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COMMENT

Reply to Comment on ‘Non-equilibrium thermodynamics of light absorption’

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Abstract. In response to the comments made by Dr Andrews, we explain why his arguments support rather than compromise the analysis published in our recent paper. Our thermodynamical description of the early steps of photosynthesis is consistent both with the established theory of quantum electrodynamics and with the known biophysics of the process. Moreover, it ties in with the non-equilibrium thermodynamics of chemical processes.

In a recent paper [2] we discussed non-equilibrium thermodynamic aspects of light absorption. We combined the thermodynamics of electromagnetic radiation as developed by Planck [1], with Hill’s theory [3] of enzymatic reactions and ‘Mosaic non-equilibrium thermodynamics’ (MNET) [4]. Since the latter approaches were successfully applied to biological free energy transduction, it is appealing to push their application towards photosynthesis and other light absorbing processes. We now reply to the comment by Dr D L Andrews [5].

The focus of our paper was on the very first step of photosynthesis, i.e. the absorption of the (Bose) photon, since this is the only point where any doubt was present in the literature. Andrews is correct in pointing at the significance of subsequent steps. But these are not different, in principle, from the rest of biochemistry. If one assigns chemical potential to the ground and excited state of the chlorophyll, chemical free energy does indeed appear at the first step. The issue whether this free energy is indeed chemical is semantic. The subsequent steps can be described with Hill’s theory or MNET.

Andrews’ discussion of time reversal symmetry in quantum field theory is identical to ours. Time reversal of induced emission appears to be missing in the semi-classical approach, if one naively regards photons as a chemical agent in the photosynthetic reaction network. This has caused confusion in the literature, since it would prevent the application of non-equilibrium thermodynamics [3]. We demonstrated, as did Andrews, that the apparent lack of reversibility is resolved in a quantum field approach.

We agree that Fock states are not familiar in biology. For this reason we offered an alternative: the neo-classical approach, which considers photons as classical, molecule-like particles and emulates Bose statistics by an activity function and an infinite series of reactions. This approach is equivalent to the quantum field treatment, and fully reversible, while avoiding any of the quantum field concepts.

We also agree that stimulated emission is not a dominant process under ‘natural’ illumination. Ratio of the stimulated and the spontaneous emission is determined by the number of photons in a given mode, as given by Planck’s distribution:

$$\langle n \rangle = \frac{1}{e^{h\nu/kT} - 1} = 0.05.$$

Here we use the same values as Andrews did ($T_r = 5762$ K, $\nu = 3.5 \times 10^{14}$ Hz, the latter one corresponds to wavelength 860 nm).

The number $\langle n \rangle = 0.05$ says that the difference between Bose and classical statistics is small. Under such conditions one could indeed ignore stimulated emission and replace the photon activity by $\langle n \rangle$. While this would simplify our approach, it would not eliminate the need to calculate the chemical potential of the photon. Moreover, such a theory would be inconsistent with the case of high light intensities. Note that stimulated emission is routinely observed with laser excitation (implying much larger $\langle n \rangle$) of photosynthetic pigment-protein complexes [6].

Andrews’ objection that ‘photon states are not influenced by temperature’ is not justified. The chemical potential of a ‘normal’ molecule depends on temperature not only through its energy. The entropy term $k_B T \ln c$ depends on temperature because this determines the ‘exchange rate’ between energy and entropy. In our description, T is the temperature and T_r is a parameter that describes the state of the photons, i.e. the intensity of the light. We considered the case $T = T_r$, to ascertain that the chemical potential of the photon is zero at thermodynamic equilibrium. Note that the effective radiation temperature may be much less than the surface temperature of the Sun and $T_r = T$ is approached with decreasing illumination. Loss of photosynthesis in approaching this equilibrium is a very relevant biological issue.

Motivated by the progress in molecular understanding, we tend to regard photosynthetic processes at the microscopic, rather than the ensemble, level. This is valid of course, but has to be complemented with the thermodynamic picture. Without the latter it would not be clear why a photon delivers the free energy

$$\mu_\gamma = h\nu \left(1 - \frac{T}{T_r} \right)$$

instead of the energy $h\nu$. The difference has a profound effect on bioenergetics.

We have demonstrated that non-equilibrium thermodynamics can be applied to light absorption. It would be worthwhile to study a more detailed application to photosynthesis and other light absorbing processes. Certainly, exciton channelling to the reaction centre is a good example of how entropy decrease is compensated by energy [7]. Checking the validity in the very first steps [8, 9] and describing how thermodynamics emerges from decoherence should be beautiful physics. Parts of it exist already in terms of density matrices and memory functions [10, 11]. At least for the case of bacteriorhodopsin the theory has helped [4].

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