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Stability of ^{4}He superlattices on graphite

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Using the variational method proposed by Lowy and Woo, we calculate the ground-state energies of the $\frac{1}{3}$- and $\frac{1}{4}$-coverage superlattices of ^{4}He physisorbed on graphite. The properly symmetrized single-particle factors in the trial wave function are constructed from expansions in an orthogonal basis set whose elements are the eigenfunctions of a Hamiltonian with a laterally averaged substrate potential. Calculation of the energy of the ^{4}He monolayer in the liquid phase is performed in a manner consistent with the superlattice calculation. The $\frac{1}{3}$-coverage superlattice is found to be stable, while the $\frac{1}{4}$-coverage monolayer chooses to remain in the liquid phase.

I. INTRODUCTION

The monolayer of ^{4}He physically adsorbed on a graphite surface has been a fascinating subject of study, particularly in view of recent interest in two-dimensional ordering. As the areal density changes, the monolayer can in principle be found in phases of two-dimensional liquid, lattice gas, and two-dimensional solid. At $\frac{1}{3}$ and $\frac{1}{4}$ coverages, the monolayer can exist in either liquid or superlattice phase.

Experimentally,[1,2] it has been observed that at $\frac{1}{3}$ coverage and near zero temperature, the adsorbed ^{4}He atoms form a registered lattice gas. There is still some uncertainty about the phase of a monolayer at $\frac{1}{4}$ coverage. A theoretical calculation was carried out by Novaco[3] comparing the ground-state energy of each superlattice with that of the liquid phase[4,5] at the same density. But the ground-state energies of the two phases were not calculated by the same method, rendering the comparison somewhat unreliable, since in some cases the energies lie very close to each other. We present here a variational calculation of the ground-state energies which treats the two phases consistently, and discuss in those terms the stability of the superlattice.

The method used was proposed by Lowy and Woo.[6] It was first applied to the solidification of bulk quantum systems and then to the solidification of ^{4}He monolayers adsorbed on graphite surfaces.[7] Substrate effects were not included in the latter. In the present calculation we include static substrate effects and bring the theory one step closer to reality. In Sec. II we first describe the system to be studied. We then motivate our choice of wave function and present the method of calculation, pointing out precisely where approximations are made. The results are given in Sec. III.

II. METHOD OF CALCULATION

We consider N helium atoms adsorbed on a graphite surface of area $\tilde{A}$. The areal density is then $n \equiv N/\tilde{A}$. The Hamiltonian of the system is given by

$$H=\sum_{i=1}^{N}\frac{-\hbar^2}{2m}\nabla_i^2+\sum_{i>j=1}^{N}v(r_{ij})+\sum_{i=1}^{N}U(\vec{r}_i) \quad . \qquad (1)$$

It includes three terms. The first term represents the kinetic energy of motion in directions both lateral and normal with respect to the substrate surface. The second term describes helium-helium interaction, r_{ij} denoting the distance between the ith and jth adatoms. The third term describes helium-substrate interaction. $\vec{r}_i$ denotes the position vector of the ith adatom, the $z=0$ plane being defined at the substrate surface with the substrate occupying the $z \leqslant 0$ half space, and the (x,y) measured from a coordinate system attached to the substrate lattice where the origin is at one adsorption site.

$$v(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^{6}] \quad , \qquad (2)$$

with $\epsilon=10.22\,^\circ\mathrm{K}$, $\sigma=2.556$ Å. $U(\vec{r})$ is taken to be the sum of pairwise contributions from all helium-carbon interactions. Again a Lennard-Jones potential is assumed

$$U(\vec{r})=\sum_k V(|\vec{r}-\vec{R}_k|) \quad ,$$

$$V(|\vec{r}-\vec{R}_k|)=\tilde{\epsilon}\left[\left(\frac{r_0}{|\vec{r}-\vec{R}_k|}\right)^{12}-2\left(\frac{r_0}{|\vec{r}-\vec{R}_k|}\right)^{6}\right] \quad , \qquad (3)$$

where $\vec{R}_k$ denotes the position of the kth carbon atom in the substrate. We take

$$\tilde{\epsilon}=15.55\,^\circ\mathrm{K} \text{ and } r_0=3.09 \text{ Å} \quad .$$

The origin of these values will be discussed in the Appendix.

