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Antenna entropy in plant photosystems does not reduce the free energy for primary charge separation

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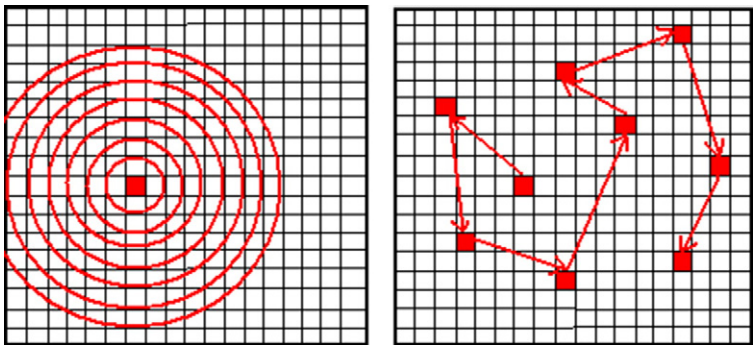
HIGHLIGHTS

- The antenna entropy does not reduce the free energy available for charge separation.
- Photosystem antenna entropy is the configurational entropy of a canonical ensemble.
- The excitation energy of a photosynthetic antenna doesn't undergo energy dilution.

GRAPHICAL ABSTRACT



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ABSTRACT

We have investigated the concept of the so-called "antenna entropy" of higher plant photosystems. Several interesting points emerge:

1. In the case of a photosystem which harbours an excited state, the "antenna entropy" is equivalent to the configurational (mixing) entropy of a thermodynamic canonical ensemble. The energy associated with this parameter has been calculated for a hypothetical isoenergetic photosystem, photosystem I and photosystem II, and comes out in the range of 3.5 - 8% of the photon energy considering 680 nm.
2. The "antenna entropy" seems to be a rather unique thermodynamic phenomenon, in as much as it does not modify the free energy available for primary photochemistry, as has been previously suggested.
3. It is underlined that this configurational (mixing) entropy, unlike heat dispersal in a thermal system, does not involve energy dilution. This points out an important difference between thermal and electronic energy dispersal.

1. Introduction

The absorption of radiant energy by the photosystems of green plants is achieved by an array of antenna pigments, of which the chlorophylls are of paramount importance. For higher plant photosystems, there are about 200–250 antenna chlorophyll (chl) molecules per photosystem, which are bound to their respective

Abbreviations: Chl, chlorophyll; PSI, photosystem I; PSII, photosystem II; LHCI, light-harvesting complex I; EET, excitation energy transfer.

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apoproteins [e.g. 1,2]. The set of energy transitions of the pigment systems are disordered due either to chemically similar pigments undergoing different interactions with the different protein binding sites [3] or to the presence of chemically different pigments. The excitation energy of the first singlet excited state is transferred, with extraordinarily high efficiency, from the antenna array to the primary chlorophyll electron donors, by a process involving the coupling of pigment transition dipoles. The single chl-chl transfer rates occur on a femtosecond–picosecond timescale [4,5]. The overall reaction centre trapping time (primary charge separation) in photosystem II has been determined to be around 300 ps [6,7], thus indicating a large number of energy-transfer steps prior to trapping, while that of photosystem I is notably shorter (~40 ps) [e.g. 8,9]. The extraordinarily fast trapping rate of photosystem I leads to a quantum efficiency of about 99% and an energy efficiency which attains values of more than 96% [10].

In recent years, there has been a resurgence of interest on the thermodynamic properties, and in particular the entropy, associated with the primary photosynthetic processes [10–22]. While such aspects as entropy changes associated with photon absorption by pigments and photosystems, configurational entropy and ergodicity, the applicability of Carnot cycle reasoning, and radiation temperature have been considered, little has been written on the so-called "antenna entropy," which will be discussed here.

During energy transfer from the antenna pigments to the reaction centre, some thermal energy and electromagnetic energy is also transferred to the environment. It is this phenomenon which lowers the quantum efficiency of photosystem primary photochemistry, σ, by a small amount. For plant PSII, $\sigma \approx 0.85$ and for PSI it is around 0.99 [8,9]. When an antenna molecule absorbs a photon, before trapping at the reaction centre, the excited state energy is delocalised (dispersed) over the pigment molecules of the photosystem at a time which is several orders of magnitude less than that of the natural excited state lifetime of the pigment and also, to reasonable approximation, considerably less than the photochemical trapping time itself. The extent of delocalisation, at thermal equilibrium, depends on the antenna characteristics and varies between the plant photosystems. It is generally thought that this energy dispersal leads to an increase in entropy, which may be analysed in statistical terms. We will call this the delocalisation (dispersal) entropy (S_D) and note that, in thermodynamic terms, it is configurational (mixing) entropy. In the photosynthetic literature, it is often referred to as "antenna entropy." We depart from the usual nomenclature as the entire pigment system is considered, including the reaction centre pigments. However, as mentioned above, little has been written in the literature on this subject. It was briefly mentioned by Schatz et al. [6], Trissl [23] and Dau [24], but in such a way as to not allow a clear understanding for real photosystems and, in some cases, with different formalisms. It is the purpose of this study to analyse this phenomenon using standard, classic, statistical mechanics theory.

