Features of photon diffusion in a dispersed medium

A V Galaktionov
Joint Institute for High Temperatures of Russian Academy of Sciences, 13 Bd.2 Izhorskaya str., Moscow125412, Russia

E-mail: andrei.v.galaktionov@gmail.com

Abstract. Energy transfer by thermal radiation in a dispersed medium with a variable refractive index is discussed. This transfer can be described by a surprisingly simple diffusion equation. The process is naturally to interpret as the photon diffusion. The diffusion equation is free from strict conditions of applicability of the radiation transfer equation, which are usually not satisfied in disperse media with densely packed inhomogeneities. Quantum constraints on the value of the photon diffusion coefficient are derived. These restrictions turn out to be similar to the conditions for the applicability of geometric optics. The lower limit of the thermal conductivity coefficient is obtained, which is easier to verify in the experiment. An independent derivation of this limitation is given from considerations of symmetry and dimension.

1. Introduction
The radiative heat transfer in absorbing-emitting and scattering media have applications in a wide variety of fields, including astrophysics, atmospheric science, biomedical optics, fuel combustion, high temperature insulators and various dispersed media [1-4]. In a number of applications, radiative heat transfer is complicated by phase transitions and changes in density or composition, which leads to a change in the refractive index of the medium and significantly complicates the calculations. In highly scattering dispersed media with densely packed inhomogeneities in the form of pores, fibers, etc. with dimensions of the order of the wavelength of thermal radiation, the correctness of the application of the transfer equation raises questions. In such materials, the requirement for the validity of the geometric optics approximation is violated. The radiation diffusion equation is free of these restrictions, much simpler, and is successfully used in many applications.

In the previous article [5], a surprisingly simple equation for the diffusion of thermal radiation was derived from the classical radiation transfer equation [3, 4] for a medium with a variable refractive index:

\[ -\nabla M_\nu \nabla N_\nu + E_\nu N_\nu = E_\nu U_{pv}(T(r)), \] (1)

where \( T \) is the temperature, \( U_{pv}(T) = 8\pi \hbar \nu^3 / c^3 (\exp(h\nu/kT) - 1) \) is the Plank spectral energy density of the equilibrium thermal radiation in a vacuum, \( \nu \) is the frequency of thermal radiation.

The equation (1) should be supplemented by the usual boundary conditions at the outer boundaries, which can be written out in the form

\[ -M_\nu \nabla N_\nu + \frac{1}{2} \frac{1-R_\nu}{1+R_\nu} (N_\nu - U_{pv}(T_{ext})) = 0, \] (2)

where \( R_\nu \) is the hemispherical reflection coefficient of the boundary and \( T_{ext} \) is the temperature of the external medium.
After solving equation (1), the divergence of radiation flux \( w(x) \) which enters as the source into the equation of total energy balance [1, 2], can easily be calculated by the formula:

\[
w(x) = \nabla q = \int E_n(U_{np}(T(r)) - N_n) \, dv,
\]

where the integration is performed over a spectrum that is essential for thermal radiation.

The coefficient \( M_v \) in equation (1) describes the exchange of momentum between radiation and matter [5]. It is related to the usual radiation diffusion coefficient by the expression \( D_v = D_v n_v^2 \), where \( D_v = 1/(k_v + \beta_v (1 - \mu_v)) \) is the usual radiation diffusion coefficient, \( k_v \) is the absorption coefficient, \( \beta_v \) is the scattering coefficient, \( n_v \) is the refractive index, \( \mu_v \) is the middle cosine of scattering. The coefficient \( E_v = k_v n_v^2 \) describes the exchange of energy between radiation and matter. The equation (1) can naturally be interpreted as the photon diffusion equation [5] due to the quantity \( N_v = U_v / n_v^2 = \int I_v / n_v^2 \, d\Omega \) is proportional to the number of photons. This assumes that the energy and momentum of a photon in a medium are determined in the same way as in a vacuum, which makes it possible to bypass the old Abraham-Minkowski controversy [6, 7].

The photon diffusion equation makes it possible to uniformly describe smooth and intermittent changes in the refractive index at the interface of phases or media. This allows to calculate heat exchange by radiation in a medium with a variable refractive index by known software packages without additional computational costs.

