Int J Thermophys (2015) 36:2705–2719
DOI 10.1007/s10765-015-1982-4

Polylogarithmic Representation of Radiative and Thermodynamic Properties of Thermal Radiation in a Given Spectral Range: II. Real-Body Radiation

Anatoliy I. Fisenko[1] · **Vladimir Lemberg**[1]

Received: 4 June 2015 / Accepted: 25 September 2015 / Published online: 13 October 2015

Abstract There are several classes of materials and space objects for which the frequency dependence of the spectral emissivity is represented as a power series. Therefore, the study of the properties of thermal radiation for these real bodies is an important task for both fundamental science and industrial applications. The general analytical expressions for the thermal radiative and thermodynamic functions of a real body are obtained in a finite range of frequencies at different temperatures. The Stefan–Boltzmann law, total energy density, number density of photons, Helmholtz free energy density, internal energy density, enthalpy density, entropy density, heat capacity at constant volume, pressure, and total emissivity are expressed in terms of the polylogarithm functions. The obtained general expressions for the thermal radiative and thermodynamic functions are applied for the study of thermal radiation of liquid and solid zirconium carbide. These functions are calculated using experimental data for the frequency dependence of the normal spectral emissivity in the visible and near-infrared range at the melting (freezing) point. The gaps between the thermal radiative and thermodynamic functions of liquid and solid zirconium carbide are observed. The general analytical expressions obtained can easily be presented in the wavenumber domain.

Keywords Emissivity · Finite frequency range · Liquid and solid zirconium carbide · Melting (freezing) temperature · Polylogarithms · Stefan-Boltzmann law · Thermodynamic functions

✉ Anatoliy I. Fisenko
afisenko@oncfec.com

1 ONCFEC Inc., 250 Lake Street, Suite 909, St. Catharines, ON L2R 5Z4, Canada

1 Introduction

It is well known that a knowledge of the spectral emissivity is necessary to measure the true temperature of a real body using non-contact optical devices [1–3]. Therefore, a great number of experimental studies have been focused on the measurement of spectral emissivity $\varepsilon(v, T)$ for various materials [4–18].

Multiwavelength emissivity models to determine the surface temperature of a real body were proposed in [19,20]. Two of the most important emissivity models are the following: (a) linear emissivity model (LEM) [21–25] and (b) log-linear emissivity model (LLE) [26–29]. The true temperature of a real body can be measured using optical multispectral radiation thermometers in conjunction with a multiwavelength emissivity model. There are other emissivity models that are based on fundamental physical principals. Such models are Maxwell, Hagen-Ruben, and Edwards [30,31].

A non-contact method for the determination of the true temperature of a real body from the "generalized" Wien's displacement law was proposed in [32–34]. The method was proven on the spectra of the thermal radiation of tungsten, tantalum, and luminous flames. The accuracy in the determination of the steady-state temperature in these cases does not exceed 2 %. Another method for representing the "generalized" Wien displacement law in terms of the logarithmic frequency or wavelength scale is proposed in [35].

It is important to note that a knowledge of the frequency dependence of the spectral emissivity also allows determination of the thermal radiative and thermodynamic properties of a real body within a finite range of frequencies. In [36–38], the thermal radiative and thermodynamic properties of materials have been studied using spectral emissivity data presented in tabular form. These materials are (a) hafnium, zirconium, and titanium carbides; (b) ZrB_2-SiC-based ultra-high temperature ceramics; and (c) molybdenum. The Helmholtz free energy density, internal energy density, enthalpy density, entropy density, heat capacity at constant volume, pressure, and the total emissivity were calculated numerically.

In [39], it was pointed out that there are several classes of materials and space objects, for which the thermal radiative and thermodynamic properties can be described within a finite spectral range of frequencies using the polylogarithms functions. This means that the frequency dependence of $\varepsilon(\nu, T)$ should be represented as a polynomial. Some of these materials and space objects are (a) zirconium, uranium, and plutonium carbides at their melting (freezing) points [40,41]; (b) noble metals at the melting temperatures [42]; (c) Fe, Co, and Ni at the melting points [43]; (d) Milky Way and other galaxies [44–46]; and others. It is essential to note that the thermal radiative and thermodynamic properties of these real bodies having emitted continuous spectra that can be calculated analytically.

In this paper, the general analytical expressions for the thermal radiative and thermodynamic functions of a real body are obtained using the frequency dependence of the spectral emissivity in the form $\varepsilon(v, T) = \sum_{i=-3}^{\infty} a_i(T)v^i$. The expressions for the Stefan–Boltzmann law, total energy density, number density of photons, Helmholtz free energy density, internal energy density, enthalpy density, entropy density, heat capacity at constant volume, total emissivity, and pressure in a finite spectral range of frequencies are expressed in terms of the polylogarithm functions. This polylogarithmic representation allows us to calculate the thermal radiative and thermodynamic properties of a real body analytically. As an example, a study of the thermal radiative and thermodynamic properties of solid and liquid zirconium carbide is performed in detail. These properties are calculated using experimental data for the normal spectral emissivity in the spectral range $0.333\ \text{PHz} \le \nu \le 0.545\ \text{PHz}$ at a melting (freezing) temperature $T = 3155$ K.

2 General Relationships for Thermal Radiative and Thermodynamic Properties of a Real Body

The radiant spectral density of a real body having emitted continuous spectra can be presented in the form,

$$I(\nu, T) = \varepsilon(\nu, T)\, I^{\mathrm{P}}(\nu, T), \tag{1}$$

where $\varepsilon(\nu, T)$ is the spectral emissivity and $I^{\mathrm{P}}(\nu, T)$ at temperature T is given by the Planck law [47]:

$$I^{\mathrm{P}}(\nu, T) = \frac{8\pi h}{c^3} \frac{\nu^3}{\mathrm{e}^{\frac{h\nu}{k_{\mathrm{B}}T}} - 1}. \tag{2}$$

Using the expression for the polylogarithm function of zero order ($\mathrm{Li}_0(x) = \frac{x}{1-x}$, $|x| < 1$, [48]), Eq. 2 can be written as

$$I^{\mathrm{P}}(\nu, T) = \frac{8\pi h \nu^3}{c^3} \mathrm{Li}_0\left(\mathrm{e}^{-\frac{h\nu}{k_{\mathrm{B}}T}}\right). \tag{3}$$

Let us present the frequency dependence of the spectral emissivity of a real body as a polynomial

$$\varepsilon(\nu, T) = \sum_{i=-3}^{\infty} a_i(T)\nu^i, \tag{4}$$

where a_i are the coefficients.

