Critical Behavior of Liquid ^{3}He

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We investigate the liquid–gas second-order phase transition in liquid ^{3}He using the variational calculations based on the cluster expansion of the energy functional. We also compute the critical point exponents of liquid ^{3}He that are in agreement with experimental data.

KEY WORDS: critical exponents; second-order phase transition; critical point.

1. INTRODUCTION

The liquids ^{3}He and ^{4}He are the only quantum liquids which exist naturally. The word "quantum liquid" comes from the fact that for these systems, the interatomic distance is at the order of their De Broglie wavelenght. ^{3}He is a liquid of strongly interacting fermionic atoms which behaves quite differently than the normal liquids at low temperature (Wilks, 1970; Kent, 1993). The properties of liquid ^{3}He have been studied using different many-body techniques (Clark and Westhaus, 1966; Nafari and Doroudi, 1995; Luijen and Meyer, 2000; Kindermann and Wetterich, 2001; Takano and Yamada, 1994; Viviani *et al.*, 1988; Pricaupenko and Treiner, 1995; Fantoni *et al.*, 1982; Krotscheck and Smith, 1983; Friman and Krotscheck, 1982). Recently, the behavior of liquid ^{3}He near its critical point has been investigated using path-integral molecular dynamics and quantum virial expansion (Müer and Luijten, 2002).

One of the most powerful techniques in many-body calculations is the variational method which is based on the cluster expansion of the energy functional (lowest order constrained variational method) (Owen *et al.*, 1977; Bordbar and Modarres, 1997, 1998; Modarres and Bordbar, 1998; Bordbar and Riazi, 2001, 2002; Bordbar, 2002a,b, 2003, 2004; Bordbar and Hashemi, 2002). This is a fully self-consistent method and does not introduce any free parameter to the

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calculations. The crucial point in this method is the functional minimization with respect to the two-body correlation function subjected to the normalization constraint which finally leads to a Euler–Lagrange differential equation. The convergence of its results has been shown by computing the three-body cluster energy term (Bordbar and Modarres, 1997).

The liquid–gas phase transition near the critical point (second-order phase transition) is an interesting subject in statistical mechanics. This behavior, critical phenomena, is caused by the existence of singularity in thermodynamic functions of the system at the transition point. The nature of these singularities in various measurable quantities at the critical point is described by the critical exponents.

In our previous paper, we have calculated some thermodynamic properties of liquid ^{3}He using the variational method, which shows a good agreement between experimental data and calculated results, especially for free energy and entropy (Bordbar and Hashemi, 2002). In this paper, we present the critical behavior of the liquid ^{3}He. We organize the paper as follows: In section 2, we obtain the critical properties of liquid ^{3}He by calculating the critical isotherm. We investigate the critical behavior of liquid ^{3}He by computing the critical point exponents in section 3.

2. CRITICAL ISOTHERMAL EQUATION OF STATE

The equation of state is the key point for investigating the second-order phase transition in a hydrostatic system. The isothermal equation of state can be calculated from the Helmholtz free energy, F:

$$P = \rho^2 \frac{\partial F}{\partial \rho}\bigg|_T , \qquad (1)$$

where P, T and $\rho = \frac{N}{V}$ are the pressure, temperature and number density, respectively. N and V are the total number of particles and volume. To obtain the free energy of liquid ^{3}He, we use the variational method explained in the appendix. The result for the equation of state at the critical temperature (critical isotherm) is shown in Fig. 1. As seen from the figure, at the critical point, the isotherm curve shows an inflection point which satisfies:

$$\frac{\partial P}{\partial \rho}\bigg|_{T_c} = \frac{\partial^2 P}{\partial \rho^2}\bigg|_{T_c} = 0, \qquad (2)$$

where T_c is the critical temperature. The calculated critical temperature, density (ρ_c) and pressure (P_c) of liquid ^{3}He are presented in Table I. The experimental results (Heller, 1967; Fisher, 1967; Pittman $et\ al.$, 1979) are also given for comparison. We can see a good agreement between these results.
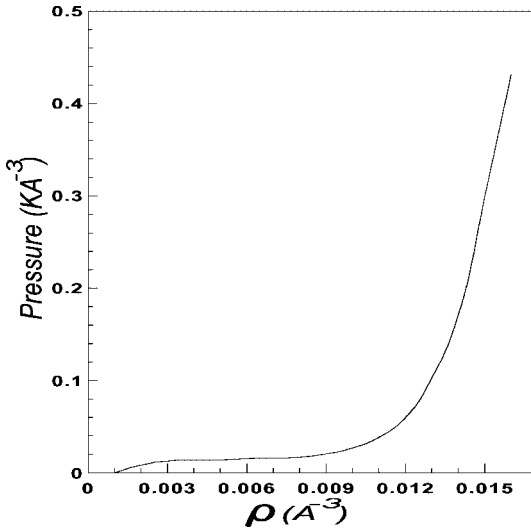
Fig. 1. The critical equation of state for liquid ^{3}He.

