PHYSICAL REVIEW A VOLUME 7, NUMBER 5 MAY 1973

# Cluster Expansion for Superlattice Physisorption: Helium Adsorbed upon Graphite*

Anthony D. Novaco
*Brookhaven National Laboratory, Upton, New York 11973*

(Received 27 December 1972)

The ground-state energy of the "$X_g = 1/3$" and "$X_g = 1/4$" superlattice states of He$^3$ and He$^4$ adsorbed on graphite is calculated via a variational wave function incorporating Jastrow factors. The single-particle factors in the wave function are constructed as an expansion in an orthogonal basis set and the Jastrow terms incorporate only lateral correlations. The ground-state energy is calculated using the Nosanow cluster expansion. The stability of the superlattice states is examined and both are found to be unstable at zero pressure. Estimates of the stability of these states to "melting" indicate the "$X_g = 1/3$" state is stable and the "$X_g = 1/4$" state is less stable or possibly unstable. The sensitivity of the results to reasonable substrate-induced many-body corrections to the adatom-adatom potential is found to be significant.

## I. INTRODUCTION

The physisorbed films of the light rare gases are the experimental systems for the study of two-dimensional quantum fluids and solids.[1] This is not only a result of the small adatom mass and weak adatom-adatom interaction, but also of the weak adatom-substrate interaction and increased importance of zero-point motion owing to the two-dimensional character of the film. The structure of the substrate surface can have a decisive role in determining the structure of the adsorbed film. However, helium adsorbed on graphite is one system where for most film densities this is not the case.[2,3]

The basal-plane surface of a graphite substrate is such that there is little hindrance to the motion of a helium atom along the surface. The basal plane consists of hexagonal rings of carbon atoms, with a point of minimum potential energy for the adsorbed helium atom which exists along a perpendicular to the surface and passes through the center of a hexagon (the adsorption site). However, the ground state of a single helium atom adsorbed upon this surface is a very delocalized Bloch wave.[2] In fact, the Wannier state constructed from the lowest band of Bloch states is about 10 °K above the ground state. Yet, even though the substrate does not dominate the dynamics of the adatom, under certain circumstances it could conceivably play an important role. Specifically, it could stabilize phases or states of the film which would be energetically unfavorable if the adatom-substrate interaction depended solely upon the perpendicular distance between adatom and substrate. There is experimental evidence that at particular values of film density, this is indeed the case—the structure of the helium film ground state being a superlattice of the basal-plane structure.[4] That is, the helium adatoms form a two-dimensional lattice whose invariant translations also leave the substrate lattice unchanged.

The strongest evidence for the existence of such superlattice states is for the "$X_g = \frac{1}{3}$" state. In this structure, the helium adatoms are visualized as forming a simple triangular lattice with the adatoms located at adsorption sites which are a factor of $\sqrt{3}$ farther apart than nearest-neighbor adsorption sites. Thus $\frac{1}{3}$ of the total number of adsorption sites are occupied. There is weaker evidence for the existence of a "$X_g = \frac{1}{4}$" state. This differs from the previous state only in that the nearest-neighbor occupied sites are spaced at a distance equal to twice the distance between nearest-neighbor adsorption sites. In this case, $\frac{1}{4}$ of the sites would be occupied. The helium-helium nearest-neighbor separation for these superlattice states, 4.25 and 4.90 Å, respectively, is 15–30% larger than that of the lowest-density bulk solid.

The present calculation is concerned with the ground-state energy and stability of the superlattice states for both He$^3$ and He$^4$ adsorbed upon graphite. For this purpose, a variational wave function incorporating Jastrow factors is used, and the ground-state energy computed using the Nosanow cluster expansion.[5,6] The interaction between the helium atoms is represented by a semiempirical hybrid potential,[7] and the helium-graphite interaction by a helium-carbon Lennard-Jones potential summed over the lattice of carbon atoms.[8]

The stability of the superlattice states under zero pressure is examined by comparing the superlattice ground-state energy per particle to the single-adatom ground-state energy. Rough estimates of the stability of the superlattice states to "melting" are made using ground-state Jastrow wave-function calculations which exist in the literature[9,10] for the two-dimensional helium liquid.

## II. BASIC HAMILTONIAN: TRIAL GROUND STATE AND CLUSTER EXPANSION

The Hamiltonian $H_N$ used to describe the system of $N$ atoms adsorbed upon a substrate surface consists of the kinetic energy of the $N$ adatoms, the interactions between these adatoms, and the interactions between the adatoms and the substrate. The substrate is assumed to be rigid and unaffected by the state of the adsorbed film. The adatom-adatom interaction is represented by a two-body central potential $v(\rho_{ij})$, where $\rho_{ij}$ is the distance between the $i$th and the $j$th adatom. The adatom-substrate interaction is represented by a nonseparable single-particle potential $U(\vec{r}_j, z_j)$, where $\vec{r}_j$ is the position vector in the surface plane of the $j$th adatom and $z_j$ is its position perpendicular to this plane. The $z=0$ plane is the plane of substrate surface atoms with the substrate occupying the entire negative $z$ half-space. The $H_N$ for such a system is

$$H_N = \sum_{j=1}^{N} \frac{-\hbar^2}{2m} \left(\nabla_j{}^2 + \frac{\partial^2}{\partial z_j{}^2}\right) + \sum_{j=1}^{N} U(\vec{r}_j, z_j) + \tfrac{1}{2} \sum_{i \neq j} v(\rho_{ij}) \; , \tag{1}$$

with $m$ being the adatom mass and $\nabla^2$ being the two-dimensional Laplacian. Typically, the potential $U$ is repulsive at small $z$, attractive at large $z$, and has a minimum at about a few angstroms away from the surface.[2,8,11] If the surface has a crystalline nature, then $U$ has a two-dimensional periodic behavior.