2. Results and discussion

It is initially necessary to define the statistical thermodynamic system model which best represents a photosystem. The simplest statistical ensemble is the microcanonical, which has the characteristics of being isolated, and thus, unable to exchange energy with the environment, and its mean energy is constant. The microstates, which specify the system in terms of the physical quantities of the "elementary" particles, in classic statistical mechanics, is determined by their position, $\mathbf{r}$, and momentum at any time. In our case, the "elementary" particles are the chl molecules bound to their apoproteins. It is clear that in the case of the chl molecules of a photosystem, the momentum may be dropped and the microstate is thus ($\mathbf{r}_1$, $\mathbf{r}_2$, … , $\mathbf{r}_N$). As a photosystem may not harbour more than a single excited state due to singlet-singlet annihilation [e.g. 25], a photosystem microstate is defined by the particular pigment on which the excited state is (transiently) localised. The entropy, S, of a microcanonical ensemble is given by the Boltzmann equation

$$S = k_B \ln \Omega, \tag{1}$$

where Ω is the number of equally accessible microstates and k_B is the Boltzmann constant. This expression has been previously used to discuss the entropy of ground and excited states in chlorophyll molecules [13] and it is also an expression of this kind which has been most commonly employed to describe the "antenna entropy," identifying $\Omega = N$, with N being the number of isoenergetic pigments [e.g. 24]. However, the constraint that all microstates must be isoenergetic renders its use in the photosynthetic antenna context doubtful.

On the other hand, the canonical ensemble, which by definition is a closed thermodynamic system but can exchange energy with the environment, seems a better choice. Microstate energy in a real photosynthetic antenna is not constant due to the presence of "spectral forms," which, for higher plant photosystems, span an energy gap in the range of 3–4 k_BT at physiological temperatures [3,26–28]. The canonical probability density, p_i, for any particular energy level E_i, which, in the present case, is equivalent to a pigment "spectral form," is given by

$$p_i = g_i e^{-E_i/k_BT} \Big/ \left(\sum_i g_i e^{-E_i/k_BT} \right);$$

E_i is the energy of the i-th spectral form, taking the lowest energy form as the reference energy, g_i is its degeneracy, and T is the temperature. This expression defines the excited state probability density distribution for a canonical photosystem under the condition that $\sum_i p_i = 1$. A photosystem is a particularly interesting case of a canonical system as it is small, with the number of microstates being of the order of 200. The photosystem phase space is accessed by EET in a few tens of picoseconds, much less than the conventional observation times (~nanoseconds), so the system is ergodic [22]. This connection between the thermodynamic ensembles and plant photosystems has not been previously made.

The photosystem delocalisation entropy (S_D) is, then, given by

$$S_D = -k_B \sum_i p_i \ln p_i = k_B (\ln Z + bU), \tag{2}$$

where $b = 1/k_BT$, $Z = \sum_i g_i e^{-bE_i}$ is the canonical partition function and U is the internal energy.

With only one pigment energy level (isoenergetic photosystem), it is readily shown that $Z = Ne^{-bE}$, and that Eq. (2) formally yields the microcanonical entropy expression, $S_D = k_B \ln N$, where N is the number of equivalent (isoenergetic) pigment sites. This is the expression used by Schatz et al. [6] and Dau [24]. However, it is, at best, a rough approximation when the energy gap between antenna pigment forms is greater than about k_BT, which is always the case in real photosystems. On the other hand, Trissl [23] took the energetically disordered antenna into consideration and wrote the expression $S = k_B \ln p$, where $p = \sum_i g_i e^{-bE_i}$, i.e. the canonical partition function, equivalent to Z in Eq. (2). However, this definition of the delocalisation entropy, which appears to be an attempt at reducing the canonical ensemble to a microcanonical one, does not consider the internal energy contribution of the canonical ensemble (Eq. (2)), and would therefore appear to be incorrect. These expressions are therefore not particularly useful in determining the S_D in a real photosystem.

In the following, we will initially investigate S_D for the general case of a hypothetical isoenergetic pigment system in order to demonstrate the effect of localisation/delocalisation of electronic energy on S_D in a simple pigment ensemble. Subsequently, both PSI and PSII of plants are considered, for which values of S_D (or TS_D) are calculated. As far as we are aware, this is the first time an effort has been made to quantify this parameter.

