Zero-Temperature Equation of State of Two-Dimensional ^{3}He

V. Grau,* J. Boronat, and J. Casulleras

*Departament de Física i Enginyeria Nuclear, Campus Nord B4-B5, Universitat Politècnica de Catalunya,
E-08034 Barcelona, Spain*

The equation of state of two-dimensional ^{3}He at zero temperature has been calculated using the diffusion Monte Carlo method. By means of a combination of the fixed-node and released-node techniques, it is shown that backflow correlations provide a very accurate equation of state. The results prove unambiguously the non-self-bound character of two-dimensional ^{3}He due to its Fermi statistics. We present solid evidence that the gas phase, predicted for the two-dimensional system, can be extrapolated to the case of ^{3}He adsorbed on a strong substrate such as graphite.

^{3}He adsorbed on strongly interacting substrates such as graphite, or on top of bulk ^{4}He or ^{4}He films, constitute experimental realizations of quasi-two-dimensional Fermi systems. In the past few decades, there has been a continued experimental effort to unveil the fascinating properties of such a nearly perfect two-dimensional Fermi liquid. Among these unique features, of particular relevance is the possibility of continuously increasing the areal density from an almost ideal gas behavior up to a strongly correlated regime. This is the experimental situation observed, for example, in the two first layers of ^{3}He adsorbed on graphite. These experimental findings indicate the nonexistence of a self-bound ^{3}He system. In contrast, Csáthy *et al.* [1] have recently studied submonolayer ^{3}He-^{4}He mixture films on H2 and claim that ^{3}He atoms appear to have condensed into a 2D self-bound liquid. Also, a recent theoretical study of mixture films points out the possibility of a dimerized ^{3}He phase in a strictly 2D geometry [2]. In fact, the question of a self-bound 2D ^{3}He phase has been discussed for a long time both from experimental [3–6] and theoretical perspectives [7–11].

Theoretical calculations concerning the 2D ^{3}He system and the ^{3}He films are scarce in comparison with the corresponding ones for the boson isotope ^{4}He. In addition to dealing with a strongly correlated system such as helium, the Fermi statistics of ^{3}He must be taken into account. In one of the pioneering works of the field, Novaco and Campbell [7] calculated the equation of state of ^{3}He adsorbed on graphite. Using lowest-order Fermi corrections, they concluded that the ^{3}He film is in a gas state, contrary to ^{4}He which exhibits a well-established self-bound character [12,13]. A comparative study of bosons and fermions in 2D was performed by Miller and Nosanow [8] using the variational method. According to their approach, and using a Wu-Feenberg expansion [14] at lowest order, ^{3}He cannot condense in 2D. More recently, Brami *et al.* [9] calculated the properties of a 2D ^{3}He film using variational Monte Carlo (VMC). They concluded that the presence of a transverse degree of freedom, not present in two dimensions, allows the system to gain enough additional binding energy to guarantee a liquid phase with a very small energy. However, a recent Green's function Monte Carlo (GFMC) calculation by Whitlock *et al.* [15], of a ^{4}He film adsorbed on graphite, has shown that the energy gain with respect to the ideal 2D system is much smaller than the one estimated in Ref. [9].

In this work, we use the diffusion Monte Carlo (DMC) method, which for bulk ^{3}He has produced, for the first time, close quantitative agreement between theoretical and experimental results for the equation of state [16]. Our aim is to achieve the same accuracy in the present study of a strictly 2D ^{3}He fluid. The energies obtained constitute upper bounds to the eigenvalues of the many-body Schrödinger equation, but the method can measure the *quality* of the bounds and provide a means of improving them. The results presented in this work show that backflow correlations are sufficient to bring the systematic error to the level of the statistical noise. The resulting equation of state implies the nonexistence of self-binding, in agreement with most experimental observations.

