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Refinement in the ultrasonic velocity data and estimation of the critical parameters for molten uranium dioxide

Abdul-Majeed Azad *

Department of Chemical and Environmental Engineering, The University of Toledo, 3052 Nitschke Hall, Toledo, OH 43606-3390, USA

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Abstract

Based on the previously reported internal pressure approach and by making use of recent and more accurate experimental measurements on the density, and heat capacity of liquid UO_2 up to ~8000 K, reliable data on the sound propagation velocity in molten uranium dioxide have been obtained. An equation of state for liquid urania has also been developed which predicts a critical temperature $(T_c) \approx 10\,500$ K, critical pressure $(P_c) \approx 219$ MPa and critical density $(\rho_c) \approx 2510\ \mathrm{kg\,m^{-3}}$.

1. Introduction

The analysis of hypothetical and undesirable yet highly improbable accidents in the liquid metal-cooled fast breeder nuclear reactors (LMFBRs) is of paramount importance for developing safety codes. A self-consistent equation of state is thus relevant to the safety of fast nuclear reactors, primarily due to the expected elevated temperatures where the vapor pressure of the fuel could be sufficiently high to produce liquid mass displacement [1]. The possible accidents with respect to the fuel could involve, fuel damage, core meltdown and reactor runaway. These mishaps could happen under various conditions of operating variables and thus warrant assessing the latter to reduce the probability of such accidents. Such analysis is relevant to predict the catastrophe and ensure the desired safety throughout the reactor and its vicinity. A reliable equation of state for the nuclear fuel, therefore, necessitates the availability of a consolidated thermodynamic and transport property database, which plays a crucial role due to the rapidly changing and severe reactivity excursions at high temperatures. Ideally, the most relevant equation of state for the fuel would be the one that is valid up to the critical point [2].

Knowledge of the speed of sound in a fluid provides an indirect measurement of some fundamental thermodynamic properties, such as isochoric specific heat, adiabatic and isothermal compressibility using the available density and isobaric heat capacity, much more easily than other conventional methods [3,4]. Many of these parameters constitute the basic components of an equation of state. The high melting temperature, wide liquid regime in conjunction with the complexity of structure in the liquid and vapor state, makes the experimental determination of some of the basic thermophysical parameters for molten UO_2 quite difficult. Moreover,

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* Tel.: +1 419 530 8103; fax: +1 419 530 8086.
E-mail address: aazad@eng.utoledo.edu

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while solid UO_2 has a pure ionic character consisting of U^{+n} and O^{-2} ions, it displays highly ionized ionic character in liquid state and a weakly ionized (or neutral) molecular character in the gas phase. Consequently, the construction of a reliable equation of state for UO_2 becomes challenging [2]. Surprisingly, there is only one solitary report on the experimental measurement on the velocity of ultrasonic waves in molten UO_2 over a rather limited temperature range in the vicinity of its melting point, viz., between 3138 and 3196 K by Slagle and Nelson [5]. The parametric relation derived by Slagle and Nelson shows that the sound velocity is proportional to the square root of temperature and can be represented as:

$$C\ (\mathrm{m\,s^{-1}}) = 5268 - 61.98\sqrt{T}. \tag{1}$$

For stoichiometric uranium oxide (O/U = 2.00) values of 3070 K [6], 3115 K [7], 3123 K [8] and 3138 K [9] have been reported as the melting point of stoichiometric uranium oxide ($UO_{2.00}$). Kapil [10] has recommended a value of 3115 K, while Finn et al. [11] have used a value of 3138 K reported by [9] for the melting point of uranium dioxide along with a density of 8662 $\mathrm{kg\,m^{-3}}$ at the melting point, in the development of the equation of state of UO_2. According to some reviews [12,13] the melting point of stoichiometric urania should be in the interval 3070 and 3140 K. Yet another experimental measurement gives a value of 3075 ± 30 K [14].

In view of the importance and the relevance of a reliable equation of state for molten UO_2, there has been a constant attempt in the published literature for several decades to improve the data on thermodynamic properties such as density, heat capacity, enthalpy and isothermal compressibility and transport properties such as thermal conductivity and thermal diffusivity both theoretically and by experimental means. This paper reports the use of such data in refining the values of sound velocity with greater accuracy. A set of thermodynamic data were also employed independently to calculate the sound velocity in molten UO_2 up to 8000 K and to compute the critical parameters by using the internal pressure approach equation of state.