2.1. Isoenergetic pigment photosystem

Upon photon absorption, the excited state energy is rapidly dispersed throughout the entire pigment system and all accessible microstates in the photosystem phase space are visited. Thus, as already mentioned, the hypothetical photosystem is ergodic and possesses configurational (mixing) entropy (S_{conf})

$$S_{conf} \equiv S_D = -k_B \sum_i p_i \ln\ p_i = k_B \ln\ N. \tag{3}$$

It will be noted, however, that unlike a thermal system, the electronic energy, while being dispersed over all microstates N, does not undergo energy dilution. This seems to constitute an exception to thermal systems. If heat, u, is initially localized in a small space portion, its diffusion throughout the system microstates is characterized by heat (energy) dilution, as described by the solution of the heat equation $\frac{\partial u}{\partial t} = k\frac{\partial^2 u}{\partial x^2}$; k is the heat diffusion coefficient and x is the distance. This is an interesting point as it is just this energy dilution which has been suggested by some to characterize the spontaneous energy dispersal of a thermal system, leading to the "inevitable free energy loss" [29–31]. Thus, thermal systems and photonic antenna systems are characterized by this fundamental difference.

In the following, we will investigate the characteristics of S_D in the hypothetical photosystem in which the purely isoenergetic property undergoes some simple energetic modifications in order to simulate S_D as a function of the degree of excited state energy delocalization/localization within the antenna. In this case, we arbitrarily consider a small group of low-energy pigments with respect to the isoenergetic pigment matrix. We take as a reference photosystem the hypothetical case of $N = 200$ isoenergetic pigments. S_D was calculated according to Eq. (2) and the data are given in Fig. 1 and Table 1.

In the first case (Fig. 1), we modulate both the energy of the low-energy pigments with respect to the antenna pigments and the number of low-energy pigments in the range 1 to 10 per antenna ($N = 200$). The rationale for these calculations is given in Appendix A. S_D has been multiplied by the temperature $T = 300$ K, in order to yield the energy associated with the delocalization entropy (S_D). It is evident that in the absence of a low-energy antenna trap, TS_D is maximal (3.16 kcal mol^{-1}). This is because energy is delocalized over the entire antenna. On the other hand, the entropic energy contribution decreases in the presence of a low-energy antenna trap and tends towards zero upon the energetic deepening of the single pigment antenna trap. The entropy decrease is, however, less as the number of low-energy pigments increases. This is due to the antenna delocalization being least in the presence of a one pigment trap (all energy being concentrated in the one pigment trap) with respect to the multi-pigment traps as, in the latter case, energy is concentrated over a greater number of trap pigments and is, hence, less delocalized. It is therefore evident, from the defining equation for free energy G,

$$G = U - TS \tag{4}$$

and in the absence of pressure and volume changes, that S_D decreases the free energy of the pigment ensemble. This effect is also evident in Table 1, where we have taken a low-energy trap of 5 pigments and have varied the trap energy in the 0–8RT energy range. If we take 680 nm as the Q_y absorption maximum of the isoenergetic pigments, the photon energy is $U = 42$ kcal mole^{-1}. Therefore TS_D, the energy associated with S_D, for the purely isoenergetic system is almost 8% of the photon energy. It should be noted that this effect decreases in the presence of an "antenna trap." It will also be noted (Table 1) that the low-energy trap lowers the occupational probability of the primary donor (see Biological significance of delocalization entropy).

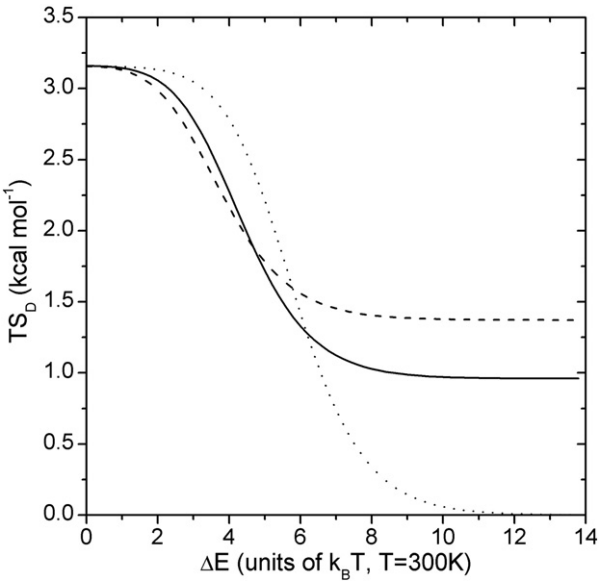

Fig. 1. Changes in the TS_D parameter as a function of low-energy antenna chlorophylls. The energy gap between the isoenergetic bulk antenna and low-energy chlorophylls is given in units of k_BT. The dotted line represents one low-energy chlorophyll. The black line represents five low-energy chlorophylls and the dashed line ten low-energy chlorophylls. The function used is given in Appendix A.

