \int_A d\vec{r} e^{-i\vec{G}\cdot\vec{r}} \int_{-\infty}^{\infty} dz M(z)^* U(\vec{r}, z) M(z) \quad (18)$$

and

$$w_{\vec{G}} = \frac{1}{A} \int_A d\vec{r} e^{-i\vec{G}\cdot\vec{r}} w(\vec{r}). \quad (19)$$

Here  $\{\vec{G}\}$  is the set of reciprocal-lattice vectors. Restricting the Fourier components of  $w(\vec{r})$  to be zero except for reciprocal-lattice vectors means that only trial states with the full symmetry of the substrate are considered here. States of reduced symmetry will be considered elsewhere.

The functions  $w(\vec{r})$  and  $U_{2D}(\vec{r})$  enter the problem as sums over all coordinates:

$$\sum_{i=1}^N U_{2D}(\vec{r}_i) = NU_0 + \sum_{\vec{G} \neq 0} U_{\vec{G}} \rho_{\vec{G}}, \quad (20)$$

$$\sum_{i=1}^N w(\vec{r}_i) = \sum_{\vec{G} \neq 0} w_{\vec{G}} \rho_{\vec{G}}, \quad (21)$$

where  $\rho_{\vec{G}}$  is the density fluctuation operator

$$\rho_{\vec{G}} = \sum_{i=1}^N e^{i\vec{G}\cdot\vec{r}_i}. \quad (22)$$

Then the energy expectation value can be expressed in terms of  $w_{\vec{G}}$  by

$$E = \frac{\langle \psi_0 | \prod_{\vec{G}} e^{w_{\vec{G}} \rho_{\vec{G}}/2} \hat{H}_{2D} \prod_{\vec{G}} e^{w_{\vec{G}} \rho_{\vec{G}}/2} | \psi_0 \rangle}{\langle \psi_0 | \prod_{\vec{G}} e^{w_{\vec{G}} \rho_{\vec{G}}} | \psi_0 \rangle}. \quad (23)$$

It is shown elsewhere<sup>16</sup> that expectation values

with this kind of functional dependence upon  $\rho_{\vec{k}}$  can be evaluated as a simple power series in the functions  $w_{\vec{G}}$ , with the result that

$$E = E_0 + NU_0 + N \sum_{p=1}^{\infty} \frac{1}{p!} \sum_{\vec{G}_1, \dots, \vec{G}_p} \left( \prod_{i=1}^p w_{\vec{G}_i} \right) Q_p(\vec{G}_1, \dots, \vec{G}_p), \quad (24)$$

where  $Q_p(\vec{G}_1, \dots, \vec{G}_p)$  depends only on  $p$ - and  $(p-1)$ -order correlation functions of  $\rho_{\vec{k}}$  in  $\psi_0$ . The correlation function  $S_p$ , necessary to define  $Q_p$ , is defined by the  $p$ th equation in the following set of equations<sup>17</sup>:

$$\langle \psi_0 | \rho_{\vec{k}_1} | \psi_0 \rangle / \langle \psi_0 | \psi_0 \rangle = N S_1(\vec{k}_1), \quad (25a)$$

$$\langle \psi_0 | \rho_{\vec{k}_1} \rho_{\vec{k}_2} | \psi_0 \rangle / \langle \psi_0 | \psi_0 \rangle = N^2 S_1(\vec{k}_1) S_1(\vec{k}_2) + N S_2(\vec{k}_1, \vec{k}_2), \quad (25b)$$

$$\begin{aligned} \langle \psi_0 | \rho_{\vec{k}_1} \rho_{\vec{k}_2} \rho_{\vec{k}_3} | \psi_0 \rangle / \langle \psi_0 | \psi_0 \rangle &= N^3 S_1(\vec{k}_1) S_1(\vec{k}_2) S_1(\vec{k}_3) \\ &+ N^2 S_1(\vec{k}_1) S_2(\vec{k}_2, \vec{k}_3) + N^2 S_1(\vec{k}_2) S_2(\vec{k}_1, \vec{k}_3) \\ &+ N^2 S_1(\vec{k}_3) S_2(\vec{k}_1, \vec{k}_2) + N S_3(\vec{k}_1, \vec{k}_2, \vec{k}_3), \end{aligned} \quad (25c)$$

etc. That is,  $S_p(\vec{k}_1, \dots, \vec{k}_p)$  is obtained from  $\langle \prod_{i=1}^p \rho_{\vec{k}_i} \rangle$  by subtracting from the latter all possible lower-order correlations, and thus represents the fundamental  $p - \rho_{\vec{k}}$  correlations. The factors of  $N$  in this definition have been chosen so that all  $S_p$  are of order  $N^0 = 1$  in the number of adatoms. In the case when  $\psi_0$  is uniform,  $S_p$  is zero for total momentum different from zero:

$$S_p(\vec{k}_1, \dots, \vec{k}_p) \propto \delta_{\vec{k}_1 + \vec{k}_2 + \dots + \vec{k}_p, 0}.$$