2. Theoretical background for sonic velocity computation

According to the internal pressure approach equation of state (IPAEOS),

$$\frac{(P+P_i)}{T} = \frac{C^2\alpha\rho C_p}{(C_p + TC^2\alpha^2)}. \tag{2}$$

In an alternate form, Eq. (2) could be written as:

$$\frac{(P+P_i)}{T} = C^2\alpha\rho\gamma, \tag{3}$$

where P, pressure (Pa); P_i, internal pressure (Pa); C, sound velocity ($\mathrm{m\,s^{-1}}$); ρ, density ($\mathrm{kg\,m^{-3}}$); α, coefficient of volume expansion (K^{-1}); C_p, heat capacity ($\mathrm{J\,kg^{-1}\,K^{-1}}$); γ, ratio of heat capacities at constant pressure and constant volume.

It has been found [17–20] that for a number of systems the value of $(P + P_i)/T$ computed as per Eq. (2) or (3) could be fitted into a linear expression of the type:

$$\frac{(P+P_i)}{T} = A - BT. \tag{4}$$

In the vicinity of critical temperature, T_c, $(P + P_i)/T$ approaches zero. Hence, under this limiting condition, we get:

$$\frac{(P+P_i)}{T} \approx 0 = A - BT_c,$$

which yields, $A = BT_c$.

So,

$$\frac{(P+P_i)}{T} = B(T_c - T). \tag{5}$$

Combining Eqs. (2) and (5), we get:

$$C = \sqrt{\frac{C_pB(T_c - T)}{[C_p\alpha\rho - T\alpha^2B(T_c - T)]}}. \tag{6}$$

Eq. (6) is a generalized expression for the computation of sonic velocity, in terms of the known values of ρ, α, and C_p as a function of temperature and an accurate value of T_c. The only unknown parameter B can be determined if sonic velocity is known at a single temperature. Obviously, the numerical value of B is inversely proportional to the critical temperature, which in the case of UO_2 shows a wide scatter. Different values of B are thus obtained depending on the choice of T_c. This in turn affects the computed values of sonic velocity and its temperature dependence [15]. In order to minimize this error, Azad and Sreedharan [16] had subsequently made use of a relationship suggested by Tecuchev and Stremousov [21] for the calculation of critical temperatures of metals and alloys from the experimental data on sound velocity. The relation could be represented as:

$$T_c = T_f + \frac{T - T_f}{1 - \frac{C^2}{C_f^2}}, \tag{7}$$

where T_f and C_f are the fusion temperature, and the sound velocity at the fusion temperature, respectively. Incorporation of this equality for T_c in Eq. (6) yields:

$$C = \sqrt{C_p\left[\frac{\alpha\rho C_f^2 - B(T - T_f)}{T\alpha^2B(T - T_f) + C_p\alpha\rho}\right]}. \tag{8}$$

It can be seen from above that elimination of T_c in terms of parameters such as T_f and C_f (that are known with a relatively better precision) in Eq. (8), could help in increasing the degree of accuracy of the values of sonic velocity estimated by the IPA formalism. However, it should again be emphasized that the errors will continue to be large if the density and heat capacity data reported in limited temperature ranges were extrapolated over an extended regime. Moreover, the value of B is still dependent on the choice of critical temperature. Keeping this in view, a consistent set of density and heat capacity data up to 8000 K, reported by Ronchi et al. [2] has been used in the present work to compute the sound velocity and its temperature dependence in molten UO_2. For a ready comparison, the thermophysical data assessed by Argonne National Laboratories' International Nuclear Safety Center [22] were also utilized.

