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Ground-state properties of the free surface of liquid ^{4}He

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We report quantum-mechanical calculations of the properties of the ground state of a slab of ^{4}He. Both variational Monte Carlo and Green's-function Monte Carlo (GFMC) methods are applied to systems of different sizes. The values for the surface tension at zero temperature obtained with different estimators give excellent agreement with experimental results. The density distributions and the thickness of the interface are also studied. We conclude that the He-He potential is accurate enough and GFMC precise enough to calculate a nontrivial inhomogeneous system.

A very significant issue in condensed-matter physics is the extent to which more or less complex systems can be quantitatively explained by our knowledge of the basic interactions and by our ability to compute their consequences accurately. A major challenge is an inhomogeneous quantum fluid such as a film or a layer of liquid ^{4}He with a free surface. By now, the bulk properties have been computed with the use of the HFDHE2 interatomic potential of Aziz *et al.*,[1] and found to be in good agreement with experiment. But the properties of a free surface are sensitive to critical details of the He-He interaction and pose a significantly greater challenge to the computational method.

Recently, the surface tension liquid ^{4}He was measured by means of a surface-wave resonance method,[2] and the relative variations with respect to γ, the extrapolation of its value at absolute zero, showed excellent agreement with those obtained by a precise capillary-rise method in a previous approach.[3] The value of γ was measured in Ref. 2 as 0.257 K/Å^2, which is 6% smaller than the value 0.274 K/Å^2 adopted in Ref. 3. Thus, the experimental situation is clear enough to justify a serious computation.

Previous attacks on this problem have left it in an unresolved state. The results on droplets[4] were not completely satisfactory, in that it is impossible to be sure whether the discrepancy in the surface tension resulted from the form of the potential or from the geometry of the system that was studied. Accordingly, we undertook a calculation of a slab of ^{4}He with a free surface. The result is very good agreement with experiment, showing that the potential is accurate enough and Green's function Monte Carlo is precise enough to calculate a system of this complexity.

Both variational Monte Carlo (VMC) and Green's function Monte Carlo (GFMC) have proved very successful in the study of the ground-state properties of quantum systems, and are described elsewhere.[5] A reason for the success of this study is that the variational wave function, also used as an importance function in the GFMC, contains appropriate three-body terms,[6]

$$\Psi_{3B}=\exp\left[-\tfrac{1}{2}\sum_{i<j}u'(r_{ij})-\tfrac{1}{4}\lambda\sum_{n}\mathbf{G}(n)\cdot\mathbf{G}(n)\right], \quad (1)$$

where

$$\mathbf{G}(n)=\sum_{i\neq n}\xi(r_{ni})\mathbf{r}_{ni}$$

and

$$u'(r_{ij})=u(r_{ij})-\lambda\xi^2(r_{ij})r_{ij}^2 .$$

The triplet correlation function is taken to be

$$\xi(r)=\left[\frac{r-r_B}{r_B}\right]^3\exp\left[-\left[\frac{r-r_t}{\omega}\right]^2\right],$$

where r_B corresponds to the walls of the box and r_t and ω are variational parameters, and the pseudopotential $u(r_{ij})$ is chosen to be of the McMillan form, $u(r)=(b/r)^5$. All the parameters in Ψ_{3B} are those for the equilibrium density and will be published elsewhere.

The film we consider has two surfaces situated symmetrically with respect to the plane $z=0$, with periodic boundary conditions in the x and y directions. One-body factors are included in the wave function to stabilize the system, and the trial wave function becomes

$$\Psi_T=\Psi_{3B}\prod_i h(z_i), \quad (2)$$

where, for $N>54$, we take $h(z)=f(z;k,z_0)$, with

$$f(z;k,z_0)=\{1+\exp[k(|z-z_{\text{c.m.}}|-z_0)]\}^{-1}.$$

For smaller systems ($N\leq 54$), we use instead $h(z)=f(z;k,z_0)f(z;-k,-z_0)$, to compensate for the effects of the use of the absolute value. The parameter z_0 controls the interface location and k determines its thickness. To guarantee translational invariance, the z component of the center of mass of the system, $z_{\text{c.m.}}$, is subtracted from z in $h(z)$.

We have studied systems with $N=27$, 54, 108, 216, and 324 particles variationally, and with $N=27$, 54, and 108 particles in the GFMC runs. The simulation area was taken to be $A=580.6$ Å^2. We have also run a system with half this area to study size effects.

