

Quantum Monte Carlo Simulation of the Second Layer Helium Film on Graphite

P.A. Whitlock

Department of Computer and Information Science,
Brooklyn College, Brooklyn, NY 11210

G.V. Chester, & B. Krishnamachari
Laboratory of Atomic and Solid State Physics,
Cornell University, Ithaca, NY 14853

January 24, 2002

Abstract

Greens function Monte Carlo and variational methods are used to study the properties of the second layer ^4He adsorbed on a smooth graphite substrate. Realistic He-He and He-carbon interactions are used in the simulation. The densities at which condensation and crystallization occur are determined and compared with experiment.

1 Introduction

The work described in this paper is a continuation of our earlier work on helium films on graphite¹, which focused on a detailed simulation study of a first layer of ^4He on a smooth graphite substrate. We have extended that work and can give a preliminary report on the second layer on graphite.

There is a wealth of experimental data on ^4He films on graphite.^{2,3,4} A good deal of attention has been focused on the appearance of commensurate solid layers. However our interests are different; we are most interested in the condensation into a fluid phase and the crystallization of the layer into an incommensurate solid. The appearance of a liquid phase should be closely related to the onset of superfluidity⁵, while the crystallization should determine the upper boundary in density for the superfluid phase⁵. From a methodological point of view we present results which will allow us to

compare a common approximation for second layer calculations with the results of a more realistic calculation. The approximation that has been widely used^{6,7} to study the second and higher layers of ^4He on graphite and other substrates is to treat one or more of the underlying layers as being the source of an effective potential for the other layers. For example the first layer of helium atoms is thought of as being the source of an effective potential for the atoms in the second layer. In this approach the first layer atoms do not play a dynamic or active role in determining the properties of the second layer, their degrees of freedom are suppressed and are replaced by an effective single particle potential. We call this type of approximation a passive effective potential (PEP) approximation. This approximation can be compared with the results of calculations in which all the degrees of freedom of both first and second layers are taken into account; i.e. the atoms in the first layer now play a full active role in the calculation of the properties of the second layer. We call this an active layer (AL) calculation. Clearly an AL calculation will involve many more degrees of freedom than the corresponding PEP calculation and will be more time consuming. One of the aims of our work on the second layer is to understand whether there are important differences in the results of these two types of calculation. We also want to understand how the binding energy of the second layer compares with that of the first layer. The first layer is confined to a very narrow density profile, perpendicular to the carbon substrate. The second layer profile is about 50% wider¹ and thus the motion of the atoms is that much closer to 3D motion; we expect that the second layer will be more tightly bound.

In Section II we give the results of both variational and exact Green's Function Monte Carlo (GFMC) calculations for the second layer using a PEP approximation. We compare the binding energy of the second layer with that of the first layer. In Section III we give the results of a preliminary AL calculation and compare these results with the corresponding PEP calculation.

There have recently been published results from a path integral simulation⁸ of the second layer using a periodic PEP. It is unfortunately difficult to make a precise comparison of our results to those of this reference. The PEP used is different, and the Aziz potential for the helium interactions is also different. A qualitative comparison is made at the end of the next section.

2 A passive effective potential approximation

The Hamiltonian for the second layer in the PEP approximation is

$$H = T + V(He, He) + V(He, S) \quad (1)$$

Here T is the kinetic energy and $V(He, He)$ the potential energy of N helium atoms. The potential $V(He, S)$ is the sum of the helium carbon potential, coming from the graphite substrate, and the potential arising from the first layer of helium atoms. The helium-helium potential is chosen to be the Aziz I⁹ potential. We have used this in two previous studies and we can thus make immediate comparisons with two dimensional (2D) helium¹⁰ and the first layer on graphite¹. The helium carbon potential is the same as that in our first layer work¹. The effective potential for the second layer is computed by assuming an Aziz I potential between a second layer atom and the atoms in the first layer. This potential is then averaged over the atoms in the first layer by assuming a uniform density and integrating through the density profile of the first layer. We chose the density of the first layer to be 0.116 \AA^{-2} . This is very close to the density at which the first layer reaches completion and the second layer starts to form.