2.2. Plant photosystem II (PSII)

We now consider S_D for the PSII complex. This photosystem binds between 200 and 250 chlorophyll pigments. We shall consider the lower limit in order to compare the results with the hypothetical isoenergetic photosystem discussed above. The pigments are bound to a number of complexes, known as chlorophyll protein complexes, the majority of which bind 10–15 chlorophylls. It has been known for many years [32,33] that there are a number of well-defined spectral pools of pigments absorbing near 650 nm (chlorophyll b) as well as chlorophyll a pools absorbing near 660 nm, 670 nm 677 nm, 680 nm, which are readily approximated in terms of Gaussian bands. These pigment pools are usually known as "spectral forms." The primary donor absorbs near 680 nm. In the following, we use the subband decomposition into spectral forms of both the absorption and fluorescence spectra for a photosystem II preparation (BBY particles) published in Zucchelli et al. [34]. From the area subtending each Gaussian, one may approximate the population of absorbing pigments in each of the five wavelength regions. On the other hand, the corresponding fluorescence subbands represent the probability density of the excited states associated with each of the absorption bands. The data are given in Table 2 as the probability values for each spectral form and the relative p_i values. It is therefore possible to calculate the S_D value for PSII (Eq. (2)). This comes out as 4.6R, which for 300 K is equivalent to $TS_D = 2.9$ kcal mole^{-1}. This value falls rather close to that of the hypothetical isoenergetic antenna (Table 1), and is therefore in broad agreement with our previous conclusion that, considering the chlorophyll/protein pigment domains, PSII is almost isoenergetic [26,35]. As the mean wavelength (first spectral moment) of the PSII absorption spectrum is around 673 nm, one estimates that TS_D is close to 7% of this energy.

2.3. Plant photosystem I (PSI-LHCI)

We shall, once again, take $N = 200$ in order to compare the results with those of PSII and the hypothetical isoenergetic photosystem. It is well known that the antenna system of PSI differs considerably from that of PSII. It consists of a large, so-called, "bulk" antenna that absorbs

Table 1
The influence of a small group of 5 low-energy pigments on the photosystem delocalization entropy (S_D) for the hypothetical isoenergetic photosystem and the occupational probability of the primary donor (p_{P^*}) for $N = 200$. S_D was calculated according to Eq. (3) in which we substituted the Boltzmann constant (k_B) with the gas constant (R) for reasons of convenience. Data are also given for the energy term associated with S_D, i.e., TS_D, in order that it may be readily compared with the photon energy. $T = 300$ K.

Photosystem (N pigments)	S_D [kcal mol^{-1} K^{-1}]	TS_D [kcal mol^{-1}]	p_{P^*}
$N = 200$ Isoenergy (IE)	$1.052 \cdot 10^{-2}$	3.16	$5.0 \cdot 10^{-3}$
$N = 195$ (IE) + 5 ($\Delta E = -2$RT)	$1.018 \cdot 10^{-2}$	3.06	$4.3 \cdot 10^{-3}$
$N = 195$ (IE) + 5 ($\Delta E = -4$RT)	$0.758 \cdot 10^{-2}$	2.27	$2.1 \cdot 10^{-3}$
$N = 195$ (IE) + 5 ($\Delta E = -8$RT)	$0.343 \cdot 10^{-2}$	1.03	$6.6 \cdot 10^{-5}$

in the spectral region around 680 nm, and a small population of low-energy pigments (red spectral forms), which absorb at wavelengths near and above that of the primary donor, usually identified as P700, with an absorption maximum at 700 nm. The red spectral forms, of which there is a small, but still unspecified number, are thought to be excitonic dimers [36–39]. This, however, does not constitute a problem for the present calculations as they are performed considering the effective monomer absorption equivalents. The red forms are mainly located in the external antenna, far from the reaction centre pigments [40]. As mentioned above, the exact number of red forms is not known. Thus, in the present case, we perform calculations in the 5–10 red forms monomer equivalent range. Owing to their low energies with respect to the bulk pigments, it has been shown that approximately 85% of the steady state fluorescence is associated with them [41]. The red forms absorb at about 3–4 k_BT below the "bulk" antenna pigments. It is therefore clear that this photosystem has an antenna which, to a rough approximation, resembles that of the hypothetical isoenergetic antenna with 5 low-energy pigments, which are low-energy shifted by 4RT (Table 1). It is therefore not surprising that the TS_D value estimated from similar Gaussian subband data to those discussed above for PSII [40], is approximately 1.8 kcal mole^{-1}. The mean absorption wavelength is near 679 nm. Thus, energy associated with TS_D is about 4% of that of the internal energy associated with this mean absorption. It is therefore evident that while electronic energy dispersal is high in the case of PSII, for PSI, it concentrates in the low-energy pigments and dispersal is reduced.