3. CRITICAL EXPONENTS

For a hydrostatic system, the two-phase coexistence conditions are

$$P_{\text{liquid}} = P_{\text{gas}}$$
$$\mu_{\text{liquid}} = \mu_{\text{gas}},$$

(3)

where the μ_{liquid} and μ_{gas} are the chemical potential of liquid and gas phases, respectively. As the temperature increases, the liquid density decreases and the gas density increases. At the critical temperature these, densities become equal. This behavior for ^{3}He is shown in Fig. 2. The order parameter $\rho_{\text{liquid}} - \rho_{\text{gas}}$, which is defined to investigate the critical behavior of this system, vanishes at the critical point. However, other thermodynamic properties diverge at this point. The critical point exponents are defined to study the asymptotic behavior of singular thermodynamic functions near the critical point. For this purpose, the following functions for the thermodynamic quantities are introduced (Garrod, 1995):

Table I. Critical point properties of liquid ^{3}He

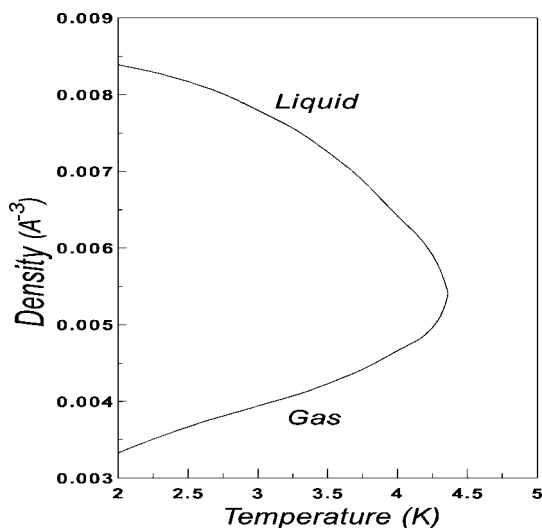|	$T_{\text{c}}(K)$	$\rho_{\text{c}}(A^{-3})$	$P_{\text{c}}(K A^{-3})$
Our results	4.36	0.0054	0.0139
Experimental results (Heller, 1967)	3.324	0.00834	0.00844
Experimental results (Pittman *et al.*, 1979)	3.317	0.00827	0.00846

Fig. 2. The liquid and gas densities versus temperature for ^{3}He.

3.1. Order Parameter

We can define the exponent β for this parameter as follows:

$$\rho_{\text{liquid}} - \rho_{\text{gas}} \sim (-\epsilon)^\beta; \quad \epsilon \longrightarrow 0^-, \tag{4}$$

where

$$\epsilon = \frac{T - T_c}{T_c}. \tag{5}$$

The critical exponent β characterizes the behavior of the order parameter and of course, the earlier function is meaningful only below the critical point in the region where the order parameter is not zero. To obtain β, we draw the order parameter as a function of ϵ on the log-log scale in Fig. 3. The slope of this figure yields the value of $\beta = 0.56239 \pm 0.01386$.

3.2. Pressure

By defining the exponent δ, we can describe the critical isotherm

$$P - P_c \sim (\rho - \rho_c)^\delta; \quad \rho \longrightarrow \rho_c, \tag{6}$$

