# Entropy production in multiple scattering of light by a spatially random medium

Christian Brosseau[1] and Dominique Bicout[2]
[1]Faculté des Sciences et Techniques, Université de Bretagne Occidentale, 6 Avenue Le Gorgeu, Boîte Postale 809, 29285 Brest Cedex, France
[2]Institut de Biologie Structurale, Laboratoire de Modélisation et de Simulation, 41 Avenue des Martyrs, 38027 Grenoble Cedex 1, France

(Received 11 July 1994)

This study reports on the problem of entropy production due to multiple scattering of light by a spatially random medium composed of uncorrelated and noninteracting spherical dielectric particles. The degree of polarization $P$ of light, in the form of plane waves, is of the nature of an order parameter for the ensemble of realizations of the fluctuating optical field. The radiation entropy takes a form analogous to the entropy of one-dimensional Ising (two-level) spin systems in contact with a heat bath. On the basis of this analysis, the degree of polarization has a different thermodynamic significance. It is argued that within this representation, one may define an effective polarization temperature $\tau$; we then show how $\tau$ depends on the degree of polarization. Light transmitted through a multiple scattering medium is depolarized by decorrelation of the phases of the electric field components and its polarization entropy increases. The effects of size of the spherical particles and of the optical depth on entropy production are studied numerically, using the Mie theory, via the Monte Carlo method. An attempt is made to interpret these results in terms of the minimization procedure (minimum entropy production) that plays a fundamental role in classical irreversible thermodynamics. One of the most remarkable aspects of this problem, where no energy exchange between radiation and scatterer takes place, is that the stationary state corresponds both to the state of minimum production of radiation entropy and to the state of maximum entropy. Thermodynamically, multiple scattering can be viewed as an order-disorder transition using the spin model. It is also emphasized that the system will tend to evolve towards a "higher polarization temperature" state. We briefly comment on the use of our treatment in interpreting the irreversibility in a scattering process.

PACS number(s): 42.25.Ja, 05.70.Ln

## I. INTRODUCTION

The irreversibility of the interaction between radiation and matter represents a scientific and philosophical landmark which continues to play a central role in our efforts to understand the nature of light. Related to this canonical problem, the entropy production due to scattering of a plane wave by a dense random medium has been of long standing interest. Previous effort has been devoted to the thermodynamic analysis of scattering phenomena using the radiative transfer theory. The literature on the subject is vast, but some representative references which we found useful are indicated in Refs. [1–14]. It is a feature of these treatments that the radiation wave is of thermal nature and that the situation involves only single scattering. The first of these restrictions limits the treatment to second-order coherence effects. The second of these restrictions makes it impossible to explain some important phenomena related to weak localization of light, such as the effect of enhanced coherent backscattering manifesting as a well-defined narrow and spatially anisotropic peak in the angular distribution of the intensity of the light scattered by a random medium at scattering angles near 180° [15].

The entropy of a radiation field was first introduced by Wien as early as 1894 [1] and its most noted success goes back to the pioneering works of von Laue [2] and Planck [3], which were the starting points of the fundamental quantization of energy. It should be also mentioned that the concept of entropy production has a pivotal role in classical irreversible thermodynamics [16,17]. Very recently it has been realized that this concept has practical applications for problems outside the traditional domain of thermodynamics, i.e., scattering [13,14,18]. This result immediately raises interesting questions regarding the behavior of entropy production during the irreversible evolution of the state of polarization. Our work to be reported here is to investigate the consequences of multiple scattering of light by a dense random collection of dielectric scatterers on entropy production. It should be noted that this situation differs from those considered by van Enk and Nienhuis [19] and Eu and Mao [20]. The former were mostly interested in investigating the connection between entropy production and kinetic effects of light on atoms or molecules, such as laser cooling and macroscopic flows in gases. The latter introduced a set of semiclassical Boltzmann equations to describe the interaction of a nonequilibrium photon (ideal) gas with matter. What we are principally concerned with is understanding the relation of the depolarization of an incident pure state of polarization to a process of entropy production and to determine its characteristic length scale. Most of the theoretical work on the transport properties of multiply scattered light has used two characteristic length scales: the elastic mean free path $l$ and the transport mean free path $l^*$, which is defined as the length over which momentum transfer becomes uncorrelated. Using a Monte Carlo method, we [21] have discovered recently that another length occurs in the problem, the depolarization length $\xi_i$ (the index $i = L, C$ refers to linear and circular incident pure states of polarization). Here we will add physical arguments leading to the introduction of the $\xi$'s. Although this subject may at first appear to be quite demanding, we will take advantage of the simplifications in the analysis by choosing isotropic and nonabsorbing scatterers.

There have been two different approaches to the important problem of irreversibility of light scattering. The first approach was initiated by Chandrasekhar [7] and Rozenberg [22] many years ago on the basis of the Boltzmann equation for an isotropic scattering medium and followed by Callies [13] and by Gudkov [14]. The second approach was initiated by Clark Jones [8]. In the first approach, a kinetic theory for treating the optical transport by a phenomenological radiative transfer approach has been introduced. In these theories, use of a statistical description for the covariances of the field by the Bethe-Salpeter integral equation characterizes irreversibility in the multiple scattering process. A further finding has been the recent demonstration that the Bethe-Salpeter equation under the ladder approximation of uncorrelated discrete scatterers results in the usual vector radiative transfer equation [23–27]. In the second approach, the author had a particular objective: he wished to understand what is different between reversible (e.g., specular reflection of a plane wave incident on a plane surface between two homogeneous isotropic media) and irreversible (e.g., wave scattering by an incoherent array) manipulations of waves. As an additional comment, we note, from these earlier studies, that the entropy production criterion [28] in the context of multiple scattering of waves by a disordered dielectric medium is a topic which has not been explicitly investigated.

The outline of this paper goes as follows. Section II outlines the basic mathematical framework in terms of which the entropic description of a plane wave field can be approached. Then we will apply these results, in Sec. III, to the problem of the depolarization of a partially polarized radiation field by a collection of uncorrelated optically inactive spheres. Section IV addresses the important question of what precisely "the irreversible evolution of the state of polarization" actually means operationally and a discussion of when our results are applicable. We also address the issue of dealing with the entropy production criteria for multiple scattering of light. Further conclusions are drawn in Sec. V, while the details of our Monte Carlo analysis are discussed in Appendix A. Additional results of the calculated degree of polarization for an incoherent superposition of beams from scatterers are derived in Appendix B.

