

Non-equilibrium thermodynamics of light absorption

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1999 J. Phys. A: Math. Gen. 32 301

(<http://iopscience.iop.org/0305-4470/32/2/006>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.105

The article was downloaded on 02/06/2010 at 07:31

Please note that [terms and conditions apply](#).

Non-equilibrium thermodynamics of light absorption

Géza Meszéna^{†§} and Hans V Westerhoff^{‡||}

[†] Department of Biological Physics, Eötvös University, Budapest, Pázmány Péter sétány 1A, H-1117 Hungary

[‡] EC Slater Institute, University of Amsterdam and Faculty of Biology, Free University Amsterdam, De Boelelaan 1087, H208, NL-1081 HV Amsterdam, The Netherlands

Received 9 March 1998, in final form 20 August 1998

Abstract. Free-energy transduction, the basic physical process underlying the phenomena of life has been described by non-equilibrium thermodynamics. However, the possibility of a thermodynamic description of the very first step, the conversion of solar energy to the free energy of the living material, has been questioned on the basis of an apparent lack of microscopic reversibility of light absorption/emission. We develop a description of light absorption that is consistent with non-equilibrium thermodynamics.

Two complementary, but equivalent ways are presented to overcome the problem with microscopic reversibility. The first one has its roots in quantum electrodynamics (which is a time-reversal invariant theory per se) but interfaces with chemical thermodynamics in a non-trivial way. The other one regards light as a classical, but non-ideal gas of photons. An activity function for this non-ideal gas is postulated to account for the Planck distribution and an infinite number of absorption/emission processes (all of which are reversible) to account for the observed kinetics.

Both approaches allow us to include the first step of photosynthesis in the canonical description of biochemical processes. The nonlinear, flow-force relationship of the process is discussed.

1. Introduction

Life is a phenomenon of non-equilibrium thermodynamics: spontaneously produced entropy is washed out of the living system by an energy flow through it [1, 2]. Schrödinger's 'negentropy', which is responsible for the non-equilibrium state of the world is created by the 'Big Bang': different constituents of the Universe cool and relax differently during the expansion [3]. Slowness of processes mediated by weak interaction preserved negentropy until today in the form of the non-equilibrium nuclear composition of the stars [4]. Some of this negentropy is delivered to Earth by sunshine and stored by photosynthetic organisms as the free-energy content of organic compounds. (Most of life is isothermal and isobaric, so free energy is the proper measure of the non-equilibrium state.) The stored free energy is utilized through biochemical processes of the different organisms [5]. Our topic is the step mediating between the inorganic and organic negentropy: photosynthetic free-energy conversion.

Biochemical transduction of free energy is well understood. Chemical thermodynamics is based on the general concepts of non-equilibrium thermodynamics [6]. Linear approximation of the flow-force relationship does not hold for chemical reactions, because reaction rates tend to be proportional to concentrations rather than to thermodynamic forces. (It is of theoretical interest that nonlinear, flow-force relationships can be derived from the assumption of linear

§ E-mail address: Geza.Meszena@elte.hu

|| E-mail address: hw@bio.vu.nl

diffusion along some internal coordinates [6]. Using these internal coordinates is, however, neither easy nor necessary in practice.) Flow-force relations are even more complicated in biochemistry because of the saturation kinetics of enzymatic reactions. A general theory of such kinetics was developed by Hill [7]. Mosaic non-equilibrium thermodynamics [5] represents a further development of the biochemical application of non-equilibrium thermodynamics. The key point is that flow-force relations are regarded as determined by the details of the protein-mediated biochemical processes rather than something ‘phenomenological’.

A major uncertainty remains, however, with respect to photosynthesis. One of the key points of chemical thermodynamics is the principle of detailed balance: all reaction rates are zero in equilibrium. This principle is stronger than the equilibrium condition itself and deeply related to microscopic reversibility and Onsager’s reciprocity [8]. But Einstein’s kinetics of light absorption/emission does not obey microscopic reversibility as no time reversal of induced emission exists. By this reason, Hill [7] questioned the very possibility of describing photosynthesis by non-equilibrium thermodynamics. This is a principal question of biological thermodynamics even if induced emission is often negligible in practice. The aim of this paper is to remove this obstacle.

