Monte Carlo calculations for liquid ^{4}He at negative pressure

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Abstract

A Quadratic Diffusion Monte Carlo method has been used to obtain the equation of state of liquid ^{4}He including the negative pressure region down to the spinodal point. The atomic interaction used is a renewed version (HFD-B(HE)) of the Aziz potential, which reproduces quite accurately the features of the experimental equation of state. The spinodal pressure has been calculated and the behavior of the sound velociy around the spinodal density has been analyzed.

67.40.Db, 67.40.Kh

Recent experiments [1–3] on cavitation in liquid ^{4}He at low temperatures have motivated the theoretical study [4–9] of liquid helium properties at low temperature and negative pressure. Some interesting questions have thus been raised, as the determination of the tensile strength (*i.e.*, the magnitude of the negative pressure at which cavitation becomes likely), and the spinodal pressure (*i.e.*, the pressure at which liquid helium becomes macroscopically unstable against density fluctuations). The standard (or classical) theory of nucleation predicts for liquid helium [10] a tensile strength rising from 8 atm at 2 K to 15 atm at 0.5 K, and the experiment around 1.5 K reported in Ref. [1] seemed to confirm this prediction. However, Maris and Xiong estimated [4,5] the spinodal pressure to be -9 atm at 0 K, so that the predictions of the standard theory must be incorrect (since the liquid cannot exists for pressures lower than the spinodal one). They also carried out an experiment [2], whose results are in contradiction with those of Ref. [1], obtaining lower values for the tensile strength. More recently, several experiments [3] providing information about the cavitation problem have been performed. Unfortunately, as they do not rely on an accurate pressure calibration, no tensile strength values are reported.

In Refs. [4,5] the spinodal pressure was estimated by fitting to the measured [11] sound velocities c as a function of pressure P several polynomial and Padé forms, and then extrapolating into the negative pressure region to determine the zero of $c(P)$. From a different point of view, the spinodal pressure was calculated in Ref. [7] using two different phenomenological models that reproduce the equation of state in the measured positive pressure region. Although an overall agreement between the phenomenological calculations and the empirical results was obtained, some questions arise, as for instance to what extent the extrapolated results depend on the form used in the fit, or on the density functional used in the calculations. It is therefore necessary to handle with a precise equation of state for liquid ^{4}He valid in the full range of pressure, down to the spinodal one.

Many-body techniques have achieved a high level of accuracy in the description of liquid helium. In particular, Monte Carlo (MC) methods [12] give exact information, apart from statistical uncertainties, on the ground state of bosonic systems both at zero and finite

temperature. The well known interatomic interaction for helium has been a key ingredient to reach an excellent agreement between the theoretical results and the experimental data. Recently, we have used a Quadratic Diffusion Monte Carlo (QDMC) method to calculate the equation of state in the positive pressure region [13]. One of the main conclusions of Ref. [13] is that the HFD-B(HE) potential suggested by Aziz *et al.* [14], hereafter referred to as Aziz II potential, improves the results obtained with the Aziz potential [15], especially when the density dependence of derivative magnitudes of the energy is considered. In this work, we have extended those calculations to lower densities, with the hope of studying without ambiguity the zero-temperature properties of homogeneous liquid ^{4}He in this zone.

The QDMC method solves stochastically the Schrödinger equation in imaginary time assuming a short-time approximation form for the Green's function [16]. The ground-state wave function is sampled in an iterative process after a time larger enough to project out higher energy components. Rigorously, the exact ground-state energy is obtained when the limit $\Delta t \to 0$ is considered. In linear DMC algorithms one has to perform calculations at several time steps, and then extrapolate to the exact value. The QDMC method, which has evidenced a quadratic dependence on Δt [13,17], improves the efficiency of the diffusion algorithm making feasible to use larger time steps than in DMC and avoiding the necessity of the extrapolation to $\Delta t = 0$.