The total energy density of thermal radiation of a real-body surface in the finite frequency range of the spectrum is defined as

$$I(\nu_1, \nu_2, T) = \frac{8\pi h}{c^3} \int_{\nu_1}^{\nu_2} \nu^3 \varepsilon(\nu, T)\, \mathrm{Li}_0\left(\mathrm{e}^{-\frac{h\nu}{k_{\mathrm{B}}T}}\right) \mathrm{d}\nu. \tag{5}$$

Using the relationship between the total energy density (Eq. 5) and the total radiation power per unit area $I^{\mathrm{SB}} = \frac{c}{4} I$, the Stefan–Boltzmann law in the finite frequency range of the spectrum takes the form,

$$I^{\mathrm{SB}}(\nu_1, \nu_2, T) = \frac{2\pi h}{c^2} \int_{\nu_1}^{\nu_2} \nu^3 \varepsilon(\nu, T)\, \mathrm{Li}_0\left(\mathrm{e}^{-\frac{h\nu}{k_{\mathrm{B}}T}}\right) \mathrm{d}\nu. \tag{6}$$

The total emissivity is represented as

$$\varepsilon(v_1, v_2, T) = \frac{I(v_1, v_2, T)}{I^{\mathrm{BB}}(v_1, v_2, T)}, \tag{7}$$

where

$$I^{\mathrm{BB}}(v_1, v_2, T) = \frac{48\pi (k_{\mathrm{B}} T)^4}{c^3 h^3} [P_3(x_1) - P_3(x_2)] \tag{8}$$

is the total energy density of blackbody surface radiation in the finite frequency range of the spectrum [49]. Here $x = \frac{hv}{k_{\mathrm{B}} T}$ and $P_3(x)$ is defined as

$$P_3(x) = \sum_{s=0}^{3} \frac{(x)^s}{s!} \mathrm{Li}_{4-s}(\mathrm{e}^{-x}), \tag{9}$$

where

$$\mathrm{Li}_{4-s}(\mathrm{e}^{-x}) = \sum_{k=1}^{\infty} \frac{\mathrm{e}^{-kx}}{k^{4-s}}, \left|\mathrm{e}^{-kx}\right| < 1 \tag{10}$$

is the polylogarithm function of the order $4 - s$ [48].

According to [47], the number density of photons of thermal radiation of a real body with a photon energy from hv_1 to hv_2 is represented in the form,

$$n = \frac{8\pi}{c^3} \int_{v_1}^{v_2} \varepsilon(v, T) v^2 \mathrm{Li}_0 \left(\mathrm{e}^{-\frac{hv}{k_{\mathrm{B}} T}}\right) \mathrm{d}v. \tag{11}$$

The Helmholtz free energy density of thermal radiation of a real body in the finite frequency range of the spectrum is defined as [47]

$$f(v_1, v_2, T) = \frac{8\pi k_{\mathrm{B}}}{c^3} \int_{v_1}^{v_2} v^2 \varepsilon(v, T) \ln \left(1 - \mathrm{e}^{-\frac{hv}{k_{\mathrm{B}} T}}\right) \mathrm{d}v. \tag{12}$$

The thermodynamic functions of thermal radiation of a real body in a finite range of frequencies are defined by the following expressions [47]:

(1) Entropy density $s = \frac{S}{V}$:

$$s = -\frac{\partial f}{\partial T}; \tag{13}$$

(2) Heat capacity at constant volume per unit volume $c_v = \frac{C_v}{V}$:

$$c_v = \left(\frac{\partial I(v_1, v_2 T)}{\partial T}\right)_V; \tag{14}$$

(3) Pressure of photons per volume $p = \frac{P}{V}$:

$$p = -f. \tag{15}$$

3 Polylogarithmic Representation of Thermal Radiative Properties of a Real-Body

To compute the total energy density for a given temperature over the finite frequency range of the spectrum, it is necessary to compute the integral in Eq. 5. In accordance with Eq. 4, the integral can be integrated by parts to give

$$I(v_1, v_2, T) = \frac{8\pi (k_B T)^4}{c^3 h^3} \sum_{i=-3}^{\infty} a_i (3+i)! \left(\frac{k_B T}{h}\right)^i A_i(x_1, x_2), \tag{16}$$

where

$$A_i(x_1, x_2) = P_{3+i}(x_1) - P_{3+i}(x_2). \tag{17}$$

Here $x = \frac{hv}{k_B T}$ and $P_{3+i}(x)$ is defined as

$$P_{3+i}\,(x) = \sum_{s=0}^{3+i} \frac{(x)^s}{s!} \mathrm{Li}_{4+i-s}(\mathrm{e}^{-x}), \tag{18}$$

where

$$\mathrm{Li}_{4+i-s}(\mathrm{e}^{-x}) = \sum_{k=1}^{\infty} \frac{\mathrm{e}^{-kx}}{k^{4+i-s}}, \; \left|\mathrm{e}^{-kx}\right| < 1 \tag{19}$$

is the polylogarithm function of the order $4+i-s$ [48].

