# Melting-pressure and density equations of ${ }^{3} \mathrm{He}$ at temperatures from 0.001 to 30 K 

Yonghua Huang and Guobang Chen<br>Cryogenics Laboratory, Zhejiang University, Hangzhou, 310027 China<br>(Received 21 June 2005; revised manuscript received 19 August 2005; published 18 November 2005)


#### Abstract

Nonsegmented equations for melting pressure and density at temperatures from 0.001 K to 30 K have been developed to fit the reference data. The maximum and average deviations between the melting pressure equation and the totaling 298 reference data are $2.17 \%$ and $0.218 \%$, respectively. For the density equations, the average deviations are $0.236 \%$ for the liquid side and $0.218 \%$ for the solid side. Both the melting pressure curve and melting density curves predicted by the submitted equations approach their minimums at about 0.315 K .


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## I. INTRODUCTION

A melting curve defines the limitation of a working substance existing in fluid state, which must be overstepped for solidification. So far, almost all the cryogenic fluids have their own standard or authoritative melting pressure equations in a wide range, except ${ }^{3} \mathrm{He}$. In the past 50 years, many theoretical and experimental researches have been put on the melting curve of the last cryogenic fluid ${ }^{3} \mathrm{He}$. Strong quantum effects at very low temperatures, no triple point existence, and superfluidity down to 2.6 mK , etc., have made ${ }^{3} \mathrm{He}$ significantly different from any other general cryogenic fluid. Such a number of interesting and unusual features of the melting curve of ${ }^{3} \mathrm{He}$ have stimulated many theoretical and experimental investigations. The melting pressure of ${ }^{3} \mathrm{He}$ is no longer monotone decreasing with temperature down to a very low degree. This implies that the melting curve would have a pressure minimum. In other words, the solid does not exist at pressures less than the minimum only even by cooling down to absolute 0 K .

In order to probe the anomalous melting properties of ${ }^{3} \mathrm{He}$, we have collected quite a number of articles on the research activities of ${ }^{3} \mathrm{He}$ since 1949 . This collection indicates that many measurements for the pressure and density (or molar volume) along the melting curve are available and united to cover a wide range. However, most of these measurements are in outdated unit systems and temperature scales as well. And the existing equations based on the measurements with narrow ranges of temperature, mostly from about 0.1 K to 1 K , cannot switch to each other smoothly. No independent and unitary equations have been reported to describe the properties on the melting curve of ${ }^{3} \mathrm{He}$ in a wide range. The traditional Simon melting equation, which has been successfully applied to other cryogenic fluids, no longer holds for ${ }^{3} \mathrm{He}$ because of the characteristics of this equation itself. In this work, the significant pressure-densitytemperature characteristics of ${ }^{3} \mathrm{He}$ along the melting curve from 0.001 K to 30 K have been suggested and examined in detail, and nonsegmented equations for the melting pressure and density in question have been developed to fit the collected reference data.

## II. REFERENCE DATA AND FORMULAS

Tables I-IV make brief summaries of the up-to-date research activities on pressure and density measurements, cal-
culations, and formulas along the melting curve of ${ }^{3} \mathrm{He}$. Most of these data are experimental measurements and smoothed values directly given by the articles cited in the tables. The rest is obtained by picking up from the curves drawn in articles by using our self-programmed software. Tables II and IV list the searched equations in their original form, without any unit conversion. The coefficients of Rusby et al.'s equation in Table II can be found in the Appendix.

