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Beer-Lambert law along non-linear mean light pathways for the rational analysis of Photoplethysmography

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Abstract. Photoplethysmography (PPG) is a technique that uses light to noninvasively obtain a volumetric measurement of an organ with each cardiac cycle. A PPG-based system emits monochromatic light through the skin and measures the fraction of the light power which is transmitted through a vascular tissue and detected by a photodetector. Part of thereby transmitted light power is modulated by the vascular tissue volume changes due to the blood circulation induced by the heart beating. This modulated light power plotted against time is called the PPG signal. Pulse Oximetry is an empirical technique which allows the arterial blood oxygen saturation (SpO\textsubscript{2} – molar fraction) evaluation from the PPG signals. There have been many reports in the literature suggesting that other arterial blood chemical components molar fractions and concentrations can be evaluated from the PPG signals. Most attempts to perform such evaluation on empirical bases have failed, especially for components concentrations. This paper introduces a non-empirical physical model which can be used to analytically investigate the phenomena of PPG signal. Such investigation would result in simplified engineering models, which can be used to design validating experiments and new types of spectroscopic devices with the potential to assess venous and arterial blood chemical composition in both molar fractions and concentrations non-invasively.

1. Introduction
Photoplethysmography is a non-invasive electro-optical technique widely used in the study and monitoring of the pulsations associated with changes in blood volume in a peripheral vascular bed [1-2]. Photoplethysmography is based on the absorption properties of vascular tissue when it is transilluminated by light. The emitted light, which is made to traverse the skin, is reflected, absorbed and scattered in the tissues and blood. The modulated light which emerges is measured using a suitable photodetector. The intensity of the light which reaches the photodetector is measured and the variations in the photodetector current are assumed to be related to blood volume changes underneath the probe [3]. These variations are amplified and recorded as a voltage signal called the photoplethysmograph (PPG). Photoplethysmography is used in the estimation of arterial oxygen saturation (SpO\textsubscript{2}) by Pulse Oximetry. Pulse Oximeters estimate arterial oxygen saturation non-invasively by shining light at two different wavelengths, red and near infrared, through vascular tissue.

Due to the fact that all commercial pulse oximetry systems are empirically calibrated it is accepted as an empirical technology by most clinicians and engineers. On the other hand a logical explanation of pulse oximetry is available. This explanation is phenomenological and based on the Beer-Lambert law [4]. Lack of the rational ground in such an explanation prevents its application in the analysis of other blood properties apart from SpO\textsubscript{2}.
The aim of this paper is to fill the gap between the rational light-tissue interaction theory and photoplethysmography. More specifically this paper presents the rational analysis that aims to develop a physical model which can be used to analytically investigate the photoplethysmogram. Such investigation would result in simplified engineering models, which can be used to design validating experiments and new types of spectroscopic devices with the potential to assess venous and arterial blood chemical composition (molar fractions and concentrations) non-invasively.

2. Background
Fundamental laws which relate measurable light and matter properties postulated in modern physics lie outside the human perception and therefore are not intuitive. Such laws may only be confirmed indirectly by experimentally validating many physical models which are mathematically derived from those laws.

Unfortunately every generalization of the known fundamental laws brings significant complexity to the rational theory and its physical models. Engineering systems which are built on top of physical models are often even more complex and not always require the best possible models predictions accuracy. Therefore, the direct utilization of the physical models derived from the best known fundamental laws is often impractical or even not feasible in engineering practice. Accepting growing amount of experimental facts, physicist of the 20th century came to the agreement that to theoretically explain some experiments, light has to be treated as consisting of particles while in other experiments as a wave in “a continuous media”. Such strange light behaviour is called wave-particle duality [5].

Many philosophical views have been proposed to rationally explain this “special” behaviour of the particles and waves mentioned above. Initiated by the famous debates between Einstein and Bohr [6-7], a dispute between people with different views on this subject is on going for decades. In this purely applied work, a neutral instrumentalist approach was chosen to avoid such discussions. From opaque bio-tissue optics literature (e.g. [8-9]), a conclusion has been made that suggests that simplified particles theory is well developed, and it is also easier to understand and to use to model biological tissues, however with certain inaccuracies.

