Chapter 2
Thermodynamics of Black-Body Radiation in a Finite Spectral Range

The thermodynamics of black-body radiation was investigated earlier for the entire range of the spectrum [1]. However, for the practical applications, we need to construct the thermodynamics of black-body radiation in the finite spectral range. In [2, 3], the thermodynamics of black-body radiation for the finite spectral range was proposed. This approach was applied by the authors to various physical [4–7] and astrophysical [2, 8, 9] problems.

In this chapter, the analytical expressions for the thermodynamic functions of black-body radiation are presented for different ranges of $x = \frac{h\nu}{k_B T}$. Based on the analytical expressions, the values of the Helmholtz free energy density, enthalpy density, entropy density, heat capacity at constant volume, and pressure are calculated. The results of these calculations are presented in Tables 6.1–6.3.

2.1 General Relationships

The thermodynamic functions of blackbody radiation in the finite frequency range of the electromagnetic spectrum are determined by the following expressions [1]:

1. Helmholtz free energy density $f = \frac{F}{V}$:

$$f(\nu_1, \nu_2, T) = \frac{8\pi k_B T}{c^3} \int_{\nu_1}^{\nu_2} \nu^2 \ln\left(1 - e^{-\frac{h\nu}{k_b T}}\right) d\nu \tag{2.1}$$

2. Entropy density $s = \frac{S}{V}$:

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$$s = -\frac{\partial f}{\partial T} \tag{2.2}$$

3. Heat capacity at constant volume per unit volume: $c_V = \frac{C_V}{V}$

$$c_V = \left(\frac{\partial I(v_1, v_2, T)}{\partial T}\right)_V . \tag{2.3}$$

4. Pressure of photons $p = -\frac{\partial F}{\partial V}$;

$$p = -f \tag{2.4}$$

5. The enthalpy density h follows from its definition,

$$h = u + p \tag{2.5}$$

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

$$g = 0 \tag{2.6}$$

7. The chemical potential density $\mu = \left(\frac{\partial g}{\partial n}\right)_{T,V}$, as seen from Eq. (2.6), is zero

$$\mu = 0 \tag{2.7}$$

2.2 Helmholtz Free Energy Density

After computing the integral in Eq. (2.1), the Helmholtz free energy density takes the following form [2] (see also Appendix B):

$$f(x_1, x_2, T) = -\frac{16\pi {k_B}^4}{c^3 h^3} T^4 C(x_1, x_2) , \tag{2.8}$$

where

$$\begin{aligned} C(x_1, x_2) &= C(x_1, \infty) - C(x_2, \infty) \\ &= \left[\left(P_3(x_1) - P_3(x_2)\right) - \frac{1}{6}\left(x_1^3 \operatorname{Li}_1(e^{-x_1}) - x_2^3 \operatorname{Li}_1\left(e^{-x_2}\right)\right)\right]. \end{aligned} \tag{2.9}$$

According to Eqs. (1.3) and (2.8), the analytical expressions for thermodynamic functions can be obtained in the finite spectral range.

2.3 Entropy Density

$$s(x_1, x_2) = \frac{64\pi {k_B}^4}{c^3 h^3} T^3 D(x_1, x_2), \tag{2.10}$$

where

$$\begin{aligned} D\big(x_1, {}^1x_2\big) &= D(x_1, \infty) - D(x_2, \infty) \\ &= \left[\Big(P_3(x_1) - P_3(x_2) \Big) - \frac{1}{24} \Big(x_1^3 \operatorname{Li}_1(e^{-x_1}) - x_2^3 \operatorname{Li}_1(e^{-x_2}) \Big) \right]. \end{aligned} \tag{2.11}$$

2.4 Heat Capacity at Constant Volume Density

$$c_V(x_1, x_2) = \frac{192\pi {k_B}^4}{c^3 h^3} T^3 E(x_1, x_2), \tag{2.12}$$

where

$$\begin{aligned} E(x_1, x_2) &= E(x_1, \infty) - E(x_2, \infty) \\ &= \left[\Big(P_3(x_1) - P_3(x_2) \Big) + \frac{1}{24} \Big(x_1^4 \operatorname{Li}_0(e^{-x_1}) - x_2^4 \operatorname{Li}_0(e^{-x_2}) \Big) \right]. \end{aligned} \tag{2.13}$$

2.5 Pressure

$$p(x_1, x_2) = \frac{16\pi {k_B}^4}{c^3 h^3} T^4 C(x_1, x_2), \tag{2.14}$$

where

$$\begin{aligned} C(x_1, x_2) &= C(x_1, \infty) - C(x_2, \infty) \\ &= \left[\Big(P_3(x_1) - P_3(x_2) \Big) - \frac{1}{6} \Big(x_1^3 \operatorname{Li}_1(e^{-x_1}) - x_2^3 \operatorname{Li}_1\big(e^{-x_2}\big) \Big) \right]. \end{aligned} \tag{2.15}$$

