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Determination of the True Temperature of Molybdenum and Luminous Flames from Generalized Wien's Displacement and Stefan–Boltzmann's Laws: Thermodynamics of Thermal Radiation

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Abstract The true temperature of thermal radiation of molybdenum and luminous flames is defined from the temperature dependences of generalized Wien's displacement and Stefan–Boltzmann's laws. For determining the true temperature of molybdenum, experimental values of either the position of the maximum of the spectral emitted density or the total emitted density are needed. It is shown that the thermal radiation of molybdenum belongs to the same universality class as that of tantalum, tungsten, and zirconium and titanium carbides. The thermodynamic functions of thermal radiation of molybdenum and luminous flames are constructed.

Keywords Generalized Wien's displacement and Stefan–Boltzmann's laws · Luminous flames · Molybdenum · True temperature

1 Introduction

The accurate determination of the true temperature of a body having emitted continuous spectra is an important problem in many technological applications for developing new products, processes, and diagnostics [1,2]. The series of non-contact measured methods used at present allow us to determine the true temperature of a body. However, these methods are limited by the measurement of the steady-state temperature [3–6] and have a limit of their application in high-speed technological processes [1–3].

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By using optical pyrometers based on Wien's law, such as color-ratio, multi-wavelength ratio, and other pyrometers, the most important radiation wavelength belongs to the visible and infrared radiation bands, depending on the materials being measured. As a result, the optical pyrometers methods for measuring the temperature of a body limit the measurement of the steady-state temperature above 3000 K.

In [7–9], a high-speed spectroscopy method for investigating the emissivity of electrically non-conducting materials at high temperature was proposed. However, the temperature of the investigated materials was defined by optical pyrometers. This means that the temperature condition attained a steady-state.

A spectroscopic-based system for providing real-time flame temperature monitoring for natural gas-fired furnaces was developed [10,11]. The flame temperature was determined by using an intensity ratio approach for paired wavelengths. In this case, it was assumed that the emissivity ratio for selected paired wavelengths is equal to 1. All these facts lead to less accuracy in defining the real flame temperature.

The method of Doppler broadening of spectral lines also has a limitation. It is unclear how to separate the effects of Doppler broadening from that appears through the phenomenon of interacting gas molecules, Lorenz broadening. Regarding other methods, see [1–3].

A general feature of the well-known methods for steady-state temperature measurements, which use a limited number of emitted spectral intensities, is the fact that they do not give a high degree of accuracy and their application cannot be used in fast measurements because of lag-time limitations [5]. Therefore, the development of new, more accurate optical non-contact methods for measurements of the temperature is a real problem.

It is well-known that a direct method for measuring the temperature of thermal radiation of a blackbody applies the Wien displacement law [12]. By using this law, the temperature of thermal radiation of a blackbody is defined from measurements of the position of the maximum of the spectral emitted density. As a result, the temperatures of surfaces of the sun and other cosmic objects were defined.

However, when we consider the thermal radiation of a real body, the application of Wien's displacement law for determining the true temperature is not correct because of the emissivity factor $\varepsilon(\nu, T)$. Therefore, there is considerable interest to generalize the Wien displacement law in the case of the thermal radiation of a body.

In [13,14], the vanishing-flux model based on information theory for the non-equilibrium extension of Wien's displacement law is proposed. It was predicted that such corrections could be very important in optical methods for temperature measurements. In [15,16], a generalized Wien displacement law is obtained by using a thermodynamic analysis involving electromagnetic zero-point radiation. However, the theoretical methods proposed above should be compared with experimental data for different substances.

In [17–20], an optical non-contact method for determining the true temperature of bodies was proposed. The performance of this method was demonstrated on the thermal radiation of tantalum, tungsten, and zirconium and titanium carbides, and luminous flames. It was shown that Wien's displacement law for the investigated bodies decreases linearly when the temperature increases. From the generalized Wien displacement law, the true temperatures were defined. The uncertainty in the determination of the steady-state temperature does not fall below 3 % in these cases. It was noted that the emitted thermal radiation of carbides, tungsten, and tantalum, belongs to the same universality class [19]. The emitted thermal radiation of luminous flames belongs to the same universality class as a blackbody [19].

