Helium Adsorption on a Lithium Substrate

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We report results of path integral Monte Carlo and density functional studies of ^{4}He adsorption on a lithium substrate at low temperature. A recently proposed, accurate potential is used to model the ^{4}He-substrate interaction. Results show evidence of continuous growth of a ^{4}He film, with a superfluid monolayer at low coverage and no well-defined layering at higher coverages. Estimated superfluid transition temperatures exhibit a coverage dependence similar to that found in recent experiments of Csathy *et al.*

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Over the past few decades, superfluidity (SF) in thin ^{4}He films adsorbed on various substrates has proven to be one of the most fascinating phenomena in condensed matter physics. One of the seminal ideas invoked in explaining the intriguing behavior of superfluid films is the Kosterlitz-Thouless (KT) concept of topological long range order [1]. In spite of its success, there remain intriguing questions about the applicability of KT theory to monolayer films on both periodic and imperfect surfaces. A key issue has been the interpretation of a substrate-dependent threshold coverage ("inert layer") above which SF occurs. Such a threshold coverage has been observed on every surface studied until now, and its physical origin remains unclear. A plausible scenario is that of a solid ^{4}He layer, either amorphous (e.g., pinned to surface defects), or ordered, either commensurate or incommensurate to the substrate. This hypothesis arises in part because nearly all surfaces studied until now adsorb one or more solid ^{4}He layers. The exceptions found thus far involve H_2, Na, and Rb surfaces [2–6]. These substrates feature such a weak attraction that no solid ^{4}He layer is expected to form [7]. A motivation for studying helium adsorption on such surfaces is the possible observation of the simplest kind of two-dimensional (2D) superfluid. There has been almost no theoretical investigation of SF on such surfaces at nonzero temperature (T). The most extensive study, by Wagner and Ceperley (WC), focused on a H_2 surface. This system features substantial substrate zero point motion, enriching but also complicating the physics [8].

We investigate here the low temperature properties of a ^{4}He film adsorbed on a Li substrate. This system has been chosen for a number of reasons. One is that it should provide the "cleanest" example of monolayer SF, as we shall indeed argue. A second goal is to clarify some helium adsorption phenomena, only partially understood, observed experimentally on a sequence of alkali metals. These include the combined wetting/superfluid transitions observed on Cs, Rb, and K and the appearance of SF in the second layer on Na [4,6,9–11]. As argued in Ref. [6], the evolution of the phase diagrams on these substrates is consistent with an increase in substrate attraction, as one moves up the alkali column in the periodic table. Recently, the various ^{4}He-alkali metal physisorption potentials have been substantially revised [12] from earlier calculations [13], primarily due to the recognition that the polarization of the electrons in the metal core significantly contributes to the van der Waals attraction of the ^{4}He atoms. A third goal is to assess the reliability of the ground state ($T = 0$) density functional (DF) method, which has been used for many such calculations. Finally, a general motivation for the present study is to investigate the finite temperature behavior of this SF film. Previous microscopic studies of such a system have only examined ground state properties and/or adopted adsorption potentials quite different from the one considered the most accurate currently available, utilized in this study.

We discuss numerical results obtained with the path integral Monte Carlo (PIMC) method, which is "exact" within numerical limits imposed by the finite size of the system studied and the computing time available. We also present results obtained, for the same system, by DF. The result is continuous growth of film at coverages beyond that corresponding to 2D liquid density. This is consistent with the new potential being even more attractive than the one previously used for this system, for which continuous wetting was predicted [14]. PIMC results at low T are in general in agreement with DF predictions with one exception: DF predicts the minimum ^{4}He coverage at which the film is stable to be some 50% above the lowest stable film coverage found here with PIMC. The superfluid behavior of the film as a function of coverage is also studied, and values of the superfluid transition temperature T_c predicted. One of the most interesting results of this work is the apparent absence of layering of the adsorbed ^{4}He film, predicted in previous calculations for this system [14,15].