2.4. Biological significance of delocalization entropy, S_D

As indicated above, a photosystem is a rather unique example of a closed (canonical) thermodynamic system. We have shown that when a photosystem harbours a chlorophyll pigment in the excited state, the pigment ensemble possesses configurational entropy (S_{conf}), which is equivalent to what we have called delocalization entropy (S_D; Eq. (3)).

However, it has also been shown that the presence of a group of low-energy antenna pigments (antenna trap) decreases S_D, which at first sight might be expected to lead to an increase in the free energy of the photosystem (Eq. (3)) with respect to an isoenergetic type photosystem. We therefore briefly consider the molar free energy (G_m), available for primary charge separation, of a photosystem suspension, taking into account that it is the free energy of the donor state (P^*) which determines the free energy available for primary charge separation. This is given in Eq. (4) for an Avogadro's number (N) of photosystems

$$G_m = N \cdot p_{P_*} \cdot G_{P_*}, \tag{5}$$

The three terms on the right-hand side of Eq. (4) are independent parameters. G_{P^*} is the intrinsic free energy of the excited primary donor and p_{P^*} is the occupational probability of the primary donor, given by the canonical ensemble probability for a particular *microstate* $p_{P^*} = e^{-bh\nu|_{P^*}} / \sum_i e^{-bh\nu|_{P_i}}$. $b = 1/k_BT$, $h\nu|_{P^*}$ is the energy of the excited primary donor and $h\nu|_{P_i}$ is the energy of the i-th pigment. It is therefore clear from Table 1 that the presence of a low-energy antenna trap, while decreasing S_D, also decreases p_{P^*}. This latter effect leads to a decrease in the molar free energy available for primary photochemical charge separation, G_m (Eq. (4)). Thus, the low-energy trap, while increasing the free energy of the photosystem antenna via S_D, decreases the free energy available for primary photochemistry. This suggests that the antenna entropy might not influence the free energy available for primary charge separation. This intriguing situation requires further comment.

In this context, we point out that the microstates which make up the photosystem macrostate include all the chlorophyll molecules, both antenna and reaction centre, and the delocalization entropy is, as always, that of the macrostate. However, it is not the macrostate which functions as the primary electron donor, but just one particular microstate which coincides with that in which the primary donor is in the excited state and, which of course, does not possess S_{conf}. This situation is analogous with that of ligand binding proteins where it is quite well known that the ligand binds to a particular protein microstate [e.g. 42]. The free energy of binding is determined by this particular microstate. The total configurational entropy of the protein is often not relevant. It is clear in both the photosystem and the ligand-binding cases that the reaction rates will depend on the occupation probability of the reactive microstate. However, this does not necessarily imply a change in the overall free energy of either system. On the basis of these considerations, we conclude that the S_D of the photosystem pigment ensemble does not modify the free energy of the primary donor, which may thus be equated with the internal energy of its excited state.

We wish to underline the unusual thermodynamic nature of this situation. It is natural to consider excited state energy transfer from the

Table 2
The energy associated with the delocalisation entropy (TS_D) and the excited state occupation probability of the primary donor (p^*) for photosystem II (BBY grana membranes). Sb_A refers to the Gaussian subband area. The data have been taken from Zucchelli et al. [34] and calculations were performed according to Eq. (2).

BBY Absorption Subbands max [nm]	Subband Area (Sb_A) (norm 200 pigments)	BBY Fluorescence Subbands max [nm]	Subband Area (p_{sub}) (norm 1)	$p_i = p_{sub}/Sb_A$	TS_D [kcal mol^{-1}] $T = 300$ K
647.5	37.58	653.4	$2.19 \cdot 10^{-2}$	$5.84 \cdot 10^{-4}$	0.097
660.0	42.86	663.6	$5.31 \cdot 10^{-2}$	$1.24 \cdot 10^{-3}$	0.212
669.6	45.76	671.7	$1.72 \cdot 10^{-1}$	$3.75 \cdot 10^{-3}$	0.572
677.5	45.97	679.7	$3.94 \cdot 10^{-1}$	$8.58 \cdot 10^{-3}$	1.119
683.9	27.84	686.5	$3.59 \cdot 10^{-1}$	$1.29 \cdot 10^{-2}$	0.930
Total	200		1.00		2.931

antenna to the primary donor as a single process. Thus, within this single process, the configurational entropy increases but this has no influence on the free energy available for primary photochemistry. This is because the energy delocalisation in the antenna is not accompanied by energy dilution, as is usual in other thermodynamic systems. In principle the free energy of P^* may be equal to the energy absorbed by an antenna molecule.