We develop two complementary, but equivalent ways of describing photon absorption/emission as a chemical reaction. Starting from first principles (that is from quantum electrodynamics) we have to deal with reactions between the chlorophyll molecule and the electromagnetic field. The other approach, which we call ‘neo-classical’, is nearer to chemical intuition. It retains the notion of individual photons chemically reacting with the absorbing molecule and simulates the Bose statistics by an activity function. Both of these approaches are in accordance with the principle of microscopic reversibility. Light reactions can be incorporated into non-equilibrium chemical thermodynamics both ways.

2. Light absorption as a chemical process

2.1. Einstein kinetics

We are interested in the very first step of photosynthesis when a photon is absorbed by a chlorophyll molecule. With chemical notation it is



where γ denotes the photon, Chl and Chl* stand for the ground and excited states of the chlorophyll molecule, respectively.

The well established kinetics of the light absorption/emission reads as [9]:

$$\begin{aligned} v_+ &= B[\gamma][\text{Chl}] \\ v_- &= (A + B[\gamma])[\text{Chl}^*] \end{aligned} \quad (2)$$

where v_{\pm} denotes the number of absorbed/emitted photons per unit time and per unit volume. Square brackets denote concentration. The (frequency-dependent) constants A and B obey the relation

$$\frac{A}{B} = \frac{8\pi\nu^2}{c^3} \quad (3)$$

where ν is the frequency and c is the velocity of light. The first and the second term in v_- represent the spontaneous and the induced emission process, respectively. Observe, that $[\text{Chl}^*]/[\text{Chl}] \rightarrow 1$ for $[\gamma] \rightarrow \infty$, while (1) taken literally as a normal (reversible) chemical reaction would predict $[\text{Chl}^*]/[\text{Chl}] \rightarrow \infty$.

The usual procedure of enclosing the electromagnetic (EM) field into a large cavity of volume V will be employed. The state density of the electromagnetic radiation in this cavity is

$$Vg(\nu) = \frac{8\pi\nu^2}{c^3}V \tag{4}$$

that is, $g(\nu) = \frac{A}{B}$ is the state density for unit volume. It is convenient to use the number of photons n in a given mode (that is with a given frequency and spin state) instead of the ‘volume/frequency interval’ photon concentration or the ‘solid angle/frequency interval’ light intensity I . The relation between these quantities is

$$\frac{4\pi}{c}I = [\gamma] = g(\nu)\langle n \rangle \tag{5}$$

where $\langle \rangle$ denotes expectation. (Note, that the number of modes in a small interval of the frequency is proportional to the volume; the density of photons is independent of that volume. One cannot ask for the density of photons in a very specific mode.) The absorption/emission rate can be rewritten as

$$\begin{aligned} v_+ &= Bg(\nu)\langle n \rangle[\text{Chl}] \\ v_- &= Bg(\nu)(\langle n \rangle + 1)[\text{Chl}^*]. \end{aligned} \tag{6}$$

In this notation, the Planck distribution of radiation in equilibrium with a black body of temperature T_r reads:

$$\langle n \rangle = \frac{1}{\exp(h\nu/k_B T_r) - 1} \tag{7}$$

where k_B is the Boltzmann constant. (For non-black body radiation this equation can be used to define the ‘temperature’ T_r of that radiation for each frequency.)

2.2. Quantum field theoretical description

According to quantum electrodynamics [10] light absorption/emission is a process in which transition between the ground and the excited chlorophyll states is coupled to the transition between the two adjacent Fock states of a mode of the EM field (figure 1):

$$|\text{Chl}, n + 1\rangle \rightleftharpoons |\text{Chl}^*, n\rangle \tag{8}$$

where $n, n + 1$ stand for the particle number of the considered mode of the field in the given state. Transition (8) is reversible. We will regard reaction (8) as a chemical reaction between the states of the EM field and the chlorophyll molecule:

$$|n + 1\rangle + \text{Chl} \rightleftharpoons |n\rangle + \text{Chl}^*. \tag{9}$$

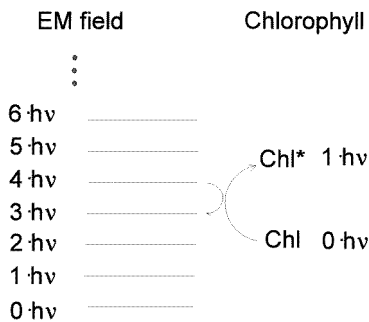


Figure 1. Emission and absorption: interaction of a molecule with the Fock space of a mode of the EM field.