3. Review of the critical temperature data for urania

An exhaustive literature survey shows that several theoretical models have been used to determine or refine the data on critical parameters for UO_2. The models used for establishing an equation of state for UO_2 and other LMFBR fuels are: law of rectilinear diameters (LRD), principles of corresponding states (PCS), significant structure theory (SST), perturbed hard sphere model (PHSM) and molecular dynamics (MD), among many. These have been excellently reviewed by Ohse et al. [23]. Other noteworthy contributions are the mean spherical approximation (MSA) [24], One fluid approximation (OFA) [25] and Debye-Hückel charged sphere approximation (DHCSA) [26,27]. The values of critical temperature assessed for molten UO_2 by these methods vary from 6744 to 9330 K. According to Robins [28], in some calculations they vary even between 5500 and 10000 K. Using a simplified semi-empirical approach based on a refined Dieterici equation, Dharmadurai [29] suggested a $T_c \approx 7500$ K for UO_2. However, some of these models and calculations have been declared 'unacceptable' by various reviewers, either due to 'the internal inconsistencies' or due to 'the particular application' [10]. In some instances, using input data from two different sources has led to T_c values as different as 6960 and 9332 K, by the same method [30,31]. A value of 10120 K for the critical temperature for uranium dioxide has recently been reported by Iosilevski et al. [32] who used the so-called Chemical (quasi-molecular) Model in their theoretical description of liquid urania. The model is based on a modified Thermodynamic Perturbation Theory (TPT) which takes into account the multi-component nature of the liquid–vapor mixture in the system that essentially consists of chemically reactive, strongly interacting neutral as well as charged molecules, atoms and ions.

The foregoing discussion clearly indicates that despite the use of highly sophisticated models, there is no consensus on the critical temperature data of uranium dioxide in the literature. As a result of this, there is no consistent set for any of the critical parameters (T_c, P_c or ρ_c) for this base nuclear material. The present attempt to compute the sonic velocity in molten UO_2 by using Eq. (8) also suffers from the lack of availability of a reliable critical temperature data. Therefore, for the illustrative purposes, the parameter B was computed by using four different T_c values, viz., 7500, 8000, 8200 and 10000 K in Eq. (6) to emphasize the need for a unique and reliable critical temperature value for urania. The values of T_c chosen here are such that they fall within the range predicted by several models as stated above. The first three T_c values are the ones used by Azad and Ganesan [15] and Azad and Sreedharan [16] in earlier works and were selected for the sake of ready comparison of the patterns in the computed sonic velocity values.

4. Results and discussion

The input data on the heat capacity, density and volume expansion coefficient in molten urania used in the calculation of the sonic velocity as a function of temperature were taken from Ronchi et al. [2] and INSC [22]. These are summarized in Table 1 in parametric forms after the raw data were least-squares fitted. The linear equations given by INSC do not give the quality of fitting in terms of a corresponding correlation factor, R^2; therefore, the raw data were re-fitted with $R^2 = 1$. For the calculations of parameter B, values of 3120 K and 1806 m s^{-1} were used for the melting temperature and the velocity of sound in molten UO_2, respectively.

Fig. 1 is a master plot for the sonic velocity in molten UO_2, using the available data on density, coefficient of volume expansion and heat capacity from different sources listed in Table 1. Curves A, B, C and D were obtained by using the experimental data reported by Ronchi et al. [2] in Eq. (6) with T_c values of 7500, 8000, 8200 and 10000 K, respectively. As mentioned in the earlier section, the parameter B is dependent on the choice of critical temperature used in Eq. (6), which in each case was computed by using a solitary value of sound velocity in UO_2 (l) at its melting point (Table 1(d)). Curves E, F, G and H represent the temperature dependence of sonic velocity in molten UO_2 obtained by using Eq. (8) with input data from Ronchi et al. [2]. Curves I through L represent the sound velocity obtained by employing the heat capacity, density and thermal expansion coefficient data recommended by INSC [22] in Eq. (8), (see Table 1).

The values of the B parameter used to compute the sound velocities represented by the curves E and I are identical to that for A, for the curves F and J are identical to that for B, for the curves G and K are identical to that for C and, for the curves H and L are same as that for the curve D. The values are listed in Table 2.

Table 1
Heat capacity, density and volume expansion coefficient for UO_2 (l)

	Temperature range T (K)	Refs.
(a) Heat capacity ($J\,kg^{-1}\,K^{-1}$)		
$C_p=$		
$277+\frac{1.1\times10^{7}}{T^{2}}\exp\left(\frac{15\,500\pm1000}{T}\right)+\frac{1.0\times10^{12}}{T^{2}}\exp\left(-\frac{35\,500\pm4000}{T}\right)$	3100–8200	[2]
$2170.5-0.7886T+7.0\times10^{-5}T^{2}$	3120–4500	[22][a]
(b) Density ($kg\,m^{-3}$)		
$\rho=$		
$10\,970/[1+9.30\times10^{-5}(T-273)]$	3100–7400	[2]
$10\,883-0.8066T+3.0856\times10^{-5}T^{2}$	3100–7400	[2][a]
$11\,757-0.9287T+2.0\times10^{-8}T^{2}$	3120–7600	[22][a]
(c) Volume expansion coefficient (K^{-1})		
$\alpha\times10^{5}=$		
$7.005+1.5284\times10^{-4}T-4.92\times10^{-8}T^{2}$	3100–7400	[2][a]
$5.6537+0.0023T-4\times10^{-7}T^{2}+4\times10^{-11}T^{3}$	3120–7600	[22][a]
(d) Other parameters		
Melting point of UO_2, T_f	3120 K	[2,22]
Sound velocity in molten UO_2 at the melting point, C_f	1806 m s^{-1}	[5]