While it is well known that the quantum efficiency of PSI is around 99% and that of PSII is around 85%, the thermodynamic, or energy, efficiency is less well understood. Earlier studies argued that the maximum thermodynamic efficiency was determined by the Carnot efficiency [14, 43–46], which was considered to be in the 50% to 70% range. However, several recent papers have disputed that the Carnot efficiency is relevant to primary photochemical processes [10,21] and, in the case of PSI it was suggested that the thermodynamic efficiency attains values of above 96% [10], only slightly lower than the quantum efficiency itself. This idea is supported by the present conclusion that S_D does not lower the free energy available for primary processes in PSI. Recent studies have also shown that upon pigment excitation into the first excited singlet state, changes in both the molecular pigment entropy and in the configurational entropy are not influenced [10,22]. Thus, it seems that there are no "inevitable free energy losses" upon light absorption and energy transfer to the primary electron donor within photosystems. This supports the conclusion that, at least in plant PSI, the thermodynamic efficiency is high, and close to that of the quantum efficiency.

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Appendix A

Given N pigments, with m pigments of energy E_1 and $(N - m)$ pigments of energy E_2 with $E_2 = E_1 - \Delta E$, with ß=b in the text, we can define the partition function Z as

$$Z = me^{-\beta E_1} + (N-m)e^{-\beta E_2} = e^{-\beta E_1}\left(m + (N-m)e^{\beta\Delta E}\right)$$

and the probability for the two types of pigments are

$$p_m = \frac{e^{-\beta E_1}}{e^{-\beta E_1}\left(m + (N-m)e^{\beta\Delta E}\right)} = \frac{1}{m + (N-m)e^{\beta\Delta E}} \quad \forall m$$

$$p_{N-m} = \frac{e^{-\beta E_2}}{e^{-\beta E_1}\left(m + (N-m)e^{\beta\Delta E}\right)} = \frac{e^{\beta\Delta E}}{\left(m + (N-m)e^{\beta\Delta E}\right)} \quad \forall (N-m)$$

Using these expressions results in

$$\begin{aligned}\sum_{i=1}^{N} p_i \ln p_i &= \sum_{i=1}^{m} p_i \ln p_i + \sum_{i=m+1}^{N} p_i \ln p_i = -\frac{m}{m + (N-m)e^{\beta\Delta E}} \ln\left(m + (N-m)e^{\beta\Delta E}\right) + \\ &+ \frac{(N-m)e^{\beta\Delta E}}{m + (N-m)e^{\beta\Delta E}} \ln \frac{e^{\beta\Delta E}}{m + (N-m)e^{\beta\Delta E}} = \\ &- \left(\frac{m}{m + (N-m)e^{\beta\Delta E}} + \frac{(N-m)e^{\beta\Delta E}}{m + (N-m)e^{\beta\Delta E}}\right) \ln\left(m + (N-m)e^{\beta\Delta E}\right) \\ &+ \frac{\beta\Delta E(N-m)e^{\beta\Delta E}}{m + (N-m)e^{\beta\Delta E}} = \\ &= -\ln\left(m + (N-m)e^{\beta\Delta E}\right) + \frac{\beta\Delta E(N-m)e^{\beta\Delta E}}{m + (N-m)e^{\beta\Delta E}}\end{aligned}$$

If we take $\Delta E = \alpha k_B T = \alpha\beta^{-1}$, S_D can then be written as:

$$S_D = -k_B \sum_{i=1}^{N} p_i \ln p_i = k_B\left[\ln\left(m + (N-m)e^{\alpha}\right) - \frac{\alpha(N-m)e^{\alpha}}{m + (N-m)e^{\alpha}}\right].$$