The present study is devoted to the subsequent development of a non-contact optical method for determining the true temperature of bodies, which was previously proposed in [17–20]. In the framework of the examples, the generalized Wien displacement law is investigated for molybdenum. By determining the law of the relationship between T and $\nu_{\max}$, the universality class to which the emitted thermal radiation of molybdenum belongs is established. The thermodynamics of thermal radiation of molybdenum and luminous flames is constructed.

2 Generalized Wien's Displacement Law and Thermodynamics of Thermal Radiation

According to [17–20], the generalized Wien's displacement law is presented in the form,

$$X_{\max} = \frac{h\nu_{\max}}{k_B T} = \left(\frac{h}{k_B T}\right)\left(1 - \frac{S_0\,\bar{S_3}}{2S_1\,\bar{S_2}}\right)\frac{S_1}{S_0}, \tag{1}$$

where k_B is the Boltzmann constant, T is the temperature, and h is the Planck constant.

Here

$$S_n = \int v^n I(v, T)\mathrm{d}v \tag{2}$$

$$\bar{S}_n = \int (\nu - \bar{\nu})^n\, I\,(\nu, T)\,\mathrm{d}\nu \tag{3}$$

are the initial Eq. 2 and central Eq. 3 moments of the distribution function $I(\nu, T)$, $n = 0, 1, 2, 3\ldots$ is the order of the moments; and $\bar{\nu} = \frac{S_1}{S_0}$.

In [18,19], it was shown that in the case of a blackbody, Eq. 1 differs negligibly from Wien's displacement law [12]. The uncertainty of the temperature in this case does not exceed 1%.

The radiant spectral density of a body is presented in the form,

$$I(\nu, T) = \varepsilon(\nu, T)I^{\mathrm{P}}(\nu, T), \tag{4}$$

where $\varepsilon(\nu, T)$ is the spectral emissivity and $I^{\mathrm{P}}(\nu, T)$ at temperature T is given by the Planck law [12]:

$$I^{\mathrm{P}}(\nu, T) = \frac{8\pi h}{c^3}\frac{\nu^3}{\mathrm{e}^{\frac{h,\nu}{k_B T}} - 1}. \tag{5}$$

According to Eq. 2, the total emitted radiant density of a body is presented in the form,

$$I(T) = S_0(T) = \int I(v, T)\mathrm{d}v. \tag{6}$$

The total emissivity of a body has the following structure:

$$\varepsilon(T) = \frac{S_0}{aT^4} = \frac{\int I(v, T)\mathrm{d}v}{aT^4}, \tag{7}$$

where $a = 7.5657 \times 10^{-16}\,\mathrm{J{\cdot}m^{-3}{\cdot}K^{-4}}$ is the blackbody constant $\left(\text{the Stefan–Boltzmann constant is } \sigma = \frac{ac}{4}\right)$.

According to [12], the thermodynamic functions of emitted thermal radiation of a body have the following expressions:

(a) Free energy:

$$F = -\frac{V}{3} S_0(T) \tag{8}$$

(b) Total energy:

$$E = \frac{V}{3}\left(T\frac{\partial S_0\,(T)}{\partial T} - S_0\,(T)\right) \tag{9}$$

(c) Entropy:

$$S = \frac{V}{3}\frac{\partial S_0(T)}{\partial T} \tag{10}$$

(d) Heat capacity at constant V:

$$C_V = \frac{VT}{3}\left(\frac{\partial^2 S_0\,(T)}{\partial^2\,(T)}\right)_V \tag{11}$$

(e) Pressure

$$P = \frac{1}{3} S_0(T) \tag{12}$$

3 Determination of the True Temperature of Molybdenum

For determining the true temperature of emitted thermal radiation of molybdenum, let us investigate the generalized Wien's displacement law (Eq. 1) at different temperatures.