[a] Parametric equations were derived by using the tabulated numerical data.

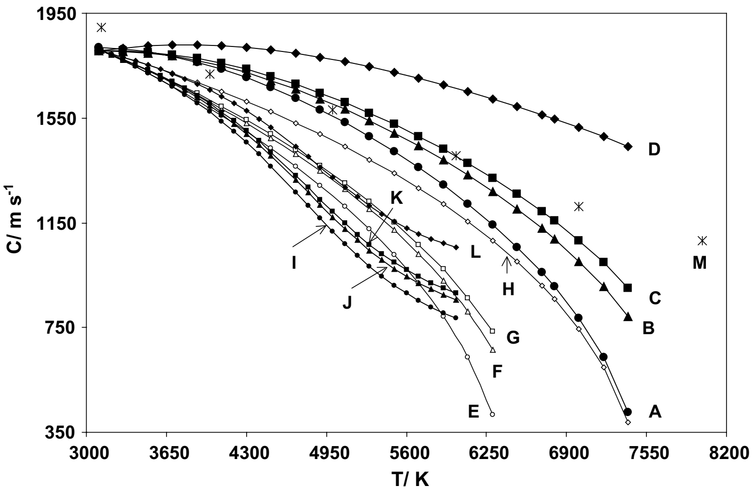

Fig. 1. Sonic velocity profiles in molten uranium dioxide as calculated by using Eqs. (6) and (8) and, the input data from Table 1. $T_c = 7500$ K, for the curves A, E and I; $T_c = 8000$ K for the curves B, F and J; $T_c = 8200$ K, for the curves C, G and K; and $T_c = 10\,000$ K, for the curves D, H and L. (See the text for the curve details).

Table 2
Values of the parameter B derived from Eq. (6) using the T_f and C_f values from Table 1(d)

Density, volume expansion coefficient and heat capacity source	Parameter B (Pa K^{-2}) at T_c (K)			
	7500	8000	8200	10000
[2]	406.1	364.7	350.4	259.0
[22]	533.6	478.9	460.0	339.7

It is evident that the choice of input data (ρ, α and C_p) and the T_c has a direct impact on B values which in turn affect the sonic velocity data presented in Fig. 1. It is interesting to note, however, that while Eq. (6) in conjunction with the experimental data of Ronchi et al. [2] yields the highest sonic velocity values (curves A through D), the scatter is significantly less when Eq. (8) is employed. This is clearly depicted by the curves E through H and I through L, which were constructed from sonic velocity data derived by using input data from Ronchi et al. [2] and INSC [22], respectively, and Eq. (8). In the absence of experimentally determined sonic velocity in molten uranium dioxide over a large temperature range, such comparison might be fortuitous. Least-squares fitted parametric equations (with correlation coefficient ~1) for each of these curves are summarized in Table 3.

The sonic velocity values thus computed are compared individually with those reported earlier by Azad and Sreedharan [16] in Fig. 2. For the sake of clarity of the presentation and better visibility the comparison is presented to Fig. 2(a) through (c). Fischer and Arnecke [34] had employed an equation of state based on the significant structure theory to derive an expression for sonic velocity in single as well as two-phase UO_2, which in turn was originally obtained by Jackson and Nicholson using the code ANLEOS [35]. Their calculation calls for the knowledge of rather complicated functions involving pressure, temperature, isochoric heat capacity and the internal energy, as a function of temperature at saturation line and their derivatives with respect to the reduced density. The temperature dependence of the sonic velocity in molten UO_2 calculated by Azad and Ganesan [15] using the above SST model and various sources of density [11,36–38], is also included in these plots. For an easy comparison, sonic velocity data at four typical temperatures, viz., 3120, 4120, 5020 and 6020 K, as derived from SSTEOS are summarized in Table 4 along with those of Azad and Sreedharan [16] and the present work. An examination of these plots suggests that the agreement of the previously estimated sonic velocity data [15,16] is somewhat better with that derived by employing Eq. (8) rather than (6), in certain temperature range.