A first estimator for γ can be obtained directly from the values of the energy. If we represent by ε_∞ and ε_N the energies per particle in the ground state of the uniform and

slab systems, respectively, the surface tension at zero temperature is given[7] by

$$\gamma = \frac{N}{A}(\varepsilon_\infty - \varepsilon_N) . \tag{3}$$

Another estimator can be obtained from the virial theorem. In the quantum case,

$$\gamma = \frac{1}{A}\int \Psi_0^* \left[-\frac{\hbar^2}{m}\sum_i \left(\frac{\partial^2}{\partial z_i^2} - \frac{\partial^2}{\partial x_i^2} \right) + \sum_{i<j} \left[\frac{x_{ij}^2 - z_{ij}^2}{r_{ij}} \right] \frac{dV(r_{ij})}{dr_{ij}} \right] \Psi_0 dr^N , \tag{4}$$

where the first term is a kinetic contribution, and has no classical counterpart.[8]

Finally, the study of systems with different N allows us to analyze the bulk, surface, and higher-order terms in the energy per particle.[4] If we define $x = A/N$ one has

$$\frac{E(N)}{N} = \varepsilon_\infty + \gamma x + \delta x^2 + \cdots . \tag{5}$$

Once we have fitted this expression to energies corresponding to different values of N, we can calculate the surface tension, which is the coefficient γ.

The pair interaction is usually truncated at a finite distance in Monte Carlo simulations, and its effect is usually estimated by a tail correction. In this case we only have periodic boundary conditions in the x and y directions, and we shall consider a truncation only in those directions, both for the total energy and for the estimator from the virial theorem. In the first case, when one assumes that the particles are uncorrelated in the region

$$\sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2} > L/2 ,$$

the corresponding two-particle density distribution factorizes to $\rho_{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \rho_{(1)}(\mathbf{r}_1)\rho_{(1)}(\mathbf{r}_2)$. The contribution per particle to the potential energy from the density beyond the cylinder of radius $L/2$ can be expressed then as

$$\varepsilon_{\text{tail}} = \frac{A\pi}{N}\int_{-\infty}^{\infty} dz_1 \int_{-\infty}^{\infty} dz_2 \int_{L/2}^{\infty} R dR \rho_{(1)}(z_1)\rho_{(1)}(z_2) \times V(R^2 + (z_1 - z_2)^2) . \tag{6}$$

A similar expression is obtained in this way for γ_{tail} from Eq. (4).

More information on the interface is provided by the single-particle density distribution $\rho_{(1)}(z)$. For instance, its profile along the coordinate z determines the width of the interface, W, which is usually defined as the distance in which $\rho_{(1)}(z)$ decreases from 0.9ρ to 0.1ρ, where ρ is the density well inside the liquid.

Table I lists the various systems and their energies and widths. We have obtained for all sizes in the VMC minimizations the same value $k = 1.0$ Å^{-1} of the thickness parameter.

The single-particle density $\rho_{(1)}(z)$ computed in the variational runs is shown in Fig. 1. Two noticeable trends are that the interior density is lower than the bulk value (0.0218 Å^{-3}) for the small systems, but it reaches this height for slabs with 10 or more atoms across ($z_{1/2} \geq 20$), and that the surface thickness W increases with the slab thickness $z_{1/2}$. There are no discernible oscillations in the surface profiles within our statistical errors.

In Fig. 2 we have plotted the density $\rho_{(1)}(z)$ obtained from GFMC calculations. This GFMC density shows large fluctuations after a few hundred iterations, a behavior that has been noticed in all previous GFMC simulations. Presumably, the cause of these fluctuations is the presence of low-lying excited states that require a large number of GFMC iterations to die out. Here, the low-lying excitations of our system have energies of the order of the two-ripplon state with total momentum zero[9] that is consistent with our boundary conditions, which has an energy of about 5.5 K. For 108 particles and $E_c/N = 25$ K, where E_c is a constant added to the Hamiltonian to make the spectrum positive,[5] each GFMC iteration will reduce this excitation by 0.997. Therefore, we expect convergence and autocorrelation times of the order of 300 iterations.

The values of the root-mean-square displacement from the plane $z = 0$, z_{rms}, are well determined by both methods. As one can see in Table I, for all the systems studied z_{rms} is linear with N. This is to be compared with the linear regime ($N > 20$) in the behavior of the root-mean-square radii of the ^{4}He droplets[4] as a function of $N^{1/3}$.

Figure 3 shows a plot of energies versus $x = A/N$ for both variational and GFMC calculations. For both

TABLE I. Energies of various ^{4}He slabs calculated using VMC and GFMC. N is the number of particles, $\sigma = N/A$, z_0 is a variational parameter, E is the energy, z_{rms} is the root-mean-squared displacement, $z_{1/2}$ is defined by $\rho(z_{1/2}) = \rho(0)/2$, W is the surface width, and γ_1 and γ_2 are the estimators given by Eqs. (3) and (4), respectively. The standard deviation of the energies is 0.03 K.