DMC [17] is a stochastic method that solves the N-body imaginary-time Schrödinger equation for the wave function $f(\boldsymbol{R}, t) = \psi(\boldsymbol{R})\Psi(\boldsymbol{R}, t)$, with $\psi(\boldsymbol{R})$ a trial wave function used for importance sampling (see Ref. [18] for a more detailed description of the actual DMC algorithm used). The first and simplest approximation for the trial wave function ψ is the Jastrow-Slater form,

$$\psi^{\mathrm{F}} = \psi_{\mathrm{J}} D^{\uparrow} D^{\downarrow}, \tag{1}$$

with a Jastrow factor $\psi_{\mathrm{J}} = \prod_{i<j}^{N} \exp[u(r_{ij})]$ accounting for the dynamical correlations induced by the interatomic potential, and $D^{\uparrow}$ ($D^{\downarrow}$) a plane-wave Slater determinant for the spin-up (spin-down) atoms.

The nodal surface provided by ψ^{F} corresponds to the 2D free Fermi gas. This is a first approximation since the real nodal surface is modified by dynamical correlations. This influence is contained in the time-dependent Schrödinger equation. Starting with ψ^{F} as zeroth order, a straightforward calculation shows that the first order correction to the wave function incorporates the so-called backflow

correlations (BF), a name used in analogy to the same type of corrections introduced by Feynman and Cohen [19] in their famous paper on the ^{4}He phonon-roton spectrum. In this new wave function ψ^{BF} the arguments of the orbitals $\varphi_\alpha(i)$ entering $D^\uparrow$ and $D^\downarrow$ are shifted under the influence of the medium,

$$\exp\{i\boldsymbol{k}_\alpha \cdot \tilde{\boldsymbol{r}}_i\} \equiv \exp\left\{i\boldsymbol{k}_\alpha \cdot \left(\boldsymbol{r}_i + \lambda_B \sum_{j \neq i}^{N} \eta(r_{ij})\boldsymbol{r}_{ij}\right)\right\}.$$

(2)

The two-body correlation factor is of McMillan type, $u(r) = -0.5(b/r)^5$, and the backflow function is approximated by a Gaussian, $\eta(r) = \exp\{-[(r - r_B)/\omega_B]^2\}$. The parameters of ψ have been optimized using VMC; the optimal values are $b = 1.16\sigma$, $\lambda_B = 0.40$, $r_B = 0.75\sigma$, and $\omega_B = 0.54\sigma$ ($\sigma = 2.556$ Å). The density dependence of this set of parameters in the region studied here is very weak and can be neglected. The interatomic interaction corresponds to the HFD-B(HE) potential from Aziz et al. [20]; its use in bulk ^{4}He [18] and ^{3}He [16] has allowed for a very accurate calculation of their respective equations of state.

The upper bound to the energy provided by the fixed-node (FN) approximation depends on the accuracy of the nodal surface of $\psi(\boldsymbol{R})$; if it is the exact, one then FN generates the eigenvalue. Otherwise, FN yields a variational estimate of the energy of the system, but provides no indication of the accuracy of this estimate. In a preceding work on bulk ^{3}He [16], we devised a combined method that incorporates FN, the released-node (RN) method, and an analytical prescription to improve $\psi(\boldsymbol{R})$. The RN method does not generally yield the exact energy, due to the growth of the boson component, but the initial slope of the energy vs the released time is readily accessible. From this slope, one can guess the difference between the FN energy and the eigenvalue; an exact wave function gener-

ates zero slope. In Fig. 1, RN results at medium density ($\rho = 0.10\sigma^{-2}$) are shown for the two trial wave functions ψ^F and ψ^{BF} reported above. The decrease of the energy going from ψ^F to ψ^{BF} is ~ 0.01 K, a small figure in absolute value but of the same relative magnitude as in bulk. More importantly, the RN energies shown in Fig. 1 illustrate the different behavior of E/N with the released time t_r: the ψ^F results show a linear decreasing trend which disappears when backflow correlations are introduced. In fact, a fit to the slope of $E/N(\psi^{BF})$ gives a value compatible with zero. This remarkable result can be combined with an estimation of the released time from $E/N(\psi^F)$ which indicates that the systematic error of the BF energies due to the nodal surface is in the mK order of magnitude, i.e., it has been brought to the level of the typical statistical errors of this work. Additional insight on the high quality of the nodal surface provided by the inclusion of backflow correlations is reached by incorporating in ψ the next-order analytical terms [16]. The results obtained with the new ψ, which includes explicit three-body correlations in the backflow operator, do not show any improvements with respect to the BF energies. Therefore, the DMC results obtained for 2D ^{3}He, using the optimized backflow correlations, are essentially exact; it is worth noticing that the same method gives unprecedented accuracy in the calculation of the bulk ^{3}He equation of state.

