Stochastic approach to recombination luminescence with retrapping in the steady state

J. R. Swandic
Naval Surface Warfare Center (Code R41), White Oak, Silver Spring, Maryland 20903-5000
(Received 2 May 1991; revised manuscript received 15 August 1991)

Due to the discrete nature of electrons and holes, fluctuations will occur in various particle densities associated with thermally stimulated luminescence. The master equation for a simple stochastic model with one trapping level and one recombination level is derived. An expansion of this equation by van Kampen's Ω-expansion method allows one to recover the usual deterministic macroscopic kinetic equations as well as to obtain the Fokker-Planck equation governing the fluctuations of the various particle numbers. A set of evolution equations for the two lowest moments of the fluctuations is then found; since the solution of the Fokker-Planck equation is a multivariate Gaussian distribution, this completely determines the statistics of the fluctuations to this order of the Ω expansion. In the steady state, one can obtain expressions for the macroscopic particle densities that are of fairly simple form in the weak-source limit. Similarly, one can find and solve in this limit the algebraic equations for the second moments and the kinetic equations for the first moments of the fluctuations. From these, one derives explicit forms for the correlation functions, in particular, for the luminescence autocorrelation function, which is a sum of exponential decays. From measurements of the autocorrelation function of a luminescent material, one can deduce the model parameters.

I. INTRODUCTION

Thermally stimulated luminescence is a widely used technique in radiation dosimetry.[1,2] To explain the relation between the observed luminescence and the radiation dose to which the sample has been exposed, one usually invokes a drastically simplified model.[3] By combining various thermoluminescence observations with those of other methods, one can determine values for the model parameters[4] and thus characterize the dosimetric properties of the material. The simplified models still contain a large number of parameters; since in thermoluminescence one only observes the recombination radiation, only a subset of these parameters can be found. Also, one must have some idea of the physical processes occurring in a given material before a particular model with its attendant assumptions and approximations can be used with confidence. The advantage of thermoluminescence is the relative ease of measurement and the apparent simplicity of the result—a luminescence curve whose peak and general shape can be related to the parameters of the simplified physical model. It would thus be useful to have another luminescence quantity that is also easy to measure, can provide qualitative information about what processes occur in the sample material, and will give quantitative estimates for the model parameters (to find the unknown ones and to serve as a check on the ones found by other methods).

As in all physical systems, there are fluctuations in the various quantities. In particular, the discrete nature of matter restricts the number of electrons, holes, and photons in the various states to integral values. The properties of such fluctuations, especially those of the thermoluminescence itself, can be exploited to glean additional information about the physical processes in the material. If the model used to describe these processes is realistic, one can also obtain values for the model parameters. In such a case, then, these parameters would have real physical meaning. In any event, fluctuations in thermoluminescence have not been considered; it would seem useful to determine what additional information they can provide.

With the goal of finding the physical processes and model parameters involved in thermoluminescent dosimetry, one could thus propose a stochastic formulation of the deterministic models and kinetic equations. This allows one to incorporate the notion of fluctuations into the usual deterministic scheme. The purpose of this paper is to present the details of such a stochastic approach, which is based on van Kampen's Ω expansion.[5] To illustrate the ideas the simplest possible model will be used, in which there is one trapping level and one recombination level. Definitions for the various quantities used and the kinetic equations for the deterministic macroscopic version of this model are presented in the next section. Then a stochastic formulation is introduced by considering the probability that the system is in a certain state (defined by the number of electrons and holes in each level) and by deriving the master equation this probability must obey. Because its coefficients are nonlinear in the number of particles, the master equation is expanded in a small parameter that decreases as the size of the system increases. From this expansion the statistics of the particle densities are developed; the usual deterministic macroscopic kinetic equations are recovered and the Fokker-Planck equation governing the fluctuations is obtained. The equations for the fluctuations of the luminescence itself are found from a slight generalization of the model. In particular, one obtains the set of evolution equations for the two lowest moments of the various fluctuating quantities. In the linear noise approximation these fluctuations are described by a multivariate Gaussian distribution that

varies in time through its dependence on the macroscopic variables of the model. In the special case of the steady state, in which all macroscopic variables are independent of time, the fluctuations obey a set of linear differential equations with constant coefficients.

Another assumption that will be made is that the production rate J of electron-hole pairs is small; all quantities can be expanded in a power series in $J^{1/2}$. The main result is an expression for the lowest-order autocorrelation function for the observed intensity, from which one can in principle obtain all the parameters of the model.