In order to guide the diffusion process a Jastrow trial wave function of the form [18]

$$\Psi_T(\mathbf{R}) = \prod_{i<j} \exp\left[-\frac{1}{2}\left(\frac{b}{r_{ij}}\right)^5 - \frac{L}{2}\exp\left(-\left(\frac{r_{ij}-\lambda}{\Lambda}\right)^2 \right) \right] \tag{1}$$

has been used in our calculations. The values of the parameters appearing in Eq. (1) ($L = 0.2$, $\lambda = 2.0\ \sigma$, $\Lambda = 0.6\ \sigma$, $b = 1.20\ \sigma$, where $\sigma = 2.556$ Å) have been fixed to optimize the Variational Monte Carlo (VMC) estimation of the energy at the equilibrium density ($\rho_0 = 0.365\ \sigma^{-3}$). The Monte Carlo simulation has been carried out with 108 particles for $\rho < 0.328\ \sigma^{-3}$ and 128 particles for $\rho \geq 0.328\ \sigma^{-3}$, maintaining an asymptotic population of 400 walkers. The errors associated to the use of both a finite volume simulation box and a finite population have been analyzed and, in all cases, are smaller than the size of the

inherent statistical fluctuations.

In Table I are reported the total energies (in K) obtained with the Aziz II potential, for different values of the density (in units of σ^{-3}). The experimental values of Ref. [19] are also displayed. The origin of the slight differences observed between theory and experiment was discussed in Ref. [13].

Derived quantities of the energy such as the pressure or the sound velocity have been obtained through a third and fourth degree interpolation, with unnoticeable changes when larger degrees were introduced in the interpolation method. The QDMC prediction of $P(\rho)$ is shown in Fig. 1 (solid line) for the whole range of densities, in comparison with experimental data for positive pressures [19]. The agreement between the Aziz II results and the experimental data is quite impressive.

At this point, we would like to draw the attention on the quality of the extrapolations coming from the previously available data, laying mainly in the positive pressure region. In the majority of microscopic calculations on liquid helium the energy per particle is parametrized using a polynomial form

$$E/N = e_0 + B\left(\frac{\rho-\rho_0}{\rho_0}\right)^2 + C\left(\frac{\rho-\rho_0}{\rho_0}\right)^3 . \qquad (2)$$

On the other hand, in calculations based on Density Functional Theory, the form

$$E/N = b\,\rho + c\,\rho^{1+\gamma} \qquad (3)$$

proposed by Stringari [20], has proved to be very efficient in describing properties of homogeneous and inhomogeneous (including an additional surface term) liquid ^{4}He. We have used both forms to fit our previous QDMC results [13], which included only one point below the equilibrium density. Proceeding in this way (*i.e.*, considering only the five last densities of Table I), we have found that although both fits are compatible with the previous results of the energy, only the second form, see Eq. (3), predicts the new QDMC results at densities lower than 0.328 σ^{-3}. This fact is reflected in Fig. 1, where the pressure derived from these fits is plotted as a function of density. The short-dashed line corresponds to the fit (2) and

the long-dashed line to the fit (3). The starting points from the left of all curves depicted in Fig. 1 correspond to the location of the spinodal point. The QDMC result for the spinodal pressure is $P_c = -9.30 \pm 0.15$ atm, corresponding to a density $\rho_c = 0.264 \pm 0.002\ \sigma^{-3}$. The fit (3) predicts $(\rho_c, P_c) = (0.266, -9.08)$ whereas the fit (2) gives $(\rho_c, P_c) = (0.292, -6.66)$. This Figure illustrates that the extrapolation from the positive pressure region to the negative one is quite sensitive to the form used in the fit. One can also see the capability of the built-in density functional given in Eq. (3) to reproduce quite accurately the equation of state of liquid ^{4}He at any density, even when only positive pressure values are used as input in the numerical fit. It is also noticeable the stability of Eq. (3) when all the QDMC energy results (Table I) are used to fix the optimal parameters b, c and γ, being their relative changes less than 5 %. In this case, the spinodal point turns out to be $(\rho_c, P_c) = (0.267, -9.16)$. If the fit (2) is extended to all the energy values, the spinodal point $(\rho_c, P_c) = (0.267, -9.24)$ comes close to the Monte Carlo prediction.