Results for the total and partial energies of the 2D ^{3}He system as a function of the surface density are reported in Table I. The potential energies per particle have been obtained using a pure estimation method [21] in order to avoid any biases coming from the trial wave function. The kinetic energy comes from the difference between the total and the potential energies. All the calculations have been carried out with 90 atoms, the finite-size simulation effects having been corrected for, and in practice eliminated, by summing up energy-tail contributions coming from both the dynamical and statistical parts. The final DMC energies are positive for any density and result from a significant cancellation between T/N and V/N, a usual feature in condensed helium. The last column in Table I contains the decrease of the energy when the nodal surface is improved by the inclusion of backflow correlations. As could be expected, $\Delta E/N$ increases with ρ as does the relevance of correlations.
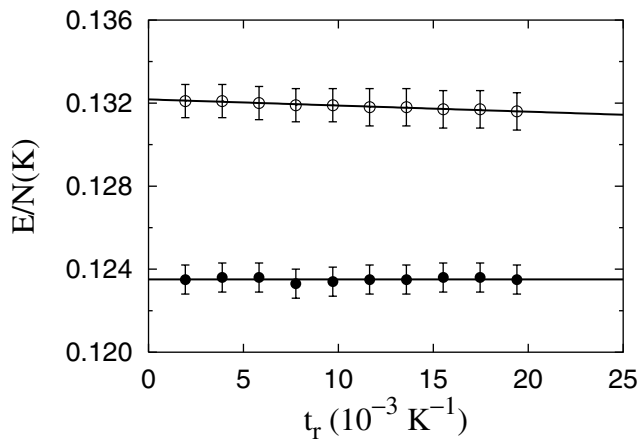

FIG. 1. RN energies as a function of the released time t_r. Empty and filled circles stand for ψ^F and ψ^{BF} as trial wave functions, respectively. Solid lines are linear fits to the calculated data.

TABLE I. DMC total and partial energies (in K) of 2D ^{3}He. The last column shows the upper bound $(E/N)^F$, relative to the DMC energies (column 1). Figures in parentheses are the statistical errors.

$\rho(\sigma^{-2})$	E/N	T/N	V/N	$\Delta E/N$
0.01	0.0262(4)	0.0884(11)	−0.0622(11)	0.003
0.06	0.0971(26)	0.6678(30)	−0.5707(30)	0.003
0.10	0.1244(18)	1.2015(70)	−1.0771(70)	0.008
0.17	0.2204(22)	2.4329(87)	−2.2125(87)	0.012
0.23	0.3939(22)	3.7414(87)	−3.3475(87)	0.038

The equation of state of 2D ^{3}He is shown in Fig. 2 for the range of densities studied. In this region, our results are well parametrized by a cubic polynomial (solid line),

$$(E/N)(\rho) = a\rho + b\rho^2 + c\rho^3, \qquad (3)$$

with optimal parameters $a = 2.376(74)$ Kσ^2, $b = -16.87(81)$ Kσ^4, and $c = 0.608(21) \times 10^2$ Kσ^6. At very small densities ($\rho \lesssim 0.05\sigma^{-2}$), the energy grows linearly as in a free Fermi gas [$E_F/N = \hbar^2/(2m)\pi\rho$] but with different slope. At medium densities, there is a clear change in the slope with a flatter region suggesting the emergence of a minimum. Nevertheless, this minimum does not appear and the energy remains always positive. For $\rho \gtrsim 0.25\sigma^{-2}$, the energy increases much faster as the density approaches the freezing point, which experimentally is observed at $\rho \simeq 0.394\sigma^{-2}$ [5].

