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Existence and nature of a helium monolayer film

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A variational calculation is presented of the energy of monolayer He films adsorbed on a surface. We find that the ground state of ^{4}He is always a liquid, in agreement with the result for a strictly two-dimensional calculation, but in disagreement with results obtained recently with perturbation theory for the case of extremely weak adsorption potentials. The calculated energies provide a bound on the regime of parameter space corresponding to a bare surface ground state. For the most part, the latter is consistent with both the conclusions obtained recently with a density functional theory and with experiments showing nonwetting for ^{4}He on Cs and Rb. For ^{3}He, calculations are presented under the assumption that the quasi-two-dimensional ground state is a gas. The resulting threshold potential for the monolayer to form is somewhat less attractive than in the ^{4}He case.

I. INTRODUCTION

Attention has been directed recently to the nature of quantum films on weak-binding substrates.[1-9] The question has been stimulated by the realization that the well depth D of individual He atoms is in some cases comparable to the binding energy of ^{4}He atoms in a three-dimensional (3D) liquid $E_B=-\mu_0=7.17$ K. Since the lateral binding energy of ^{4}He atoms in ideal 2D is quite small (of order 0.8 K), there arises the possibility that He films may not be stable relative to bulk. Indeed, specific predictions have been made of ^{4}He nonwetting and prewetting behaviors in the case of alkali metal and H_2 substrates; experimental evidence of both kinds of behavior has been seen. For the case of Cs, the data indicate that there exist low temperature (T) nonwetting and a wetting transition at T near 2 K.

This paper addresses $T=0$ properties of a film in order to establish whether the hypothetical film actually exists on a given surface and to quantify its properties. To accomplish this we determine variationally the energy per particle, E, of a quasi-two-dimensional (Q2D) He monolayer film. We then ask whether

$$\Delta E=E+\mu_0 \tag{1}$$

is positive or negative. If $\Delta E<0$, it means that the monolayer film is stable relative to both the bulk liquid and the bare surface. This means that such a monolayer film may exist at unsaturated conditions. The word "may" is used because we cannot exclude the possibility that other film states may be more energetically stable. We can, however, definitely exclude in this case the possibility of complete nonwetting, i.e., a bare surface, for $\mu<\mu_0$.

The results of the present calculations are twofold. First, we establish rigorously an extended domain of gas-surface interaction strength such that some film exists; the limited scope of our variational wave function's parameter search precludes a definite statement about the existence, and possible greater stability, of multilayer films. Second, we find that the calculated ^{4}He monolayer film is stable relative to 2D evaporation; that is, it is a liquid. This conclusion contradicts that obtained previously for some weak-binding surfaces, using perturbation theory and other methods.[4]

Recent studies of weak-binding have found it convenient to describe the He-surface interaction in terms of a two-parameter potential:

$$V(z)=C_3\left[\left[\frac{4C_3^2}{27D^2z^9}\right]-\frac{1}{z^3}\right] . \tag{2}$$

Here z is the He distance above the surface, D is the well depth, and C_3 is the van der Waals coefficient of the nonretarded asymptotic potential. Numerical values are presented for many surfaces in Ref. 10. We ignore any x,y corrugation effects for two reasons (in addition to simplicity): corrugation effects are expected to be small in the important case of weak binding, due to the large equilibrium distance, and the variational theorem shows that the corrugation term in the potential can only lower the energy further, below our calculated upper limit. Previous variational studies of Q2D He have taken account of x,y corrugation, but they have not probed the regime of weak adsorption potential.[11]

In the following section we present the variational calculation describing the hypothetical ^{4}He monolayer film. Section III compares these results to those of two related studies. One is an analogous study of adsorption which uses a phenomenological density functional to explore films of variable thickness.[2,3] The other is the previously mentioned set of approximate calculations pertinent to the state of the monolayer film. Section IV addresses ^{3}He briefly, summarizes our results and discusses other calculations and experiments.