The variational wave function Ψ is taken as the product of the single adatom wave functions $\phi(\vec{r}_i)$ and a Feenberg-Jastrow variational factor $e^{u(r_{jk})/2}$:

$$\Psi(\vec{r}_1,\vec{r}_2\ldots,\vec{r}_N)=\prod_{i=1}^{N}\phi(\vec{r}_i)\prod_{j>k=1}^{N}e^{u(r_{jk})/2} \quad . \tag{4}$$

Since the adatom is bound in the z direction and experiences a periodic potential provided by the substrate, the single adatom wave function is chosen to be the product of two expandable factors

$$\phi(\vec{r})=e^{t(\vec{\rho})/2}\chi(z) \quad . \tag{5}$$

We write the exponent of the first factor as

$$t(\vec{\rho})=\sum_{\vec{G}\geqslant 0} t_{\vec{G}}e^{i\vec{G}\cdot\vec{\rho}} \quad , \tag{6}$$

where $\vec{\rho}$ stands for the two-dimensional position vector $\vec{\rho}\equiv(x,y)$ and $\{\vec{G}\}$ represents a set of two-dimensional reciprocal-lattice vectors that corresponds to the superlattice structure assumed. By expanding $t(\vec{\rho})$ in this way, the single adatom wave function becomes properly symmetrized on the substrate surface. The coefficients $\{t_{\vec{G}}\}$ will then be determined as variational parameters. A liquid phase of the monolayer corresponds to a constant surface part of the single adatom wave function, thus $\{t_{\vec{G}}\}=0$. In contrast, when the monolayer finds itself in registry with the substrate surface, at least one member of the set $\{t_{\vec{G}}\}$ has to be finite. It is in this sense that our calculation of the ground-state energies is consistent for the two phases.

The second factor in $\phi(\vec{r})$ is written as

$$\chi(z)=\sum_{\nu} C_\nu M_\nu(z) \quad , \tag{7}$$

where $M_\nu(z)$ denotes the νth bound-state wave function of the adatom in a laterally averaged substrate potential. Details of calculating $M_\nu(z)$ are given in the Appendix. $\{C_\nu\}$ will be determined variationally. We normalize $\chi(z)$ by the condition

$$\int_0^\infty \chi^2(z)\,dz=1 \quad . \tag{8}$$

Finally, in Ψ, we take

$$u(r)=-(a\sigma/r)^5 ,$$

where a represents yet one more variational parameter.

The expectation value of the ground-state energy E can be expressed in the exact form

$$\begin{aligned}E=&\int P^{(1)}(\vec{r}_1)\left[-\frac{\hbar^2}{4m}\left(\frac{1}{2}\nabla^2_{1\rho}t(\vec{\rho}_1)+\frac{\partial^2}{\partial z_1^2}\ln\chi(z_1)\right)+U(\vec{r}_1)\right]d\vec{r}_1\\&+\tfrac{1}{2}\int P^{(2)}(\vec{r}_1,\vec{r}_2)\left(-\frac{\hbar^2}{4m}\nabla^2_1 u(r_{12})+v(r_{12})\right)d\vec{r}_1\,d\vec{r}_2 \quad ,\end{aligned} \tag{9}$$

where $P^{(1)}(\vec{r}_1)$ and $P^{(2)}(\vec{r}_1,\vec{r}_2)$ are the one- and two-particle distribution functions, respectively, the general definition of the n-particle distribution function being

$$P^{(n)}(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_n)=\frac{N!}{Z(N-n)!}\int d\vec{r}_{n+1}\,d\vec{r}_{n+2}\cdots d\vec{r}_N|\Psi|^2 \quad , \tag{10}$$

where

$$Z=\int d\vec{r}_1\cdots d\vec{r}_N|\Psi|^2 \quad . \tag{11}$$

In solving for $P^{(1)}(\vec{r}_1)$ and $P^{(2)}(\vec{r}_1,\vec{r}_2)$, we start from the generalized Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) integral equations. These equations are obtained by taking the gradients of $P^{(1)}(\vec{r}_1)$ and $P^{(2)}(\vec{r}_1,\vec{r}_2)$ with respect to $\vec{r}_1$. From Ref. 6,