In [21] the experimental values of the spectral emissivity $\varepsilon(\nu, T)$ for molybdenum at different temperatures are presented. Using the method proposed in [22], the frequency initial moments of the radiant spectral density for molybdenum are calculated

Table 1 Temperature dependence of the initial moments $S_n = \int_{\nu_1}^{\nu_2} \nu^n I(\nu, T)\,d\nu$ of the radiant spectral density for molybdenum

T (K)	$S_0 \times 10^{-4}$ ($J \cdot m^{-3}$)	$S_1 \times 10^{11}$ ($J \cdot m^{-3} \cdot s^{-1}$)	$S_2 \times 10^{25}$ ($J \cdot m^{-3} \cdot s^{-2}$)	$S_3 \times 10^{39}$ ($J \cdot m^{-3} \cdot s^{-3}$)
1200	1.201	0.169	0.278	0.531
1400	3.176	0.504	0.943	2.057
1600	6.936	1.221	2.561	6.295
1800	13.450	2.599	6.032	16.485
2000	23.910	5.022	12.750	38.240

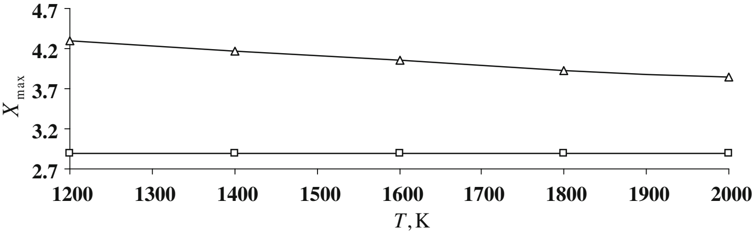

Fig. 1 Investigation of the generalized Wien displacement law for molybdenum: □ blackbody; △ molybdenum

at different temperatures and are presented in Table 1. The temperature dependence of the generalized Wien displacement law (Eq. 1) for molybdenum is represented in Fig. 1. As seen in Fig. 1, the generalized Wien's displacement law X_{max} with good accuracy is approximated by the equation,

$$X_{max} = \frac{h\nu_{max}}{kT} = a' - b'T, \tag{13}$$

where $a' = 4.99$ and $b' = 5.75 \times 10^{-4}\,K^{-1}$. The constants a' and b' are estimated using the least-squares method. From Eq. 13, the true temperature of molybdenum has the following form:

$$T = c'\left[1 - \left(1 - d'\upsilon_{max}\right)^{\frac{1}{2}}\right], \tag{14}$$

where $c' = 8.67 \times 10^3$ K and $d' = 4.44 \times 10^{-15}$ s.

As clearly seen from Eq. 14 for determining the true temperature of molybdenum, the experimental value of the position of the maximum of the radiant spectral density is needed.

Now let us compare the calculated value for the true temperature of molybdenum (Eq. 14) with the experimental data. In accordance with the experimental data [21], at the temperature $T' = 2000$ K, the value of $\nu_{max} \approx 0.93 \times 10^{14}\,s^{-1}$. After substituting the experimental value ν_{max} in Eq. 14, the calculated value of the temperature for molybdenum is equal to $T = 2027\,\mathrm{K}$. The uncertainty in the determination of the true temperature in this case is no larger than 2 %.

In [21], it is noted that the bodies at high temperature emit radiation as a blackbody. This conclusion is in agreement with our calculation. As seen in Eq. 13, the properties of emitted radiation of molybdenum coincide with that of a blackbody at the temperature $T = 3770\,\mathrm{K}$.

It is important to note that a similar law of the relationship (Eq. 14) between the temperature T and the position of the spectral radiance maximum $\nu_{\max}$ has been obtained for both zirconium and titanium carbides, tantalum, and tungsten [17–20]. This means that the emitted radiations of molybdenum, tantalum, tungsten, and zirconium and titanium carbides belong to the same universality class. The constants c' and d' for molybdenum differ from the same constants in [17–19]. It appears that this difference can be related to the difference of frequency ranges when the frequency moments were calculated. This question and another related to comparing the accuracy of temperature obtained from various frequency ranges will be the focus of our future research.

4 Thermodynamics of Thermal Radiation of Molybdenum and Luminous Flames

4.1 Molybdenum

Now let us construct the thermodynamic functions of thermal radiation of molybdenum in the temperature range $1200\,\mathrm{K} \le T \le 2000\,\mathrm{K}$. According to Eq. 6, the generalized Stefan–Boltzmann law could be presented in the following form:

$$I(T) = S_0(T) = \int_{\nu_1}^{\nu_2} I(\nu, T)\mathrm{d}\nu = \varepsilon(T)aT^4, \tag{15}$$

where $\varepsilon(T)$ is the total emissivity of molybdenum and the integral is evaluated over the spectral band ν_1 and ν_2.

