

^3He Vapor Pressure near Its Critical Point

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Abstract Between 0.65 K and 3.2 K, the temperature dependence of the vapor pressure P of ^3He is defined by the International Temperature Scale of 1990 (ITS-90). However, the ITS-90 vapor pressure equation was not designed to be consistent with the scaling law required for the second temperature derivative of the vapor pressure in the vicinity of the liquid-vapor critical point. In this paper, two scaling-type equations are used to describe the ^3He vapor pressure in the region near the critical point. The first scaling equation contains two unknown coefficients which are obtained by taking as reference the temperature \bar{T} at which the product $(T_c - T)P$ presents a maximum ($\bar{T} = 2.56736$ K). The second scaling equation contains three unknown coefficients which are obtained by using as references \bar{T} and $T_{\text{up}} = 3.2$ K, the upper value of the ITS-90 interval. In both equations we take for the critical temperature and pressure the values $T_c = 3.31554$ K and $P_c = 114632.7$ Pa. The proposed equations, specially the second one, are satisfactorily compared with experimental data for P and dP/dT within the temperature range $(T_c - T)/T_c \leq 0.065$ and with semiempirical data for d^2P/dT^2 within the temperature range $0.0001 \leq (T_c - T)/T_c \leq 0.03$.

Keywords ^3He · Vapor pressure equation · Critical point · Scaling equation

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1 Introduction

Between 0.65 K and 3.2 K, the International Temperature Scale of 1990 (ITS-90) is defined in terms of the vapor pressure vs. temperature relation of ^3He by [1–3]

$$T_{90} = \sum_{n=0}^9 A_n \left(\frac{\ln P - B}{C} \right)^n, \quad (1)$$

where P is the vapor pressure in Pa, and the values of the coefficients A_n and the constants B and C are given in Table 1. The ITS-90 interpolating equation (1) for ^3He vapor pressure has not been extended above 3.2 K because of the uncertainty of measurements at temperatures near the critical point. Furthermore, (1) was not designed to be consistent with the scaling theory that predicts a divergence of the second derivative of the vapor pressure w.r.t. temperature at the critical point. The purpose of this work is to use two different scaling equations in order to describe the temperature dependence of the ^3He vapor pressure in the region near the critical point. The first equation is the simplest scaling equation containing only two unknown coefficients whose values are determined by taking as reference the temperature \bar{T} at which the function $\phi = (T_c - T)P$ presents a maximum. The second one is the simplest extended scaling equation containing only three unknown coefficients whose values are determined by using as references \bar{T} and $T_{\text{up}} = 3.2$ K, the upper value of the ITS-90 interval. In this paper, we take $T_c = 3.31554$ K and $P_c = 114\,632.7$ Pa (859.816 Torr), as the values for the ^3He critical temperature and pressure. We find that this choice of T_c and P_c is corroborated by the good agreement between theoretical equations and the P and dP/dT experimental data reported by Behringer et al. [4] in the range from ~ 3.1 K to T_c . Furthermore, the proposed extended scaling equation provides for the second derivative d^2P/dT^2 a temperature dependence consistent with the one reported by Anisimov et al. [5] from the analysis of the so-called Yang-Yang anomaly in ^3He near the critical point. Therefore, the present work can also be of relevance for scaling theory. In this context, we would like to mention that recently Zhong and Bartmatz [6] considered parametric expressions to calculate the isothermal susceptibility, specific heat and coexistence curve near the ^3He liquid-vapor critical point. Although these parametric expressions provide the complete crossover behavior from the critical point to the region far away from it, from a practical point of view it is convenient to consider a single explicit equation for the temperature dependence of the saturated vapor pressure $P(T)$.