The trial ground state used is a slightly modified version of the Nosanow trial ground state used for bulk quantum solids.[5] For an $N$-atom system, the trial ground state for the adsorbed film is

$$\Psi_N(\vec{r}_1, z_1, \ldots, \vec{r}_N, z_N) = \prod_{i=1}^{N} \phi_i(\vec{r}_i, z_i) \prod_{1 \leq j < k \leq N}\!\!\prod f(|\vec{r}_j - \vec{r}_k|) \; , \tag{2}$$

where

$$\phi_i(\vec{r}_i, z_i) = \phi(\vec{r}_i - \vec{R}_i, z_i) \tag{3}$$

and $\vec{R}_i$ is a two-dimensional lattice vector of the superlattice. For the cases considered, every adatom sees the same environment. The $\phi_j$ are normalized so that $\langle \phi_j | \phi_j \rangle = 1$. The overlap between neighboring $\phi_j$ is assumed to be negligible, so exchange effects are not considered. The Jastrow factor $f(r)$ is, following Nosanow, chosen to be of the form

$$f(r) = e^{-Bu(r)} \; , \tag{4}$$

with $u(r)$ being an analytic function which is a reasonable fit to the interatomic potential $v$, and $B$ being a variational parameter. The advantages of such a form for $f(r)$ when doing cluster expansions have been known for some time.[6] Note that only lateral correlations are incorporated into the wave function.[12,13] This simplifies the calculations and is justified by the narrowness of typical adatom wave functions in the $z$ direction.[2]

The Nosanow cluster expansion gives a prescription for the calculation of the ground-state energy $E_0 = \langle \Psi_N | H_N | \Psi_N \rangle$ as a summation of the cluster terms involving matrix elements $\langle \Psi_M | H_M | \Psi_M \rangle$ with $M = 1, 2, \ldots, N$. The cluster expansion is, of course, useful insofar as this summation can be well approximated by a cluster expansion involving only small values of $M$. The evaluation of $E_0$ for the $\Psi_M$ of Eq. (2) and the $H_N$ of Eq. (1) follows directly from the general form of the expansion.[5,6] The first few terms of the expansion are given in Table I. The calculation of the ground-state wave function and energy then reduces to the truncation of the sum for $E_0$ and the minimization of $E_0$ as a function of the variational parameters. For this purpose, the single-particle function $\phi_j$ is expanded in terms of some relevant basis set with the expansion coefficients treated as variational parameters.

## III. INTERATOMIC POTENTIALS AND SINGLE-PARTICLE STATES

The two-body potential used for the helium-helium interaction is the Morse-$V_{DD}$ potential, a semi-

TABLE I. Nosanow cluster expansion for the adsorbed film,

$$E_0 = \sum_{M=1}^{N} E_{0M}.$$

$$E_{01} = E_{01T} + E_{01U},$$

$$E_{01T} = \frac{-\hbar^2}{2m} \sum_{j=1}^{N} \langle \phi_j | \nabla_j{}^2 | \phi_j \rangle,$$

$$E_{01U} = \sum_{j=1}^{N} \langle \phi_j | \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial z_j{}^2} + U_j | \phi_j \rangle;$$

$$E_{02} = E_{02V} + E_{02T} + E_{02U},$$

with

$$E_{02V} = \frac{1}{2} \sum_{j \neq k} \frac{\langle \phi_j \phi_k | f_{jk}{}^2 V_{jk} | \phi_j \phi_k \rangle}{\langle \phi_j \phi_k | f_{jk}{}^2 | \phi_j \phi_k \rangle},$$

$$E_{02T} = \sum_{i \neq j} \left( \frac{\langle \phi_i \phi_j | T_i f_{ij}{}^2 | \phi_i \phi_j \rangle}{\langle \phi_i \phi_j | f_{ij}{}^2 | \phi_i \phi_j \rangle} - \langle \phi_i | T_i | \phi_i \rangle \right),$$

$$E_{02U} = \sum_{i \neq j} \left( \frac{\langle \phi_i \phi_j | U_i f_{ij}{}^2 | \phi_i \phi_j \rangle}{\langle \phi_i \phi_j | f_{ij}{}^2 | \phi_i \phi_j \rangle} - \langle \phi_i | U_i | \phi_i \rangle \right);$$

and

$$E_{03} = E_{03V} + E_{03T} + E_{03U}, \text{ etc.},$$

where

$$U_j = U(\vec{r}_j, z_j),$$

$$T_j = \frac{-\hbar^2}{4m} \left( \nabla_j{}^2 + \frac{\partial^2}{\partial z_j{}^2} \right) \ln \phi(\vec{r}_j, z_j) \, ,$$

$$V_{ij} = V(|\vec{r}_i - \vec{r}_j|)$$

for

$$V(r) = v(r) - (\hbar^2/2m) \nabla^2 \ln f(r)$$

and

$$f_{ij} = f(|\vec{r}_i - \vec{r}_j|).$$

TABLE II. Parameters for the Morse-$V_{DD}$ helium-helium potential and Lennard-Jones helium-carbon potential.