In accordance with Eq. 6, the Stefan–Boltzmann law in the finite frequency range of the spectrum takes the form,

$$I^{\mathrm{SB}}(v_1, v_2, T) = \frac{2\pi (k_B T)^4}{c^2 h^3} \sum_{i=-3}^{\infty} a_i (3+i)! \left(\frac{k_B T}{h}\right)^i \left[P_{3+i}(x_1) - P_{3+i}(x_2)\right] \quad . \tag{20}$$

The total radiation power I_{total} emitted by a heated surface area S of a real body is defined as

$$I_{\mathrm{total}} = S I^{\mathrm{SB}}(v_1, v_2, T). \tag{21}$$

In accordance with Eqs. 7, 8, 16, and 17, the total emissivity can be presented in the form,

$$\varepsilon(v_1, v_2, T) = \frac{\sum_{i=-3}^{\infty} a_i(T)(3+i)! \left(\frac{k_B T}{h}\right)^i \left[P_{3+i}(x_1) - P_{3+i}(x_2)\right]}{6[P_3(x_1) - P_3(x_2)]} \quad . \tag{22}$$

Using Eq. 4 and after computing the integral in Eq. 11, the polylogarithmic representation of the number density of photons of thermal radiation of a real body can be written as

$$n = \frac{8\pi}{c^3} \sum_{i=-2}^{\infty} a_i \left(\frac{k_\mathrm{B} T}{h}\right)^{3+i} (2+i)! B_i(x_1, x_2), \tag{23}$$

where

$$B_i(x_1, x_2) = P_{2+i}(x_1) - P_{2+i}(x_2). \tag{24}$$

In conclusion of this paragraph, it is essential to note that the analytical expressions obtained above in the case of blackbody radiation, when $a_i = 0$ and $a_0 = 1$, take well-known expressions [47].

4 Thermodynamics of Real-Body Thermal Radiation

After computing the integral in Eq. 12, the general expressions for the thermodynamic functions of thermal radiation of a real body can be expressed in terms of the polylogarithm functions as follows:

(1) Helmholtz free energy density f:

$$f = -\frac{8\pi k_\mathrm{B}^4}{c^3 h^3} T^4 \sum_{i=-2}^{\infty} a_i (2+i)! \left(\frac{k_\mathrm{B} T}{h}\right)^{i} C_i(x_1, x_2), \tag{25}$$

where

$$C_i(x_1, x_2) = \left\{ \left[P_{3+i}(x_1) - P_{3+i}(x_2)\right] - \frac{1}{(3+i)!} \left(x_1^{3+i} \mathrm{Li}_1(\mathrm{e}^{-x_1}) - x_2^{3+i} \mathrm{Li}_1(\mathrm{e}^{-x_2})\right) \right\}. \tag{26}$$

(2) Entropy density s:

$$s = \frac{8\pi k_\mathrm{B}^4}{c^3 h^3} T^3 \sum_{i=-2}^{\infty} a_i \left(\frac{k_\mathrm{B} T}{h}\right)^{i} (2+i)!(4+i) D_i(x_1, x_2), \tag{27}$$

where

$$D_i(x_1, x_2) = \left\{ \left[P_{3+i}(x_1) - P_{3+i}(x_2)\right] - \frac{1}{(4+i)!} \left[x_1^{3+i} \mathrm{Li}_1(\mathrm{e}^{-x_1}) - x_2^{3+i} \mathrm{Li}_1(\mathrm{e}^{-x_2})\right] \right\}. \tag{28}$$

(3) Heat capacity at constant volume per volume, c_V:

$$c_V = \frac{8\pi k_\mathrm{B}^4}{c^3 h^3} T^3 \sum_{i=-2}^{\infty} a_i \left(\frac{k_\mathrm{B}}{h}\right)^{i} T^i (4+i)! E_i(x_1, x_2), \tag{29}$$

where

$$
\begin{aligned}
&E_i(x_1, x_2) \\
&\quad = \left\{ \left[P_{3+i}(x_1) - P_{3+i}(x_2) \right] + \frac{1}{(4+i)!} \left[x_1^{4+i} \mathrm{Li}_0(\mathrm{e}^{-x_1}) - x_2^{4+i} \mathrm{Li}_0(\mathrm{e}^{-x_2}) \right] \right\}.
\end{aligned} \tag{30}
$$

(4) Pressure p:

$$
p = \frac{8\pi k_\mathrm{B}^4}{c^3 h^3} T^4 \sum_{i=-2}^{\infty} a_i (2+i)! \left(\frac{k_\mathrm{B} T}{h} \right)^i C_i(x_1, x_2), \tag{31}
$$

where

$$
\begin{aligned}
&C_i(x_1, x_2) \\
&\quad = \left\{ \left[P_{3+i}(x_1) - P_{3+i}(x_2) \right] - \frac{1}{(3+i)!} \left(x_1^{3+i} \mathrm{Li}_1(\mathrm{e}^{-x_1}) - x_2^{3+i} \mathrm{Li}_1(\mathrm{e}^{-x_2}) \right) \right\} .
\end{aligned} \tag{32}
$$

By definition [47], $f = u - Ts$, (where u is the internal energy density), we obtain the analytical expression for u,

$$
\begin{aligned}
u(x_1, x_2, T) &= f + Ts \\
&= \frac{8\pi (k_\mathrm{B} T)^4}{c^3 h^3} \sum_{i=-3}^{\infty} a_i (3+i)! \left(\frac{k_\mathrm{B} T}{h} \right)^i A_i(x_1, x_2),
\end{aligned} \tag{33}
$$

where $A(x_1, x_2)$ is defined by Eq. 17.

The enthalpy density h follows from its definition, $h = u + p$, giving

$$
h(x_1, x_2, T) = \frac{8\pi k_\mathrm{B}^4}{c^3 h^3} T^4 \sum_{i=-2}^{\infty} a_i \left(\frac{k_\mathrm{B} T}{h} \right)^i (2+i)!(4+i) D_i(x_1, x_2). \tag{34}
$$

The Gibbs free energy density g, by definition, is $h - Ts$, thus

$$
g(x_1, x_2, T) = 0. \tag{35}
$$

This result coincides with the result obtained for the blackbody radiation [47]. This mean, that the normal spectral emissivity of a real body has no thermodynamic effect on the Gibbs free energy.