$$\nabla_1 P^{(1)}(\vec{r}_1)=P^{(1)}(\vec{r}_1)\nabla_1\ln\phi^2(\vec{r}_1)+\int d\vec{r}_2 P^{(2)}(\vec{r}_1,\vec{r}_2)\nabla_1 u(r_{12}) \tag{12}$$

and

$$\nabla_1 P^{(2)}(\vec{r}_1,\vec{r}_2)=P^{(2)}(\vec{r}_1,\vec{r}_2)[\nabla_1\ln\phi^2(\vec{r}_1)+\nabla_1 u(r_{12})]+\int d\vec{r}_3 P^{(3)}(\vec{r}_1,\vec{r}_2,\vec{r}_3)\nabla_1 u(r_{13}) \quad . \tag{13}$$

Before proceeding further, we shall introduce some reasonably reliable[8] approximations on the adatom-adatom correlations in order to reduce mathematical complexities. Since the adatoms are very well localized in a plane parallel to the surface, we assume correlations between the adatoms in the z direction negligible compared to correlations in the lateral directions. So, instead of being functions of $\vec{r}$, the interaction v and the correlating factor u become functions of $\vec{\rho}$ only. Correspondingly, we can write

$$P^{(1)}(\vec{r}_1)=P_\rho^{(1)}(\vec{\rho}_1)\chi^2(z_1) \tag{14}$$

and

$$P^{(2)}(\vec{r}_1,\vec{r}_2)=P_\rho^{(2)}(\vec{\rho}_1,\vec{\rho}_2)\chi^2(z_1)\chi^2(z_2) \quad , \tag{15}$$

where $P_\rho^{(1)}(\vec{\rho}_1)$ and $P_\rho^{(2)}(\vec{\rho}_1,\vec{\rho}_2)$ are now the one- and two-particle distribution functions on a plane, defined by

$$P_\rho^{(n)}(\vec{\rho}_1,\vec{\rho}_2,\ldots,\vec{\rho}_n)=\frac{N!}{(N-n)!}\frac{\int d\vec{\rho}_{n+1}\cdots d\vec{\rho}_N\left[\prod_{i=1}^{N}e^{t(\vec{\rho}_i)}\prod_{j<k=1}^{N}e^{u(\rho_{jk})}\right]}{\int d\vec{\rho}_1\cdots d\vec{\rho}_N\left[\prod_{i=1}^{N}e^{t(\vec{\rho}_i)}\prod_{j<k=1}^{N}e^{u(\rho_{jk})}\right]} \quad . \tag{16}$$

The distribution function in the z direction reduces to the square of the wave function in that direction, as shown.

Equations (12) and (13) take on the two-dimensional form

$$\nabla_{1\rho}P_\rho^{(1)}(\vec{\rho}_1)=P_\rho^{(1)}(\vec{\rho}_1)\nabla_{1\rho}t(\vec{\rho}_1)+\int P_\rho^{(2)}(\vec{\rho}_1,\vec{\rho}_2)\nabla_{1\rho}u(\rho_{12})d\vec{\rho}_2 \tag{17}$$

and

$$\nabla_{1\rho}P_\rho^{(2)}(\vec{\rho}_1,\vec{\rho}_2)=P_\rho^{(2)}(\vec{\rho}_1,\vec{\rho}_2)[\nabla_{1\rho}t(\vec{\rho}_1)+\nabla_{1\rho}u(\rho_{12})]+\int d\vec{\rho}_3P_\rho^{(3)}(\vec{\rho}_1,\vec{\rho}_2,\vec{\rho}_3)\nabla_{1\rho}u(\rho_{13}) \quad , \tag{18}$$

where

$$\nabla_\rho\equiv\left[\frac{\partial}{\partial x},\frac{\partial}{\partial y}\right] \quad .$$

Guided by previous work,[6] we write

$$P_\rho^{(2)}(\vec{\rho}_1,\vec{\rho}_2)\equiv P_\rho^{(1)}(\vec{\rho}_1)P_\rho^{(1)}(\vec{\rho}_2)g(\vec{\rho}_1,\vec{\rho}_2) \quad ,$$

and apply Kirkwood's superposition approximation to $P_\rho^{(3)}(\vec{\rho}_1,\vec{\rho}_2,\vec{\rho}_3)$

$$P_\rho^{(3)}(\vec{\rho}_1,\vec{\rho}_2,\vec{\rho}_3)=P_\rho^{(1)}(\vec{\rho}_1)P_\rho^{(1)}(\vec{\rho}_2)P_\rho^{(1)}(\vec{\rho}_3)g(\vec{\rho}_2,\vec{\rho}_3)g(\vec{\rho}_1,\vec{\rho}_3)g(\vec{\rho}_1,\vec{\rho}_2) \quad .$$

