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Application of Exergy for Research on Increasing the Usefulness of Solar Radiation by Dispersing It into Monochromatic Beams

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Abstract

Energy determines the ability of matter to work. However, in the given environment, the real usefulness to perform work is determined by exergy. This study covers not only solar, but also any monochromatic thermal radiation. The value of such radiation was determined by its exergy and the ratio of its exergy-to-energy. A novelty in this work is to demonstrate by means of exergy that the usefulness of thermal polychromatic radiation can be increased by its dispersion to monochromatic radiation. This effect is the greater, the lower the temperature of the radiation. Analogies of this effect to the exergetic effect of gas separation have been indicated. The effect of the increase in exergy in the process of radiation dispersion was interpreted by means of a cylinder-piston system that explains this effect with the influence of environmental radiation. The concept of quasi-monochromatic and cumulated radiation was introduced into dispersion considerations and the change in the energetic, entropic and environmental components of the exergy of radiation beams was analyzed. Considerations were illustrated with appropriate examples of calculations considering dispersion of high-temperature radiation, such as extraterrestrial solar radiation and dispersion of low-temperature radiation from water vapor.

Keywords

Radiation Exergy, Monochromatic Radiation, Solar Radiation, Water Vapor Radiation, Light Dispersion, Exergy-Energy Ratio

1. Introduction

The radiation of the Sun can be considered as thermal radiation that comes from a body with a temperature higher than absolute zero. Solar radiation plays a large role as an energy source. Therefore, various energetic and exergetic analyzes of this radiation and the processes of its use are widely carried out. For example, it can be concluded that the practical value of solar radiation, measured by exergy, differs from the energy of this radiation and is always about 6.7% less.

The main part of solar energy is visible white light, which, for example, by means of a prism or by diffraction (**Figure 1**), can be split into radiation of different colors. Colored light is also obtained through filters that allow only a given color to pass. The unicolor radiation is monochromatic radiation. The spectrum of solar radiation also contains invisible radiation, which of course is also characterized by wavelength, or frequency. Invisible radiation can be also dispersed, but remains invisible. An example of a single-color light is also laser light, which, however, is not covered by these considerations. Radiation of fluorescent phenomena is also neglected. Current considerations apply only to heat radiation, also called thermal radiation, which occurs due to surface temperature. The theory of such thermal radiation was formulated by Planck [1].

The subject of this theoretical study is the exergetic effect of dispersion of thermal radiation and the results of the exergetic analysis of monochromatic radiation arising during dispersion are the original contribution of this work to the knowledge of radiation exergy.

The literature on this topic is not very developed. Badescu (1988) [2] proposed a formula for the component of the exergy spectrum per unit volume. Moreno *et al.* (2003) [3] considered the reduction and splitting of the quantum states of photons. The exergy of monochromatic radiation was originally mentioned by Candau (2003) [4], then also discussed by Chu and Liu (2009) [5], and a more detailed analysis of monochromatic radiation was presented by Petela [6]. Badescu [7] thought about a solar power station in space or on the surfaces of planets, based on Carnot's efficiency, and analyzed the efficiency of monochromatic radiation converters. However, the exergetic effect of radiation dispersing, analyzed in this paper, has never been taken into account.

An extended overview of the exergy of thermal radiation can be found in [8]. The energy and entropy of thermal radiation are considered here according to Planck (1914) [1]. Data on the solar radiation spectrum come from Kondratyev (1954) [9].

2. Basic Equations

We begin with radiation, which is considered arbitrary, but non-polarized,

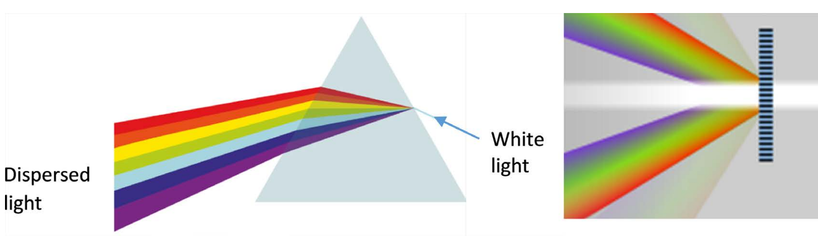

Figure 1. Dispersion and diffraction of a white light.

uniform radiation propagating in a solid angle of 2π. Uniform radiation means that the energy and entropy spectra do not depend on direction. The exergy formula for such radiation b, J/m^2 is as follows [10]:

$$b = 2\pi \int_{\nu} i_{b,0,\nu} \mathrm{d}\nu - 2\pi T_0 \int_{\nu} L_{b,0,\nu} \mathrm{d}\nu + \frac{\sigma}{3} T_0^4 \quad (1)$$

where:

T_0 - absolute temperature of environment, K,

ν - vibration frequency, 1/s,

$i_{b,0,\nu}$ - directional normal monochromatic radiation intensity of non-polarized radiation, depending on frequency ν, J/(m^2 sr),

$L_{b,0,\nu}$ - entropy of this intensity, dependent on frequency ν, J/(m^2 K sr),

σ - Boltzmann constant for black radiation, $\sigma = 5.6693 \times 10^{-8}$ W/(m^2 K^4).

To clarify, according to Planck [1], the number 2 before the sums of intensity and entropy in formula (1) takes into account that both components of polarized radiation in two perpendicular planes are equal.

Waves of heat radiation are characterized by wavelength λ, propagation velocity c and frequency ν, ($\lambda\nu = c$). In experimental studies, it is more convenient to measure the wavelength. However, in theoretical analyses, it is often convenient to use a frequency that does not change when radiation passes from one medium to another, although it changes the propagation speed. Both integrals in Equation (1) can also be expressed as dependent on the wavelength:

$$\int i_{b,0,\nu} \mathrm{d}\nu = \int i_{b,0,\lambda} \mathrm{d}\lambda \quad (2)$$

$$\int L_{b,0,\nu} \mathrm{d}\nu = \int L_{b,0,\lambda} \mathrm{d}\lambda \quad (3)$$

where:

λ - wavelength, m,

$i_{b,0,\lambda}$ - directional normal monochromatic radiation intensity of non-polarized radiation, depending on wavelength λ, W/(m^3 sr),

$L_{b,0,\lambda}$ - entropy of $i_{0,\lambda}$, dependent on wavelength λ, W/(m^3 K sr).

The black radiation intensity appearing in the formula (1), is expressed [1] as follows:

$$i_{b,0,\nu} = \frac{h\nu^3}{c^2} \frac{1}{\exp\left(\frac{h\nu}{kT}\right) - 1} \quad (4)$$

and the entropy of the black radiation intensity:

$$L_{b,0,\nu} = \frac{k\nu^2}{c^2} \left[(1+X)\ln(1+X) - X \ln X \right] \quad \text{where } X \equiv \frac{c^2 i_{0,\nu}}{\nu^3 h} \quad (5)$$

where:

c - is the speed of propagation of radiation in vacuum, $c = 2.9979 \times 10^8$ m/s,

k - Boltzmann constant, $k = 1.3805 \times 10^{-23}$ J/K,

h - Planck's constant, $h = 6.625 \times 10^{-34}$ J s,

T - radiation temperature, K.

The black radiation intensity appearing in formula (1) can also be expressed as a function of the wavelength λ, [1]:

$$i_{b\,0\,\lambda} = \frac{c_0^2 h}{\lambda^5} \frac{1}{\exp\left(\frac{c_0 h}{k\lambda T}\right) - 1} \tag{6}$$

and correspondently the entropy of the black radiation intensity as function of wavelength λ:

$$L_{b,0,\lambda} = \frac{c_0 k}{\lambda^4}\left[(1+Y)\ln(1+Y) - Y\ln Y\right] \quad \text{where } Y \equiv \frac{\lambda^5 i_{b,0,\lambda}}{c_0^2 h} \tag{7}$$

Monochromatic radiation occurs only in an infinitesimally small range of wavelengths from λ to λ + dλ. However, one can also consider quasi-monochromatic radiation for a small but finite range from λ to $\lambda + \Delta\lambda$. In both cases, radiation can be understood either as only the considered component of the spectrum, not separated from this polychromatic radiation, or radiation separated from the polychromatic spectrum, characterized by such a spectrum in which the radiation intensity is for all wavelengths equal to zero, except for the considered wavelength (dλ or $\Delta\lambda$). It can be assumed that by applying an appropriate filter, separated radiation of the required spectrum can be obtained.

If the dependence of the intensity i and entropy of L, neither on the frequency ν nor on the wavelength λ, in the form of equations is unknown, then these two quantities have to be determined on the basis of measured data for intensity i, and in Equation (1) discretization is used:

$$b = 2\pi\sum i_{0,\nu}\Delta\nu - 2\pi T_0\sum L_{b,0,\nu}\Delta\nu + \frac{\sigma T_0^4}{3} \tag{8}$$

or using wavelength instead of frequency:

$$b = 2\pi\sum i_{0,\lambda}\Delta\lambda - 2\pi T_0\sum L_{b,0,\lambda}\Delta\lambda + \frac{\sigma T_0^4}{3} \tag{9}$$

For the solar radiation, it is assumed that the intensity $\boldsymbol{i}$ arrives from black surface of the sun, therefore the entropy $\boldsymbol{L}$ of this intensity is calculated also as for a black radiation.

3. Components of Radiation Exergy

The formula for physical exergy B of a substance contains the environmental temperature T_0, the enthalpy and entropy (H, S) for the substance under consideration and (H_0, S_0) for that substance in equilibrium with the environment:

$$B = H - H_0 - T_0(S - S_0) \tag{10}$$

Equation (10) can be rewritten in the form:

$$B = H - T_0 S + (T_0 S_0 - H_0) \tag{11}$$

which reveals the three components of exergy; energetic (H), entropic ($-T_0S$) connecting to the environment through the involvement of T_0 and purely environmental ($T_0S_0 - H_0$).