In Figure 2 is displayed the sound velocity c as a function of pressure P. The points are the experimental values of Ref. [11], and the solid line corresponds to the QDMC results. The accuracy provided by the Aziz II potential is again remarkable, giving results for the sound velocity in close agreement with the experiment. It can be seen that c drops to zero very fast when approaching the spinodal point. The behavior of c near P_c is expected to be of the form $c \propto (P - P_c)^\nu$, being ν the critical exponent. It is known [7] that $\nu = 1/4$ provided that the quantity

$$P_c'' = \left(\frac{\partial^2 P}{\partial \rho^2} \right)_{\rho_c} \tag{4}$$

be different from zero. Our QDMC estimation of P_c'' is 1200 ± 100 Kσ^3. Therefore, the clear departure from zero of P_c'' guarantees that $\nu = 1/4$, in disagreement with the Maris' model [6] which, explicitly taking the value $P_c'' = 0$, predicts $\nu = 1/3$. Nevertheless, in the positive pressure region the experimental values are very well reproduced by the above form with ν close to 1/3. In fact, we have found that for pressures only slightly higher than P_c and up to almost solidification pressure, the behavior is also $c \propto (P - P_c)^\nu$ with the exponent given

by [7]

$$\nu = \nu_0 \equiv -P_c\,\kappa_0\,u_0\ , \tag{5}$$

where κ_0 is the isothermal compressibility

$$\kappa = \frac{1}{\rho}\left(\frac{\partial\rho}{\partial P}\right)_T \tag{6}$$

and u_0 is the Grüneisen constant

$$u = \frac{\rho}{c}\frac{\partial c}{\partial\rho}\ , \tag{7}$$

both quantities evaluated at the saturation density ρ_0. Our QDMC results give for these quantities the values $\kappa_0 = 0.01231 \pm 0.00005$ atm^{-1} and $u_0 = 2.81 \pm 0.04$ with $\rho_0 = 0.3645 \pm 0.0003\ \sigma^{-3}$, to be compared with the experimental values [11] $\kappa_0^{\rm exp} = 0.01230$ atm^{-1}, $u_0^{\rm exp} = 2.84$ and $\rho_0^{\rm exp} = 0.3646\ \sigma^{-3}$. The QDMC result for the exponent (5) is $\nu_0 = 0.322 \pm 0.007$, close to the value 1/3 pointed out in Refs. [5,6].

The power-law behavior of c is shown in Figures 3 and 4. The quantity $(c/c_0)^{1/\nu}$, where c_0 is the sound velocity at the equilibirium density, is displayed in Figure 3 against $1 - P/P_c$. When $\nu = \nu_0$ a straigth line is obtained in a very wide range of pressures (Fig. 3), whereas the case $\nu = 1/4$ manifests a nearly quadratic behavior. However, for pressures close to the spinodal pressure one can see (Fig. 4) that the linear behavior is obtained taking the critical exponent as 1/4.

To summarize, we have calculated the equation of state of liquid ^{4}He in a QDMC framework using the Aziz II potential from the spinodal point up to the solidification point. The characteristics of the spinodal point have been evaluated without the uncertainty of the extrapolation from the positive pressure data. As a byproduct, we have noted that our QDMC results are very well fitted by the form (3), giving thus additional support to this purely phenomenological density functional.

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FIGURES

FIG. 1. Pressure as a function of density. Points: experimental results [19], solid line: QDMC result, short-dashed line: fit (2), and long-dashed line: fit (3). The fits (2) and (3) include only the results from .328 to .438 σ^{-3}.

FIG. 2. The sound velocity as a function of pressure. The experimental points are taken from Ref. [11], and the solid line corresponds to the QDMC results.

FIG. 3. Power-law behavior of the sound velocity using as a critical exponent ν_0 (5) and 1/4.

FIG. 4. Same as Figure 3 for pressures close to the spinodal one. To illustrate more clearly the power-law behavior, the quantity $(c/c_0)^{1/\nu} / (1 - P/P_c)$ has been plotted against $1 - P/P_c$ for the values $\nu = \nu_0$ and 1/4.

TABLES

TABLE I. Results for the total energies (in K) at several densities (in σ^{-3}) from the QDMC calculations with the Aziz II potential and experiment [19].

ρ	E/N	E/N (exp)
0.264	-6.376 ± 0.010	
0.267	-6.441 ± 0.010	
0.285	-6.692 ± 0.010	
0.300	-6.892 ± 0.010	
0.310	-7.011 ± 0.010	
0.328	-7.150 ± 0.010	
0.365	-7.267 ± 0.013	-7.17
0.401	-7.150 ± 0.016	-7.03
0.424	-6.877 ± 0.022	-6.77
0.438	-6.660 ± 0.017	-6.55