Equations (17) and (18) then reduce to coupled equations for $P^{(1)}(\vec{\rho})$ and $g(\vec{\rho}_1,\vec{\rho}_2)$

$$\nabla_{1\rho}\ln P_\rho^{(1)}(\vec{\rho}_1)=\nabla_{1\rho}t(\vec{\rho}_1)+\int P_\rho^{(1)}(\vec{\rho}_2)g(\vec{\rho}_1,\vec{\rho}_2)\nabla_{1\rho}u(\rho_{12})d\vec{\rho}_2 \tag{19}$$

and

$$\nabla_{1\rho}\ln g(\vec{\rho}_1,\vec{\rho}_2)=\nabla_{1\rho}u(\rho_{12})+\int d\vec{\rho}_3P_\rho^{(1)}(\vec{\rho}_3)g(\vec{\rho}_1,\vec{\rho}_3)[g(\vec{\rho}_2,\vec{\rho}_3)-1]\nabla_{1\rho}u(\rho_{13}) \quad . \tag{20}$$

These two equations should be solved simultaneously. A complete iterative procedure begins with guessing a $P_\rho^{(1)}(\vec{\rho}_3)$ in Eq. (20). One solves for $g(\vec{\rho}_1,\vec{\rho}_2)$ by iteration, and then substitutes it into Eq. (19) to obtain a new $P_\rho^{(1)}$, which is in turn substituted into Eq. (20) for the determination of a new $g(\vec{\rho}_1,\vec{\rho}_2)$. These steps are to be repeated until convergence. In practice, we shall solve each equation only once. The first guess for $P_\rho^{(1)}(\vec{\rho}_3)$ is $n\equiv N/\tilde{A}$, the mean number density, so that Eq. (20) reduces to the BBGKY equation for a two-dimensional liquid.[5] $g(\vec{\rho}_1,\vec{\rho}_2)$ reduces to $g(\rho_{12})$, the radial distribution function for the uniform liquid. In close-packed lattice one expects weak directional dependences of $g(\vec{\rho}_1,\vec{\rho}_2)$.

In solving the first BBGKY equation (19), we follow the method described in Ref. 7. It will be outlined briefly here for completeness.

We expand $P_\rho^{(1)}(\vec{\rho}_1)$, first in the series

$$P_\rho^{(1)}(\vec{\rho})=n\exp\left[\sum_{\vec{G}\geq 0}b_{\vec{G}}e^{i\vec{G}\cdot\vec{\rho}}\right] \tag{21}$$

and then in the series

$$P_\rho^{(1)}(\vec{\rho}) = n \sum_{\vec{G} \geq 0} a_{\vec{G}} e^{i\vec{G}\cdot\vec{\rho}} . \tag{22}$$

By definition, the first relation between the coefficients $a_{\vec{G}}$ and $b_{\vec{G}}$ is established

$$a_G = \frac{1}{A} \int_{\text{cell}} \exp\left[\sum_{\vec{G}'} b_{\vec{G}'} e^{i\vec{G}'\cdot\vec{\rho}} \right] e^{-i\vec{G}\cdot\vec{\rho}} d\vec{\rho} , \tag{23}$$

where A is the area of the unit cell of the superlattice structure. The integration is performed over the unit cell.

Substituting these two expansions into Eq. (19), we find a second relation between $a_{\vec{G}}$ and $b_{\vec{G}}$ for each given choice of the trial wave function

$$b_G = t_G + n a_G F(G) , \tag{24}$$

where

$$F(G) = -\frac{2\pi}{G} \int_0^\infty g(\rho) u'(\rho) \rho J_1(g\rho) d\rho, \quad G \neq 0 , \tag{25}$$

$$F(G=0) = -\pi \int_0^\infty g(\rho) u'(\rho) \rho^2 d\rho , \tag{26}$$

and in Eq. (25) $J_1(x)$ is a Bessel function of order 1. Substituting Eq. (24) into Eq. (23), we obtain

$$a_G = \frac{1}{A} \int_{\text{cell}} \exp\left[\sum_{\vec{G}'} [t_{\vec{G}'} + n a_{\vec{G}'} F(G')] e^{i\vec{G}'\cdot\vec{\rho}} \right] \times e^{-i\vec{G}\cdot\vec{\rho}} d\vec{\rho} . \tag{27}$$

$\{a_{\vec{G}}\}$ can then be solved from Eq. (27) by iteration.