References

[1] D. Mauzerall, N.L. Greenbaum, The absolute size of a photosynthetic unit, Biochim. Biophys. Acta 974 (1989) 119–140.
[2] P. Galka, S. Santabarbara, T.H.K. Thi, H. Degand, P. Morsomme, R.C. Jennings, E.J. Boekema, S. Caffarri, Functional analyses of the plant photosystem I-light-harvesting complex II supercomplex reveal that light-harvesting complex II loosely bound to photosystem II is a very efficient antenna for photosystem I in state II, Plant Cell 24 (2012) 2963–2978.
[3] G. Zucchelli, D. Brogioli, A.P. Casazza, F.M. Garlaschi, R.C. Jennings, Chlorophyll ring deformation modulates electronic transitions in chlorophyll–protein complexes and generates spectral forms, Biophys. J. 93 (2007) 2240–2254.
[4] H. van Amerongen, L. Valkunas, R. van Grondelle, Photosynthetic Excitons, World Scientific, Singapore, 2000.
[5] T. Mancal, L. Valkunas, Exciton dynamics in photosynthetic complexes by coherent and incoherent light, New J. Phys. 12 (2010).
[6] G.H. Schatz, H. Brock, A.R. Holzwarth, Kinetic and energetic model for the primary processes in photosystem-II, Biophys. J. 54 (1988) 397–405.
[7] E. Engelmann, G. Zucchelli, A.P. Casazza, D. Brogioli, F.M. Garlaschi, R.C. Jennings, Influence of the photosystem I—light harvesting complex I antenna domains on fluorescence decay, Biochemistry 45 (2006) 6947–6955.
[8] E. Wientjes, I.H.M. van Stokkum, H. van Amerongen, R. Croce, Excitation-energy transfer dynamics of higher plant photosystem I light-harvesting complexes, Biophys. J. 100 (2011) 1372–1380.
[9] R.C. Jennings, G. Zucchelli, S. Santabarbara, Photochemical trapping heterogeneity as a function of wavelength in plant photosystem I (PSI-LHCI), Biochim. Biophys. Acta 1827 (2013) 779–785.
[10] R.C. Jennings, S. Santabarbara, E. Belgio, G. Zucchelli, The Carnot efficiency and plant photosystems, Biophysics 59 (2014) 230–235.
[11] R.C. Jennings, E. Engelmann, F.M. Garlaschi, A.P. Casazza, G. Zucchelli, Photosynthesis and negative entropy production, Biochim. Biophys. Acta 1709 (2005) 251–255.
[12] R.C. Jennings, E. Belgio, A.P. Casazza, F.M. Garlaschi, G. Zucchelli, Entropy consumption in primary photosynthesis, Biochim. Biophys. Acta 1767 (2007) 1194–1197.
[13] R.S. Knox, W. Parson, Entropy production and the second law in photosynthesis, Biochim. Biophys. Acta 1767 (2007) 1189–1193.
[14] J. Lavergne, Commentary on "Photosynthesis and negative entropy production" by Jennings and co-workers, Biochim. Biophys. Acta 1757 (2006) 1453–1459.
[15] Z.S. Chen, S.P. Mo, Effective temperature and exergy of monochromic blackbody radiation, Prog. Nat. Sci. 17 (2007) 1250–1254.
[16] Z.S. Chen, S.P. Mo, P. Hu, Recent progress in thermodynamics of radiation-exergy of radiation, effective temperature of photon and entropy constant of photon, Sci. China E. Technol. Sci. 51 (2008) 1096–1109.
[17] S. Lems, H.J. van der Kooi, J.D. Arons, Exergy analyses of the biochemical processes of photosynthesis, Int. J. Exergy 3 (2010) 333–351.
[18] G. Renger, The light reactions of photosynthesis, Curr. Sci. 98 (2010) 1305–1319.
[19] A.V. Melkikh, V.D. Seleznev, O.I. Chesnokova, Analytical model of ion transport and conversion of light energy in chloroplasts, J. Theor. Biol. 264 (2010) 702–710.
[20] S. Naoki, Scientific Elan Vital: entropy deficit or inhomogeneity as a unified concept of driving forces of life in hierarchical biosphere driven by photosynthesis, Entropy 14 (2012) 233–251.
[21] D. Mauzerall, Thermodynamics of primary photosynthesis, Photosynth. Res. 116 (2013) 363–366.
[22] R.C. Jennings, G. Zucchelli, Ergodicity, configurational entropy and free energy in pigment solutions and plant photosystems: influence of excited state lifetime, Biophys. Chem. 187–188 (2014) 29–32.
[23] H.W. Trissl, Long-wavelength absorbing antenna pigments and heterogeneous absorption bands concentrate excitons and increase absorption cross-section, Photosynth. Res. 35 (1993) 247–263.
[24] H. Dau, On the relation between absorption and fluorescence emission spectra of photosystems: derivation of a Stepanov relation for pigment clusters, Photosynth. Res. 48 (1996) 139–145.
[25] V. Barzda, V. Gulbinas, R. Kananavicius, V. Cervinskas, H. van Amerongen, R. van Grondelle, L. Valkunas, Singlet-singlet annihilation kinetics in aggregates of trimers of LHCII, Biophys. J. 80 (2001) 2409–2421.
[26] R.C. Jennings, R. Bassi, F.M. Garlaschi, P. Dainese, G. Zucchelli, Distribution of chlorophyll spectral forms in the chlorophyll protein complexes of photosystem II, Biochemistry 32 (1993) 3203–3210.
[27] R. Cattaneo, G. Zucchelli, F.M. Garlaschi, L. Finzi, R.C. Jennings, A thermal broadening analysis of the absorption spectra of the D1/D2/cytochrome B-559 complex in terms of gaussian decomposition subbands, Biochemistry 34 (1995) 15267–15275.
[28] J. Adolphs, F. Mueh, M.El-A. Madjet, M.S. Busch, T. Renger, Structure-based calculations of optical spectra of photosystem I suggest an asymmetric light-harvesting process, J. Am. Chem. Soc. 132 (2010) 3331–3343.
[29] H.S. Leff, Thermodynamic entropy: the spreading and sharing of energy, Am. J. Phys. 64 (1996) 1261–1271.
[30] H.S. Leff, Entropy: its language and interpretation, Found. Phys. 37 (2007) 1744–1766.
[31] F.L. Lambert, Configurational entropy revisited, J. Chem. Educ. 84 (2007) 1548–1550.
[32] C. French, J.S. Brown, M.C. Lawrence, Four universal forms of chlorophyll a, Plant Physiol. 49 (1972) 421–429.
[33] G. Zucchelli, R.C. Jennings, F.M. Garlaschi, The presence of long wavelength chlorophyll a spectral forms in the light harvesting chlorophyll harvesting a/b protein complex II, J. Photochem. Photobiol. B 6 (1990) 381–394.
[34] G. Zucchelli, R.C. Jennings, Garlaschi, Independent fluorescence emission of the chlorophyll spectral forms in higher plant photosystem II, Biochim. Biophys. Acta 1099 (1992) 163–169.