The photon diffusion equation, in contrast to the transfer equation, does not use the concept of a ray. Therefore, it is free from the requirement to fulfill the geometric optics approximation, which is a necessary condition for the applicability of the radiation transfer equation. This condition is usually violated in many dispersed media with densely packed inhomogeneities such as pores, inclusions, fibers, etc. And although the transfer equation has been successfully used for a long time in such medium, strictly speaking, this is incorrect. It is useful to try to derive the diffusion equation or some more general equation directly from the fluctuation electrodynamics [8, 9], bypassing the transfer equation. This theory is free from the limitations of geometric optics and, perhaps, may circumvent the above problems. However, below we will see that this path, most likely, will not allow one to significantly expanding the limits of geometric optics.

2. Quantum constraints on the photon diffusion coefficient

In the equation (1), the photon diffusion coefficient \( M_v \) has the dimension of length and, by analogy with the elementary kinetic theory, can be written in the form \( M_v = <l>_v / 3 \), where \( <l>_v \) is the average path length of a photon with a frequency \( v \).

The mean free path of a photon in a medium \( <l>_v \) describes the exchange of momentum between radiation and matter and has the dimension of length. Therefore, there is a temptation to write an estimate for it based on the quantum uncertainty relation coordinate-momentum \( \delta x \cdot \delta p \geq \frac{1}{2} \hbar \). Since \( <l>_v \approx \delta x, \delta p \approx h v / c \), we obtain \( <l>_v \approx h / (h v / c) = c / v = \lambda_v \). Thus, from the uncertainty relation follows a lower estimate for the minimum possible value of the photon diffusion coefficient:

\[
M_v \geq \frac{<l>_v}{3} = \text{const} \cdot \frac{c}{v} \approx \text{const} \cdot \lambda_{vac}, \tag{4}
\]

where const \( \approx 1 / 6\pi \) is some constant of the order of unity. Its possible value is discussed below. In other words, the photon diffusion coefficient in a medium cannot be less than the order of the radiation wavelength \( \lambda_{vac} \) in vacuum.

It is important to note that relation (4), on the one hand, is new and unusual, since it represents a quantum-mechanical constraint on the dissipative coefficient in an irreversible diffusion process. On the other hand, this relationship is not unexpected, since it is very similar to the requirement for the validity of the geometric optics approximation \( <l>_v \gg \lambda \). Another interesting and important point is that the quantum Planck constant \( \hbar \) will drop out of the quantum constraint (4).
Strictly speaking, applying the usual coordinate-momentum uncertainty relation to a photon is completely incorrect. The photon does not have three coordinate operators, there is no wave function in the coordinate representation, and hence the usual Heisenberg uncertainty relation coordinate-momentum loses its meaning. This is an old problem of determining the wave function of a photon, formulated in the famous paper by Newton and Wigner [10].

The problem of the photon wave function is part of the general problem of quantum theory about the impossibility of matching parts of the observed physical quantities to a self-adjoint operator, i.e. observable in the usual quantum mechanical sense [11]. The square of the modulus of the wave function is the probability density of finding a particle in space. This means that it is not possible to find out exactly where the photon is, even in a "blurry" quantum-mechanical sense. At least up to the photon wavelength. Many authors have tried to solve these problems using various approaches - statistical generalizations of the concepts of observables, the development of the theory of quantum measurements, generalizations of the concept of the wave function [11–16]. However, it has not yet been possible to create a single generally accepted consistent theory, although there are a number of theories in varying degrees of development.

One of the possible approaches to solving this problem by generalizing the concept of the wave function was proposed by I. Bialynicki-Birula [17] and J. E. Sipe [18]. This approach is called the theory of "energy density wave functions" in coordinate space [14]. And the uncertainty relation has the form $\delta r \delta \rho \geq 4 \hbar$. That is, the photon turns out to be more “smear” in three-dimensional space than an ordinary particle with a nonzero rest mass $\delta r \delta \rho \geq \frac{3}{2} \hbar$. This approach gave an estimate for the diffusion coefficient of the form

$$M_\nu \geq \frac{4}{3\pi} \lambda_{\text{vac}}. \quad (5)$$

The constant in expression (5) still needs to be refined on the basis of a more rigorous theory and, possibly, will be changed by a value of the order of unity. Moreover, with a "naive" approach to the derivation of this restriction, the constant in (5) should be replaced by $1/6\pi$.