We have carried out both variational and GFMC calculations. The optimized variational function was used as the importance function for the GFMC calculation. The variational function has the same form as those used in our first layer work;

$$\Psi_T = \Phi_J \Phi_3 \Phi_S. \quad (2)$$

In the solid phase an additional factor Φ_G is used. Φ_J is a standard Jastrow factor, with two body correlations of the Macmillan form. Φ_3 is a triplet correlation function and Φ_S is a product of single particle orbitals which depend only on z , the coordinate perpendicular to the substrate. All these function are for N helium atoms contained in a rectangular simulation box and free to move in the z direction. The value of N ranged from 80 to 96. The additional factor Φ_G in the solid phase, is the product of Gaussian localization factors with a parameter c to define the degree of localization. The explicit forms of Φ_J , Φ_3 , Φ_S and Φ_G are given in reference 1. The single particle orbitals in the factor Φ_S are taken to be the ground state wave function of a helium atom moving in the PEP we have previously described. This potential is shown in figure 1, where it is compared with the helium carbon potential which binds the first layer to the graphite substrate. This second layer potential has a minimum of approximately -50K. The helium

carbon potential contributes about -25K and the remainder comes from the PEP of the first layer. Table I shows the values of the variational parameters as a function of density in both the fluid and solid phases.

Table II shows the variational and GFMC energies at four liquid densities and three solid densities of the second layer. We define the binding energy of the second layer as the total energy per particle minus the energy of a single helium atom in the PEP; this has a value of -29.02 K. These energies are shown in the fourth column. The fifth column gives the energies of the first layer at the same areal densities. These were obtained from our fitted equations of state¹. We see that the second layer is, as we expect, significantly more bound. The increase in the binding energy ranges from 6% at the lowest liquid density to 30% at the highest solid density. As we have pointed out this comes about because the second layer atoms have a much wider density profile, in the z direction, than those in the first layer. The data in Table II suggest that the second layer energy will have a minimum between 0.0426 \AA^{-2} and 0.0530 \AA^{-2} . Thus the density at which the second layer condenses to form a liquid phase will be somewhat above that found for the first layer, 0.0443 \AA^{-2} . The GFMC calculations show that the second layer solid phase has a lower energy at $0.08 \text{ atoms \AA}^{-2}$. At $0.07 \text{ atoms \AA}^{-2}$ the fluid and solid phases have almost the same GFMC energies. We conclude that the second layer crystallizes at a density close to $0.08 \text{ atoms \AA}^{-2}$ and that at the density 0.07 \AA^{-2} it is in a two phase region where the solid coexists with the liquid phase. This result is in agreement with the experimental neutron scattering data¹¹. It is important to notice that the variational results predict that the second layer will have crystallized by a density of 0.07 \AA^{-2} . This is not in agreement with experiment¹¹. Superfluidity has been observed⁵ in the second layer in the density range 0.05 \AA^{-2} to 0.07 \AA^{-2} . The upper density is clearly in the region where we believe the film has entered a two phase region which may well suppress the superfluid phase. We have recently calculated an additional value for the energy at a density of 0.0485 \AA^{-2} . The value we find is $-30.03 \pm 0.02 \text{ K}$. A fit to our energy values as a function of density yield a minimum value for the binding energy of $-3.03 \pm .03 \text{ K}$ at a density of 0.0483 \AA^{-2} . We see that the binding energy of the second layer is about 0.1 K (10%) lower than that of the first layer. Moreover the density at which a uniform fluid phase first forms, 0.0483 \AA^{-2} , is appreciably higher than the corresponding density for the first layer (0.0426 \AA^{-2}). Our value is now quite close to the value suggested by the superfluidity experiments⁵. Further refinements in the model of the second layer may well bring the condensation temperature into agreement with experimental value.

The last column of Table II shows the energies of the 2D system at the same areal density. These energies were again obtained from our fitted equations of state¹⁰. The difference in energy between the second layer and the 2D system are significant. Ranging from 10%, at the lowest density, to 40% at the highest. In our previous work we suggested that the 2D equation of state might be a good approximation to use to calculate the chemical potential of the second layer. This approximation has been used fairly frequently^{6,7}. Our new calculations throw some doubt on this method. However we need more data at other densities in order to see how well this approximation works.

In a recent paper Pierce and Manousakis⁸, using path integral techniques, have located the condensation density and the density at which the incommensurate crystal forms. Their condensation density is 0.048 \AA^{-2} and the crystallization density is 0.074 \AA^{-2} . We have already pointed out that their model for the second layer differs from ours in that the PEP potential is periodic and that the Aziz potential is also different. The condensation density is consistent with our data while the crystallization density is somewhat lower than ours.