The transition matrix element between these states is

$$\begin{aligned} V_{\text{Chl},n+1;\text{Chl}^*,n} &= \langle \text{Chl}, n+1 | -\frac{q}{m} \mathbf{p} \mathbf{A} | \text{Chl}^*, n \rangle \\ &\sim \langle n+1 | \hat{a}^+ | n \rangle e \langle \text{Chl} | \mathbf{p} | \text{Chl}^* \rangle \end{aligned} \quad (10)$$

where q and m are the charge and the mass of the electron, \mathbf{p} is the operator of the (electron) momentum, \mathbf{A} is the operator of the vector potential of the EM field [10]. \hat{a}^+ is the photon creation operator and e is the polarization vector of the mode of interest. By the relation $\langle n+1 | \hat{a}^+ | n \rangle = \sqrt{n+1}$ one can get

$$V_{\text{Chl},n+1;\text{Chl}^*,n} = \alpha \sqrt{n+1} \quad (11)$$

where α contains the electron wavefunctions but does not depend on light intensity (the photon number).

According to Fermi's golden rule the transition rate of reaction (8) in either direction is

$$w = \frac{2\pi}{\hbar} g(\nu) |V_{\text{Chl},n+1;\text{Chl}^*,n}|^2 = \frac{2\pi}{\hbar} g(\nu) |\alpha|^2 (n+1). \quad (12)$$

(Note, that w measures the combined transition rate to/from any of the mode of the EM field within the natural line-width of the transition rather than the transition to/from a very specific mode.) The equality of the forward and backward rate constants is a consequence of the time-reversal symmetry of quantum electrodynamics represented by the relation

$$V_{\text{Chl},n+1;\text{Chl}^*,n} = V_{\text{Chl}^*,n;\text{Chl},n+1}^* \quad (13)$$

The rate constant (in either direction) is proportional to the number of photons present in the *more excited* state of the EM field. That is, in the case of absorption the rate is proportional to the number of photons *before* the transition, but in the case of emission it is proportional to the number of photons *after* the transition. Expressing the rate constants in terms of the photon number *before* the transition leads to kinetics that break time-reversal symmetry [11]. Absorption/emission kinetics (6) is reproduced (with $B = 2\pi|\alpha|^2/\hbar$) by summing up for the different Fock states. In quantum electrodynamics the description of spontaneous and stimulated emissions are not distinguished. A combined emission process is the reversal of the absorption process.

For thermal radiation characterized by the radiation temperature T_r one has to deal with a mixture of different Fock states. The probability, that the number of photons in the mode of interest equals n , is

$$p_n = \frac{1}{Z} \exp\left(-n \frac{h\nu}{k_B T_r}\right) \quad (14)$$

where

$$Z = \sum_{n=0}^{\infty} \exp\left(-n \frac{h\nu}{k_B T_r}\right) = \frac{1}{1 - \exp(-h\nu/k_B T_r)} \quad (15)$$

is the partition function. These probabilities play the role of concentration for the Fock states.

The chemical potential of the state characterized by photon number n is

$$\begin{aligned} \mu_n^{\text{EM}} &= nh\nu + k_B T \ln p_n \\ &= nh\nu \left(1 - \frac{T}{T_r}\right) + k_B T \ln \left[1 - \exp\left(-\frac{h\nu}{k_B T_r}\right)\right] \end{aligned} \quad (16)$$

where T stands for the temperature of the living system. (In this paper chemical potential is calculated 'per molecule' rather than 'per mol'.) We will characterize the out-of-equilibrium state of the EM field (with respect to the system with temperature T) with this chemical

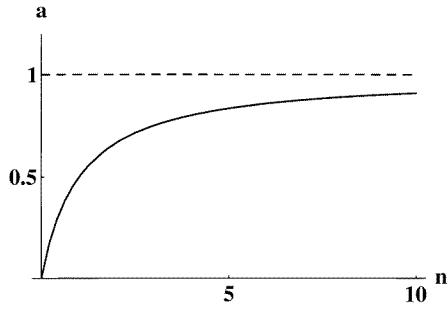


Figure 2. The photon activity.

potential rather than with T_r . For thermal equilibrium ($T_r = T$) μ_n^{EM} becomes independent of n .