Note that

$$S_2(\vec{k}, -\vec{k}) = S_0(k), \quad (26)$$

where  $S_0(k)$  is the liquid structure function of state  $\psi_0$ :

$$\begin{aligned} S_0(k) &= \frac{1}{N} \langle \psi_0 | \rho_{\vec{k}} \rho_{-\vec{k}} | \psi_0 \rangle / \langle \psi_0 | \psi_0 \rangle \\ &= 1 + 2\pi n \int_0^{\infty} dr r [g_0(r) - 1] J_0(kr), \end{aligned} \quad (27)$$

where  $J_0$  is the Bessel function of order zero. In addition to  $S_p$ , there is another correlation function  $\mathcal{T}_p$  which appears in the definition of  $Q_p$ , and depends upon  $\hat{H}_0$  (the uniform part of  $\hat{H}_{2D}$ ).  $\mathcal{T}_p$  is defined by the  $p$ th equation below combined with the definition of  $S_p$ :

$$\langle \psi_0 | \rho_{\vec{k}_1} (H_0 - E_0) | \psi_0 \rangle / \langle \psi_0 | \psi_0 \rangle = N \mathcal{T}_1(\vec{k}_1), \quad (28a)$$

$$\begin{aligned} \langle \psi_0 | \rho_{\vec{k}_1} \rho_{\vec{k}_2} (\hat{H}_0 - E_0) | \psi_0 \rangle / \langle \psi_0 | \psi_0 \rangle \\ = N^2 \mathcal{T}_1(\vec{k}_1) S_1(\vec{k}_2) + N^2 S_1(\vec{k}_1) \mathcal{T}_1(\vec{k}_2) + N \mathcal{T}_2(\vec{k}_1, \vec{k}_2), \end{aligned} \quad (28b)$$

$$\begin{aligned} \langle \psi_0 | \rho_{\vec{k}_1} \rho_{\vec{k}_2} \rho_{\vec{k}_3} (\hat{H}_0 - E_0) | \psi_0 \rangle / \langle \psi_0 | \psi_0 \rangle \\ = N^3 \mathcal{T}_1(\vec{k}_1) S_1(\vec{k}_2) S_1(\vec{k}_3) + N^3 S_1(\vec{k}_1) \mathcal{T}_1(\vec{k}_2) S_1(\vec{k}_3) \\ + N^3 S_1(\vec{k}_1) S_1(\vec{k}_2) \mathcal{T}_1(\vec{k}_3) + \sum N^2 \mathcal{T}_1(\vec{k}_\alpha) S_2(\vec{k}_\beta, \vec{k}_\gamma) \\ + \sum N^2 S_1(\vec{k}_\alpha) \mathcal{T}_2(\vec{k}_\beta, \vec{k}_\gamma) + N \mathcal{T}_1(\vec{k}_1, \vec{k}_2, \vec{k}_3), \end{aligned} \quad (28c)$$

etc. That is, the definition of  $\mathcal{T}_p$  is obtained from the definition of  $S_p$  by replacing one  $S_\alpha$  factor by  $\mathcal{T}_\alpha$  in all possible ways in each term of the definition of  $S_\alpha$ . Thus the summations in (28c) are over all distinct terms. Note that the  $\mathcal{T}_p$  vanish if  $\psi_0$  is the ground state of  $\hat{H}_0$  with energy  $E_0$ .

With this lengthy set of definitions, the coefficient of  $\prod_{i=1}^p w_{\vec{G}_i}$  in the expression for the energy expectation value  $E$  is

$$\begin{aligned} Q_p(\vec{G}_1, \dots, \vec{G}_p) \\ = \mathcal{T}_p(\vec{G}_1, \dots, \vec{G}_p) + \sum_{i=1}^p \frac{U_{\vec{G}_i}}{w_{\vec{G}_i}} S_p(\vec{G}_1, \dots, \vec{G}_p) \\ - \sum_{i \neq j} \frac{\hbar^2}{8m} \vec{G}_i \cdot \vec{G}_j S_{p-1}(\vec{G}_1, \dots, \vec{G}_i + \vec{G}_j, \dots, \vec{G}_p), \end{aligned} \quad (29)$$

where the arguments of  $S_{p-1}$  in the last term exclude  $\vec{G}_i$  and  $\vec{G}_j$  but include  $\vec{G}_i + \vec{G}_j$ , and  $S_{p-1}$  vanishes if any of its arguments are zero, with the exception that  $S_1(0) = 1$ . Note that the second term contains  $w_{\vec{G}_i}$  and would be included with the  $p-1$  coefficient if a strict power series in  $w_{\vec{G}}$  were intended in the expression for  $E$ . It is expected, however, that  $U_{\vec{G}}$  and  $w_{\vec{G}}$  will be comparable and that the ratio should be treated as order unity.