The Fermi statistics of ^{3}He atoms is the key point underlying the non-self-bound character of 2D ^{3}He. This conclusion is drawn from the comparison between the real system and a fictitious 2D ^{3}He boson system. In Fig. 3, the DMC equation of state of both systems is compared. Boson ^{3}He would show a liquid phase with a binding energy $(E/N)_0 = -0.1189(23)$ K at an equilibrium density $\rho_0 = 0.1311(17)\sigma^{-2}$. The lighter mass of the ^{3}He atom is responsible for the large reduction of binding energy of boson ^{3}He with respect to liquid ^{4}He: Using the same potential, the ^{4}He equilibrium point is $(0.284\sigma^{-2}, -0.897$ K) [13]. Some previous theoretical calculations on 2D ^{3}He used the boson model as a reference system [7,8]. On top of this, dominant Fermi corrections were added to introduce the correct statistics. This perturbative approach,

known as Wu-Feenberg expansion [14], starts at zeroth order by simply adding E_F/N to the boson energy. This crude estimation is plotted in Fig. 3. As one can see, the kinetic term E_F/N leads to a large overestimation of E/N, and only for $\rho < 0.03\sigma^{-2}$ can it be considered a reasonable approximation. The successive terms in the Wu-Feenberg series show a nonmonotonic behavior and, in general, a very slow convergence: At medium densities ($\rho \simeq 0.1\sigma^{-2}$) the next-order term is negative and approximately 100 times smaller than the zeroth order [11]. Therefore, although the present results modify quantitatively those approximate calculations, previous conclusions about the gaslike character of ^{3}He are not altered.

Relevant quantities from the experimental standpoint are the density dependence of the pressure $P(\rho)$ and the speed of sound $c(\rho)$. Both functions are shown in Fig. 4. They have been obtained from the polynomial fit to the DMC energies (3) through the thermodynamic relations $P(\rho) = \rho^2[d(E/N)/d\rho]$ and $c(\rho) = [m^{-1}(dP/d\rho)]^{1/2}$. The pressure remains very low up to $\rho \simeq 0.20\sigma^{-2}$, and from then on increases much faster due to the small ^{3}He mass and the rapid decrease with density of the mean distance between particles, due to the reduced dimensionality. An approximate estimate for the latter comes from $2(4\pi\rho)^{-1/2}$; at $\rho = 0.25\sigma^{-2}$ it amounts to only 2.88 Å, a smaller value than in bulk ^{3}He at freezing, 4.32 Å. The speed of sound presents three different regimes as a function of ρ. At very small densities, $c(\rho)$ increases approximately like $\rho^{1/2}$ as it would correspond to a free 2D Fermi gas. Then, $c(\rho)$ reaches a plateau up to $\rho \simeq 0.08\sigma^{-2}$. In this region, the speed of sound increases although the
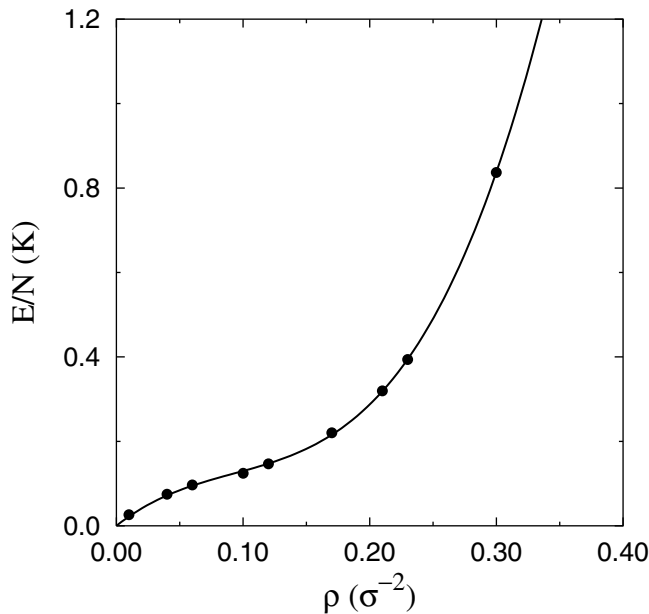

