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# Minimum entropy production in photosynthesis

C.D. Andriesse*, M.J. Hollestelle

*Faculty of Physics and Astronomy, Utrecht University, Princetonplein 5, 3584 CC Utrecht, The Netherlands*

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**Abstract**

In this paper a flux-coupling model of photosynthesis is presented. By requiring minimum entropy production, it is found that the photosynthetic efficiency is essentially given by the square root of $D/\lambda$. $D$ and $\lambda$ are the diffusion coefficient and thermal conductivity of the rate-limiting processes in the chloroplast, respectively. For experimental values of $D$ and $\lambda$, the efficiency is found to be 2.4–7.5%, with a likely value of 6.1%, whereas C4-plants are known to have an efficiency of 6.2%. We conclude that the process of photosynthesis is in quantitative agreement with the principle of minimum entropy production. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Photosynthesis; Photosynthetic efficiency; Plant cell wall; Entropy production; Diffusion processes

## 1. Introduction

Although the mechanism of photosynthesis is understood in considerable detail, there is as yet no fundamental explanation of the low efficiency. This efficiency is the small energy fraction available for the synthesis that is left after incidental losses in the absorption and degradation of photons, plus those in the transfer of excitations [1,2]. So it might seem that photosynthetic efficiency should be determined directly by the details of specific molecular processes, rather than indirectly by general physical principles. However, one can look at photosynthesis as a process where energy-rich organic molecules emerge from simple, energy-poor molecules when the latter are absorbing solar photons. In this perspective, it is just another of the many processes where a flux of matter is coupled to a flux of energy. For such processes a fundamental theory exists, namely that of non-equilibrium thermodynamics [3,4]. When this theory is applied, one can find a simple relation between the efficiency of photosynthesis and common transport properties of the chloroplast, under the condition that a minimum of entropy will be produced. That condition seems to be fulfilled. For the likely range of diffusion

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* Corresponding author.

*E-mail address:* C.D.Andriesse@phys.uu.nl (C.D. Andriesse).

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coefficients we calculate efficiencies of 2.4–7.5%, in agreement with measured values.

## 2. Theory

Let us consider a model process with energy exchange between a photon 1 and a composite particle 2 (see Fig. 1); 2 is the loose combination of a $H_2O$ and a $CO_2$ molecule. Energy is exchanged through an excitation 3 of the chloroplast, by which energy-rich electron/proton pairs from the $H_2O$ ultimately react with the $CO_2$. This results in heat, radiated away by a photon 4, and a new composite particle 5; 5 is the loose combination of a $[CH_2O]$ (unit carbohydrate molecule) and an $O_2$.

In reality the exchange involves many interactions, not one single excitation. In reality also, the particles 2 and 5 are not linked; the pertinent molecules (and intermediate forms) participate in these interactions only at distinct moments. A more realistic graph, with details about the various excitations and molecules, would, however, still show a sequence of photons that is somehow coupled to a sequence of molecules. The idea of a sequence is essential, since a single photon will not suffice to produce a particle 5 with the $[CH_2O]$; approximately 10 solar photons are needed. Our graph is meant to show the simplest possible coupling of a flux of molecules (or matter) $j_D$ to a flux of photons (or energy) $j_T$.

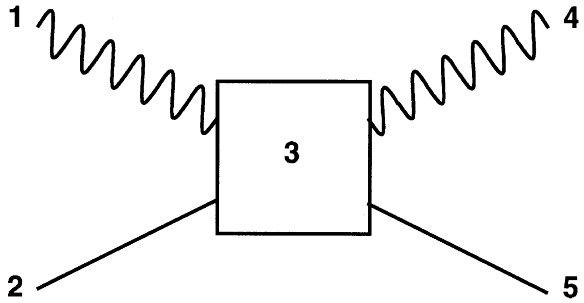

Fig. 1. Diagram of fluxes through the chloroplast. Details of the excitation 3 are omitted and replaced by a 'black box', since only the influxes (1 and 2) and the effluxes (4 and 5) are important.

Will this coupling be fixed by common transport properties for matter and energy of the chloroplast? One is tempted to say no. It would be surprising if the relation between $j_D$ and $j_T$ were only determined by the diffusion coefficient $D$ and the thermal conductivity $\lambda$. Flux coupling results from the sharing of the driving 'forces' $\nabla n$ and $\nabla T$, gradients of the atomic density $n$ and the temperature $T$ (the equivalent of energy). Whereas normally $\nabla n$ is only driving $j_D$ and $\nabla T$ only $j_T$, in the present case of photosynthesis $\nabla T$ is also driving $j_D$ and $\nabla n$ also $j_T$. This suggests that the coupling would be fixed by unknown cross-coefficients and not by $D$ and $\lambda$.

