

OPTICAL PROCESSES IN SOLIDS

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1

Radiation field

1.1 Maxwell equations for electromagnetic field

Early in the nineteenth century, people already realized that light was better described by a wave model than by a corpuscular model on the basis of experimental confirmation of the interference effect. However, they were not yet aware of an entity that could oscillate and propagate in a vacuum, unlike the case of a sound wave which they knew to be a compressional wave of air. The answer came from an apparently different area: later in that century, Maxwell formulated the experimental laws relating the spatial and temporal changes of electric and magnetic fields into a set of simultaneous equations which are now called by his name. He found the set to have a solution describing an electromagnetic wave which propagates in a vacuum, and this wave was indentified with light since the predicted velocity of the former exactly agreed with that of the latter already known at that time.

Maxwell's equations for the electric field \mathbf{E} and magnetic field \mathbf{H} are given as a set of the following four equations^{1,2}

$$\nabla \times \mathbf{E} = -\partial \mathbf{B} / \partial t, \quad (1.1.1)$$

$$\nabla \times \mathbf{H} = \partial \mathbf{D} / \partial t + \mathbf{J}, \quad (1.1.2)$$

$$\nabla \cdot \mathbf{D} = \rho, \quad (1.1.3)$$

$$\nabla \cdot \mathbf{B} = 0. \quad (1.1.4)$$

Here $\nabla \equiv (\partial/\partial x, \partial/\partial y, \partial/\partial z)$ denotes a vector differential operator, \times the vector product and \cdot the scalar product. Therefore, $\nabla \cdot \mathbf{B}$ represents $\text{div} \mathbf{B} \equiv (\partial/\partial x)B_x + \dots$ and $\nabla \times \mathbf{E}$ represents $\text{rot} \mathbf{E} \equiv [(\partial/\partial y)E_z - (\partial/\partial z)E_y, \dots, \dots]$.

For the *electric flux density* \mathbf{D} and *magnetic flux density* \mathbf{B} , we have also linear relations which are exact in a vacuum and hold approximately in many ordinary

(neither ferroelectric nor ferromagnetic) materials for weak fields:

$$\mathbf{D} = \epsilon \mathbf{E}, \quad (1.1.5)$$

$$\mathbf{B} = \mu \mathbf{H}. \quad (1.1.6)$$

The *dielectric constant* ϵ and the *magnetic permeability* μ are material constants, while in a vacuum they are universal constants written as ϵ_0 and μ_0 . The most recent value of ϵ_0 is $8.854\,187\,817 \times 10^{-12} \text{ F m}^{-1}$, while $\mu_0 = 4\pi \times 10^{-7} \text{ N A}^{-2}$ by definition.

Matter with a *charge density* ρ is subject to the *Lorentz force* with density \mathbf{f} and velocity \mathbf{v} which is given by

$$\mathbf{f} = \rho(\mathbf{E} + \mathbf{v} \times \mathbf{B}). \quad (1.1.7)$$

This equation should be added to (1.1.1–1.1.4) for a consistent description of interacting particles and fields satisfying the conservation laws of energy and momentum, as will be seen below.

Taking the divergence of (1.1.2) and using (1.1.3), one gets the *continuity equation* describing the conservation of charge through the *electric current* \mathbf{J} :

$$\partial\rho/\partial t + \nabla \cdot \mathbf{J} = 0. \quad (1.1.8)$$

Under the proportionality (1.1.5, 1.1.6), the energy density of the fields is given by

$$U \equiv (\mathbf{D} \cdot \mathbf{E} + \mathbf{B} \cdot \mathbf{H})/2, \quad (1.1.9)$$

as is seen by integrating it over the volume V and taking its time derivative:

$$d/dt \int_V U dV = \int_V (\partial\mathbf{D}/\partial t \cdot \mathbf{E} + \partial\mathbf{B}/\partial t \cdot \mathbf{H}) dV.$$

With the use of eqs. (1.1.1, 1.1.2), the identity: $\nabla \cdot (\mathbf{E} \times \mathbf{H}) = \mathbf{H} \cdot \nabla \times \mathbf{E} - \mathbf{E} \cdot \nabla \times \mathbf{H}$ and the partial integration to be balanced by the surface integral, one finally obtains the energy conservation relation:

$$d/dt \int_V U dV = - \int_V (\mathbf{J} \cdot \mathbf{E}) dV - \int_s S_n ds. \quad (1.1.10)$$

Here the first integral on the right hand side (r.h.s.) represents the energy dissipated as *Joule's heat* and the second the energy lost through the surface s (suffix n denotes the component outward-normal to the surface element ds) by the flow:

$$\mathbf{S} \equiv \mathbf{E} \times \mathbf{H}, \quad (1.1.11)$$

which is called the *Poynting vector*.