## II. PSEUDOSPIN ANALYSIS OF THE ENTROPY OF A CLASSICAL STOCHASTIC WAVE FIELD

In this section we describe the entropic properties of a partially polarized plane wave field. To begin with, we emphasize that there has been much interest in the algebraic description of polarization in recent years. In particular, Simon and Mukunda [29] derived some applications of SU(2) transformations for polarization modifying optical systems which are intensity invariant and outlined Hamilton's geometric theory of turns for SU(2) and noncompact SU(1,1)=SL(2,R). Other works that need to be mentioned concern Hopf fibration and congruence properties of Clifford parallels [30] and Berry-Pancharatnam geometric phase for polarization circuits of light on Poincaré sphere [31], to mention but a few. All these works concerned pure states and polarization preserving transformations, i.e., entropy invariant. The purpose of this section is to add to the discussion of the algebraic properties of polarization by considering the more general situation of mixed states.

We are concerned with a narrow band optical field, which can be represented by an ensemble of realizations, which we shall assume to be statistically stationary at least in the wide sense. The entropy contains information about the second-order temporal correlations of the electric field components of the wave [32]. It may be also viewed as a measure of the purity of states. A natural approach to describing the entropy of a partially polarized plane quasimonochromatic radiation field is provided by the method formulated by Brosseau [33] and reviewed by Barakat and Brosseau [34]. Since a central part of the discussion will deal with the concept of entropy, we first begin by presenting some of its technical properties that will be useful to us hereafter. In the interest of brevity, we will not rederive these properties here, but will merely recapitulate the ones we require since the interested reader can find a full discussion in Refs. [33,34]. There are two steps in the approach. In the first step we specify the degrees of freedom of the classical stochastic field in such a way that we will operate with a two-level system description of the plane wave. The second step is to specify the entropy measure. For this purpose a convenient way of doing this is to use the Von Neumann measure $S(\mathbf{D}) = -\mathrm{tr}[\mathbf{D}\ln(\mathbf{D})]$, which rests on the spectral expansion of $\mathbf{D}$ [35]. Here $\mathbf{D}$ is the density matrix which characterizes the second-order statistics of the fluctuating field at a particular point in space. The averaging is taken over the ensemble of realizations of the optical field. We have shown previously that this description relies on two ingredients: the convexity and the spectral description of the polarization states [33]. Both properties are of topological nature and may be simply visualized through the Poincaré sphere representation embedded in the three-dimensional Stokes space. For instance, the Krein-Millman theorem, which states that a compact convex set is completely determined by its extreme points, implies that every mixed state (i.e., partially polarized) can be written as nonunique convex combinations of pure states (i.e., completely polarized). As elaborated elsewhere [33], the degree of polarization expressed in terms of one of the two rotational invariants [36] of $\mathbf{D}$

$$P \equiv [1 - 4\det(\mathbf{D})]^{1/2} \tag{2.1}$$

indicates to which the system has ordered and is of the nature of an order parameter. In Ref. [33] we were able to write, using the spectral decomposition theorem, a closed-form equation for the polarization entropy

$$S(P)=-\ln[s(P)]\ ,$$
$$\text{with } s(x)=\tfrac{1}{2}(1+x)^{(1+x)/2}(1-x)^{(1-x)/2}\ . \qquad (2.2)$$

It may be noted that this important formula can also be derived using a minimum entropy production principle [37]. For $x$ varying between 0 and 1, $s(x)$ takes values between $\frac{1}{2}$ and 1; $s(x)$ is a bijective strictly increasing function. Three other important points should be noted. First, the entropy in (2.2) depends only on $P$ and not on the detailed state of polarization: for instance, it is the same for both linear and circular polarizations. Second, it satisfies the inequalities $S(P=1)\leq S\leq S(P=0)$. Third, both the entropy of the strictly monochromatic radiation and the entropy of pure states of polarization are equal to zero. This formula is useful for studying the entropy transformation $\Delta S(\mathbf{M})$ of a partially polarized plane wave field by interaction with a linear optical medium, $\mathbf{M}$ being the notation for the Mueller $4\times4$ polarization matrix. As an illustrative example, a maximum entropy argument can serve as a method for determining the Mueller matrix for Rayleigh scattering [18].

A bit of physical interpretation of Eq. (2.2) might be helpful at this point by introducing the analogy of this two-level description with a one-dimensional Ising spin system in contact with a heat bath. The Hamiltonian assigned to a particular configuration of spins is $-J\sum_{i,j=1}^{N}\sigma_i\sigma_j$, with each site $\mathbf{r}_i$ having a spin $\sigma_i=\pm1$. The summation extends over the neighboring pairs of spins and $J$ stands for the nearest neighbor spin-spin coupling. In standard discussions of statistical physics the entropy per spin of such a one-dimensional system has the form (e.g., see Ref. [38])

$$\frac{S(y)}{Nk}=\ln[2\cosh(y)]-y\tanh(y)\ , \qquad (2.3)$$

where $y\equiv J\beta$, $\beta\equiv1/kT$ is the inverse temperature, and $k$ is Boltzmann's constant. Now by a straightforward calculation Eq. (2.3) can be verified to be identically equal to (2.2) if one makes use of the expression

$$\frac{1}{\tau}=\frac{1}{2}\left[\ln\left[\frac{1+P}{1-P}\right]\right] \qquad (2.4)$$

and sets $\tau\equiv kT/J$, which defines an effective polarization temperature. A feature particularly to be emphasized in connection with Eq. (2.4) is that it should not be confused with the radiance temperature obtained using Planck's spectral law [3,39]. In Fig. 1 we depict the behavior of $\tau P$ as a function of $P$. We first observe that $\tau$ is a monotonic decreasing function of $P$. It also shows clearly that $\tau\sim P^{-1}$ for very small values of $P$ and we observe a dramatic change as $P$ approaches 1 from below. In the limit of $P\rightarrow1$, the polarization temperature may be evaluated as $\tau\sim P^{-1}(1-P)^{\alpha}$. The exponent $\alpha$ is found to be equal to 0.225. At this point two comments are in order. Just as in the study of the Ising system, one can determine the thermodynamic functions for the partially po-