Yet the opposite is true. Recently it has been shown that $(j_D/j_T)^2 = knD/\lambda$ is a useful approximation [5]. Here $k$ is Boltzmann's constant. This result is found as part of the solution of a special problem (offering another case of flux coupling), but it is valid for all processes with a minimum of entropy production. One has to start with the definition of entropy production, which is

$$\partial(s/k)/\partial t = -j_D \cdot \nabla n/n - j_T \cdot \nabla T/T \tag{1}$$

where $s/k$ is a volume-dependent number, namely, the logarithm of the probability of a configuration in that volume. One has to add the phenomenological equations

$$j_D = -(nD)\nabla n/n - C\nabla T/T \tag{2}$$

$$j_T = -\Gamma \nabla n/n - (\lambda/k)\nabla T/T \tag{3}$$

where $C$ and $\Gamma$ are the above mentioned cross coefficients, with which the fluxes $j_D$ an $j_T$ can be eliminated from Eq. (1). The minimum of entropy production is obtained from $\partial^2(s/k)/(\partial t \partial \nabla n) = 0$ and $\partial^2(s/k)/(\partial t \partial \nabla T) = 0$, which gives two further equations. Together with Eqs. (2) and (3) one now has four equations for eight variables (namely, the two fluxes, the two 'forces', the two proper transport coefficients and the two cross coefficients). So, one can find four other equations, each with four variables, of which one is

$$(j_D/j_T)^2 = (nD)/(\lambda/k). \tag{4}$$

For details of the calculation one is referred to ref. [5].

We stress that minimum entropy production is taken as a *principle*. In fact we have no proof for its validity in the case of photosynthesis. It can only be proved, if: (i) the entropy production is a quadratic function of the gradients behind the fluxes; and (ii) the cross-coefficients are symmetric [3]. Condition (i) will be fulfilled when the system is close to equilibrium (where fluxes are proportional to the gradients), but what is close [6]? This question has been recently discussed in terms of decaying fractal structures, which determine the entropy production in the approach to equilibrium [7]. But condition (ii) may be violated, since anti-symmetric components of the cross-coefficients, and therefore, microscopic irreversibility [8], cannot be a priori excluded. Our *principle* implies reversibility as an approximation.

Irreversibility will make the ratio $j_D/j_T$ smaller than given by Eq. (4). The reason is that in this case a larger fraction of $j_T$ is converted into heat, that is: directed to the efflux 4 instead of to efflux 5 (see Fig. 1). The less reversible the process is, the smaller is $j_D/j_T$, and it is not possible to give a lower limit.

## 3. Transport coefficients

Before discussing likely values of the transport coefficients, we recall that $D$ and $\lambda/(kn)$, the diffusivity as it is called, are theoretically equal when $n$ approaches zero (the ideal-gas limit) and that $D$ is smaller than $\lambda/(kn)$ when $n$ is finite, so that $knD/\lambda < 1$. The flux ratio $j_D/j_T$, being always less than 1, can be simply related to $\eta$, the energy efficiency of photosynthesis. The fluxes consist of molecules and photons and, thus, they are expressed in entities per square metre per second. But $\eta$ is the ratio of energies in these fluxes, expressed in joule per square metre per second. So $j_D$ has to be multiplied by $(\Delta G)$, the Gibbs-energy per molecule, and $j_T$ by $(h\nu)$, the energy per photon, or $\eta = (\Delta G)/(h\nu)\cdot(j_D/j_T)$. Note that we do not need to speak of the ten or so solar photons required for the synthesis of $[CH_2O]$; the numbers are accounted for in the fluxes. For $(\Delta G)$ of one unit carbohydrate we take $7.95 \times 10^{-19}$ joule, 1/6 of the value obtained in the original, extensive oxidation experiments of glucose [9]. For $(h\nu)$ of a solar photon we take $2.92 \times 10^{-19}$ joule, pertaining to the red light with a wavelength of 680 nm that is best absorbed by chlorophyll-*a* [10]. With $(\Delta G)/(h\nu) = 2.72$ we get an efficiency of $\eta = 2.72\sqrt{knD/\lambda}$, where $n$ will be approximately $3.3 \times 10^{28}$ molecules/m$^3$, a typical value for water and condensed matter in general.