1.2 Electromagnetic wave

Under the absence of charge ρ and current \mathbf{J} , (1.1.1–1.1.6) reduce to homogeneous equations for the fields. Putting (1.1.5, 1.1.6) into (1.1.1, 1.1.2) and making use of the identity: $\nabla \times \nabla \times \mathbf{E} = \nabla(\nabla \cdot \mathbf{E}) - (\nabla^2)\mathbf{E}$, where $\nabla^2 \equiv (\nabla \cdot \nabla) = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$, one obtains

$$\nabla^2 \mathbf{E} - \epsilon\mu \partial^2 \mathbf{E} / \partial t^2 = 0 \quad (1.2.1)$$

and a similar equation for \mathbf{B} . Equation (1.2.1) has a solution describing a plane wave

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_0 \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)] \quad (1.2.2)$$

which propagates with *wave vector* \mathbf{k} ($k = 2\pi/\lambda$, where λ is the *wavelength*), *angular frequency* $\omega (= 2\pi\nu$, where ν is the frequency) and velocity $c = \omega/k$ given by

$$c = (\epsilon\mu)^{-1/2}. \quad (1.2.3)$$

In a vacuum, (1.2.3) reduces to $c_0 = (\epsilon_0\mu_0)^{-1/2} (= 2.997\,924\,58 \times 10^8 \text{ m s}^{-1}$, the most recent value), which was found to agree with the velocity of light as mentioned above. The \mathbf{E} wave (1.2.2) and the corresponding \mathbf{B} wave of the same form satisfy

$$\mathbf{k} \cdot \mathbf{E}_0 = 0, \quad \mathbf{k} \cdot \mathbf{B}_0 = 0, \quad \mathbf{B}_0 = i(\mathbf{k}/\omega) \times \mathbf{E}_0 \quad (1.2.4)$$

as is seen from (1.1.1, 1.1.3 and 1.1.4). Namely, we have a *transverse* wave with \mathbf{k} , \mathbf{E}_0 and \mathbf{B}_0 forming a right-handed system with \mathbf{B}_0 lagging behind \mathbf{E}_0 by phase difference $\pi/2$. From (1.1.9, 1.1.11) and (1.2.3, 1.2.4) one finds that $\mathbf{S} = c(\mathbf{k}/k)U$, namely that the energy density U is conveyed towards the direction of \mathbf{k} with velocity c .

Similarly to the energy conservation, one can derive the momentum conservation relation from (1.1.7) and the Maxwell equations. One can see from this relation that the electromagnetic wave has momentum density U/c in the direction of propagation \mathbf{k}/k , although we do not give the derivation here.

As the electromagnetic wave passes from a vacuum into a material, the velocity c_0 and hence the wavelength $\lambda_0 = c_0/\nu$ decrease to c and $\lambda = c/\nu$, respectively, since ν does not change due to the continuity of the field at the surface. The ratio

$$n \equiv c_0/c = (\epsilon\mu/\epsilon_0\mu_0)^{1/2}, \quad (1.2.5)$$

which is called *refractive index* of the material, relates the refraction angle θ to the incidence angle θ_0 through the law of refraction: $\sin \theta = (1/n) \times \sin \theta_0$.

1.3 Canonical equations of motion for electromagnetic waves

The wave equation (1.2.1) is a differential equation of second order in time t which is similar to the Newtonian equation of motion of a particle, whereas the original simultaneous equations (1.1.1, 1.1.2) for \mathbf{E} and \mathbf{B} are of first order in t , similar to the *canonical equations* of motion for the position coordinate q and the momentum p . The canonical form is more convenient, especially when one constructs quantum mechanical and quantum electrodynamical equations from the classical ones.