The difference between the chemical potential of the adjacent states is

$$\mu_\gamma = \mu_{n+1}^{\text{EM}} - \mu_n^{\text{EM}} = h\nu \left(1 - \frac{T}{T_r}\right). \quad (17)$$

This has been recognized as the chemical potential of the photon [5, 12]. It is the free energy delivered to the chlorophyll molecule by absorbing a photon. It is nothing else, than the energy of the photon multiplied by the Carnot efficiency which is expected from the picture of the two heat baths. It is zero in thermal equilibrium $T = T_r$.

2.3. Neo-classical approach

Here we consider a description, which regards photons as ‘normal’ particles of a classical, but non-ideal gas (cf [5]). The non-ideal nature of the photon gas is supposed to account for the difference between the Bose and the Boltzmann distribution. Non-ideality is described by the activity a .

Postulate 1. *The activity of the photon gas is*

$$a = \frac{\langle n \rangle}{\langle n \rangle + 1} = \frac{[\gamma]}{[\gamma] + g(\nu)}. \quad (18)$$

Note, that $a \approx \langle n \rangle$ for low photon concentrations ($\langle n \rangle \ll 1$) and the activity remains finite for $\langle n \rangle \rightarrow \infty$ (figure 2).

The chemical potential of this gas as a function of the frequency reads:

$$\mu_\gamma(\nu) = h\nu + k_B T \ln a(\nu). \quad (19)$$

In equilibrium ($T = T_r$) the condition $\mu_\gamma(\nu) = 0$ (corresponding to the lack of a conservation law for the radiation) leads to the activity-distribution

$$a(\nu) = \exp\left(-\frac{h\nu}{k_B T_r}\right). \quad (20)$$

The photon concentration follows a different frequency dependence. From equations (18)–(20) one obtains:

$$[\gamma] = \frac{g(\nu) \cdot a(\nu)}{1 - a(\nu)} = \frac{g(\nu)}{\exp[(h\nu - \mu_\gamma)/k_B T] - 1} \quad (21)$$

which reproduces the Planck distribution (7). In the case of out of equilibrium, when $T_r \neq T$, the chemical potential of the photons can be calculated substituting (20) into (19):

$$\mu_\gamma(\nu) = h\nu + k_B T \ln \exp\left(-\frac{h\nu}{k_B T_r}\right) = h\nu \left(1 - \frac{T}{T_r}\right) \quad (22)$$

in agreement with (17).

Our activity function reproduces the equilibrium thermodynamics of the photon gas. Now we have to make an assumption about the kinetic behaviour of the system.

Postulate 2. *There is an infinite series of the emission/absorption processes*



The postulated reactions are reversible microscopically and have the same rate constant in either direction: k .

The absorption and emission rates derive from summing up all the processes:

$$v_+ = \sum_{l=1}^{\infty} ka^l [\text{Chl}] = \frac{ka}{1-a} [\text{Chl}] = kn [\text{Chl}] \quad (24)$$

$$v_- = \sum_{l=1}^{\infty} ka^{l-1} [\text{Chl}^*] = \frac{k}{1-a} [\text{Chl}^*] = k(n+1) [\text{Chl}^*].$$

With the identification $k = Bg(\nu)$ the kinetics (6) has been reproduced.

3. Onsager reciprocity and flow-force relationships

Let us first recapitulate the non-equilibrium thermodynamics of an ordinary chemical reaction [5]. One of the possible choices for the extensive variables is the concentrations c_i . (Depending on the reaction network, these variables are not necessarily independent.) Entropy production reads as

$$\sigma = \frac{1}{T} \sum_i J_i \mu_i \quad (25)$$

where

$$J_i = \frac{dc_i}{dt} \quad (26)$$

are the chemical flows and μ_i s are the chemical potentials. Onsager's reciprocal relationships state that

$$\left(\frac{\partial J_i}{\partial \mu_j} \right)_{\text{eq}} = \left(\frac{\partial J_j}{\partial \mu_i} \right)_{\text{eq}} \quad (27)$$

where the subscripts denote thermodynamic equilibrium. Note that this relationship remains valid even if the extensives we use are not independent (theorem 1 of chapter 6 in [6]). Consider a specific chemical reaction, for instance