FIG. 2. Energy per particle of 2D ^{3}He as a function of the density. The statistical error bars are smaller than the size of the symbols. The solid line corresponds to a third-degree polynomial fit (3) to the DMC data.
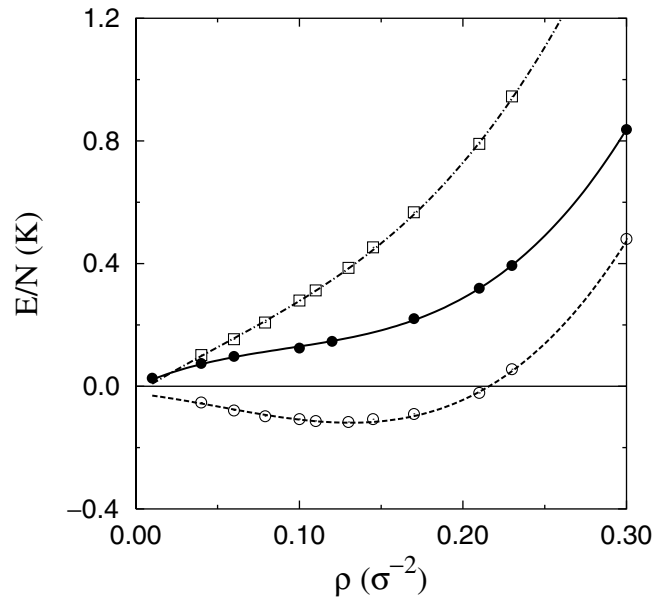

FIG. 3. Influence of the Fermi statistics on the energy of 2D ^{3}He. Filled and empty circles correspond to Fermi and Bose ^{3}He, respectively. Squares represent the sum of the boson energy and the Fermi gas kinetic energy. The lines are polynomial fits to the data.
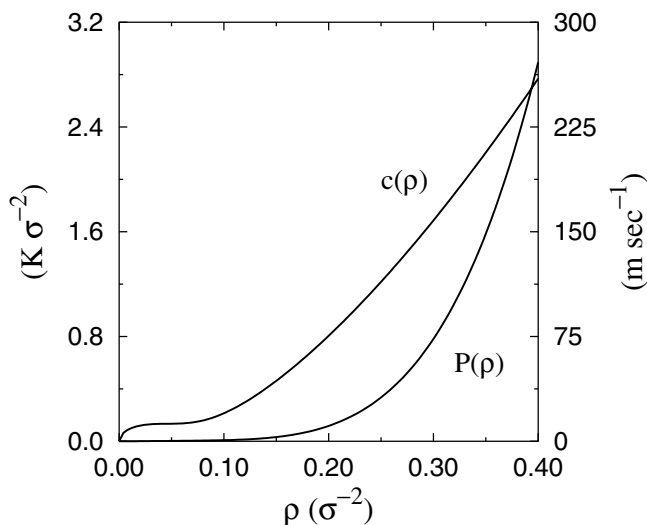
FIG. 4. Density dependence of the pressure and speed of sound of 2D ^{3}He.

slope is very small; this behavior is a direct consequence of the flattening exhibited by the energy for the same range of densities (see Fig. 2). Finally, in the third regime, $c(\rho)$ again increases with ρ in a more common way.

The 2D system constitutes a model for a film adsorbed on a strong substrate such as graphite. A question that naturally emerges is to what extent the presence of a transverse degree of freedom would modify the ^{3}He properties. First, the nodal surface could be different from the one of the 2D system. However, a key result of this work in 2D, and the previous one in 3D [16], is that the real nodal surface in both cases is essentially given by backflow effects. In a film, the particle-particle backflow correlations would be mainly contained in the surface plane. Furthermore, both the not-in-plane contributions and the particle-substrate correlations, being perpendicular to the surface plane, should have a small effect on the backflow wave function. Therefore, the Fermi statistics of a thin ^{3}He film can be safely considered within the idealized 2D geometry. Second, the additional degree of freedom perpendicular to the substrate could by itself lower the energy in an amount large enough to allow for the existence of a liquid phase. In fact, a VMC calculation of ^{3}He and ^{4}He films adsorbed on graphite by Brami et al. [9] concludes for the former the existence of a self-bound system with a binding energy of ~ 200 mK at an equilibrium density $\sim 0.131\sigma^{-2}$. To our knowledge, there are not DMC or GFMC calculations of ^{3}He films on graphite that can confirm that variational prediction. However, Whitlock et al. [15] performed GFMC calculations for ^{4}He films adsorbed on the same substrate, and found a decrease in energy with respect to 2D that is much smaller than the results from Ref. [9]. Even at the variational level, and using the same wave function and graphite-helium potential, Whitlock et al. [15] were not able to reproduce the ^{4}He energy reported in Ref. [9] (-0.7 vs -1.9 K).