The infinite series for  $E$  in terms of  $w$  is truncated at finite order under the assumption that the product  $w^p Q_p$  is small beyond some value of  $p$ . In particular, consider the truncation where only the  $p=2$  term is retained. Then, the approximate expression for  $E$  is

$$E = E_0 + NU_0 + \frac{N}{2} \sum_{\vec{G}} w_{\vec{G}} w_{-\vec{G}} Q_2(\vec{G}, -\vec{G}), \quad (30)$$

where

$$\begin{aligned} Q_2(\vec{G}, -\vec{G}) &= \langle \psi_0 | \rho_{\vec{G}} \rho_{-\vec{G}} (\hat{H}_0 - E_0) | \psi_0 \rangle / \langle \psi_0 | \psi_0 \rangle \\ &+ (U_{\vec{G}}/w_{\vec{G}} + U_{-\vec{G}}/w_{-\vec{G}}) S_0(G) + (\hbar^2/4m) G^2. \end{aligned} \quad (31)$$

Extremizing  $E$  with respect to  $w_{-\vec{G}}$  gives

$$\begin{aligned} w_{\vec{G}} &= -U_{-\vec{G}} S_0(G) / \left( \frac{\hbar^2 G^2}{4m} + \frac{\langle \psi_0 | \rho_{\vec{G}} \rho_{-\vec{G}} (\hat{H}_0 - E_0) | \psi_0 \rangle}{N \langle \psi_0 | \psi_0 \rangle} \right) \\ \text{and energy} \end{aligned} \quad (32)$$

$$E = E_0 + NU_0 - \frac{\frac{1}{2} N \sum_{\vec{G}} |U_{\vec{G}}|^2 S_0(G)^2}{[\hbar^2 G^2/4m + \langle \psi_0 | \rho_{\vec{G}} \rho_{-\vec{G}} (\hat{H}_0 - E_0) | \psi_0 \rangle / N \langle \psi_0 | \psi_0 \rangle]}. \quad (33)$$

The condition that this extremum be a minimum is that the denominator be positive. The value of  $\rho_{\vec{G}}$  in state  $\psi_{2D}$  can be read directly from (24), (31), and (32) as the coefficient of  $U_{-\vec{G}}$ . In the lowest order in  $w$  this gives

$$\begin{aligned} \rho_{\vec{G}} &\equiv (1/N) \langle \psi_{2D} | \rho_{\vec{G}} | \psi_{2D} \rangle / \langle \psi_{2D} | \psi_{2D} \rangle \\ &= -U_{\vec{G}} S_0(G)^2 \left/ \left( \frac{\hbar^2 G^2}{4m} + \frac{\langle \psi_0 | \rho_{\vec{G}} \rho_{-\vec{G}} (\hat{H}_0 - E_0) | \psi_0 \rangle}{N \langle \psi_0 | \psi_0 \rangle} \right) \right., \end{aligned} \quad (34)$$

in which case the energy becomes

$$E = E_0 + NU_0 + \frac{1}{2}N \sum_{\vec{G} \neq 0} U_{-\vec{G}} \rho_{\vec{G}}. \quad (35)$$

We can make use of an identity to show that in a special case this approximation for  $E$  is equivalent to the inclusion of the contribution of single Feynman-phonon states to the ground-state energy in second-order perturbation theory. The necessary identity is

$$\begin{aligned} \langle \psi_0 | \rho_{-\vec{k}} (\hat{H}_0 - E_0) \rho_{\vec{k}} | \psi_0 \rangle \\ = \langle \psi_0 | \rho_{-\vec{k}} \rho_{\vec{k}} (\hat{H}_0 - E_0) | \psi_0 \rangle + N \hbar^2 k^2 / 2m. \end{aligned} \quad (36)$$

Now the normalized single Feynman-phonon state defined in terms of  $\psi_0$  is

$$|\vec{k}\rangle = \rho_{\vec{k}} |\psi_0\rangle / [NS_0(k)]^{1/2}; \quad (37)$$

so the energy shift obtained above can be reexpressed using Eqs. (33), (36), (37), (26a) and (26b) as

$$\delta E = - \sum_{\vec{G}} \frac{|\langle \psi_0 | \hat{H}_1 | \vec{G} \rangle|^2}{[2\langle \vec{G} | \hat{H}_0 - E_0 | \vec{G} \rangle - \hbar^2 G^2 / 2m S_0(G)]}, \quad (38)$$

where

$$\hat{H}_1 = \sum_{\vec{G} \neq 0} U_{\vec{G}} \rho_{\vec{G}}. \quad (39)$$

This expression has the form of second-order perturbation theory if

$$\langle \vec{G} | \hat{H}_0 - E_0 | \vec{G} \rangle = \hbar^2 G^2 / 2m S_0(G) = e_{BF}(G), \quad (40)$$

which is the Bijl-Feynman form of the excitation spectrum. Thus this equality holds when  $\psi_0$  is the ground state of  $\hat{H}_0$ , but it also holds in the less restrictive case when  $\psi_0$  gives  $\hat{H}_0$  its minimum expectation among all Jastrow functions.<sup>18</sup> We assume in the remainder of this paper that  $\psi_0$  is sufficiently close to the optimum Jastrow function that we can approximate  $\langle \vec{G} | \hat{H}_0 - E_0 | \vec{G} \rangle$  by  $e_{BF}(G)$ . This also leads to the replacement of the denominator in Eq. (34) by  $\hbar^2 G^2 / 4m$ .