The energy expression, in terms of the variational function $u(\rho)$, $t(\vec{\rho})$, and $\chi(z)$, now appears as

$$\frac{E}{N} = \frac{\hbar^2}{8m} \sum_{\vec{G} \geq 0} a_{-\vec{G}} t_{\vec{G}} G^2 + \sum_{\vec{G} \geq 0} \sum_{\nu,\nu'} a_{\vec{G}} C_\nu C_{\nu'} \frac{1}{A} \int_{\text{cell}} \int_0^\infty e^{i\vec{G}\cdot\vec{\rho}_1} M_\nu(z_1) M_{\nu'}(z_1) U(\vec{r}_1) \, d\vec{\rho}_1 \, dz$$
$$+ n\pi \sum_{\vec{G} \geq 0} a_{-\vec{G}} a_{\vec{G}} \int_0^\infty g(\rho) \left[v(\rho) - \frac{\hbar^2}{4m} \nabla_\rho^2 u(\rho) \right] \rho J_0(G\rho) \, d\rho - \frac{\hbar^2}{4Nm} \int P_\rho^{(1)}(\vec{\rho}_1) \chi^2(z_1) \frac{\partial^2}{\partial z_1^2} \ln\chi(z_1) \, d\vec{\rho}_1 \, dz_1 , \tag{28}$$

where $J_0(G\rho)$ is a Bessel function of order zero. The last term is the kinetic energy that corresponds to motion of the adatom in the z direction. It can be reduced to a simpler form by means of the normalization relation

$$\int P_\rho^{(1)}(\vec{\rho}_1) \, d\vec{\rho}_1 = N ,$$

used in conjunction with results shown in the Appendix. The final expression for the energy per adatom is given by

$$\frac{E}{N} = \frac{\hbar^2}{8m} \sum_{\vec{G} \geq 0} a_{\vec{G}} t_{\vec{G}} G^2 + \sum_{\vec{G} \geq 0} \sum_{\nu,\nu'} a_{\vec{G}} C_\nu C_{\nu'} \frac{1}{A} \int_{\text{cell}} \int_0^\infty e^{i\vec{G}\cdot\vec{\rho}_1} M_\nu(z_1) M_{\nu'}(z_1) U(\vec{r}_1) \, d\vec{\rho}_1 dz_1$$
$$+ n\pi \sum_{\vec{G} \geq 0} a_{\vec{G}} a_{\vec{G}} \int_0^\infty g(\rho) \left[v(\rho) - \frac{\hbar^2}{4m} \nabla_\rho^2 u(\rho) \right] \rho J_0(G\rho) \, d\rho + \sum_\nu C_\nu^2 E_\nu^z - \sum_{\nu,\nu'} C_\nu C_{\nu'} \int_0^\infty M_\nu(z) M_{\nu'}(z) \bar{U}(z) \, dz . \tag{29}$$

Specifically, the variational parameters $\{C_\nu\}$ are determined by minimizing the energy with respect to $\{C_\nu\}$ under the condition that $\sum_\nu C_\nu^2 = 1$. We solve on the computer the set of equations

$$\frac{\partial(E/N)}{\partial C_\nu} + \lambda C_\nu = 0 , \tag{30}$$

where λ is a Lagrange multiplier.

III. RESULTS

The lateral pair distribution functions at densities corresponding to $\frac{1}{3}$ and $\frac{1}{4}$ coverages are shown in Fig. 1. The areal densities are 0.0641 and 0.0481 Å^{-2}, respectively. In both cases the value of the parameter a which minimized the energy is 1.18.