If this is the only reaction operating, the chemical flows defined above are not independent:

$$-J_A = -J_B = J_C = J \quad (29)$$

where J is the chemical flow of this specific reaction. Onsager reciprocity (27) for this reaction reads as

$$\left(\frac{\partial J}{\partial \mu_A} \right)_{\text{eq}} = \left(\frac{\partial J}{\partial \mu_B} \right)_{\text{eq}} = - \left(\frac{\partial J}{\partial \mu_C} \right)_{\text{eq}}. \quad (30)$$

Dependences $\frac{\partial J}{\partial \mu_i}$ are not affected by the presence of other reactions, so (30) remains valid even if this reaction is a part of a reaction network.

Onsager reciprocity is related to the principle of detailed balance. Detailed balance requires $J = 0$ in equilibrium, when $X = \mu_A + \mu_B + \mu_C = 0$. This, in turn, implies (30). Detailed balance is stronger than the (phenomenological) equilibrium condition $J_i = 0$ if more than one reaction is present. Onsager reciprocity/detailed balance is a consequence of the time-reversal symmetry of the underlying molecular processes [8]. The main point is that, according to (30), the flow is determined through the combination $X = \mu_A + \mu_B + \mu_C = 0$ (the thermodynamic force) near to equilibrium.

For ideal solutions and ordinary reaction the forward and backward rates of the reaction (28) are

$$\begin{aligned} v_1 &= k_1[A][B] \\ v_{-1} &= k_{-1}[C] \end{aligned} \quad (31)$$

while the chemical potentials are

$$\mu_i = \mu_i^0 + k_B T \ln[i] \quad (i = A, B, C). \quad (32)$$

This type of kinetics is referred to as canonical. Kinetics is non-canonical in many cases: saturation effect of the protein has to be taken into account in an enzyme reaction, for instance [5].

Using the detailed balance condition

$$\frac{k_1}{k_{-1}} = \exp\left(\frac{\mu_A^0 + \mu_B^0 - \mu_C^0}{k_B T}\right) \quad (33)$$

(31) can be written in the form

$$\begin{aligned} v_1 &= k \exp\left(\frac{\mu_A + \mu_B}{k_B T}\right) \\ v_{-1} &= k \exp\left(\frac{\mu_C}{k_B T}\right) \end{aligned} \quad (34)$$

where

$$k = k_1 \exp\left(-\frac{\mu_A^0 + \mu_B^0}{k_B T}\right) = k_{-1} \exp\left(-\frac{\mu_C^0}{k_B T}\right). \quad (35)$$

The $J = v_1 - v_{-1}$ chemical current can be expressed as the function of the $X = \mu_A + \mu_B - \mu_C$ chemical force [5]:

$$J = k_1[A][B] \left[1 - \exp\left(-\frac{X}{k_B T}\right)\right] = k_{-1}[C] \left[\exp\left(\frac{X}{k_B T}\right) - 1\right]. \quad (36)$$

Near the equilibrium this flow-force relation becomes proportional. The linearity condition $X \ll k_B T$ is rarely valid, however. One can demonstrate easily that (30) is satisfied. For enzyme-catalyzed reactions, the rate constant k becomes proportional to the free enzyme concentration, which, in turn, depends on the reactant concentrations (the enzyme saturation). This leads to a flow-force relationship more complicated than (36) but keeps the $[\exp(\frac{X}{k_B T}) - 1]$ dependence and adherence to detailed balance [7]. (Enzymes cannot break time-reversal symmetry, so they have to catalyze the back reaction just as well as the forward one.)

We shall now derive the analogous flow-force relation for light absorption/emission. The chemical potential of the ground and the excited state chlorophyll reads as follows:

$$\begin{aligned} \mu &= \mu_0 + k_B T \ln[\text{Chl}] \\ \mu^* &= \mu_0^* + k_B T \ln[\text{Chl}^*]. \end{aligned} \quad (37)$$