Note that in the zero-density limit ( $n \rightarrow 0$ ),  $S_0 = 1$ , and  $\delta E$  is the energy shift for a single adatom on the surface. Since  $S_0$  can be either greater than or less than 1.0, depending upon density and  $G$  value, the effect of the periodic potential can be

either to increase or decrease the liquid binding energy. To see this, it is convenient to write the liquid binding energy to second order, noting that the "vacuum zero" is a single adatom on the surface. The liquid binding energy per adatom is  $\bar{\epsilon}(n)$ , where

$$-\bar{\epsilon}(n) = \frac{1}{N} E_0 - \sum_{\vec{G} \neq 0} |U_{\vec{G}}|^2 [S_0(G)^2 - 1.0] \left/ \frac{\hbar^2 G^2}{2m} \right. . \quad (41)$$

The binding is enhanced when the adatom-adatom interaction is such as to form a structure which allows all adatoms to sit in potential wells formed by the substrate. However, if the match is not close, then the binding energy will—in general—be decreased since some adatoms will be in regions of high potential energy. Thus there is a competition between the substrate-adatom interaction and the adatom-adatom interaction to determine the structure of the liquid.

All that is needed to complete the calculation is to find the optimum values of the variational parameter(s) in  $u(r)$  and the optimum functional form for  $M(z)$ . To accomplish the latter, the function  $M(z)$  is expanded in an orthonormal basis set  $M^\nu$  with

$$M(z) = \sum_{\nu} C^{\nu} M^{\nu}(z) \quad (42)$$

and

$$\int dz M(z)^2 = 1.$$

The  $C^\nu$  are treated as variational parameters, and the minimization of the ground-state energy with respect to these  $C^\nu$  parameters leads to an eigenvalue equation for the  $C^\nu$ . This process could be complicated by the fact that not only  $U_0$  but also  $E_0$  and  $\delta E$  are functions of  $C^\nu$ . The terms  $U_0$  and  $\delta E$  depend upon  $C^\nu$  via the definitions of  $U_0$  and  $U_{\vec{G}}$ , while  $E_0$  depends on  $C^\nu$  through  $v_{2D}$ . At this stage in the calculation, the dynamics of the lateral and perpendicular motions are partially decoupled by varying only  $U_0$  and  $\delta E$  with respect to the  $C^\nu$ . Since the term  $\delta E$  depends upon  $C^\nu$  in a nonlinear fashion, the term  $U_0 + \delta E$  is minimized in an iterative manner, using an initial set of  $\bar{\rho}_{\vec{G}}$  to generate values of  $C^\nu$ , using these new values of  $C^\nu$  to generate a new set of  $\bar{\rho}_{\vec{G}}$ , and continuing this cycle until stable values  $\bar{\rho}_{\vec{G}}$  are found. The set of  $C^\nu$  and  $\bar{\rho}_{\vec{G}}$  used for the calculation of  $v_{2D}$  is that set found for zero density. This is in keeping with the decoupling procedure. The physical interpretation of this decoupling is a statement that the zero-point oscillations perpendicular to the surface are little affected by compressing the liquid in the lateral dimensions.

The eigenvalue equation for  $C^\nu$  is found by in-

serting (42) into the equations for  $U_0$  and  $U_{\vec{G}}$ , and then differentiating with respect to  $C^\nu$  with  $\sum(C^\nu)^2 = 1$  as a constraint. Noting that  $\delta E$  is a quadratic function of  $C^\nu$ , the resulting equation for  $C^\nu$  is

$$\sum_{\nu'} \left( U_0^{\nu\nu'} + \sum_{\vec{G}} \bar{\rho}_{\vec{G}} U_{\vec{G}}^{\nu\nu'} \right) C^{\mu'} = \delta C^\nu, \quad (43)$$

where  $U_0^{\nu\nu'}$  and  $U_{\vec{G}}^{\nu\nu'}$  are given by

$$U_0^{\nu\nu'} = \frac{1}{A} \int_A d\vec{r} \int_{-\infty}^{\infty} dz M^\nu(z) \times \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} + U(\vec{r}, z) \right) M^{\nu'}(z) \quad (44)$$

and

$$U_{\vec{G}}^{\nu\nu'} = \frac{1}{A} \int_A d\vec{r} \int_{-\infty}^{\infty} dz M^\nu(z) U(\vec{r}, z) e^{-i\vec{G}\cdot\vec{r}} M^{\nu'}(z).$$

Once stable values of  $C^\nu$  have been determined,  $U_0$  and  $\delta E$  are calculated using

$$U_0 = \sum_{\nu\nu'} C^\nu U_0^{\nu\nu'} C^{\nu'} \quad (45)$$

and

$$U_{\vec{G}} = \sum_{\nu\nu'} C^\nu U_{\vec{G}}^{\nu\nu'} C^{\nu'}.$$

When this has been done, there remains but to minimize  $(1/N)E = (1/N)E_0 + U_0 + (1/N)\delta E$  as a function of the variational parameters in  $u(r)$ . This is done at constant density. The ground-state energy is the optimized energy for density  $n$ , minimized as a function of  $n$ .