By using the temperature dependence $S_0(T)$ taken from Table 1, the second column, the temperature dependence of $\varepsilon(T)$ is presented in Fig. 2. As seen in Fig. 2, the total emissivity of molybdenum increases with increasing temperature, and to a good accuracy, is approximated by the expression,

$$\varepsilon(T) = \frac{S_0(T)}{aT^4} = BT^{1.85}, \tag{16}$$

where $B = 1.59 \times 10^{-7}\,\mathrm{K}^{-1.85}$.

Here it is important to note that the following expression $\varepsilon(T) = m + nT$ could also be used as the approximating function of $\varepsilon(T)$. Here $m = -0.109$ and $n = 0.155 \times 10^{-3}\,\mathrm{K}^{-1}$. However, this expression for determining the true temperature from the experimental data is less convenient in comparison to Eq. 16. Later on, we will use the expression (Eq. 16) for constructing the thermodynamics of thermal radia-

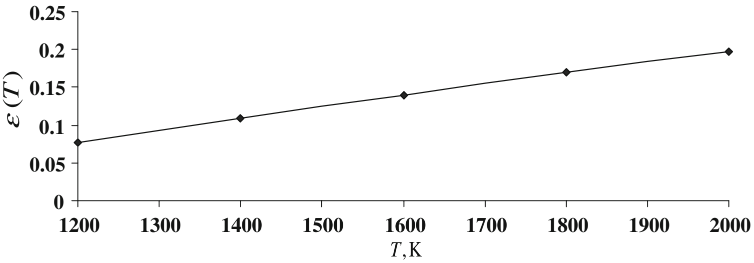

Fig. 2 Temperature dependence of the total emissivity $\varepsilon(T) = \frac{S_0(T)}{aT^4}$ for molybdenum

tion of molybdenum. Substituting Eq. 16 in Eq. 15, the generalized Stefan–Boltzmann law for molybdenum takes the following form:

$$S_0(T) = K_0 T^{5.85}, \tag{17}$$

where $K_0 = 1.20 \times 10^{-22}\ \mathrm{J \cdot m^{-3} \cdot K^{-5.85}}$. Equation 17 allows us to determine the true temperature of molybdenum in the form,

$$T = D(S_0)^{\frac{1}{5.85}}, \tag{18}$$

where $D = 5.59 \times 10^3\ \mathrm{J}^{-\frac{1}{5.85}} \cdot \mathrm{m}^{\frac{3}{5.85}} \cdot \mathrm{K}$.

As seen from Eq. 18 in determining the true temperature of molybdenum from experimental data, only precise measurements of the total emitted thermal radiation is necessary.

By using Eqs. 8, 9, 10, 11, and 12, the thermodynamic functions of thermal radiation of molybdenum have the following forms:

(a) Free energy:

$$F = -\frac{VK_0}{3} T^{5.85}$$

(b) Total energy:

$$E = 1.62 V K_0 T^{5.85}$$

(c) Entropy:

$$S = 1.95 V K_0 T^{4.85}$$

(d) Heat capacity at constant V:

$$C_V = 9.46 V K_0 T^{4.85}$$

(e) Pressure

$$P = \frac{K_0}{3} T^{5.85}$$

Now let us compare the calculated value for the total emissivity of molybdenum (Eq. 16) with literature data. According to Eqs. 7 and 16, the calculated total emissivity of molybdenum at 1773 K is equal to $\varepsilon(T) = 0.163$. In accordance with the experimental data taken from [23], the total emissivity of molybdenum, unoxidized at 1773 K, is equal to 0.19. Here it is important to note that the difference between the calculated and experimental values $\varepsilon(T)$ of molybdenum could be explained by the difference in the surface states of molybdenum and its degree of oxidation in [21,23]. However, at $T = 2273$ K, the experimental value of the total emissivity is $\varepsilon(T) = 0.24$ [23]. By extrapolating Eq. 16 in the high-temperature region, the calculated value is equal to $\varepsilon(T) = 0.25$ and is in good agreement with literature data. It means that the influence of surface states and its degree of oxidation could be negligible in the high-temperature region. However, for proving this fact, additional research should be conducted.