Before the least-squares fitting, procedures for converting temperatures measured on various scales to the currently accepted ITS-90 temperature scale and converting data from various sources to consistent units (SI units) for analysis have been completed first. The temperature scales are also listed in Tables I and III. Second, the data selection process is important and necessary. Systematic errors in the experimental data sets and methods of thermometry will certainly affect the quality of the state equation. To minimize the effects of such factors, care is taken to analyze each data set used in the development of the equation for consistency with independent measurements along the melting curve. Much effort has been performed to avoid using experimental data that contain large systematic errors in the fitting process. It should be pointed out that not all the listed data sets, but only those marked with " *" in Tables I and III have been used during the final fitting. Those not-used data given here are good references for the comparison in the following text of this paper. For melting pressures, it is found that observations at temperatures below 1 K are numerous and overlapped. Since the numerical differences between these early measurements due to temperature scales and methods of thermometry and manometry are worthwhile, it is complicated to convert all these data for the sake of consistency. Furthermore, it is not necessary to make such a conversion because Rusby et al. 's ${ }^{11}$ small interval data published in 2003 are the most advanced data, which cover the whole range from 1 mK to 1 K and have been well accepted internationally. So, in our fitting program, only Rusby et al.'s data were adopted for the region below 1 K . At temperatures from 1 K to 30 K , reference data included in the least-squares fit were from Grilly and Mills ${ }^{2,4,9}$ and Sherman and Edeskuty, ${ }^{5}$ totaling 298 points. For melting densities, the guidelines for data selection are: (1) using numerical data listed in tables given in articles instead of data pickedup from curves, and (2) data

TABLE I. Melting pressure measurements and smoothed values.

| Year | Author | Ref. | Points | $T$ range (K) | $P$ range (MPa) | Temperature scale/Thermometer |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1953 | Weinstock et al. | 1 | 29 | 0.1551-1.594 | 2.943-6.066 | $T_{\text {CMN mag }}{ }^{\text {a }}$ |
| 1955 | Mills et al. * | 2 | Curve | 1.44-29.85 | 5.69-343.94 | 1.9-5.2 K: v.p. ${ }^{4} \mathrm{He} \mathrm{T}_{48}$ $5.2-12 \mathrm{~K}: \mathrm{Cu}-\mathrm{Ci} \mathrm{Fe}$ thermoc. $12-24.5 \mathrm{~K} \text { v.p. } \mathrm{n}-\mathrm{H}_{2}$ $24.5-31 \mathrm{~K}: \text { v.p. } \mathrm{Ne}$ |
| 1959 | Baum et al. | 3 | 11 | 0.12-0.7 | 2.969-3.354 | $T_{\text {CMN mag }}{ }^{\text {b }}$ |
| 1959 | Grilly and Mills* | 4 | 29 | 1.332-30.184 | 5.061-348.607 | $<5.2 \mathrm{~K}$ : v.p. ${ }^{4} \mathrm{He}_{58}$ <br> $5.2-12 \mathrm{~K}: \mathrm{Cu}-\mathrm{Ci} \mathrm{Fe}$ thermoc. $\begin{gathered} 12-24.5 \mathrm{~K}: \text { v.p. n- } \mathrm{H}_{2} \\ 24.5-31 \mathrm{~K}: \text { v.p. } \mathrm{Ne} \end{gathered}$ |
| 1960 | Sherman and Edeskuty* | 5 | 14 | 1.07-3.1 |  | $\mathrm{T}_{55 \mathrm{E}}$ |
| 1961 | Mills et al. | 6 | 10+Curve | 0.3-1.2 | 2.929-4.5698 | $\mathrm{T}_{55 \mathrm{E}}$ |
| 1963 | Anderson et al. | 7 | $43+$ Curve | 0.02-0.7 | 2.926-3.308 | $T_{\text {CMN mag }}$ |
| 1969 | Scribner et al. | 8 | $31+$ Curve | 0-0.7 |  | $>0.5 \mathrm{~K}$ : v.p. ${ }^{4} \mathrm{He} \mathrm{T}_{58}$ and ${ }^{3} \mathrm{HeT}_{62}$ $<0.5 \mathrm{~K}: T_{\text {CMN mag }}\left(\mathrm{T}_{58}, \mathrm{~T}_{62}\right.$ calibrated) |
| 1971 | Grilly* | 9 | 18+Curve | 0-1.8 | 2.937-6.858 | $\mathrm{T}_{62}$, v.p. ${ }^{3} \mathrm{He}$ |
| 1986 | Greywall | 10 | 68 | 0.0009-0.25 |  | $T_{\text {CMN mag }}$, NBS-CTS1983 |
| 2003 | Rusby et al. * | 11 | 220 | 0.001-1 |  | PLTS-2000 |