The chemical potential density $\mu = \left(\frac{\partial g}{\partial n} \right)_{T,V}$, as seen from Eq. 35, is zero

$$
\mu(x_1, x_2, T) = 0. \tag{36}
$$

It is not difficult to show that Eqs. 16, 20, 23, 25, 27, 29, 31, 33, and 34 in the semi-infinite range of frequencies, when $\varepsilon(v, T) = 1$, take the well-known expressions for the thermal radiative and thermodynamic functions of blackbody radiation [47].

In conclusion, it should be noted that the obtained analytical expressions for the thermal radiative and thermodynamic functions of a real body in a finite range of frequencies can easily be presented in the wavenumber ($\tilde{v}$) domain. In this case, we should use the following relationships [50]:

$$v = c\tilde{v} \tag{37}$$

$$\mathrm{d}v = c\mathrm{d}\tilde{v} \tag{38}$$

$$\int_{v_1}^{v_2} I^{\mathrm{P}}(v, T)\mathrm{d}v = \int_{\tilde{v}_1}^{\tilde{v}_2} I^{\mathrm{P}}(\tilde{v}, T)\mathrm{d}\tilde{v}. \tag{39}$$

Note that using different spectral units produces the same result, because it represents the same physical quantity.

5 Thermal Radiative and Thermodynamic Properties of Liquid and Solid Zirconium Carbide

Now let us consider an example related to the study of the thermal radiative and thermodynamic properties of liquid and solid zirconium carbide using experimental data for the normal spectral emissivity in the visible and near-infrared range at melting/freezing temperature.

It is well known that the rapid development of space and missile technologies requires ultra-high temperature ceramics with the melting temperature up to 4273 K [51,52]. Zirconium carbide is a good candidate material for using it in environments with extreme temperatures. Applications of ZrC are (a) nuclear fuel coating in high temperature Generation IV reactors [53]; (b) thermal shield in aerospace applications [54]; (c) solar energy receiver with low emissivity and high absorptivity [55]; etc. Thus, the investigation of the thermal radiative and thermodynamic properties of zirconium carbide under extreme conditions is a research domain of great interest both for basic science and industrial applications.

In [41], the radiance spectra of zirconium carbide were measured in the frequency range (0.333 PHz $\leq v \leq$ 0.545 PHz) at temperature $T = 3155$ K during the melting and freezing arrests while cooling and heating the samples. The measured normal spectral emissivity of solid and liquid zirconium carbide is approximated by the following analytical expression:

$$\varepsilon(\nu, T) = \sum_{i=-2}^{0} \tilde{a}_i v^i = \tilde{a}_0 + \tilde{a}_{-1}\nu^{-1} + \tilde{a}_{-2}\nu^{-2}, \tag{40}$$

where

$$\begin{aligned}\text{Solid ZrC: } \tilde{a}_0 = 0.6968;\ \tilde{a}_{-1} = -8.2503 \times 10^{13}\ \text{Hz};\\ \tilde{a}_{-2} = 1.4739 \times 10^{28}\ \text{Hz}^2\end{aligned} \tag{41}$$

$$\text{Liquid ZrC: } \tilde{a}_0 = 0.86663;\ \tilde{a}_{-1} = -2.6018 \times 10^{14}\ \text{Hz};$$
$$\tilde{a}_{-2} = 4.4587 \times 10^{28}\ \text{Hz}^2. \tag{42}$$

The gap between the normal spectral emissivity of solid and liquid ZrC is observed in the spectral frequency range from 0.333 PHz to 0.545 PHz [41]. The normal spectral emissivity of both solid and liquid zirconium carbide increases with increasing v.

Using the general expressions for the thermal radiative and thermodynamic functions of a real-body obtained above and Eq. 40, in the case of zirconium carbide, we obtain

(1) The total energy density in the finite frequency range of the spectrum:

$$I = \tilde{a}_0 I_0 + \tilde{a}_{-1} I_{-1} + \tilde{a}_{-2} I_{-2}, \tag{43}$$

where

$$I_0 = \frac{48\pi (k_\mathrm{B}T)^4}{c^3h^3}\left[P_3(x_1) - P_3(x_2)\right], \tag{44}$$
$$I_{-1} = \frac{16\pi (k_\mathrm{B}T)^3}{c^3h^2}\left[P_2(x_1) - P_2(x_2)\right], \tag{45}$$
$$I_{-2} = \frac{8\pi (k_\mathrm{B}T)^2}{c^3h}\left[P_1(x_1) - P_1(x_2)\right]. \tag{46}$$

(2) The total radiation power per unit area in the finite frequency range (Stefan–Boltzmann law):

$$I^{\mathrm{SB}} = \tilde{a}_0 I_0^{\mathrm{SB}} + \tilde{a}_{-1} I_{-1}^{\mathrm{SB}} + \tilde{a}_{-2} I_{-2}^{\mathrm{SB}}, \tag{47}$$

where

$$I_0^{\mathrm{SB}} = \frac{12\pi (k_\mathrm{B}T)^4}{c^2h^3}\left[P_3(x_1) - P_3(x_2)\right], \tag{48}$$
$$I_{-1}^{\mathrm{SB}} = \frac{4\pi (k_\mathrm{B}T)^3}{c^2h^2}\left[P_2(x_1) - P_2(x_2)\right], \tag{49}$$
$$I_{-2}^{\mathrm{SB}} = \frac{2\pi (k_\mathrm{B}T)^2}{c^2h}\left[P_1(x_1) - P_1(x_2)\right]. \tag{50}$$

(3) Total emissivity:

$$\varepsilon(v_1, v_2, T) = \frac{\tilde{a}_0 I_0 + \tilde{a}_{-1} I_{-1} + \tilde{a}_{-2} I_{-2}}{I^{\mathrm{BB}}(v_1, v_2, T)}. \tag{51}$$

$I^{\mathrm{BB}}(v_1, v_2, T)$ is determined by Eq. 8.