In the same way, the components of radiation exergy can be considered. To obtain the formula for the exergy of black emission, in equation (10) the enthalpy of a substance is replaced by the corresponding σT^4 emission of black radiation, while the entropy of the substance corresponds to the entropy $4\sigma T^3/3$ of the emission. The exergy b of black emission is therefore:

$$b = \sigma T^4 - \sigma T_0^4 - T_0\left(\frac{4}{3}\sigma T^3 - \frac{4}{3}\sigma T_0^3\right) \tag{12}$$

Equation (12) can be converted into a form with three characteristic components revealing the contribution of environment (ambient) A, entropy S and emitted energy E:

$$b = A + S + E \tag{13}$$

where:

$$A = \sigma\frac{T_0^4}{3} \tag{14}$$

$$S = -\frac{4}{3}\sigma T_0 T^3 \tag{15}$$

$$E = \sigma T^4 \tag{16}$$

The environmental exergy component A is always positive. In the considered case of non-dispersed black radiation this component depends only on the environmental temperature. The energetic component E represents the intensity of radiation and is always positive. However, the entropic component S is always negative. These components ($A' + S' + E' = 100\%$) are shown in **Figure 2** for temperatures T below 600 K and in **Figure 3** for temperatures T higher than 600

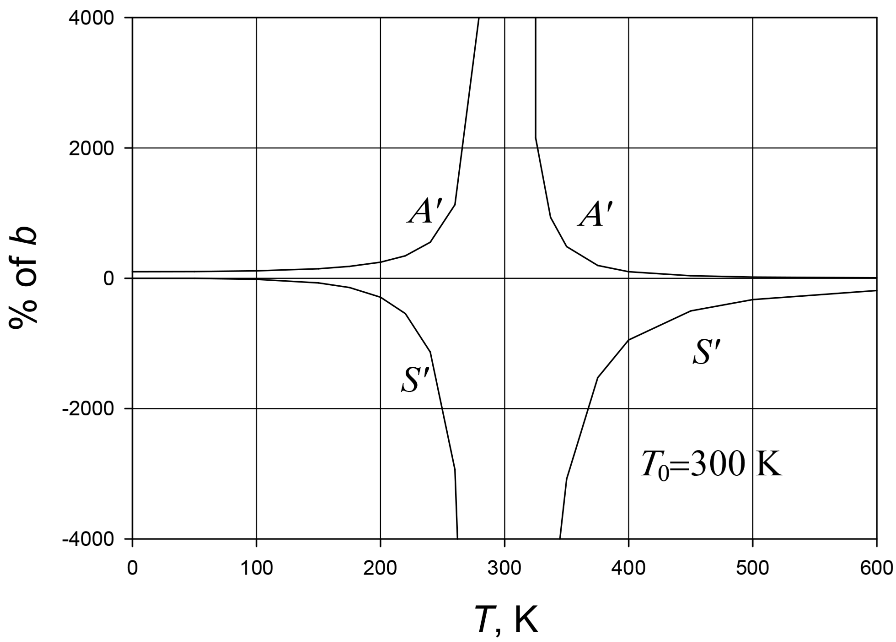

Figure 2. Percentage components A, S and E of exergy b at low temperature.

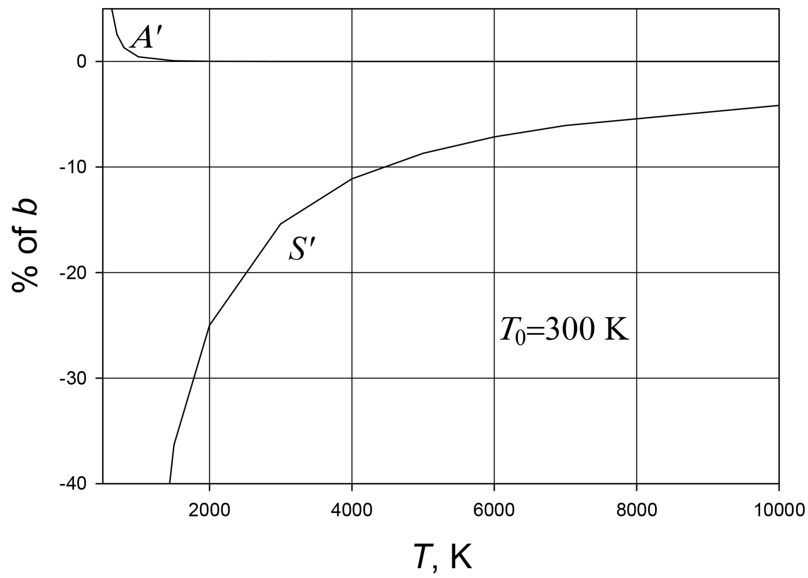

Figure 3. Percentage components A, S and E of exergy b at high temperature.

K. The ambient temperature is T_0 = 300 K. In the first case, **Figure 2**, (for example, for T = 450 K, A = 37.2%, S = −502.3%, E = 565.1%), all components have counting values so the emission exergy of the black surface should be calculated using the known complete formula [10] resulting e.g. from the rearranged Equation (12):

$$b = \frac{\sigma}{3}\left(3T^4 - 4T_0T^3 + T_0^4\right) \tag{17}$$

However, in the second case, in **Figure 3**, it is shown that the environment component can be neglected for radiation temperatures T > ~1000 K, (for example for T = 1500 K, A = 0.07%, S ≈ −25%, E ≈ 125%), and the following simplified formula can be used:

$$b = \frac{\sigma}{3}\left(3T^4 - 4T_0T^3\right) \tag{18}$$

In exergy analyses, for comparative purposes, the exergy-to-energy ratio ψ is used. For example, for blackbody radiation at temperature T, this ratio is, Petela, 1961 [10]:

$$\psi = 1 + \frac{1}{3}\left(\frac{T_0}{T}\right)^4 - \frac{4}{3}\frac{T_0}{T} \tag{19}$$

For radiation temperatures T > ~1000 K, according to (18), the formula (19) can be simplified:

$$\psi = 1 - \frac{4}{3}\frac{T_0}{T} \tag{20}$$

The ratio of ψ plays a similar role as Carnot's efficiency for heat engines, since this ratio indicates a certain relative potential of the maximum work available from radiation. It is worth noting that this ratio does not describe how to get maximum work, but only expresses that the search for a way is justified. This ratio was first introduced by R. Petela, [10]. Based on later articles by Landsberg and Press, who discussed the formula (19) without changing it, it was sometimes called in the literature by three names, the Petela-Landsberg-Press ratio, although there is no rule that everyone who confirmed the newly found formula becomes its co-author.

On the basis of the discussed formulas for polychromatic radiation, represented by the full spectrum of radiation, further considerations are carried out on the exergy of monochromatic radiation.

4. Undispersed Monochromatic Black Radiation

By analogy with Equation (10), you can write the following formula for the exergy of undispersed monochromatic black radiation propagating in a unit of solid angle [6]:

$$b_\lambda = \left(i_{0,\lambda}\right)_T - \left(i_{0,\lambda}\right)_{T_0} - T_0\left[\left(L_{0,\lambda}\right)_T - \left(L_{0,\lambda}\right)_{T_0}\right] \tag{21}$$

By analogy with Equation (12), exergy b_λ, expressed by Equation (21), is the sum of the components presented in Equation (13):

$$A_\lambda = T_0\left(L_{0,\lambda}\right)_{T_0} - \left(i_{0,\lambda}\right)_{T_0} \tag{22}$$

$$S_\lambda = -T_0\left(L_{0,\lambda}\right)_T \tag{23}$$

$$E_\lambda = \left(i_{0,\lambda}\right)_T \tag{24}$$

The sum of the percentage values of these components is 100%, and some examples of such values, depending on the wavelength λ, are shown in **Figure 4**. Three graphs show values for three different radiation temperatures T, (6000, 1000 and 280 K), at the same environment temperature T_0 = 300 K, while the other three graphs refer to three different ambient temperatures T_0, (300, 2000 and 150 K), at the same radiation temperature T = 6000 K. The entropic component S_λ is always negative. At high radiation temperature T, the energetic component E_λ is larger than 100%. The environmental component A_λ becomes relatively relevant when the radiation temperature T is low or the environment temperature T_0 is relatively high. At constant values of T and T_0, the environmental component A_λ increases as the wavelength λ increases.

By analyzing the Equation (1), for polychromatic radiation, and the Equation (21), for monochromatic radiation, it can be deduced that the environmental component of monochromatic radiation A_λ, W/(m^3 sr), presented by the formula (22), after integration in the range from $\lambda = 0$ to $\lambda = \infty$ and at T_0 = 300 K, reaches the polychromatic component value $A = \sigma T_0^4/3 = 153.1\ \mathrm{W/m^2}$.

Based on Equation (21), the ratio of exergy-to-energy ψ_λ, for monochromatic unseparated radiation, is:

$$\psi_\lambda = \frac{b_\lambda}{\left(i_{0,\lambda}\right)_T} \tag{25}$$

Figure 5 shows the calculated values of ψ_λ as a function of λ for five temperature

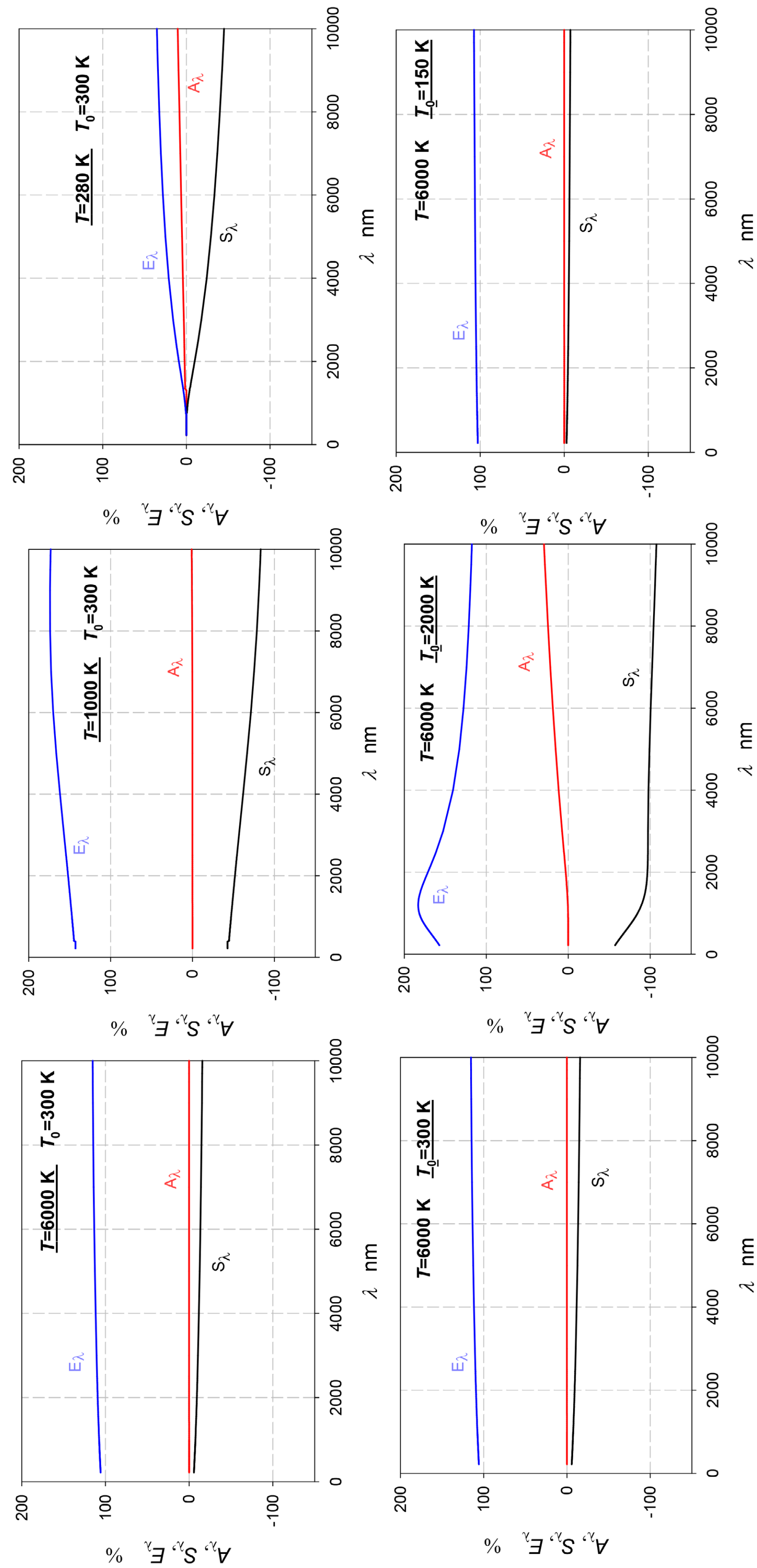

Figure 4. Exemplary values of components of black radiation exergy at temperature T as function of wavelength λ and environment temperature T_0.

