Generalized formulation of free energy and application to photosynthesis

Hwe Ik Zhang, M.Y. Choi *

Department of Physics and Center for Theoretical Physics, Seoul National University, Seoul 151-747, Republic of Korea

HIGHLIGHTS

- We generalize the free energy for a photon system not at thermal equilibrium.
- The thermodynamic aspects of primary photosynthetic processes are probed.
- The photosynthetic energy conversion is described in terms of the free energy transduction.
- An analytic expression for the photosynthetic efficiency is derived.

ARTICLE INFO

ABSTRACT

The origin of free energy on the earth is solar radiation. However, the amount of free energy it contains has seldom been investigated, because the free energy concept was believed to be inappropriate for a system of photons. Instead, the origin of free energy has been sought in the process of photosynthesis, imposing a limit of conversion given by the Carnot efficiency. Here we present a general formulation, capable of not only assessing accurately the available amount of free energy in the photon gas but also explaining the primary photosynthetic process more succinctly. In this formulation, the problem of "photosynthetic conversion of the *internal energy* of photons into the *free energy* of chlorophyll" is replaced by simple "free energy transduction" between the photons and chlorophyll. An analytic expression for the photosynthetic efficiency is derived and shown to deviate from the Carnot efficiency. Some predictions verifiable possibly by observation are also suggested.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Nonequilibrium phenomena, especially living activities, are in general carried out by the drive of free energy. As change occurs only toward the decrease of free energy, no animate or inanimate activities can be performed without spending free energy. A crucial question then arises: Where does the free energy come from in the first place? This question has yet to be well addressed scientifically.

Common sense dictates the ultimate source of "useful energy" (which really means the free energy) to be solar energy. But the literal meaning of "solar energy" is the *internal energy* of solar radiation. Therefore, depending on the presumption that the system of photons contains *accessible free energy* within itself, either of the following questions may arise: (1) What is the amount of the accessible free energy contained in the photon system? (2) What fraction of the internal energy of the photon system can be converted into free energy of another system (e.g., chlorophyll)?

---

* Corresponding author.
  E-mail addresses: zm530@hanmail.net (H.I. Zhang), mychoi@snu.ac.kr (M.Y. Choi).

While considerable pursuits have been given to the second question, there have been so far few taking the position that the photon system contains available free energy, as posed in the first question. This is related with the view that it is rather infeasible to discuss the free energy of photons without reference to the system with which they interact and in which they are converted into work [1]. In fact the belief that free energy involved in a process may be defined only for the process at equilibrium is still prevalent [2] although there are suggestions for nonequilibrium processes involving information [3,4]. Thus the major motive has been to explain the workings of photosynthesis rather than to assess the source of free energy and existing studies deal with the conversion of the energy, rather than the free energy, of photons. Specifically, it is often accepted that the photosynthetic conversion of the internal energy of photons into the free energy of chlorophyll is described by the Carnot cycle equation [5]. As we will see, however, even the problem of understanding the workings of photosynthesis is not satisfactory without the premise that the photon system itself is interpreted to contain a certain amount of free energy. We will henceforth argue that the free energy could be defined meaningfully for a photon system not in thermal equilibrium and probe, on this basis, the thermodynamic aspects of primary photosynthetic processes.

2. Generalized formulation of free energy

When solar photons, which should have been produced in equilibrium at the solar temperature, arrive on the earth, they should neither remain in equilibrium at the solar temperature nor adjust to the ambient temperature on earth. To study such a nonequilibrium situation, we propose a general formulation of free energy, based on the principle of maximum entropy [6], extended to the principle of maximum caliber [7].

According to the principle, the state of an effectively isolated thermodynamic system in given volume (like the photon system within given volume traveling the interstellar space) is given by the one that maximizes the entropy of the system, $S = -k\sum_i P_i \log P_i$, subject to given constraints, where k is Boltzmann's constant and $\{P_i\}$ ($i = 1, 2, 3, \ldots$) is the probability distribution over the energy eigenstates with eigenvalues $\{E_i\}$. In particular, when the internal energy U is given, the probability distribution, which maximizes the entropy under the constrains $\sum_i P_i = 1$ and $\sum_i P_i E_i = U$, is well known to be the *canonical distribution*: $P_i = Z^{-1}e^{-\beta_c E_i}$ with the partition function $Z \equiv \sum_i e^{-\beta_c E_i}$ and Lagrange's multiplier $\beta_c \equiv (kT_c)^{-1}$. Correspondingly, the maximized entropy reads $S = -k\sum_i P_i \log P_i = U/T_c + k \log Z$, where the *canonical temperature* T_c is determined by the constraint $U = \sum_i P_i E_i = -(\partial/\partial\beta_c) \ln Z$. Notice that *the only condition* imposed on this argument is that the entropy should be maximized for given energy. We will call this condition and the resulting formulation "canonical" to designate this particular property.

On the other hand, this canonical formulation is applicable regardless of whether or not the system is in thermal contact with a reservoir. Even if the reservoir is disconnected, it would remain canonically associated with T_c, because it is the most probable situation. When it comes in contact with another reservoir at temperature T not equal to T_c but the thermal exchange between them is not yet initiated, the "canonical association" between the energy U and entropy S is still maintained. In such a transient situation, which is a hallmark of nonequilibrium, the canonical temperature T_c serves as an internal parameter which simply relates U and S remaining in canonical association.

Equipped with such robustness of the canonical association between U and S, we now define two kinds of free energy relative to temperature T: usual (equilibrium) free energy $F(T)$ and general free energy $\mathcal{F}(T; T_c)$ as

$$F(T) = -kT \log Z = U - TS$$
$$\mathcal{F}(T; T_c) = U_c - TS_c, \tag{1}$$

where U_c and S_c are canonically associated values at canonical temperature T_c, and U and S are equilibrium values at the ambient temperature T. Note that this corresponds to a special case of the nonequilibrium free energy suggested in Refs. [3,4]. Namely, with the probability distribution given by the canonical distribution at temperature T_c, the nonequilibrium free energy in Refs. [3,4] reduces to Eq. (1). In particular, when $T = T_c$, the general free energy reduces to the equilibrium one: $\mathcal{F}(T; T) = F(T)$.

Now suppose that a system having energy U_c and entropy S_c, canonically associated at canonical temperature T_c, is placed (normally in a steady state) at a location with temperature T. This corresponds to the situation that the system becomes in contact with a reservoir at temperature T. Then the system, which may receive heat Q from the reservoir, will do work W until the energy and entropy reduce to the equilibrium values U and S at temperature T. The first law of thermodynamics, i.e., energy conservation requires $Q = W + U - U_c$ while the second law states $S - S_c - Q/T \geq 0$. In consequence we obtain

$$W = Q + U_c - U \leq W_m = \mathcal{F}(T; T_c) - F(T), \tag{2}$$

which states that the maximum possible work W_m performable by the system at temperature T is simply the difference between the (nonequilibrium) *general free energy* and the equilibrium free energy both defined relative to temperature T. This difference can be called the net free energy or the *accessible free energy* of the system.

We now define the thermodynamic *accessibility* of the system at temperature T, which measures the maximum possible work performable per unit internal energy available in the system:

$$\eta \equiv \frac{W_m}{U_c} = \frac{\mathcal{F}(T; T_c)}{U_c} - \frac{F(T)}{U_c}. \tag{3}$$