

van der Waals study of liquid-vapor coexistence in ${}^4\text{He}$

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An augmented van der Waals theory is used to study the liquid-vapor coexistence and critical constants T_c , ρ_c , and P_c of ${}^4\text{He}$. The reference system is taken as hard spheres, the properties of which are computed by the path-integral Monte Carlo method. The results of this "mean-field" theory are shown to be in semiquantitative agreement with experiment. Predictions for the Lennard-Jones and HFDHE2 helium pair potentials are compared.

I. INTRODUCTION

In this paper we report on the calculation of the liquid-vapor coexistence curve of ${}^4\text{He}$ by an augmented van der Waals theory. In van der Waals's work¹ the key sources of the two-phase region and the existence of a critical point were elucidated by the well-known equation of state

$$P = \frac{k_B T}{v - (4\pi/6)\sigma^3} - a\rho^2, \quad (1)$$

where $\rho = 1/v = N/V$ is the number density, σ represents an effective molecular diameter, and a characterizes the "mean-field" attraction between molecules. The liquid-vapor phase transition can be viewed as a competition between the first term due to the repulsion between hard spheres and the second term reflecting the attraction between the molecules that tends to induce condensation. Above the critical temperature T_c , defined by

$$\left(\frac{\partial P}{\partial \rho}\right)_{T_c} = 0, \quad \left(\frac{\partial^2 P}{\partial \rho^2}\right)_{T_c} = 0, \quad (2)$$

the pressure is monotonically increasing function of ρ , whereas below T_c there is a "van der Waals" loop for which the standard equal-area construction yields the coexisting liquid and vapor densities ρ_l and ρ_v and the coexistence pressure P_{coex} .

If the potential energy is of the pairwise form, $V = \sum_{ij} v(r_{ij})$ (where r_{ij} is the distance between atoms i and j), then the form of Eq. (1) can be argued from the first-order perturbation theory result for the free energy²

$$f(\rho, T) \approx f_0(\rho, T) + \frac{1}{2} \rho \int \Delta v(r) g_0(r; \rho, T) d^3 r, \quad (3)$$

where the pair potential is broken up into repulsive and attractive parts by³

$$v_0(r) = \begin{cases} v(r) + \epsilon, & r < r_m, \\ 0, & r > r_m, \end{cases}$$

$$\Delta v(r) = \begin{cases} -\epsilon, & r < r_m, \\ v(r), & r > r_m, \end{cases}$$

with ϵ the magnitude of $v(r)$ at its minimum r_m . In this equation, f is the Helmholtz free energy per particle of the system with potential $v(r)$; f_0 and $g_0(r)$ are, respectively, the free energy and radial distribution function of the reference system with potential $v_0(r)$. The mass m is the same in both systems.

From the application of the relation $P = \rho^2 (\partial f / \partial \rho)_T$ to Eq. (3) one finds

$$P \approx P_0 + \frac{1}{2} \rho^2 \frac{\partial}{\partial \rho} \left[\rho \int \Delta v(r) g_0(r; \rho, T) d^3 r \right], \quad (4)$$

and so the pressure breaks up into the pressure of the reference system P_0 plus a contribution due to the attractive forces. These are the analogs of the first and second terms, respectively, in van der Waals's equation of state,⁴ which can be thought of as a model of the more realistic Eq. (4). In this work we use simulation results for the quantum hard-sphere free energy and radial distribution function computed by the path-integral Monte Carlo (PIMC) method⁵ and, hence, we compute the first-order free energy in Eq. (3) essentially exactly. The details of these computations may be found in Ref. 5; we only mention that here, as in our previous work, the particles are assumed to obey Boltzmann statistics rather than Bose statistics. This approximation should be quite accurate at nearly all of the temperatures considered in this paper.

Equation (3) has often been used as the basis for perturbative studies of *classical* liquids,^{6,7} such as the square-well and Lennard-Jones potentials. With recent improvements in computational power and in the PIMC algorithm^{5,8} it is now relatively straightforward to compute f_0 and $g_0(r)$ for the quantum hard-sphere reference system at finite temperatures in the fluid phase. The study of the ${}^4\text{He}$ liquid-vapor phase transition is of interest because the coexistence region is strongly affected by the quantum nature of the system. Indeed, the critical temperature T_c and critical density ρ_c are 35% and 50%, respectively, of the values for the classical system with the same pair potential. The suppression of the critical constants can be argued by noting that the "quantum-mechanical smearing" of each particle's position [roughly

by the de Broglie thermal wavelength $\lambda_T \sim (\hbar^2 / mk_B T)^{1/2}$ makes the particles appear “larger” and thus, the system is at a *higher* effective density. The well depth ϵ of $v(r)$ is effectively *reduced*, being replaced by a “smeared” average of order λ_T about the minimum. Because T_c should scale roughly as this effective well depth, T_c is, therefore, reduced by quantum effects. In the work presented here, these heuristic “quantum smearing” ideas are accounted for by using a fully quantum mechanical reference system.