II. THERMOLUMINESCENCE MODEL AND KINETIC EQUATIONS

In a sample of real material there are an unknown number and type of impurities and defects. Upon irradiation electron-hole pairs form; in this paper the model is considered in which the electrons migrate to traps and the holes migrate to recombination centers. Upon thermal activation the electrons escape from the traps, enter the conduction band, and eventually recombine with the holes in the recombination centers, which results in the emission of light. If the sample is continuously irradiated at a constant rate, electrons and holes will be generated continuously in the sample, and a nonzero (but in most cases small) steady state will exist. Such a situation has several advantages. It allows one to calculate more easily the fluctuations and to interpret them more readily in terms of the model parameters. In an experiment, it is easier to measure fluctuations about a constant mean field than about a rapidly varying signal as occurs in thermoluminescence studies. The detailed physical processes that occur are ignored and replaced by simple parameters to describe the complicated physics.

In a unit volume of the sample material there are N metastable traps, in which n electrons are trapped. Upon thermal activation there is a probability $s\exp(-E/k_BT)$ that in unit time an electron will leave a trap and enter the conduction band, where E is the energy depth of the trap below the conduction band, T is the temperature, k_B is the Boltzmann constant, and s is a pre-exponential factor. There are n_c electrons per unit volume in the conduction band; the probability per unit time that a conduction electron falls into a trap or into a recombination center is A_n and A_m, respectively. Each of the m_v holes per unit volume in the valence band has probability B_m per unit time to enter a recombination center. There are m holes per unit volume in the recombination centers of which there are M per unit volume. In this simple model there is only one trap level and one recombination level; there is no direct recombination from the traps, only through the conduction band. The intensity of the luminescence, I, is determined by the rate of recombination of electrons and holes; every recombination results in photon emission, and recombination is the only loss mechanism for the holes. All photons escape from the sample without absorption or other interaction. Replace the complicated details of the interaction of the incident radiation with the sample and of the production of the electron-hole pairs by the parameter J, which is the number of electrons (or holes) produced in a unit volume of the sample in a unit time interval. The electrons and holes are introduced into the conduction and valence band, respectively.

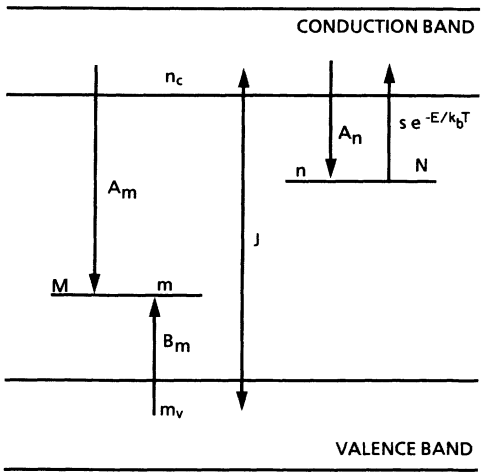

FIG. 1. Energy levels, transition probabilities, and electron, hole, and level densities for a simple generalized kinetic model that allows electron-hole production during luminescence.

The model is illustrated by Fig. 1 and satisfies the kinetic equations

$$\frac{dm}{dt} = -A_m m n_c + B_m (M-m) m_v \ , \tag{1}$$

$$\frac{dm_v}{dt} = -B_m (M-m) m_v + J \ , \tag{2}$$

$$\frac{dn}{dt} = A_n (N-n) n_c - s e^{-E/k_B T} n \ , \tag{3}$$

$$\frac{dn_c}{dt} = -A_m m n_c - A_n (N-n) n_c + s e^{-E/k_B T} n + J \ . \tag{4}$$

These are not independent, since

$$\frac{dm}{dt} + \frac{dm_v}{dt} = \frac{dn}{dt} + \frac{dn_c}{dt} \ . \tag{5}$$

For this model, conservation of charge leads to

$$m + m_v = n + n_c \ . \tag{6}$$

When J and m_v are set equal to zero, one recovers the usual kinetic equations for thermoluminescence.[6,7] The source term J can be expressed in terms of physical quantities as

$$J = \sum_k \int_E dE \, I_{\rm inc}(E) \sigma_k(E) N_k \ , \tag{7}$$

where $I_{\rm inc}(E)$ is the incident radiation flux at energy E and $\sigma_k(E)$ is the cross section for radiation of energy E to produce an electron-hole pair by interacting with sample component k, of which there are N_k per unit volume. The energy emitted per unit sample volume by electron-hole recombination is given by

$$I = A_m m n_c \ . \tag{8}$$

In this model this emission is due to fluorescence as well as to thermoluminescence. Integration of (1)–(4) for a given source J in the limit of very small $s \exp(-E/k_B T)$ allows one to calculate the initial values for the usual thermoluminescence case.[8]