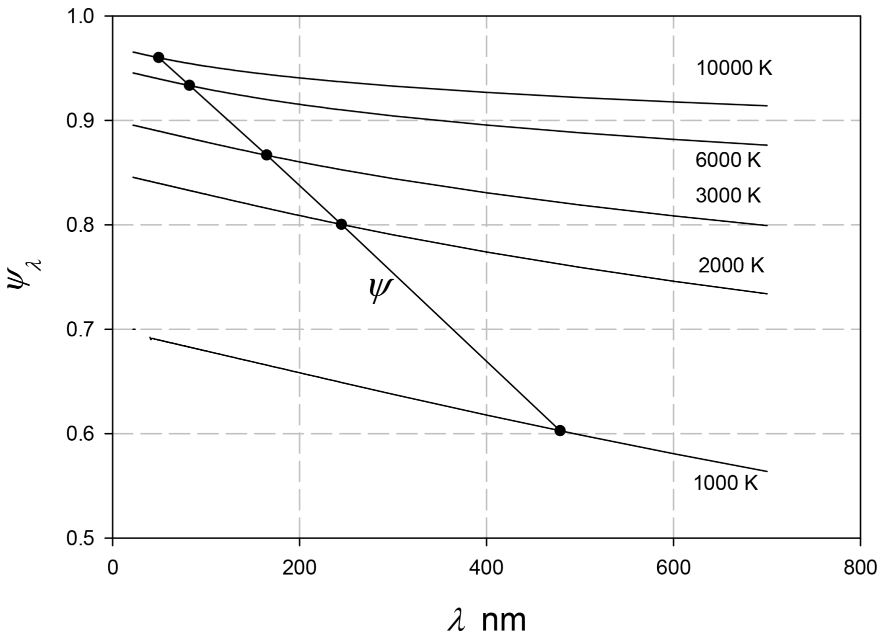

Figure 5. The exergy-to-energy ratios ψ and ψ_λ as a function of wavelength λ and temperature T of black radiation.

values T, at environmental temperature T_0 = 300 K. The formulas (25), (6) and (7) were used in the calculations. For comparison, the value of ψ calculated from the formula (20) is also shown.

For each of all 5 temperatures considered T, **Figure 5** shows that the exergy-to-energy ratio ψ_λ of undispersed monochromatic radiation increases with a decrease in wavelength λ and can reach even values greater than ψ calculated for total polychromatic black radiation. Both the ratios ψ and ψ_λ decrease as the radiation temperature decreases and the wavelength λ increases. In other words, for any given temperature, the thermodynamic value of monochromatic radiation, measured by exergy, is the closer to the energy, the smaller the wavelength, and therefore the higher the frequency. The question now arises as to how the exergy of polychromatic radiation will change when it is optically separated into monochromatic beams.

5. Exergetic Effect of Dispersion of Radiation

These considerations are conducted on the assumption that dispersed rays do not change the solid angle of their spread, while changing the direction of their propagation at the changed plane angle does not affect its exergy. It was assumed that the dispersion of radiation causes a change in its spectrum without changing temperature, which means that dispersed non-polychromatic beams, with the exception of exergy, have energy and entropy values such as they had when they were part of undispersed polychromatic radiation. It is also assumed that there is no loss of energy when dispersing of radiation, e.g. that the heat released can be neglected.

Radiation dispersing can generate exergy. To theoretically explain this possibility, let's apply Equation (1). Based on the relationship (2) and (3), Equation (1) can also be written using wavelengths instead of vibration frequencies. Suppose that the polychromatic radiation, the exergy of which is determined by the formula (1), has been dispersed into a count of n beams, the spectrum of which consists of the intensity of radiation only in the appropriate intervals: $\Delta\lambda_1, \Delta\lambda_2, \cdots, \Delta\lambda_n$. The radiation exergy of each dispersed beam can also be calculated by the formula (1). The sum b_d of the exergies of all the dispersed beams is therefore:

$$\begin{aligned} b_d &= 2\pi\left(\int_0^{\Lambda_1} i_{b,0,\lambda}\mathrm{d}\lambda - T_0\int_0^{\Lambda_1} L_{b,0,\lambda}\mathrm{d}\lambda\right) + 2\pi\left(\int_{\Lambda_1}^{\Lambda_2} i_{b,0,\lambda}\mathrm{d}\lambda - T_0\int_{\Lambda_1}^{\Lambda_2} L_{b,0,\lambda}\mathrm{d}\lambda\right) + \cdots \\ &+ 2\pi\left(\int_{\Lambda_{n-1}}^{\infty} i_{b,0,\lambda}\mathrm{d}\lambda - T_0\int_{\Lambda_{n-1}}^{\infty} L_{b,0,\lambda}\mathrm{d}\lambda\right) + n\frac{\sigma}{3}T_0^4 \end{aligned} \tag{26}$$

where integration limits are:

$$\begin{aligned} \Lambda_1 &= \Delta\lambda_1 \\ \Lambda_2 &= \Delta\lambda_1 + \Delta\lambda_2 \\ &\vdots \\ \Lambda_{n-1} &= \sum_{i=1}^{i=n-1}\Delta\lambda_i \end{aligned}$$

The sum of all integrals in Equation (26) is equal to the sum of two integrals in Equation (1). The difference between the exergy of dispersed beams and the non-dispersed radiation is therefore:

$$b_d - b = (n-1)\frac{\sigma}{3}T_0^4 \tag{27}$$

By introducing the degree of $\varepsilon = b_d/b$ as a measure of the increase in radiation exergy by dispersion and using the Equations (13) and (14), the Equation (27) may be changed as follows:

$$\varepsilon = 1 + (n-1)\frac{A}{A+E+S} \tag{28}$$

Since the ratio $A/(A + S + E)$ is always positive, the formula (28) shows that for $n > 1$, radiation dispersion always gives an increase in exergy, $\varepsilon > 1$. For black radiation, using the formulae (14), (15) and (16) in (28), the following is obtained:

$$\varepsilon = 1 + \frac{n-1}{1 + 3\left(\frac{T}{T_0}\right)^4 - 4\left(\frac{T}{T_0}\right)^3} \tag{29}$$

The degree of ε depends on the radiation temperature T, the ambient temperature T_0 and the number of n beams obtained by dispersions. The dependence (29) for black radiation at T_0 = 300 K is illustrated by diagram in **Figure 6**.

For example, as shown in **Figure 6**, for T = 800 K, if n = 40 then ε = 1.5075. The greater the number of n separated beams from polychromatic radiation, the

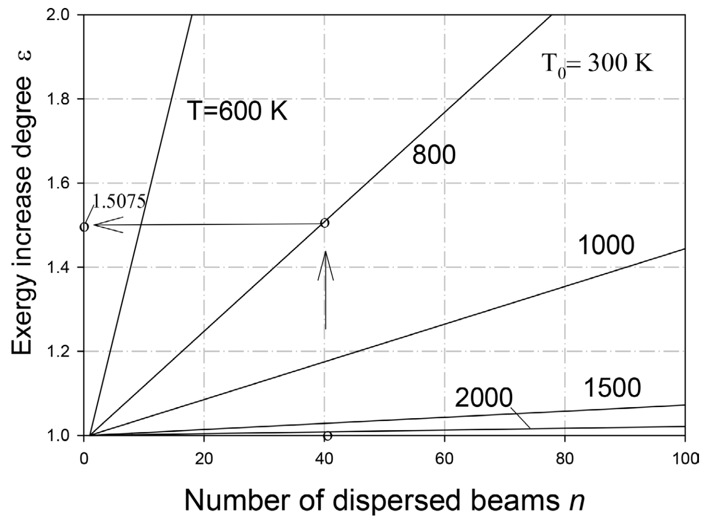

Figure 6. The degree ε of increase in exergy as a function of black radiation temperature T and the number n dispersed beams at environment temperature $T_0 = 300$ K.

greater the generation of exergy can be expected. The formula (29) also shows that at any temperatures T and T_0, when $n \to \infty$, also to infinity aims the exergy increase degree, $\varepsilon \to \infty$. The lower the radiation temperature T, the smaller the number of n dispersed beams causes a remarkable increase in exergy by dispersing radiation.

Solar radiation is characterized by high temperature and a significant increase in exergy by dispersion, for example $\varepsilon = 1.05$ at $T = 6000$ K and $T_0 = 300$ K, occurs only at the number of dispersed beams $n = 22{,}401$. However, in some exceptional surroundings with a temperature of $T_0 = 2000$ K, this solar radiation will reach $\varepsilon = 1.05$ already at $n = 8$. The calculation examples later show in more detail the dispersion effect for high-temperature solar radiation and low-temperature water vapor.

Summarizing, it can be observed that if the exergy of an initially undispersed radiation flux of a given spectrum is calculated, then according to the formula (8) the environmental component A is taken only once. However, when the initial radiation is dispersed, a series of new dispersed beams are formed, each of which has its own spectrum. Therefore, by summing up the exergy of all n dispersed beams, each of which is also calculated using the formula (8), one obtains a total exergy greater by the number $(n - 1)$ of the environment components. Therefore, the dispersion process increases total exergy.

It seems peculiar that the separation of any radiation beam can be carried out optically in a process without any driving input. For comparison, however, it is worth mentioning the analogy to the separation of gaseous components. In addition to the differential pressure required for the transport of gases, the separation of the components is carried out without any input using molecular sieves. For example, the exergy of ambient air is zero, while the sum of the exergies of the separated components from such air is greater than zero.

The effect of increasing the exergy of products in the process of gas separation, or radiation dispersion, occurs as a result of interaction with the environment. In the case of radiation, this effect arises in the fact that environmental radiation has a full black spectrum, which confronts the spectrum of dispersed radiation without radiation intensity in some wavelength ranges. For further interpretation of such increasing exergy, one of the methods of deriving the formula on the exergy of radiation can be used. The method involves calculating the work performed by radiation in a frictionless cylinder-piston system filled with gas. Such a model was used [11] for radiation considered as a photon gas (**Figure 7**).

The system is located in a vacuum, which is filled only with environment radiation at temperature T_0. The cylinder contains only considered radiation trapped inside, at temperature T. The system is in an adiabatic state because, thanks to its perfect insulation and perfect mirror like walls, there is no heat exchange with surroundings, neither by convection, nor conduction, nor by radiation. The radiation pressure depends only on the temperature, and the higher the temperature, the higher the pressure. Therefore, for different temperatures $T \neq T_0$, there is a different pressure on both sides of the piston, which moves the piston to the left ($T_0 > T$) or to the right ($T > T_0$), in both cases performing work determining the exergy of trapped radiation.

The dispersed radiation with a spectrum with no radiation intensity in some wavelength ranges could be imagined using the model of two cylinder-piston systems (**Figure 8**). For example, one cylinder is filled with any quasi monochromatic radiation in a given wavelength range at $T > T_0$, and another cylinder represents the absence of radiation ($T = 0$) in all other wavelength ranges. The sum of the work done in both systems determines the exergy of the quasi monochromatic radiation under consideration. The absence of radiation in the dλ wavelength range in the spectrum can be interpreted as a kind of monochromatic

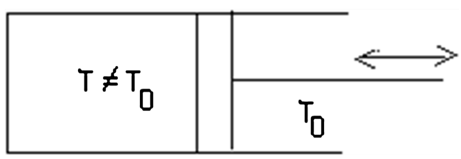

Figure 7. Radiation trapped in a cylinder with a piston.