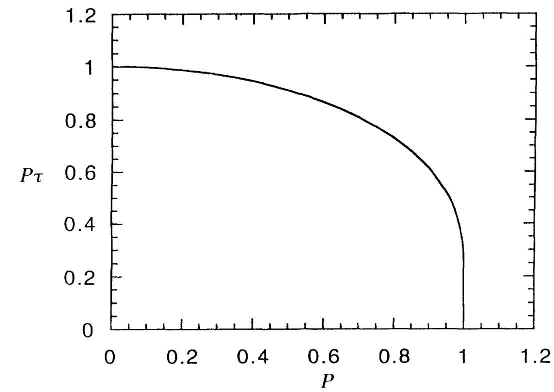


FIG. 1. Radiation temperature $\tau$ as a function of degree of polarization. See Eq. (2.4).

larized radiation field. Using the thermodynamics of the canonical ensemble the partition function is given by

$$Z=2(1-P^2)^{-1/2}\ . \qquad (2.5)$$

Equation (2.5) can be used to find other thermodynamic quantities such as the free energy and the internal energy (see Table I). In like fashion, as one defines in thermodynamics the equilibrium temperature such as $1/T\equiv\partial S/\partial U$ [38], we may prove that the polarization temperature verifies $1/\tau\equiv\partial S/\partial U=-\partial S/\partial P$. The "specific heat" can be found by a simple expression

$$C=\frac{1-P^2}{\tau^2}\ . \qquad (2.6)$$

One can see that the specific heat has a maximum at a degree of polarization such that $P_0\ln[(1+P_0)/(1-P_0)]=2$, i.e., $P_0=\tau_0=0.834$. For later purpose it will also be useful to consider a correlation length by analogy with the Ising model. We assume a finite correlation length $\xi$ for $S(\mathbf{r})$, where $\xi$ is defined as usual by the expression

$$\langle S(\mathbf{r}_i)S(\mathbf{r}_j)\rangle\sim\exp\left[-\frac{|\mathbf{r}_i-\mathbf{r}_j|}{\xi}\right]\ ,$$
$$|\mathbf{r}_i-\mathbf{r}_j|\rightarrow\infty\ . \qquad (2.7)$$

Upon making the substitution, we found that the correlation length behaves as $l[|\ln(P)|]^{-1}$. At small $P$, we expect the correlations to decay to zero.

To close this section we emphasize that Eq. (2.2) is in fact quite general, holding not only for optical radiations, but indeed whenever the stochastic field can be represented as plane waves, e.g., neutron flux. A second paper (in preparation) deals with the case of nonplane waves (applications in the area of near-field optics [40]) for which the analogy is served through the consideration of spin 1. We now illustrate the generality of our approach by considering the problem of multiple scattering of waves by a spatially dense random medium and its connection to a process of entropy production.

TABLE I. Comparison of the thermodynamic functions for the Ising spin-$\frac{1}{2}$ system and for the partially polarized radiation. $a$ is the lattice constant of the spin model. We have set $\beta J \equiv y$. Within the spin model, functions have been normalized to number of spins. Thermodynamic functions have similar expressions, provided thermodynamic temperature $T \equiv J/ky$ is changed into polarization temperature $\tau^{-1} \equiv \frac{1}{2}\ln[(1+P)/(1-P)]$.

| Ising spin system | Quantity | Partially polarized plane wave field |
|---|---|---|
| $2\cosh(y)$ | partition function | $2(1-P^2)^{-1/2}$ |
| $-J\tanh(y)$ | internal energy | $-P$ |
| $k\{\ln[2\cosh(y)]-y\tanh(y)\}$ | entropy | $-\ln[\frac{1}{2}(1+P)^{(1+P)/2}(1-P)^{(1-P)/2}]$ |
| $-\frac{y}{J}\ln[2\cosh(y)]$ | free energy | $\frac{1}{4}\ln\left[\frac{1+P}{1-P}\right]\ln\left[\frac{(1-P^2)}{2}\right]$ |
| $y^2[1-\tanh^2(y)]$ | specific heat | $\frac{1}{4}(1-P^2)\ln\left[\frac{(1+P)}{1-P}\right]$ |
| $a\lvert\ln[\tanh(y)]\rvert^{-1}$ | correlation length | $l\lvert\ln(P)\rvert^{-1}$ |

## III. MULTIPLE SCATTERING AND ENTROPY PRODUCTION

We now come to our main interest, which is the study of how the entropy production behaves as a function of the size of the particles and of the optical depth. Consider a quasimonochromatic plane wave field that is incident normally along the $z$ axis upon a plane-parallel slab, of finite thickness $d$ ($d \gg l$) in the $z$ direction and of infinite extent in the $x,y$ directions, composed of uncorrelated spherical particles of an optically inactive material and of radius $a$ suspended in a liquid. These particles undergo Brownian motion which produces a set of realizations of disorder evolving randomly in time. The transmitted light is measured in the $z$ direction. The slab is assumed to be free of absorption and we consider only the weak scattering limit (i.e., $kl \gg 1$) in the sense that the elastic mean free path $l \equiv 1/\phi\sigma$ is much larger than the wavelength of the radiation: consequently, the ensemble average behavior of wave transmission may be described by a classical diffusion process. Here $\phi$ is the concentration of scatterers, $\sigma$ is the scattering cross section, and $k$ is the wave vector in the scattering medium. Under these circumstances the typical number of scattering events across the slab is on the order of $(d/l)^2$.