${ }^{2}$ Corrected to thermodynamic temperatures (Ref. 12).
${ }^{\text {b }}$ Calibrated against ${ }^{4} \mathrm{He}$ vapor pressure temperature scale.
should cover the interested region as comprehensively as possible. Finally, only data from Grilly and Mills, ${ }^{4,6,9}$ and Sherman and Edeskuty ${ }^{5}$ are adopted. After converting the temperature scale and unit, a plot of these density data shows that they join with each other smoothly.

All the data marked with an asterisk in Tables I and III unite to cover a wide range from about 0.001 K to 30 K , which comes into being the basis of the derivation of our equations to be introduced in the following sections.

## III. DERIVATION OF EQUATIONS

On the basis of the reference data in previous section, the authors have developed equations for pressure and densities on both liquid and solid sides along the melting curve.

## A. Melting pressure equation

The anomalous melting properties of $\mathrm{He}^{3}$ are heavily dependent upon the behavior of Fermi liquid and the spin sys-

TABLE II. Melting pressure formulas in literatures.

| Year | Author | Ref | Equation | Units | T range (K) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1955 | Mills et al. | 2 | $P=25.16+20.08201 T^{1.517083}$ | $\mathrm{kg} / \mathrm{cm}^{2} ; \mathrm{K}$ | 1.844-29.88 |
| 1959 | Grilly et al. | 4 | $P=27.256-0.64696 T+16.0205 T^{2}-1.39505 T^{3}$ | kg/cm ${ }^{2}$; K | 1.2-3.1 $\alpha$ Solid $\rightarrow$ Liquid |
|  |  |  | $P=3.873+30.5539 T+4.08176 T^{2}$ | $\mathrm{kg} / \mathrm{cm}^{2} ; \mathrm{K}$ | 3.2-4.4 $\beta$ Solid $\rightarrow$ Liquid |
| 1960 | Sydoriak et al. | 13 | $P=28.91+32.20(T-0.330)^{2}$ | atm; K | 0.3-0.5 |
| 1960 | Sherman et al. | 5 | $P=24.559+16.639 T^{2}-2.0659 T^{3}+0.11212 T^{4}$ | atm; K | 1.07-3.1 |
| 1961 | Mills et al. | 6 | $P=28.91+32.20(T-0.330)^{2}$ | atm; K | 0.33-1.2 |
| 1963 | Anderson et al. | 7 | $P=425+485(0.3191-T)^{2}+546.5(0.3191-T)^{3}$ | psi; K | 0.03-0.4 |
| 1968 | Zeisse et al. | 14 | $\begin{gathered} P=29.107+0.25537(t)^{2}-0.05700(t)^{3}+0.01625(t)^{4} \\ 100 t=T-299.028 \end{gathered}$ | atm; mK | 0.012-0.6 |
| 1969 | Scribner et al. | 8 | $P=28.94+25.86(T-0.318)^{2}$ | atm; K | 0.26-0.38 |
| 1986 | Greywall | 10 | $P_{m}-P_{A}=\sum_{n=-3}^{+5} a_{n}(T)^{n}$ | bar; mK | 0.0009-0.25 |
| 2003 | Rusby et al. | 11 | $P_{m}=\sum_{i=-3}^{+9} a_{i}(T)^{i}$ | MPa; K | 0.001-1 |

TABLE III. Density measurements and calculations along the melting curve of ${ }^{3} \mathrm{He}$.