II. VARIATIONAL METHOD—^{4}He

We write the Hamiltonian as

$$H=-\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2+\sum_{i=1}^{N}V(z_i)+\sum_{i=1}^{N}\sum_{j>i}^{N}U(r_{ij}) , \tag{3}$$

where $U(r)$ is the He-He interaction.[12]

Let ϵ be the ground-state energy of the single-particle potential:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dz^2}\varphi_0(z)+V(z)\varphi_0(z)=\epsilon\varphi_0(z) . \tag{4}$$

If $|\Psi\rangle$ denotes the exact ground state of the total Hamiltonian H, we define the binding energy per particle, E_B, through

$$\frac{1}{N}\frac{\langle\Psi|H\Psi\rangle}{\langle\Psi|\Psi\rangle}-\epsilon\equiv-E_B . \tag{5}$$

In a variational calculation, the expectation value of H is calculated in a trial state $|\Psi_v\rangle$. This yields a rigorous lower bound to the binding energy.

We have considered variational Bose wave functions that are products of single-particle functions $\varphi(z)$ and translationally invariant (in 3D) many-body wave functions of the Jastrow type. It is convenient to factor out the exact ground state of the adsorption potential explicitly, and write

$$\varphi(z)=\varphi_0(z)\tilde{\varphi}(z) ,$$

$$\psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)=\prod_i\tilde{\varphi}(z_i)\prod_{j>i}\exp[-\tfrac{1}{2}u(r_{ij})] , \tag{6}$$

$$\langle\mathbf{r}_1,\ldots,\mathbf{r}_N|\Psi_v\rangle=\left[\prod_i\varphi_0(z_i)\right]\psi(\mathbf{r}_1,\ldots,\mathbf{r}_N) ,$$

so that, assuming Ψ_v is normalized, one obtains a variational estimate of the binding energy of the film, given by (we omit the explicit coordinate dependence of the wave functions)

$$E_B^v=-\frac{1}{N}\int d^3r_1\cdots d^3r_N\Psi_v^2\sum_i\left[-\frac{\hbar^2}{2m}\left[\frac{1}{\psi}\nabla_i^2\psi+2\frac{d}{dz_i}\ln(\varphi_0)\frac{\partial}{\partial z_i}\ln(\psi)\right]+\sum_{j>i}U(r_{ji})\right] . \tag{7}$$

These integrals are suitable for Monte Carlo evaluation using the Metropolis algorithm. A code, previously used for calculations of three-dimensional He,[13] was modified and extensively tested. For instance, the variational results of Ref. 14 were reproduced when the film was confined in the z direction by a very narrow single-particle wave function.

We simulate a system of $N=64$ atoms, with periodic boundary conditions in the (x,y) directions, and free boundary conditions in the z direction. Test runs with twice as many particles show that size effects are negligible. The density is varied by choosing a unit cell of appropriate size. Following Ref. 14, the Jastrow pseudopotential is chosen of the from $u(r)=(b/r)^m$. All results presented below are obtained with $\tilde{\varphi}=1$. In general no significant improvement in the energy could be obtained by a simple analytical ansatz for $\tilde{\varphi}$.

III. RESULTS FOR ^{4}He

We begin by studying the binding energy of a He film on several alkali metal substrates. Table I shows the adsorption potential parameters used, and the adsorption energies, ϵ. Table II summarizes the results of our variational calculations at fixed coverage, $\rho=0.0321$ Å^{-2} (at this rather low density, variational and Green's function Monte Carlo results agree to better than 15% for 2D helium.[14] We show the total energy of the film (relative to ϵ), $-E_B$; the potential energy contribution,

$$E_P=\left\langle\frac{1}{2}\sum_{i\neq j}U(r_{ij})\right\rangle ;$$

the two-dimensional kinetic energy contribution,

$$T_{\parallel}=\left\langle\frac{\hbar^2}{2m}\sum_i\frac{\partial^2}{\partial x_i^2}+\frac{\partial^2}{\partial y_i^2}\right\rangle ;$$

the total energy of the film (also relative to ϵ) obtained in first-order perturbation theory following Ref. 4; and, finally, the optimized variational parameter, b; in all cases, $m=5$.[15] We also present our variational results

TABLE I. Well depth (K), Van der Waals dispersion (K Å^3), and ground-state energy (K) of the adsorption potential for ^{4}He (ϵ_4) and ^{3}He (ϵ_3) on selected alkali surfaces.