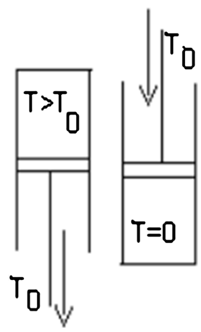

Figure 8. Quasi monochromatic radiation considered with use of the two cylinder-piston systems.

radiation "vacuum", which allows the environmental radiation pressure to manifest its usefulness in this range. It could therefore be noted that the factor that triggers the work from the environment may be partial pressure in the case of gases and a non-polychromatic spectrum in the case of radiation.

6. Solar Radiation

6.1. Exergy of Extraterrestrial Solar Radiation

Solar radiation is an example of relatively high-temperature radiation. The spectrum of solar radiation is determined by measurements [9]. The 114 values $i_{0,\lambda}$ of radiation intensity for successive wavelengths λ are shown in the corresponding columns 3 and 2 of **Table A1** (Appendix), some of whose rows are shown as a sample in **Table 1**. With the appropriate selections, this data make it possible to study the solar radiation spectrum from different viewpoints.

The input values for the present considerations are in **Table A1** columns 2 - 6. The part of input, relating to the white light, is shown by the wavelength ranges distinguished as shaded rows with respective primary colors. Taking the wavelength intervals $\Delta\lambda$ from column (4) and based on the relation $\nu = c/\lambda$, (2) and (3), the respective frequency intervals $\Delta\nu$ were determined. The radiation intensity or its entropy (in columns 5 or 6), were calculated with formulae 4 or 5 in which the average value of ν in the considered interval, was used.

Column 7 in **Table A1** shows monochromatic radiation b_ν calculated based on adapted equation (8) and with taking into account the solid angle ($\pi \times 2.16 \times 10^{-5}$) in which the solar radiation propagates:

$$\left(b_\nu\right)_n = \left[2\left(i_{0,\nu}\Delta\nu\right)_n - 2T_0\left(L_{0,\nu}\Delta\nu\right)_n + \frac{\sigma T_0^4}{3\pi}\right]2.16\times10^{-5}\pi \tag{30}$$

The considerations in Section 5 show that the number $n = 114$ quasi-monochromatic components of high-temperature radiation is so small that the environmental component of exergy can be omitted ($A = \sigma T_0^4/3\pi \approx 0$) when calculating

Table 1. Sample data (some selected rows) on the spectral distribution of extraterrestrial solar radiation reaching the atmosphere (columns 2 and 3), (Kondratyev, 1954) and other columns used in the analysis of monochromatic radiation exergy.

#	λ	$i_{0,\lambda}$	$\Delta\lambda$	$i_{0,\nu}\Delta\nu$	$L_{0,\nu}\Delta\nu$	b_ν	ψ_ν	$(i_{0,\nu}\Delta\nu)_\lambda$	$(L_{0,\nu}\Delta\nu)_\lambda$	$b_{\Delta\nu}$	$\psi_{\Delta\nu}$
1	2	3	4	5	6	7	8	9	10	11	12
1	220	10	10	96	0.21	0.13	0.9613	96	0.21	0.13	0.9613
2	230	26	10	265	0.54	0.34	0.9481	361	0.75	0.46	0.9448
3	240	31	10	309	0.64	0.40	0.9458	670	1.38	0.86	0.9417
…	…	…	…	…	…	…	…	…	…	…	
113	6000	1	1000	126	0.51	0.15	0.8970	1,007,866	2263.01	1275.71	0.9326
114	7000	1	1000	64	0.29	0.08	0.9007	1,007,930	2263.31	1275.78	0.9326
Total				**10,079,300**	**2263.31**	**1275.78**					

both the exergy of monochromatic radiation in a non-dispersed beam as well as separated beams. Thus, the value b_ν, in column 7 of Table A1, calculated by the formula (30), corresponds to the quasi-monochromatic exergy in the non-dispersed beam of radiation or to the separated beams. For example, the value in column 7, (row 3 – shaded in grey) is calculated as:
$b_\nu = (2\times 3090 - 2\times 300\times 0.64)\times\pi\times 2.16\times 10^{-5} = 0.3967 \approx 0.4$. The corresponding exergy-to-energy ratio (column 8) is
$\psi_\nu = (2\times 3090 - 2\times 300\times 0.64)/2\times 3090 = 0.9458$. Columns 9 - 12 are discussed later. All calculations results given in Tables are rounded.

Data from Table A1 were also used in the adapted formula (8) to calculate the exergy b of undispersed extraterrestrial solar radiation reaching the Earth:

$$b = \left(2\sum_{n=1}^{n=114} \left(i_{0,\nu}\Delta\nu\right)_n - 2T_0 \sum_{n=1}^{n=114} \left(L_{0,\nu}\Delta\nu\right)_n + \frac{\sigma T_0^4}{3\pi} \right) 2.16\times 10^{-5}\pi \tag{31}$$

The sums of the products $\Sigma(i_{0,\nu}\Delta\nu)$ = 10,079,300 W/(m^2 sr), (column 5) and $\Sigma(L_{0,\nu}\Delta\nu)$ = 2263.31 W/(m^2 K sr), (column 6), were used in (31), and T_0 = 300 K was assumed:

$$\begin{aligned} b &= \left(2\times 10079300 - 2\times 300\times 2263.31 + \frac{5.6693\times 10^{-8}\times 300^4}{3\pi} \right)\times\pi\times 2.16\times 10^{-5} \\ &= 1367.9 - 92.151 + 0.00331 = 1275.78\ \mathrm{W/m^2} \end{aligned} \tag{32}$$

The calculation (32) shows the values of the components of the calculated exergy b. A value of extraterrestrial solar radiation energy E = 1367.9 W/m^2, reaching an area of 1 m^2 that is perpendicular to the direction of the Sun, was obtained. The exergy of this radiation b = 1275.8 W/m^2 (also shown at the bottom of column 7) and the corresponding ratio of exergy-to-energy ψ = 1275.78/1367.9 = 0.9326, (114-th row of column 12). The environmental influence expressed as A = 0.00331 in equation (32) is negligible compared to the components of radiation energy E = 1367.9 and entropy S = 92.151.

6.2. Exergy-to-Energy Ratio of Extraterrestrial Solar Radiation

Since the spectrum of real solar radiation is given in the form of intensity data for the finite wavelength intervals, only quasi-monochromatic solar radiation, based on equation (8), can be considered. As discussed in Section 6.1, due to the relatively small value of the environment component of solar radiation exergy, the exergy of monochromatic separated and unseparated radiation is practically the same. Dispersion of solar radiation does not increase the exergy. However, it can be analyzed the dependence of the monochromatic exergy-to-energy ratio on the wavelength. In order to better demonstrate the specificity of this dependency, it is proposed to carry out the analysis in two ways. First, quasi-monochromatic exergy b_λ is studied. Secondly, cumulative exergy $b_{\Delta\lambda}$ will be observed, which is the sum of the gradually added values of these quasi-monochromatic exergies with an increase in wavelength range from 0 to the successively increasing λ. In both cases, the data from Table A1 are used in the calculations.

6.2.1. Quasi Monochromatic Radiation

For each n-th of all 114 rows ($n = 1, 2, \cdots, 114$) in Table A1, the values of quasi-monochromatic exergy b_ν, are taken from column 7. The corresponding quasi monochromatic radiation energy e_ν is calculated from the formula:

$$(e_\nu)_n = 2\left(i_{0,\nu}\Delta\nu\right)_n 2.16\times10^{-5}\pi \tag{33}$$

and the corresponding exergy-to-energy ratio ψ_ν is:

$$(\psi_\nu)_n = \frac{(b_\nu)_n}{(e_\nu)_n} = (\psi_\lambda)_n \tag{34}$$

For example, for radiation at λ = 240 nm, the data from the third row (n = 3) of Table 1 (shaded in grey), the monochromatic exergy $b_\nu \approx 0.40$, and the corresponding energy e_ν results from (33):

$$e_\nu = 2\times3090\times2.16\times10^{-5}\pi = 0.4194\ \text{W/m}^2 \tag{35}$$

From the formula (34) follows $\psi_\nu = \psi_\lambda = 0.9458$, as shown in column 8, (shaded in gray).

6.2.2. Cumulative Monochromatic Radiation

A cumulative exergy $b_{\Delta\nu}$ is calculated based on the formula (8) interpreted as follows:

$$(b_{\Delta\nu})_j = \left(2\sum_{n=1}^{n=j}\left(i_{0,\nu}\Delta\nu\right)_n - 2T_0\sum_{n=1}^{n=j}\left(L_{0,\nu}\Delta\nu\right)_n\right)2.16\times10^{-5}\pi \tag{36}$$

where n is the current index of the summed products ($n = 1, 2, \cdots, j$) and j is the current index of considered cumulative exergy value ($j = 1, 2, \cdots, 114$).

For example, calculation for radiation in the wavelength range from 220 to 240 nm is presented. The sums of intensity and entropy contain only three components (j = 3) taken as the first three values from columns 5 and 6 (Table 1) respectively and shown in the 3rd row of columns 9 and 10 respectively (shaded in orange). The formula (36) shows:

$$b_{\Delta\nu} = (2\times6700 - 2\times300\times1.38)\times2.16\times10^{-5}\pi = 0.86\ \text{W/m}^2 \tag{37}$$

The corresponding energy $e_{\Delta\nu}$ is calculated similarly to the energy in the formula (35):

$$e_{\Delta\nu} = 2\times6700\times2.16\times10^{-5}\pi = 0.91\ \text{W/m}^2 \tag{38}$$

The corresponding cumulative exergy-energy ratio is:

$$\psi_{\Delta\nu} = \frac{b_{\Delta\nu}}{e_{\Delta\nu}} \tag{39}$$

and, for the considered example, has the value $\psi_{\Delta\nu} = \psi_{\Delta\lambda}$ = 0.86/0.91 = 0.9417, as shown in Table 1, column 12, row 3 (orange color).