Since it is difficult to use the coordinate-momentum uncertainty relation for a photon, we will obtain an estimate based on the time-energy uncertainty relation. The time–energy uncertainty relation

$$\delta t \cdot \delta E \geq \frac{1}{2} \hbar \quad (6)$$

has been a controversial issue since the advent of quantum theory. Its appropriate formalization, validity, and possible meanings are still under discussion [19].

Nevertheless, it allows a slightly different look at the process of photons diffusion in a medium. Since the acts of emission, absorption and scattering of photons are independent, it is natural to assume that the lifetime of a photon is distributed according to Poisson's law $\nu \propto e^{-t/\tau}$ with an average lifetime $\tau$. From this and the obvious relation $\Delta x = c \Delta t$ it follows that the free path of the photon also obeys Poisson's law $l \propto e^{-\epsilon x}$, where the extinction coefficient is $\epsilon = 1/c\tau$. This corresponds to the well-known Beer – Lambert – Bouguer law. For the Poisson process, the mathematical expectation and variance are $\langle \nu \rangle = \sigma_\nu = \tau$ and $\langle l \rangle = \sigma_l = 1/\epsilon = c\tau$.

To calculate $\delta E$, we note that either the photon exist ($E = h\nu$), or it does not exist ($E = 0$), and it is natural to assign the probability 1/2 to both states. Hence we have $\delta E = \sqrt{\langle E^2 \rangle - \langle E \rangle^2} = E/2$. Then from the uncertainty relation (6) it follows $\geq 1/2\pi\nu$, $\langle l \rangle = \sigma_l \geq c/2\pi\nu = \lambda_{\text{vac}}/2\pi$, whence

$$M_\nu \geq c/6\pi\nu = \lambda_{\text{vac}}/6\pi. \quad (7)$$

This value of the constant coincides with the value obtained in the "naive" derivation of the coordinate-momentum from the uncertainty relation and is almost an order of magnitude less than the constant in (5). Thus, the question of the exact value of the constant in relation (4) and its rigorous derivation is still open. Further, for definiteness, we will use the constant from relation (7).
3. The lower limit of the thermal conductivity

Experimental verification of the obtained limitations of the photon diffusion coefficient requires complex optical spectral measurements of a dispersed media. For comparison with experiment, let us calculate on its basis an estimate for the coefficient of radiation thermal conductivity, the values of which are much easier to measure or find in the literature.

To calculate the lower limit of the possible values of the radiative thermal conductivity coefficient, one can use the well-known Rosseland approximation

$$\Lambda_{\text{rad}} = \int_{0}^{\infty} d\nu c M_N \frac{\partial U_{\nu}(T)}{\partial T} (T).$$

Using estimate (7), this integral is easy to calculate

$$\Lambda_{\text{rad}} \geq 2\zeta(3) k^3 \frac{\pi^2}{c^2 \hbar^2} T^2,$$

where $\zeta(3) = 1.202$ is the Riemann zeta function, $2\zeta(3)/\pi^2 = 0.24357$, $k$ is the Boltzmann constant. The coefficient in expression (9) has the value $2\zeta(3) k^3 / \pi^2 c^2 \hbar^2 = 1.92278 \cdot 10^{-10}$ W/mK. At room temperature ($T = 300 K$), we obtain for the thermal conductivity coefficient $\Lambda_{\text{rad}} \geq 1.73 \cdot 10^{-5}$ W/mK, which is approximately three orders of magnitude less than the thermal conductivity of the best nano-structural heat insulators based on aerogel ($\approx 0.01$ W/mK) [20]. Considering that the radiation component in these materials is about $4 \cdot 10^{-3}$ W/mK, that is, only two orders of magnitude more than the theoretical limit, and then we are not so far from reality. Moreover, if we use estimate (5) and change the constant in (7), then the discrepancy will be reduced to one order.