| Morse-$V_{DD}$ helium-helium | Lennard-Jones helium-carbon |
|---|---|
| $\epsilon_0 = 12.14$ °K | $\tilde{\epsilon}_0 = 14.5$ °K |
| $\alpha = 6.23$ | $\rho_0 = 3.34$ Å |
| $\rho_1 = 2.975$ Å | |
| $\rho_2 = 3.5975$ Å | |
| $C_6 = 1.02 \times 10^4$ °K Å$^6$ | |
| $C_8 = 2.77 \times 10^4$ °K Å$^8$ | |

empirical hybrid potential which reasonably accounts for the virial coefficient data, the crossed-molecular-beam scattering, and the theoretical potential.[7,14] Although it may not be the very best potential available, it is much better than the standard Lennard-Jones potential[7] and is certainly adequate for present purposes. The functional form is

$$v(\rho) = \begin{cases} \epsilon_0\left(e^{-2\alpha(1-\rho/\rho_1)} - 2e^{-\alpha(1-\rho/\rho_1)}\right), & \rho \leq \rho_2 \\ -C_6/\rho^6 - C_8/\rho^8 \ , & \rho \geq \rho_2 \end{cases} \tag{5}$$

with the numerical values of the parameters given in Table II.

The interaction of a helium atom with the graphite substrate is represented, in typical fashion, by a sum over all carbon atoms of a two-body helium-carbon potential.[8] The carbon atoms are assumed to be fixed at their ideal lattice sites, with the surface basal plane assumed to be geometrically identical to the interior ones. This assumed substrate structure is an idealized one. The helium-carbon interatomic potential used is a Lennard-Jones potential, so $U(\vec{r}, z)$ is given by

$$U(\vec{r}_i, z_i) = \sum_j \tilde{\epsilon}_0 \left[(\rho_0/\rho_{ij})^{12} - 2(\rho_0/\rho_{ij})^6\right] \ , \tag{6}$$

with $\tilde{\epsilon}_0$ and $\rho_0$ being the parameters characterizing the helium-carbon pair and $\rho_{ij}$ being the distance between the $i$th helium atom and the $j$th carbon atom. In principle the sum in Eq. (6) extends over all carbon atoms; in practice some truncation is necessary. The details of the evaluation of $U$ are given in Appendix A.

While the helium-helium interaction is well characterized, the same cannot be said of the helium-carbon interaction. In recent calculations, the parameters $\tilde{\epsilon}_0$ and $\rho_0$ were estimated by use of the geometric mean interpolation rule using as knowns the helium-helium and carbon-carbon parameters.[2,15] These estimates are 17.0 °K for $\tilde{\epsilon}_0$ and 3.34 Å for $\rho_0$. The extent to which such estimates are reliable can be assessed by comparing such estimates for unlike rare-gas pairs (e.g., helium-argon) to those values of $\tilde{\epsilon}_0$ and $\rho_0$ deduced from crossed-molecular-beam experiments.[16] Typically, the interpolation estimate for $\rho_0$ is within a few percent of the experimental fit, but the interpolation estimate of $\tilde{\epsilon}_0$ can be too large by as much as a factor of 2. The inference is that the interpolation estimate for $\tilde{\epsilon}_0$ of the helium-carbon pair is likewise too large. This assertion is substantiated by the theoretical binding energies for helium adsorbed on graphite being roughtly 30% larger than experimental measurements indicate. The interpolation values of $\tilde{\epsilon}_0$ and $\rho_0$ result in a theoretical binding energy of 189 °K,[2] while experimental measurements place this number in the range 145–155 °K.[17–19]

One way of circumventing the above difficulty is to use the experimental data to fix the value of $\tilde{\epsilon}_0$.[18] For $13.5 \leq \tilde{\epsilon}_0 \leq 14.5$ °K, the theoretical binding energy for a He$^4$ adatom upon graphite ranges from about 140 to 156 °K.

The calculation of the binding energy of a single adatom upon a periodic substrate can be performed in a straightforward manner.[2,20] The single-adatom Hamiltonian $H_1$ is

$$H_1 = \frac{-\hbar^2}{2m}\left(\nabla^2 + \frac{\partial^2}{\partial z^2}\right) + U(\vec{r}, z) \ . \tag{7}$$

Briefly, the ground state of $H_1$ is expanded in an orthogonal basis set, suitably chosen and truncated. Since the ground state $\psi_0(\vec{r}, z)$ is a Bloch state, it can be expanded as

$$\Psi_0(\vec{r}, z) = \sum_{\vec{K}, \nu} C^{\nu}_{\vec{K}} \, e^{i\vec{K}\cdot\vec{r}} M^{\nu}(z) \ , \tag{8}$$

with the two-dimensional vector $\vec{K}$ being a reciprocal-lattice vector for the direct lattice associated with $U(\vec{r}, z)$. The set of functions $M^{\nu}(z)$ is an orthonormal basis of discrete states. The details of $M^{\nu}(z)$ are given in Appendix B.