It is convenient to introduce the *vector* and *scalar potentials*, $\mathbf{A}(\mathbf{r}, t)$ and $\phi(\mathbf{r}, t)$, in place of the electromagnetic fields, $\mathbf{E}(\mathbf{r}, t)$ and $\mathbf{B}(\mathbf{r}, t)$. According to one theorem in vector analysis, the divergence-free field \mathbf{B} (eq. (1.1.4)) can be written as a rotation of the vector potential \mathbf{A} :

$$\mathbf{B} = \nabla \times \mathbf{A}. \quad (1.3.1)$$

Putting this into (1.1.1), one obtains

$$\nabla \times (\mathbf{E} + \partial \mathbf{A} / \partial t) = 0. \quad (1.3.2)$$

According to another theorem, the rotation-free field as given in (\dots) of (1.3.2) can be written as a gradient of the scalar potential ϕ :

$$\mathbf{E} + \partial \mathbf{A} / \partial t = -\nabla \phi. \quad (1.3.3)$$

A *general* solution of the set of inhomogeneous equations (1.1.1–1.1.4) for ϕ and \mathbf{A} is given as the sum of a *particular* solution of the set and a general solution of the homogeneous equations (obtained by putting $\mathbf{J} = 0$ and $\rho = 0$ in (1.1.1–1.1.4)). One particular solution which is well known is the *retarded potentials* $\phi(\mathbf{r}, t)$ and $\mathbf{A}(\mathbf{r}, t)$ due to the charge and current densities ρ and \mathbf{J} as their respective sources at the spacetime point $(\mathbf{r}', t' = t - |\mathbf{r} - \mathbf{r}'|/c)$, with the common integration kernel (over \mathbf{r}') being coulombic: $|\mathbf{r} - \mathbf{r}'|^{-1}$, as it should be. This solution plays an especially important role in studying how the oscillating charge and current as sources give rise to electromagnetic waves at a remote location. We will not give the derivation here, leaving it to the standard text books.^{1,2}

We are here concerned with a general solution of the homogeneous equations, namely a superposition of the electromagnetic waves which are given by

$$\mathbf{A}(\mathbf{r}, t) = \mathbf{A}_0 \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)], \quad \mathbf{A}_0 = \mathbf{E}_0 / i\omega = (ik^{-2}) \mathbf{k} \times \mathbf{B}_0, \quad (1.3.4)$$

as can be confirmed by eqs. (1.3.1, 1.3.3). They also satisfy the wave equation of the form (1.2.1). The wave vector \mathbf{k} can take arbitrary values in infinitely extended space. A more realistic situation is a confined space such as a cavity. For the

sake of simplicity, let us consider a cube of side L and impose a cyclic boundary condition

$$\mathbf{A}(\mathbf{r} + L\hat{i}, t) = \mathbf{A}(\mathbf{r} + L\hat{j}, t) = \mathbf{A}(\mathbf{r} + L\hat{k}, t) = \mathbf{A}(\mathbf{r}, t) \quad (1.3.5)$$

where \hat{i}, \hat{j} and \hat{k} are unit vectors along the three sides of the cube. Then \mathbf{k} in (1.3.4) takes only discrete values:

$$k_x = 2\pi n_x/L, k_y = 2\pi n_y/L, k_z = 2\pi n_z/L \quad (1.3.6)$$

where n_x, n_y and n_z can take independently all integer values, inclusive of negative values and zero.[†] Then the number of possible modes with k_x within a small interval dk_x is given by $dn_x = (L/2\pi)dk_x$ and similarly for y and z components. Since the electromagnetic wave is a transverse wave and there are two possible directions of polarization (defined to be along \mathbf{E}_0) for a given wave vector \mathbf{k} , the number per volume of possible modes contained within the spherical shell between k and $k + dk$ is given by

$$\begin{aligned} 2dn/V &= 2 \times 4\pi k^2 dk / 8\pi^3 = 2 \times 4\pi \rho(\omega) d\omega, \\ \rho(\omega) &\equiv \omega^2 / 8\pi^3 c_0^3. \end{aligned} \quad (1.3.7)$$