In general the set of kinetic equations (1)–(4) cannot be solved analytically; one must resort to numerical solutions. There is one observed quantity, I, while there are seven sample parameters, A_n, A_m, B_m, s, E, N, and M, four initial conditions, $m(0)$, $n(0)$, $m_v(0)$, and $n_c(0)$, and two parameters that can be manipulated by the experimentalist, J and T. To obtain values for at least some of the sample parameters one usually incorporates results from several different sets of experimental measurements.[4] The kinetic equations govern the evolution of the macroscopic concentration of electrons and holes, whereas in any real system there are always fluctuations about the expected values. Since such fluctuations usually provide additional information about a system, it appears useful to study the fluctuations associated with the model in Fig. 1 and (1)–(4). To that end the next section takes up a stochastic formulation of the luminescence model of this section.

III. STOCHASTIC FORMULATION

In the previous section the discrete number of electrons and holes was described by continuous, differentiable functions. This was possible since the quantities are macroscopic; the number of particles is so large that any discrete change is relatively continuous. In reality, the number of particles is an integer (usually very large) and any changes (usually very small) are also integral as well as instantaneous. A continuous, differentiable function is still available, however, in the quantity $p(k,l,m,n|t)$, the probability that at time t there are k holes in the valence band, l electrons in the conduction band, m holes in recombination centers, and n electrons in traps. The four numbers k, l, m, and n are not independent; from (6)

$$k+m=l+n \ . \tag{9}$$

The formulation of a kinetic equation for $p(k,l,m,n|t)$ and its solution under suitable approximations will follow the work of van Kampen.[9] Consider the small change in p that occurs in a short time Δt by relating the probability there are k, l, m, n particles at time $t+\Delta t$ to the probabilities at time t that are connected to k, l, m, n by a single transition, i.e., that an electron leaves the conduction band and recombines with a hole, that a conduction electron becomes trapped, that a trapped electron is excited to the conduction band, that a hole leaves the valence band and enters a recombination center, and that an electron and hole produced by irradiation enter the conduction and valence bands. In the limit Δt goes to zero this leads to the master equation

$$\begin{aligned}\frac{d}{dt}p(k,l,m,n|t)=&\frac{A_m}{\Omega}(E_l E_m-1)lmp(k,l,m,n|t)+\frac{A_n}{\Omega}(E_l E_n^{-1}-1)l(N-n)p(k,l,m,n,|t)\\&+\sigma(E_l^{-1}E_n-1)np(k,l,m,n,|t)+\frac{B_m}{\Omega}(E_k E_m^{-1}-1)k(M-m)p(k,l,m,n|t)\\&+\Omega J(E_k^{-1}E_l^{-1}-1)p(k,l,m,n,|t)\ ,\end{aligned} \tag{10}$$

where for convenience the quantity

$$\sigma \equiv s e^{-E/k_B T} \tag{11}$$

and the step operator E defined by

$$E_n f(n,m)=f(n+1,m) \tag{12}$$

are introduced.

One difference between the deterministic quantities m_v, n_c, m, n and the probabilistic ones k,l,m,n is that the former refer to particle numbers per unit volume of the sample whereas the latter refer to the number of particles in the entire sample. This difference is expressed by the relation $m_v = k/\Omega$ and similarly for the other quantities; here Ω is the volume of the sample. This produces different units for the coefficients; for example, $[A(m_v)]$ is in units of $\mathrm{cm^3\,s^{-1}}$ while $[A(k)]$ is in units of $\mathrm{s^{-1}}$. To maintain the more customary former units, in which the coefficients do not depend on Ω, the explicit Ω dependence is shown in (10).[10] For convenience the source term J is taken to be a deterministic quantity, so that it has no fluctuations. The master equation (10) is still correct when any of the four quantities k,l,m,n vanish if the corresponding terms with $k-1$, $l-1$, $m-1$, $n-1$ are dropped. The equations for $m=M$ and $n=N$ have a natural cutoff. Since particles are continuously generated via J, there need not be an absolute upper limit on $(k+m)$ or $(l+n)$. A suitable initial condition for (10) is

$$p(k,l,m,n,|t=0)=\delta(k,k_0)\delta(l,l_0)\delta(m,m_0)\delta(n,n_0) \ . \tag{13}$$

Each process considered in (10) can affect in two ways the probability that a particular number of particles exists: The probability increases if another state changes into the state in question, and the probability decreases if this state changes into any other state. This balance has the immediate consequence of conserving the total probability. The kinetic equation for the expected value $\langle k \rangle$ of a quantity such as k can be derived by multiplying (10) by k and summing over the four variables; it contains the higher-order moment in $k(M-m)$. This difficulty (nonclosure of the moment equations) arises because the coefficients of the p's in (10) are not linear in the particle

numbers. To obtain the expected values and the fluctuations of the particle numbers, one must use a more sophisticated systematic expansion of the master equation. One such method is the Ω expansion of van Kampen,[5] which is discussed in the next section.