where $\epsilon = 0$ ($T = T_c$). In Fig. 4, $P - P_c$ as a function of $\rho - \rho_c$ is shown. The value of δ obtained from this figure is 3.31032 ± 0.08192.
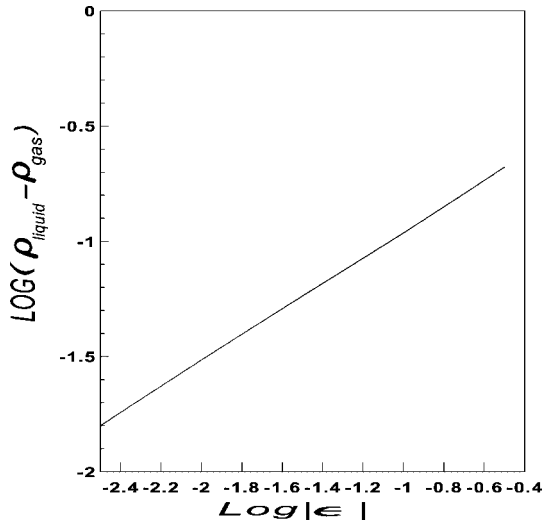
Fig. 3. The order parameter versus ϵ on log–log scale for ^{3}He.

3.3. Heat Capacity

The exponent α' and α characterize the behavior of specific heat (C_V) below and above the critical temperature, respectively, along the critical isochore
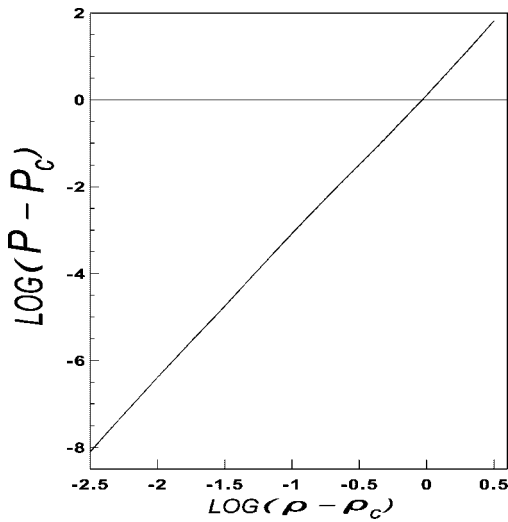

Fig. 4. The $P - P_c$ versus $\rho - \rho_c$ at critical temperature (T_c) for ^{3}He.
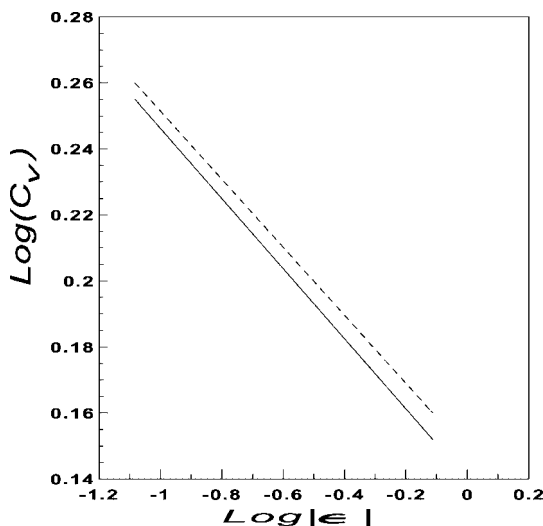
Fig. 5. Specific heat along the critical isochore as a function of ϵ above (full curve) and below (dashed curve) critical temperature for ^{3}He.

$(V = V_c)$

$$C_{V_c} = (-\epsilon)^{-\alpha'}; \quad \epsilon \longrightarrow 0^-,$$

$$C_{V_c} = (\epsilon)^{-\alpha}; \quad \epsilon \longrightarrow 0^+. \tag{7}$$

In Fig. 5, the specific heat along the critical isochore versus ϵ is shown. The values $\alpha' = 0.1018 \pm 0.0001$ and $\alpha = 0.10609 \pm 0.0014$ are extracted from Fig. 5.

3.4. Isothermal Compressibility

For describing the behavior of isothermal compressibility (K) near the critical point, the exponents γ and γ' are defined to be

$$K = (-\epsilon)^{-\gamma'}; \quad \epsilon \longrightarrow 0^-,$$

$$K = (\epsilon)^{-\gamma}; \quad \epsilon \longrightarrow 0^+, \tag{8}$$

The calculated values of isothermal compressibility shown in Fig. 6 leads to $\gamma = 1.05343 \pm 0.01077$ and $\gamma' = 1.05343 \pm 0.01077$.