Table 1 Constants for (1), 0.65–3.2 K

A_0	1.053447	A_6	0.006596
A_1	0.980106	A_7	0.088966
A_2	0.676380	A_8	−0.004770
A_3	0.372692	A_9	−0.054943
A_4	0.151656	B	7.3
A_5	−0.002263	C	4.3

2 The ³He Critical Point

The range of values of T_c and P_c for ³He from several experimental sources and theoretical studies has been compiled recently by Huang and Chen [7]. Taking into account only measurements reported since 1970, it is observed that the value of T_c on ITS-90 varies from 3.3153 K (3.3086 K on 1958 ⁴He scale, T_{58}) [8] to 3.3175 K ($T_{58} = 3.3105$ K) [9]. Huang and Chen [7] recommend $T_c = 3.3157 \pm 0.0006$ K as a mean value which is reasonably consistent with the above range. However, very recently Hahn et al. [10], using the quasistatic thermogram technique for measuring the liquid-vapor coexistence curve of ³He near its critical point, have obtained the value $T_c = 3.315540 \text{ K} \pm 4 \mu\text{K}$, which is practically the same than the value obtained by Zhong et al. [11] from a ³He critical point study and from Barmatz et al. [12] from heat capacity and susceptibility measurements near the ³He critical point. In the present work we take $T_c = 3.31554$ K as the ³He critical temperature.

On the other hand, the value of P_c reported in the literature varies from 114 586.6 Pa (859.47 Torr) [13] to 114 723.9 Pa (860.5 Torr) [9]. Huang and Chen [7] recommend $P_c = 114 603.91$ Pa (859.6 Torr) as a mean value into the above range. In the present work we take the value $P_c = 114 632.7$ Pa (859.816 Torr) provided experimentally by Behringer et al. [4] for the ³He critical pressure.

3 The Simplest Scaling Vapor-Pressure Equation and Srinivasan’s Criterion

Scaling theory predicts that the second derivative of the vapor pressure with respect to temperature at the critical point diverges as

$$\frac{d^2 P}{dT^2} \approx B(T_c - T)^{-\alpha}, \tag{2}$$

where B is a positive, substance-dependent critical amplitude and α is the critical exponent for specific heat at constant volume C_V . Integrating (2) twice and taking the critical point as reference, one obtains

$$P = P_c + A_1(T_c - T) + B_1(T_c - T)^{2-\alpha}, \tag{3}$$

where A_1 and B_1 are substance-dependent coefficients given by: $A_1 = -\left(\frac{dP}{dT}\right)_{T=T_c} \equiv -\alpha_c$, α_c being the so-called critical Riedel parameter which gives the slope of the vapor pressure curve at the critical point, and $B_1 = B/(1 - \alpha)(2 - \alpha) > 0$. Equation (3) is the simplest vapor-pressure equation compatible with scaling theory.

Recently [14], we have proposed a method for deriving the A_1 and B_1 coefficients in (3) by using the Srinivasan criterion [15]: for all fluids, the function $\phi(T) = (T_c - T)P$ presents a maximum at a temperature \bar{T} in the high temperature region. The fact that $\phi(T)$ goes through a maximum at \bar{T} is mathematically expressed by the relation

$$\left[\frac{d\phi(T)}{dT} \right]_{T=\bar{T}} = -\bar{P} + (T_c - \bar{T}) \left(\frac{dP}{dT} \right)_{T=\bar{T}} = 0, \tag{4}$$

where $\bar{P} = P(\bar{T})$. From (3) and (4) one easily obtains the relations

$$A_1 = \frac{(3 - \alpha)\bar{P} - (2 - \alpha)P_c}{(1 - \alpha)(T_c - \bar{T})}, \tag{5}$$

$$B_1 = \frac{P_c - 2\bar{P}}{(1 - \alpha)(T_c - \bar{T})^{2-\alpha}}. \tag{6}$$

Therefore if \bar{T} and \bar{P} are known, (3) with A_1 and B_1 given by (5) and (6), provides the vapor pressure in terms of the critical pressure P_c and the critical exponent α .