6.2.3. Comparison of Monochromatic and Cumulative Radiation

Data of Table A1 have been used in Figure 9 which shows the calculated values of the ψ_λ (black line) from column 8 and the values $\psi_{\Delta\lambda}$ (red line) from column

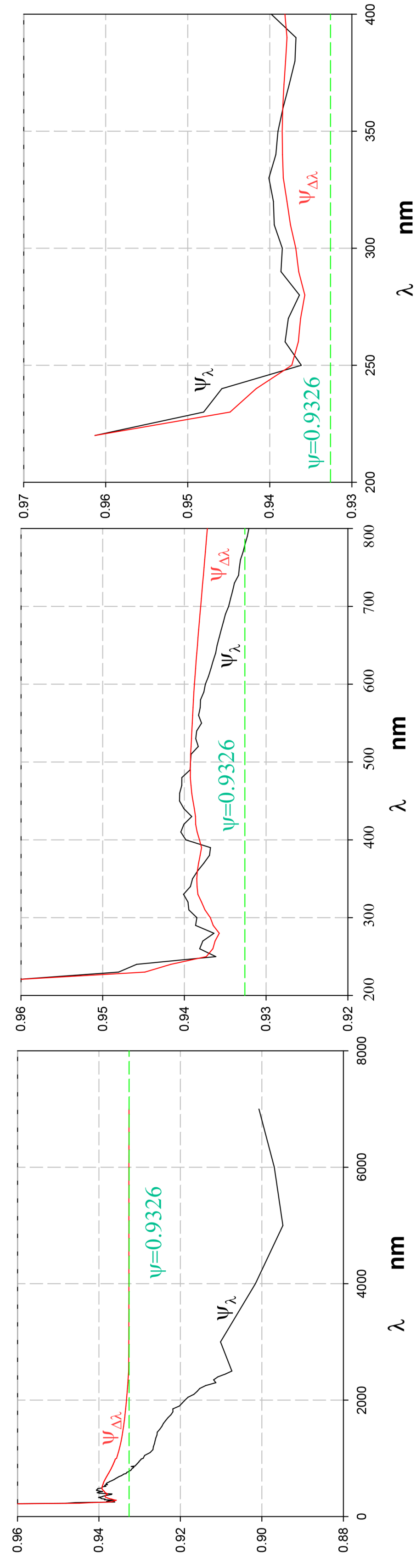

Figure 9. The ratios ψ_λ and $\psi_{\Delta\lambda}$ as a function of wavelength λ.

12, as a function of wavelength λ, (column 2). For comparison, a horizontal (green) line representing the exergy-to-energy ratio of $\psi = 0.9326$ for total solar radiation is also shown (column 12, row 114). The left part of Figure 9 shows both exergy-to-energy ratios, as they vary over the entire wavelength range from 200 to 7000 nm. The ratio of $\psi_{\Delta\lambda}$ (red line) for cumulative exergy decreases from 0.9613 to $\psi = 0.9326$ for total solar radiation. However, the ratio of ψ_λ (black line) for quasi-monochromatic exergy, from a value of 0.9613 decreases more and reaches a value of 0.9007. The remaining parts of Figure 9 show the considered relationships for the wavelength ranges of 200 - 800 and 200 - 400 nm respectively, in order to better demonstrate that in these wavelength ranges the exergy-to-energy ratio of quasi-monochromatic radiation may be greater or smaller than such ratio for cumulative radiation, $\psi_\lambda > \psi_{\Delta\lambda}$.

As seen in Figure 9, the quasi-monochromatic and cumulative energy-to-exergy ratios (black and red lines) increase with decreasing λ, which means that generally the smaller the wavelength λ (and the higher the vibration frequency ν), the higher the exergy values of radiation beams. It can also be observed that exergy beams, b_λ, with a wavelength of less than about 800 nm (or a frequency greater than 3.75×10^{14} 1/s), have a ratio greater than $\psi = 0.9326$ for total radiation.

However, the cumulative ratio (red), although decreases as the wavelength increases, is always greater than the mean value of $\psi = 0.9326$ and gradually diminishes to this value. Figure 9 (middle) better shows clearly that in the range of λ from about 250 to 500 nm, quasi monochromatic beams have mostly a higher ratio (black line) compared to the corresponding value of the cumulative ratio (red line). Figure 9 (right) better presents cumulative and quasi monochromatic ratios in the range of small wavelengths (below 250 nm).

It is noted that in general, the smaller the wavelength, (or the higher the frequency), the greater the exergy of the monochromatic radiation beam. It can be expected that exergy is particularly high for such short wavelength radiation like ultra violet ($\sim 10^{-8}$ m), x-ray ($\sim 10^{-10}$ m), or gamma radiation (10^{-12} m). Thermodynamic analysis, including exergy, has not been applied into processes where such high-frequency radiation takes place.

6.3. Visible Light of Solar Radiation

White light can be dispersed into radiation beams of different colors. Each color has its own wavelength range. For example, a violet beam has the wavelength range $\Delta\lambda$ = 380 - 450 nm, which corresponds to the rows 17 – 24 of Table A1, (violet shaded). This wavelength range corresponds to the frequency range $\Delta\nu = 7890 \times 10^{11}$ - 6662×10^{11} 1/s. Table 2 shows the violet data extracted from Table A1.

Based on formula (8), the cumulative exergy $b_{\Delta\nu,viol}$ of the violet beam separated from solar radiation is:

$$b_{\Delta\nu,viol} = \left[2\sum_{n=17}^{n=24} \left(i_{0,\nu}\Delta\nu\right)_n - 2T_0 \sum_{n=17}^{n=24} \left(L_{0,\nu}\Delta\nu\right)_n \right] 2.16\times10^{-5}\pi \tag{40}$$

Columns 9 and 10 (Table 2) show the cumulated products from columns 5 and 6 respectively. The sums of these products (in bold), shown in row 24, columns 9 and 10, are used respectively in formula (40):

$$b_{\Delta\nu,viol} = (2\times 928170 - 2\times 300\times 187.63)\times 2.16\times 10^{-5}\pi = 118.33\ \mathrm{W/m^2} \quad (41)$$

Analogous to (38), the corresponding energy $e_{\Delta\nu,viol}$ is calculated as follow:

$$e_{\Delta\nu,viol} = 2\times 928170\times 2.16\times 10^{-5}\pi = 125.97\ \mathrm{W/m^2} \quad (42)$$

The ratio of exergy-to-energy for violet is $\psi_{\Delta\nu,viol}$ = 118.33/125.97 = 0.9394. Table 3 shows the results of similar calculations for other colors and for comparison also shows data on the entire solar radiation (bottom row).

The results obtained suggest that the maximum ability of dispersed white light to perform work (expressed by the ratio ψ) is greater compared to the value 0.9326 for undispersed polychromatic solar radiation. For example, such a difference for a violet beam is: 100 × (0.9394 − 0.9326)/0.9326 = 0.7%. The values of the exergy-to-energy ratio for the considered colors are 0.8% - 0.3% higher than the value (0.9326) for solar radiation, which may be a practical guideline.

Table 2. Data of the solar spectrum in violet range [9], and some calculation results.

#	λ	$i_{0,\lambda}$	$\Delta\lambda$	$i_{0,\nu}\Delta\nu$	$L_{0,\nu}\Delta\nu$	b_ν	ψ_ν	$(i_{0,\nu}\Delta\nu)_\lambda$	$(L_{0,\nu}\Delta\nu)_\lambda$	$b_{\Delta\nu}$	$\psi_{\Delta\nu}$
1	2	3	4	5	6	7	8	9	10	11	12
17	380	683	10	6832	14.44	8.69	0.9369	6832	14.44	8.69	0.9369
18	390	727	10	7265	15.39	9.24	0.9368	14,097	29.83	17.92	0.9367
19	400	1137	10	11,369	22.89	14.50	0.9398	25,466	52.72	32.42	0.9380
20	410	1287	10	12,869	25.63	16.43	0.9404	38,335	78.35	48.84	0.9388
21	420	1294	10	12,942	25.94	16.51	0.9401	51,277	104.28	65.35	0.9390
22	430	1208	10	12,082	24.61	15.40	0.9391	63,359	128.89	80.74	0.9390
23	440	1405	10	14,053	28.16	17.93	0.9401	77,412	157.05	98.67	0.9392
24	450	1541	10	15,405	30.58	19.67	0.9406	**92,817**	**187.63**	118.33	0.9394
Total				**92,817**	**187.63**						

Table 3. Data for different colors of white light

Color	Approximate wavelength range nm	Energy W/m²	Exergy W/m²	Exergy/energy ratio
Violet	380 - 450	125.97	118.33	0.9394
Blue	460 - 500	105.70	99.341	0.9398
Green	510 - 560	119.57	112.20	0.9383
Yellow	570 - 590	58.744	55.089	0.9378
Red	600 - 760	247.29	231.21	0.9350
Solar radiation	220 - 7000	1367.9	1275.8	0.9326

6.4. Temperature of the Quasi Monochromatic Components of Solar Radiation

One of the possibilities of the use of data in Table A1 could also be the determination of the temperature of quasi monochromatic extraterrestrial solar radiation. For example, assuming that the measured radiation intensities come from a sun with a black surface, the values in columns 2 and 3 of Table A1 can be used in formula (6) to calculate the surface temperature of the Sun. The results of such calculations used in Figure 10 show the interpretation of the temperature of the Sun's surface as a function of wavelength.

The temperature of visible radiation (in the wavelength range 380 - 760 nm) varies from 5406 to 5817 K. The highest temperature in this range is 6004 K for a wavelength of 460 nm. For a wavelength greater than about 3000 nm, temperature values are determined with smaller reliability, since the assumed wavelength ranges used in discretization are relatively large.

7. Radiation of Water Vapor

7.1. Polychromatic Radiation of Water Vapor

However, as mentioned before, significant effects of increasing exergy by dispersing radiation appear for radiation of low temperature, like for example radiation of water vapor. Measurement data (Jacob, 1957) was used for a water vapor layer of equivalent thickness 1.04 m at 473 K. The characteristic product of the thickness and the partial pressure of vapor is 10.4 m kPa. The radiation energy of vapor is emitted to the hemispherical enclosure, and the exergy of this radiation arriving at 1 m^2 of the enclosing hemispherical wall may be calculated on the basis of the formula (9) appropriately adapted. The radiation is assumed

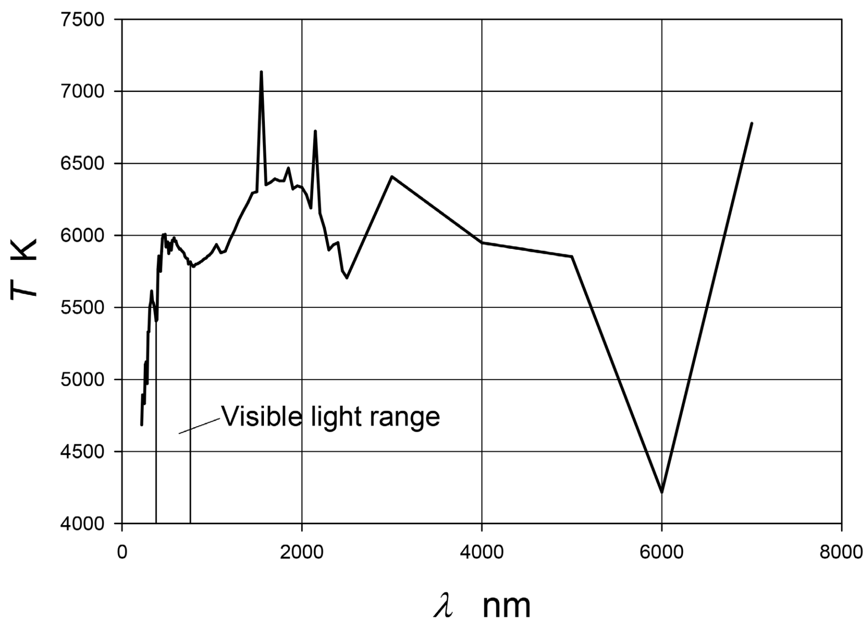

Figure 10. Solar radiation temperature T as function of wavelength λ, calculated based on spectrum measured by Kondratyev.

as the uniformly propagating within a solid angle 2π and instead of the frequency ν, the wavelength λ is used. The entire measured radiation spectrum of water vapor as a function of wavelength λ was approximately represented [10] by seven ($n = 7$) rectangles with height $i_{0,\lambda}$ and of wideness $\Delta\lambda$, as shown in Table 4, (column 3 and 4). The data in column 2 - 4 of Table 4 is taken as input for further consideration. It is assumed that the environment temperature $T_0 = 300$ K. To calculate exergy b of polychromatic water vapor radiation, formula (9) is used in the following form Petela, 1961 [10]:

$$b = 2\pi\sum_{n=1}^{n=7}\left(i_{0,\lambda}\Delta\lambda\right)_n - 2\pi T_0\sum_{n=1}^{n=7}\left(L_{0,\lambda}\Delta\lambda\right)_n + \frac{\sigma T_0^4}{3} \tag{43}$$

The measured data in column 2 and 3 (Table 4) were used to calculate the values in columns 7 to 12. The sums of products $\Sigma i_{0,\lambda}\cdot\Delta\lambda = 242.1$ W/(m² sr), (green), and $\Sigma L_{0,\lambda}\cdot\Delta\lambda = 0.7291$ W/(m² K sr), (blue), taken from Table 4 (columns 5 and 6 respectively), are used in (43):

$$\begin{aligned} b &= 2\pi\times 242.1 - 2\pi\times 300\times 0.7291 + \frac{5.6693\times 10^{-8}}{3}300^4 \\ &= 1521 - 1374.3 + 153.1 = 299.8\ \mathrm{W/m^2} \end{aligned} \tag{44}$$

Calculated exergy of polychromatic vapor radiation $b = 299.8$ W/m² and the corresponding ratio of exergy-to-energy $\psi = 299.8/1521 = 0.197$. The results are very similar to those originally obtained [10].

