

## EQUATION OF STATE AND THERMOPHYSICAL PROPERTIES OF HELIUM-3\*

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Experimental data for the thermophysical properties of  $^3\text{He}$  were mined into a searchable database. Equilibrium equations along the vapor-liquid and liquid-solid lines were proposed. A general equation of state for normal fluid  $^3\text{He}$  based on the Debye specific heat model was developed. Calculations by the Debye fluid  $^3\text{He}$  state equation differ from the reference experimental data generally within  $\pm 1\%$  for the  $p$ - $v$ - $T$ ,  $\pm 0.9\%$  for the specific heat and  $\pm 1\%$  for the velocity of sound. A graphical computer program was developed to simplify the calculation of  $^3\text{He}$  properties over a wide range for temperature from 0.01 K to 300 K and pressures up to 15 MPa.  $^3\text{He}$   $T$ - $s$  and  $p$ - $h$  diagrams were plotted.

### INTRODUCTION

Helium-3 is a rare and expensive isotope of helium that is selectively used in some mK refrigeration technologies. Its normal boiling temperature is 3.197 K, and it becomes superfluid below 0.0026 K, in marked contrast to (the ordinary)  $^4\text{He}$  with a normal boiling temperature of 4.23 K and which transitions to a superfluid phase below 2.1768 K. With appropriate design, use of  $^3\text{He}$  results in improved efficiency and/or significantly lower refrigeration temperatures. However, in contrast to the widely used database, equation of state, and computer codes for  $^4\text{He}$ , no reference data, equation, and codes were available for  $^3\text{He}$  until recently. Equilibrium equations over wide ranges with high precision along the vapor-liquid [1, 2] and liquid-solid lines [3] were proposed. Based on classical thermodynamics and quantum mechanics, a framework for developing a general  $^3\text{He}$  state equation was constructed [4]. The Debye specific heat model for crystal was successfully applied to a cryogenic fluid for the first time. With this new concept and framework, a general equation of state working both for compressed liquid and normal gaseous  $^3\text{He}$  was proposed [5, 6]. A graphical computer program was developed to simplify the calculation of  $^3\text{He}$  properties over a wide range of temperature from 0.01 K to 300 K (even 1500 K) and pressures up to 15 MPa.  $^3\text{He}$   $T$ - $s$  and  $p$ - $h$  diagrams were plotted [7]. This paper summarizes these results and introduces the current research status on the thermophysical properties of  $^3\text{He}$ . Due to the space limitation, coefficients for all the equations will not be included.

## DATA MINING

Measurements are necessary for understanding the thermophysical behavior of a substance and developing its equation of state. Experimental data especially for the following  $^3\text{He}$  properties have been mined over the last 4 years: (1) vapor pressure and saturation density measurements; (2) melting pressure and density measurements; (3)  $p$ - $\rho$ - $T$  data in the compressed liquid and gas region; (4)  $p$ - $\rho$ - $T$  data near the critical region and critical values; (5) heat capacity  $c_v$ - $\rho$ - $T$  and  $c_p$ - $\rho$ - $T$  data for compressed liquid, normal gas, and saturation curves; (6) sound speed  $u$ - $p$ - $T$  data; and (7) thermal conductivity, viscosity, and surface tension. Refer to references [1-3] for details of these data.

## LIQUID-VAPOR EQUILIBRIUM EQUATIONS

A vapor pressure equation and a saturated density equation are essential components of state equations for any substances. For developing the  $^3\text{He}$  state equation, these two vapor-liquid equilibrium equations consequently must be valid from about 0.01 K to the critical temperature 3.3157 K. In the critical region, they should be in agreement with well known scaling laws. The  $^3\text{He}$  vapor pressure equation has often been used to define the international temperature scales below about 3.2 K. Our vapor pressure equation [2], adopting the latest critical parameters measurements (3.3157 K, 114.6 kPa) [1], extends the temperature range up to the critical temperature and down to the superfluid transition temperature. The equation

$$\ln(p) = \sum_{k=-1}^n a_k T^k + b \ln(T) \quad (1)$$

agrees with the current ITS-90 temperature scale within 90  $\mu\text{K}$  between 0.65 and 3.2 K.  $p$  is pressure in Pascal,  $T$  is temperature in K, and  $a_k$  are fitted constants [2]. Close to the critical point, equation (2)

$$p_r = 1 - \left[ A(1-T_r)^{2-\alpha} + \sum_{i=1}^6 C_i(1-T_r)^i \right] \quad (2)$$