It is interesting to compare the obtained estimate (9) with radiative heat transfer in a vacuum gap between two parallel plates, for example, thick polished copper discs. According to the predictions of the theory of heat transfer by a fluctuating electromagnetic field [8, 9], as the plates with different temperatures approach each other, the energy flux of thermal radiation between them should increase. Estimate (9) also predicts an increase in heat flux, but this increase begins at noticeably large distances between the discs and is in good agreement with the measurement results [21]. However, a detailed analysis and interpretation of the results by a large array of such experiments is not always possible, laborious, and goes beyond the scope of this work.

4. The estimate derivation from dimension and symmetry considerations

The above constraints (7), (9) are closely related to the Abraham-Minkowski problem, the problem of determining the photon coordinate operators and the photon wave function and are based on the controversial time-energy uncertainty relation. Therefore, their derivation, interpretation and consequences can cause fair criticism. Fortunately, inequality (9) can be obtained in a completely independent way solely from considerations of symmetry and dimension, which will be an additional argument in favor of their validity. It turns out that estimate (9) is closely related to another fundamental problem of modern physics - the problem of substantiating the second law of thermodynamics, which contradicts the time reversibility of the laws of mechanics.

Landau and Lifshitz pointed out that “is to be existed an inequality that contains the quantum constant $\hbar$, which provides validity of the law and is satisfied in real nature” [22 sec.8 p.32]. Let’s find an answer on the following simple question. What additional fundamental constants does this inequality contain? We discuss simplest case of a homogeneous isotropic medium without chemical reactions and external fields. Indeed, in general case may appear only additional constants, but included constants could not disappear. On the other hand, common mechanism of irreversibility must work at the simplest case as well. Consider a large system initially diverted from thermodynamic equilibrium. Conditions of the system are uniform temperature and pressure. We examine the system at asymptotically large time $t \to \infty$. Since the pressure usually reaches the steady state faster than temperature, we assume that pressure has already been uniform and explore entropy increasing due to final temperature equalizing.

The desirable inequality must strengthen the second law of thermodynamics $dS/dt \geq 0$. Since the entropy $S$ is additive thermodynamic function, in the right side of the inequality must be an integral over
a volume. Under the integral must be a local [23] (i.e. differential) non-linear operator \( F \) that acts on the temperature distribution \( dS/dt \geq \int F(T(r))dV \geq 0 \). From the existence of equilibrium \( dS/dt = 0 \) follows that \( F(T(r)) = T_0 = \text{const} \). Because the medium is isotropic and uniform, the operator does not depend on coordinates and must locally satisfy translation and rotation symmetries. This means that it is commutative with infinitesimal operators of the symmetry 

\[ \forall \delta r \forall \delta \varphi, \varphi \mathbf{r} + \delta \varphi \mathbf{r} \mathbf{r} \mathbf{r} \mathbf{r} \delta \mathbf{r} \].

Thus, operator \( F \) has to be a function of the operator nabla \( \nabla \). Expanding operator \( F \) into Taylor series by operator nabla and nonlinearity, using Curie principle [24], and noting that it is positive scalar operator, we obtain that first term of the expansion must be quadratic and equal 

\[ F(\nabla) \equiv \vartheta(\nabla^2) + \cdots \].

That is distribution \( dS/dt \geq \int (\nabla^2) dV \geq 0 \), where positive constant \( \vartheta \) is to be found in terms of 

fundamental physical constants.

Now as fundamental physical constants may be accepted the Plank quantum constant \( h \), light velocity in vacuum \( c \), gravitational constant \( \gamma \), masses of elementary particles, fine structure constant \( \alpha = e^2 / ch \) (or electron charge \( e \)), and constants of weak and strong interactions. Experience suggests that thermodynamic equilibrium arises in systems that consist of various collections of elementary particles. Thus, masses of elementary particles and gravitational constant must be excluded from the universal constant \( \vartheta \). The constants of weak and strong interactions must be also excluded because the equilibrium arrives in systems without nuclear reactions (e.g., “cold” hydrogen that involves stable protons and electrons). These assumptions agree with results of relativistic quantum kinetic theory of diluted systems, which shows that micro and macro irreversibilities are independent [25]. Success of the electroweak interaction theory causes to exclude the fine structure constant. Therefore, only the quantum constant \( h \) and light velocity \( c \) are available.