(4) Number density of photons with a photon energy from hv_1 to hv_2:

$$n = \tilde{a}_0 n_0 + \tilde{a}_{-1} n_{-1} + \tilde{a}_{-2} n_{-2}. \tag{52}$$

where

$$n_0 = \frac{16\pi k_{\mathrm{B}}^3}{c^3 h^3} T^3 \left\{[P_2(x_1) - P_2(x_2)]\right\}, \tag{53}$$

$$n_{-1} = \frac{8\pi k_{\mathrm{B}}^2}{c^3 h^2} T^2 \left\{[P_1(x_1) - P_1(x_2)]\right\}, \tag{54}$$

$$n_{-2} = \frac{8\pi k_{\mathrm{B}}}{c^3 h} T \left\{[P_0(x_1) - P_0(x_2)]\right\}. \tag{55}$$

(5) Helmholtz free energy density f:

$$f = \tilde{a}_0 f_0 + \tilde{a}_{-1} f_{-1} + \tilde{a}_{-2} f_{-2}, \tag{56}$$

where

$$f_0 = -\frac{16\pi k_{\mathrm{B}}^4}{c^3 h^3} T^4 \left\{[P_3(x_1) - P_3(x_2)] - \frac{1}{6}\left(x_1^3 \mathrm{Li}_1(\mathrm{e}^{-x_1}) - x_2^3 \mathrm{Li}_1(\mathrm{e}^{-x_2})\right)\right\}, \tag{57}$$

$$f_{-1} = -\frac{8\pi k_{\mathrm{B}}^3}{c^3 h^2} T^3 \left\{[P_2(x_1) - P_2(x_2)] - \frac{1}{2}\left(x_1^2 \mathrm{Li}_1(\mathrm{e}^{-x_1}) - x_2^2 \mathrm{Li}_1(\mathrm{e}^{-x_2})\right)\right\}, \tag{58}$$

$$f_{-2} = -\frac{8\pi k_{\mathrm{B}}^2}{c^3 h} T^2 \left\{[P_1(x_1) - P_1(x_2)] - \left(x_1 \mathrm{Li}_1(\mathrm{e}^{-x_1}) - x_2 \mathrm{Li}_1(\mathrm{e}^{-x_2})\right)\right\}. \tag{59}$$

(6) Entropy density s:

$$s = \tilde{a}_0 s_0 + \tilde{a}_{-1} s_{-1} + \tilde{a}_{-2} s_{-2}, \tag{60}$$

where

$$s_0 = \frac{64\pi k_{\mathrm{B}}^4}{c^3 h^3} T^3 \left\{[P_3(x_1) - P_3(x_2)] - \frac{1}{24}\left(x_1^3 \mathrm{Li}_1(\mathrm{e}^{-x_1}) - x_2^3 \mathrm{Li}_1(\mathrm{e}^{-x_2})\right)\right\}, \tag{61}$$

$$s_{-1} = \frac{24\pi k_{\mathrm{B}}^3}{c^3 h^2} T^2 \left\{[P_2(x_1) - P_2(x_2)] - \frac{1}{6}\left(x_1^2 \mathrm{Li}_1(\mathrm{e}^{-x_1}) - x_2^2 \mathrm{Li}_1(\mathrm{e}^{-x_2})\right)\right\}, \tag{62}$$

s

$$s_{-2} = \frac{16\pi k_{\mathrm{B}}^2}{c^3 h} T \left\{[P_1(x_1) - P_1(x_2)] - \frac{1}{2}\left(x_1 \mathrm{Li}_1(\mathrm{e}^{-x_1}) - x_2 \mathrm{Li}_1(\mathrm{e}^{-x_2})\right)\right\}. \tag{63}$$

(7) Heat capacity at constant volume per unit volume c_V:

$$c_V = \tilde{a}_0 c_{V_0} + \tilde{a}_{-1} c_{V_{-1}} + \tilde{a}_{-2} c_{V_{-2}}, \tag{64}$$

Table 1 Calculated values of the thermal radiative and thermodynamic functions of thermal radiation of solid and liquid zirconium carbide emitted by a heated surface per unit area of the sample in the finite frequency range 0.333 PHz $\leq \upsilon \leq$ 0.545 PHz at the eutectic temperature 3155 K

Quantity	Zirconium carbide		Gaps between solid and liquid phases
	Solid phase	Liquid phase	
$I(\nu_1, \nu_2, T)$ (J·m^{-3})	8.968×10^{-3}	7.675×10^{-3}	1.23×10^{-3}
$I^{SB}(\nu_1, \nu_2, T)$ (W·m^{-2})	6.721×10^{5}	5.753×10^{5}	0.968×10^{5}
ε	0.584	0.500	0.084
f (J·m^{-3})	-1.743×10^{-3}	-2.167×10^{-3}	0.424×10^{-3}
s (J·m^{-3}·K^{-1})	3.869×10^{-6}	3.528×10^{-6}	0.341×10^{-6}
p (J·m^{-3})	1.743×10^{-3}	2.167×10^{-3}	-0.424×10^{-3}
c_V (J·m^{-3}·K^{-1})	1.002×10^{-5}	8.965×10^{-6}	1.037×10^{-6}
n (m^{-3})	3.357×10^{16}	2.866×10^{16}	0.491×10^{16}

where

$$c_{V_0} = \frac{192\pi k_B^4}{c^3 h^3} T^3 \left\{ [P_3(x_1) - P_3(x_2)] + \frac{1}{24}\left(x_1^4 \mathrm{Li}_0(\mathrm{e}^{-x_1}) - x_2^4 \mathrm{Li}_0(\mathrm{e}^{-x_2}) \right) \right\}, \tag{65}$$

$$c_{V_{-1}} = \frac{48\pi k_B^3}{c^3 h^2} T^2 \left\{ [P_2(x_1) - P_2(x_2)] + \frac{1}{6}\left(x_1^3 \mathrm{Li}_0(\mathrm{e}^{-x_1}) - x_2^3 \mathrm{Li}_0(\mathrm{e}^{-x_2}) \right) \right\}, \tag{66}$$

$$c_{V_{-2}} = \frac{16\pi k_B^2}{c^3 h^1} T \left\{ [P_1(x_1) - P_1(x_2)] + \frac{1}{2}\left(x_1^2 \mathrm{Li}_0(\mathrm{e}^{-x_1}) - x_2^2 \mathrm{Li}_0(\mathrm{e}^{-x_2}) \right) \right\}. \tag{67}$$