The single-adatom binding energy of a helium atom is calculated using a seven-plane wave and a six-$M^{\nu}(z)$ basis. The sum over $\vec{K}$ includes the point $\vec{K}=0$ and its six nearest neighbors. The sum over $\nu$ includes the six most fundamental modes. With this 42-function basis and helium-carbon parameters of 14.5 °K for $\tilde{\epsilon}_0$ and 3.34 Å for $\rho_0$, the He$^4$ binding energy is 156.3 °K and that of He$^3$ is 149.4 °K. For the purposes of the present calculation, this is in satisfactory agreement with experiment. Thus these values of $\tilde{\epsilon}_0$ and $\rho_0$ are used for the remainder of the calculation.

The basic nature of the quantum states and band-structure shape is virtually unchanged upon reducing $\tilde{\epsilon}_0$ from 17.0 to 14.5 °K. The only noticeable change is a shift upwards and very slight compression of the band structure.[2]

## IV. CLUSTER EXPANSION FOR HELIUM UPON GRAPHITE

The particular nature of the helium-graphite system makes certain simplifications in $\Psi_N$ reasonable *a priori*. Since the ground state of a single adatom is nearly separable,[2] the single-particle term of $\Psi_N$—that is, the $\phi_j$ term—is written

$$\phi_j(\vec{r}_j, z_j) = \psi_j(\vec{r}_j)\sum_\nu C^\nu M^\nu(z) \quad , \tag{9}$$

with the $C^\nu$ to be determined variationally, and the $M^\nu(z)$ functions being the same basis set used in Sec. III for the single-adatom Bloch state. The single-adatom ground state is nearly cylindrically symmetric,[2] so that it is reasonable to use a cylindrically symmetric form for $\psi_j(\vec{r}_j)$. Furthermore, the calculations for the bulk solid[5] showed little effect upon replacing a Hartree single-particle term by a Gaussian. Therefore, the form chosen for $\psi_j(\vec{r}_j)$ is the Gaussian form

$$\psi_j(\vec{r}_j) = (A/2\pi)^{1/2} e^{-(A/4)(\vec{r}_j - \vec{R}_j)^2} \quad , \tag{10}$$

where $A$ is a variational parameter. This choice for $\psi_j$ means that $E_{01T} = \hbar^2 AN/4m$ and $E_{02T} = E_{03T} = 0$. Finally, the narrowness of the $M^\nu(z)$ functions simplifies the calculation of $E_{02V}$ since, for values of $r_{ij} = |r_i - r_j|$ where $\phi_j\phi_i$ is not negligible,

$$\int dz_i\, dz_j |M^\nu(z_i)|^2 v(\rho_{ij}) |M^{\nu'}(z_j)|^2 = v(r_{ij}) \tag{11}$$

to within 1%.

The cluster expansion for $\langle \Psi_N | H_N | \Psi_N \rangle$ is truncated by neglecting $E_{02U}$ and all three-body and higher clusters, so that $E_0$ is calculated via

$$E_0 = E_{01T} + E_{01U} + E_{02V} \quad . \tag{12}$$

The variational parameters are determined by minimization of this truncated series. Higher-order terms can then be calculated in order to assess the effect of their omission. The functional form used for $u(r)$ is

$$u(r) = e^{-2\alpha(1 - r/\rho_1)} - 2e^{-\alpha(1 - r/\rho_1)} \quad , \quad 0 \le r < \infty \tag{13}$$

with the values of parameters $\alpha$ and $\rho_1$ being those of Eq. (5).

The energy per adatom is, using Eq. (12),

$$\epsilon \equiv \frac{1}{N} E_0 = \frac{\hbar^2 A}{4m} + \sum_{\nu\nu'} C^\nu H^{\nu\nu'} C^\nu + \frac{1}{2}\sum_{j=2}^{N} \frac{\langle \psi_1\psi_j | V(r_{1j}) f^2(r_{1j}) | \psi_1\psi_j \rangle}{\langle \psi_1\psi_j | f^2(r_{1j}) | \psi_1\psi_j \rangle} \quad , \tag{14}$$

$$H^{\nu\nu'} \equiv \int_{-\infty}^{\infty} dz\, M^\nu(z) M^{\nu'}(z) \int dr^2 |\psi_1(\vec{r})|^2 \times [E^\nu \delta^{\nu\nu'} - U_m(z) + U(\vec{r}, z)], \tag{15}$$

$$V(r) \equiv v(r) - (\hbar^2/2m)\nabla^2 \ln f(r), \tag{16}$$

with $U_m(z)$ and $E^\nu$ given in Appendix B. For a given value of $A$, $\epsilon$ is minimized by the vector $C^\nu$, which is the eigenvector of $H^{\nu\nu'}$ having the lowest eigenvalue $\epsilon^0(A)$. Once $\epsilon^0(A)$ has been determined numerically, it can be minimized as a function of of $A$