Further analysis seems to have rather theoretical significance. It is assumed that every 1 m² of the considered irradiated surface surrounding the hemisphere is able to disperse the incoming vapor radiation. The resulting dispersed beam in the space behind this surface can therefore be assessed by exergy.

Table 4. Measured (Jacob, 1957) spectrum of water vapour radiation, used for quasi-monochromatic considerations.

1	2	3	4	5	6	7	8	9	10	11	12
#	λ	$i_{0,\lambda}$	$\Delta\lambda$	$i_{0,\lambda}\cdot\Delta\lambda$	$L_{0,\lambda}\cdot\Delta\lambda$	b_λ	ψ_λ	$(i_{0,\lambda}\cdot\Delta\lambda)$	$(L_{0,\lambda}\cdot\Delta\lambda)$	$b_{\Delta\lambda}$	$\psi_{\Delta\lambda}$
1	2.69	5.0	0.66	3.3	0.0076	159.4	7.690	3.3	0.0076	159.4	7.690
2	6.15	45.7	2.8	128.0	0.3283	338.3	0.421	131.3	0.3359	344.7	0.418
3	7.95	17.2	0.8	13.76	0.0433	157.9	1.826	145.0	0.3792	349.5	0.384
4	9.80	3.7	2.9	10.73	0.0452	135.3	2.007	155.7	0.4244	331.7	0.339
5	14.8	6.4	7.1	45.44	0.1687	120.5	0.422	201.2	0.5931	299.2	0.237
6	21.0	5.1	5.3	27.03	0.0871	158.7	0.935	228.2	0.6802	304.8	0.213
7	26.8	2.2	6.3	13.86	0.0489	148.1	1.700	242.1	0.7291	299.8	0.197
Total				242.1	0.7291	1218.3					

Columns: 1) Successive number; 2) Wavelength, λ μm; 3) Monochromatic radiation intensity, $i_{0,\lambda}$ (10^{-6}), W/(m³ sr); 4) Assumed wavelength range, $\Delta\lambda$ μm; 5) Product $i_{0,\lambda}\cdot\Delta\lambda$, W/(m² sr); 6) Product $L_{0,\lambda}\cdot\Delta\lambda$, W/(m² K sr); 7) Exergy of monochromatic radiation, b_λ, W/m², (formula 45); 8) Ratio of exergy-to-energy of monochromatic radiation, ψ_λ, (formula 47); 9) Additively cumulated product, $(i_{0,\lambda}\cdot\Delta\lambda)$ W/(m² sr); 10) Additively cumulated product, $(L_{0,\lambda}\cdot\Delta\lambda)$, W/(m² K sr); 11) Additively cumulated exergy of monochromatic radiation intensity, $b_{\Delta\lambda}$, W/m², (formula 49); 12) Ratio of exergy-to-energy of radiation, $\psi_{\Delta\lambda}$, (formula 51). (Table presents the rounded values, although the calculations were carried out without rounding).

7.2. Quasi Monochromatic Radiation of Water Vapor

Equation (9) is used to calculate the seven values b_λ of quasi-monochromatic radiation shown in column 7 (Table 4). So, for each n-th of all 7 rows ($n = 1, 2, \cdots, 7$), the following formula was used:

$$\left(b_\lambda\right)_n = 2\pi\left(i_{0,\lambda}\Delta\lambda\right)_n - 2\pi T_0\left(L_{0,\lambda}\Delta\lambda\right)_n + \frac{\sigma T_0^4}{3} \quad (45)$$

The quasi monochromatic radiation energy e_λ is equal to the first member of the right side of the Equation (45):

$$\left(e_\lambda\right)_n = 2\pi\left(i_{0,\lambda}\Delta\lambda\right)_n \quad (46)$$

The corresponding exergy-to-energy ratio ψ_λ, (column 8) is:

$$\left(\psi_\lambda\right)_n = \frac{\left(b_\lambda\right)_n}{\left(e_\lambda\right)_n} \quad (47)$$

For example, for a wavelength of λ = 9.8 μm, equation (45) uses the data from the fourth row (n = 4) of Table 4 to obtain the value:

$$b_\lambda = 2\times\pi\times10.73 - 2\times\pi\times300\times0.0452 + \frac{5.6693\times10^{-8}\times300^4}{3} = 135.3\ \mathrm{W/m^2} \quad (48)$$

shown in column 7. The energy of quasi-monochromatic radiation e_λ is equal to the first member of the right side of the equation (48): e_λ = 2·π·10.73 = 67.42 W/m^2.

The formula (47) gives ψ_λ = 135.3/67.42 = 2.007, as shown in column 8, row 4, Table 4. It turns out that the exergy-to-energy ratio for the water vapor under consideration may be greater than 1.

7.3. Cumulative Radiation of Water Vapor

As in the case of solar radiation analysis, it is also possible to consider the exergy of cumulated vapour radiation $b_{\Delta\lambda}$ using the formula (36), in which, however, the solid angle of propagation of radiation 2π and the environmental component of exergy should be taken into account as follows:

$$\left(b_{\Delta\lambda}\right)_j = 2\pi\sum_{n=1}^{j}\left(i_{0,\lambda}\Delta\lambda\right)_n - 2\pi T_0\sum_{n=1}^{j}\left(L_{0,\lambda}\Delta\lambda\right)_n + \frac{\sigma T_0^4}{3} \quad (49)$$

where n is the current index of the summed products ($n = 1, 2, \cdots, j$) and j is the current index of considered cumulative exergy value ($j = 1, 2, \cdots, 7$).

For example, for radiation in the wavelength range from 2.69 to 7.95 μm, the sums of energy and entropy contain only the first three values from columns 5 and 6, (j = 3) and these sums are shown in the third row of columns 9 and 10, respectively. The formula (49) gives the value:

$$b_{\Delta\lambda} = 2\times\pi\times145.0 - 2\times\pi\times300\times0.3792 + \frac{5.6693\times10^{-8}\times300^4}{3} = 349.5\ \mathrm{W/m^2} \quad (50)$$

which is shown in column 11, (row 3). Based on (49) the corresponding radiation energy $e_{\Delta\nu}$ = 2·π·145 = 911.2 W/m^2.

The corresponding cumulative exergy-to-energy ratio is:

$$\psi_{\Delta\lambda} = \frac{b_{\Delta\lambda}}{e_{\Delta\lambda}} \tag{51}$$

and for the case under consideration it is $\psi_{\Delta\lambda}$ = 349.5/911.2 = 0.384, as shown in column 12, (row 3).

7.4. Comparison of Quasi-Monochromatic and Cumulative Radiation of Water Vapor

The data from **Table 4**, used in the **Figure 11**, show how, depending on the wavelength λ (column 2), the value ψ_λ from column 8 (black line) and the value $\psi_{\Delta\lambda}$ from column 12 (red line) depend. In the wavelength range 2.69 - 6.15 μm, the red line covers the black line exactly. For comparison, a horizontal (green) line representing the exergy-to-energy ratio ψ = 0.1971 for polychromatic vapor radiation is also shown.

In the case of the water vapor under consideration, the ratio of $\psi_{\Delta\lambda}$, (red line), with increasing wavelength λ, as in the case of solar radiation, starts changing from a high value, even well above 1, and then decreases relatively smoothly, reaching a value of 0.1971 for the considered polychromatic radiation. However, the ratio of ψ_λ, after decreasing in the wavelength range of 2.69 – 6.15 μm, in which it changes the same way as $\psi_{\Delta\lambda}$, changes not smoothly, reaching values of ψ_λ = 1.7 for λ = 26.8 μm. Comparison of **Figure 9**, for solar radiation, to **Figure 11**, for water vapor, illustrates the effect of environment temperature in case of high and low radiation temperatures. The accuracy of diagrams in **Figure 11** can be influenced by the replacing of the measured spectrum with only seven rectangular areas.

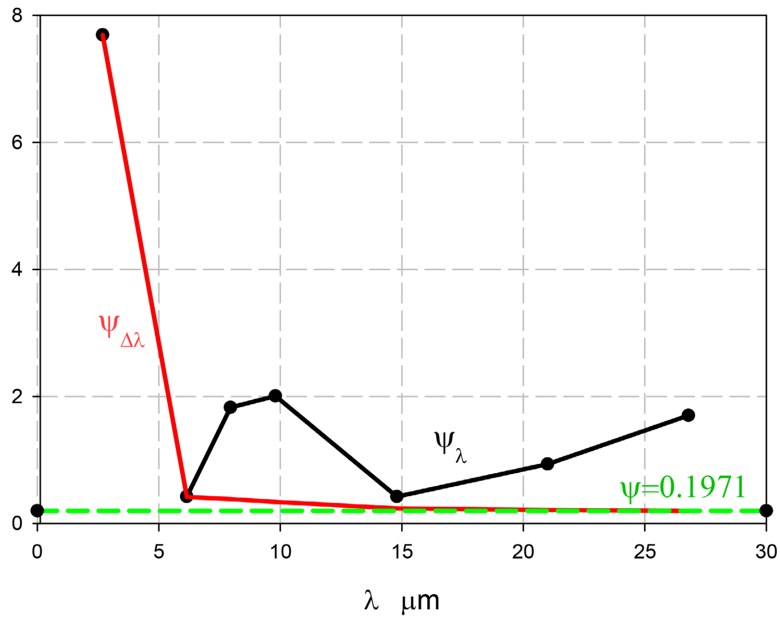

Figure 11. Quasi monochromatic and cumulative exergy-to-energy ratios ψ_λ, $\psi_{\Delta\lambda}$, as a function of the wavelength λ, for water vapor.