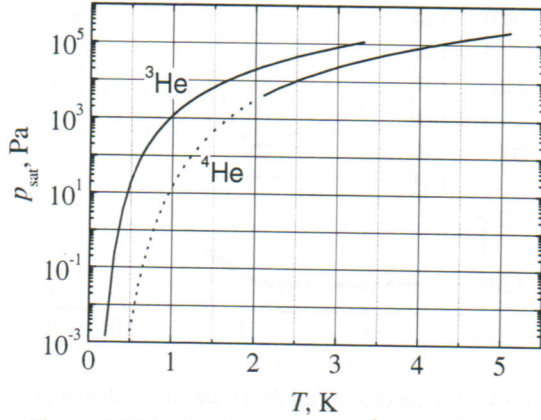
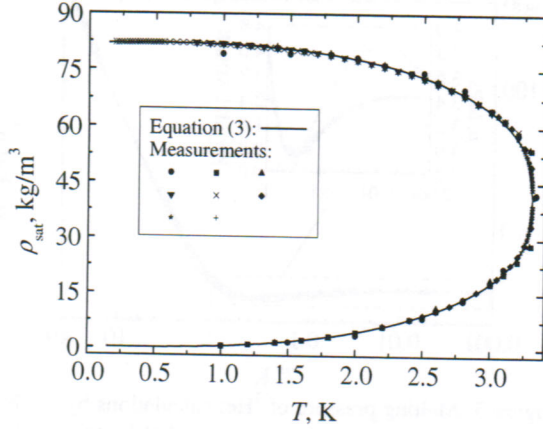
was used to realize a smooth switch to the critical point, which follows the scaling law and agrees with the reference measurements within a relative rms error 0.00013%. In equation (2),  $p_r = p/p_c$ ,  $T_r = T/T_c$ , and  $p_c$  and  $T_c$  are the critical pressure and temperature.  $\alpha$  is a critical index,  $\alpha = 0.105$ . The vapor pressure curve of  $^3\text{He}$  in contrast to  $^4\text{He}$  is shown in Figure 1. It can be seen that the vapor pressures of  $^3\text{He}$  are several orders higher than that of  $^4\text{He}$  below about 2 K, which hints at the potential for much lower cooling temperatures by evaporation refrigeration.

For the density along the vapor-liquid equilibrium line, the following dimensionless equation was proposed [1],

$$\rho / \rho_c = 1 \pm (c_1 \tau^\beta + c_2 \tau^{1+\beta} + c_3 \tau^{2+\beta} + c_4 \tau^{3+\beta}) + c_5 \tau + c_6 \tau^2 \quad (3)$$

where  $\tau = (T_c - T)/T_c$ ,  $\rho_c = 41.191 \text{ kg/m}^3$ ,  $c_1$ - $c_6$  are the coefficients [1] obtained by least squares regression, and  $\beta$  is a critical index to describe the density dependence near the



Figure 1 Vapor pressure curves of  $^3\text{He}$  and  $^4\text{He}$ Figure 2 Saturated density curve of  $^3\text{He}$ 

critical point. The sign “ $\pm$ ” is used to distinguish the liquid and vapor branches. “+” is for liquid and “-” is for vapor. To our knowledge, no saturated density equation has ever been published for any other substances working down to such a low temperature at  $0.06T_c$ . In this dimensionless form, the deviations caused by the differing temperature scales will affect our results only negligibly, although the old temperature scales have been converted to ITS-90. The agreement between equation (3) and the reference measurements is shown in Figure 2.

### LIQUID-SOLID EQUILIBRIUM EQUATIONS

Liquid  $^3\text{He}$  obeys Fermi-Dirac statistics. The departure from classical behavior occurs roughly at the temperature where the thermal de Broglie wavelength is on the order of the mean interparticle spacing. This temperature is of order 1 K for liquid  $^3\text{He}$  (depending on the density). Well below this Fermi degeneracy temperature, the specific heat and the entropy will both be linear functions of the absolute temperature. On the other hand, in the range of temperatures above 0.01 K, the nuclear spins of the  $^3\text{He}$  atoms comprising the solid should be almost fully disordered. For spin 1/2 nuclei this required that the solid entropy  $S_s$  should be equal to  $R\ln 2$  per mole. For these two basic reasons, the melting properties of  $\text{He}^3$  are anomalous. At extremely low temperatures, the entropy of liquid  $^3\text{He}$   $S_l$  will be less than that of solid  $S_s$ . When the temperature goes up, like any normal substance,  $S_s$  becomes greater than  $S_l$ . Since the molar volume of liquid  $^3\text{He}$   $V_l$  is always greater than that of solid  $V_s$ , according to the Clausius-Clapeyron equation,  $dp_m/dT = (S_l - S_s)/(V_l - V_s)$ , the melting pressure curve must have a minimum at the place where the liquid entropy line intersects the solid entropy line. Hence, a melting pressure equation in the form of rational expression was derived as