Mean-field expressions such as Eq. (3) have long been known to break down in the critical region. The reason is that the approximation ignores large scale fluctuations in the density (induced by the attraction between atoms) that are all important near the critical point. For example, the prediction of the mean-field theory for the order-parameter exponent β , $\rho_l - \rho_v \sim (T_c - T)^\beta$, will be $\beta = \frac{1}{2}$ rather than the experimental value closer to $\beta = \frac{1}{3}$. Nevertheless, nonuniversal quantities computed within the theory, such as T_c , ρ_c , and the coexistence curve, are reasonably close to the experimental values (within roughly 25%) and so the simple theory can be useful in studying the dependence on mass and interatomic potential of these quantities.

II. RESULTS

In this work the reference free energy and pair distribution function in Eq. (3) are replaced by the values of the quantum hard-sphere (HS) system:

$$\begin{aligned} f_0(\rho, T) &\approx f_{\text{HS}}(\rho, T), \\ g_0(r; \rho, T) &\approx g_{\text{HS}}(r; \rho, T). \end{aligned} \quad (5)$$

The hard-sphere diameter σ is selected to match the *s*-wave scattering length of the potential v_0 . In Ref. 5 we demonstrated that this choice is a fairly accurate approximation for helium, even for densities in the solid phase.⁹ From the expression for $f(\rho, T)$ in Eq. (3), one can use the standard Maxwell double-tangent construction to locate the liquid-vapor phase transition along each isotherm.

The helium pair potentials used here are the standard Lennard-Jones (LJ) 6-12 potential with the de Boer-Michels parameters¹⁰

$$\begin{aligned} v(r) &= 4\epsilon[(a/r)^{12} - (a/r)^6], \\ \epsilon &= 10.22 \text{ K}, \\ a &= 2.556 \text{ \AA}, \end{aligned} \quad (6)$$

and the HFDHE2 potential of Aziz *et al.*¹¹ The HFDHE2 potential is the result of an elaborate fit to experimental data on gaseous (two-body) helium. The LJ potential has a minimum of 10.22 K at pair separation $r_m = 2.87 \text{ \AA}$, while the HFDHE2 potential has a minimum of 10.8 K at separation $r_m = 2.95 \text{ \AA}$. Exact Monte Carlo calculations away from the critical point by Kalos, Lee, Whitlock, and Chester¹² and by Ceperley and Pollock⁸ have shown that the HFDHE2 potential is superior to the LJ in reproducing thermodynamical and structural prop-

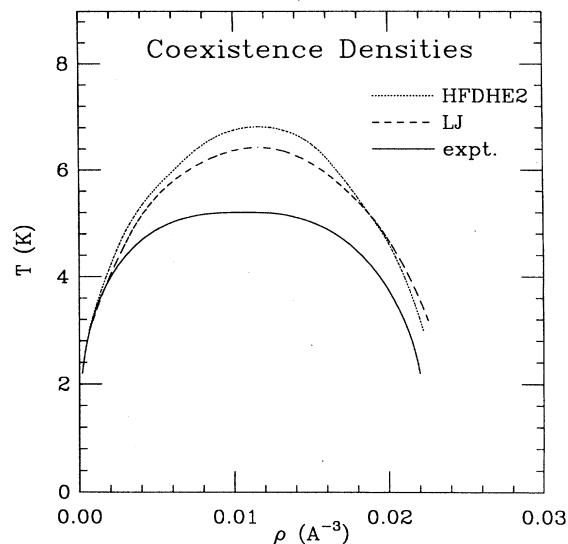


FIG. 1. ^4He liquid and vapor coexistence densities in particles per \AA^3 . The lower curve (solid) denotes the experimentally measured coexistence and the upper curve denotes the predictions of the first-order quantum hard-sphere perturbation theory for the two pair-potentials discussed in the text. The maximum of each curve corresponds to T_c .

erties of liquid and solid helium. The *s*-wave scattering lengths of the repulsive part v_0 of the LJ and HFDHE2 potentials are 2.138 and 2.203 \AA , respectively. The 3% difference in the effective hard-sphere diameter and the 5% difference in well depths may be thought of as characterizing the differences between the two potentials.