The actual numerical procedure that we employed to compute the polarization entropy is presented in Appendix A. Equation (A2) characterizes the polarization behavior of the transmitted light in the far field. Most of the effort of our simulations has been devoted to study the effects of the size parameter $ka$ and of the optical thickness $d/l^*$. Results of the computer simulation of the entropy and of the entropy production for various situations are shown in Figs. 2 and 3. To quantify the behavior of entropy we scanned a large range of values of $ka$. The dependence on the optical thickness is illustrat-

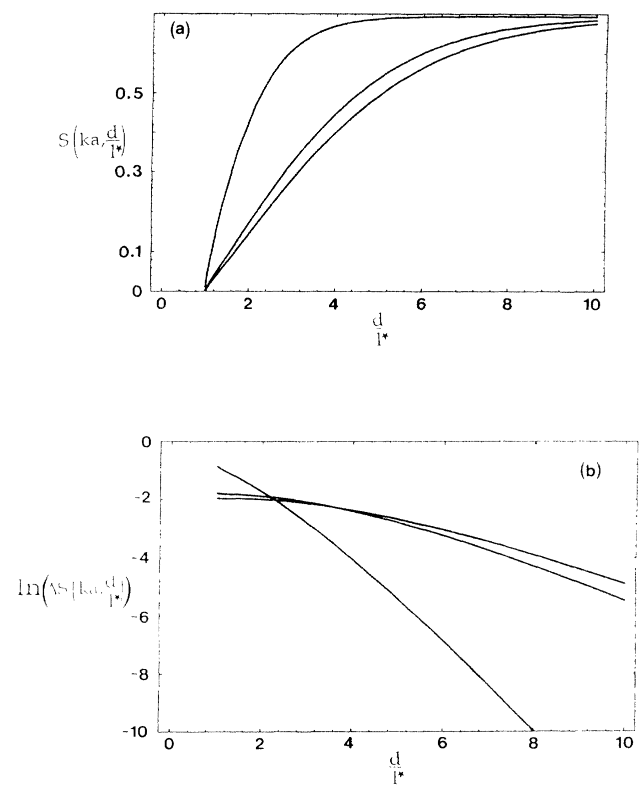


FIG. 2. (a) Polarization entropy as a function of optical thickness $d/l^*$ for a circularly polarized incident light beam and fixed values of the size parameter $ka$. The values of $ka$ from the top are 10, 1, and 0.1. (b) Optical thickness dependence of entropy production $\Delta S \equiv S(ka,(d+l^*)/l^*) - S(ka,d/l^*)$, plotted as $\ln(\Delta S)$ vs $d/l^*$, for a circularly polarized incident light beam and fixed values of the size parameters $ka$. The values of $ka$ from the top are 3.5, 5, and 7.

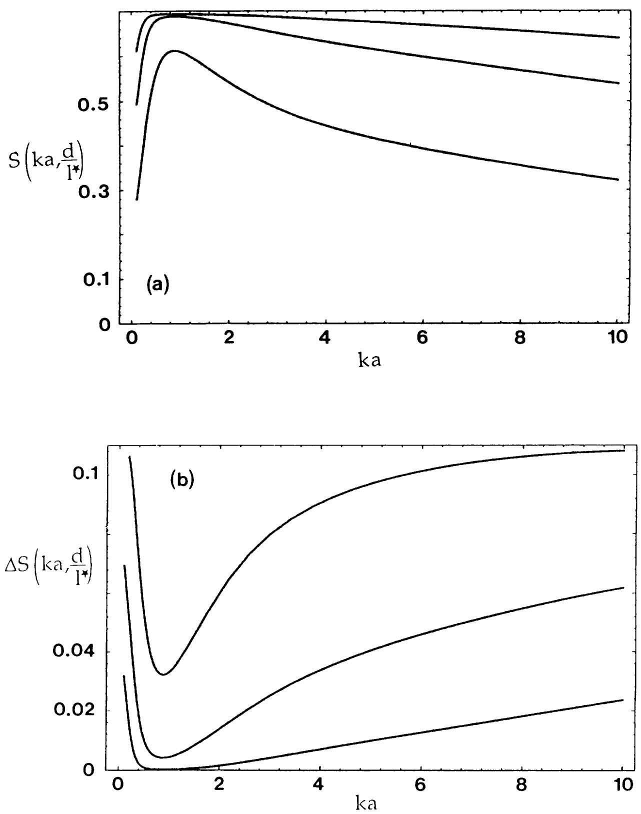


FIG. 3. (a) Polarization entropy as a function of size parameter $ka$ for a circularly polarized incident light beam and fixed values of the optical thickness $d/l^*$. The values of $d/l^*$ from the top are 7, 5, and 3. (b) Entropy production as a function of size parameter for a circularly polarized incident light beam and fixed values of the optical thickness $d/l^*$. The values of $d/l^*$ from the top are 10, 1, and 0.1.

ed in Fig. 2(a) for incident circularly polarized waves. Since identical behavior is observed for incident linearly polarized waves, we concentrate on the circularly polarized case only. This figure shows the values of the length scale to attain the state of maximum entropy for $ka \ll 1$, $ka \sim 1$, and $ka \gg 1$. It is clear from looking at Fig. 2(b) that the entropy production $\Delta S$ falls off exponentially with the optical thickness for $d/l^* \gg 1$. We also find that the two plots for $ka = 0.1$ and 10 have an initial slope at $d/l^* = 1$, which is equal to zero. We defer to Sec. IV the discussion of the physical reasons of why the depolarization process actually implies that the system should tend to produce entropy according to an exponential law. In Fig. 3(a) we have plotted the entropy as a function of $ka$ for a set of $d/l^*$ values. The entropy goes up quickly for $ka < 1$ (forward and backward scattered directions are equivalent) and decreases slowly for large values of $ka$ (scattering predominantly in the forward direction), indicating a strong anisotropy effect. We can also see a maximum for $ka \sim 1$. The dependence of the entropy production on $ka$, hence on the degree of forwardness of the scattering, is depicted in Fig. 3(b). This figure shows a comparison between the size dependence of the entropy production for fixed values of $d/l^*$. Notice that a minimum of entropy production at $ka \sim 1$, corresponding to a maximum of entropy, separates a domain of decreasing entropy production for small particles from a domain of increasing entropy production for large particles. As before this behavior is interpreted as arising from the anisotropy property of the scattering. Furthermore, if we compare the three curves in Figs. 3(a) and 3(b), it is interesting to see that $S$ ($\Delta S$) is significantly larger (smaller) when $d/l^*$ increases.

## IV. MULTIPLE SCATTERING AND IRREVERSIBILITY

This section has three basic objectives. The first of these is to clarify operationally what is meant by the irreversible evolution of the wave during scattering. Related to this, the second objective is to justify the introduction of the characteristic length scale of depolarization by a thermodynamic argument. The third objective is to discuss entropy production criteria for our specific situation.