3 An active second layer calculation

In this section we present some preliminary results of a calculation that removes the PEP approximation and treats both the first and second layers on an equal footing. We maintain the approximation of a smooth carbon substrate; thus each atom in the first and second layers sees a helium-carbon potential which is a function of z alone. The Hamiltonian for the system is

$$H = H_1 + H_2 + V_{12} \quad (3)$$

Here H_1 is the Hamiltonian for the atoms in the first layer and is given by

$$H_1 = T_1 + V_{11} + V_{1C} \quad (4)$$

where T_1 is the kinetic energy of the atoms in the first layer, V_{11} is the Aziz interaction for these atoms and V_{1C} is the helium carbon potential. The Hamiltonian for the second layer H_2 has the same form as H_1 . The interaction potential between the layers is V_{12} and is the sum of the two body interactions between the atoms in the first layer and those in the second layers. In our calculations, we have assumed the atoms belong to either to the first or second layers. This will be an accurate approximation

as long as there are very few exchanges between the atoms in these layers. Since the first layer is a very dense triangular solid it strongly repels the second layer atoms and exchanges are rare. It is known experimentally that the first layer density increases by about 5% as the density of the second layer increases from that of a dilute gas to the highest density of 0.08 \AA^{-2} . We can readily allow for this effect by maintaining the equality of the chemical potentials of the two layers. In our preliminary work we have not allowed for this small correction.

Our variational wave function for the two layer calculation has the form

$$\Psi_T^{(1,2)} = \Psi_T^{(1)} \Psi_T^{(2)} \Phi_J^{(1,2)} \quad (5)$$

Here $\Psi_T^{(1)}$ stands for a trial function of the form given by Eqn (2). We note that in $\Psi_T^{(1)}$ the orbitals in the factor $\Phi_S^{(1)}$ are single particle functions taken to be the ground state of a helium atom in the helium carbon potential for the first layer. In $\Psi_T^{(2)}$ the single particle orbitals are the ground state of a helium atom in a potential which is the sum of the helium carbon potential and the PEP provided by the first layer. While we have abandoned the PEP approximation in the Hamiltonian, Eqn (3), we have used it to define the orbitals in the trial wave function, $\Psi_T^{(2)}$. The factor $\Phi_J^{(1,2)}$ is a Jastrow factor, of the Macmillan form, which correlates the particles in the first layer with those in the second layer. Thus each particle in the second layer is explicitly correlated with each particles in the first layer.

We have carried out variational calculations with a first layer at a density of 0.116 \AA^{-2} (132 atoms) and the second layer at a density of 0.0421 \AA^{-2} (48 atoms). The wave function given by Eq.(5) was optimized to yield a total energy of -95.89 ± 0.02 K. We can compare this with a weighted sum of the energy of the first layer and the energy of the second layer. The weights being given by the fraction of the total number of atoms that are in each of these layers. This weighted sum give an energy of -96.92 ± 0.06 K. These energies are about 1K, or 1%, apart. This suggests that the PEP approximation for the second layer is quite accurate. In figure 2 we show the density profile in z direction for both layers. In this profile there are 132 atoms in the first layer and 48 in the second and the profile has been normalized to unity. This figure clearly shows that there is essentially zero overlap between these layers.

How does the binding energy of the second layer change when we compare the results of the PEP calculation with the AL calculation? The binding energy in the PEP calculation was defined as the total energy per particle minus the binding energy of a single particle in the PEP. We use the

analogous definition for the AL calculation. This single particle energy is now the difference in energy of the first layer with a single particle in the second layer and the energy of the first layer alone. Both energies are large because they contain the binding energy of N particles in the first layer to the carbon substrate. If we run a simulation with 30 particles in the first layer then this contribution is 30 times the single particle energy in the first layer, -140 K approximately. We are thus faced with the difficulty of subtracting two numbers of the order of 4,200 K. To overcome this difficulty we obtain our single particle energy by correlated sampling. In this method the energy estimators for the first layer with a single particle in the second layer and for the first layer alone are both evaluated for each configuration in the MC simulation and then the difference is taken. The binding energy is then the average of these differences over the MC run. Our preliminary calculations using this method suggest that the second layer binding energy may be significantly reduced in magnitude.

4 Conclusions

The calculations we have carried out for the second layer of ^4He on graphite show significant changes in both the condensation and crystallization densities when compared with the first layer values. Both densities are close to those suggested by the observation of superflow in the second layer⁵. A more realistic model of the second layer in which the first layer is treated as an active substrate suggest that the commonly used effective potential approximation requires careful examination. We plan to extend these calculations to cover more densities in both the fluid and the solid phases and thus obtain an accurate equation of state for the second layer.

Acknowledgments

This work was partially supported by the National Science Foundation under Grant No. DMR 9200409 and by the Office of Naval Research Grant No. N00014-96-1-1-1057.