The difference in the concentration-independent part of the chemical potentials equals the excitation energy:

$$\mu_0^* - \mu_0 = h\nu. \quad (38)$$

The net rate of absorption reads (from equation (6)):

$$\begin{aligned}
 J &= v_+ - v_- = Bg(\nu)\{\langle n \rangle[\text{Chl}] - (\langle n \rangle + 1)[\text{Chl}^*]\} \\
 &= Bg(\nu)\langle n \rangle[\text{Chl}] \left(1 - \frac{[\text{Chl}^*]}{[\text{Chl}]} \cdot \frac{\langle n \rangle + 1}{\langle n \rangle} \right) \\
 &= B[\gamma][\text{Chl}] \left[1 - \exp\left(\frac{\mu^* - \mu - h\nu}{k_B T}\right) \exp\left(\frac{h\nu}{k_B T_r}\right) \right] \\
 &= B[\gamma][\text{Chl}] \left[1 - \exp\left(-\frac{X}{k_B T}\right) \right] \tag{39}
 \end{aligned}$$

where the thermodynamic force is

$$X = \mu + \mu_\gamma - \mu^*. \tag{40}$$

This flow-force relation is analogous to the one derived above for normal chemical kinetics.

(39) implies that photon absorption/emission obeys the Onsager reciprocity

$$\left(\frac{\partial J}{\partial \mu}\right)_{\text{eq}} = \left(\frac{\partial J}{\partial \mu_\gamma}\right)_{\text{eq}} = -\left(\frac{\partial J}{\partial \mu^*}\right)_{\text{eq}} \tag{41}$$

which is a consequence of the underlying time-reversal symmetry. We note that for the Onsager reciprocity to obtain, only chemical equilibrium is required, given by $\mu + \mu_\gamma = \mu^*$. It is not required that the photons are in thermal equilibrium ($\mu_\nu = 0$; $T = T_r$) with the system.

4. Discussion

4.1. The picture we obtained

The aim of this paper was to examine if photosynthesis can be described just like any other free-energy transduction process in biochemistry, or whether it requires a separate formalism. The equilibrium thermodynamics of light is well-known[12]. However, non-equilibrium thermodynamics of light absorption and emission is needed to incorporate photosynthesis into the non-equilibrium thermodynamic description of enzymatic processes. Non-equilibrium thermodynamics has been shown to be consistent with chemical [6, 8, 13] and biochemical kinetics [5, 7]. However, with respect to the standard kinetic description of photochemistry, an apparent inconsistency with microscopic reversibility of non-equilibrium thermodynamics has been noted [5, 7]. This paper has removed this inconsistency.

As a consequence, light can now be viewed as a substrate of the photosynthetic reaction centre. The flow-force relation for a simple absorption-emission process was derived. Calculating the analogous relation for an enzymatic process, that is, taking into consideration enzyme saturation, is straightforward. As the general concepts of chemical thermodynamics apply to this step, the very first step of biochemistry can be included, as a mosaic, into the mosaic non-equilibrium thermodynamics picture.

4.2. Comparison of the two approaches

Of course, light remains a very special substrate, in that it follows Bose–Einstein statistics, while the classical, Boltzmann statistics is an excellent approximation for the normal substrates. The apparent lack of microscopic reversibility is a consequence of the improper mixing of classical and quantum concepts. The problem does not exist in the QED description. In this theory, the quantum field rather than the photons are the subject of description. If one wishes to keep the structure of this theory, Fock states have to be regarded as the chemical agents. The probabilities of the different Fock states play the role of the concentrations.

In the quantum field theory, the spontaneous *and* the induced emission *together* have the true time reversal of the absorption: when searching for the microscopic reversal of each process, the former two processes should be considered as a single process. Note, that spontaneous emission is ignored in the quantum mechanical treatment, which is valid for $\langle n \rangle \gg 1$. (In that limit the difference between n and $n + 1$ becomes irrelevant.) Quantum mechanics is a time-reversible theory in its own right, so it gives the same rate constant for absorption and for (induced) emission, which are the exact time reversals of each other in this limit.

We also developed another option here, which is more in line with the chemical way of thinking because it keeps the notion of individual photons. ([5] contains an earlier version of this idea.) A special form of activity to account for Bose statistics and an infinite series of emission and absorption processes to reproduce the linear intensity dependence were postulated. It takes both spontaneous and induced emission into account explicitly and postulates stimulated absorption as the microscopic reversal of stimulated emission ($l = 2$ in (23)). Higher-order stimulated absorption and emission are postulated in pairs similar to the quantum mechanical symmetry mentioned above. Needless to say, these reactions must not be seen as independently observable elements of physical reality.