4.2 Luminous Flames

Let us now construct the thermodynamics of thermal radiation of luminous flames. It is known [24] that luminous flames (soot-forming flames) emit radiation in a continuum similar to that of solid-body radiation. Diffusion flames and flames of over-rich mixtures of organic fuel are typical examples of the latter.

In [19] and [20], the true temperature of a series of luminous flames, in the case when $K_\nu L \ll 1$, was determined by using the generalized Wien's displacement law (Eq. 1). Here, K_ν is the absorption coefficient for the frequency ν, and L is the thickness of the absorbing layer.

According to Eq. 6 and [19,20], the generalized Stefan–Boltzmann law for luminous flames has the following structure:

$$I(T) = S_0(T) = \int_0^\infty \varepsilon(\upsilon, T) I(\upsilon, T) \mathrm{d}\upsilon = \varepsilon_0 A_0(\alpha) T^{\alpha+4}, \tag{19}$$

where

$$A_0(\alpha) = \frac{8\pi}{c^{3+\alpha}} \frac{k_\mathrm{B}^{4+\alpha}}{h^{3+\alpha}} \int_0^\infty \frac{x^{3+\alpha}}{\mathrm{e}^x - 1} \mathrm{d}x.$$

Here ε_0 is a constant in the equation showing the variation of the spectral emissivity $\varepsilon(\nu, T)$ with ν [19–24], $x = \frac{h\upsilon}{k_\mathrm{B} T}$, and α takes different values for different flames (see Table 2). The constant ε_0 is determined from experimental data.

Table 2 Calculated values of the constant A_0

FLAME	α	$A_0 \times 10^{-12}$ $(\mathrm{J \cdot m^{-(3+\alpha)} \cdot K^{-(4+\alpha)}})$
Acetone	1.43	2.40
Amyl acetate	1.39	1.90
Coal–gas/air	1.29	1.06
Benzene/air	1.23	0.75
Nitrocellulose	1.14	0.46
Benzene/NO	1.05	0.28
Acetylene/air	0.66–0.75	0.03–0.05

Values of α are taken from [24]
Constants $c, k,$ and h [21] are: $c = 2.998 \times 10^8\ \mathrm{m \cdot s^{-1}}$, $k = 1.38 \times 10^{-23}\ \mathrm{J \cdot K^{-1}}$, and $h = 6.626 \times 10^{-34}\ \mathrm{J \cdot s}$

By using Eq. 19, the true temperature of thermal radiation of luminous flames is presented in the form,

$$T = \left(\frac{S_0(T)}{A_0(\alpha)\varepsilon_0} \right)^{\frac{1}{\alpha+4}} \tag{20}$$

As seen from Eq. 20 in determining the true temperature of luminous flames from experimental data, only precise measurements of the total radiance density are necessary.

The total emissivity (Eq. 7) of luminous flames has the structure,

$$\varepsilon(T) = \frac{\varepsilon_0 A_0(\alpha)}{a} T^{\alpha}. \tag{21}$$

According to Eqs. 8, 9, 10, 11, and 12, the thermodynamic functions of thermal radiation of luminous flames have the following expressions:

(a) Free energy:

$$F = -\frac{V}{3}\varepsilon_0 A_0(\alpha) T^{\alpha+4}$$

(b) Total energy:

$$E = \frac{V(\alpha+3)}{3}\varepsilon_0 A_0(\alpha) T^{\alpha+4}$$

(c) Entropy:

$$S = \frac{V(\alpha+4)}{3}\varepsilon_0 A_0(\alpha) T^{\alpha+3}$$

(d) Heat capacity at constant V:

$$C_V = \frac{V(\alpha+4)(\alpha+3)}{3}\varepsilon_0 A_0(\alpha) T^{\alpha+3}$$

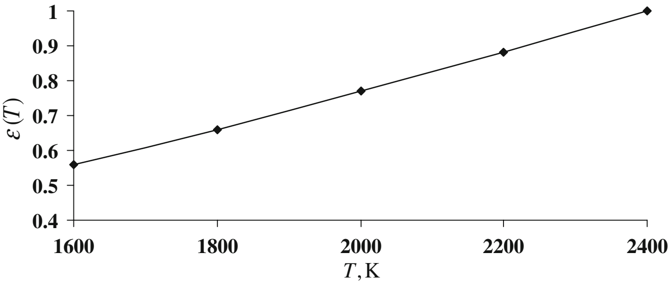

Fig. 3 Temperature dependence of the total emissivity $\varepsilon(T)$ for acetone: $\alpha = 1.43$; $\varepsilon_0 = 4.62 \times 10^{-9}\,\mathrm{m}^{\alpha}$

