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Ergodicity, configurational entropy and free energy in pigment solutions and plant photosystems: Influence of excited state lifetime

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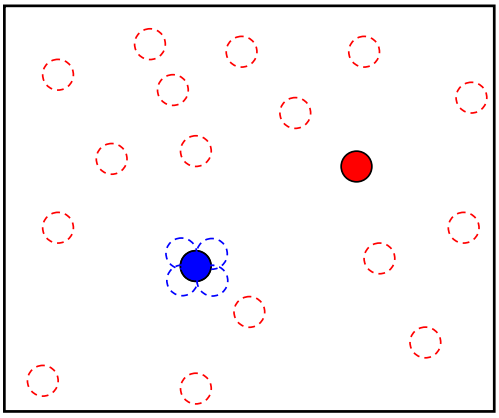
HIGHLIGHTS

- We consider ergodicity and configurational entropy for pigments and for photosystems.
- Pigments display broken ergodicity.
- Photosystem suspensions display both ergodic and broken ergodic behaviour.

GRAPHICAL ABSTRACT



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ABSTRACT

We examine ergodicity and configurational entropy for a dilute pigment solution and for a suspension of plant photosystem particles in which both ground and excited state pigments are present. It is concluded that the pigment solution, due to the extreme brevity of the excited state lifetime, is non-ergodic and the configurational entropy approaches zero. Conversely, due to the rapid energy transfer among pigments, each photosystem is ergodic and the configurational entropy is positive. This decreases the free energy of the single photosystem pigment array by a small amount. On the other hand, the suspension of photosystems is non-ergodic and the configurational entropy approaches zero. The overall configurational entropy which, in principle, includes contributions from both the single excited photosystems and the suspension which contains excited photosystems, also approaches zero. Thus the configurational entropy upon photon absorption by either a pigment solution or a suspension of photosystem particles is approximately zero.

1. Introduction

The aim of this study is to examine the ergodicity and the configurational entropy of: i) a pigment solution in which, upon illumination, some of the pigment molecules absorb a photon and transit to the excited state while the (usually) great majority remain in the unexcited ground state; ii) a suspension of photosynthetic photosystems which, under illumination, will also contain a mixture of particles, some of which will harbour an excited state (and which may therefore perform photochemistry) and many of which will not.

Ergodicity and configurational entropy are thought of as being related characteristics. The most common interpretation of ergodicity is that the time average of a single particle trajectory is equivalent to the

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overall ensemble average. This implies that, given enough time, a system will explore all points in its phase space. It is this latter aspect which connects ergodicity with configurational entropy. In statistical mechanics the configurational entropy (S^{conf}) is related to the distribution, or position, of particles in subsets, or microstates, in phase space. At equilibrium, i.e. when all microstates, or a representative number of them, are accessed, S^{conf} may be given by the Boltzmann entropy

$$S^{conf} = k_B \ln \Omega \tag{1}$$

where k_B is the Boltzmann constant and Ω is the thermodynamic probability of the microcanonical ensemble, and is defined as the number of equally accessible microstate conformations in a given macrostate $\Omega = \Omega(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$, where $\mathbf{x}_i$ are the n-th particle positions in the phase space. This implies that all microstates are isoenergetic, which is usually not the case for photosystems. The microcanonical ensemble, by definition, is unable to exchange energy with its surrounds, i.e. it is an isolated system.

On the other hand the Gibbs entropy (S^G) recognises that microstates may not be equally accessible, due to energy differences, and energy exchange with the environment is allowed

$$S^G = -k_B \sum_{i=1}^{\Omega} p_i \ln p_i, \tag{2}$$

where p_i is the probability of occurrence of the i-th microstate and the sum is extended over all microstates (Ω). This is the expression describing a canonical ensemble at equilibrium and, in general terms, is the most commonly used. It readily represents the plant photosystems in which there is considerable pigment energy disorder (e.g. [1]) and which exchanges energy with its environmental bath.

In the case of a non-equilibrium system which, over time, evolves towards equilibrium, Mauro and co-workers introduced time-dependent Gibbs entropy [2]. To this end a conditional probability $\rho_{i,j}(t)$ is introduced [2–4] as the probability of the system of occupying the j-th microstate starting from the initially prepared i-th microstate. This conditional probability satisfies the following requirements: $\sum_j \rho_{i,j}(t) = 1$; $\lim_{t\to 0} \rho_{i,j}(t) = \delta_{i,j}|^{=1 \text{ for } i=j}_{=0 \text{ for } i\neq j}$; $\lim_{t\to\infty} \rho_{i,j}(t) = P^{eq}_j$, where P^{eq}_j is the probability, at equilibrium, of the j-th state. For a system starting in the i-th microstate, the configurational entropy is