Turn first to the physical significance of irreversibility. The important problem of irreversibility in matter-radiation interactions has been the subject of some considerable debate (see, e.g., Refs. [4–13] for recent discussions). We first recall some results of an important paper of Clark Jones [8]. In this paper the emphasis was on obtaining a list of reversible and irreversible operations on a beam of light. By means of heuristic arguments, this author assigned to a partially polarized beam two temperatures $T_1$ and $T_2$ and two values of entropy flux by Planck's radiation formula [$S_1 = S(T_1)$ and $S_2 = S(T_2)$]. When the beam is totally unpolarized (i.e., $T_1 = T_2 = T_u$), $S_1 = S_2 = S_u$. On the other hand, for a completely polarized light (i.e., $T_1 \neq 0$ and $T_2 \neq 0$), $S_1 \neq 0$ independent of the polarization form considered and $S_2 = 0$. The entropy becomes a function of macroscopic variables such as the radiance, frequency, and temperature. Then, to quote Clark Jones, "the pleasant position has now been achieved where both a temperature and an entropy are associated with any given beam of light. It is now possible to decide the question of reversibility or irreversibility by thermodynamic criteria. According to the second principle of thermodynamics, an operation on a beam of light (supposed an isolated system) will be reversible if the total entropy is unchanged and irreversible if the total entropy increases natural processes in which the total entropy decreases are of course impossible" [8]. The postulate of Clark Jones is that the principles of macroscopic equilibrium thermodynamics are compatible with the description of the interaction of polarized light with any optical system. However, this simple thermodynamic analysis raised some criticisms [13,41] as the following consideration shows. Let us consider the simple mixing of two completely polarized (one right circularly, indexed $r$; the other left circularly, indexed $l$): from the Clark Jones point of view, the two components have temperature $T_r = T_l = T_1$ and entropy $S_1$. As a consequence of the extensive character of entropy, we get for the mixture

$S=2S_1$ and $T=T_1$, which is incompatible with the fact that an incoherent superposition of two completely polarized beams can lead to a partially polarized light beam, even a completely unpolarized beam (see Appendix B for details). The key point to be stressed here is that any linear interaction is reversible if and only if $S$ remains invariant under the transformation $\mathbf{D}\to\mathbf{D}'$ and if no absorption occurs; otherwise it is irreversible. As a direct consequence, it is easy to prove that any unitary transformation $\mathbf{D}\to\mathbf{D}'=\Lambda\mathbf{D}\Lambda^{-1}$ constitutes a reversible operation on a beam of light, e.g., rotation of the state of polarization. From this point of view the problem of irreversibility can be understood when dissipation occurs in the medium (e.g., by selective absorption of states) or alternatively when taking into account correlations of phases and amplitudes of the field components induced by any interaction for which $\Delta S\neq 0$: this could be achieved in practice by either a dilatating interaction ($\Delta S<0$, e.g., induced by a polarizer) or by a contracting depolarizing interaction ($\Delta S>0$, e.g., induced by a polarization scrambler) [33].

At this stage, it remains to explain more precisely why a depolarization process actually implies that the system should tend to increase its entropy. Waves propagating through a strongly disordered medium emerge diffusively scattered in all directions. The effect of multiple scattering on the propagation of waves is to randomize the incident wave vector direction, the phase of the electric field vector, and its polarization. Let us first assume that the medium is static, i.e., this would be the case for a particular realization of the spatial disorder and that the wave is either monochromatic or quasimonochromatic, but with a coherence length which exceeds the characteristic path length $d^2/l^*$, i.e., spectral bandwidth $\Delta\omega \ll cl^*/d^2$. In such a case the time-invariant speckle pattern of scattered light, in which each speckle spot has a definite state of pure polarization, is characteristic of the given realization of disorder [32]. Experimentally, it has been shown by Freund that changing the polarization of the incident wave results in well-defined changes of the speckle pattern and this can be used to reconstruct the Stokes vector of the incident beam by making speckle correlation measurements on the diffusively scattered light [42]. In this monochromatic limit there is no entropy production and the scattering process appears to be reversible. In the opposite situation, i.e., $\Delta\omega \gg cl^*/d^2$, the speckle pattern is washed out and entropy can be produced. In like fashion, if the average is taken over all realizations of disorder, e.g., by rotating the sample, the speckle pattern is washed out and entropy can be produced. In that situation, after undergoing a sufficiently large number of scattering events and ensemble averaging the properties of the wave, the information contained in polarization is lost [21,32,43]. The irreversible radiative transfer from a low polarization temperature state to a high polarization temperature state results in a simple exponential law for the production of radiation entropy. The exponential law for the production of radiation entropy can be justified as follows. The production of radiation entropy is given by

$$\Delta S = S\left(ka, \frac{d+l^*}{l^*}\right) - S\left(ka, \frac{d}{l^*}\right) = \ln\left(\frac{s\left[P\left(ka, \frac{d}{l^*}\right)\right]}{s\left[P\left(ka, \frac{d+l^*}{l^*}\right)\right]}\right) . \tag{4.1}$$

Straightforward expansion leads to $\ln[s(x)] = \ln(2)+x^2/2+O(x^4)$ for $x\approx 0$. Substituting this result into Eq. (4.1) and making use of Eq. (A1) in the limit $d/\xi \gg 1$, i.e., $P\cong(2d/l)\sinh(1/\xi)\exp(d/\xi)$, Eq. (4.1) can be rewritten as

$$\Delta S \sim \left(\frac{d}{l^*}\right)^2 \exp\left(-2\frac{d}{\xi}\right) = \left(\frac{d}{l^*}\right)^2 \exp\left(-2\frac{d}{l^*}\frac{l^*}{\xi}\right) , \quad \frac{d}{l^*} \gg 1 , \tag{4.2}$$

which is consistent with the linearity observed of the large-optical thickness behavior of $\Delta S$, in the semilogarithmical plot in Fig. 2(b). It is remarkable that this exponential law is valid for both small-diameter ($ka \ll 1$) and large-diameter ($ka \gg 1$) spheres [Fig. 2(b)]. We like to emphasize that the exponential law was anticipated in an earlier study by heuristic arguments (see Fig. 3 in Ref. [18]).