### III. OPERATION ASPECTS OF THE HELIUM PROBLEM

The substrate is modeled by a rigid array of substrate atoms having a well defined crystalline structure and an ideal surface.<sup>4-9</sup> The plane of substrate surface atoms forms the  $z=0$  plane, with the substrate occupying the entire negative- $z$  half-space. The interaction between the substrate and a given helium adatom is calculated by using a lattice sum of a two-body potential. The form of this potential is Lennard-Jones with

$$V(\rho) = \epsilon_0 [(\rho_0/\rho)^{12} - 2(\rho_0/\rho)^6] \quad (46)$$

and the values of  $\epsilon_0$  and  $\rho_0$  depending upon the particular substrate atom. Three substrates were studied: graphite with a basal plane surface; graphite preplated with a monolayer of close-packed neon; and graphite preplated with a monolayer of close-packed argon. Table I contains the various

TABLE I. Lennard-Jones potential parameters.

	He-C	He-Ne	He-Arg
$\epsilon_0$ (°K)	14.5	16.7	25.4
$\rho_0$ (Å)	3.34	3.0	3.40

TABLE II. Beck potential parameters.<sup>a</sup>

	Bare He-He interaction	Effective <sup>4</sup> He- <sup>4</sup> He interaction on the basal plane of graphite.
$A$	$4.638 \times 10^6$	$3.819 \times 10^6$
$a^2$	0.4556	0.2212
$B$	2.71	1.93
$\alpha$	4.39	4.35
$\beta$	$3.746 \times 10^{-4}$	$3.746 \times 10^{-4}$
$C_6$	$1.00685 \times 10^4$	$1.00685 \times 10^4$

<sup>a</sup>Energy units: °K. Distance unit: Å.

values of  $\epsilon_0$  and  $\rho_0$ . Details of the actual calculation of the substrate potential are found elsewhere.<sup>6,9,12</sup>

The helium-helium potential is the Beck potential

$$v(\rho) = A e^{-(\alpha\rho + \beta\rho^6)} - \frac{C_6}{(a^2 + \rho^2)^3} \left( 1 + \frac{B + 3a^2}{a^2 + \rho^2} \right). \quad (47)$$

This is an excellent representation of the helium-helium potential in vacuum. In using this potential, the assumption is that the substrate does not affect the interaction between the adatoms. This is not strictly true,<sup>18,20</sup> but the picture is not clear enough at present to attempt to include this effect. The size of this effect is probably about 10%.<sup>19</sup> The potential  $v_{2D}$  is strictly to be had in tabulated form only, but this is inconvenient. Therefore once  $v_{2D}$  was calculated, the tabulated values were used to fit a function having the form of the Beck potential, but with  $A$ ,  $\alpha$ ,  $\beta$ ,  $a^2$ , and  $B$  determined by a least-squares fit to  $v_{2D}$ . To insure that  $v_{2D} \rightarrow v$  as  $r \rightarrow \infty$  the value of  $C_6$  was not varied. The values of all parameters for both  $v$  and  $v_{2D}$  are to be found in Table II. The least-squares fit to  $v_{2D}$  is excellent. For instance, with  $2.0 \text{ Å} < r < 6.0 \text{ Å}$ , the fitted function and  $v_{2D}$  are indistinguishable (deviations  $\sim 10^{-2}$  °K).

The functional form chosen for  $u(r)$  is the usual WKB (Lennard-Jones)

$$u(r) = -(a/r)^5. \quad (48)$$

This allows a simple scaling with density for  $g_0(r)$  and  $S_0(Q)$ .<sup>21</sup> Thus  $a$  is the only true variational parameter in  $\psi_0$ .

The basis set  $M^\nu(z)$  is the set of bound energy eigenfunctions for the helium atom in the one-dimensional Morse potential<sup>22</sup>

$$V_M(z) = D(e^{-2\beta(z-z_0)} - 2e^{-\beta(z-z_0)}). \quad (49)$$

The method of choosing the best values of  $D$ ,  $\beta$ , and  $Z_0$  are described elsewhere.<sup>12</sup> The values are to be found in Table III. The expansion in the set  $M^\nu(z)$  usually involved a truncation at four or six states. This means that the calculated heats of

TABLE III. Morse potential parameters.

	He-C	He-Ne	He-Ar
$D$ (°K)	310	95.0	106.0
$Z_0$ (Å)	3.115	2.8	3.09
$\alpha_0^a$	12	6	6

$$^a\alpha_0 = (2/\beta) (2mD/\hbar^2)^{1/2} - 1.$$

adsorption are in error by one or two degrees Kelvin. Considering the uncertainty of the substrate-adatom interaction, this is a very small uncertainty. However, the effects of the truncation on quantities like the liquid binding energy are much smaller, since the standard reference for all results is the energy of a single adatom on the surface.

The effects of truncating the  $M^p$  basis set will largely cancel and can be ignored as long as the  $M(z)$  functions used are the same for both the single atom (zero density) and liquid states. Also, the energies of both states should be calculated to the same order as in Eq. (41) to avoid truncation errors due to the plane-wave expansion. With the set of  $M^p$  used, adding or deleting a basis function of two would change  $U_{\bar{G}}$  (and thus the binding energy) by a few per cent. The effects of truncating the plane-wave expansion are much smaller.