$$\ln(p) = \frac{c_1 + c_3 \ln T + c_5 (\ln T)^2 + c_7 (\ln T)^3 + c_9 (\ln T)^4 + c_{11} (\ln T)^5}{1 + c_2 \ln T + c_4 (\ln T)^2 + c_6 (\ln T)^3 + c_8 (\ln T)^4 + c_{10} (\ln T)^5} \quad (4)$$

where  $p$  is the melting pressure in MPa,  $T$  is the temperature in K, and  $c_1 - c_{11}$  are fitted coefficients [3]. The suggested working range for this melting pressure equation is 0.001–30 K, although it could be extended up to 35 K reliably. For equation (4), when the temperature  $T \rightarrow 0$ , that is  $\ln(T) \rightarrow -\infty$ ,  $\ln(p)$  approaches its limit  $c_{11}/c_{10} = 1.3486$ , that is  $p = 3.852$  MPa. At pressures lower than this value, one can never solidify  $^3\text{He}$ . The agreement between equation (4) and the reference experimental data is illustrated in Figure 3.

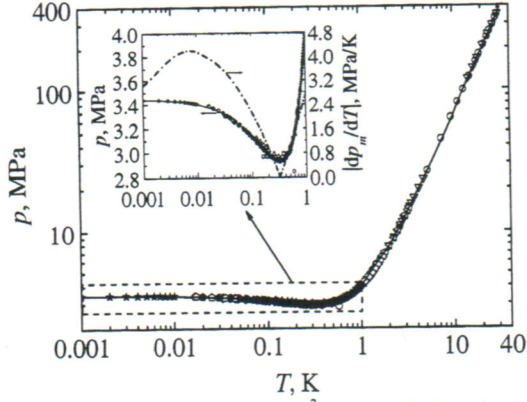


Figure 3 Melting pressure of  $^3\text{He}$ : calculations by equation (4) (line), measurements (symbols)

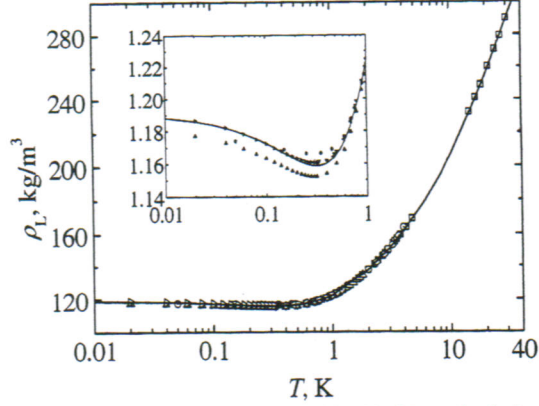


Figure 4 Melting density on the liquid side: calculations by equation (5) (line), measurements (symbols)

It is interesting to find that the shape of density plots along the melting curve looks similar to that of the melting pressure. In view of the successful application of the rational form to melting pressure, the density equations for both the liquid and solid along the melting curve of  $^3\text{He}$  are also of a similar form of a rational expression except without any logarithm functions due to the small numerical magnitude of the density variation,

$$\rho = \frac{c_1 + c_3 T + c_5 T^2 + c_7 T^3 + c_9 T^4 + c_{11} T^5}{1 + c_2 T + c_4 T^2 + c_6 T^3 + c_8 T^4 + c_{10} T^5} \quad (5)$$

where  $\rho$  is the liquid or solid density along the melting curve, in  $\text{kg/m}^3$ ,  $T$  is temperature in K, and the  $c_i$ 's are fitted coefficients, different for liquid and solid. The agreement between equation (5) and the reference experimental data are shown in Figure 4 and Figure 5.