	D	C_3	ϵ_4	ϵ_3
Li	17.05	1350	−8.97	−8.01
Na	10.44	1068	−4.84	−4.21
K	6.26	812	−2.44	−2.05
Cs	4.41	673	−1.49	−1.21

TABLE II. Columns 1, 2, 3: variational results for total, potential, and in-plane kinetic energies of two-dimensional ^{4}He (first row) and ^{4}He films on various alkali surfaces. Column 4: total energy in first-order perturbation theory. 1-σ uncertainty on last digit is given in parentheses. All energies in K/particle; the adsorption ground-state energies have been subtracted out [see Eq. (7)]. Column 5: best value of the variational parameter b. Coverage $\rho=0.0321$ Å^{-1}.

	$-E_B^v$	E_P	$T_{\parallel}$	$-E_B^1$	b (Å)
2D	−0.67(1)	−3.28(2)	2.61(2)	−0.67(1)	3.05
Li	−0.70(1)	−2.88(2)	1.77(2)	−0.52(2)	3.0
Na	−0.81(1)	−2.84(2)	1.57(2)	−0.35(2)	3.0
K	−0.94(1)	−2.61(2)	1.22(2)	−0.20(2)	2.95
Cs	−0.97(1)	−2.43(2)	1.04(2)	0.04(2)	2.95

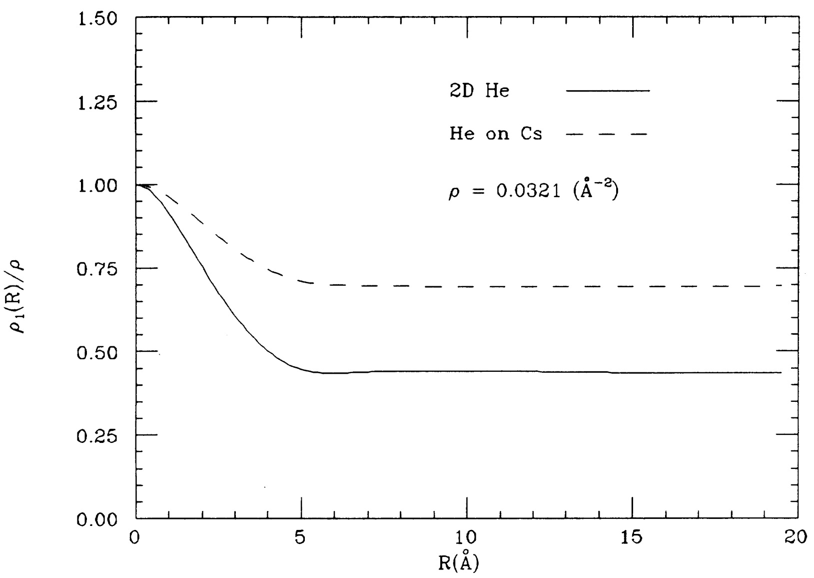

FIG. 1. Normalized one-body density matrix [Eq. (8)]; R denotes distance on the plane of the surface.

for two-dimensional He for comparison.