#### IV. RESULTS

The results of the calculation described above as applied to helium adsorbed on several different substrates are contained in this section. The quantity of interest is the binding energy of the condensed phase (the quasi-two-dimensional liquid) represented by the trial function. It must therefore be calculated relative to the ground-state energy of the single adatom on the substrate. This invokes the familiar difficulty of comparing the energy of two different phases (vapor and liquid in this case) when only the approximate energy of one or both of the phases can be determined. An immediate casualty of such a procedure is the variational principle: The calculated binding energy is no longer a variational lower bound on the exact binding energy.

The chief approximation in the above analysis of the condensed phase is the use of a trial function which is separable in the  $z$  and  $\vec{r}$  coordinates. While a similar approximation is of no real calculational advantage for the single-adatom ground state, it is nevertheless used in that case to make more valid a comparison of the two energies to deduce the binding energy. For the case of helium adsorbed on graphite, an additional 0.3 °K binding energy can be realized for the vapor phase by using a nonseparable wave function. While this is a very small fraction of the heat of adsorption, it is comparable to some of the lateral binding energies

listed below, and is therefore a source of uncertainty in the numerical results.

##### A. Helium adsorbed on the basal plane of graphite

The Morse parameters for the determination of  $M^p(z)$  for a single  $^4\text{He}$  atom on the basal plane of graphite are given in Table III. Six eigenfunctions of the Morse potential provided rapid convergence. Using these  $M^p$  functions, the zeroth and first Fourier coefficient of  $U_{2D}(\vec{r})$  were

$$U_0 = -150.8 \text{ }^\circ\text{K},$$

$$U_{\bar{G}_0} = -1.56 \text{ }^\circ\text{K}.$$

The contribution of the periodic potential to the single adatom energy is obtained from Eq. (38) by setting  $S_0(k)$  equal to 1:

$$\delta E = - \sum_{\bar{G}} |U_{\bar{G}}|^2 / \frac{\hbar^2 G^2}{2m} = -0.27 \text{ }^\circ\text{K}. \quad (50)$$

To determine the binding energy of the condensed phase,  $E_0$  and  $S_0(k)$  must be calculated from  $v_{2D}(r)$ , which is in turn dependent upon the function  $M(z)$  which is to be determined self-consistently at zero density. In the case of  $^4\text{He}$  adsorbed on graphite, the effects of self-consistency are negligible. Then  $v_{2D}(r)$  is fit by a Beck potential with parameters shown in Table II. The only effect of  $M(z)$  is to slightly soften the core compared to the bare potential, which will only show up at very high densities—well into the solid range.

The binding energy  $\bar{\epsilon}$  [Eq. (41)] depends upon the variational parameter  $a$  through both  $E_0$  and  $S_0(k)$ . The results of the minimization are shown in Fig. 1. The binding energy of 0.62 °K at equilibrium density 0.0365 Å<sup>-2</sup> is in close agreement with previous calculations for a uniform substrate<sup>13,14</sup> [although those calculations use a slightly different  $v(r)$ ]. The effect of the periodic potential is very small, as can be seen from Table IV. The only real effect manifested in this calculation is a periodic variation in the density. The density varies from 135% (at the adsorption site) to 82% (over a carbon atom) of the average density. This is in good agreement with single-particle calculations, where the variations were slightly larger due to the nonseparable wave function.<sup>6</sup>

Note that a major effect of the substrate may be one which is not included in this calculation, i. e., the effect of substrate mediation of the interaction such as via the exchange of substrate phonons.<sup>19</sup> To test the sensitivity of the binding energy to changes in the adatom-adatom potential, the above calculation was repeated using an interatomic potential which differs by about 10% from the Beck potential at the minimum. The result of that calculation was a binding energy of about 1 °K at a density of approximately 0.04 Å<sup>-2</sup>, indicating a large sensitivity in the binding energy.

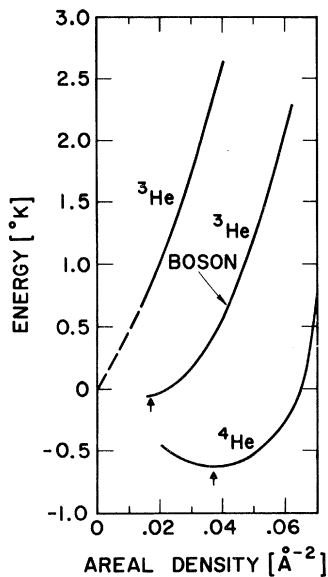


FIG. 1. Negative of the binding energy  $[-\bar{\epsilon}(n)]$  for helium adsorbed on the basal plane of graphite. Arrows indicate the equilibrium densities. Dashed line approaching the  ${}^3\text{He}$  curve is the energy per particle for noninteracting  ${}^3\text{He}$ .