PIMC is a well-established computational tool to investigate physical properties of quantum many-body systems at finite temperature (see [16]). Here, we use PIMC to simulate N interacting ^{4}He atoms, interacting via the

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accepted Aziz pair potential [17]. Helium atoms move inside a simulation box in the shape of a parallelepiped of dimensions $L_x \times L_y \times L_z$, with periodic boundary conditions in all directions. The two bases of area $A = L_x \times L_y$ model Li substrates. For a given coverage Θ, L_x, and L_y are fixed so as to obtain a cross-sectional area $A = N/\Theta$. In most of our calculations we set $L_x = L_y$, but for values of Θ above 0.056 Å^{-2} we also performed a few simulations with a rectangular cell, in order to allow for different initial arrangements of the ^{4}He atoms, including a 2D triangular lattice. Values of Θ between 0.0360 and 0.1400 Å^{-2} are considered, at several temperatures in the range $T = 0.5$–2 K. L_z is chosen large enough (typically of the order of 4–5 times L_x, L_y) that, at all coverages considered, ^{4}He atoms remain in the vicinity of one of the two Li substrates during the entire simulation. Each run consists of typically 108 "passes" (see Ref. [16]). The interaction between the ^{4}He atoms and the Li surface is modeled by a "3-9" potential:

$$V(z) = \frac{4C^3}{27D^2z^9} - \frac{C}{z^3}, \tag{1}$$

where z is the distance of the ^{4}He atom from the Li surface. Here, $C = 1422$ K Å^3 is the van der Waals interaction coefficient and $D = 17.87$ K is the well depth. These values have been obtained from *ab initio* calculations of the physisorption potential $V(z)$ for a ^{4}He atom and an alkali substrate by Chizmeshya, Cole, and Zaremba (CCZ) [12]. Such calculations employ a jellium model of the metal, a Hartree-Fock approximation to the "overlap" electron-atom interaction, and an electron gas method to determine the dielectric response, using dynamical image plane parameters obtained by Liebsch [18]. The CCZ potentials are significantly deeper than those used in earlier studies [13] of these systems, which overestimated the repulsion and underestimated the attraction. The revised, deeper potentials yield estimates of wetting temperatures and contact angles on Cs and Rb much closer to experimental values than those offered by the previous potentials [6,19]. An important feature of our model, based on the potential $V(z)$, is the lack of surface corrugation. Such a translational invariance, implicit in the jellium model, is a realistic consequence of the fact that the motion of the ^{4}He atoms begins at a plane some 4–5 Å above that of the Li nuclei [12]. The number N of ^{4}He atoms in our studies varies between 25 and 64. For any given Θ, PIMC results for structural and energetic properties of ^{4}He films feature negligible dependence on N, whereas results for the ^{4}He superfluid fraction $\rho_S(\Theta, T)$ show expected finite-size effects. We shall return to this point later in the Letter. The time step utilized in all PIMC calculations is $\tau = 0.025$ K^{-1}, which has been empirically found suitable for simulations of this type [16]. Figures 1 and 2 present results of our calculations for the correlation functions $n(z)$ and $g(R)$. The former is the laterally averaged ^{4}He density as a function of the distance z from the Li substrate. It is defined as $n(z) = (1/A)\int dx\, dy\, \rho(x, y, z)$, ρ being the PIMC-computed 3D ^{4}He density. The correlation function $g(x, y)$ is defined as

$$g(x, y) = \frac{1}{\Theta^2}\int dx'\, dy'\, n(x + x', y + y')n(x', y'), \tag{2}$$

with $n(x, y) = \int dz\, \rho(x, y, z)$. Because of the cylindrical symmetry that the infinite system enjoys, we average over the angular dependence, i.e., take $g(x, y) \equiv g(R)$, with $R = \sqrt{x^2 + y^2}$. The first comment concerns the comparison of PIMC and DF results; in Fig. 1, density profiles $n(z)$ computed using both PIMC (at $T = 0.5$ K) and DF (at $T = 0$) are shown. In general, the agreement between the two calculations is fairly good, at all coverages considered. On the other hand, DF predicts a stable