[35] R.C. Jennings, F.M. Garlaschi, R. Bassi, G. Zucchelli, A. Vianelli, P. Dainese, A study of photosystem II emission in terms of the antenna chlorophyll protein complexes, Biochim. Biophys. Acta 1183 (1993) 194–200.
[36] E. Engelmann, T. Tagliabue, N.V. Karapetyan, F.M. Garlaschi, G. Zucchelli, R.C. Jennings, CD spectroscopy provides evidence for excitonic interactions involving red shifted chlorophyll forms in photosystem I, FEBS Lett. 499 (2001) 112–115.
[37] T. Morosinotto, S. Castelletti, J. Breton, R. Bassi, R. Croce, Mutation analysis of Lhca1 antenna complex. Low energy absorption forms originate from pigment-pigment interactions, J. Biol. Chem. 277 (2002) 36253–36261.
[38] R. Croce, T. Morosinotto, S. Castelletti, J. Breton, R. Bassi, The Lhca antenna complexes of higher plants photosystem I, Biochim. Biophys. Acta 1556 (2002) 29–40.
[39] R. Croce, A. Chojnicka, T. Morosinotto, J.A. Ihalainen, F. van Mourik, J.O. Dekker, R. Bassi, R. van Grondelle, The low energy forms of photosystem I light harvesting complexes: spectroscopic properties and pigment–pigment interaction characteristics, Biophys. J. 93 (2007) 2418–2428.
[40] R. Croce, G. Zucchelli, F.M. Garlaschi, R.C. Jennings, A thermal broadening study of the antenna chlorophylls in PSI-200, LHCI, and PSI core, Biochemistry 37 (1998) 17355–17360.
[41] R. Croce, G. Zucchelli, F.M. Garlaschi, R. Bassi, R.C. Jennings, Excited state equilibration in the photosystem I light-harvesting I complex: P700 is almost isoenergetic with its antenna, Biochemistry 35 (1996) 8572–8579.
[42] R.A. Copeland, Evaluation of Enzyme Inhibitors in Drug Discovery, Second edition Wiley, New Jersey, 2013.
[43] L.N.M. Duysens, The photochemical apparatus, its structure and function, in: R.C. Fuller (Ed.), The path of light energy in photosynthesis, Brookhaven Symp. Biol, Brookhaven Natl. Lab, NY, 1958, p. 18.
[44] G. Meszena, H.V. Westerhoff, Non-equilibrium thermodynamics of light absorptiion, J. Phys. A Math. Gen. 32 (1999) 301–311.
[45] J. Lavergne, P. Joliot, in: W.A. Cramer (Ed.), Energy Transduction in Membranes, Biophysical Society, 2000, (http://www.biophysics.org/education/lavergne.pdf).
[46] R.S. Knox, Primary processes in photosynthesis, in: J. Barber (Ed.), Photosynthetic Efficiency an Exciton Transfer and Trapping, Elsevier/North Holland, Amsterdam, 1977, p. 55.