While it can be concluded that  ${}^4\text{He}$  forms a self-bound quasi-two-dimensional liquid in preference to a two-dimensional vapor when adsorbed on the basal plane of graphite, experimental<sup>1</sup> and theoretical<sup>12,23</sup> considerations indicate the possibility of several other phases of  ${}^4\text{He}$  on graphite. In particular at high two-dimensional densities there may exist a solid-like phase with lattice spacing largely uncorrelated with the periodicity of the substrate. At intermediate densities there seems to be one or more superlattice phases where the helium atoms form a two-dimensional lattice which is a superlattice of the basal plane structure, i.e., whose invariant translations also leave the substrate lattice unchanged. An important question is the location of the phase boundaries of these various phases. To determine this one is required to do an accurate calculation of the ground-state energies of each of these phases. While one of us has calculated the ground-state energies of the superlattice state,<sup>12</sup> the approximations necessary in that calculation differ sufficiently from the ones invoked here so that a comparison of the energies is not meaningful due to the very small energy differences. We should point out, however, that the formalism developed here is capable in principle of describing transitions of this type. It would be necessary to include functions  $w(\vec{r})$  which have the symmetry of the superlattice phase (or the solid phase) and then to include terms from Eq. (24) beyond quadratic terms in the new Fourier coefficients  $w_{\vec{r}}$  which arise because of the reduced sym-

metry. This is beyond the scope of our current study.

The effects of mass and statistics upon the liquid state were determined by repeating the calculation for  ${}^3\text{He}$ . The effect of lowering the mass to mass three is of course to increase the zero-point energy of the condensed phase. The (fictitious) mass-three-boson problem gave a binding energy of  $0.05^\circ\text{K}$  at a density between  $0.015$  and  $0.02 \text{ \AA}^{-2}$ , i.e., at about half the density of  ${}^4\text{He}$  (see Fig. 1). Introducing the Fermi statistics also must reduce the binding energy. Indeed, the lowest-order correction is just the energy of the Fermi sea, which when added to the Bose energy gave a positive energy per particle at all densities. The energy to this order is shown in Fig. 1. This leads us to conclude that  ${}^3\text{He}$  is probably not self-bound in two dimensions. Our conclusions at very low densities are based upon extrapolations in the variational parameter  $a$  and therefore cannot be completely trusted. There are also second-order correlated basis-function corrections which may change these results.<sup>15</sup> Furthermore, we have not investigated the effects of changing the two-body potential. It is clear, however, that since the  ${}^3\text{He}$  fermion ground-state energy must lie above the  ${}^3\text{He}$  boson ground-state energy, the liquid must occur at very low densities if it occurs at all. This theoretical conclusion agrees with the experimental conclusions of Eckardt *et al.*,<sup>24</sup> although it must be noted that their substrate- ${}^4\text{He}$  liquid—is very different from the solid type considered here.

#### B. Helium adsorbed on neon-plated graphite

We report here some preliminary results concerning the effect of preplating the graphite by a close-packed layer of neon or argon. This additional layer is assumed to provide the entire periodic part of the substrate-atom potential, which in both cases is more strongly varying than for pure graphite. We do not determine the  $C'$  in  $M(z)$  self-consistently, which is a cruder approximation than above because of the increased importance of the periodic potential. For  $v_{2D}(r)$  we use that obtained for bare graphite. Finally,  $E_0$  is minimized as a function of  $a$  and then the correction  $\delta E$  due to the periodic potential is added.

The number density of the neon layer is  $0.122$  and  $0.079 \text{ \AA}^{-2}$  for the argon layer. The results are shown in Fig. 2. For the neon-plated system there is an equilibrium indicated near density

TABLE IV.  $\delta E/N$  for  ${}^4\text{He}$  adsorbed on the basal plane of graphite.

$n(\text{\AA}^{-2})$	0.02	0.03	0.04	0.05	0.06	0.07
$\delta E/N(^{\circ}\text{K})$	0.01	0.01	0.02	0.03	0.04	0.05



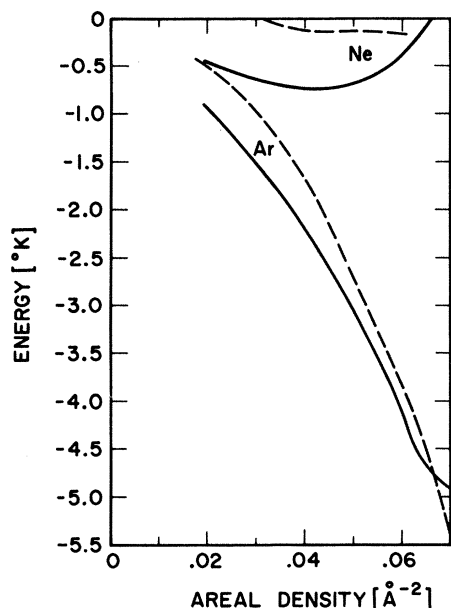


FIG. 2. Negative of the binding energy  $[-\bar{\epsilon}(n)$ ; solid lines] and the substrate contribution to the energy  $[\delta E/N$ ; dashed lines] for  ${}^4\text{He}$  adsorbed on graphite preplated by a close-packed layer of neon (Ne) and by a close-packed layer of argon (Ar).

$0.04 \text{ \AA}^{-2}$ . We note in passing that the density of a superlattice of  ${}^4\text{He}$  occupying one triangular sublattice of adsorption sites (the "triangular lattice gas") would be  $0.04067 \text{ \AA}^{-2}$ . The relationship of the equilibrium configuration of our present calculation to the superlattice structure needs to be explored further.