Radiation cannot reach a steady state without interaction with matter. This idea implies specific constraints on the entropy production. The principle of minimum entropy production was first discussed systematically by Prigogine, who argued, using ideas from the thermodynamics of irreversible processes (Onsager reciprocity theorem), that the entropy production reaches its absolute minimum rate in the steady state consistent with the constraints which prevent the system from reaching equilibrium. Reference is made to Prigogine, as well as Glansdorff and Prigogine [16], for an overview. Another entropy production minimum principle was put forward by Tykodi [17]. By the approach of Tykodi, the entropy production is a minimum in the steady state. The topic of entropy production criterion has been the subject of some considerable debate (see, e.g., Ref. [44] for two recent discussions). In an important paper, Essex discussed why we should expect the Glansdorff-Prigogine and Tykodi minimum principles to apply for problems of radiative transfer [12]. The situation discussed in Sec. III is a remarkable example where there are no conserved quantities other than the energy for which the steady state is characterized by both maximum entropy and minimum production of entropy.

## V. CONCLUDING REMARKS

In this final section we summarize several aspects of the work described above. We have studied the thermodynamic properties of a plane radiation field. Just as in the study of thermodynamic equilibrium temperature, it is possible to define a polarization temperature. The formalism presented here is consistent with the second principle of thermodynamics. Theoretical discussion of depolarization has exploited a remarkable analogy with an order-disorder transition which permitted us to specify the radiative entropy and its production upon interaction with matter. Using such a framework we have been able to obtain a number of results which are of importance in interpreting the polarization effects in multiply scattered classical wave propagation by an optically dense medium. By studying ensemble-averaged properties over the system of diffusing scatterers we found that the production of radiation entropy decreases as the exponential of the optical depth of the medium. One can also conclude that the wave evolves towards its maximum entropy state, i.e., its higher polarization temperature state. Our results are quite general and may be used in other contexts for which waves are multiply scattered by a random medium, e.g., lidar exploration of the atmosphere and the ocean, optical imaging.

Many interesting questions remain. Ultimately, in this line of research, it would be desirable to characterize the entropy production for a nonlinear random scattering medium (i.e., when Onsager's reciprocity relationships are not valid). For such a system the state of minimum entropy production is no longer the state to which the system evolves, i.e., instabilities due to nonequilibrium dissipative structures [16]. Whether the exponential law for entropy production is a general state of affairs needs to be studied more carefully. In a future study, we plan also to investigate the influence of particulate shape (e.g., circular cross-sectioned cylindrical fibers) on entropy production.

## ACKNOWLEDGMENTS

We have benefited from many helpful discussions with A. S. Martinez and J. M. Schmitt. We wish also to thank Professor Craig Bohren, at the Pennsylvania University, for stimulating correspondence on various aspects of this subject. This research was started while C.B. was at Fourier University, Grenoble, France, the hospitality of which is acknowledged gratefully.

## APPENDIX A

In a recent Brief Report [21] we presented a Monte Carlo simulation treatment which accounts for the transmission of light through a dielectric medium which multiply scatters the probing light. In this appendix we briefly review the scattering laboratory (SLAB) procedure [21]. We assume that the medium is of the kind considered in Sec. III. Although developed for a general purpose, calculations are confined to the important case of uncorrelated, optically inactive spherical particles. A wave in such a medium is described by a random walk in which the mean length of each random step is given by $l$. The multiply scattered light results in a random speckle pattern whose intensity correlation function has been already measured [32].

We were able to write a closed-form equation of the degree of polarization of light transmitted in the far zone of the scattering medium

$$P_i=\frac{d}{l}\frac{\sinh\left[\frac{1}{\xi_i}\right]}{\sinh\left[\frac{d}{\xi_i}\right]}\ , \tag{A1}$$

where $\xi_i=(\zeta_i l/3)^{1/2}$ [$i=L$ ($C$) is the notation for a linear (circular) state of polarization] refer to the characteristic lengths of depolarization of the incident field for the slab geometry [21]. This analysis applies equally well for large spheres provided that $l$ is changed into the transport mean free path $l^*=1/\phi\sigma^*=l/[1-\langle\cos(\theta)\rangle]$. Here the transport scattering cross section for each scatterer is defined in the usual way as $\sigma^*=\int\sigma(\theta)[1-\cos(\theta)]d\Omega$ and $\langle\cos(\theta)\rangle$ is the mean cosine of the scattering angle $\theta$.

In our Monte Carlo analysis, each scattering is assumed to be elastic and is described by the standard Mie theory. The input parameters are the relative refractive index $m\equiv n_S/n_M=1.20$, where $n_S$ and $n_M$ are the refractive indices of the spheres ($n_S=1.59$ for polystyrene) and of the surrounding medium ($n_M=1.33$ for water), the size parameter $ka$ and $kl^*=1000$. Results of the corresponding Mie calculations are shown in Fig. 4, where the characteristic lengths of depolarization for incident linearly $\xi_L/l$ and circularly $\xi_C/l$ polarized light are plotted versus the dimensionless size parameter $ka$. In the case of particles large compared to the wavelength, a linearly or circularly polarized wave becomes depolarized over a distance that is significantly greater than the mean free path. It happens that

$$P_i\cong\frac{d}{l^*}\frac{\sinh\left[\frac{l^*}{lf(ka)}\right]}{\sinh\left[\frac{d}{lf(ka)}\right]} \tag{A2}$$

provides a reasonable fit to the $ka$ dependence of these lengths if the function $f$ is taken as a polynomial expansion. For instance, Fig. 4 depicts the fit to the numerical

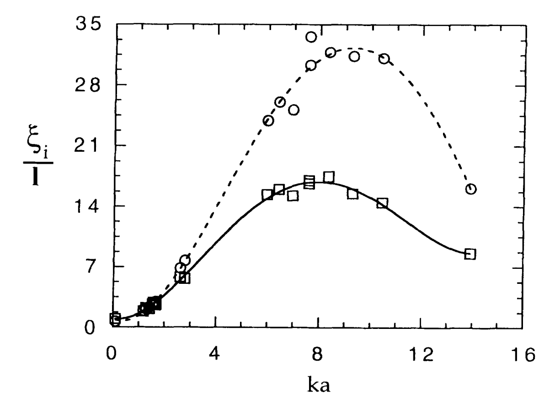


FIG. 4. Characteristic length of depolarization as a function of $ka$ fitted by a fourth-order polynomial expansion in $ka$ [see Eq. (A2)]. Linearly (solid line) and circularly (dotted line) polarized waves impinging on a slab composed of uncorrelated spherical particles of radius $a$ suspended in a liquid.

data concerning incident linearly and circularly polarized waves. Recent experiments have measured the depolarization length scales of light scattered from a random distribution of latex polystyrene microspheres ($1.23 < ka < 5.89$) in distilled water and are in good agreement with our simulation data [21].