2.6 Enthalpy Density

$$h(x_1, x_2, T) = \frac{64\pi k_B{}^4}{c^3 h^3} T^4 D(x_1, x_2), \tag{2.16}$$

where

$$\begin{aligned} D\left(x_1, {}^1x_2\right) &= D(x_1, \infty) - D(x_2, \infty) \\ &= \left[\left(P_3(x_1) - P_3(x_2)\right) - \frac{1}{24}\left(x_1^3 \operatorname{Li}_1(e^{-x_1}) - x_2^3 \operatorname{Li}_1(e^{-x_2})\right)\right]. \end{aligned} \tag{2.17}$$

The Tables 6.1–6.3 provide the numerical data for the following thermodynamic functions:

(a) Absolute values of coefficients: $C(x, \infty)$, $D(x, \infty)$ and $E(x, \infty)$ as a function of $x = \frac{h\nu}{k_B T}$ (Table 6.1);
(b) Normalized values of thermodynamic functions, $\frac{f(x,\infty)}{T^4}$, $\frac{s(x,\infty)}{T^3}$, $\frac{c_V(x,\infty)}{T^3}$, $\frac{p(x,\infty)}{T^4}$, $\frac{h(x,\infty)}{T^4}$ at different $x = \frac{h\nu}{k_B T}$ (Table 6.2);
(c) Fractional values of coefficients, $C_{\text{Normalized}}$, $D_{\text{Normalized}}$, $E_{\text{Normalized}}$ as a function of $x = \frac{h\nu}{k_B T}$ (Table 6.3).

2.7 Black-Body Radiative and Thermodynamic Functions for Different Domains

It should be noted that the obtained analytical expressions for the radiative and thermodynamic functions of black-body radiation can be easily transformed to the wavenumber ($\tilde{\nu}$) or wavelength (λ) domains. In these cases, we should use the following relationships:

$$\nu = \frac{c}{\lambda}, \quad \nu = c\widetilde{\nu} \tag{2.18}$$

$$d\nu = -\frac{c}{\lambda^2} d\lambda, \quad d\nu = c d\widetilde{\nu} \tag{2.19}$$

Planck function in the frequency domain ν is a well-known function [3] given by:

$$I^{\mathrm{P}}(\nu, T) d\nu = \frac{8\pi h}{c^3} \frac{\nu^3}{e^{\frac{h\nu}{k_B T}} - 1} d\nu. \tag{2.20}$$

Using the relationship [3] and Eqs. (2.18)–(2.20)

$$I^{\mathrm{P}}(\nu,T)d\nu = I^{\mathrm{P}}(\widetilde{\nu}(\nu),T)d\widetilde{\nu} = -I^{\mathrm{P}}(\lambda(\nu),T)d\lambda, \tag{2.21}$$

we obtain:

(a) Wavelength domain λ:

$$I^{\mathrm{P}}(\lambda,T)d\lambda = \frac{8\pi hc}{\lambda^5\left[\exp^{\left(\frac{hc}{\lambda\, k_{\mathrm{B}}T}\right)} - 1\right]}d\lambda \tag{2.22}$$

(b) Wave number domain $\widetilde{\nu}$:

$$I^{\mathrm{P}}(\widetilde{\nu},T)d\widetilde{\nu} = \frac{8\pi hc\,\widetilde{\nu}^3}{\left[\exp^{\left(\frac{h\widetilde{\nu}c}{k_{\mathrm{B}}T}\right)} - 1\right]}d\widetilde{\nu}. \tag{2.23}$$

Using Eqs. (2.20) and (2.22), and Eq. (2.23), the relationship between integrals in the finite spectral range for different domains is defined as:

$$\int_{\nu_1}^{\nu_2} I^{\mathrm{P}}(\nu,T)\mathrm{d}\nu = -\int_{\lambda_1}^{\lambda_2} I^{\mathrm{P}}(\lambda,T)\mathrm{d}\lambda = \int_{\widetilde{\nu}_1}^{\widetilde{\nu}_2} I^{\mathrm{P}}(\widetilde{\nu},T)\mathrm{d}\widetilde{\nu} = I(x_1,x_2,T), \tag{2.24}$$

Here, the function $I(x_1,x_2,T)$ is defined by Eq. (1.3)

$$I(x_1,x_2,T) = \frac{48\pi(k_{\mathrm{B}}T)^4}{c^3h^3}[P_3(x_1) - P_3(x_2)]. \tag{2.25}$$

The arbitrary variable x can be represented in all three domains as follows:

$$x = \frac{h\nu}{k_{\mathrm{B}}T} = \frac{hc}{\lambda k_{\mathrm{B}}T} = \frac{h\widetilde{\nu}}{k_{\mathrm{B}}T}. \tag{2.26}$$

As seen, the results of these integrals are identical because any variable substitution does not affect the value of the calculated integral. Thus, the solution is independent on the choice of the domain. Therefore, all analytical expressions for thermal radiative and thermodynamic functions of black-body radiation, obtained in Chaps. 1 and 2, have the same structure for the wavenumber and wavelength domains.

Note that using different domains produce the same results, because it represents the same physical quantity. This means that the calculated values presented in Tables 6.1–6.3 are valid for different domains.

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