There is a striking difference between the results of first-order perturbation theory and those of our variational calculation. According to the former, the spread of the wave function in the third dimension always results in a decrease of the binding energy; for $\rho=0.0321$ Å^{-2}, there is no binding at all for He on Cs. (Note that the perturbative calculation, carried out with a variational two-dimensional wave function, actually underestimates this unbinding effect relative to the result obtained with the Green's function Monte Carlo ground state). Our nonperturbative calculations show instead that the binding energy increases in all cases as a consequence of the motion of the atoms in the z direction. This breakdown of perturbation theory points to a substantial wave-function renormalization, and its origin should be traced to the hard-core character of the He-He interaction. This causes the many-body wave function to go rapidly to zero whenever two atoms get closer than the hard-core diameter, yielding as a consequence a high kinetic energy. When out-of-plane motion is allowed, these close encounters are much rarer, and the curvature of the wave function decreases substantially. Thus, the increase in potential energy (which is the only contribution in first-order perturbation) is outweighed by a simultaneous decrease in kinetic energy.

A straightforward check of this interpretation is provided by the calculation of the one-body density matrix, off-diagonal in the $\mathbf{R}\equiv(x,y)$ coordinate:

$$\rho_1(R) = \int d^3r_1 \cdots d^3r_N \psi(\mathbf{r}_1+\mathbf{R},\ldots,\mathbf{r}_N)\psi(\mathbf{r}_1,\ldots,\mathbf{r}_N) . \tag{8}$$

Figure 1 shows the result of a variational calculation of

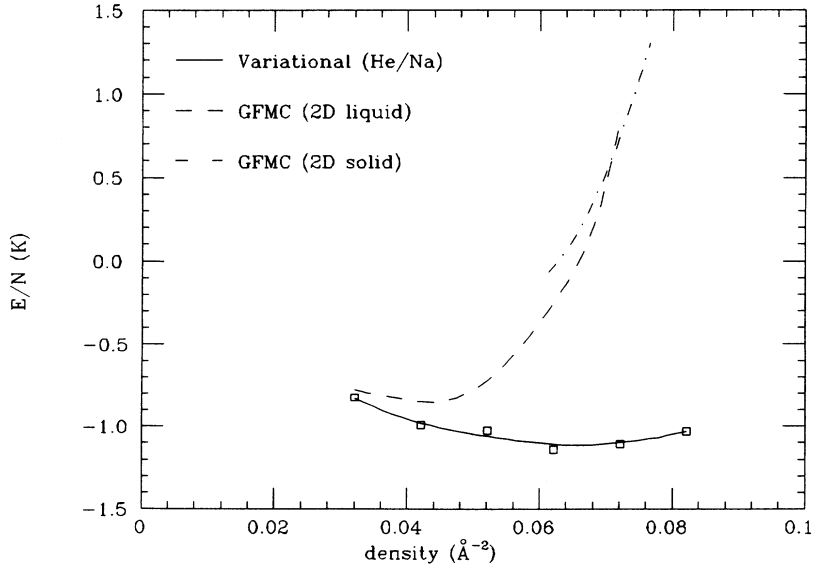

FIG. 2. Energy per particle of 2D and Q2D ^{4}Helium. Green's function Monte Carlo resutls for 2D liquid (dashed line) and triangular solid (dash-dotted line) from Ref. 14. Variational results for ^{4}He on the surface of Na from Eq. (7) (squares).