We have presented the whole critical exponents for the ^{3}He in Table II. The experimental results (Heller, 1967; Fisher, 1967; Pittman *et al.*, 1979) are also given for the comparison in Table II. There is a good agreement between our calculations for the critical exponents and the experimental results. From Table II, it can be
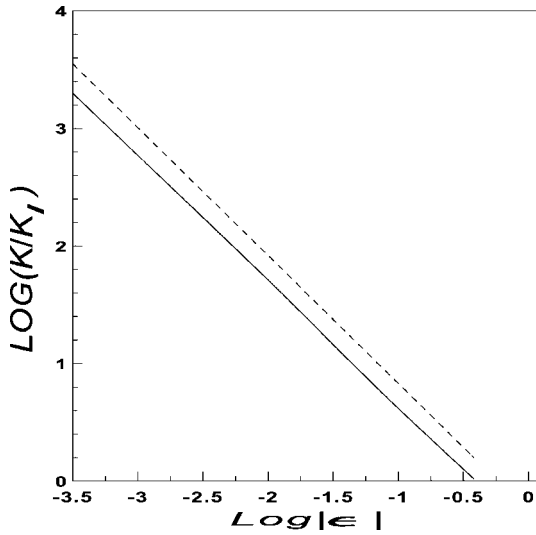
Fig. 6. Isothermal compressibility as a function of ϵ above (full curve) and below (dashed curve) critical temperature for ^{3}He. K_I is the ideal fermi gas compressibility at $\rho = \rho_c$ and $T = T_c$.

seen that the Griffiths and Rushbrooke inequalities (Huang, 1987; Griffiths, 1965) are satisfied by our results for the critical exponents of ^{3}He,

$$\alpha + 2\beta + \gamma \geq 2$$
$$\alpha + \beta(1 + \delta) \geq 2. \tag{9}$$

4. SUMMARY AND CONCLUSION

The liquid–gas phase transition near the critical point is of special interest in statistical mechanics. In this paper, we have computed the critical equation of state for liquid ^{3}He which led to critical density, temperature and pressure of this

Table II. Critical exponents for ^{3}He

	β	δ	α'	α	γ	γ'
Our results	0.5624	3.3103	0.1018	0.1061	1.0534	1.0560
	± 0.0139	± 0.0819	± 0.0001	± 0.0014	± 0.0108	± 0.0093
Experimental results (Heller, 1967)	~ 0.361	~ 4.21	~ 0.105	~ 0.105	~ 1.17	~ 1.17
Experimental results (Pittman *et al.*, 1979)	0.322 ± 0.002	—	—	—	1.19 ± 0.01	—

system. The critical exponents, β, δ, α and γ for this system are computed. The calculated critical exponents satisfies the Griffiths and Rushbrooke inequalities. A comparison between our results and experimental data is made, which shows a good agreement between theoretical calculation and experimental results.

APPENDIX

In this section, we give a brief review to obtain the free energy of liquid ^{3}He using the lowest order constrained variational method based on the cluster expansion of the energy functional (Owen et al., 1977; Bordbar and Modarres, 1997, 1998; Modarres and Bordbar, 1998; Bordbar and Riazi, 2001, 2002; Bordbar, 2002a,b, 2003, 2004; Bordbar and Hashemi, 2002). In this method, we choose a trial many-body wave-function as

$$\Psi = \left\{ \prod_{i<j} f(ij) \right\} \Phi, \tag{10}$$

where $f(ij)$ is the two-body correlation function and Φ the Slater determinant of non-interacting particles wave-functions (plane waves). We then apply the cluster expansion to the energy per particle (Clark, 1979) and keep one- and two-body energy terms,[4]

$$E = \frac{1}{N} \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = E_1 + E_2, \tag{11}$$

where

$$E_1 = \sum_i \frac{\hbar^2 k_i^2}{2m} n(k_i), \tag{12}$$

$$E_2 = \frac{1}{2N} \sum_{ij} \langle ij | w(12) | ij - ji \rangle. \tag{13}$$

In the earlier equations, $n(k_i)$ is the Fermi-Dirac distribution function and

$$w(12) = \frac{\hbar^2}{m} (\nabla_{12} f(12))^2 + f^2(12)V(12), \tag{14}$$

where $V(12)$ is the interatomic potential. In the thermodynamic limit, Eqs. (12) and (13) read:

$$E_1 = \frac{\hbar^2}{2m\rho\pi^2} \int_0^\infty n(k)k^4 \, dk, \tag{15}$$

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[4] It is shown that higher order energy terms are ignorable when we are dealing with short-range potential (Bordbar and Modarres, 1997).