### DEBYE FLUID $^3\text{He}$ EQUATION OF STATE

The above independent phase equilibrium equations for  $^3\text{He}$  on the vapor-liquid saturation line and the melting line, with the superfluid transition lines, sketch the basic phase diagram of  $^3\text{He}$ . However, the thermodynamic properties in the normal liquid and gas regions are of great interest. By observing the amazing similarity between the  $^3\text{He}$  specific heat measurements [8] and the Debye specific heat model which has been successfully used to explain the thermophysical mechanism of solid/crystal, a Debye equation of state for fluid  $^3\text{He}$  using the Helmholtz potential function was developed. The fundamental assumption for this theory is that the Debye temperature  $\Theta$  is a function only of density for fluid rather than a constant as for solids. The equation is written as

$$A = \underbrace{-\Theta H_0}_{(I)} + \underbrace{\frac{1}{1 + e^{C_1(\tau-1)}} \sum_{i=1}^4 \frac{\delta^i (C_{2i+5} \tau^2 + C_{2i+6} \tau^4)}{1 + e^{i C_2(\delta-1)}}}_{(II)} + \underbrace{\sum_{i=1}^3 C_{i+14} \delta^i}_{(III)} + \underbrace{\sum_{i=1}^2 \left[ \frac{\delta^i}{1 + e^{C_3(\delta-1)}} (C_{2i+16} + C_{2i+17} \frac{1}{1 + e^{C_4(\tau-1)}}) \right]}_{(IV)} \quad (6)$$

$$+ \underbrace{\frac{(1 - e^{-C_5 \tau})^2}{1 + e^{C_6(1/\delta-1)}} \sum_{i=1}^4 [(C_5 \tau)^{i-3} \cdot (C_{3i+19} + C_{3i+20} \delta + C_{3i+21} \delta^2)]}_{(V)} - \underbrace{C_{34} \tau}_{(VI)} - \underbrace{C_{35}}_{(VII)}$$



$$H_0 = \int_0^{\tau/\Theta} \int_0^{\tau/\Theta} [9R_m y^2 \int_0^{\tau/y} \frac{x^4 e^x dx}{(e^x - 1)^2}] dy dz \quad (7)$$

where  $A$  is the Helmholtz energy, the Debye theta  $\Theta = C_{36}\delta^{2/3}(1 + C_{37}\delta + C_{38}\delta^2)$ ,  $R_m$  is the gas constant,  $\delta = \rho/\rho_c$ ,  $\tau = T/T_c$ , and the  $C_i$ 's are fitted constants [5, 6]. In Eq. (6), the term indexed (I) is the basic Debye function. Grouped terms (II) attempt to fit the conventional thermodynamics near critical point. Terms (III) stand for the compressibility of the liquid, which is independent of temperature. Terms (IV) are used for the 2nd and 3rd virial components for low density. Terms (V) describe both the linear specific heat of a Fermi fluid at very low temperatures and contribute to the specific heat by the decay of spin alignment at relatively higher temperatures but below 1 K. Term (VI) gives zero for entropy at  $p = 0$ ,  $T = 0$  in the compressed liquid. Term (VII) is chosen so that the Helmholtz energy  $A$  is adjusted to zero for  $p = 0$ ,  $T = 0$  in the liquid phase. In groups (II), (IV), and (V), the Fermi function  $1/(1+e^x)$  is widely used as the cutoff function instead of the traditional exponential (or BWR functions)  $\exp(-x^2)$ .

The lower limit of 0.01 K for equation (6) is above the superfluid transition at 0.0026 K. The upper limit of 300 K is a reliable extrapolation although the upper limit of available  $^3\text{He}$  property measurements is 60 K. With the Debye state equation, all state properties, e.g.,  $p$ - $V$ - $T$  relations, specific heats, thermal expansion, and sound velocity for  $^3\text{He}$  could be determined from the Helmholtz energy by standard thermodynamics. For instance, Figure 6 and Figure 7 compare the calculations by equation (6) with the isothermal  $p$ - $V$ - $T$  experimental data from Bogoyavlenskii *et al.* up to 13 K [9] and from Karnus *et al.* up to 60 K [10]. Figure 8 shows the agreement between the calculated isochoric specific heat by equation (6) and the measurements from Greywall [8]. According to a comprehensive analysis, the uncertainty of the state equation was inferred between calculations and reference data as follows: for  $p$ - $\rho$ - $T$ , the percent errors of the calculated density values are estimated to be  $\pm 1\%$  for the gas and  $\pm 0.7\%$  for the normal compressed liquid, respectively. The errors in calculated heat capacity values are generally within  $\pm 0.9\%$  in the liquid region but a maximum 6.32% appears around 15 K in the gas region, where only one reference data source is available. The uncertainty for velocity of sound calculations is usually on the order of  $\pm 1\%$  in the liquid region.

