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

Robert C. Jennings *, Giuseppe Zucchelli

Consiglio Nazionale delle Ricerche, Istituto di Biofisica, sede di Milano, via Giovanni Celoria 26, 20133 Milan, Italy
Dipartimento di Bioscienze, Università degli Studi di Milano, via Giovanni Celoria 26, 20133 Milan, Italy

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
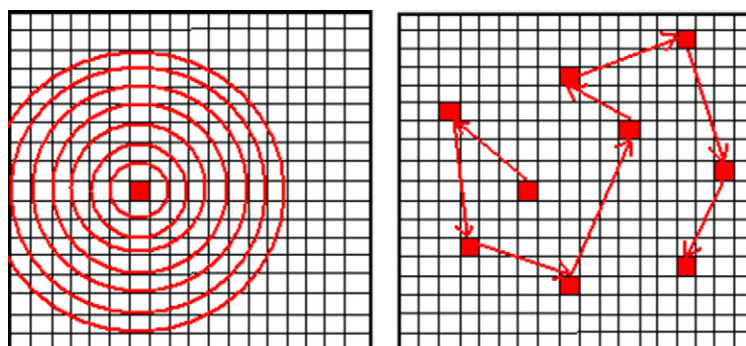
ABSTRACT

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

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, **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 ($\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$). 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 $k_B T$ 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

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

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

With only one pigment energy level (isoenergetic photosystem), it is readily shown that $Z = N e^{-bE}$, 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 $k_B T$, 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 $p = \sum g_i e^{-bE_i}$, 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.