$$S^{conf}_i(t) = -k_B \sum_j \rho_{i,j}(t) \ln \rho_{i,j}(t). \tag{3}$$

In the limit $t \to \infty$, $S^{conf}_i(t)$ approaches the maximum equilibrium value $S^{conf} = -k_B \sum_j P^{eq}_j \ln P^{eq}_j$ whereas, when t tends towards zero, $\lim_{t\to 0} S^{conf}_i(t) = 0$. In other words, in the long time limit all microstates "j" are accessed, equilibrium is attained and S^{conf}_i is maximal. The system is ergodic. On the other hand, in the short time limit S^{conf}_i will tend towards zero, which may be imagined in terms of a single configurational microstate. In this limit the system is non-ergodic due to the short time not allowing the system to explore the entire phase space, or a representative part of it. We have considered a system prepared in the i-th microstate. The same conclusions are reached also considering the total configurational entropy evaluated in terms of all the possible initially prepared microstates of the system, weighted by their probability of occurrence. There is a rich and extensive literature on these points in relation to the liquid/glass transition (e.g. [2–9]).

2. Discussion

We shall now address the pigment systems of interest, i.e. both a dilute pigment solution and a suspension of plant photosystems.

2.1. A dilute solvated pigment solution

We now apply the general aspects mentioned above to a dilute pigment solution illuminated by a series of short (picosecond) flashes that excite a subset of the total pigments. For the pigment solution we can imagine a cubic lattice whose cells are the size of the average solvent volume per pigment molecule (V_{mol}). In the case of excited state pigments intermingled with ground state pigments, and when the particle distribution is statistically spread over the equally accessible states (relaxed system), the root mean square displacement of molecular motion, r, during the excited state lifetime is $r \ll \sqrt{3} V_{mol}^{\frac{1}{3}}$, when compared to the greatest distance inside the cube. V_{mol} is a function of the pigment concentration. We therefore compare r and $V_{mol}^{\frac{1}{3}}$ for dilute solutions of several pigments of biological importance, where the root mean square displacement is given by the Einstein expression for three dimensional diffusion

$$r = (6Dt)^{\frac{1}{2}}, \tag{4}$$

where D is the diffusion coefficient and t is the diffusion time considered.

We do not know the exact values of D for solvated pigments, however these values are known for the most commonly employed solvents. As these solvents have a lower molecular mass with respect to the pigments themselves, it is reasonable to assume that $D_{solvent} > D_{pigment}$. For these estimates we, therefore, use the solvent values, noting that they are expected to be an overestimate of the pigment values. For the organic solvents normally used to dissolve pigments $D \approx 1 \times 10^{-9}$ m^2 s^{-1}. The time (t) of interest is the excited state lifetime (τ) of the particular pigment. For dissolved chlorophyll this is about 5 ns, while for carotenoids it is around 10 ps. In this way one estimates $r < 5.5$ nm for chlorophyll and $r < 0.24$ nm for carotenoids. In the case of 2τ, $r < 7.7$ nm for chlorophyll and $r < 0.34$ nm for carotenoids.

In order to achieve an initially random distribution of excited state pigments intermingled with ground state pigments it is necessary to consider an optically thin sample ($OD \leq 0.01$). On the basis of the molarity corresponding to this optical density for chlorophyll and carotenoids one estimates $V_{mol}^{\frac{1}{3}} \geq 200$ nm for chlorophylls and ≥ 400 nm for carotenoids. This means that the time to travel these distances is $t > 7 \cdot 10^{-6}$ s for chlorophyll and $t > 27 \cdot 10^{-6}$ s for carotenoids, three and six order of magnitude longer than the respective lifetime. The extreme brevity of the excited state lifetime of chlorophyll and carotenoids implies that $S^{conf}_i(t)$ (Eq. (3)) remains close to the short time limit and, thus, tends towards zero. In other words, due to the brevity of the excited state lifetime, the system is unable to relax, in the sense that it is unable to access a representative part of the entire configurational phase space. Due to the brevity of the particle excited state lifetime, the particle solution does not possess the configurational degrees of freedom characteristic of long lived states. Thus the pigment solution under consideration is a non-ergodic system. These points have not been previously recognised as far as we are aware.

During personal discussions the comment has been made that "even though the lifetime brevity does not allow access to a representative part of the phase space, all microstates are potentially present". We consider this comment erroneous as, due to the short lifetime of the excited states, one might say that the pigments are "unaware" of other, potentially accessible, microstates. We underline that this comment is in agreement with the principle of causality, as pointed out by Kivelson and Reiss [7]. To state the opposite would violate the principle of causality. The short lifetime sets restrictions that prevent the system to be found in any of its potentially accessible states.

Another observation which is sometimes made is that "there is no need for pigment diffusion to occur in order to access all microstates as, under continuous illumination, the pigments are randomly excited and all microstates will therefore be automatically occupied". As the pigment solution is non-ergodic, as discussed above, this line of thought is