Using the data on selected thermodynamic properties (viz., ρ, α, β_T and C_p) compiled by Iosilevski et al. [1] in the range 3120–8000 K for $UO_{2.00}$ along the boiling line, sonic velocity in molten urania was computed by invoking the simple relationship between the isothermal compressibility (β_T, Pa^{-1}) and sonic velocity:

$$\beta_T = \frac{\gamma}{C^2 \rho}. \tag{9}$$

It can be easily shown [33] that:

$$\gamma = \frac{C_p + TC^2\alpha^2}{C^2 \rho C_p}. \tag{10}$$

Thus, Eq. (9) can be simplified as:

$$C = \sqrt{\frac{C_p}{\beta_T \rho C_p - T\alpha^2}}. \tag{11}$$

The results of Eq. (11) are listed in Table 5 and are plotted in Fig. 1 as curve M (asterix). This calculation also allowed the use of Eq. (2) to compute $(P + P_i)/T$ as a function of temperature.

The least-squares fitting method gave the following linear equation to describe the temperature dependence of the curve M in the range $3120\ \text{K} \leqslant T \leqslant 8000\ \text{K}$:

$$C\ (\text{m s}^{-1}) = 2408.2 - 0.1677T. \tag{12}$$

Iterative fitting of the $(P + P_i)/T$ values in the temperature range of 5000–7000 K, yielded the following linear relationship similar to that predicted by the IPAEOS for other liquids [15–20,39,40] and shown in Eq. (4):

Table 3
Parametric equations describing the temperature dependence of the sonic velocity depicted for curve A through I in Fig. 1

Sonic velocity (m s^{-1})	T_c (K)	Comments
$2716.2 - 0.57573T + 1.3641 \times 10^{-4}T^2 - 1.3447 \times 10^{-8}T^3$	7500	[2], Eq. (6), curve A
$1765.0 + 0.036748T + 4.7978 \times 10^{-6}T^2 - 3.6784 \times 10^{-9}T^3$	8000	[2], Eq. (6), curve B
$1588.1 + 0.14867T - 1.8845 \times 10^{-5}T^2 - 1.8335 \times 10^{-9}T^3$	8200	[2], Eq. (6), curve C
$1106.7 + 0.4205T - 7.1358 \times 10^{-5}T^2 + 2.7937 \times 10^{-9}T^3$	10000	[2], Eq. (6), curve D
$4538.7 - 1.7758T + 3.9885 \times 10^{-4}T^2 - 3.4932 \times 10^{-8}T^3$	7500	[2], Eq. (8), curve E
$3310.8 - 0.90366T + 1.9328 \times 10^{-4}T^2 - 1.8441\text{x}\ 10^{-8}T^3$	8000	[2], Eq. (8), curve F
$3075.9 - 0.7390T + 1.5448 \times 10^{-4}T^2 - 1.5231 \times 10^{-8}T^3$	8200	[2], Eq. (8), curve G
$3752.4 - 1.1853T + 2.4226 \times 10^{-4}T^2 - 1.9270 \times 10^{-8}T^3$	10000	[2], Eq. (8), curve H
$5.7656 \times 10^{-8}T^3 - 8.0837 \times 10^{-4}T^2 + 3.3026T - 2407.9$	7500	[22], Eq. (8), curve I
$5.4489 \times 10^{-8}T^3 - 7.6831 \times 10^{-4}T^2 + 3.1695T - 2275.7$	8000	[22], Eq. (8), curve J
$5.4195 \times 10^{-8}T^3 - 7.6486 \times 10^{-4}T^2 + 3.1636T - 2282.1$	8200	[22], Eq. (8), curve K
$4.3546 \times 10^{-8}T^3 - 6.2507 \times 10^{-4}T^2 + 2.6367T - 1675.1$	10000	[22], Eq. (8), curve L