Figure 1 shows the function $\phi(T)$ for ^3He obtained from (1) with $T_c = 3.31554$ K. This function presents a maximum at $\bar{T} = 2.56736$ K ($\bar{T}_r = \bar{T}/T_c = 0.774343$) for which $\bar{P} = 48234.14$ Pa. On the other hand, we take for the critical exponent α the theoretically accepted value $\alpha = 0.109$ [16, 17]. This value is very close to the value $\alpha = 0.105 \pm 0.015$ reported by Brown and Meyer [18] from the experimental study of the specific-heat C_V of ^3He near its critical point. Then, using $\alpha = 0.109$, $T_c = 3.31554$ K and $P_c = 114\,632.7$ Pa, (5) and (6) lead to the coefficients of (3) given in the second column of Table 2. With these values, the percent deviations between P and dP/dT obtained from (3) and from the ITS-90 (1) in the overlapped range from \bar{T} to 3.2 K are shown by dashed lines in Fig. 2. The average of the absolute relative deviation (AARD) is of 0.15% for P and 0.46% for dP/dT , while the maximum absolute relative deviation (MARD) is of 0.23% for P and 0.76% for dP/dT .

Fig. 1 Function $\phi(T) = (T_c - T)P$ for ^3He obtained from the ITS-90 (1) and with $T_c = 3.31554$ K. This function presents a maximum at $\bar{T} = 2.56736$ K

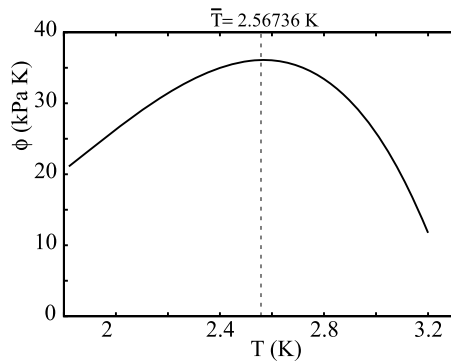
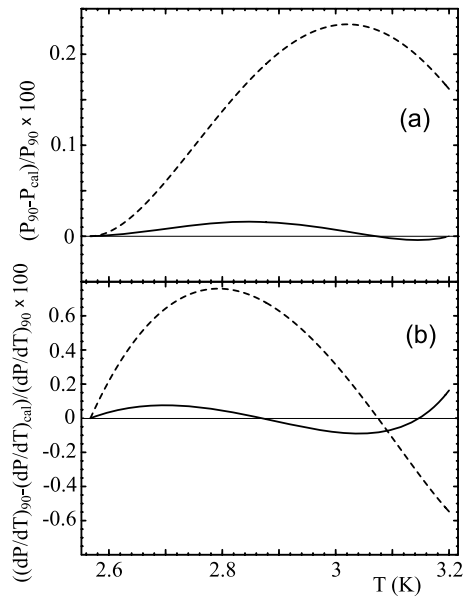


Table 2 Parameters for (3) and (9)

Parameters	Equation (3)	Equation (9)
α	0.109	0.109
Δ	–	0.52
T_c (K)	3.31554	3.31554
P_c (Pa)	114 632.7	114 632.7
A_1 (Pa K $^{-1}$)	–115 995.5	–118 332.2
B_1 (Pa K $^{\alpha-2}$)	35285.99	43496.84
B_2 (Pa K $^{\alpha-2-\Delta}$)	–	–6029.163

Fig. 2 Pressure (a) and dP/dT (b) relative differences between ITS-90 (1) and (3) (dashed lines), and between ITS-90 (1) and (9) (thick solid lines) from $\bar{T} = 2.56736$ K to 3.2 K using the values of the coefficients given in Table 2



4 An Extended Scaling Vapor-Pressure Equation

The assumption of simple scaling, like in (2), is only asymptotically valid as the critical point is approached. This assumption breaks down as one moves away from the critical point where higher order terms become important. An amplification of the temperature range should require the use of extended scaling equations for which the original power law is the leading term. There are several scaling theories that extend the asymptotic range of (2) [19–23]. In most of them the vapor pressure is given as a sum of two contributions

$$P(T) = A(T) + (T_c - T)^{2-\alpha} \sum_{n=1}^{\infty} B_n (T_c - T)^{\gamma_n}, \tag{7}$$

where $A(T)$ is the regular part of the pressure and the γ_n 's ($\gamma_1 = 0$) are correction-to-scaling exponents. The function $A(T)$ can be any analytic function of T such that $A(T_c) = P_c$ and $A'(T_c) = (dA/dT)_{T_c} = -\alpha_c$, but it is usually expressed as a power series of $(T_c - T)$ with integer exponents,

$$A(T) = P_c + \sum_{n=1}^{\infty} A_n (T_c - T)^n, \tag{8}$$

with $A_1 = -\alpha_c$.