The two leading corrections to $\epsilon$ are $\epsilon_{2U} = (1/N)E_{02U}$ and $\epsilon_{3V} = (1/N)E_{03V}$, with the main contributions to these terms involving the nearest-neighbor clusters.[5] The corrections are given by

$$\epsilon_{2U} = \sum_{j\neq 1}\left( \frac{\langle \psi_1\psi_j | \tilde{U}_1 f_{1j}^2 | \psi_1\psi_j \rangle}{\langle \psi_1\psi_j | f_{1j}^2 | \psi_1\psi_j \rangle} - \langle \psi_1 | \tilde{U}_1 | \psi_1 \rangle \right), \tag{17a}$$

$$\epsilon_{3V} = \frac{1}{2} \sum_{\substack{j\neq 1\\ l\neq 1\\ j\neq l}} \left( \frac{\langle \psi_1\psi_j\psi_l | f_{1j}^2 f_{1l}^2 f_{jl}^2 V_{1j} | \psi_1\psi_j\psi_l \rangle}{\langle \psi_1\psi_j\psi_l | f_{1j}^2 f_{1l}^2 f_{jl}^2 | \psi_1\psi_j\psi_l \rangle} - \frac{\langle \psi_1\psi_j | f_{1j}^2 V_{1j} | \psi_1\psi_j \rangle}{\langle \psi_1\psi_j | f_{1j}^2 | \psi_1\psi_j \rangle} \right) \; ; \tag{17b}$$

$$\tilde{U}_j \equiv \tilde{U}(r_j) \equiv \sum_{\nu\nu'} C^\nu C^{\nu'} \int_{-\infty}^{\infty} dz_j\, M^\nu(z_j) M^{\nu'}(z_j) \times U(r_j, z_j). \tag{18}$$

## V. RESULTS, CONCLUSIONS, AND REMARKS

For the sake of convenience, the energy origin is chosen to be $\overline{E}_0$, the ground-state energy of a single adatom in the laterally averaged substrate potential

$$\overline{U}(z) \equiv (1/\Omega) \int \int_\Omega d^2r\, U(\vec{r}, z) \ , \tag{19}$$

with $\Omega$ being the area of the unit cell. One advantage of using $\overline{E}_0$ as the origin is that the results are then relatively insensitive to changes in the helium-carbon Lennard-Jones parameters. Changes in $\overline{\epsilon}_0$ as large as 30% do little but change the value of $\overline{E}_0$. Using the method of Sec. III, $\overline{E}_0$ is $-149.1$ °K for He$^3$ and $-155.8$ °K for He$^4$. Subtracting $\overline{E}_0$ from the results of Sec. III, the ground-state energy of the single adatom in the potential $U(\vec{r}, z)$ is $-0.3$ °K for He$^3$ and $-0.5$ °K for He$^4$.

For both the "$\frac{1}{3}$" and "$\frac{1}{4}$" superlattice states of He$^4$, $E_0$ given by Eq. (12) is not very sensitive to changes in the variational parameters $A$ and $B$. In part, this is due to the competition of the "lateral" and "substrate" contributions to $E_0$. The $E_{01T}$ and the $E_{02V}$ terms combine to increase as a function of the parameter $A$, while the $E_{01U}$ term decreases. The lack of sensitivity to variations in $B$ is caused, in part, by the increased value of $A$ with the potential $U(\vec{r}, z)$ as compared to the potential $\overline{U}(z)$. Numerical calculations show that 15% variations in $A$ and $B$ about their *optimum* values cause less than 0.1 °K changes in $E_0$.

For the "$\frac{1}{3}$" superlattice state, which has an areal density $\rho = 0.0641$ Å$^{-2}$, the value of $A$ which minimizes $E_0$ is 40% larger than that value obtained by replacing $U(\vec{r}, z)$ by $\overline{U}(z)$. For the "$\frac{1}{4}$" state (areal density 0.0481 Å$^{-2}$) the increase is 30%. This shows the localization effect upon the adatom due to the substrate potential. Furthermore, this increase in the value of $A$ causes a very slight but significant decrease in $\overline{z}$, the average distance of the adatom from the surface. This slight decrease

TABLE III. Ground-state energies.

| | Areal density (Å$^{-2}$) | Energy per adatom (°K) |
|---|---|---|
| He$^4$ ($\bar{E}_0=-155.8$ °K) | | |
| Ideal gas | 0.0 | −0.5 |
| Superlattice ($X_g=\frac{1}{3}$) | 0.06407 | 0.0 |
| Superlattice ($X_g=\frac{1}{4}$) | 0.04805 | +0.6 |
| Liquid state | 0.06407 | +0.6 |
| Liquid state | 0.04805 | −0.3 |
| Liquid state | 0.036 | −0.6 |
| He$^3$ ($\bar{E}_0=-149.1$ °K) | | |
| Ideal gas | 0.0 | −0.3 |
| Superlattice ($X_g=\frac{1}{3}$) | 0.06407 | +3.4 |
| Superlattice ($X_g=\frac{1}{4}$) | 0.04805 | +2.6 |

in $\bar{z}$ results in about a 0.4 °K decrease in $E_0$. Similar effects occur for the "$\frac{1}{4}$" superlattice state. The He$^4$ ground-state energies, listed in Table III, are 0.0 °K per adatom for the "$\frac{1}{3}$" superlattice state and 0.6 °K per adatom for the "$\frac{1}{4}$" state. The increase in energy upon decrease in density is a reflection of the extent to which the higher-density state is able to take advantage of the periodic substrate potential. Table IV lists the appropriate values of $A$ and $B$. The parameter $a$ in that table is the helium-helium nearest-neighbor distance.