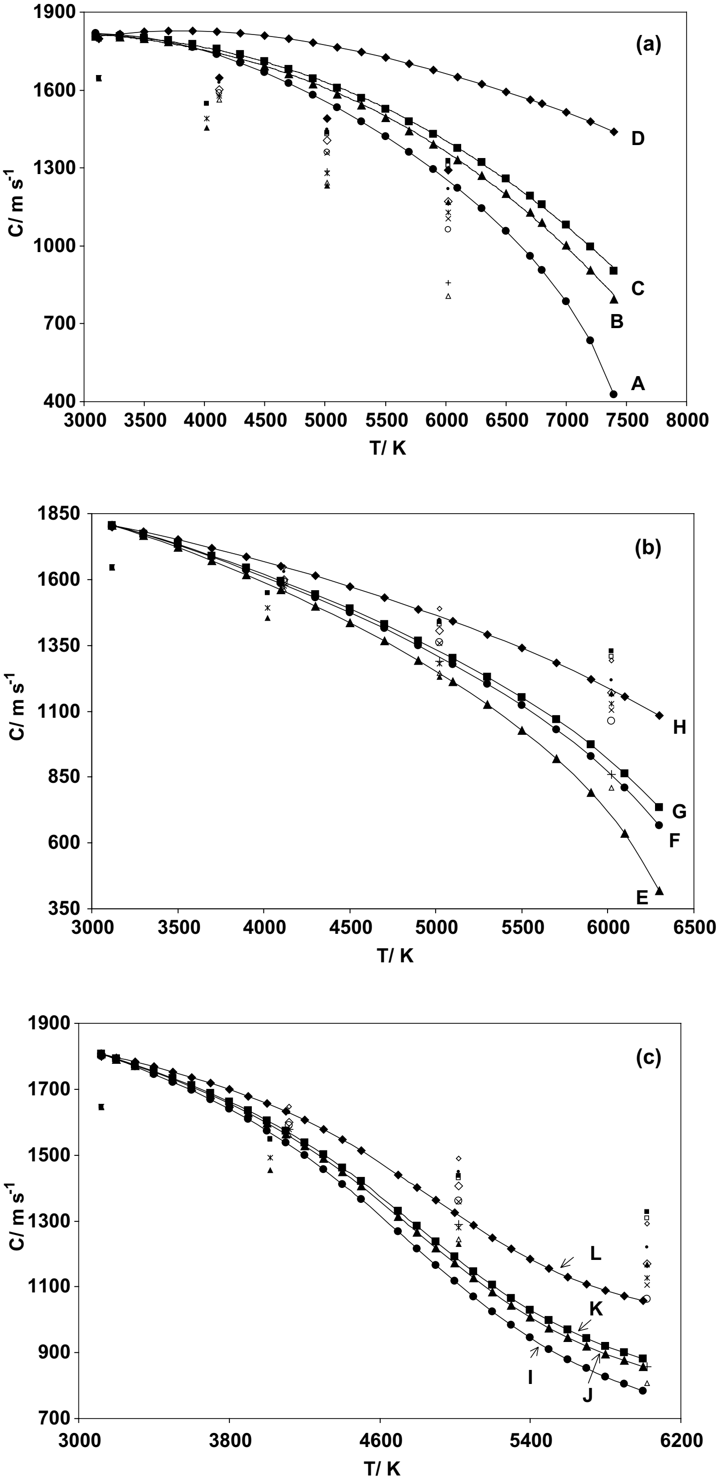

Fig. 2. Sonic velocity profiles in molten UO_2 using: (a) the input data from Ronchi et al. [2] and Eq. (6), (b) the input data from Ronchi et al. [2] and Eq. (8), and (c) the input data from INSC [22] and Eq. (8). Single-valued data points are those predicted by SSTEOS [15] and Azad and Sreedharan [16] and are listed in Table 4 at 3120, 4120, 5020 and 6020 K.