The practical application of (7) and (8) requires the series to be truncated at some finite order. Equation (3) is the simplest version of these truncated equations. Several truncated expressions, different from (3), have been used in the literature for vapor pressure near the critical point [7, 24, 25]. This truncation process mainly depends on

the range below the critical temperature used to correlate experimental data. In this paper we shall use the truncated Wegner expansion [20]

$$P = P_c + A_1(T_c - T) + B_1(T_c - T)^{2-\alpha} + B_2(T_c - T)^{2-\alpha+\Delta}, \quad (9)$$

where Δ (also denoted by θ) is the Wegner leading correction-to-scaling exponent.

We take for the critical exponents α and Δ in (9), the theoretically accepted values of $\alpha = 0.109$ and $\Delta = 0.52$ [16, 17]. Once the values of the exponents α and Δ are fixed, the coefficients A_1 , B_1 and B_2 in (9) are calculated by taking two reference points: the point ($\bar{T} = 2.56736$ K, $\bar{P} = 48234.14$ Pa) corresponding to the maximum of the product $(T_c - T)P$, and the point ($T_{\text{up}} = 3.2$ K, $P_{\text{up}} = 101\,662.1$ Pa) corresponding to the upper temperature of the ITS-90 interval. Using condition (4) and (9), one obtains the set of linear equations

$$\begin{aligned} A_1(T_c - \bar{T}) + B_1(2 - \alpha)(T_c - \bar{T})^{2-\alpha} + B_2(2 - \alpha + \Delta)(T_c - \bar{T})^{2-\alpha+\Delta} &= -\bar{P}, \\ A_1(T_c - \bar{T}) + B_1(T_c - \bar{T})^{2-\alpha} + B_2(T_c - \bar{T})^{2-\alpha+\Delta} &= \bar{P} - P_c, \\ A_1(T_c - T_{\text{up}}) + B_1(T_c - T_{\text{up}})^{2-\alpha} + B_2(T_c - T_{\text{up}})^{2-\alpha+\Delta} &= P_{\text{up}} - P_c. \end{aligned} \quad (10)$$

Solving this set of equations one obtains the coefficients of (9) given in the third column of Table 2. The percent deviations between P and dP/dT obtained from (9) and from the ITS-90 (1) in the overlapped range from \bar{T} to 3.2 K are shown by thick solid lines in Fig. 2. The AARD is of 0.0077% for P and 0.055% for dP/dT , while the MARD is of 0.016% for P and 0.16% for dP/dT . The temperature differences between calculations by (9) and the T_{90} (1) are smaller than 0.13 mK in the range from 2.45 K to 3.2 K.

Finally, we would like to remark that Fig. 2 shows that the ITS-90 scale is continuously extended by (9), i.e., there is no *kink* at 3.2 K in P and only a very small change arises in the first derivative dP/dT . Therefore, (9) provides a rather smooth extension of the vapor pressure representation given by the ITS-90 scale.

5 Comparison with Experimental Data near the Critical Point

Values for the vapor pressure P and its derivative dP/dT below 3.2 K can be obtained from the interpolating equation (1). From this point to the critical point high-resolution measurements of the vapor pressure values (P and dP/dT) along the coexistence curve have been reported by Behringer et al. [4] in a technical report provided us by H. Meyer. These unsmoothed data correspond to Figs. 2 and 3 of [7]. We have converted these data to the ITS-90 by considering that no conversion is needed [26] between ITS-90 and l'Échelle Provisoire de Température de 1976 (EPT-76; T_{76}) and by using Table 3 of [27] and Table 2 of [28] for the difference $T_{76} - T_{58}$. The experimental data for P and dP/dT are shown in Figs. 3a and 3c, respectively. One can observe a small bump for dP/dT over the region $3.2968 < T < 3.3108$ K. Behringer et al. [8] pointed out that this anomalous behavior might arise from an instrumental effect associated with the strain gauge.