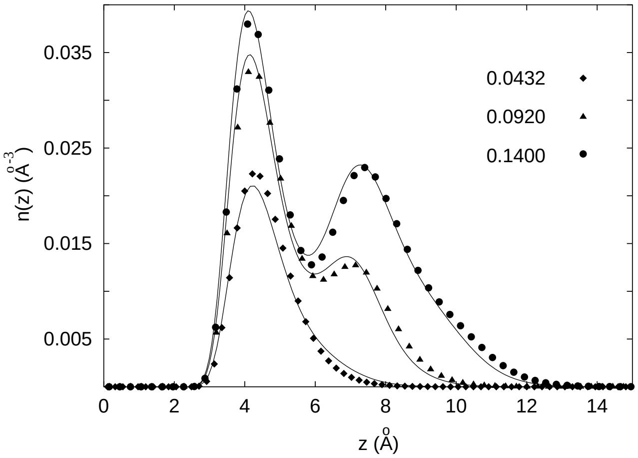

FIG. 1. Filled symbols show density profiles $n(z)$ for a ^{4}He film on a Li substrate, computed by PIMC at $T = 0.5$ K, at various ^{4}He coverages, expressed in Å^{-2}. Statistical uncertainties are smaller than symbol sizes. Solid lines represent the corresponding density profiles computed by DF at $T = 0$.

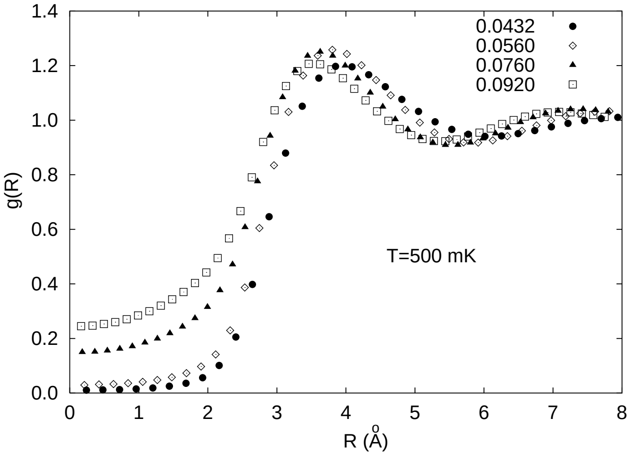

FIG. 2. Density correlation function $g(R)$, defined as in (2), for ^{4}He adsorbed on a Li substrate, computed by PIMC at $T = 0.5$ K, at various ^{4}He coverages, expressed in Å^{-2}.

^{4}He film to exist only for coverages above 0.056 Å^{-2}. What we observe for ^{4}He on Li clearly depends on the coverage Θ, as seen in Figs. 1 and 2. Consider now for definiteness a coverage $\Theta = 0.0432$ Å^{-2}, henceforth referred to as Θ_e, which corresponds to the theoretical value of the 2D ^{4}He equilibrium density [20]; the "spread" of $n(z)$, defined as the full width at half maximum, is $\delta z \sim 2$ Å, much larger than what is found, for example, on graphite [21], where $\delta z \sim 0.3$ Å. This is a result of the very shallow and broad adsorption potential in the Li case. The evolution of $n(z)$ as the density increases is similar to what is found by WC on a H_2 surface [8]. One observes in Fig. 1 that the second layer is not well defined, particularly if compared to what is observed on graphite, for example.