3. Theoretical method
In the current work, light is accepted as a flux of elementary particles – photons. Speed of photons is equal to the speed of light. This speed is defined by the electromagnetic properties of the media where light propagates. Light photon can be emitted absorbed or scattered by an optical electron of an atom or molecule, collectively called matter particle. Light photon energy is insufficient to interact with atom electrons at inner orbits or with atomic nucleus. Photon energy is proportional to the light wavelengths and the proportionality coefficient is the Plank constant.

Postulated fundamental laws, enumerated below were deduced by analysis of the following physical models: Beer-Lambert law, Monte Carlo light scattering modelling and light energy transport integral equation. These physical models can be used to confirm practical validity of the postulated laws by deriving their experimentally confirmed equations:
1) Number of photons in a small volume of light beam is sufficiently large to be accurately represented by a continuous vector field of light energy density.
2) Photons do not interact with each other: motion of one photon does not affect motion of another.
3) Light photons travel along straight lines in free Galilean space between interactions with matter particles.
4) Matter particle cross-section has a defined shape which in most cases is approximated by spheres, to achieve isotropic matter simplification.
5) Number of matter particles in a small volume of matter is sufficiently large to be accurately represented by a continuous scalar field of matter particles density or concentration.
6) Distance between matter particles is greater than maximum matter particle dimension.
7) Mass of the matter sample is equal to the sum mass of all its matter particles.
If one assumes that the chances of a photon to hit different points of a matter particle cross-section are equiprobable (i.e. uniform light beam profile) then the probability of photon-optical electron interaction would depend on the probability distribution of an electron presence along its orbit. The probability of photon scattering by an electron can be numerically described in terms of geometrical probabilities. Thus, photon-electron scattering probability can be described by the defined molecular cross-section shape of a certain area. Because molecules orientations in biological media are randomized, the average effect of such media on the light beam is isotropic. Therefore, the defined shape of molecular cross-section can be approximated with a round shape of some averaged area. The sphere is the only stereometric figure, which has the round as its planimetric projection at any direction. Thus, molecular cross-section of a defined shape in matter with a high average isotropy can be approximated with a circle.

Notice that the matter particle term is postulated; it does not necessary approximate a real atom or molecule. Similarly, spherical shape of the matter particle enforces isotropy of the homogeneous media; while real homogeneous media is not necessarily isotropic (i.e. it must be experimentally verified for each derived physical model).

8) Matter particles average motion speed is negligible in respect to the light photon speed.
9) Average light photons dimensions are negligible in respect to the average matter particles dimensions.
10) Light-matter interactions do not significantly change interacting electrons energy.
11) Matter media with homogeneously distributed inhomogeneities at larger modelled scale can be approximated by a homogeneous media.

A light beam that travels through matter does not have any effect on the matter’s ability to absorb or scatter the following (in time) or overlapping (in space) light beams passing through the same matter. The latter simplifying assumption is used to substitute the real biological tissue matter with homogeneously distributed inhomogeneities (such as tissue layers or blood) by a simpler homogeneous matter model with some averaged optical absorption and scattering coefficients. In Pulse oximetry, for example, blood with a large number of macro bodies is approximated by a homogeneous liquid with averaged optical characteristics [4, 10].

Thus, elementary principles of the light-matter interaction given in this section represent a theoretical method utilized in the current work. Those principles can be used to derive the well recognized Beer-Lambert law, Monte Carlo light scattering modelling and light energy transport integral equation, as well as some tissue optics models. Such derivation (which will not take part in this paper) validates the simplified fundamental laws of the light-matter interaction introduced in this section. Such common basis also allows drawing similarities and finding relationships between parameters used in different light-matter interaction models.

The following section analyses the light energy propagation within highly scattering media from the position of elementary principles introduced above.