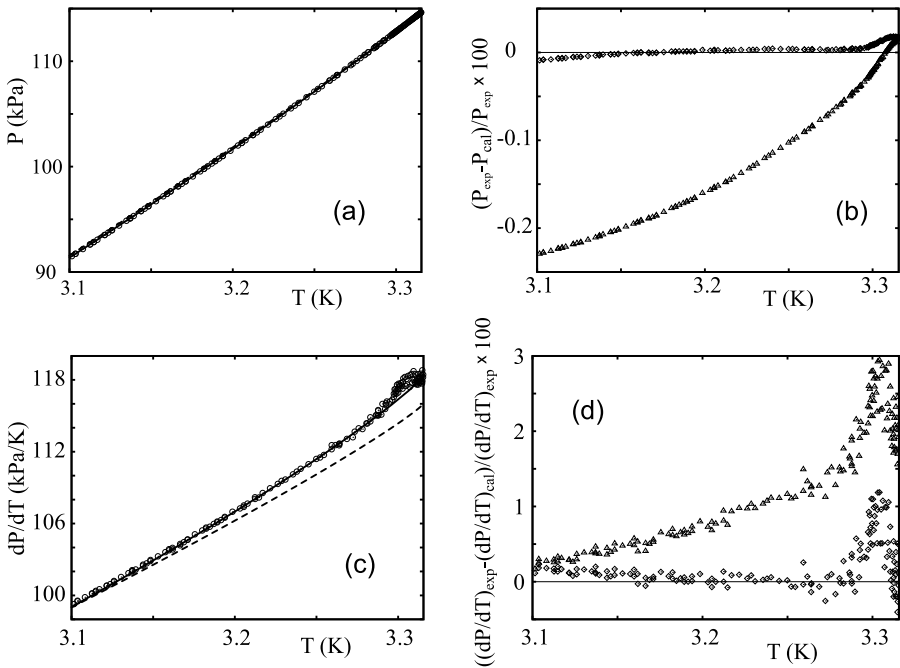


Fig. 3 *Left:* comparison for pressure (a) and dP/dT (c) of ^3He along the vapor-liquid coexistence curve between experimental data (circles) by Behringer et al. [4] and calculated values by using (3) (dashed lines), and (9) (thick solid lines) from 3.1 K to T_c . *Right:* pressure (b) and dP/dT (d) relative differences between experimental data and (3) (triangles), and between experimental data and (9) (diamonds) from 3.1 K to T_c . For the theoretical equations the values of the coefficients given in Table 2 have been used

Figures 3a and 3c also show the comparison, in the range from 3.1 K to T_c , between the experimental data for P and dP/dT and the calculated data from (3) and (9) using the coefficients given in Table 2. Percent deviations between experimental and calculated data are shown in Fig. 3b for P and in Fig. 3d for dP/dT . Without considering the data on the bump region, using (3), percent deviations are smaller than 0.23% for P and smaller than 2% for dP/dT , while (9) leads to percent deviations smaller than 0.009% for P and smaller than 0.25% for dP/dT .

We would like to remark the excellent agreement between experimental data and those calculated from (9). Note that in Figs. 3c and 3d, for $T \geq 3.2$, relative deviations from the scaling prediction are $\sim 0.005\%$ for P and of the same order than the dispersion of the experimental data ($\sim 0.2\%$) for dP/dT . These deviations are similar than those obtained between theoretical and ITS-90 equations for $\bar{T} \leq T \leq 3.2$. Table 3 shows a comparison among the values for T_c , P_c and α_c given by some authors (including those reported by Durieux et al. [29] on the ETP-76) and those reported in this work.