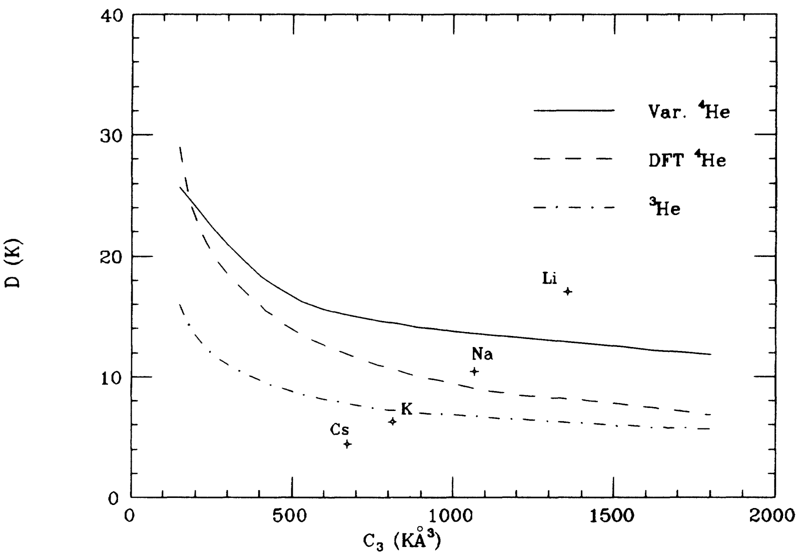

FIG. 3. Domain of existence of a He film on weak-binding substrates, as a function of the substrate potential. A ^{4}He monolayer film is found to be stable above the solid line (variational calculation) or dashed line (density functional theory of Ref. 2). For ^{3}He, the analogous curve (dash-dotted) lies below these others, indicating a less stringent condition for the existence of a film.

ρ_1 for two-dimensional He and for a He film on Cs (both at coverage $\rho=0.0321$ Å^{-2}). Note that ρ_1 is isotropic in the (x,y) plane, and is related to the two-dimensional kinetic energy per particle as follows:

$$T_{\parallel}=-\frac{\hbar^2}{m\rho}\left[\frac{\partial^2}{\partial R^2}\rho_1(R)\right]_{R=0} . \tag{9}$$

That is, the kinetic energy is proportional to the curvature of ρ_1 at the origin. Also note that the condensate fraction calculated in quasi-2D is 50% higher than in strictly 2D due to the diminished role of the hard core.

The substantial decrease of $T_{\parallel}$ due to the motion in the third dimension accounts for another remarkable difference between 2D and Q2D He, that is the weak dependence of the binding energy on the coverage. We have carried out a study of the energy as a function of coverage for Q2D He on a Na substrate. The results are shown in Fig. 2, together with the 2D energy per particle from Green's function Monte Carlo (GFMC).[14]

IV. CONCLUSIONS

We have found a variational result for the ground-state energy of surfaces characterized by the adsorption potential (2). We show in Fig. 3 the evaluation of the condition that ΔE vanishes; that is, that the computed binding energy equals that of bulk liquid He. As discussed in the Introduction, this represents an upper limit in the C_3-D plane to the domain in which some film exists. Below this line there exists the possibility of complete nonwetting at $T=0$. We may compare this result to the result obtained by Cheng *et al.*[2] for the same problem using a phenomenological density-functional method.

The latter curve is compatible with the present result insofar as it lies below it, except for the regime of very small C_3. Two sets of comments are appropriate to this finding. The first is that the Cheng *et al.* results correspond to a prewetting transition, meaning a coverage discontinuity as a function of chemical potential. Just above this curve, the jump diverges, but asymptotically it corresponds to the 2D condensation transition studied here. The second comment is that experiments have now confirmed these predictions in several respects: Cs and Rb, but not Na, are nonwetting surfaces at very low temperatures.[5-7] Cs and Rb exhibit prewetting transitions, with a wetting temperature of order 2 and 1 K, respectively.[16]

To make definitive predictions requires either that one go beyond the variational method, e.g., Green's function Monte Carlo method, or that one extends the class of variational states considered here. While thin films may be successfully addressed without substantially greater computational effort than used here, the prewetting phenomenon requires treatment of thick films, which can be considerably more difficult. The reason is simply that the trial wave function ought to incorporate a reasonable estimate of the film's configuration; this is not easy when the layers lose their meaning, which happens a few Å from the substrate.

We now address briefly ^{3}He, for which we assume that the ground state is a gas.[17] Under these circumstances, the ground-state energy is just equal $-\epsilon$. Then the threshold condition for the stability of such a film is $\epsilon=\mu_0$, where μ_0 is 2.47 K for ^{3}He.[18] Figure 3 shows the corresponding curve to lie below that of ^{4}He. This implies that some surfaces will bind a ^{3}He film, but not a ^{4}He film. This is intriguing in view of the fact that when mixtures are adsorbed on more conventional surfaces, the heavier isotope segregates to the substrate.

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