4. Scattered light power distribution
The left part of figure Figure 1, shows the light flux envelope between emitter and detector in a highly scattering matter like vascular tissue which is known as “banana”.

This banana shaped envelope represents a space area along which most photons travel from the light emitter to the light detector. Such envelop can be obtained by light scattering modelling on the homogeneous plain semi-infinite matter models utilizing the Monte Carlo method to solve the light radiation transfer equation [9, 11-12]. It might also be obtained by measuring the light radiant intensities at various points within the matter sample volume in vitro [8]. This “banana” shaped envelop is used in the following section to derive the Beer-Lambert law for non-linear mean light pathways which can be utilized to determine light absorbing components concentrations within highly scattering matter such as blood glucose in vascular tissue.

To construct the Beer-Lambert integrals in scattering matter the following question should be answered: are photons motions absolutely random within the banana shaped envelop? Light pulse
propagation delay experiments suggest otherwise. In both dynamic and quasistationary cases directional integrals (i.e. light radiation transfer equation) which define photons scattering directions are the same [9]. Thus, another observation can be made:

- Mean photon scattering trajectories are the same for the dynamic and quasistationary light radiation transfer equations.

Practical implication of the above statement is that the photons scattering “banana” envelope in the pulse propagation delay experiments are no different from the “banana” envelope in quasistatic experiments where continuous light is utilized (e.g. photoplethysmography).

To illustrate the results of the photons motion combined from both light pulse propagation delay experiments, and light transfer equation solution with Monte Carlo analysis, consider Figure 1. Let’s light pulse power emitted by the light emitter is $P_{E\lambda}$. Assume that $\int P_{E\lambda}$ is the total fraction of the emitted light pulse energy which went through the vascular tissue and was captured by the light detector (Figure 1, left). A fraction of the emitted light pulse power $P_{E\lambda}$ captured by the detector is widened in time (Figure 1, right). The light energy transport equation suggests that the light pulse widening occurs only because of the time during which light photons cover the distance between emitter and detector (photon absorption-emission delay is neglected). Time interval “I” during which the first part of the light pulse power arrives to the light detector corresponds to the shortest distance in the banana envelope (Figure 1). Time interval “II” corresponds to the longer distance, and so on up to the end of the light pulse propagation time interval “VI”. The conclusion of such an analysis is as follows:

- Despite that the individual light photons motion is determined statistically by the photon scattering and scattering phase distribution functions, the light energy propagation pathways are deterministic and not random.

The conclusion above leads to the key concept of this paper, which would allow components concentrations evaluation within highly scattering matter, such as blood glucose within vascular tissue. This concept is the Beer-Lambert law along non-linear mean light pathways.

5. Beer-Lambert law along non-linear mean light pathways
Light energy propagation between emitter and detector within highly scattering matter is deterministic and can be split into a series of smaller “canoe” shaped envelops within which certain fraction of light energy propagates through the matter (Figure 2, left). Forms of those envelops determine the shape of

![Figure 1](image_url)
the detected response for emitted short light pulses in the light pulse propagation delay experiments (Figure 2, right). Each such envelope can be approximated by the mean light pathway, going through the envelope centre. In this approximation, fractions of the light energy corresponding to each envelope are propagating along the mean light pathways (Figure 2, right). It is possible to prove that when thinner envelopes are used to split the whole “banana” shape, the more accurate the mean light pathways approximation will be. Each mean light pathway corresponds to the certain light pulse propagation delay time interval (Figure 2). Thus, individual mean light pathways can be selected from the “banana” envelope. One of such mean light pathways corresponds to the “canoe” envelope along which most of the light energy propagates through the scattering matter. This higher energy light pathway in the scattering matter is referred in the current work as the \textit{ridge light pathway} and denoted by zero indexes in the corresponding variables (Figure 2).

Thus, after introducing the concept of the light propagation pathway in the scattering matter, light intensity can also be introduced for the resulting scattered light. Light intensity can be computed for each point of the mean light pathway curve along its tangent and at the emitter-detector direction.