The set of all $u_{\mathbf{k}}(\mathbf{r}) = L^{-3/2} \exp(i\mathbf{k} \cdot \mathbf{r})$ with \mathbf{k} given by (1.3.6) forms an orthonormal complete set such that $(u_{\mathbf{k}}, u_{\mathbf{k}'}) \equiv \int d\mathbf{r} u_{\mathbf{k}'}^*(\mathbf{r}) u_{\mathbf{k}}(\mathbf{r}) = \delta_{\mathbf{k}, \mathbf{k}'}$. However, in order to expand the vector potential $\mathbf{A}(\mathbf{r}, t)$, one has to prepare the set of vector basis functions

$$\mathbf{A}_{\mathbf{k}j}(\mathbf{r}) = \mathbf{e}_{\mathbf{k}j} u_{\mathbf{k}}(\mathbf{r}) \quad (j = 1, 2) \quad (1.3.8)$$

with the use of the two possible directions of polarization $\mathbf{e}_{\mathbf{k}j}$ for each \mathbf{k} which satisfy $\mathbf{e}_{\mathbf{k}j} \perp \mathbf{k}$ (transverse wave!) and $\mathbf{e}_{\mathbf{k}j} \cdot \mathbf{e}_{\mathbf{k}j'} = \delta_{jj'}$. Denoting the set $(\mathbf{k}j)$ simply by κ , one can see that (1.3.8) form an orthonormal set in the following sense:

$$\int d\mathbf{r} \mathbf{A}_{\kappa}^*(\mathbf{r}) \cdot \mathbf{A}_{\kappa'}(\mathbf{r}) = \delta_{\kappa\kappa'}. \quad (1.3.9)$$

Then one can expand

$$\mathbf{A}(\mathbf{r}, t) = (4\epsilon)^{-1/2} \sum_{\kappa} [q_{\kappa}(t) \mathbf{A}_{\kappa}(\mathbf{r}) + q_{\kappa}^*(t) \mathbf{A}_{\kappa}^*(\mathbf{r})]. \quad (1.3.10)$$

Although the first term in $[\dots]$ is sufficient as an expansion, the addition of the second term automatically assures that the three components of the vector $\mathbf{A}(\mathbf{r}, t)$

[†] A more realistic electromagnetic boundary condition for the real-valued waves of the form $\sin(\mathbf{k} \cdot \mathbf{r}) \sin(\omega t)$ may be that the waves vanish at the boundary surface, which gives possible k values without the factor 2 on the right hand sides of (1.3.6) but confines them to positive values. The two effects cancel out, keeping the number of possible modes within the interval $(k, k + dk)$, as given by (1.3.7), unchanged. Other possible shapes of the cavity do not change (1.3.7) as long as we are concerned with the majority of k values which are much greater than $1/L$.

are *real* quantities for any t . (The prefactor with ϵ , the dielectric constant, is for the normalization of energy, as will be seen later.) It is convenient to introduce *real*-valued dynamical coordinates

$$Q_\kappa(t) \equiv [q_\kappa(t) + q_\kappa^*(t)]/2 \quad (1.3.11)$$

instead of the complex-valued q_κ s. In order that each term in (1.3.10) represents a running wave as in eq. (1.2.2), $q_\kappa(t)$ should vary as $\exp(-i\omega_\kappa t)$ where $\omega_\kappa \equiv \omega_\kappa$. The time derivative of (1.3.11) is then given by

$$dQ_\kappa/dt = -i\omega_\kappa(q_\kappa - q_\kappa^*)/2. \quad (1.3.12)$$

By introducing the momentum $P_\kappa \equiv dQ_\kappa/dt$ as an independent dynamical variable, one can rewrite the complex q_κ , with the use of (1.3.11, 1.3.12), as

$$q_\kappa = Q_\kappa + (i/\omega_\kappa)P_\kappa. \quad (1.3.13)$$

Now the energy density (1.1.9) can be rewritten as

$$U = (\epsilon/2)[(\partial\mathbf{A}/\partial t)^2 + c^2(\nabla \times \mathbf{A})^2]$$

with the use of eqs. (1.1.5, 1.1.6) and (1.3.1, 1.3.3). Putting (1.3.10, 1.3.13) into this expression and integrating over the volume which is the cube, one obtains

$$H \equiv \int U dr = \sum_\kappa (P_\kappa^2 + \omega_\kappa^2 Q_\kappa^2)/2 \quad (1.3.14)$$

with the use of (1.3.9). The total energy of the transverse electromagnetic field is thus reduced to a Hamiltonian H of an assembly of harmonic oscillators indexed with κ . In fact, the canonical equations of motion: $dQ_\kappa/dt = \partial H/\partial P_\kappa$ and $dP_\kappa/dt = -\partial H/\partial Q_\kappa$ give an harmonic oscillation with angular frequency ω_κ .