$$E_2 = \frac{2\pi\rho\hbar^2}{m} \int_0^\infty \left[f'^2(r) + \frac{m}{\hbar^2} f^2(r)V(r) \right] \left[1 - \frac{1}{2}\left(\frac{\gamma(r)}{\rho} \right)^2 \right] r^2 \, dr, \quad (16)$$

where ρ is the number density,

$$\rho = \frac{1}{\pi^2} \int_0^\infty n(k)k^2 \, dk, \quad (17)$$

$$\gamma(r) = \frac{1}{\pi^2} \int_0^\infty \frac{\sin kr}{kr} n(k)k^2 \, dk, \quad (18)$$

and $f'(r) = \frac{\partial f(r)}{\partial r}$.

At this point, we minimize the energy functional with respect to the two-body correlation function, $f(r)$, to obtain the following Euler–Lagrange differential equation

$$\left\{ \frac{2m}{\hbar^2} f(r)V(r) + 2\lambda f(r) \right\} \left[1 - \frac{1}{2}\left(\frac{\gamma(r)}{\rho} \right)^2 \right] - \frac{\partial}{\partial r}\left[2f'(r)\left[1 - \frac{1}{2}\left(\frac{\gamma(r)}{\rho} \right)^2 \right] \right] = 0,$$

$$(19)$$

where λ is the Lagrange multiplier that imposed the normalization condition $\langle \Psi | \Psi \rangle = 1$. By solving Eq. (19), using the numerical technique, the two-body correlation function, $f(r)$ and therefore the energy of the system are obtained. This finally leads to the free energy function of the system

$$F = E - TS, \quad (20)$$

where T and S are the temperature and entropy per particle of the systems (Fetter and Walecka, 1971).

To calculate the free energy of liquid ^{3}He, we use the Aziz interatomic potential (Aziz *et al.*, 1979) in Eqs. (16) and (19)

$$V(r) = \epsilon \left\{ Ae^{-\alpha r/r_m} - \left[C_6 \left(\frac{r_m}{r} \right)^6 + C_8 \left(\frac{r_m}{r} \right)^8 + C_{10}\left(\frac{r_m}{r} \right)^{10} \right] f(r) \right\}, \quad (21)$$

where

$$f(r) = \begin{cases} e^{-\left(\frac{Dr_m}{r} - 1 \right)^2}; & \dfrac{r}{r_m} \le D \\[2mm] 1; & \dfrac{r}{r_m} > D, \end{cases} \quad (22)$$

and

$$\frac{\epsilon}{k_B} = 10.8K, \quad A = 0.5448504 \times 10^6 \quad (23)$$

$$\alpha = 13.353384, \quad r_m = 2.9673A, \quad (24)$$

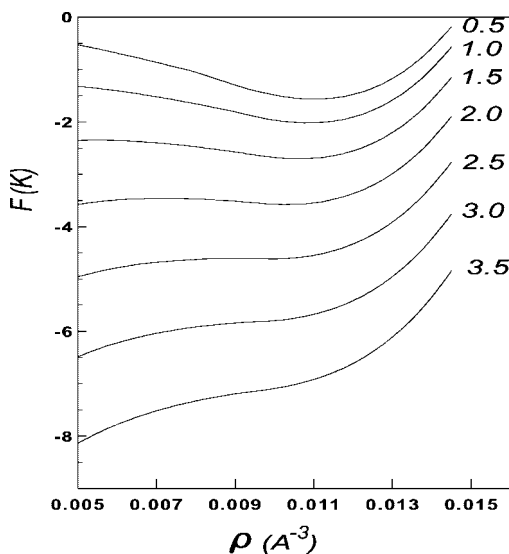$$C_6 = 1.37732412, \quad C_8 = 0.4253785, \quad (25)$$

Fig. 7. The free energy of liquid ^{3}He as a function
of number density at different temperatures.

$$C_{10} = 0.178100, \quad D = 1.241314. \tag{26}$$

The realistic Aziz Potential agrees with the He–He scattering experimental data which satisfies the following criteria:

- It has a short-range repulsive part which is described by exponential form.
- It has also a long-range attractive tail which includes the multiple interactions.

A realistic potential between helium atoms must have the criteria. Our results for the free energy calculations of the liquid ^{3}He are given in Fig. 7 (Bordbar and Hashemi, 2002).

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