The absence of layering is a second consequence of the weak attraction; it occurs because the ill-defined first layer provides an even weaker and less localized potential for subsequent adsorption. PIMC also permits one to study the evolution of the ^{4}He film with temperature; however, for all values of Θ considered here the dependence of $n(z)$ on T is weak. This can also be rationalized as a consequence of the loss of layering. In the contrasting case of strong layering, the onset of the second layer is considerably T dependent, through an Arrhenius-type behavior [22]. Concerning the film evolution, we note two additional points. One is that there appears no evidence, in $g(R)$, of the formation of a 2D solid near $\Theta \sim 0.07$ Å^{-2}, in contrast to the case of ^{4}He on graphite [21]. This is related to the second point, namely, that growth beyond the monolayer regime commences near this density. This value was predicted previously to represent the onset of second layer formation on Li, but the basis for that onset value was an oversimplified, mean field model of layering [7]. The results for the correlation function $g(R)$ are consistent with our interpretation of the $n(z)$ behavior. At low coverage, $g(R)$ is found to be nearly identical to the ground state pair distribution function computed for 2D ^{4}He [23]. As we have already remarked, however, ^{4}He motion in the z direction is significant, as can also be appreciated from the values of the kinetic energy per ^{4}He atom, $\langle k \rangle$, reported in Table I. Again, at $\Theta = \Theta_e$ $\langle k \rangle \sim 7$ K at $T = 0.5$ K, more than twice as large as the corresponding value for 2D ^{4}He at the same coverage and temperature [23]. As coverage increases, deviation from the 2D behavior develops. Especially noteworthy is the growth of $g(R)$ for values of r less than the hard core size ($\sim$2.6 Å) of the helium interatomic potential. This manifests atomic motion beyond the monolayer region. This smooth growth of the film beyond the monolayer is consistent with both other predictions and trends from experimental data for other surfaces, which imply continuous ^{4}He film growth on a Li surface [6]. The last column of Table I reports the values of the total energy of each ^{4}He atom, ϵ. This quantity is found to have a minimum $\epsilon_m \sim -9.65$ K at around $\Theta \sim 0.046$ Å^{-2}; one may compare this value with -16.6 K, obtained by WC for a H_2 substrate, at the same coverage found here [8]. The presence of a minimum of $\epsilon(\Theta)$ at some finite Θ is consistent with a prewetting transition, predicted for this system [7]. We now turn to the superfluid behavior, which is a subject of particular interest because it has been studied experimentally for surfaces other than Li [24–26] and has been predicted by KT theory to have a specific form near the SF transition [1]. $\rho_S(\Theta, T)$ is the fraction of ^{4}He film that, for a given ^{4}He coverage Θ, can flow without dissipation parallel to the Li substrate (i.e., in our case, to the xy plane). In this Letter, we compute by PIMC $\rho_S(\Theta, T, N)$, i.e., the superfluid fraction for a system with N ^{4}He atoms. Calculation is performed as illustrated in Ref. [16]. In order to provide theoretical estimates of the superfluid transition temperature $T_c(\Theta)$, one should in principle extrapolate numerical results for $\rho_S(\Theta, T, N)$, obtained for several systems with different numbers of particles N, to the thermodynamic limit ($N \rightarrow \infty$). Such a procedure is impractical, however, as the computation of $\rho_S(\Theta, T, N)$ by PIMC becomes rather demanding for $N > 30$. Instead, we rely on a more convenient scheme, adopted in Refs. [23,27] to study SF in 2D ^{4}He. $T_c(\Theta)$ for the infinite system is determined quite accurately by fitting the values of $\rho_S(\Theta, T, N)$ for a system of relatively small size; the fitting function arises within KT scaling theory, and depends on two parameters, namely, the effective vortex core energy (E_c) and diameter (d). Just as in Ref. [23], we use values of $\rho_S(\Theta, T, N)$ with $N = 25$ to obtain $T_c(\Theta)$ at the various coverages considered. Note that, although the fitting does not determine d very accurately, the value of $T_c(\Theta)$ in the thermodynamic limit depends only on E_c [23]. The fit is very accurate at all coverages, except at the lowest one considered, $\Theta = 0.0360$ Å^{-2}, where it fails. It should also be noted that at this coverage, unlike at all others, $\rho_S(\Theta, T, N)$ does not tend to 1 as $T \rightarrow 0$, but rather saturates at about 0.85–0.90, as reported also on H_2 by WC [8]. We interpret this as indicative of the instability of a 2D ^{4}He film at the spinodal density, estimated to be near 0.0350 Å^{-2} [28].

TABLE I. Normal-to-superfluid transition temperature T_c (K) as a function of the coverage Θ (Å^{-2}, first column). Also reported are the values of the fitting parameters d (Å^{-2}) and E_c (K). For the lowest coverage no accurate fit could be obtained. The last two columns report kinetic ($\langle k \rangle$) and total energy (ϵ) per ^{4}He atom (K) at a temperature $T = 0.5$ K, computed by PIMC on a 25-particle system. Numbers in parentheses are statistical uncertainties, on the last digit.