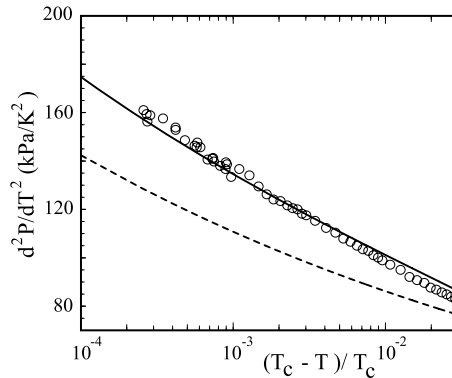
On the other hand, in the coexistence region, the so-called Yang-Yang relation [30] for the two-phase specific heat C_V is

$$\frac{\rho C_V}{T} = \frac{d^2 P}{dT^2} - \rho \frac{d^2 \mu}{dT^2}, \tag{11}$$

Table 3 Critical parameters for ^3He

	Behringer et al. [4]	Durieux et al. [29]	Huang et al. [7]	Equation (9)
T_c (K)	3.31537	3.3162	3.3157	3.31554
P_c (Pa)	114 632.7	114 657.2	114 603.9	114 632.7
α_c (Pa K $^{-1}$)	118 438.1	116 806.7	117 489.1	118 332.2

Fig. 4 Comparison for d^2P/dT^2 of ^3He along the vapor-liquid coexistence curve between semiempirical data (circles) by Anisimov et al. [5] and calculated values by using (3) (dashed line) and (9) (thick solid line). For the theoretical equations the values of the coefficients given in Table 2 have been used



where ρ is the density and $d^2\mu/dT^2$ the second temperature derivative of the chemical potential along the liquid-vapor saturation curve. Equation (11) has been used recently by Anisimov et al. [5] in order to analyze the near-critical behavior of d^2P/dT^2 for ^3He . In this analysis, experimental C_V data reported by Brown and Meyer [18] were used, while $d^2\mu/dT^2$ was determined by using an analytical equation proposed to fit experimental $d\mu/dT$ data reported by Behringer et al. [8]. The values (circles) for d^2P/dT^2 obtained by Anisimov et al. are shown in Fig. 4 on a semi-log scale within the temperature range $0.0001 \leq (T_c - T)/T_c \leq 0.03$. The theoretical predictions for d^2P/dT^2 obtained from the second temperature derivative of (3) and (9) using the coefficients given in Table 2 are also shown in Fig. 4. One can see that the result obtained from the extended scaling expression, (9), is in good agreement with the semiempirical data reported by Anisimov et al.

6 Conclusions

Two simple scaling equations have been used to provide the temperature dependence of the ^3He vapor pressure in the high-temperature range from $\bar{T} = 2.56736$ K to the critical temperature $T_c = 3.31554$ K, \bar{T} being the temperature at which the product $(T_c - T)P$ presents a maximum. The first considered vapor pressure equation corresponds to the simplest equation compatible with the scaling law for the second derivative at the critical point, while the second one corresponds to a Wegner-type extended scaling equation truncated after the first order in the correction-to-scaling exponent. By considering $T_c = 3.31554$ K, $P_c = 114632.7$ Pa and the critical exponents as input data, the remaining parameters of both scaling equations are calculated

by taking as reference two temperatures in the ITS-90 scale: \bar{T} and the upper temperature of this scale, $T_{\text{up}} = 3.2$ K. The proposed scaling equations are compared with high-resolution experimental data for P and dP/dT in the near-critical region over the range $(T_c - T)/T_c \leq 0.065$ and with semiempirical data for d^2P/dT^2 over the range $0.0001 \leq (T_c - T)/T_c \leq 0.03$. We have found that the considered extended scaling equation, (9), provides a simple expression to predict with a rather good accuracy the temperature dependence of the ^3He vapor pressure both with respect to the ITS-90 data and with respect to the experimental data in the near-critical region.

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