The thermal radiative and thermodynamic functions of liquid and solid ZrC such as the total energy density, the total radiation power per unit area, total emissivity, Helmholtz free energy density, entropy density, pressure, heat capacity at constant volume, and number density of photons are calculated in the finite frequency range 0.333 PHz $\leq \upsilon \leq$ 0.545 PHz at the eutectic temperature 3155 K. Their values are presented in Table 1. As seen, the gaps between these functions are observed.

Now let us calculate the same properties of thermal radiation emitted by a heated surface area S of a zirconium carbide sample.

According to [41], the zirconium carbide sample under investigation is a disk about 1 mm thick and around 10 mm in diameter. Then, in accordance with Eq. 21, the total radiation powers emitted by a surface area S of the ZrC sample in solid and liquid phases are defined as

$$\text{Solid ZrC: } I^{SB}_{\text{Solidtotal}}(T) = S I^{SB}_{\text{Solid}}(\upsilon_1, \upsilon_2, T) \tag{68}$$

$$\text{Liquid ZrC: } I^{SB}_{\text{Liquidtotal}}(T) = S I^{SB}_{\text{Liquid}}(\upsilon_1, \upsilon_2, T), \tag{69}$$

where $I^{SB}_{Liquid}(v_1, v_2, T)$ and $I^{SB}_{Solid}(v_1, v_2, T)$ are the total radiation powers emitted by a heated surface per unit area of the ZrC sample. Their values are presented in Table 1.

The surface area S of the zirconium carbide sample under investigation can be determined as

$$S = 2\pi \left(\frac{d}{2}\right)^2 + \pi hd = 1.885 \times 10^{-4}\ \mathrm{m}^2. \tag{70}$$

Then, in accordance with Eq. 32 and Table 1, Eqs. 68 and 69 take the following values:

$$\text{Solid ZrC: } I^{SB}_{Solidtotal} = SI^{SB}_{Solid}(v_1, v_2, T) = 7.379 \times 10^2\ \mathrm{W} \tag{71}$$

$$\text{Liquid ZrC: } I^{SB}_{Liquidtotal} = SI^{SB}_{Liquid}(v_1, v_2, T) = 9.178 \times 10^2\ \mathrm{W}. \tag{72}$$

A volume of the ZrC sample under study can be calculated using the following expression:

$$V = \pi h \left(\frac{d}{2}\right)^2 = 7.854 \times 10^{-8}\ \mathrm{m}^3. \tag{73}$$

Using Eq. 73 and Table 1, for the total energies of the ZrC sample in solid and liquid phases, we obtain

$$\text{Solid ZrC: } I_{Solidtotal}(T) = VI_{Solid}(v_1, v_2, T) = 4.102 \times 10^{-9}\ \mathrm{J} \tag{74}$$

$$\text{Liquid ZrC: } I_{Liquidtotal}(T) = VI_{Liquid}(v_1, v_2, T) = 5.102 \times 10^{-9}\ \mathrm{J}. \tag{75}$$

In accordance with Eq. 73 and Table 1, the total numbers of photons N_{total} emitted by solid and liquid ZrC in the finite frequency range 0.333 PHz $\leq v \leq$ 0.545 PHz at temperature $T = 3155$ K are calculated and take the following values:

$$\text{Solid ZrC: } N_{Solidtotal} = Vn_{Solid} = 3.486 \times 10^{10} \tag{76}$$

$$\text{Liquid ZrC: } N_{Liquidtotal} = Vn_{Liquid} = 4.336 \times 10^{10}. \tag{77}$$

Now let us calculate the thermodynamic functions of thermal radiation of liquid and solid ZrC emitted by a heated surface area S of the sample. Using Eq. 73 and Table 1, for the total Helmholtz free energies F_{total}, we obtain

$$\text{Solid ZrC: } F_{Solidtotal} = a_{Solid}V = -1.367 \times 10^{-9}\ \mathrm{J} \tag{78}$$

$$\text{Liquid ZrC: } F_{Liquidtotal} = a_{Liquid}V = -1.701 \times 10^{-9}\ \mathrm{J}. \tag{79}$$

In Table 2, the calculated values of thermal radiative and thermodynamic functions of thermal radiation of liquid and solid zirconium carbide emitted by a heated surface area S of the sample are presented in the finite frequency range from 0.333 PHz to 0.545 PHz at the eutectic melting (freezing) temperature $T = 3155$ K. As can be clearly seen, the gaps between the thermal radiative and thermodynamic functions of liquid and solid zirconium carbide are observed.

Now let us compare the obtained results with the experimental data. In [56], the experimental data of the normal total emissivity of stoichiometric zirconium carbide are presented in the temperature range 2300 K $\leq T \leq$ 2900 K for wavelengths

Table 2 Calculated values of the thermal radiative and thermodynamic functions of thermal radiation of solid and liquid zirconium carbide emitted by a heated surface area S of the sample in the finite frequency range 0.333 PHz $\leq \upsilon \leq$ 0.545 PHz at the eutectic temperature 3155 K