The above procedure may seem to be artificial because in defining P_κ by (1.3.12) we have made use of a solution yet to be obtained. However, this artifice is common to the canonical formalism in which the formula defining the momentum $P \equiv m dQ/dt$ with mass m is to be derived from one of the canonical equations of motion: $dQ/dt = \partial H/\partial P$ ($= P/m$ for a general motion which is not harmonic). Introduction of P as an independent variable has the merit of lowering the differential equations of motion to first order in time as compared to the Newtonian equations of motion which are of second order. This facilitates the time-integration a great deal, so as to more than cover the demerit of doubling the number of independent variables. The canonical formalism turns out to be more natural in statistical mechanics in which P and Q are independent variables, and to be indispensable for quantum mechanics in which P and Q are mutually conjugate variables subject to the uncertainty relation.

1.4 Thermal radiation field

We are now in a position to describe that experimental fact whose deviation from the predictions of classical physics provided a clue to the discovery of quantum mechanics. It is well known, even in daily experience, that the glowing radiation emitted by a hot body shifts from red to yellow, namely toward shorter wavelengths, as the temperature increases. The observed spectral distribution of this radiation in an idealized situation, namely in a cavity which is in thermal equilibrium with its wall, depends only on the temperature but not on the material of the wall, as shown schematically by the solid lines in Fig. 1.1. The broken lines are the spectra predicted by the classical theory available at that time, late in the 19th century when the experiments were done. One finds that the theory deviates from the observation significantly in the short-wavelength region.

Let us trace this theoretical prediction which was based on the classical mechanics and statistical mechanics applied to an assembly of harmonic oscillators representing the radiation field as mentioned in the preceding section. A harmonic oscillator with Hamiltonian given by $H(Q, P) = P^2/2 + \omega^2 Q^2/2$, which is in thermal equilibrium at temperature T , obeys the Boltzmann distribution: the probability of finding the system within a small region of the phase space (Q, P) is proportional to

$$\exp[-\beta H(Q, P)]dQdP, \text{ with } \beta \equiv 1/k_B T \quad (1.4.1)$$

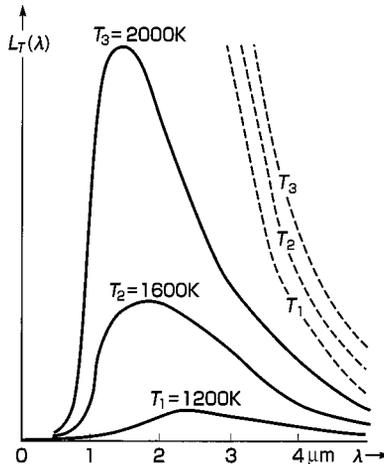


Fig. 1.1 The spectral distribution of energy density, L_T , of thermal radiation field at various temperatures. Solid lines are experimental results (shown schematically) which can be fitted by the quantum hypothesis of Planck. Broken lines are the predictions of classical field theory.

where k_B is the Boltzmann constant. Consider the region of the phase space which is surrounded by an ellipse given by $H(Q, P) = E$. Its area is given by

$$s(E) = \pi(2E/\omega^2)^{1/2}(2E)^{1/2} = E/\nu \quad (1.4.2)$$

where $\nu = \omega/2\pi$ is the frequency. Integrating (1.4.1) over the elliptic shell between E and $E + dE$ whose area is given by dE/ν , one obtains the Boltzmann distribution for the energy: $\exp(-\beta E)dE/\nu$. The statistical average of the energy is then given by

$$\begin{aligned} \langle\langle E \rangle\rangle &= \int_0^\infty E \exp(-\beta E)d(E/\nu) / \int_0^\infty \exp(-\beta E)d(E/\nu) \\ &= \beta^{-1} = k_B T \end{aligned} \quad (1.4.3)$$

which does not depend on the frequency ν of the oscillator for the electromagnetic wave concerned.