| Year | Author | Ref. | Liquid Points | Solid Points | $T$ range (K) | Temperature scale |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1959 | Grilly and Mills* | 4 | 29 | 29 | 1.332-30.184 | $<5.2$ K: v.p. ${ }^{4} \mathrm{He}_{58}$ $5.2-12 \mathrm{~K}: \mathrm{Cu}-\mathrm{Ci} \mathrm{Fe}$ thermoc. $12-24.5 \mathrm{~K}:$ v.p. n- $\mathrm{H}_{2}$ 24.5-31 K: v.p. Ne |
| 1960 | Sherman and Edeskuty* | 5 | 24 | 0 | 0.05-3.99 | $\mathrm{T}_{55 \mathrm{E}}$ |
| 1960 | Sydoriak et al. | 13 | Curve | Curve | 0.32-1.2 | $<5.2 \mathrm{~K}$ : v.p. ${ }^{4} \mathrm{He} \mathrm{T}_{58}$ |
| 1961 | Mills et al. * | 6 | 10+Curve | 10+Curve | 0.33-1.2 | $\mathrm{T}_{55 \mathrm{E}}$ |
| 1963 | Anderson et al. | 7 | 16 | 16 | 0.02-0.32 | $T_{\text {CMN mag }}$ |
| 1971 | Grilly* | 9 | 34 | 34 | 0.02-1.8 | $\mathrm{T}_{62}$, v.p. ${ }^{3} \mathrm{He}$ |

tems of the solid and liquid phases. Liquid ${ }^{3} \mathrm{He}$ obeys FermiDirac 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 on the order of 1 K for liquid ${ }^{3} \mathrm{He}$ (depending on the density). Well below this temperature (called the Fermi degeneracy temperature $T_{\mathrm{F}}$ ), 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 ${ }^{3} \mathrm{He}$ 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. Based on these considerations, as shown in Fig. 1, one is able to explore the implications of the liquidsolid phase equilibrium by the famous Clausius-Clapeyron equation,

$$
\begin{equation*}
\frac{d p_{m}}{d T}=\frac{\Delta S_{m}}{\Delta V_{m}}=\frac{S_{l}-S_{s}}{V_{l}-V_{s}} \tag{1}
\end{equation*}
$$

For ${ }^{3} \mathrm{He}$, the molar volume of liquid $V_{l}$ is always greater than that of solid $V_{s}$, so the denominator is always positive. On the other hand, the numerator will change sign as one cools into the Fermi degenerate region because $S_{l}$ will become less than the constant solid entropy $S_{s}=R \ln 2$ corresponding to random spin orientation, so at the lowest temperatures the slope of the melting curve becomes negative. At the higher temperatures, the entropy of the liquid will be greater than
$R \ln 2$ per mole so that the slope of the melting becomes positive. Figure 1 implies that the melting curve will have a minimum at the place where the liquid entropy curve intersects the solid entropy curve.

The authors find it difficult to derive an exact theoretical equation that excellently represents the above-mentioned slope behavior of the melting pressure curve for ${ }^{3} \mathrm{He}$. Instead, various general polynomial equations and their combinations with exponential terms were tried empirically. Unfortunately, none of the equation forms that had been successfully applied to other cryogenic fluids can perfectly fit the selected reference data of ${ }^{3} \mathrm{He}$. On the other hand, it is not difficult to find that the pressure of ${ }^{3} \mathrm{He}$ varies from about 3 MPa to 400 MPa when the temperature increases from 0.001 K to 30 K . Such a large variation of the numerical magnitudes may require using logarithm functions. At the same time, we noticed that a rational equation in the form of a polynomial divided by a polynomial has two branches on both sides of its vertical asymptote. The tendency of the left branch meets the requirement in question. However, the melting-pressure equation should also be reasonably simple so as to be useful in thermodynamic calculations. Obviously, more terms may be put into an equation to get better agreement with the collected data, but complexity is the penalty. After many trials, the following empirical equation is suggested for the melting-pressure behavior of ${ }^{3} \mathrm{He}$ as a function of temperature,

$$
\begin{equation*}
\ln (P)=\frac{c_{1}+c_{3} \ln T+c_{5}(\ln T)^{2}+c_{7}(\ln T)^{3}+c_{9}(\ln T)^{4}+c_{11}(\ln T)^{5}}{1+c_{2} \ln T+c_{4}(\ln T)^{2}+c_{6}(\ln T)^{3}+c_{8}(\ln T)^{4}+c_{10}(\ln T)^{5}} \tag{2}
\end{equation*}
$$