## APPENDIX B

The purpose of this appendix is to find some bounds on the values of the degree of polarization of an incoherent mixture of partially polarized light beams. The method is based on the utilization of the concavity property of entropy and the linear superposition of polarization states for an incoherent mixture, i.e., if many beams are fitted together, one loses the information that tells from which ensemble a special beam stems, and therefore entropy increases. We start from the expression of the density matrix of the mixture

$$\mathbf{D}=\sum_{k=1}^{N}\lambda_k \mathbf{D}_k , \tag{B1}$$

where $D_k$ represent the density matrix for the $k$th light beam and $\lambda_k$ are the intensity weights ($\lambda_k = I_k/\sum_{k=1}^{N} I_k$ and $\sum_{k=1}^{N}\lambda_k=1$, $k\in\langle 1,N\rangle$ with $I_k$ denoting the intensity of the $k$th light beam) of the different components of the mixture. Using the concavity and superposition properties, one obtains the expression

$$\sum_{k=1}^{N}\lambda_k S(\mathbf{D}_k)\le S(\mathbf{D})\le \sum_{k=1}^{N}\lambda_k S(\mathbf{D}_k)-\sum_{k=1}^{N}\lambda_k \ln(\lambda_k) . \tag{B2}$$

The term $\sum_{k=1}^{N}\lambda_k\ln(\lambda_k)$ occurring on the right-hand side of inequality (B2) represents the mixing entropy contribution. Then (B2) can be rewritten in the form

$$\prod_{k=1}^{N}(\lambda_k)^{\lambda_k}\prod_{k=1}^{N}[s(P_k)]^{\lambda_k}\le s(P)\le \prod_{k=1}^{N}[s(P_k)]^{\lambda_k} , \tag{B3}$$

where the function $s(x)$ is defined by Eq. (2.2). Because $\prod_{k=1}^{N}[s(P_k)]^{\lambda_k}$ takes a value between $\frac{1}{2}$ and 1, there exists a unique value noted $P_\pi$ verifying

$$P_\pi = s^{-1}\left[\prod_{k=1}^{N}[s(P_k)]^{\lambda_k}\right] . \tag{B4}$$

Therefore we find that

$$s(P_\pi)\prod_{k=1}^{N}(\lambda_k)^{\lambda_k}\le s(P)\le s(P_\pi) . \tag{B5}$$

Two cases may occur. On the one hand, if $\frac{1}{2}\le s(P_\pi)\prod_{k=1}^{N}(\lambda_k)^{\lambda_k}\le 1$, then there exists a unique value $P^*$ given by $P^* = s^{-1}[s(P_\pi)\prod_{k=1}^{N}(\lambda_k)^{\lambda_k}]$ with

$$P^*\le P\le P_\pi , \tag{B6a}$$

or equivalently, in terms of polarization temperatures,

$$\tau_\pi \le \tau \le \tau^* . \tag{B6b}$$

On the other hand, if $0 < s(P_\pi)\prod_{k=1}^{N}(\lambda_k)^{\lambda_k} < \frac{1}{2}$, we have $0\le P\le P_\pi$. Because the function $x^\alpha$ with $0<\alpha\le 1$ is bijective strictly increasing one can also prove the inequality

$$P\le P_\pi \le P_m , \tag{B7a}$$

or equivalently formulated as

$$\tau_m \le \tau_\pi \le \tau , \tag{B7b}$$

where $P_m$ (to which corresponds $\tau_m$) is defined as the extremum of the degrees of polarization of the different beams.

To illustrate our results, let us consider the special but important case of the mixing of two pure states (i.e., $P_1=P_2=1$ and $\tau_1=\tau_2=0$) of equal intensity ($\lambda_1=\lambda_2=\frac{1}{2}$). It follows from the above treatment that $P_\pi=1$; hence $0\le P\le 1$. Consequently the resultant wave is a mixed state (i.e., a finite polarization temperature), except when the two states are orthogonally polarized for which the mixture leads to unpolarized light or when the two density matrices are identical for which $P$ remains equal to 1.


[1] W. Wien, Ann. Phys. (Leipzig) **52**, 132 (1894).

[2] M. von Laue, Ann. Phys. (Leipzig) **20**, 365 (1906); **23**, 1 (1907).

[3] M. Planck, *The Theory of Heat Radiation* (Dover, New York, 1959); see also P. T. Landsberg, *Thermodynamics with Quantum Statistical Illustrations* (Wiley-Interscience, New York, 1961) for an interesting discussion of the Planck entropy of pencil of radiation. The radiation temperature for a completely polarized pencil of radiation of frequency $\nu$ is defined as $1/T_\nu \equiv \partial s_\nu/\partial u_\nu$, where $s_\nu=(k\nu^2/c^2)[(1+x_\nu)\ln(1+x_\nu)-x_\nu\ln(x_\nu)]$ is the specific entropy and $x_\nu \equiv 1/[\exp(h\nu/kT)-1]$, with $h$ the Planck constant and $c$ the velocity of light *in vacuo;* see also R. Barakat, Opt. Acta **30**, 1171 (1983) for an extended derivation.

[4] P. Rosen, Phys. Rev. **96**, 555 (1954).

[5] A. Ore, Phys. Rev. **98**, 887 (1955).

[6] R. Wildt, Astrophys. J. **123**, 107 (1956); **140**, 1343 (1964); **143**, 363 (1966); **146**, 418 (1966); **174**, 69 (1972).

[7] S. Chandrasekhar, *Radiative Transfer* (Dover, New York, 1960).

[8] R. Clark Jones, J. Opt. Soc. Am. **53**, 1314 (1963).

[9] J. Oxenius, J. Quant. Spectrosc. Radiat. Transfer **6**, 65 (1966).

[10] W. Kröll, J. Quant. Spectrosc. Radiat. Transfer **7**, 715 (1967).

[11] A. Rueda, J. Opt. Soc. Am. **63**, 573 (1973).

[12] C. Essex, Astrophys. J. **285**, 279 (1984).

[13] U. Callies, Beitr. Phys. Atmosph. **62**, 212 (1989); U. Callies and F. Herbert, J. Appl. Math. Phys. **39**, 242 (1988).