The order of magnitude of the shift in energy that appears in a ^{3}He film with respect to the 2D system can be estimated from the GFMC results for the ^{4}He liquid [15], taking into account the different mass of the two isotopes in the approximate kinetic-energy correction. For example, at densities $\rho = 0.065\sigma^{-2}, 0.131\sigma^{-2}$, and $0.170\sigma^{-2}$, the energy shifts are $\Delta E/N = -0.005$, -0.022, and -0.037 K, to be compared with the 2D energies $E/N = 0.100, 0.159$, and 0.220 K, respectively. Therefore, the energy shift is by far too small to change the conclusion that, similar to the strictly 2D fluid, a thin ^{3}He film is not self-bound.

*Present address: Departament d'Enginyeria Mecànica, Universitat Politècnica de Catalunya, Barcelona, Spain.

[1] G. A. Csáthy, E. Kim, and M. H. W. Chan, Phys. Rev. Lett. **88**, 045301 (2002).

[2] E. Krotscheck, J. Paaso, M. Saarela, and K. Schörkhuber, Phys. Rev. Lett. **85**, 2344 (2000).

[3] K. D. Morhard, C. Bäuerle, J. Bossy, Y. Bunkov, S. N. Fisher, and H. Godfrin, Phys. Rev. B **53**, 2658 (1996).

[4] A. Casey, M. Patel, J. Nyéki, B. P. Cowan, and J. Saunders, J. Low Temp. Phys. **110**, 293 (1998).

[5] C. Bäuerle, Y. Bunkov, A. S. Chen, S. N. Fisher, and H. Godfrin, J. Low Temp. Phys. **110**, 333 (1998).

[6] P. C. Ho and R. B. Hallock, Phys. Rev. Lett. **87**, 135301 (2001).

[7] A. D. Novaco and C. E. Campbell, Phys. Rev. B **11**, 2525 (1975).

[8] M. D. Miller and L. H. Nosanow, J. Low Temp. Phys. **32**, 145 (1978).

[9] B. Brami, F. Joly, and C. Lhuillier, J. Low Temp. Phys. **94**, 63 (1994).

[10] B. E. Clements, E. Krotscheck, and M. Saarela, Phys. Rev. B **55**, 5959 (1997).

[11] B. Krishnamachari and G. V. Chester, Phys. Rev. B **59**, 8852 (1999).

[12] P. A. Whitlock, G. V. Chester, and M. H. Kalos, Phys. Rev. B **38**, 2418 (1988).

[13] S. Giorgini, J. Boronat, and J. Casulleras, Phys. Rev. B **54**, 6099 (1996).

[14] F. Y. Wu and E. Feenberg, Phys. Rev. **128**, 943 (1962).

[15] P. A. Whitlock, G. V. Chester, and B. Krishnamachari, Phys. Rev. B **58**, 8704 (1998).

[16] J. Casulleras and J. Boronat, Phys. Rev. Lett. **84**, 3121 (2000).

[17] J. B. Anderson, J. Chem. Phys. **63**, 1499 (1975).

[18] J. Boronat and J. Casulleras, Phys. Rev. B **49**, 8920 (1994).

[19] R. P. Feynman and M. Cohen, Phys. Rev. **102**, 1189 (1956).

[20] R. A. Aziz, F. R. W. McCourt, and C. C. K. Wong, Mol. Phys. **61**, 1487 (1987).

[21] J. Casulleras and J. Boronat, Phys. Rev. B **52**, 3654 (1995).