Rough estimates for the ground-state energy of the adsorbed He$^4$ liquid can be made by using a trial wave function in which the liquid ground state is totally uncorrelated with the substrate. Thus $\Psi_N^{\mathrm{liq}}$ is written

$$\Psi_N^{\mathrm{liq}}=\prod_{i=1}^{N}\left(\sum_{\nu} C^{\nu} M^{\nu}(z_i)\right)\prod_{1\le j<k\le N}\prod f(r_{jk}) , \qquad (20)$$

with $f(r)$ being the Jastrow factor used in the two-dimensional liquid ground-state calculations[9,10] and the vector $C^\nu$ is to be determined variationally. The calculation of the ground-state energy per adatom for the $\Psi_N^{\mathrm{liq}}$ of Eq. (20) and the $H_N$ of Eq. (1) is simply the sum of two terms, since Eq. (12) still applies. The first term is the ground-state energy of a strictly two-dimensional He$^4$ liquid, and the second is $\bar{E}_0$, the ground state of a single adatom in the potential $\bar{U}(z)$. The evaluation of the first term is given in Ref. 9 for the standard Lennard-Jones helium-helium interaction. In view of the difference in interatomic potentials and the lack of substrate correlations in Eq. (20), any comparisons between the liquid state and the superlattice state can only be taken as suggestive. However, with this reservation in mind, the results of Ref. 9 give an energy per adatom of − 0.6 °K for $\rho=0.035$ Å$^{-2}$, − 0.3 °K for $\rho=0.0481$ Å$^{-2}$, and + 0.6 °K for $\rho=0.0641$ Å$^{-2}$. These values complete the He$^4$ section of Table III.

The results tabulated in Table III do indicate specific stability conditions for the He$^4$ film. Both superlattice states have a higher energy per adatom than the adsorbed ideal gas, indicating that they are not self-bound and can only exist under pressure. On the other hand, the liquid calculation for $\rho=0.035$ Å$^{-2}$ is highly suggestive of this state being self-bound on the substrate surface, but at this point, the 0.1 °K difference between the gas and the liquid must be considered within the "noise" of the calculation. The comparison of the superlattice states to the liquid states suggest that the "$\frac{1}{3}$" state is stable to melting, but the "$\frac{1}{4}$" state is not. Thus at $\rho=0.0481$ Å$^{-2}$, the liquid state seems energetically favored, but at $\rho=0.0681$ Å$^{-2}$, it is the superlattice state which is so favored. However, the tentative nature of the comparisons with the liquid calculation must again be emphasized, and more detailed comparisons must await a liquid ground-state calculation with a better interatomic potential and some estimate as to the substrate correlation in the liquid state. What is quite noticeable from the calculation is the small differences in energy for densities below 0.068 Å$^{-2}$, and this effect can be seen in the experiments.[17] Tables III and IV also list the relevant values for He$^3$ superlattice and single-adatom states. The behavior is quite similar to He$^4$. Comparisons with liquid-state calculations are not made because of a lack of such calculations for the fermion system.

Because of the small energy differences between the states, the stability of these states may be affected by many-body corrections to the helium-helium interactions. For example, adatom-phonon interactions can increase the attraction between helium atoms by about 1 °K.[21] The dielectric effect of the substrate may also be of this magnitude.[22] To show the sensitivity of the calculation to such effects, if the ground-state energy of the "$\frac{1}{3}$" state is recalculated with an $\epsilon_0$ increased by 25%, this state becomes self-bound. Also, along similar lines, the summation of two-body potentials to obtain the adatom-substrate potential of the helium-graphite system is only a model of the actual substrate potential, although a commonly used one. If the actual shape of the substrate potential is very different from the result of such summations, this

TABLE IV. Wave-function parameters for the superlattice states.

| | | $Aa^2$ | $B$ |
|---|---|---|---|
| He$^4$ | $X_g=\frac{1}{3}$ | 51 | 0.07 |
| | $X_g=\frac{1}{4}$ | 34 | 0.09 |
| He$^3$ | $X_g=\frac{1}{3}$ | 46 | 0.06 |
| | $X_g=\frac{1}{4}$ | 31 | 0.07 |

could also affect the stability. The sensitivity of the calculation to these effects is caused by the smoothness of the substrate potential, so that for the superlattice states there is a delicate balance between the substrate effects and the adatom-adatom effects.

Calculations for the bulk helium solid show that the effects of the higher clusters are small. In view of the fact that these effects can be expected to be smaller for the superlattice states, and with the many-body corrections to the helium-helium interaction not yet fully assessed, it is not worthwhile to fully explore the remaining cluster terms. There are three main reasons why these remaining cluster terms are smaller here than in bulk. First, because of the two-dimensional nature of the adsorbed state, there are simply fewer neighbors of a given adatom, causing the higher clusters to have a smaller weight than in bulk. Second, the interatomic spacing for the superlattice states is larger than that in bulk, and the cluster expansion is known to converge faster for lower densities. Third, the substrate potential causes a narrowing of the single-particle Gaussians, and this also increases the convergence of the expansion.