Let us rewrite (1.3.7), the number of normal modes of electromagnetic wave within a small interval dk of wave number, into that within an interval $d\lambda$ of wavelength, making use of the relation $k = 2\pi/\lambda$. The number per unit volume of the cavity space is then given by $8\pi\lambda^{-4}d\lambda$. Multiplying this by the energy per mode (1.4.3), one obtains the energy density per λ of the thermal radiation field

$$L_T(\lambda) = 8\pi k_B T \lambda^{-4} \quad (1.4.4)$$

which diverges at shorter wavelengths, as shown by the broken lines in Fig. 1.1.

In 1900, Planck put forth a working hypothesis,³ by which he could *provisionally* evade the discrepancy of the theoretical prediction from the experimental result; that concerned with the mechanics, not with the statistical distribution. In classical mechanics, one tacitly assumes that the energy of a particle in motion can take continuous values as exemplified by the continuous distribution shown in the integral of (1.4.3). For a harmonic oscillator with frequency ν , he *tentatively replaced* the continuous values by the following set of *discrete* values:

$$E_n = nh\nu \quad (n = 0, 1, 2, \dots). \quad (1.4.5)$$

Here, h is an empirical constant to be determined later. The integral in (1.4.3) is then to be replaced by a summation, with the following result:

$$\begin{aligned} \langle\langle E \rangle\rangle &= \sum_{n=0}^{\infty} nh\nu \exp(-\beta nh\nu) / \sum_{n=0}^{\infty} \exp(-\beta nh\nu) \\ &= h\nu / [\exp(\beta h\nu) - 1] = h\nu \langle\langle n \rangle\rangle. \end{aligned} \quad (1.4.6)$$

(Note: the summation in the denominator gives $f(\beta) = [1 - \exp(-\beta h\nu)]^{-1}$ so that the numerator can be written as $-df(\beta)/d\beta$.) Hence, (1.4.4) was replaced by

$$L_T(\lambda) = 8\pi\lambda^{-5}hc_0 / [\exp(hc_0/k_B T\lambda) - 1]. \quad (1.4.7)$$

Planck could reproduce the experimental spectra shown schematically in Fig. 1.1. at all temperature by the new formula (1.4.7) by choosing an appropriate value for h , the only adjustable parameter. In spite of this brilliant success, it took some time before people realized the physical meaning of the working hypothesis (1.4.5) which seemed so absurd from the viewpoint of classical physics. However, the constant h introduced by him as an empirical parameter played a pivotal role in the groping effort for new physical principles until quantum mechanics was discovered a quarter of a century later. And in fact Planck's hypothesis, (1.4.5), was successfully derived subsequently when quantum mechanics was established, as will be described in Sections 2.2 and 2.3. Planck's constant h is now a universal constant governing the entire quantum world. Its value is $6.626\,068\,76 \times 10^{-34}$ J s according to a recent measurement.

Returning to the problem of thermal radiation, we find that the new formula (1.4.7) reduces to the classical one (1.4.4) in the limit of high temperature or long wavelength, namely when $k_B T \lambda / hc_0 = k_B T / h\nu \gg 1$. The spectral maximum of the quantal expression (1.4.7) appears at λ_{\max} which is related to T by

$$\lambda_{\max} T = (hc_0/4.966k_B) = 0.290 \text{ cm K.} \quad (1.4.8)$$

This reproduces Wien's displacement law, the empirical law which had been found before Planck put forth his hypothesis.

In contrast to traditional spectroscopy in which λ has been chosen as the variable, it is more convenient to choose an angular frequency $\omega = 2\pi c_0/\lambda$. Then the energy density in ω -space, defined by $W_T(\omega)d\omega = L_T(\lambda)d\lambda$, is given by

$$W_T(\omega) = (\hbar\omega^3/\pi^2c_0^3)\langle\langle n \rangle\rangle = (\hbar\omega^3/\pi^2c_0^3)/[\exp(\beta\hbar\omega) - 1], \quad (1.4.9)$$

where we have defined $\hbar \equiv h/2\pi$ which is nowadays more frequently used than h . It takes its maximum value at

$$\hbar\omega_{\max} = 2.821k_B T \quad (1.4.10)$$

which is different from the photon energy corresponding to the λ_{\max} of (1.4.8), namely $hc_0/\lambda_{\max} = 4.966k_B T$.