By above definition fractions of the emitted light energy propagate along various mean pathways. Then, in the absence of light absorption \((\mu_a = 0)\), light intensity within the envelope does not change due to the scattering. In the presence of light absorption \((\mu_a \neq 0)\), light intensity degrades along the mean pathways according to the Beer-Lambert law, apart from the fact that the Beer-Lambert integral sum is taken along the mean light pathways rather than a straight line:

\[
I_{pl\lambda} = -\log I_{Ep\lambda} = \mu_{at\lambda} \cdot l_{pl\lambda}
\]  

(1)

\(l_{pl\lambda}\) is the mean light pathway corresponding to the \(pi\) fraction of the transmitted light power in the vascular tissue \([cm]\) (Figure 2); \(\mu_{at\lambda}\) is the absorption coefficient for the whole light pathway in the scattering sample \([cm^{-1}]\).

Let us suppose that there are \(m\) matter segments along the mean light pathway with different absorption coefficients (three segments example is shown in Figure 3, right), then the following equation can be stated:

\[
A_{pl\lambda} = -\log I_{Ep\lambda}^{Dpl\lambda} = \mu_{at\lambda} \cdot \left( \sum_{j=0}^{m} \mu_{atsj\lambda} \cdot l_{pisj\lambda} \right)
\]  

(2)
is the light detector’s active area and in the case of similar detector sensitivity along the whole active area then \( I_{\text{DPi}} \sim P_{\text{D}} \) [W cm\(^{-2}\)]; \( m_\lambda + 1 \) is the number of homogeneous segments along light pathway \( p_i \) within the scattering matter (\( m_\lambda + 1 = 3 \) in example in Figure 3, right); \( \tilde{\mu}_{\text{atsj}} \) total absorption coefficient tilde within scattering matter segment \( sj \) [-]; \( l_{\text{pisj}} \) part of the mean light pathway \( p_i \) within the scattering matter segment \( sj \) [cm].

According to the absorbance superposition for composite samples, each absorption coefficient in (2) can be further extended by absorptivities and concentrations of absorbing components present in the light pathway segment \( sj \):

\[
\tilde{\mu}_{\text{atsj}} = \sum_{k=0}^{n_{sj}} a_{k\lambda} \cdot c_{ksj} \tag{3}
\]

\( n_{sj} \) is the number of light absorbing components in the segment \( j \) [-]; \( a_{k\lambda} \) is the Beer-Lambert law absorptivity of the absorbing component \( k \) at wavelength \( \lambda \) [L mol\(^{-1}\) cm\(^{-1}\)]; \( c_{ksj} \) is the concentration of the light absorbing component \( k \) in the light pathway segment \( j \) [mol l\(^{-1}\)].

Thus, in scattering samples such as blood, the Beer-Lambert law absorptivity coefficient \( a_{k\lambda} \) can be measured using the variable light path length method, by making the sample width variation small compared to the mean path length of the photon free flight. If such small sample width variation causes light absorption variations that are below detectable threshold then the sample width variation can be increased with the corresponding light intensity measurements correction for scattering [13].

Further analysis of the PPG phenomena can be done using the proposed Beer-Lambert law along non-linear mean light pathways and assuming that the cardiac blood pulsation does not significantly change the mean light pathways distribution and only alters their lengths \( l_{\text{pis}} \). This analysis methodology is similar to the common phenomenological analysis as described in many sources on Pulse oximetry such as [4]. The only significant difference is that the light energy summation has to be done over all the mean light pathways within the vascular tissue.

6. Conclusion and further work

The Beer-Lambert law along non-linear mean light pathways is the physical model that is presented in this paper. It allows the application of the Beer-Lambert law analysis to the highly scattering media such as human vascular tissue. Further work is needed to derive the generic fixed wavelengths PPG equations based on (1)-(3) which theoretically will allow evaluation of any arterial blood chemical component molar fraction or concentration.
References