In the Equation (45), the exergy components introduced into the consideration by the formula (13), can be determined as follows:

$$A = \frac{\sigma}{3} T_0^4 \tag{52}$$

$$E = 2\pi \sum \left(i_{0,\lambda} \Delta\lambda \right) \tag{53}$$

$$S = -2\pi T_0 \sum \left(L_{0,\lambda} \Delta\lambda \right) \tag{54}$$

The components, A, E and S are used with a subscript of λ for quasi monochromatic or with subscript $\Delta\lambda$ for cumulated exergy values and the respective radiation beams $b_{\Delta\lambda} = A_{\Delta\lambda} + E_{\Delta\lambda} + S_{\Delta\lambda}$ and $b_\lambda = A_\lambda + E_\lambda + S_\lambda$, are analyzed. The way of calculation of these components (in W/m^2) of cumulative exergy is shown in Table 5, and for quasi-monochromatic exergy components is shown in Table 6. It is seen how the environment component A becomes significant, when a low temperature radiation is considered. The environmental component $A_{\Delta\lambda}$ = 153.1 W/m^2, (at T_0 = 300 K) in the case of cumulative exergy $b_{\Delta\lambda}$, is added only once for the entire spectrum within $\Delta\lambda$, while in the case of quasi monochromatic exergy b_λ, of dispersed beams, this component is added for each individual wavelength λ.

It can be noted that the cumulative exergy for the entire spectrum of the vapor is only 299.8 W/m^2, while the sum of monochromatic exergy for the seven separate beams reaches 1218.3 W/m^2, as shown in red in Tables 4-6. However, the sums of energy intensity and entropy are the same, (Table 4, in green and blue respectively).

Table 5. Exergy for the cumulative radiation spectrum of the considered water vapor.

Row in Table 4	$A_{\Delta\lambda}$	$E_{\Delta\lambda}$ 2π·	$S_{\Delta\lambda}$ 2π·300·	$b_{\Delta\lambda}$
1	153.1	3.3	−0.0076	159.4
2	153.1	3.3 + 128.0 = 131.3	−(0.0076 + 0.3283) = −0.3359	344.7
3	153.1	3.3 + 128.0 + 13.77 = 145.0	−(0.0076 + 0.3283 + 0.0433) = −0.3792	349.5
…	…	…	…	…
7				**299.8**

Table 6. Exergy for the quasi monochromatic radiation spectrum of the considered water vapor

Row in Table 4	A_λ	E_λ 2π·	S_λ 2π·300·	b_λ
1	153.1	3.3	−0.0076	159.4
2	153.1	128.0	−0.3283	338.3
3	153.1	13.77	−0.0433	157.9
…	…	…	…	…
Total				**1218.3**

The components of exergy for the water vapor under consideration are shown in the diagram (**Figure 12**). Radiation exergy, $B_{\Delta\lambda}$ or B_λ, (red line) is the algebraic sum of three components, which are entropic, $S_{\Delta\lambda}$ or S_λ, (green line), environmental $A_{\Delta\lambda}$ or A_λ, (black dashed line), and energetic, shown together with the environmental $E_{\Delta\lambda} + A_{\Delta\lambda}$ or $E_\lambda + A_\lambda$, (blue line). Cumulative exergy $B_{\Delta\lambda}$ (left red) is relatively smaller than any monochromatic exergy B_λ (right red).

Based on the calculation (44), the ratio of exergy-to-energy for the polychromatic vapor radiation under consideration was determined to be $\psi = 299.8/1521 = 0.197$ as shown in **Table 4**, column 12, row 7. In the theoretical reasoning, the dispersion process can be estimated by the ratio of exergy-to-energy ψ_{disp} determined as the exergy sum of dispersed monochromatic beams related to the total energy of radiation. The values from **Table 4** are used as follows:

$$\psi_{disp} = \frac{\sum_{n=1}^{n=7}(b_\lambda)_n}{2\pi\sum_{n=1}^{n=7}(i_{0,\lambda}\Delta\lambda)_n} = \frac{1218.3}{2\pi\cdot 242.1} = 0.8 \qquad (55)$$

The present theoretical considerations have shown that the dispersion of radiation allows to increase the exergy-to-energy ratio from 0.197 to 0.8. For comparison, the formula (19), for any black radiation at a temperature of the considered vapor 473 K, (200 C), gives a value of $\psi = 0.2083$.

8. Conclusions

The considerations in this theoretical work constitute a cognitive contribution to the field of radiation exergy. This exergy has been analyzed as consisting of three components that represent energy, entropy, and the environment. For high-temperature radiation, such as solar radiation, the environmental component in the exergy of polychromatic and monochromatic radiation is meaningless. However, the lower the temperatures of such radiations, the greater the impact of the environment. To illustrate this rule, solar radiation has been compared to water vapor radiation.

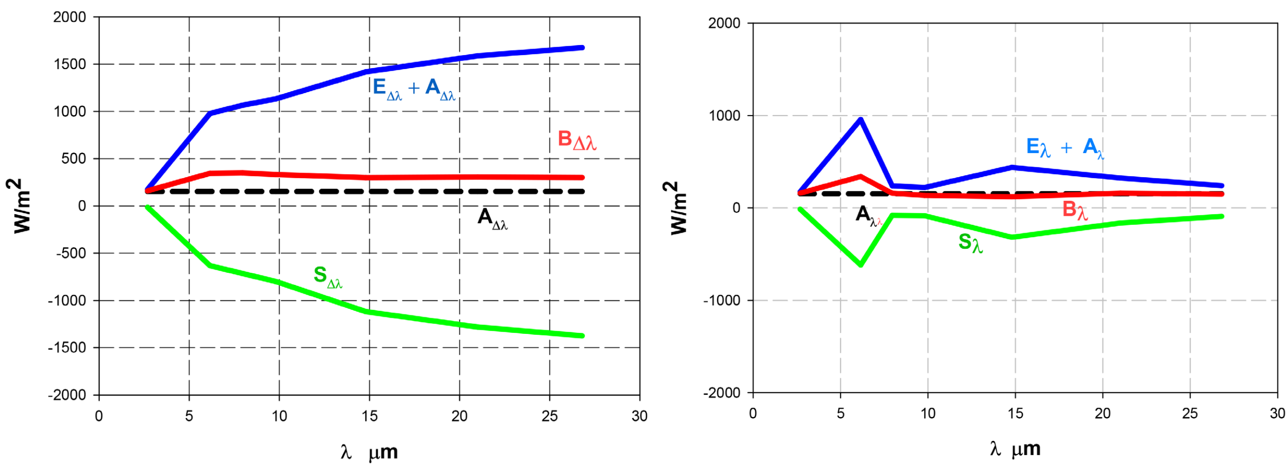

Figure 12. Components of cumulative exergy (left) and quasi-monochromatic exergy (right).

The spectrum presented by quasi-monochromatic or cumulative radiation was for the first time studied using exergy. It was found that for these two types of radiation, the ratio of exergy-to-energy is smaller, the greater the wavelength. That is, the lower the wavelength (or higher frequency), the more valuable the energy, (measured by exergy) of each of these considered types of radiation.

However, the main finding is that dispersion of polychromatic radiation can increase exergy, and the dispersion process does not require any driving input, which means that it occurs for free. That is, the exergy of polychromatic radiation before dispersion is less than the sum of the exergies of all dispersed beams. An interpretation of this phenomenon has been proposed and an analogy has been cited to the increase in exergy during gas separation. The lower the radiation temperature, the greater the effect of the increase in exergy.

The dispersing of visible sunlight generates color beams, all of which have a monochromatic exergy-to-energy ratio slightly greater than such a ratio for undispersed polychromatic solar radiation.

The presented analyses may be a motivation for further research of optical phenomena from a thermodynamic point of view. Exergy effects or reversibility of optical processes could be analyzed. A more detailed analysis of exergy for the process of radiation dispersion could be carried out. Exergy analysis of processes in which visible sunlight is dispersed or involved are ultraviolet, X-ray or gamma rays could also be considered. These analyses can help to make better use of monochromatic radiation, particularly dispersed solar radiation, on Earth or elsewhere.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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Nomenclature

A environment contribution component to exergy
b radiation exergy, W/m^2
B exergy consisting of three components
c speed of propagation of radiation in vacuum $c = 2.9979 \times 10^8$ m/s
e radiation energy, W/m^2
E energy contribution component to exergy
h Planck's constant, $h = 6.625 \times 10^{-34}$ J s
H enthalpy of substance, J
i directional radiation density, J/(m^2 sr) or W/(m^3 sr)
i successive number
j successive number
k Boltzmann constant, $k = 1.3805 \times 10^{-23}$ J/K
L normal entropy of radiation intensity, J/(m^2 K sr) or W/(m^3 K sr)
n number of beams
n successive number
S entropy of substance, J/K
S entropy contribution component to exergy
T absolute temperature, K

Greek

ε degree of exergy increase
Λ integration limit, m
λ wavelength, m
ν vibration frequency, 1/s
ψ exergy-to-energy ratio
σ Boltzmann constant for black radiation, $\sigma = 5.6693 \times 10^{-8}$ W/(m^2 K^4)

Subscripts

b black
$viol$ violet beam
λ wavelength
$\Delta\lambda$ interval of wavelength
ν frequency
0 environment
0 directional normal

Appendix

Table A1. Spectral Distribution of Extraterrestrial Solar Energy Radiation Arriving at the Atmosphere, (column 2 and 3), Kondratyev (1954), and Other Columns, Used in Analyses of Monochromatic Radiation Exergy.

#	λ	$i_{0,\lambda}$	$\Delta\lambda$	$i_{0,\nu}\Delta\nu$	$L_{0,\nu}\Delta\nu$	b_ν	ψ_ν	$(i_{0,\nu}\Delta\nu)_\lambda$	$(L_{0,\nu}\Delta\nu)_\lambda$	$b_{\Delta\nu}$	$\psi_{\Delta\nu}$
1	2	3	4	5	6	7	8	9	10	11	12
1	220	10	10	96	0.21	0.13	0.9613	96	0.21	0.13	0.9613
2	230	26	10	265	0.54	0.34	0.9481	361	0.75	0.46	0.9448
3	240	31	10	309	0.64	0.40	0.9458	670	1.38	0.86	0.9417
4	250	41	10	412	0.96	0.52	0.9362	1082	2.34	1.38	0.9373
5	260	98	10	978	2.10	1.25	0.9381	2060	4.44	2.62	0.9365
6	270	126	10	1257	2.69	1.60	0.9377	3317	7.13	4.21	0.9362
7	280	112	10	1118	2.45	1.42	0.9364	4435	9.58	5.63	0.9357
8	290	263	10	2633	5.47	3.35	0.9386	7068	15.05	8.98	0.9365
9	300	304	10	3044	6.32	3.88	0.9385	10112	21.37	12.86	0.9368
10	310	452	10	4515	9.19	5.76	0.9395	14627	30.57	18.61	0.9375
11	320	529	10	5287	10.73	6.74	0.9396	19914	41.30	25.35	0.9379
12	330	645	10	6449	12.96	8.23	0.9401	26363	54.25	33.57	0.9384
13	340	635	10	6354	12.95	8.10	0.9393	32717	67.20	41.67	0.9385
14	350	672	10	6721	13.75	8.57	0.9390	39438	80.95	50.23	0.9385
15	360	693	10	6927	14.31	8.82	0.9384	46365	95.26	59.05	0.9384
16	370	692	10	6920	14.47	8.81	0.9376	53285	109.73	67.85	0.9383
17	380	683	10	6832	14.44	8.69	0.9369	60117	124.17	76.54	0.9381
18	390	727	10	7265	15.39	9.24	0.9368	67382	139.56	85.77	0.9379
19	400	1137	10	11369	22.89	14.50	0.9398	78751	162.44	100.27	0.9381
20	410	1287	10	12869	25.63	16.43	0.9404	91620	188.07	116.69	0.9384
21	420	1294	10	12942	25.94	16.51	0.9401	104562	214.01	133.20	0.9386
22	430	1208	10	12082	24.61	15.40	0.9391	116644	238.61	148.59	0.9387
23	440	1405	10	14053	28.16	17.93	0.9401	130697	266.77	166.52	0.9388
24	450	1541	10	15405	30.58	19.67	0.9406	146102	297.35	186.18	0.9390
25	460	1589	10	15891	31.56	20.29	0.9406	161993	328.91	206.46	0.9391
26	470	1581	10	15810	31.53	20.18	0.9403	177803	360.44	226.64	0.9392
27	480	1603	10	16031	31.97	20.46	0.9403	193834	392.41	247.09	0.9393
28	490	1488	10	14876	30.18	18.96	0.9393	208710	422.59	266.05	0.9393
29	500	1527	10	15274	31.01	19.47	0.9393	223984	453.60	285.52	0.9393
30	510	1525	10	15251	31.00	19.44	0.9392	239235	484.60	304.95	0.9392
31	520	1422	10	14222	29.33	18.11	0.9383	253457	513.93	323.06	0.9392
32	530	1482	10	14825	30.42	18.88	0.9386	268282	544.35	341.94	0.9391
33	540	1485	10	14847	30.52	18.91	0.9385	283129	574.86	360.85	0.9391
34	550	1419	10	14193	29.46	18.07	0.9379	297322	604.32	378.91	0.9390