Method	N	σ (Å^{-2})	z_0 (Å)	E (K)	z_{rms}	$z_{1/2}$	W (Å)	γ_1	γ_2
VMC	27	0.047	1.8	−2.43	2.22	3.3	2.8	0.198	0.19
VMC	54	0.093	3.6	−4.06	3.48	5.6	3.1	0.244	0.27
VMC	108	0.186	7.3	−5.31	5.84	9.8	3.5	0.257	0.29
VMC	216	0.372	14.6	−5.98	10.28	17.6	4.3	0.264	0.30
VMC	324	0.558	22.1	−6.16	14.70	25.6	5.0	0.296	0.28
GFMC	27	0.047	···	−2.75	2.27	3.3	3.0	0.203	···
GFMC	54	0.093	···	−4.65	3.47	5.6	3.1	0.230	···
GFMC	108	0.186	···	−5.69	5.86	10.0	3.7	0.266	···

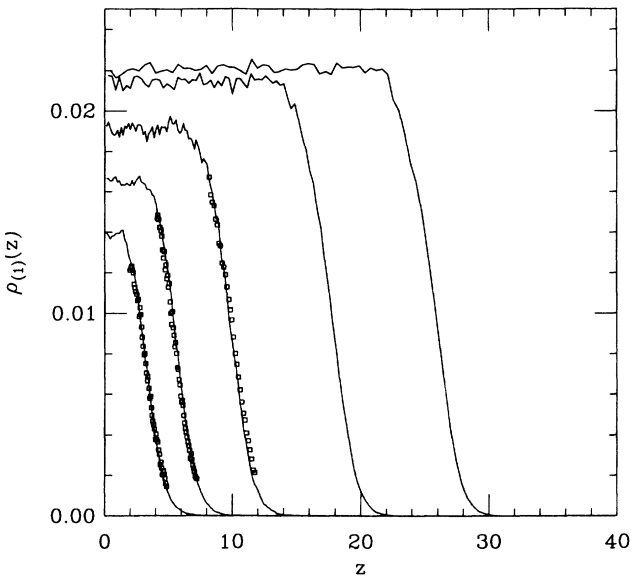

FIG. 1. Profiles of the density distribution $\rho_{(1)}(z)$ for the systems with $N=27$, 54, 108, 216, and 324 particles obtained from variational calculations. Values from the GFMC runs for the density in the interface are shown with boxes. The excellent agreement with the mixed estimation indicates the quality of the trial function. z is in Å.

methods, we have fit the energies to a quadratic polynomial, according to Eq. (5), and we have included in the fits calculated infinite system values of -6.69 ± 0.02 (Ref. 10) and -7.12 ± 0.02 (Ref. 11), respectively. The coefficients are shown in Table II. We extract a surface tension of 0.265 ± 0.006 K/Å^2 and 0.272 ± 0.011 K/Å^2 from the GFMC and VMC fits, respectively. This value should be compared to the experimental values of 0.257 (Ref. 2) and 0.274 (Ref. 3). The VMC calculations give an upper bound to $E(N)$ while the GFMC calculations give exact results within statistical errors. The closeness of the results indicates the good quality of the trial function, even though it has very simple assumptions about the interface. The other two estimators that we have defined here provide values of γ which are less reliable. With the first estimator, Eq. (3), we improve the value obtained by Liu, Kalos, and Chester, but still it is correct only for N large. The value of the virial estimator is very sensitive to the variational parameters, changing much faster than the energy, and so we have to consider larger errors than the statistical ones.

There are several possible sources of error beyond the statistical errors shown. No three-body potential was used. Since the HFDHE2 potential predicts the bulk liquid equation of state rather well,[11] this should not be too bad an approximation. The addition of a three-body Axelrod-Teller potential gives poor results for the bulk equation of state. This indicates that any three-body potential effects will have to be compensated by a different two-body potential. The finite lateral dimensions are a source of systematic error. In bulk calculations, simulation boxes similar to our lateral dimensions reduced the size dependence to less than the statistical error. Our calculations for systems of different area show that this dependence might be here a little larger than the statistical error. The fit to Eq. (5) is another source of systematic error.