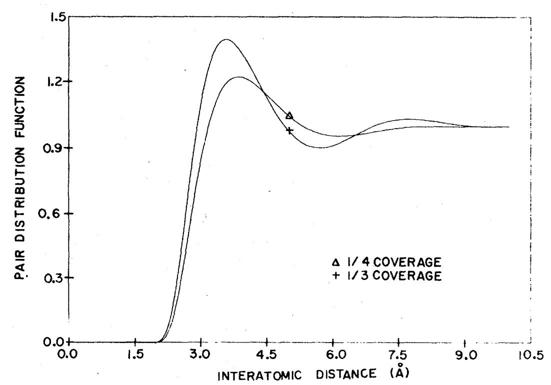

FIG. 1. Lateral pair distribution functions as calculated for $\frac{1}{4}$ and $\frac{1}{3}$ coverages.

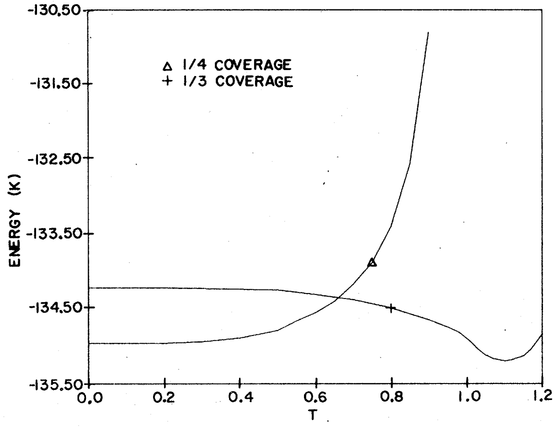

FIG. 2. Ground-state energies for the $\frac{1}{4}$-coverage and $\frac{1}{3}$-coverage monolayers as functions of the variational parameter T.

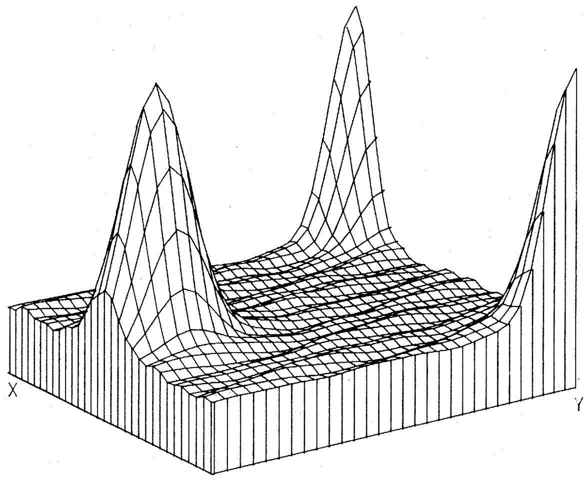

FIG. 3. $P_\rho^{(1)}(\rho)$: lateral distribution of adatoms in the $\frac{1}{3}$-coverage monolayer.

As mentioned in Sec. II, if the absolute minimum in the energy is obtained only when the set $\{t_{\vec{G}}\}$ equals the null set, we conclude that no periodic structure is stable with respect to the liquid configuration. Alternatively, if there is some nonzero set $\{t_{\vec{G}}\}$ such that the energy of the corresponding periodic configuration is less than the liquid (at the same density) energy, this particular superlattice structure will be stable with respect to the liquid.

We vary the first nontrivial t_{G_1}, where $\vec{G}_1$ stands for the first vector in the reciprocal-lattice space, in order to obtain the energy minimum. We denote this t_{G_1} by T and set the rest of the elements of the set $\{t_{\vec{G}}\}$ temporarily to zero. Furthermore, in calculating the one-particle distribution we use the values of the coefficients $a_{\vec{G}}$, $b_{\vec{G}}$, and $F(G)$, for $|\vec{G}|$ out to the tenth nearest-neighbor distance in the reciprocal-lattice space. This means retaining 73 terms in the Fourier series sum. The energy expectation value as a function of T is shown in Fig. 2.

In the $\frac{1}{4}$ coverage case, the energy increases monotonically with T. No minimum exists at finite T. The minimum that occurs at $T=0$ establishes a stable liquid phase with energy of -135.0 K per particle. There is no sign of a registered superlattice.

For the $\frac{1}{3}$ coverage, however, there is a minimum at finite T. The stable phase is a registered superlattice. The ground-state energy is -135.2 K per particle and the corresponding $T=1.1$. Figure 3 shows $P_\rho^{(1)}(\vec{\rho})$ and the extent of localization.