Note, that only these two constants appear in basic mechanical inequalities, namely Einstein’s restriction of highest velocity and Heisenberg’s indeterminacy principle. The other constants appear only in equalities. From dimension considerations, we obtain \( \vartheta \approx 1 / ch^2 \) implying that entropy is dimensionless quantity and temperature measures in energy units. In SI units we accordingly have \( \vartheta \approx k^3 / ch^2 \), where \( k \) is the Boltzmann constant. Finally, we have

\[ dS/dt \geq \frac{k^3}{h^2 c} \int (\nabla^2) dV. \] (10)

Here a numerical constant about unity is omitted, like in any expressions derived by dimension considerations. Comparing this inequality with known expression for entropy risen by thermal conductivity \( dS/dt = \int \Lambda (\nabla^2)^2 / T^2 dV \), implying that Fourier conduction law \( q = -\Lambda \nabla T \) holds. Thus, inequality (10) may be interpreted as existence of fundamental lower bound for thermal conductivity

\[ \Lambda \geq \frac{k^3}{h^2 c} T^2. \] (11)

Inequalities (10, 11) are valid only in asymptotic sense \( t, V \to \infty, (\nabla^2)^2 \to 0 \). Comparing inequalities (9) and (11), it is easy to see that they coincide up to a constant, which has yet to be refined.

Inequalities (10, 11) include both constants of basic mechanical inequalities. Therefore, solution of the irreversibility problem is to be sought in relativistic quantum theory, which is reversible according to CPT theorem [26]. Other attempts are presumably doomed to failure. It is important to note that estimate (10) was obtained without any assumptions about the properties of the medium and the mechanisms of heat transfer. It does not require Fick’s Law to be valid. Moreover, the numerical constants in estimates (7) and (11), generally speaking, do not have to coincide. In estimate (11), the constant can be larger. The consequences of estimate (10) are of a very general nature and can work in very different areas of physics. However, a discussion of the various implications of this assessment is beyond the scope of this article.

5. Conclusions

In the diffusion limit for a medium with a variable refractive index we obtain a surprisingly simple equation, which is naturally interpreted as the photons diffusion equation, the momentum and energy of
which are the same as in vacuum. The coefficients of this equation describe the exchange of momentum and energy between radiation and matter. This allows us to bypass the well-known Abraham-Minkowski problem on the consistent definition of the energy-momentum tensor of an electromagnetic wave in a medium.

The photon diffusion coefficient has the dimension of length and describes the exchange of momentum between radiation and matter. This makes it possible to obtain an estimate for it from below, based on the coordinate-momentum or energy-time uncertainty relations. The estimate turns out to be of the order of the radiation wavelength in vacuum, and the quantum constant drops out of it. This means that the limits of applicability of the photon diffusion equation \( \langle l \rangle_{\nu} \geq \lambda_{\nu}/2\pi \) cannot be made much wider than the limit of geometric optics \( \langle l \rangle_{\nu} \gg \lambda \). However, since a photon, strictly speaking, has no wave function in the coordinate representation and the coordinate operator along its propagation, these estimates are not strict and the constant in them may differ by an order of magnitude. The question of the exact value of the constant in the estimate is still open.

Integration over the spectrum of the quantum estimate of the photon diffusion coefficient makes it possible to obtain an estimate from below for the radiative thermal conductivity, which is easier to verify experimentally. Its value at room temperature is only one to two orders of magnitude lower than the observed values of thermal conductivity of heat insulators based on aerogel.

A similar estimate for the minimum possible value of the thermal conductivity coefficient, which is proportional to the square of the temperature, can be obtained independently from macroscopic considerations of symmetry and dimension as the next term in the law of entropy increasing. Perhaps this is exactly the assessment that Landau and Lifshitz wrote about [22 sec.8 p.32]. The presence in the estimation of both a quantum constant and the speed of light indicates that macroscopic irreversibility is an essentially relativistic quantum effect. The validity of this estimate and the exact value of the numerical constant must and can be verified experimentally.

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