Quantity	Zirconium carbide		Gaps between solid and liquid phases
	Solid phase	Liquid phase	
$I_{\text{total}}\,(\nu_1, \nu_2, T)$ (J)	7.043×10^{-10}	6.027×10^{-10}	1.015×10^{-10}
$I^{\text{SB}}_{\text{total}}\,(\nu_1, \nu_2, T)$ (W)	1.267×10^{2}	1.084×10^{2}	0.182×10^{2}
F_{total} (J)	-1.369×10^{-10}	-1.702×10^{-10}	3.330×10^{-11}
S_{total} (J·K^{-1})	3.039×10^{-13}	2.771×10^{-13}	2.678×10^{-14}
P_{total} (J)	1.369×10^{-10}	1.702×10^{-10}	-3.330×10^{-11}
$C_{V_{\text{total}}}$ (J·K^{-1})	7.870×10^{-13}	7.041×10^{-13}	8.144×10^{-14}
N_{total}	2.636×10^{9}	2.251×10^{9}	0.385×10^{9}

The surface area of the sample is $S = 1.885 \times 10^{-4}$ m^2. The volume of the sample is $V = 7.854 \times 10^{-8}$ m^3

between 0.6 µm and 6.0 µm. In [57], the normal spectral emissivity was measured in the wavelength range 0.6 µm $\leq \lambda \leq$ 4.0 µm at different temperatures 2100 K, 2270 K, 2470 K, and 2670 K. Let us extrapolate these experimental data to the ultra-high temperature range up to 3155 K. At $T = 3155$ K, the values of the normal total emissivity are (a) $\varepsilon(T) \approx 0.47$ [56], and (b) $\varepsilon(T) \approx 0.49$ [57]. According to Table 1, the calculated values for normal total emissivity in the solid and liquid phases are (a) $\varepsilon(T) = 0.584$ for solid phase and (b) $\varepsilon(T) \equiv 0.50$ for liquid phase, respectively. As seen, the calculated value for the normal total emissivity of liquid zirconium carbide, presented in Table 1, is in good agreement with experimental data. This fact confirms that at the temperature 3155 K, the melting occurs and the liquid phase exists.

6 Conclusions

Using the expression for the normal spectral emissivity in the form $\varepsilon\,(\nu, T) = \sum_{i=-3}^{\infty} a_i \upsilon^i$, the thermal radiative and thermodynamic properties of a surface of the real body are studied in a finite range of frequencies. The general analytical expressions for the Stefan–Boltzmann law, total energy density, number density of photons, Helmholtz free energy density, enthalpy density, internal energy density, entropy density, heat capacity at constant volume, and pressure in various frequency ranges and different temperatures are obtained. In the case of blackbody radiation, these expressions reproduce the well-known equations for blackbody radiation in a semi-infinite range of frequencies.

The general expressions obtained in this work is applied to the study of the thermal radiative and thermodynamic properties of solid and liquid zirconium carbide using the experimental data for the frequency dependence of the normal spectral emissivity at melting (freezing) point. The calculated values of the total radiation power per unit area, total energy density, number density of photons, Helmholtz free energy density, enthalpy density, internal energy density, entropy density, heat capacity at constant volume, and pressure in a spectral range 0.333 PHz $\leq \upsilon \leq$ 0.545 PHz at temperature $T = 3155$ K are presented in Table 1. The value for the normal total emissivity of liquid zirconium carbide presented in Table 1 is in a good agreement with the experimental data.

In Table 2, the thermal radiative and thermodynamic functions of thermal radiation of solid and liquid ZrC emitted by a heated surface area S of the sample are presented. The volume of the sample is $V = 7.854 \times 10^{-8}\ \text{m}^3$. The existence of the gaps between the thermal radiative and thermodynamic functions of solid ZrC and that of liquid ZrC in the visible range are confirmed.

In conclusion, it is important to note the following. In [30,40], and [42–46], the normal spectral emissivity is represented as a series. Thus, the general analytical expressions for the thermal radiative and thermodynamic functions obtained in this paper can be applied to study of real bodies such as (a) luminous flames; (b) cobalt, iron, and nickel at melting points; (c) uranium and plutonium carbides at melting temperatures; and (d) Milky Way and other galaxies. As a result, the thermal radiative and thermodynamic functions of these real bodies can be described using polylogarithm functions.

These and other topics will be points of discussion in subsequent publications.

Acknowledgment The authors cordially thank Professor N.P. Malomuzh for fruitful discussions.

References

1. L. Michalski, K. Eckersdorf, J. Kucharski, J. McGhee, *Temperature Measurements* (Wiley, Chichester, 2001)
2. E.C. Magison, *Temperature Measurements in Industry* (Research Triangle Park, ISA, 1990)
3. H. Fukuyama, Y. Waseda (eds.), High-temperature measurements of materials, *Advances in Materials Research* (Springer, Berlin, 2008), p. 204
4. T. Riethof, B. Acchione, E. Branyan, High-temperature spectral emissivity studies on some refractory metals and carbides, *Temperature, Its Measurement and Control in Science and Industry* (Reinhold Publishing Corporation, New York, 1962)
5. S. Meng, H. Chen, J. Hu, Z. Wang, Mater. Des. **32**, 377 (2011)
6. M. Bober, H.U. Karow, K. Muller, High Temp. High Press. **12**, 161 (1980)
7. D.D. Soerensen, S. Clausen, J.B. Mercer, L.J. Pedersen, Comput. Electron. Agric. **109**, 52 (2014)
8. R. Ke, Y. Zhang, Y. Zhou, Optik. Int. J. Light Electron Opt. **125**, 6991 (2014)
9. A. Adibekyan, C. Monte, M. Kehrt, B. Gutschwager, J. Hollandt, Int. J. Thermophys. **36**, 283 (2015)
10. F. Tairan, T. Peng, D. Minghao, Meas. Sci. Technol. **26**, 015003 (2015)
11. K. Nakazawa, A. Ohnishi, Int. J. Thermophys. **31**, 2010 (2010)
12. A. Barducci, D. Guzzi, P. Marcoionni, I. Pippi, IEEE Trans. Geosci. Remote Sens. **42**, 1521 (2004)
13. T. Matsumoto, A. Cezairliyan, D. Basak, Int. J. Thermophys. **20**, 943 (1999)
14. C. Cagran, G. Pottlacher, Int. J. Thermophys. **28**, 697 (2007)
15. S. Krishnan, G.P. Hansen, R.H. Hauge, J.L. Margrave, High Temp. Sci. **29**, 17 (1990)
16. S. Krishnan, P.C. Nordine, J. Appl. Phys. **80**, 1735 (1996)
17. Y.S. Touloukian, D.P. DeWitt, Thermal radiative properties: metallic elements and alloys, *Thermophysical Properties of Matter*, vol. 7 (IFI/Plenum, New York, Washington, 1970)
18. D.J. Watmough, R. Oliver, Nature **219**, 622 (1968)
19. C.D. Wen, I. Mudawar, Int. J. Heat Mass Transf. **47**, 3591 (2004)
20. B.K. Tsai, R.L. Shemaker, D.P. DeWitt, B.A. Cowans, Z. Dardas, W.N. Delgass, G.J. Dail, Int. J. Thermophys. **11**, 269 (1990)
21. M.F. Hopkins, SPIE Int. Soc. Opt. Eng. **2599**, 294 (1996)
22. M.A. Khan, C.D. Allemand, T.W. Eager, Rev. Sci. Instrum. **62**, 403 (1991)