The two main improvements in the bulk-solid calculation are the replacement of $\Pi_i \phi_i$ by a correlated Gaussian function and the use of a $t$-matrix approach for the calculation of $f(r)$.[23-25] In the bulk solid, the correlated Gaussian form can be argued on the basis of the translational invariance of the basic Hamiltonian. Thus the correlated Gaussian corresponds to a Debye model of zero-point motion as opposed to an Einstein model. Since the substrate potential breaks the translational invariance of the basic Hamiltonian, these arguments cannot be used, and it might be expected that the Einstein model for $\Psi_N$ has more validity for the superlattice state than it does for the bulk solid. The effect of the form of $f(r)$ would also be expected to have less effect for the superlattice states because of the narrowing effect of the substrate potential. In particular, it is known that the Nosanow form for $f(r)$ is not adequate to describe the very small $r_{ij}$ behavior of $\Psi_N$,[6] but this is just the region whose importance is decreased by the narrowing effect. However, exact quantitative effects can only be determined by explicit calculation.

## ACKNOWLEDGMENTS

The author would like to thank Dr. V. J. Emery and Dr. W. A. Steele for interesting discussions, and would like to express special thanks to Dr. H. Horner, several discussions with whom resulted in the author's beginning the above calculation.

## APPENDIX A

Two approximations in the lattice sum for $U(\vec{r}, z)$ are used. The effects of both approximations, tested numerically against the limit of Eq. (6), are found to result in errors which were less than 0.1 °K for all regions of space where the helium wave functions are not negligible.

The first approximation is the treating of all basal planes except the first or surface plane as two-dimensional continuums. The sum over carbon atoms in a lower plane becomes an integral which can be evaluated analytically.[8] The second approximation is the truncation of the sum over all carbon atoms in the first plane such as to include only those carbon atoms within a distance $\rho_c$. The contributions of the remaining carbon atoms in the first plane are calculated via the continuum approximation. The final result for $U(\vec{r}, z)$ is

$$U(\vec{r}, z) = \sum_{\rho_j < \rho_c} \tilde{\epsilon}_0 \left[ \left(\frac{\rho_0}{\rho_j}\right)^{12} - 2\left(\frac{\rho_0}{\rho_j}\right)^{6} \right] + \frac{8\pi\tilde{\epsilon}_0}{\sqrt{27}} \frac{\rho_0^2}{a^2} \left\{ 0.1\left(\frac{\rho_0}{\rho_c}\right)^{10} - 0.5\left(\frac{\rho_0}{\rho_c}\right)^{4} + \sum_{j=1}^{\infty} \left[ 0.1\left(\frac{\rho_0}{z+j\eta}\right)^{10} - 0.5\left(\frac{\rho_0}{z+j\eta}\right)^{4} \right] \right\} , \tag{A1}$$

with $a$ being the basal-plane carbon-carbon nearest-neighbor distance and $\eta$ the distance between basal planes. The values for these parameters are $a = 1.415$ Å, $\eta = 3.50$ Å, and $\rho_c = 10.32$ Å.

## APPENDIX B

The basis set $M^{\nu}(z)$ is the set of bound-state solutions to the Schrödinger equation for the adatom (mass $m$) in a Morse potential[26]

$$U_m = D(e^{-2\beta(z-z_0)} - 2e^{-\beta(z-z_0)}) , \tag{B1}$$

with $D$, $z_0$, and $\beta$ chosen in such a manner that $\alpha_0 = (2/\beta)(2mD/\hbar^2)^{1/2} - 1$ is a positive integer. In particular, $\alpha_0$ is fixed at some convenient value, with $D$ and $z_0$ adjusted so as to minimize the ground-state energy of the adatom in the potential

$$\overline{U}(z) = (1/\Omega) \int\int_{\Omega} d^2 r\, U(\vec{r}, z) , \tag{B2}$$

with $\Omega$ being the unit-cell area. Tests for the effect of the finite basis set can be made by increasing $\alpha_0$. The basis set so determined for the calculations in Sec. III are defined by the parameters

| | $D$ (°K) | $z_0$ (Å) | $\alpha_0$ |
|---|---|---|---|
| $He^3$ | 322.0 | 3.19 | 12 |
| $He^4$ | 312.3 | 3.115 | 12 |

The energy spectrum for these states is given by

$$E^{\nu} = -D\left(1 - \frac{2\nu - 1}{\alpha_0 + 1}\right)^2 , \quad \nu = 1 \cdots \leq 1 + \tfrac{1}{2}\alpha_0 . \tag{B3}$$

The numerical evaluation of any matrix element involving

$$\langle M^{\nu'}(z)|\frac{\partial^2}{\partial z^2}|M^{\nu}(z)\rangle$$

is achieved via

$$\langle M^{\nu'}|\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial z^2}|M^{\nu}\rangle = E^{\nu}\delta^{\nu\nu'} - \langle M^{\nu'}|U_m(z)|M^{\nu}\rangle \,. \qquad \text{(B4)}$$

---

*Work performed under the auspices of the U.S. Atomic Energy Commission.