IV. EXPANSION OF THE MASTER EQUATION

Since the relative size of fluctuations decreases as the system becomes larger, it is natural to approximate (10) by an expansion in the small parameter Ω^{-1}.[5] To do so one must display explicitly the Ω dependence of all the terms in the equation. Now $p(k,l,m,n|t)$ itself has some characteristic dependence on Ω. For a linear system of k particles the fluctuations are of the order $k^{1/2}$, so their relative effect on the macroscopic properties goes like $k^{-1/2}$. Thus, the relative importance of the fluctuations depends on the size of the system (denoted by Ω). One expects p to have a sharp peak around Ω with a width $\sim\Omega^{1/2}$. To incorporate these observations into an expansion of the master equation, define k, l, m, and n by the relations[11]

$$k=\Omega\rho(t)+\Omega^{1/2}\tau\ , \tag{14}$$

$$l=\Omega\phi(t)+\Omega^{1/2}\xi\ , \tag{15}$$

$$m=\Omega\psi(t)+\Omega^{1/2}\eta\ , \tag{16}$$

$$n=\Omega\chi(t)+\Omega^{1/2}\xi\ , \tag{17}$$

where ρ, ϕ, ψ, and χ are as yet undefined functions and τ, ξ, η, and ζ are variables more directly tied to the fluctuations. The first set of terms, in Ω, are macroscopic; if they are chosen to follow the motion of the peak in time, the p will not depend on Ω when expressed as functions of τ, ξ, η, and ζ. Then write

$$p(k,l,m,n|t)=p(\Omega\rho+\Omega^{1/2}\tau,\ \Omega\phi+\Omega^{1/2}\xi,\ \Omega\psi+\Omega^{1/2}\eta,\ \Omega\chi+\Omega^{1/2}\zeta|t)=\Pi(\tau,\xi,\eta,\zeta|t)\ . \tag{18}$$

Since

$$E_\tau\Pi(\tau)=\Pi(\tau+\Omega^{-1/2})=\left[1+\Omega^{-1/2}\frac{\partial}{\partial\tau}+\frac{1}{2}\Omega^{-1}\frac{\partial^2}{\partial\tau^2}+\cdots\right]\Pi(\tau)\ , \tag{19}$$

the master equation (10) can be written with explicit Ω dependence as

$$\begin{aligned}\frac{d}{dt}p(k,l,m,n,|t)&=\frac{\partial\Pi}{\partial t}-\Omega^{1/2}\left[\frac{\partial\Pi}{\partial\tau}\frac{d\rho}{dt}+\frac{\partial\Pi}{\partial\xi}\frac{d\phi}{dt}+\frac{\partial\Pi}{\partial\eta}\frac{d\psi}{dt}+\frac{\partial\Pi}{\partial\zeta}\frac{d\chi}{dt}\right]\\
&=A_m\Omega^{-1}\{\Omega^{-1/2}(\partial_\xi+\partial_\eta)+\Omega^{-1}[\partial_\xi\partial_\eta+\tfrac{1}{2}(\partial_\xi^2+\partial_\eta^2)]+\cdots\}(\Omega\phi+\Omega^{1/2}\xi)(\Omega\psi+\Omega^{1/2}\eta)\Pi\\
&\quad+A_n\Omega^{-1}\{\Omega^{-1/2}(\partial_\xi-\partial_\zeta)+\Omega^{-1}[-\partial_\xi\partial_\zeta+\tfrac{1}{2}(\partial_\xi^2+\partial_\zeta^2)]+\cdots\}\\
&\quad\times(\Omega\phi+\Omega^{1/2}\xi)[\Omega(N-\chi)-\Omega^{1/2}\zeta]\Pi\\
&\quad+\sigma\{\Omega^{-1/2}(-\partial_\xi+\partial_\zeta)+\Omega^{-1}[-\partial_\xi\partial_\zeta+\tfrac{1}{2}(\partial_\xi^2+\partial_\zeta^2)]+\cdots\}(\Omega\chi+\Omega^{1/2}\zeta)\Pi\\
&\quad+B_m\Omega^{-1}\{\Omega^{-1/2}(\partial_\tau-\partial_\eta)+\Omega^{-1}[-\partial_\tau\partial_\eta+\tfrac{1}{2}(\partial_\tau^2+\partial_\eta^2)]+\cdots\}\\
&\quad\times(\Omega\rho+\Omega^{1/2}\tau)[\Omega(M-\psi)-\Omega^{1/2}\eta]\Pi\\
&\quad+J\Omega\{\Omega^{-1/2}(-\partial_\tau-\partial_\xi)+\Omega^{-1}[\partial_\tau\partial_\xi+\tfrac{1}{2}(\partial_\tau^2+\partial_\xi^2)]+\cdots\}\Pi\ .\end{aligned} \tag{20}$$