Continued

35	560	1477	10	14766	30.47	18.80	0.9383	312088	634.79	397.71	0.9390
36	570	1456	10	14560	30.14	18.54	0.9381	326648	664.93	416.25	0.9389
37	580	1459	10	14590	30.22	18.57	0.9380	341238	695.15	434.82	0.9389
38	590	1413	10	14134	29.47	17.99	0.9376	355372	724.63	452.80	0.9388
39	600	1396	10	13957	29.19	17.76	0.9374	369329	753.81	470.55	0.9388
40	610	1353	10	13530	28.47	17.21	0.9371	382859	782.28	487.76	0.9387
41	620	1321	10	13215	27.94	16.80	0.9368	396074	810.22	504.55	0.9386
42	630	1291	10	12906	27.41	16.40	0.9365	408980	837.63	520.95	0.9386
43	640	1259	10	12589	26.86	15.99	0.9362	421569	864.49	536.95	0.9385
44	650	1238	10	12376	26.48	15.72	0.9360	433945	890.98	552.66	0.9384
45	660	1210	10	12104	26.01	15.37	0.9357	446049	916.98	568.03	0.9383
46	670	1182	10	11825	25.51	15.01	0.9355	457874	942.49	583.04	0.9383
47	680	1155	10	11545	25.01	14.65	0.9352	469419	967.50	597.69	0.9382
48	690	1127	10	11273	24.52	14.30	0.9350	480692	992.01	611.99	0.9381
49	700	1091	10	10905	23.86	13.83	0.9346	491597	1015.87	625.82	0.9380
50	710	1063	10	10634	23.35	13.48	0.9343	502231	1039.22	639.30	0.9379
51	720	1039	10	10392	22.91	13.17	0.9341	512623	1062.14	652.47	0.9378
52	730	1016	10	10156	22.47	12.87	0.9339	522779	1084.60	665.34	0.9378
53	740	974	10	9737	21.71	12.33	0.9334	532516	1106.31	677.67	0.9377
54	750	960	10	9597	21.43	12.16	0.9333	542113	1127.73	689.83	0.9376
55	760	943	10	9427	21.09	11.94	0.9331	551540	1148.82	701.76	0.9375
56	770	914	10	9141	20.55	11.57	0.9328	560681	1169.38	713.33	0.9374
57	780	892	10	8920	20.13	11.29	0.9326	569601	1189.50	724.62	0.9374
58	790	868	10	8677	19.66	10.98	0.9323	578278	1209.17	735.59	0.9373
59	800	849	10	8486	19.29	10.73	0.9321	586764	1228.45	746.32	0.9372
60	810	835	10	8354	19.01	10.57	0.9320	595118	1247.46	756.89	0.9371
61	820	819	10	8185	18.65	10.35	0.9320	603303	1266.11	767.24	0.9370
62	830	802	10	8023	18.34	10.15	0.9317	611326	1284.45	777.38	0.9370
63	840	785	10	7854	18.00	9.93	0.9316	619180	1302.44	787.31	0.9369
64	850	769	10	7692	17.66	9.72	0.9314	626872	1320.11	797.03	0.9368
65	860	753	10	7530	17.13	9.53	0.9321	634402	1337.23	806.55	0.9368
66	870	738	10	7383	17.03	9.33	0.9311	641785	1354.26	815.87	0.9367
67	880	723	10	7228	16.71	9.13	0.9310	649013	1370.97	825.00	0.9366
68	890	708	10	7082	16.40	8.95	0.9309	656095	1387.37	833.95	0.9366
69	900	694	10	6935	16.10	8.76	0.9307	663030	1403.47	842.70	0.9365
70	910	680	10	6795	15.80	8.58	0.9306	669825	1419.27	851.28	0.9364
71	920	666	10	6655	15.51	8.40	0.9305	676480	1434.78	859.68	0.9364
72	930	652	10	6523	15.24	8.24	0.9303	683003	1450.02	867.91	0.9363
73	940	638	10	6383	14.93	8.06	0.9302	689386	1464.95	875.97	0.9363
74	950	626	10	6255	14.65	7.90	0.9301	695641	1479.60	883.86	0.9362

Continued

75	960	613	10	6126	14.38	7.73	0.9300	701767	1493.98	891.59	0.9361
76	970	600	10	6001	14.12	7.57	0.9298	707768	1508.10	899.16	0.9361
77	980	588	10	5875	13.85	7.41	0.9297	713643	1521.95	906.57	0.9360
78	990	576	10	5758	13.59	7.26	0.9296	719401	1535.54	913.83	0.9360
79	1000	565	50	29653	70.11	37.39	0.9292	749054	1605.65	951.22	0.9357
80	1050	515	50	24580	58.42	30.98	0.9288	773634	1664.07	982.20	0.9355
81	1100	448	50	21418	51.89	26.96	0.9274	795052	1715.96	1009.16	0.9353
82	1150	402	50	19283	47.16	24.25	0.9268	814335	1763.12	1033.41	0.9351
83	1200	371	50	17826	43.67	22.42	0.9266	832161	1806.78	1055.82	0.9349
84	1250	340	50	16339	40.17	20.54	0.9264	848500	1846.96	1076.36	0.9347
85	1300	313	50	15048	37.08	18.92	0.9262	863548	1884.04	1095.27	0.9346
86	1350	287	50	13831	34.17	17.38	0.9261	877379	1918.21	1112.65	0.9344
87	1400	263	50	12673	31.44	15.92	0.9258	890052	1949.65	1128.57	0.9343
88	1450	242	50	11696	29.06	14.69	0.9257	901748	1978.71	1143.26	0.9342
89	1500	219	50	10604	26.57	13.31	0.9251	912352	2005.28	1156.57	0.9341
90	1550	249	50	9655	24.36	12.11	0.9246	922007	2029.64	1168.68	0.9340
91	1600	182	50	8842	22.43	11.09	0.9242	930849	2052.07	1179.77	0.9339
92	1650	166	50	8067	20.62	10.11	0.9236	938916	2072.69	1189.88	0.9338
93	1700	152	50	7358	18.95	9.22	0.9231	946274	2091.64	1199.09	0.9337
94	1750	138	50	6686	17.40	8.37	0.9223	952960	2109.04	1207.46	0.9336
95	1800	126	50	6116	16.02	7.65	0.9218	959076	2125.05	1215.11	0.9335
96	1850	118	50	5729	15.00	7.17	0.9219	964805	2140.06	1222.27	0.9335
97	1900	104	50	5087	13.61	6.35	0.9202	969892	2153.66	1228.62	0.9334
98	1950	96	50	4661	12.58	5.82	0.9196	974553	2166.24	1234.44	0.9333
99	2000	88	50	4269	11.63	5.32	0.9189	978822	2177.86	1239.76	0.9333
100	2050	80	50	3913	10.76	4.88	0.9181	982735	2188.62	1244.63	0.9332
101	2100	72	50	3520	9.86	4.38	0.9167	986255	2198.48	1249.00	0.9331
102	2150	76	50	3234	9.15	4.02	0.9159	989489	2207.63	1253.02	0.9331
103	2200	61	50	2984	8.51	3.71	0.9153	992473	2216.14	1256.72	0.9330
104	2250	55	50	2698	7.83	3.35	0.9138	995171	2223.97	1260.07	0.9330
105	2300	49	50	2411	7.21	2.98	0.9113	997582	2231.18	1263.05	0.9329
106	2350	46	50	2268	6.75	2.81	0.9118	999850	2237.92	1265.85	0.9329
107	2400	43	50	2089	6.29	2.58	0.9108	1001939	2244.22	1268.43	0.9328
108	2450	38	50	1874	5.77	2.31	0.9089	1003813	2249.99	1270.74	0.9328
109	2500	35	500	1440	4.53	1.77	0.9074	1005253	2254.51	1272.51	0.9327
110	3000	22	1000	1654	5.04	2.04	0.9101	1006907	2259.55	1274.55	0.9327

Continued

111	4000	7	1000	588	2.01	0.72	0.9016	1007495	2261.56	1275.26	0.9327
112	5000	3	1000	245	0.94	0.30	0.8948	1007740	2262.50	1275.56	0.9326
113	6000	1	1000	126	0.51	0.15	0.8970	1007866	2263.01	1275.71	0.9326
114	7000	1	1000	64	0.29	0.08	0.9007	1007930	2263.31	1275.78	0.9326
Total				1007930	2263.31	1275.78					

Columns: 1) Successive number; 2) Wavelength, λ (10^9), m; 3) Monochromatic radiation intensity, $i_{0,\lambda}$ (10^{-10}), W/(m^3 sr); 4) Assumed wavelength range, $\Delta\lambda$, (10^9), m; 5) Product $i_{0,\nu}\cdot\Delta\nu$ (10^{-1}), W/(m^3 sr); 6) Product $L_{0,\nu}\cdot\Delta\nu$, W/(m^2 K sr); 7) Exergy of monochromatic radiation, b_ν, W/m^2, (formula 16) 8) Ratio of exergy b_ν to energy of monochromatic radiation, ψ_ν, (formula 19) 9) Additively cumulated product, $i_{0,\nu}\cdot\Delta\nu$ (10^{-1}), W/(m^2 sr); 10) Additively cumulated product, $L_{0,\nu}\cdot\Delta\nu$, W/(m^2 K sr); 11) Additively cumulated exergy of monochromatic radiation intensity, $b_{\Delta\nu}$, W/m^2, (formula 36) 12) Ratio of exergy-to-energy of radiation, $\psi_{\Delta\nu}$, (formula 39). (Table presents the rounded values, although the calculations were carried out without rounding).