Table 4
Sonic velocity in molten UO_2 from different models

Reference	T_c (K)	C (m s^{-1})			
		3120 K	4120 K	5020 K	6020 K
Curve A	7500	1839.4	1719.3	1562.5	1260.2
Curve B	8000	1814.6	1740.6	1605.0	1357.6
Curve C	8200	1812.1	1752.5	1627.6	1400.1
Curve D	10000	1808.9	1823.3	1772.8	1661.6
Curve E	7500	1829.6	1566.7	1281.5	718.1
Curve F	8000	1812.8	1578.9	1312.3	852.1
Curve G	8200	1811.4	1588.3	1322.3	902.6
Curve H	10000	1827.4	1633.6	1469.6	1192.5
Curve I	7500	1789.5	1524.2	1111.8	778.4
Curve J	8000	1789.0	1551.7	1166.7	848.5
Curve K	8200	1788.9	1559.0	1180.4	867.5
Curve L	10000	1789.3	1623.3	1318.0	1045.4
SSTEOS [15]	–	1645.3	1453.6[a]	1230.2	1168.2
		1647.3	1409.9[a]	1279.8	1127.7
		1646.2	1547.8[a]	1431.0	1308.2
		1646.9	1548.3[a]	1308.2	1328.0
IPAEOS [16]	7500	1798.8	1628.2	1448.1	1219.0
		1798.8	1565.9	1312.6	994.60
		1798.8	1576.9	1358.7	1104.8
		1798.8	1561.5	1244.8	807.80
IPAEOS [16]	8000	1798.8	1646.2	1490.3	1291.7
		1798.8	1589.6	1359.7	1063.8
		1798.8	1600.4	1405.7	1170.3
		1798.8	1578.3	1289.2	858.50

[a] At 4020 K.

Table 5
Selected thermodynamic properties of stoichiometric UO_2 along the boiling line [1]

T (K)	ρ (kg m^{-3})	α (K^{-1})	C_p (J kg^{-1} K^{-1})	β_T (Pa^{-1})	C (m s^{-1})	P (Pa) [1]	P (Pa) [11]
3120	8871	1.09E−04	511.2	3.95E−11	1896.98	3.98E03	3.00E03[a]
4000	8125.7	9.50E−05	399.2	5.29E−11	1716.45	1.47E05	2.50E05
5000	7353.6	1.08E−04	371.8	7.57E−11	1581.52	2.33E06	6.44E06
6000	6533.3	1.34E−04	416.1	1.17E−10	1406.53	2.02E07	6.08E07
7000	5679.7	1.81E−04	524.2	1.97E−10	1211.41	1.12E08	3.20E08
8000	4876.1	2.83E−04	851.7	3.30E−10	1080.32	3.88E08	5.30E08[b]

The sound velocity computed by using these data with the help of Eq. (11) is also listed (column 6). The temperature dependence of the sonic velocity computed from Eq. (11) is shown in Fig. 1 as curve M. Vapor pressures over liquid UO_2 reported in [1,11] are listed in column 7 and 8. (See the text for details).

[a] Calculated from the parametric equation for the vapor pressure over UO_2 (l) from [11].

[b] At 7364.8 K.

$$(P+P_{\mathrm{i}})/T\ (\mathrm{MPa\ K^{-1}}) = 2.6873 - 2.5395\times10^{-4}T. \tag{13}$$

It has been shown elsewhere [20,41] that as the temperature increases, $(P + P_{\mathrm{i}})/T \approx 0$, and $T \to T_{\mathrm{i}}$, so that Eq. (4) could be approximated as:

$$0 = A - BT_{\mathrm{i}} \quad \text{or,} \quad A = BT_{\mathrm{i}} \tag{14}$$

T_{i} is the intercept of the straight line represented by Eq. (4) with the x-axis.

Thus, under such assumption Eq. (13) gives, $T_{\mathrm{i}} = 10582$ K.

Similarly, at the critical temperature, $(P + P_{\mathrm{i}})/T \approx P_{\mathrm{c}}/T_{\mathrm{c}}$, so that:

$$\frac{P_{\mathrm{c}}}{T_{\mathrm{c}}} = A - BT_{\mathrm{c}}. \tag{15}$$

By combining Eqs. (14) and (15), we get:

$$T_{\mathrm{i}} - T_{\mathrm{c}} = \frac{P_{\mathrm{c}}}{BT_{\mathrm{c}}}. \tag{16}$$

Assuming the ideal gas behavior of the UO_2 vapor in the vicinity of the critical temperature, the difference between the intercept (of the line $(P + P_i)/T$ vs. T) T_i and the theoretical critical temperature can be approximately deduced from Eq. (16).