23. Th Duvaut, D. Georgeault, J.L. Beaudoin, Infrared Phys. Technol. **36**, 1089 (1995)
24. J.L. Gardner, T.P. Jones, M.R. Davies, High Temp. High Press. **13**, 459 (1981)
25. J.L. Gardner, High Temp. High Press. **12**, 699 (1980)
26. M. Hoch, High Temp. High Press. **24**, 607 (1992)
27. M. Hoch, Rev. Sci. Instrum. **63**, 2274 (1992)
28. G.R. Gathers, Int. J. Thermophys. **13**, 361 (1992)
29. G.R. Gathers, Int. J. Thermophys. **13**, 539 (1992)
30. R. Siegel, J.R. Howell, *Thermal Radiation Heat Transfer* (McGraw-Hill, New York, 1972). p
31. D.K. Edwards, I. Catton, Advances in the thermophysical properties at extreme temperatures and pressures. In: Proceedings of third symposium on thermophysical properties 1965, p. 189
32. A.I. Fisenko, S.N. Ivashov, J. Phys. D **32**, 2882 (1999)
33. S.N. Ivashov, A.I. Fisenko, J. Eng. Phys. **57**, 838 (1990)
34. V.A. Ershov, A.I. Fisenko, Combust. Explos. Shock Waves **28**, 159 (1992)
35. Z.M. Zhang, X.J. Wang, J. Thermophys. Heat Transf. **24**, 222 (2010)
36. S.N. Ivashov, A.I. Fisenko, Int. J. Thermophys. **30**, 1524 (2009)
37. A.I. Fisenko, V. Lemberg, Int. J. Thermophys. **33**, 513 (2012)
38. A.I. Fisenko, V. Lemberg, Int. J. Thermophys. **34**, 486 (2013)
39. A.I. Fisenko, V. Lemberg, Int. J. Thermophys. **36**, 1627 (2015)
40. D. Manara, F. De Bruycker, K. Boboridis, O. Tougait, R. Eloirdy, M. Malki, J. Nucl. Mater. **426**, 126 (2012)
41. D. Manara, H.F. Jackson, C. Perinetti-Casoni, K. Boboridis, M.J. Welland, L. Luzzi, P.M. Ossi, W.E. Lee, J. Eur. Ceram. Soc. **33**, 1349 (2013)
42. H. Watanabe, M. Susa, H. Fukuyama, K. Nagata, Int. J. Thermophys. **24**, 223 (2003)
43. H. Watanabe, M. Susa, H. Fukuyama, K. Nagata, Int. J. Thermophys. **24**, 473 (2003)
44. W.T. Reach, E. Dwek, D.J. Fixsen, T. Hewagama, J.C. Mather, R.A. Shafer, A.J. Banday, C.L. Bennett, E.S. Cheng, R.E. Eplee Jr, D. Leisawitz, P.M. Lubin, S.M. Read, L.P. Rosen, F.G.D. Shuman, G.F. Smoot, T.J. Sodroski, E.L. Wright, AP J. **451**, 188 (1995)
45. L. Spinoglio, M.A. Malkan, H.A. Smith, E. González-Alfonso, J. Fischer, AP J. **623**, 123 (2005)
46. A.I. Fisenko, V. Lemberg, Res. Astron. Astrophys. **15**, 939 (2015)
47. L.D. Landau, E.M. Lifshitz, *Statistical Physics, Course of Theoretical Physics*, vol. 5 (Pergamon Press, Oxford, New York, 1980)
48. M. Abramowitz, I.A. Stegun, *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables* (Dover Publications, New York, 1965)
49. A.I. Fisenko, V. Lemberg, Astrophys. Space Sci. **352**, 221 (2014)
50. D.S. Birney, G. Gonzalez, D. Oepser, *Observational Astronomy*, 2nd edn. (Cambridge University Press, Cambridge, UK, 2006)
51. E. Wuchina, E. Opila, M. Opeka, W. Fahrenholtz, I. Talmy, Interface **16**, 30 (2007)
52. P.T.B. Shaffer, Engineering properties of carbides, *Engineered Materials Handbook*, vol. 4, Ceramics and Glass (ASM International, Metals Park, Ohio, 1991), p. 1217
53. W. Doonyapong, J. Nucl. Mater. **396**, 149 (2010)
54. S.R. Levine, E.J. Opila, M.C. Halbig, J.D. Kiser, M. Singh, J.A. Salem, J. Eur. Ceram. Soc. **22**, 2757 (2002)
55. E. Sani, L. Mercatelli, F. Francini, J.L. Sans, D. Sciti, Scripta Mater. **65**, 75 (2011)
56. T.E. Zapadaeva, V.A. Petrov, V.V. Sokolov, High Temp. **18**, 76 (1980)
57. P.T.B. Shaffer, J. Am. Ceram. Soc. **46**, 177 (1963)