Note that the smallness of the coefficient δ does not imply that we have reached the asymptotic regime. The

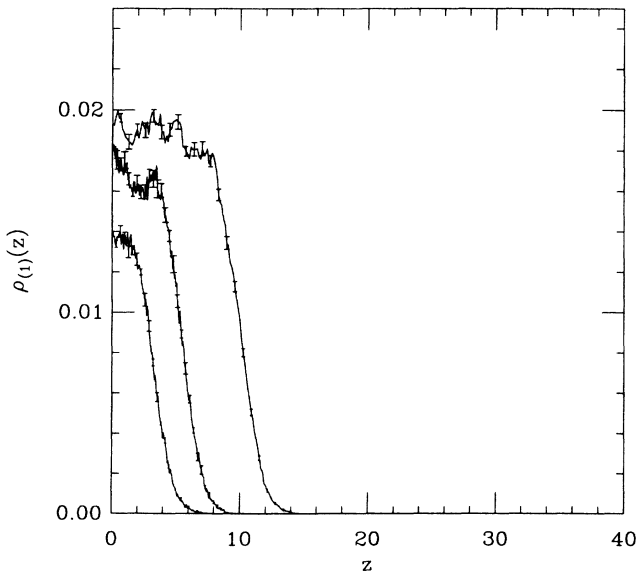

FIG. 2. Profiles of $\rho_{(1)}(z)$ for the systems $N=27$, 54, and 108 obtained from the GFMC calculations. The values plotted and the error bars are from averages in 200 bins over the last 12 sets of 500 configurations in runs of 2500 iterations where the sample sets were taken with a separation of 100 iterations. z is in Å.

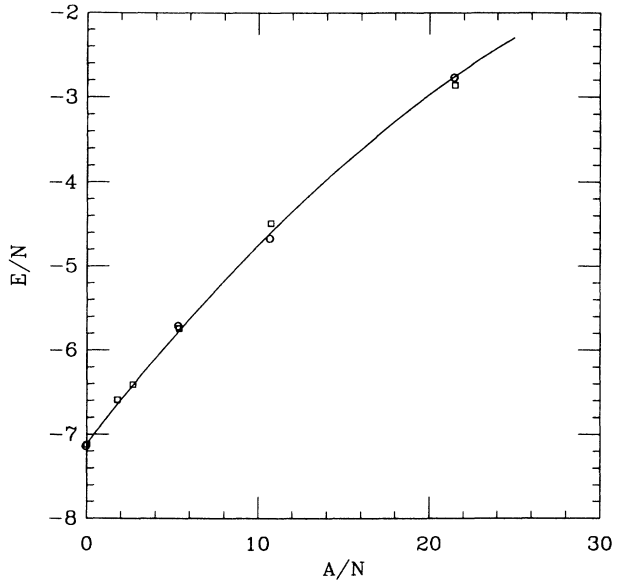

FIG. 3. Energies per particle from Table I vs $x=A/N$, both for GFMC (circles) and VMC (squares). The curve is the second-degree polynomial fit to the GFMC values, as shown in Table II. The values for VMC have been shifted by $\varepsilon_\infty(\text{GFMC})-\varepsilon_\infty(\text{VMC})$ for the purpose of comparison. E is in K and A is in Å^2.

TABLE II. Results of the fit of the energies from Table I to a second-degree polynomial, according to Eq. (5). The case $N=27$ with VMC has not been included.

Method	ε_∞	γ	δ
VMC	-6.68 ± 0.03	0.272 ± 0.011	-0.0027 ± 0.0011
GFMC	-7.11 ± 0.02	0.265 ± 0.006	-0.0029 ± 0.0003

whole term has to be considered instead, since the expansion is in $x=A/N$. Fits to higher-degree polynomials[12] indicate that the truncation of the series at the x^2 term may be warranted.

As mentioned previously, other calculations have been done in the past on finite ^{4}He systems. A slab was calculated by Liu *et al.*[7] using VMC. Their results are in qualitative agreement with our results, but since they used the Lennard-Jones potential quantitative agreement cannot be expected. Furthermore, their wave function did not contain three-body correlations. Their calculated surface tension is 0.21 K/Å^2.

Pandharipande *et al.*[4] have done simulations of ^{4}He droplets with both GFMC and VMC using the HFDHE2 potential. These simulations have the advantage that no tail corrections or periodic boundary conditions need to be introduced. Although they were mostly concerned with questions of droplet structure and saturation, they fit their energies for these spherical systems to a polynomial in $N^{-1/3}$ and extracted a surface tension of 0.30 K/Å^2. The slow convergence of the spherical system with particle number makes extracting a surface tension more difficult. Further, the area to use is obvious in the slab geometry, but is less obvious for the spheres. Their surface profiles also show qualitatively similar structure to ours, though we find the thickness W closer to the value by Liu *et al.*

It is very reassuring that our knowledge of the He-He interaction and our numerical techniques are now good enough to permit the calculation of properties of inhomogeneous quantum systems. We plan to extend our calculations to ^{4}He on a substrate.

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