The validity of this model has been verified in the case of LMFBR coolant, viz., sodium [15,17,33], where Eq. (2) yields $T_i = 2652$ K and from Eq. (16), $T_i - T_c \sim 18$ K. However, at the critical point, for a Van der Waals gas, $(P + P_i)/T = 4P_c/T_c$ is a more reasonable correction. Incorporating this, the value of T_c for liquid sodium then works out to be 2581 K ($4P_c/T_c \sim 71$ K) which compares well with a T_c value of 2634 K assuming a Van der Waals gas behavior for sodium vapors in the critical region. The theoretically estimated values of T_c for sodium are in excellent agreement with the experimental values as well. Fink and Leibowitz [42] have recently tabulated the critical temperature values for sodium that range from 2485 to 2573 K; the recommended T_c value for sodium is 2503.7 ± 12 K. It is worth pointing out that in the case of the first five alkali metals (Li to Cs) the scatter ($T_i - T_c$) was found to be 21 ± 2 K [20]. It was mentioned earlier that while solid UO_2 has a pure ionic character consisting of U^{+n} and O^{-2} ions, it displays highly ionized ionic character in liquid state and a weakly ionized (or neutral) molecular character in the gas phase. Such behavior is akin to that observed in alkali metal melts where the M^+ ions are embedded in a free flowing electron well. Hence, the application of the methodology to the molten urania seems valid.

As stated in the previous section, the uncertainty with regard to the critical pressure is as large as for the critical temperature in the case of UO_2 (*l*). Hence, it is rather difficult to validate Eq. (16) by selecting a P_c value randomly. However, by extending the trend observed in liquid sodium and other alkali metals to liquid uranium dioxide, and assuming $T_i - T_c \sim 4 \times (20\ \text{K})$, T_c was computed as $T_c = T_i - 80 = 10582 - 80 \approx 10500$ K. This estimation is in fair agreement with a value of 10120 K, recently predicted by Iosilevski et al. and Gryaznov et al. [1,25] for the critical temperature of UO_2 (*l*). This agreement demonstrates that the extension and incorporation of the above assumption in our critical temperature calculation is valid, since the estimated value is quite close (within 3.6%) to the recently reported value from an independent and different model. At the same time, it is not outrageously different from the spectrum of data available in the literature on this property of UO_2 (*l*).

By introducing the estimated critical temperature of molten uranium dioxide in Eq. (15), the critical pressure (P_c) is found to be 219 MPa which is in good agreement with the upper limit of the estimates ranging between 100 and 240 MPa [10,29,31]. Iosilevski et al. and Gryaznov et al. [1,25] on the other hand, have reported a value of 965 MPa based on their equation of state calculations. It should be pointed out that the vapor pressure data reported by Iosilevski et al. [1] is somewhat different from that reported by Finn et al. [11]. It is likely that the much exaggerated value of P_c derived by them is due to this difference in the vapor pressure data, though the authors [1] have not commented on this inconsistency. For a ready comparison, the vapor pressures over liquid UO_2 reported by these researchers are summarized in Table 5 (column 7 and 8).

Using the widely accepted value of the compressibility factor Z_c (~0.27) and other critical parameters, viz., critical temperature and critical pressure derived in this work for liquid urania in the equation, $Z_c = \frac{P_c V_c}{R T_c}$, the critical density ρ_c for UO_2 was calculated to be 2510 kg m^{-3}. This is in excellent agreement with the value of 2610 kg m^{-3} predicted by Iosilevski et al. and Gryaznov et al. [1,25]. Fischer et al. [31] have compared the critical constants for UO_2 evaluated by different authors and find that the critical temperature ranges between 6960 and 9330 K ($T_{c,\text{average}} \sim 8043$ K), critical pressure between 123 and 201 MPa ($P_{c,\text{average}} \sim 149$ MPa) and critical density between 1630 and 3160 kg m^{-3} ($\rho_{c,\text{average}} \sim$ 2120 kg m^{-3}).

5. Conclusions

The speed of ultrasound waves in molten uranium oxide was recalculated by employing recent and more accurate set of physical properties of liquid urania, and using a simple equation of state based on the concept of internal pressure in liquids. The sonic velocity was dependent on the value of the parameter B whose determination relies on the choice of critical temperature of the system. Substitution of critical temperature with a more accurately known quantity (melting point) appears to yield data that are in better conformity with one another as well as with those predicted by other models. The IPAEOS was also utilized to compute the critical parameters for UO_2 (*l*). The predicted critical parameters are: $T_c \sim 10500$ K, $P_c \sim 219$ MPa and $\rho_c \sim$ 2510 kg m^{-3}.

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