[14] N. D. Gudkov Opt. Spektrosk. **68**, 224 (1990) [Opt. Spectrosc. (USSR) **68**, 130 (1990)].

[15] For a review of some of these contributions, see, for instance, F. C. Mackintosh and Sajeev John, Phys. Rev. B **40**, 2383 (1989); M. P. van Albada and A. Lagendjik, Phys. Rev. Lett. **55**, 2692 (1985); P. E. Wolf and G. Maret, *ibid.* **55**, 2696 (1989); Y. Kuga and A. Ishimaru, J. Opt. Soc. Am. A **1**, 831 (1984).
[16] See, for instance, the developments of the Brussels School: I. Prigogine, *Thermodynamics of Irreversible Processes* (Wiley, New York, 1971); S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (North-Holland, Amsterdam, 1962).
[17] R. Tykodi, *Thermodynamics of Steady States* (Macmillan, New York, 1967).
[18] D. Bicout and C. Brosseau, J. Phys. I **2**, 2047 (1992).
[19] S. J. van Enk and G. Nienhuis, Phys. Rev. A **46**, 1438 (1992).
[20] B. Chan Eu and K. Mao, Physica A **180**, 65 (1992).
[21] D. Bicout, C. Brosseau, A. S. Martinez, and J. M. Schmitt, Phys. Rev. E **49**, 1767 (1994).
[22] G. V. Rozenberg, Usp. Fiz. Nauk **56**, 77 (1955).
[23] B. Wen, L. Tsang, D. P. Winenbrenner, and A. Ishimaru, IEEE Trans. Geosci. Remote Sens. **28**, 46 (1990).
[24] C. E. Siewert, Astrophys. J. **245**, 1080 (1981).
[25] A. A. Golubentzev, Zh. Eksp. Teor. Fiz. **86**, 47 (1984) [Sov. Phys. JETP **59**, 26 (1984)].
[26] Yu. A. Kravtsov, S. M. Rytov, and V. I. Tatarskii, Usp. Fiz. Nauk **115**, 239 (1975) [Sov. Phys. Usp. **18**, 118 (1975)].
[27] A Ishimaru, *Wave Propagation and Scattering in Random Media* (Academic, New York, 1978).
[28] E. T. Jaynes, in *Annual Review of Physical Chemistry*, edited by S. Rabinovitch (Annual Reviews, Palo Alto, 1980).
[29] R. Simon and N. Mukunda, Phys. Lett. A **138**, 474 (1989).
[30] B. Jurco, Czech. J. Phys. B **37**, 1035 (1987).
[31] See *Geometric Phases in Physics*, edited by A. Shapere and F. Wilczek (World Scientific, Singapore, 1989); S. Pancharatnam, Proc. Ind. Acad. Sci. A **44**, 247 (1956); M. V. Berry, J. Mod. Phys. **34**, 1401 (1987).
[32] When the radiation is of thermal origin, the temporally random signals representing the electric field components can be described by zero mean stationary Gaussian random processes by virtue of the central-limit theorem; e.g., see I. Freund, Opt. Commun. **81**, 251 (1991); I. Freund, M. Kaveh, R. Berkovits, and M. Rosenbluh, Phys. Rev. B **42**, 2613 (1990) for a detailed study of the statistics of laser speckle patterns in multiple scattering dense random media (i.e., dispersions of micrometer sized particle in a polymer matrix and diffuse coatings). We assume here that a second-order statistics description of the field suffices to completely specify the multiple scattering process. Higher-order correlation functions could be introduced, but would obscure the results.
[33] Arguments suggesting a two-level method for the derivation of entropy in polarization optics were first formulated by C. Brosseau, C. R. Acad. Sci. Sér. B **310**, 181 (1990). Dilatating or contracting mechanisms of depolarization proceeding either by decorrelation of the phases and the amplitudes of the electric field components induced by the interaction with the material medium or by selective absorption of states have been reviewed by C. Brosseau, Optik (Stuttgart) **88**, 109 (1991).
[34] R. Barakat and C. Brosseau, J. Opt. Soc. Am. A **10**, 529 (1993).
[35] The following reference is very valuable: A. Wehrl, Rev. Mod. Phys. **50**, 221 (1978).
[36] The other invariant is $\mathrm{tr}(\mathbf{D})=1$.
[37] C. Brosseau (unpublished).
[38] See, for example, L. E. Reichl, *A Modern Course in Statistical Physics* (Arnold, London, 1980); R. Balescu, *Equilibrium and Non-Equilibrium Statistical Mechanics* (Wiley-Interscience, New York, 1975).
[39] As a historical note, it should be mentioned that the first attempt to assign a temperature to a monochromatic radiation was done by E. Weidemann, Ann. Phys. (Leipzig) **34**, 446 (1888).
[40] M. Born and E. Wolf, *Principles of Optics*, 6th ed. (Pergamon, Oxford, 1980).
[41] Professor Bohren kindly informed us that Clark Jones published one or two more papers on the entropy of radiation after his 1953 paper (Ref. [8]). Clark Jones published these additional papers because of his disappointment at the reception of his first paper; however, we were unable to locate them in the archival literature.
[42] I. Freund, Opt. Lett. **15**, 1425 (1990). Similarly, for diffusing (Brownian motion) scatterers, if the speckle pattern is studied on a time scale short compared to the multiple scattering dephasing time $\tau=cl^{*2}/\omega d^2D$, where $D$ is the particle-diffusion constant, then a well-defined speckle pattern is again obtained with no entropy production; see, for instance, M. Rosenbluh, M. Hoshen, I. Freund, and M. Kaveh, Phys. Rev. Lett. **58**, 2754 (1987).
[43] M. P. van Albada and A. Lagendijk, Phys. Rev. B **36**, 2353 (1987); E. Akkermans, P. E. Wolf, R. Maynard, and G. Maret, J. Phys. (Paris) **49**, 77 (1988).
[44] M. J. Klein and P. H. E. Meijer, Phys. Rev. **96**, 250 (1954); see also M. J. Klein, *ibid.* **98**, 1736 (1955). As emphasized by M. J. Klein, the MEP gives a characterization of the stationary state that is not generally equivalent to the characterization of the equilibrium state, in contrast to the maximum entropy method.