TABLE IV. Correlations for density along the melting curve of ${ }^{3} \mathrm{He}$.

| Year | Author | Ref | Equation | Units | $P$ range |
| :--- | :---: | :---: | :---: | :---: | :---: |
| 1959 | Grilly et al. | 4 | $V_{\mathrm{f}}=-3.2482+51.1102\left(P_{m}+1.075\right)^{-0.161532}$ | $\mathrm{~kg} / \mathrm{cm}^{2} ; \mathrm{cm}^{3} / \mathrm{mol}$ | $50-3555 \mathrm{~kg} / \mathrm{cm}^{2}$ |
|  |  |  | $\Delta V_{m}=1.56464-0.39023 \log _{10}\left(P_{m}-29.998\right)$ | $\mathrm{kg} / \mathrm{cm}^{2} ; \mathrm{cm}^{3} / \mathrm{mol}$ | $51-128 \mathrm{~kg} / \mathrm{cm}^{2}$ |
|  |  | $\Delta V_{m}=1.51053-0.30825 \log _{10}\left(P_{m}-42.581\right)$ | $\mathrm{kg} / \mathrm{cm}^{2} ; \mathrm{cm}^{3} / \mathrm{mol}$ | $146-3555 \mathrm{~kg} / \mathrm{cm}^{2}$ |  |



FIG. 1. (Color online) An idealized sketch map of the entropy of liquid and solid ${ }^{3} \mathrm{He}$ along the melting curve.
where $P$ is melting pressure in MPa , and $T$ is temperature in K. The coefficients $c_{1}-c_{11}$ are listed in Table V. The suggested working range for this melting pressure equation is $0.001 \mathrm{~K}-30 \mathrm{~K}$, however, an extension of Eq. (2) to higher temperatures up to 35 K is also dependable. The melting pressure will be a very high value of 550 MPa at 40 K , which is hard to realize in actual experiments. For Eq. (2), when temperature $T \rightarrow+0$, that is $\ln (T) \rightarrow-\infty, \ln (P)$ approaches its limit $c_{11} / c_{10}=1.3486$, that is $P=3.852 \mathrm{MPa}$. It should be noted that the solid ${ }^{3} \mathrm{He}$ has two different phases, $\alpha$ (bcc structure) and $\beta$ (hcc structure), as show in Fig. 2. The measurements by Grilly and Mills ${ }^{4}$ on the solid $\alpha$-liquid boundary and solid $\beta$-liquid boundary join smoothly. The solid $\alpha$-solid $\beta$ transition line intersects with the melting curve at a point with the temperature 3.154 K (ITS-90 scale). It can be seen that the solid line plotted in Fig. 2 predicted by Eq. (2) smoothly and continuously connects the measurements on the coexistence line of liquid and both $\alpha$ and $\beta$ solid.

## B. Density equations along the melting curve

It is interesting to see that the shape of density plots along the melting curve looks quite similar to that of the melting


FIG. 2. (Color online) Transition between two crystalline phases of solid ${ }^{3} \mathrm{He}$ and normal liquid ${ }^{3} \mathrm{He}$.
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 ${ }^{3} \mathrm{He}$ are also in a similar form of rational expression except without any logarithm functions due to the small numerical magnitude of the density variation,

$$
\begin{equation*}
\rho=\frac{c_{1}+c_{3} T+c_{5} T^{2}+c_{7} T^{3}+c_{9} T^{4}+c_{11} T^{5}}{1+c_{2} T+c_{4} T^{2}+c_{6} T^{3}+c_{8} T^{4}+c_{10} T^{5}} \tag{3}
\end{equation*}
$$

where $\rho$ is the liquid or solid density along the melting curve, unit in $\mathrm{kg} / \mathrm{m}^{3}$; and $T$ is temperature in K. Different coefficients, also listed in Table V, are obtained for liquid and solid respectively.