For $\lambda$ we propose to take 0.607 W m$^{-1}$ K$^{-1}$, the normal thermal conductivity of water [11]. This is the only realistic choice for a chloroplast that is drenched with water, where the high-frequency motions of water molecules will take care of the energy transport. The uncertainty about this value is at most a few percent (as is the case for $n$). Under normal environmental conditions for photosynthesis the dependence of $\lambda$ (and $D$) on the temperature and pressure is irrelevant.

The uncertainty about the value of $D$ is greater, since it is not entirely clear which motion is relevant. In contrast to the thermal conductivity, the diffusion coefficient is linked to the low-frequency motions of molecules through the chloroplast. Should we take the $D$ for $CO_2$ or the $D$ for glucose, both in a watery environment? The first choice can be motivated by hints that intercellular diffusion of $CO_2$ could be a limiting process in the photosynthesis [12]. For $CO_2$ in water under normal conditions one measures $D = 1.95 \times 10^{-9}$ m$^2$ s$^{-1}$ [13,14]. The other choice can be motivated by the large size of molecules like $[CH_2O]_6$, which will make them slower than $CO_2$. In that case the efflux, not the influx, would be the limiting process. As a matter of fact, the diffusion coefficient for glucose in water is almost 3 times smaller: under normal conditions one measures $D = 0.67 \times 10^{-9}$ m$^2$ s$^{-1}$ [11]. Being so much smaller, it probably is more relevant than the value for $CO_2$. How certain is it? In wet cells $D$ is expected to lie between 1 and $0.1 \times 10^{-9}$ m$^2$ s$^{-1}$, where the upper limit is for glucose diffusion through aqueous solutions and the lower limit for glucose diffusion across cell walls [10]. We do not speak of diffusion of glucose in a perpendicular direction, in the plane of those walls, for which $D$ will be two orders of magnitude smaller [15]. The faster and more relevant diffusion across the walls may pass through ‘channels’ between the polysaccharides and proteins from which the walls are made [16].

Since only a lower limit for this diffusion has been given, one wonders whether structural information can help to find the real value, or real values. Comparative studies of cell walls in flowering plants have led to the recognition of two basically different structures [17]. All dicotyledons and some monocot families have type I walls, which consist of a pectin matrix with wide pores of 4 to perhaps 10 nm. Other monocot families have entirely different walls of type II based on GAXs, between which the pores are tight. Can one thus, expect the diffusion through type I walls to be easier than through type II walls? No, since pore sizes alone don’t determine the diffusion of glucose. Other differences, particularly in the charge density, which is higher in type I than in type II, will have an effect as well. Unfortunately it is not yet possible to relate $D$ to cell wall structure.

## 4. Discussion and conclusion

The above values for $n$, $\lambda$ and $D$, inserted in $\eta = 2.72\sqrt{knD/\lambda}$, give the efficiencies shown in Table 1. We get the correct order of magnitude, and more than that. For any crop growing under ideal conditions $\eta$ is expected to be close to 7% [10]. In practice, C4-plants convert, on average, 14 $\mu$g $CO_2$/joule of intercepted daylight in [$CH_2O$], and 11 $\mu$g in C3-plants [18].

These data are transformed in $\mu$g [$CH_2O$]/joule absorbed photosynthetically-active radiation when we multiply by 0.28, and this again in $\eta$ by multiplying with the heat of formation of 0.0159 joule $\mu g^{-1}$ [$CH_2O$]. So we have 6.2% for the efficiency of C4-plants and 4.9% for C3-plants — in both cases average values with a spread of 0.5% (according to the error in the transformation factor 0.28). The 6.2% measured for the most efficient plants fits very well to the $0.67 \times 10^{-9}$ $m^2\ s^{-1}$ measured for glucose diffusion in water, but the precision of that fit can have no significance, considering the simplicity of our calculation.