[1] J. G. Dash, J. Low Temp. Phys. **3**, 301 (1970).

[2] D. E. Hagen, A. D. Novaco, and F. J. Milford, in *Proceedings of the Second International Symposium on Adsorption-Desorption Phenomena, Florence* (Academic, London, 1971).

[3] M. Bretz and J. G. Dash, Phys. Lett. **26**, 963 (1971).

[4] M. Bretz and J. G. Dash, Phys. Lett. **27**, 647 (1971).

[5] L. H. Nosanow, Phys. Rev. **146**, 120 (1966); J. H. Hetherington, W. J. Mullin, and L. H. Nosanow, Phys. Rev. **154**, 175 (1967).

[6] R. A. Guyer, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1969), Vol. 23.

[7] L. W. Bruch and I. J. McGee, J. Chem. Phys. **46**, 2959 (1967).

[8] A. D. Crowell and R. B. Steele, J. Chem. Phys. **34**, 1347 (1961).

[9] C. E. Campbell and M. Schick, Phys. Rev. A **3**, 691 (1971).

[10] M. D. Miller, C-W Woo, and C. E. Campbell, Phys. Rev. A **6**, 1942 (1972).

[11] F. Ricca, Nuovo Cimento Suppl. **5**, 339 (1967).

[12] W. H. Lai and C-W. Woo, Phys. Lett. A **41**, 170 (1972).

[13] H. W. Jackson, Phys. Rev. **180**, 184 (1969).

[14] J. M. Farrar and Y. T. Lee, J. Chem. Phys. **56**, 5801 (1972).

[15] R. Hellemans, A. Van Itterbeck, and W. Van Dael, Physica (Utr.) **34**, 429 (1967).

[16] R. B. Bernstein and J. T. Muckerman, in *Advances in Chemical Physics*, edited by J. A. Hirschfielder (Interscience, New York, 1967), Vol. 12, p. 466.

[17] R. L. Elgin and D. L. Goodstein, in Proceedings of the Thirteenth International Conference on Low Temperature Physics (unpublished).

[18] W. A. Steele (private communication).

[19] E. Lerner and J. G. Daunt, J. Low Temp. Phys. **10**, 299 (1973).

[20] A. D. Novaco and F. J. Milford, Phys. Rev. A **5**, 783 (1972).

[21] M. Schick and C. E. Campbell, Phys. Rev. A **2**, 1591 (1970).

[22] C. E. Campbell (private communication).

[23] T. R. Koehler, Phys. Rev. Lett. **18**, 654 (1967).

[24] H. Horner, Z. Phys. **205**, 72 (1967).

[25] R. H. Glyde and F. C. Khanna, Can. J. Phys. **50**, 1143 (1972).

[26] P. M. Morse, Phys. Rev. **34**, 57 (1929).

---

PHYSICAL REVIEW A VOLUME 7, NUMBER 5 MAY 1973

# Scaled Particle-Quasilattice Model of Liquid Water*

Donald E. O'Reilly
*Argonne National Laboratory, Argonne, Illinois 60439*

(Received 27 November 1972)

A quasilattice model for liquid water is formulated which in first approximation is based on the ice VII and ice Ic structures. Values of the work required to create a molecular vacancy are computed from the observed density and scaled particle theory of liquids. The isothermal compressibility of water is computed and is in good agreement with experiment. A modified Stokes–Einstein relation for the nuclear relaxation time is shown to give good agreement with recent deuteron relaxation data.

As is well known,[1] liquid water exhibits anomalous characteristics in density and compressibility versus temperature as well as other unusual physical properties. The temperature dependence of density, isothermal compressibility, and rotational correlation times of most liquids may be reasonably well accounted for by a simple quasilattice model of the liquid state in which it is assumed that the short-range structure of the liquid is face-centered cubic with molecular vacancies.[2] However, water has a decidedly tetrahedral structure as was clearly shown in the recent molecular-dynamics calculations of Rahman and Stillinger.[3] In the present work we propose that in zeroth approximation a suitable quasilattice for liquid water is the body-centered-cubic ice VII structure with molecular vacancies. We will compute the density $\rho$ of the liquid from the density $\rho_s$ of the hypothetical ice VII quasilattice and the probability $p_v$ of a molecular vacancy as follows[2]:

$$\rho = \rho_s(1-p_v) \,. \qquad (1)$$

In Eq. (1), $p_v$ is equal to $e^{-w/kT}$, where $w$ is the reversible work required to form a vacancy of molecular dimension. $w$ is conveniently calculated from the scaled particle theory of liquids[4] in which $w$ is expressed in terms of temperature ($T$), pressure ($P$), number density ($\rho_l$), and cavity radius ($\bar{r}$) as follows:

$$w(r) = \tfrac{4}{3}\pi\bar{r}^3 P + K_0 + 4\pi\bar{r}^2\sigma_0(1-2\delta/\bar{r}) \,, \qquad (2)$$

where $K_0$, $\sigma_0$ (surface tension), and $\delta$ are expressed as a function of $T$, $P$, and $\rho_l$ in Ref. 4(b). Equation (2) is valid for $\bar{r} > \frac{1}{2}\sigma$, where $\sigma$ is the colli-