## IV. RESULTS AND DISCUSSION

## A. Accuracy of the melting pressure equation

Figure 3 shows the agreement of the calculations by Eq. (2) (solid line) with the experimental and calculated data listed in Table I. The area around the $P_{\text {min }}$ has been enlarged

TABLE V. Coefficients for Equations (2) and (3).

|  |  | Equation (3) |  |
| :---: | :---: | :---: | :---: |
| Coefficients | Equation (2) | Liquid side | Solid side |
| $c_{1}$ | 1.387061 | 119.026135 | 125.106337 |
| $c_{2}$ | -0.47739621 | 0.26598247 | 0.744874167 |
| $c_{3}$ | $1.173634148 \times 10^{-2}$ | 8.959606 | 63.4602862 |
| $c_{4}$ | 0.329447888 | 0.259048 | $5.69419341 \times 10^{-2}$ |
| $c_{5}$ | 0.563607496 | 73.0945524 | 60.44224356 |
| $c_{6}$ | -0.09599502 | -0.35192157 | $9.606419123 \times 10^{-2}$ |
| $c_{7}$ | -0.111889 | -59.347 | -15.834 |
| $c_{8}$ | $1.36493847 \times 10^{-2}$ | 0.15613338 | 0.17301133 |
| $c_{9}$ | $1.570888538 \times 10^{-2}$ | 19.37724 | 30.6121475 |
| $c_{10}$ | $-7.7718566 \times 10^{-4}$ | $3.8934088 \times 10^{-3}$ | $3.11169498 \times 10^{-3}$ |
| $c_{11}$ | $-1.045706897 \times 10^{-3}$ | 1.9364125 | 1.699408157 |



FIG. 3. (Color online) Melting pressure of ${ }^{3} \mathrm{He}$ vs temperature: solid curve shows calculated results by Eq. (2).
to show the specialty of the ${ }^{3} \mathrm{He}$ melting pressure. Figure 4 gives the relative residuals between the calculations by the equation and the measurements.

It can be seen from Figs. 3 and 4 that Eq. (2) well represents the characteristics of the melting pressure of ${ }^{3} \mathrm{He}$. The maximum and average residuals in percent between Eq. (2) and the 298 reference data in the temperature range from 0.001 K to 30 K are $2.17 \%$ and $0.218 \%$, respectively. In the range $0.001 \mathrm{~K}-1 \mathrm{~K}$, our melting pressure equation agrees with the equation presented by Rusby et al. ${ }^{11}$ within $0.16 \%$, as shown in Fig. 5. Rusby et al.'s equation has been used to define the Provisional Low Temperature Scale from 0.9 mK to 1 K , which was adopted by the Comité International des Poids et Measures in October 2000.

Another important characteristic of Eq. (2) to be examined is the phenomenon of the melting-pressure minimum. When ${ }^{3} \mathrm{He}$ was first solidified in 1951 by Osborne et al., ${ }^{15,16}$ the observation of a melting pressure minimum ${ }^{17}$ was precluded due to the measurement technique, which resulted in the capillary leading to the sample chamber blocked with solid. Consequently, observation of $P>P_{\min }$ at $T<T_{\min }$ by


FIG. 4. (Color online) Residuals between the calculated results by Eq. (2) and reference data.


FIG. 5. The residuals between Eq. (2) and Rusby et al.'s equation.
sensing the pressure in the capillary becomes impossible. Baum et al. ${ }^{3}$ directly detected the minimum in $P_{m}(T)$ using a variation of the blocked-capillary procedure. At 1.2 K the sample chamber was filled to a pressure that would ensure the maintenance of two-phase equilibrium over the region to be investigated. At the same time, Bernardes and Primakoff ${ }^{18,19}$ led in 1959 to a fairly accurate prediction of an alignment temperature 0.37 K for the pressure minimum due to crystal lattice theory of ${ }^{3} \mathrm{He}$. A number of other investigations ${ }^{7,20}$ employing the blocked capillary as well as different techniques have amply substantiated the minimum in $P_{m}(T)$. Table VI lists a brief summary of determinations of the location of the minimum of the melting curve of ${ }^{3} \mathrm{He}$.