Table 1
Comparison of predicted efficiencies $\eta_p$ of photosynthesis, for relevant values of the diffusion coefficient $D$, with measured efficiencies $\eta_m$ for C3- and C4-plants and the expected maximum (see text)

| $\eta_p$(%) | $D(10^{-9}\ m^2/s)$ | $\eta_m$(%) | Comment |
|---|---|---|---|
| 2.4 | 0.10 | | min of $D$ |
| | | 4.9 | C3-plants |
| 6.1 | 0.67 | 6.2 | C4-plants |
| | | ~ 7 | ‘ideal crop’ |
| 7.5 | 1.0 | | max of $D$ |

Apart from the distinction between C4- and C3-plants, one may consider other differences in photosynthesis. Plants can of course be distinguished by the end products of the $CO_2$ conversion, i.e. their specific tissues of proteins, carbohydrates, lipids, lignin and organic acids. In building these tissues, maize and sorghum (C4-plants) convert 2.4 and 2.7 $\mu$g $CO_2$/joule of intercepted daylight; but barley, wheat, sugar beet and rice (C3-plants) only 1.2, 1.5, 1.8 and 2.1 $\mu$g, respectively, [19]. These values are much lower than the above 14 and 11 $\mu$g and point to substantial losses. However, since they refer to plant-specific mechanisms for fixing the initially formed [$CH_2O$] in more stable stocks, they should not be compared with our theory.

We conclude that photosynthesis is in quantitative agreement with the principle of minimum entropy production. In the evolution that led to the performance of C4-plants in the terrestrial environment, we can see a natural tendency to make the entropy that is generated in fluxes as small as possible.

One can speculate about the applicability of our treatment to other, more primitive, photosynthetic organisms. In the purple membrane bacteriorhodopsin of *Halobacterium salinarum*, for instance, $\eta$ seems to have a somewhat higher value [20]. Should this be ascribed to faster diffusion?

In any case there is no reason why flux coupling would not be effective here.

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## References

[1] D.O. Hall, K.K. Rao, Photosynthesis, Edward Arnold, London, 1987.

[2] N.R. Baker (Ed.), Photosynthesis and the Environment, Kluwer, Dordrecht, 1996.

[3] S.R. de Groot, P. Mazur, Non-equilibrium Thermodynamics, Dover, New York, 1984.

[4] G. Nicolis, I. Prigogine, Self-organization in Non-equilibrium Systems, Wiley, New York, 1977.

[5] C.D. Andriesse, On the relation between stellar mass loss and luminosity, Astrophys. J. 539 (2000) 364–365.

[6] L.E. Reichl, A Modern Course in Statistical Physics, Edward Arnold, London, 1998.

[7] T. Gilbert, J.R. Dorfman, P. Gaspard, Entropy production, fractals, and the relaxation to equilibrium, Phys. Rev. Lett. 85 (2000) 1606–1609.

[8] H.B.G. Casimir, On Onsager's principle of microscopic reversibility, Rev. Mod. Phys. 17 (1945) 343–350.

[9] K. Burton, H.A. Krebs, The free-energy changes associated with the individual steps of the tricarboxylic acid cycle, glycolysis and alcoholic fermentation and with the of the pyrophosphate groups of adenosinetriphosphate, Biochem. J. 54 (1953) 94–107.

[10] P.S. Nobel, Introduction to Biophysical Plant Physiology, Freeman, San Francisco, 1974.

[11] D.R. Lile, Handbook of Chemistry & Physics, Chem. Rubber Co, Cleveland, 1994.

[12] D.F. Parkhurst, K.A. Mott, Intercellular diffusion limit to CO2 uptake in leaves, Plant Physiol. 94 (1990) 1024–1032.

[13] C.S. Ho, J.F. Shanahan, Carbon dioxide transfer in bioreactors, CRC Crit. Rev. Biotech. 4 (1986) 185–252.

[14] C.S. Ho, M.D. Smith, J.F. Shanahan, Carbon dioxide transfer in biochemical reactors, Adv. Biochem. Eng. 35 (1987) 83–125.

[15] J. Whitmarsh, Mobile electron carriers in thylakoids, Encycl. Plant Physiol. 19 (1986) 508–527.

[16] J.E. Varner, L.-S. Lin, Plant cell wall architecture, Cell 56 (1989) 231–239.

[17] N.C. Carpita, D.M. Gibeaut, Structural models of primary cell walls in flowering plants, Plant J. 3 (1993) 1–30.

[18] J. Goudriaan, H.H. van Laar, Modelling Potential Crop Growth Processes, Kluwer, Dordrecht, 1994.

[19] S.N. Azam–Ali, N.M.J. Crout, R.G. Bradley, Perspectives in modelling resource capture by crops, in: J.L. Monteith, R.K. Scott, M.H. Unsworth (Eds.), Resource Capture by Crops, Nottingham Univ. Press, 1994.

[20] H.V. Westerhoff, W. Crielaard, K.J. Hellingwerf, Global bioenergetics, in: P. Gräber (Ed.), Bioenergetics, Birkhäuser Verlag, Basel, 1997.