A graphical computer program "He3Pak" was developed to simplify the calculation of  $^3\text{He}$  properties over a wide range for temperatures from 0.01 K to 300 K and pressures up to 15 MPa.  $T$ - $s$  and  $p$ - $h$  diagrams for  $^3\text{He}$  in this region were plotted for engineering applications. Additional experimental measurements on some of the properties, such as specific heat, would be useful for temperatures above 20 K to improve the accuracy of the equation of state.

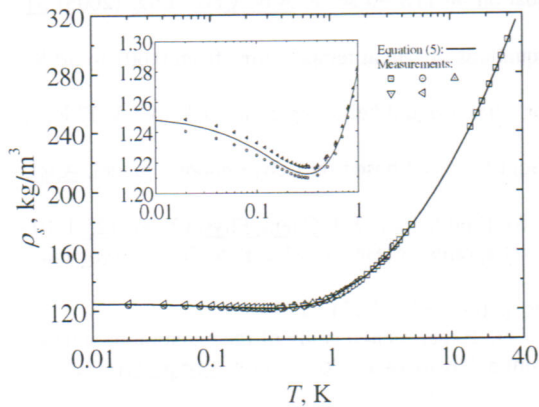


Figure 5 Melting density on the solid side: calculations by equation (5) (line), measurements (symbols)

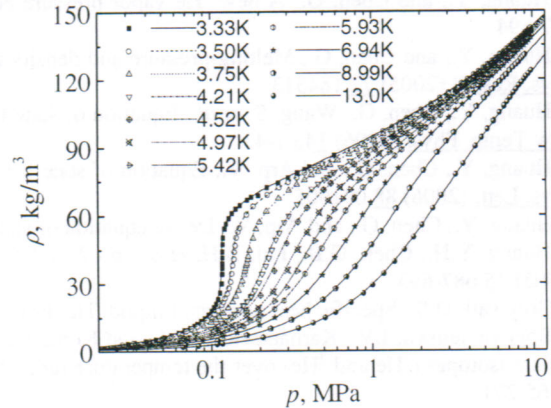


Figure 6 Comparison of calculated  $p$ - $\rho$ - $T$  (lines) with measurements from Bogoyavlenskii *et al.* [9] (symbols)

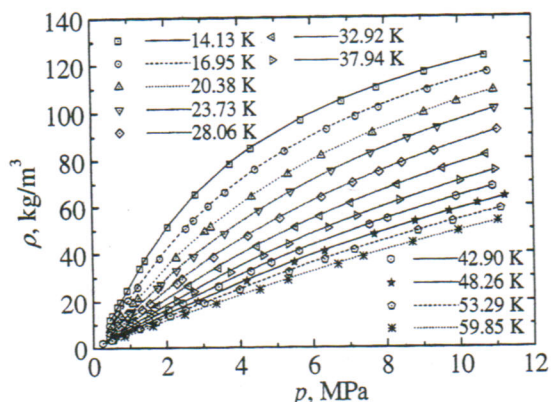


Figure 7 Comparison of calculated  $p$ - $\rho$ - $T$  (lines) with measurements from Karnus *et al.* [10] (symbols)

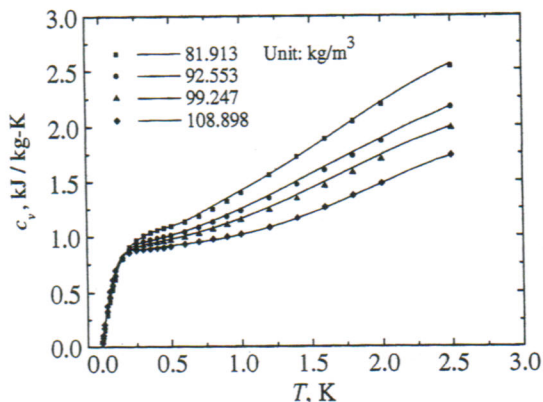


Figure 8 Comparison of calculated  $c_v$ - $p$ - $T$  (lines) with measurements from Greywall [8] (symbols)

## TRANSPORT PROPERTIES

Transport properties are totally different from thermodynamic properties and can not be derived from the state equation. Currently we are extending the work at NIST on  $^3\text{He}$  thermodynamic properties to the transport properties. A literature survey on thermal conductivity, viscosity, surface tension, etc. of  $^3\text{He}$  has been completed and all published data were collected. Graphs for isobars, isotherms, and isochors were generated for assisting curve fitting.

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