References

- [1] P.A. Whitlock, G.V. Chester and B. Krishnamachari, Phys. Rev. B. 58 (1998).
- [2] J.G. Dash and J. Ruvalds, eds. "Phase Transitions in Surface Films," (Plenum, N.Y., 1980); H. Taub, G. Torzo, H.J. Lauter, and S.C. Fain, Jr., eds. "Phase Transitions in Surface Films 2" (Plenum, N.Y., 1991); "Excitations in two and three dimensional quantum fluids," edited by A.F.G. Wyatt and H.G. Lauter (Plenum Press, New York, 1991).
- [3] D.S. Greywall and P.A. Busch, Phys. Rev. Lett. 67, 3535 (1991); D.S. Greywall, Phys. Rev. B 47, 309 (1993); G. Zimmerli, G. Mitura, and M.W.H. Chan, Phys. Rev. Lett. 68, 60 (1992).
- [4] R.B. Hallock in Progress in Low Temperature Physics, Vol. XIV, page 321 (North Holland, Amsterdam 1995).
- [5] P.A. Crowell and J.D. Reppy, Phys. Rev. 53, 2701 (1996).
- [6] B.E. Clements, J.L. Epstein, E. Krotscheck, and M. Saarela, Phys. Rev. B 48, 7450 (1993); B.E. Clements, H. Forbert, E. Krotscheck, and M. Saarela, J. Low Temp. Physics 95, 849 (1994).
- [7] C.E. Campbell and M. Schick, Phys. Rev. A 3, 691 (1971).
- [8] M. Pierce and E. Manousakis, Phys. Rev. Lett. 81, 156 (1998).
- [9] R.A. Aziz, V.P.S. Nain, J. S. Carley, W.L. Taylor and G.T. McConville, J. Chem. Phys. 70, 4330, (1979).
- [10] P.A. Whitlock, G.V. Chester, and M.H. Kalos, Phys. Rev. B 38, 2418 (1988).
- [11] H.J. Lauter, H.P. Schildberg, H. Goldfrin, H. Wiechert, and R. Haensel, Can. J. Phys. 65, 1435 (1987).

Figure Captions

Fig. 1 The effective potential for atoms in the second layer (- - - - - - - -) compared with the helium carbon potential for atoms in the first layer (_____). The second layer PEP was calculated as described in the text. It has a minimum of approximately -50 K at a position of 5.6 Å above the carbon substrate. The helium carbon potential is -180 K deep at a distance 2.8 Å above the substrate.

Fig. 2 The density profile from a two layer calculation. The coordinate z is normal to the carbon substrate. There are 132 atoms in the first layer and 48 in the second layer. The profile has been normalized to unity.

$\rho(A^{-2})$	b(A)	c	$\lambda_t(A^2)$	$s_t(A)$	$\omega_t(A)$	$r_t(A)$
0.0426 ℓ	3.093	-	-8.50	2.045	1.278	6.39
0.0536 ℓ	3.093	-	-2.61	2.045	1.278	6.39
0.0700 ℓ	3.093	-	-1.96	2.045	1.278	6.39
0.0800 ℓ	3.093	-	-1.96	2.045	1.278	6.39
0.0700 s	2.888	0.268	-6.56	2.096	12.78	7.256
0.0800 s	2.837	0.421	-6.56	2.096	12.78	7.256
0.0850 s	2.863	0.459	-6.56	2.096	12.78	7.256

Table 1: The parameters, for the optimized wave functions for the liquid (ℓ), and solid (s) phases of the film. The second column gives the value of b in the Macmillan pseudo potential and c in the third column is the localization parameter in the Gaussian orbitals. The parameters λ , s , w and r define the triplet-correlation.

$\rho(A^{-2})$	$E_{var} (^{\circ}K)$	$E_{GFMC} (^{\circ}K)$	$E_2(K)$	$E_1 (^{\circ}K)$	$E_{2D} (^{\circ}K)$
0.0426 ℓ	-29.551 ± 0.009	-29.982 ± 0.007	-0.96 ± 0.01	-0.90 ± 0.01	-0.83
0.0536 ℓ	-29.076 ± 0.002	-29.98 ± 0.01	-0.96 ± 0.01	-0.79 ± 0.01	-0.71
0.0700 ℓ	-26.94 ± 0.02	-29.03 ± 0.02	-0.01 ± 0.02	0.32	-0.56
0.0800 ℓ	-24.72 ± 0.02	-27.68 ± 0.02	1.34 ± 0.02	1.88	2.37
0.0700 s	-28.227 ± 0.008	-29.01 ± 0.02	0.01 ± 0.02	0.39	0.55
0.0800 s	-27.16 ± 0.02	-27.99 ± 0.01	1.03 ± 0.01	1.52	1.85
0.0850 s	-26.27 ± 0.03	-27.24 ± 0.02	1.78 ± 0.02	2.49	2.90

Table 2: E_{var} and E_{GFMC} are the values of the variational and GFMC energies for the second layer respectively. The fourth column, E_2 , gives the values of the binding energy, $E_2 = E_{GFMC} - E_B$. The fifth column gives, for comparison, the binding energy of the first layer⁽¹⁾ and the last column gives the energy of the 2D system¹⁰. All energies are per particle.