The energy minimum on close-packed argon occurs at high densities, where our calculation is

inadequate primarily because the simple variational parametrization of our Jastrow function cannot properly represent the structure of the wave function at these densities. Furthermore, the contribution of  $\delta E$  (shown in Fig. 2) overwhelms the remaining terms. Nevertheless, we may take the present calculations to indicate that the periodic potential dominates the energetics of helium adsorbed on argon-plated graphite and forces the helium to high densities which would ordinarily be characteristic of a solid helium phase. Similar conclusions may be drawn from experiments on helium adsorbed on argon-plated copper.<sup>3</sup>

## V. DISCUSSION

We have investigated the effect of the structure of the substrate on the liquid-like condensed phase of adsorbed helium. We have included the effects of the finite thickness of the monolayer and the effect of the periodicity of the substrate. For helium adsorbed on the basal plane of graphite the substrate effects are nearly negligible and the helium may be considered as seeing a nearly perfect two-dimensional environment. We conclude that  ${}^4\text{He}$  has a weakly bound quasi-two-dimensional liquid phase, while  ${}^3\text{He}$  is probably never self-bound in its ground state. A preliminary investigation of helium adsorbed on neon-plated graphite and argon-plated graphite produces substantially different results. In both cases the substrate drives the condensed phase to higher densities, probably solid densities for the argon case.

The primary sources of uncertainty in the results described here are the adatom-substrate potentials used and many-body corrections to the helium-helium interaction due to the presence of the substrate.

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<sup>1</sup>M. Bretz, J. G. Dash, D. C. Hickernell, E. O. McClean, and O. E. Vilches, *Phys. Rev. A* **8**, 1589 (1973), and references cited therein.  
<sup>2</sup>R. Siddon and M. Schick, *Phys. Rev. A* **9**, 907 (1974); **9**, 1753 (1974).  
<sup>3</sup>W. D. McCormick, D. L. Goodstein, and J. G. Dash, *Phys. Rev.* **168**, 249 (1970); G. A. Stewart and J. G. Dash, *Phys. Rev. A* **2**, 918 (1970).  
<sup>4</sup>F. Ricca, C. Pisani, and E. Garrone, *J. Chem. Phys.* **51**, 4079 (1969).  
<sup>5</sup>A. D. Novaco and F. J. Milford, *J. Low Temp. Phys.* **3**, 307 (1970).  
<sup>6</sup>D. E. Hagen, A. D. Novaco, and F. J. Milford, in *Proceedings of the Second International Symposium of Adsorption-Desorption Phenomena, Florence* (Academic, New York, 1971).

<sup>7</sup>F. Ricca, C. Pisani, and E. Garrone, in Ref. 6.  
<sup>8</sup>F. J. Milford and A. D. Novaco, *Phys. Rev. A* **4**, 1136 (1971).  
<sup>9</sup>A. D. Novaco and F. J. Milford, *Phys. Rev. A* **5**, 783 (1972); **6**, 526 (1972).  
<sup>10</sup>H.-W. Lai, C.-W. Woo, and F. Y. Wu, *J. Low Temp. Phys.* **3**, 463 (1970).  
<sup>11</sup>H.-W. Lai, C.-W. Woo, and F. Y. Wu, *J. Low Temp. Phys.* **5**, 499 (1971); H.-W. Lai and C.-W. Woo, *Phys. Lett. A* **41**, 170 (1972).  
<sup>12</sup>A. D. Novaco, *Phys. Rev. A* **7**, 1653 (1973).  
<sup>13</sup>C. E. Campbell and M. Schick, *Phys. Rev. A* **3**, 691 (1971).  
<sup>14</sup>M. D. Miller, C.-W. Woo, and C. E. Campbell, *Phys. Rev. A* **6**, 1942 (1972).  
<sup>15</sup>See the discussion of bulk liquid  ${}^3\text{He}$  in E. Feenberg, *Theory of Quantum Fluids* (Academic, New York, 1969), and references cited therein.  
<sup>16</sup>C. E. Campbell, *J. Math. Phys.* (to be published).  
<sup>17</sup>F. Y. Wu, *J. Math. Phys.* **9**, 1923 (1971).  
<sup>18</sup>C. E. Campbell and E. Feenberg, *Phys. Rev.* **188**, 396 (1969).

<sup>19</sup>M. Schick and C. E. Campbell, Phys. Rev. A 2, 1591 (1970).

<sup>20</sup>O. Sinanađlu and K. S. Pitzer, J. Chem. Phys. 32, 1279 (1960).

<sup>21</sup>W. L. McMillan, Phys. Rev. 138, A442 (1965).

<sup>22</sup>P. M. Morse, Phys. Rev. 34, 57 (1929).

<sup>23</sup>C. E. Campbell and M. Schick, Phys. Rev. A 5, 1919 (1972).

<sup>24</sup>J. R. Eckardt, D. O. Edwards, P. P. Fatouros, F. M. Gasparini, and S. Y. Shen, Phys. Rev. Lett. 32, 706 (1974).