The origin of the activity function (18) of this ‘neo-classical’ approach can be understood on the basis of the factors $|\langle n + 1 | \hat{a}^+ | n \rangle|^2 = n + 1$ of quantum electrodynamics. Consider two Fock states of a Bose gas with particle numbers n_1 and n_2 and energies E_1 and E_2 . Interaction with the environment of temperature T causes transitions between these states with rates

$$\begin{aligned} w_{1 \rightarrow 2} &= n_1 k_{1 \rightarrow 2} (n_2 + 1) \\ w_{2 \rightarrow 1} &= n_2 k_{2 \rightarrow 1} (n_1 + 1) \end{aligned} \quad (42)$$

where

$$\frac{k_{1 \rightarrow 2}}{k_{2 \rightarrow 1}} = \exp\left(\frac{E_1 - E_2}{k_B T}\right). \quad (43)$$

The condition of detailed equilibrium $w_{1 \rightarrow 2} = w_{2 \rightarrow 1}$ leads to the relation

$$\frac{n_1 / (n_1 + 1)}{n_2 / (n_2 + 1)} = \frac{k_{2 \rightarrow 1}}{k_{1 \rightarrow 2}} = \exp\left(-\frac{E_1 - E_2}{k_B T}\right). \quad (44)$$

This equation makes it clear, that the combination $a_i = n_i / (n_i + 1)$ plays the same role in Bose statistics as the particle number n_i does in Boltzmann statistics. Consequently, using the activity a_i instead of n_i , one can mimic Bose–Einstein statistics. The fact that this activity function levels off at high particle numbers corresponds to Bose condensation at low temperatures.

This connection establishes the equivalence of the two approaches. As the quantum electrodynamics treatment (section 2.2) is rooted in the first principles of physics, the validity of the neo-classical description (section 2.3) is also established. We have two ways to write the light absorption/emission process into a form of reversible chemical reaction. The overall flow-force relationship (section 3) is already independent of this choice as it depends on the observable kinetics only.

4.3. Photon chemical potential

Recognizing the situation $\mu + \mu_\gamma = \mu^*$ as chemical equilibrium was important to establish light reactions as chemical processes obeying Onsager reciprocity. That is, the non-zero photon chemical potential μ_γ is an essential element of the picture. It is the difference between chemical potentials of the adjacent Fock states in the quantum electrodynamics description

while it is the real chemical potential of the photons in the neo-classical one. In any way, it measures the maximal free energy the system can gain during absorption of a single photon.

The photon chemical potential (17) is proportional to the frequency ν for radiation characterized by a radiation temperature T_r . It must be so [5] because of the possibility of the reaction

$$\gamma_A \rightleftharpoons \gamma_B + \gamma_C \quad (45)$$

if

$$\nu_A = \nu_B + \nu_C. \quad (46)$$

(Some matter is needed to catalyze this reaction.) That is, (17) represents an internal chemical equilibrium in the radiation even if it is out of equilibrium with the system of temperature T .

The photon chemical potential has also been introduced by Würfel [16] in an equilibrium thermodynamics context. He described non-thermal radiation by the temperature of the emitting body and a non-zero chemical potential. His definition for the photon chemical potential was equivalent to ours except that we used the temperature of the absorbing (living) material as the reference temperature. The role of Carnot efficiency in radiant energy conversion was already stressed by Mortimer and Mazo [17] and Ross [18].

The photon chemical potential is of great biological interest. A photon that is used for photosynthesis e.g. 700 nm wavelength carries an energy 1.7 eV. Its chemical potential is, however, only 1.25 eV [14, 21, 23]. (Here the effective radiation temperature in an algae suspension is used.) Splitting a water molecule (the most important step of photosynthesis) at pH 6 requires 1.3 eV for each of the four electrons involved. Consequently, although the *energy* of a single photon would suffice, the fact that the photon delivers free energy, rather than energy, makes water splitting by a single photon impossible [14, 23]. This fact had a profound effect: a complicated system, the photosynthetic electron transport chain (that is life) was needed to develop oxygen atmosphere [24, 25].