To ascertain these findings, we fix T at the value that minimizes the energy, and vary the energy with respect to t_{G_2}, where $\vec{G}_2$ is the second-nearest-neighbor vector in the reciprocal-lattice space. We find the minimum occurring at $t_{G_2}=0$.

We also consider the phase of a "slightly structured liquid" with the mean density of 0.0641 Å^{-2} (corresponding to $\frac{1}{3}$ coverage) and small fluctuations of the density commensurate with the periodicity of the substrate. Our calculations show that the "slightly structured liquid" seems to be slightly more stable than the uniform liquid. But the difference between

TABLE I. Variational parameters as determined in calculations for $\frac{1}{4}$ and $\frac{1}{3}$ coverages.

Parameter	Value for $\frac{1}{3}$ coverage	Value for $\frac{1}{4}$ coverage
a	1.18	1.18
T	1.1	0.0
C_1	-0.999	1.000
C_2	-3.94×10^{-2}	-3.06×10^{-3}
C_3	-1.59×10^{-2}	5.10×10^{-4}
C_4	-8.21×10^{-3}	-2.58×10^{-4}
C_5	4.34×10^{-3}	-1.46×10^{-4}
C_6	-2.23×10^{-3}	8.74×10^{-5}

the two energies is small compared to our numerical uncertainty; the result is thus not decisive. What is certain is that the superlattice phase is significantly more stable than either of the two liquid phases, the energy difference being about 1 K.

Table I lists the variational parameters determined for both cases. We observe C_1 is much larger than the rest of the elements of the set $\{C_\nu\}$. This fact justifies the assumption of neglecting the correlation between helium-helium atoms in the z direction.

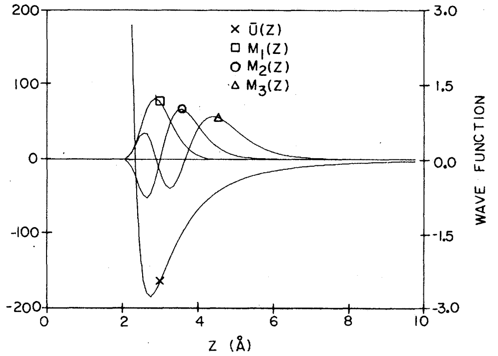

FIG. 4. Laterally averaged ^{4}He-substrate potential $\bar{U}(z)$ and the three lowest bound states $M_1(z)$, $M_2(z)$, and $M_3(z)$ in the normal direction.

ACKNOWLEDGMENT

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APPENDIX

The basis set $\{M_\nu(z)\}$ whose elements represent an orthonormal basis of discrete states is obtained by solving the one-dimensional Schrödinger equation for a single adatom

$$-\frac{\hbar^2}{2m}\frac{\partial^2 M_\nu(z)}{\partial z^2} + \bar{U}(z) = E_\nu^z M_\nu(z) \ . \qquad \text{(A1)}$$

The potential $\bar{U}(z)$ is the lateral average of the adatom-substrate potential $U(\vec{r})$ [Eq. (3)]. Explicitly it is given by the expression

$$\bar{U}(z) = \frac{1}{A}\int_{\text{cell}} d\vec{\rho}\, U(\vec{\rho},z)$$

$$= \frac{4\pi\tilde{\epsilon}}{A}\sum_{n=0}^{\infty}\left[0.1\frac{r_0^{12}}{(z+nd)^{10}} - 0.5\frac{r_0^6}{(z+nd)^4}\right] ,$$

where A is the area of the substrate unit cell, and $d = 3.37$ Å is the layer spacing.

Now given a choice of the pair $(\tilde{\epsilon}, r_0)$ the Schrödinger equation (A1) can be solved numerically. To make a specific choice of $(\tilde{\epsilon}, r_0)$ we follow the method of Carlos and Cole[9]: We choose the values of $\tilde{\epsilon}$ and r_0 that give a good fit between this calculated energy eigenvalue spectrum and the surface-bound-state spectrum obtained from measurements of ^{4}He scattering by graphite.[10] This approach gives the optimal Lennard-Jones potential parameters $\tilde{\epsilon} = 15.5$ K and $r_0 = 3.09$ Å. In Fig. 4 we present a plot of $\bar{U}(z)$ and the wave functions corresponding to the three lowest bound states.

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