The melting pressure minimum $P_{\text {min }}$ and its corresponding temperature $T_{\text {min }}$ calculated by Eq. (2) with $d P / d T=0$ are 2.93113 MPa and 0.31586 K , respectively. These values are in good quantitative agreement with those latest researches listed in Table VI, especially the most recent results given by Rusby et al. ${ }^{11}$ as the PLTS-2000 scale definition.

## B. The performance of the density equations

Figures 6 and 7 show the agreement of Eq. (3) with the melting-density reference data versus temperature. The average deviations for the liquid and solid sides are $0.236 \%$ and $0.218 \%$ respectively. The behavior of liquid melting density $\rho_{\mathrm{L}}$ at $T<1 \mathrm{~K}$ is illustrated clearly in Fig. 6. One should notice that measurements in the liquid by Grilly ${ }^{9}$ are obviously greater than others bellow about 0.7 K . The fact of the other results bearing the same kind of deviation below 0.3 K is that Scribner and Adams et al. used the Mills' data for calibration. Equation (3) bias toward the Mills et al. data, whose error was estimated at less than $0.1 \%$.

The density minimum calculated by Eq. (3) for liquid along the melting curve locates at 0.3152 K , which leads to $\rho_{\mathrm{L} \min }=115.8533 \mathrm{~kg} / \mathrm{m}^{3}$; for solid, $T_{\text {Smin }}=0.3151 \mathrm{~K}, \rho_{\text {Smin }}$ $=121.2091 \mathrm{~kg} / \mathrm{m}^{3}$. It is interesting to find that these temperatures are almost the same as that of the melting-pressure curve predicted by Eq. (2).

## C. The relationship between the melting pressure and density

Of even more concern, when combining Figs. 3, 6, and 7, is the trend similarity of melting-density curves and melting-

TABLE VI. Summary of determinations of the location of the minimum of the melting curve of ${ }^{3} \mathrm{He}$.

| Year | Author | Ref. | $\begin{gathered} P_{\min } \\ (\mathrm{MPa}) \end{gathered}$ | $\begin{gathered} T_{\min } \\ (\mathrm{K}) \end{gathered}$ | Method |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1959 | Baum et al. | 3 | $2.96882 \pm 0.01^{\text {a }}$ | $0.32 \pm 0.004$ | Resistance strain gauge pressure measurement; powdered cerium magnesium nitrate (CMN) sphere thermometry |
| 1961 | Mills et al. | 6 | $2.92931 \pm 0.002$ | $0.323 \pm 0.005$ | Spring-loaded bellows, differential-pressure measurement; corrected ${ }^{3} \mathrm{He}$ vapor pressure thermometry |
| 1961 | Lee et al. | 21 | $2.94958 \pm 0.01$ | $0.32 \pm 0.01$ | Observation of density |
| 1961 | Anderson et al. | 20 | $2.93372 \pm 0.01$ | $\ldots$ | Melting of plug |
| 1963 | Anderson et al. | 7 | $2.93336 \pm 0.007$ | $0.319 \pm 0.005$ | Resistance strain gauge pressure measurement; observations of compressional cooling; powdered CMN, cylinder thermometry |
| 1968 | Zeisse et al. | 14 | $2.94856 \pm 0.03$ | $0.299 \pm 0.021$ | Capacitance strain gauge; NMR thermometry |
| 1969 | Scribner et al. | 8 | $2.93235 \pm 0.003$ | $0.318 \pm 0.006$ | Capacitance strain gauge pressure measurements; powdered CMN, cylinder thermometry |
| 1971 | Grilly et al. | 9 | $2.93153 \pm 0.003$ | $0.319 \pm 0.003$ |  |
| 2003 | Rusby et al. | 11 | 2.93113 | 0.31524 | Calculation by a correlation |
| 2005 | This paper |  | 2.93113 | 0.31586 | Calculation by Eq. (2) |

${ }^{\text {a }}$ Reference 7 has pointed out that $\sim 0.03 \mathrm{MPa}$ systematic error appears in the pressure measurements of Baum et al.
pressure curve. This implies an interesting relationship between these two properties along the melting curve.