Note that there are other factors beyond Carnot efficiency which reduce the amount of free energy that can be gained from light absorption. The physiological requirement of non-zero reaction rates requires $\mu + \mu_\gamma > \mu^*$ decreasing further the energy conversion efficiency ('finite-time thermodynamics' [22]). The maximum efficiency of solar energy conversion is also lower than the Carnot efficiency because a fraction of the absorbed light is radiated back and is inevitably lost [19, 20].

Light absorption can also be regarded as pure heat transfer. In that view absorption of energy $h\nu$ corresponds to the transfer of entropy $h\nu/T_r$ at the radiation temperature. The maximal free energy gained by a system at temperature T during this absorption event is $h\nu(1 - T/T_r)$ [5, 14]. The same free energy transfer was regarded here as chemical work. Despite the fact that we used T_r to parametrize the radiation, here radiation was not regarded as another heat bath. Radiation has instead been regarded as being out of *chemical* equilibrium with the environment. We have the same freedom here as in laser physics where the excited state:ground state ratio is often characterized by a (sometimes negative) temperature value, but we opted to use the opposite choice to be compatible with the chemical description. A more general way would be to use exentropy as the ultimate measure of negentropy [15].

Acknowledgments

We thank Katalin Martinás and Stanislaw Sientiutycz for discussions, the Netherlands organisation for scientific research (NWO) for support, and the European Union for financing a visit of GM to the Netherlands.

References

- [1] Schrödinger E 1944 *What is Life? The Physical Aspects of the Living Cell* (Cambridge: Cambridge University Press)
- [2] Nicolis G and Prigogine I 1977 *Self-Organization in Non-Equilibrium Systems* (New York: Wiley-Interscience)
- [3] Alpher R A and Marx G 1992 The creation of free energy *Vistas Astron.* **35** 179–214
- [4] Marx G 1988 Week universe *Festi-Val-Festschrift for Val Telegdi* ed K Winter (Amsterdam: Elsevier)
- [5] Westerhoff H V and Van Dam K 1987 *Thermodynamics and Control of Biological Free Energy Transduction* (Amsterdam: Elsevier)
- [6] De Groot S R and Mazur P 1962 *Non-Equilibrium Thermodynamics* (Amsterdam: North-Holland)
- [7] Hill T L 1977 *Free Energy Transduction in Biology* (New York: Academic)
- [8] Onsager L 1931 *Phys. Rev.* **37** 405–26
- [9] Einstein A 1917 *Z. Phys.* **18** 121
- [10] Louisell W H 1973 *Quantum Statistical Properties of Radiation* (New York: Wiley)
- [11] Feynman R P, Leighton R B and Sands M L 1964 *Feynman Lectures on Physics* vol III (Reading, MA: Addison-Wesley)
- [12] Planck M 1914 *The Theory of Heat radiation* (Philadelphia, PA: Blakistons)
- [13] Keizer J 1987 *Statistical Thermodynamics of Nonequilibrium Processes* (Berlin: Springer)
- [14] Knox R S 1977 Photosynthetic efficiency and exciton transfer and trapping *Primary Processes of Photosynthesis* ed J Barber (Amsterdam: Elsevier) p 55
- [15] Martínás K and Ayres R 1994 Entropy, physical information and economic values *ISEAD Working Paper* 94/05/EPS
- [16] Würfel P 1982 *J. Phys. C: Solid State Phys.* **15** 3967–85
- [17] Mortimer R G and Mazo R M J. *Chem. Phys.* **35** 1013–17
- [18] Ross R T J. *Chem. Phys.* **45** 1–7
- [19] De Vos A and Pauwels H 1981 *Appl. Phys.* **25** 119–25
- [20] Ries H 1983 *Appl. Phys. B* **32** 153–6
- [21] Duysens L N M 1958 *Brookhaven Symp. Biol.* **11** 10–25
- [22] Sieniutycz S and Shiner J S 1994 Thermodynamics of irreversible processes and its relation to chemical engineering: second law analyses and finite time thermodynamics *J. Non-Equilib. Thermodynam.* **19** 303–48
- [23] Westerhoff H V, Crielaard W and Hellingwerf K J 1997 Global bioenergetics *Bioenergetics* ed P Gräber and G Milazzo (Basel: Birkhauser) pp 57–94
- [24] Sagan C 1994 The search for extraterrestrial life *Sci. Am.* **70**
- [25] Sagan C *et al* 1993 A search for life on earth from the Galileo spacecraft *Nature* **365** 715–21