In Fig. 1 we display our results for the liquid-vapor

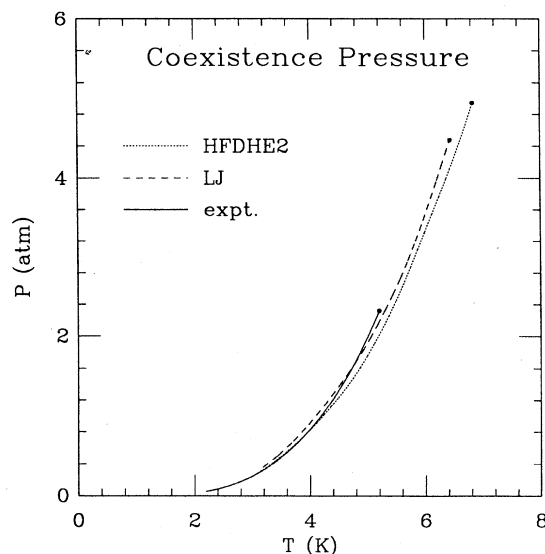


FIG. 2. ^4He coexistence pressure P_{coex} in atmospheres as a function of temperature T in kelvin near the critical point. The solid curve denotes the experimentally measured values, while the others denote the predictions of the first-order quantum hard-sphere perturbation theory for the two pair potentials discussed in the text.

phase diagram of ^4He using the LJ and HFDHE2 potentials along with the experimental values given by McCarty's fit.¹³ Both potentials overestimate the critical temperature T_c , as is expected in mean-field theory (recall the Bragg-Williams treatment of the Ising ferromagnet¹⁴). We find $T_c=6.4$ and 6.8 K for the LJ and HFDHE2, respectively, and these may be compared to the experimental value of $T_c=5.2$ K. The critical density is $\rho_c=0.0116 \text{ \AA}^{-3}$ for both potentials, while the experimental result is $\rho_c=0.0105 \text{ \AA}^{-3}$. For a classical system with the pair potentials used here, one would have $T_c \approx 13$ K and $\rho_c \approx 0.020 \text{ \AA}^{-3}$. The Monte Carlo statistical sampling errors are estimated to be roughly 4% for T_c and $\sim 2\text{--}3\%$ for the coexistence densities. Since the same Monte Carlo data are used for both potentials, any systematic differences (say in T_c) are estimated to much higher accuracy. The LJ potential yields T_c closer to the experimental value than HFDHE2 does, although away from the critical region the LJ results deviate more from experiment than do those of HFDHE2. For example, below 5 K the liquid coexistence density ρ_l in LJ is in poorer agreement with experiment than is the HFDHE2 prediction. Also, the vapor density ρ_v in the case of LJ crosses through the experimental value at about 3.8 K, while the HFDHE2 value evidently matches onto experiment as T is decreased. We note that the ratio of LJ to HFDHE2 critical temperatures is found to be 0.94 which correlates well with the ratio of well depths $\epsilon_{LJ}/\epsilon_{HF}=0.95$. Figure 2 shows the coexistence pressure as a function of temperature for the two potentials and for experiment.¹³ Again, away from the critical point we see that the LJ prediction crosses through the experimental curve, whereas the HFDHE2 apparently matches onto it. We find the critical pressures to be $P_c=4.5$ and 4.9 atm for

the LJ and HFDHE2 potentials, respectively. The large discrepancy from the experimental value of 2.3 atm is due to the large slope of P_{coex} near T_c : A 25% change in T_c gives rise to roughly a factor of two change in P_{coex} .

In this study we have shown that in ^4He one obtains semiquantitative agreement with experiment for the coexistence curve and critical constants (T_c and ρ_c) by treating the attractive well to first-order in hard-sphere perturbation theory.¹⁵ Previously, perturbation theories similar to the one used here have been applied only to classical systems.⁷ Thus, we have shown that a comparable level of accuracy can be achieved in strongly quantum-mechanical systems such as ^4He . We are presently collaborating with Parola and co-workers¹⁶ in an attempt to apply their quite successful hierarchical reference theory of fluids (HRT) to the LJ and HFDHE2 models of ^4He discussed here. Parola and co-workers¹⁶ have shown that the HRT yields the correct critical exponents and very accurate ($\sim 1\text{--}3\%$) values for nonuniversal properties (such as T_c , ρ_c , and P_c) of simple classical fluids. It is, therefore, hoped that the HRT (along with additional approximations required to treat quantum-mechanical systems) will provide accurate results for the critical point of ^4He .

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