Θ	T_c	d	E_c	$\langle k \rangle$	ϵ
0.0360	⋯	⋯	⋯	6.49(1)	−9.30(1)
0.0385	0.58(1)	5.7(3)	1.92(4)	6.63(1)	−9.57(1)
0.0432	0.69(1)	4.6(2)	2.47(5)	6.99(1)	−9.62(1)
0.0480	0.78(1)	4.1(2)	2.87(7)	7.44(1)	−9.64(1)
0.0560	0.88(1)	4.1(2)	3.06(4)	8.21(1)	−9.61(2)
0.0760	1.10(1)	3.0(2)	3.50(4)	9.21(1)	−9.25(3)
0.0920	1.23(1)	2.3(1)	3.61(3)	9.66(1)	−9.00(3)
0.1400	1.42(2)	4.1(3)	3.4(1)	11.30(3)	−8.44(4)

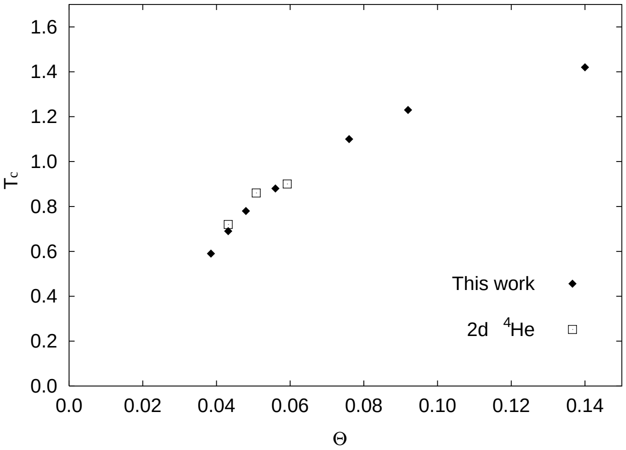

FIG. 3. Estimated ^{4}He superfluid transition temperature T_c (K), for various coverages Θ (Å^{-2}) (filled diamonds). Also shown are PIMC results for 2D ^{4}He (boxes), from Ref. [27]. Statistical uncertainties are smaller than the symbol size.

Transition temperatures $T_c(\Theta)$ are reported in Table I, together with the values of E_c and d, and shown in Fig. 3. Also shown are estimated values of $T_c(\Theta)$ for 2D ^{4}He, from Ref. [27]. Within their statistical uncertainties, these two calculations are in agreement. Our conclusion is that, despite the importance of atomic motion in the z direction, at low coverage the physics of the adsorbed ^{4}He film is remarkably close to that of an ideal two-dimensional system. This fact was also reported in a recent preliminary account of this work [29]. The smoothness of $T_c(\Theta)$ is consistent with the absence of layering; no evidence of discontinuous behavior is found, for example, near $\Theta \sim 0.07$ Å^{-2}, corresponding to the completion of the first layer.

The trend shown by the results in Fig. 3 is quite similar to that of experimental data by Csathy *et al.* for ^{4}He on a variety of relatively weak substrates, including H_2, HD, D_2, Ne, and Ar [26]. The only difference between results on different substrates is the value of $\Theta_\circ$, i.e., the onset coverage below which no SF is observed. The results shown in Fig. 3 suggest a nonzero value of $\Theta_\circ$, roughly around 0.035 Å^{-2}, for our system as well. We believe such a threshold onset coverage, close to that observed for H_2 [26], to reflect a property of 2D ^{4}He, namely, the spinodal decomposition, rather than any particular feature of the substrate, which is strong enough to stabilize a monolayer film at low coverage. On the other hand, for experimental substrates the onset coverage $\Theta_\circ$ is empirically found to depend roughly linearly on the value of the parameter D characterizing the adsorption potential. As yet unexplained, this intriguing dependence will be the subject of future investigations.

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