(e) Pressure

$$P = \frac{1}{3}\varepsilon_0 A_0(\alpha) T^{\alpha+4}$$

Consider the example of acetone ($\alpha = 1.43$) in more detail. According to Eq. 21 and Table 2, the total emissivity $\varepsilon(T)$ of acetone is presented in the form,

$$\varepsilon(T) = 3.172 \times 10^3 \varepsilon_0 T^{1.43}. \qquad (22)$$

As seen from Eq. 22, for obtaining the temperature dependence of the total emissivity $\varepsilon(T)$, the values ε_0 should be determined from experimental data. Here let us estimate the value ε_0 by taking into consideration the fact that the total emissivity $\varepsilon(T) \le 1$. Thus, we obtain

$$\varepsilon_0 \le 0.315 \times 10^{-3} T^{-1.43}. \qquad (23)$$

According to Eq. 23, it is not difficult to show that in the temperature range $1600\ \mathrm{K} \le T \le 2400\ \mathrm{K}$, the constant $\varepsilon_0 \le 4.62 \times 10^{-9}\,\mathrm{m}^{\alpha}$.

Let us construct thermodynamics of thermal radiation of acetone by using the upper limit for $\varepsilon_0 = 4.62 \times 10^{-9}\,\mathrm{m}^{\alpha}$. In this case, the temperature dependence of the total emissivity Eq. 22 is presented in Fig. 3. The thermodynamic functions of acetone have the following structures: (a) true temperature: $T = 4.73 \times 10^3\,(S_0(T))^{\frac{1}{5.43}}$; (b) free energy: $F = -3.696 \times 10^{-21} V T^{5.43}$; (c) total energy: $E = 1.637 \times 10^{-20} V T^{5.43}$; (d) entropy: $S = 2.01 \times 10^{-20} V T^{4.43}$; (e) heat capacity at constant V: $C_V = 8.89 \times 10^{-20} V T^{4.43}$; and (f) pressure: $P = 3.696 \times 10^{-21} T^{5.43}$.

In conclusion, it is important to note that the dependence of the total emitted thermal density $I(T)$ on the temperature T has a similar power law for molybdenum (Eq. 16), the optically thin luminous flames (Eq. 19), and the blackbody [12].

5 Conclusion

In this article, the true temperature of molybdenum is defined from either generalized Wien's displacement or Stefan–Boltzmann's laws. In the first case, for determining the true temperature, the experimental value of the position of the maximum of the spectral emitted density is needed. In the second one, precise measurements of the total radiance density are necessary.

It has been shown that the thermal continuum radiation of molybdenum has a similar relationship between T and $\nu_{\max}$ (Eq. 14) and belongs to the same universality class of bodies as investigated in [17–19].

Thermodynamics of thermal radiation of molybdenum and luminous flames is constructed. The true temperature of luminous flames is determined from the generalized Stefan–Boltzmann law. In this case, precise measurements of the total radiance density are necessary.

It has been shown that the temperature dependence of the total emitted thermal intensity $I(T)$ upon T has a similar behavior for molybdenum, luminous flames, and a blackbody. In time, let us note that the emitted continuum thermal radiations of bodies, which have a similar power law, can be identified as belonging to the same universality class.

At present, it is important to investigate other flames, metals, carbides, and bodies, which have emitted continuous spectra for establishing the temperature behaviors for generalized Wien's displacement and Stefan–Boltzmann's laws. As a result, the different universality classes of thermal radiation of bodies with different laws will be developed.

Special attention should be paid to the determination of the true temperature and the construction of thermodynamics of thermal radiation of luminous flames in the case when $K_\nu L \sim 1$. This will lead to the existence of another universality class of luminous flames.

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

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