According to the Clausius-Clapeyron equation [Eq. (1)], the slope of the melting pressure is directly associated with the relative magnitudes of the molar volume (or density) change along the melting curve. As mentioned in Sec. III A, at not sufficiently high as well as not sufficiently low temperatures, we shall assume that the solid entropy is $R \ln 2$ over the entire region of interest. Under this assumption, we can take both the solid expansion coefficient and specific heat to be zero. Hence, the solid molar volume will be a function of pressure only. This reflects the curve similarity between the density and pressure.

The consistency of melting-pressure minimum and density minimum can be explained as following. In thermodynamics, the thermal expansion coefficient $\alpha$ can be expressed as


FIG. 6. (Color online) Eq. (3) fits the melting density reference data in the liquid side.

$$
\begin{equation*}
\alpha=\beta \frac{d P_{m}}{d T}-\frac{1}{\rho} \frac{d \rho}{d T} \tag{4}
\end{equation*}
$$

or

$$
\begin{equation*}
\alpha=\left(\beta-\frac{1}{\rho} \frac{d \rho}{d P_{m}}\right) \frac{d P_{m}}{d T} \tag{5}
\end{equation*}
$$

where $\beta$ is the compressibility coefficient. From the observation that $\beta$ remains finite and $d \rho / d P_{m}$ is nearly constant as $P_{m} \rightarrow P_{\text {min }}$, then according to Eq. (5), $\alpha \rightarrow 0$ as $T \rightarrow T_{\text {min }}$. From Eq. (4), $d \rho / d T$ must also become zero at $T_{\min }$. These clues help to demonstrate the essential correlations or thermodynamic consistency between the pressure and density along the melting curve.


FIG. 7. (Color online) Eq. (3) fits the melting density reference data in the solid side.

## V. SUMMARY

Nonsegmented equations for ${ }^{3} \mathrm{He}$ melting pressure and density in the temperature range from 0.001 K to 30 K have been developed to fit the measurements. The maximum and average deviation in percent between the melting pressure equation and the 298 reference data are $2.17 \%$ and $0.218 \%$, respectively. For the density equations, the average deviation is $0.236 \%$ for the liquid side and $0.218 \%$ for the solid side. Both the melting-pressure equation and the melting-density equations predict almost the same tem-
perature, about 0.315 K at the pressure and/or density minimum.

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## APPENDIX

The Coefficients for Rusby et al.'s equation as referenced in Table II, are as follows:
$\mathrm{a}_{-3}=-1.3855442 \times 10^{-12}$
$\mathrm{a}_{2}=1.5417437 \times 10^{1}$
$\mathrm{a}_{-2}=4.5557026 \times 10^{-9}$
$\mathrm{a}_{3}=-3.5789853 \times 10^{1}$
$\mathrm{a}_{-1}=-6.4430869 \times 10^{-6}$
$\mathrm{a}_{4}=7.1499125 \times 10^{1}$
$a_{0}=3.4467343 \times 10^{0}$
$a_{5}=-1.0414379 \times 10^{2}$
$a_{1}=-4.4176438 \times 10^{0}$
$\mathrm{a}_{6}=1.0518538 \times 10^{2}$
$a_{7}=-6.9443767 \times 10^{1}$
$\mathrm{a}_{8}=2.6833087 \times 10^{1}$
$\mathrm{a}_{9}=-4.5875709 \times 10^{0}$
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