Expand this equation as a series in the system volume Ω, with terms proportional to $\Omega^{1/2}$, Ω^0, $\Omega^{-1/2}$, and so on. The leading term, in $\Omega^{1/2}$, must vanish so (20) will not diverge as Ω becomes infinitely large; this condition is satisfied if

$$-\frac{d\rho}{dt}=B_m\rho(M-\psi)-J\ , \tag{21}$$

$$-\frac{d\phi}{dt}=A_m\phi\psi+A_n\phi(N-\chi)-\sigma\chi-J\ , \tag{22}$$

$$-\frac{d\psi}{dt}=A_m\phi\psi-B_m\rho(M-\psi)\ , \tag{23}$$

$$-\frac{d\chi}{dt}=-A_n\phi(N-\chi)+\sigma\chi\ , \tag{24}$$

which are just the macroscopic kinetic equations (1)–(4) upon making the identification $\rho\rightarrow m_v$, $\phi\rightarrow n_c$, $\psi\rightarrow m$, and $\chi\rightarrow n$. The initial conditions are

$$\rho(0)=k_0/\Omega,\quad \phi(0)=l_0/\Omega\ ,\qquad \psi(0)=m_0/\Omega,\quad \chi(0)=n_0/\Omega\ . \tag{25}$$

There is also the conservation relation

$$\rho+\psi=\phi+\chi\ . \tag{26}$$

Now gather together the terms in (20) that are proportional to Ω^0, to obtain

$$\frac{\partial \Pi}{\partial t} = A_m(\partial_\xi+\partial_\eta)(\phi\eta+\psi\xi)\Pi + A_m\phi\psi[\partial_\xi\partial_\eta+\tfrac{1}{2}(\partial_\xi^2+\partial_\eta^2)]\Pi$$
$$+ A_n(\partial_\xi-\partial_\zeta)[-\phi\zeta+(N-\chi)\xi]\Pi + A_n\phi(N-\chi)[-\partial_\xi\partial_\zeta+\tfrac{1}{2}(\partial_\xi^2+\partial_\zeta^2)]\Pi$$
$$+\sigma(-\partial_\xi+\partial_\zeta)\zeta\Pi+\sigma\chi[-\partial_\xi\partial_\zeta+\tfrac{1}{2}(\partial_\xi^2+\partial_\zeta^2)]\Pi$$
$$+B_m(\partial_\tau-\partial_\eta)[(M-\psi)\tau-\rho\eta]\Pi+B_m\rho(M-\psi)[-\partial_\tau\partial_\eta+\tfrac{1}{2}(\partial_\tau^2+\partial_\eta^2)]\Pi+J[\partial_\tau\partial_\xi+\tfrac{1}{2}(\partial_\tau^2+\partial_\xi^2)]\Pi\ . \quad (27)$$

This is a linear Fokker-Planck equation whose solution is a multivariate Gaussian distribution.[12] One need only find the two lowest moments to determine the solution completely. To this end define the mean or expected values

$$\langle\tau\rangle = \int\int\int\int \tau\Pi\, d\tau\, d\xi\, d\eta\, d\zeta \quad (28)$$

and similarly for the other three fluctuation variables. Normalize the probability density Π by imposing the condition

$$\int\int\int\int \Pi\, d\tau\, d\xi\, d\eta\, d\zeta = 1\ . \quad (29)$$

Since the fluctuations are finite, the integral over all fluctuation space of any spatial derivatives of Π will vanish by partial integration. Multiply (27) successively by τ, ξ, η, and ζ and integrate each resulting equation over all of fluctuation space, $d\tau\, d\xi\, d\eta\, d\zeta$. Integrate by parts to obtain the first moment equations

$$\frac{\partial}{\partial t}\langle\tau\rangle = -B_m(M-\psi)\langle\tau\rangle + B_m\rho\langle\eta\rangle\ , \quad (30)$$

$$\frac{\partial}{\partial t}\langle\xi\rangle = -[A_m\psi+A_n(N-\chi)]\langle\xi\rangle - A_m\phi\langle\eta\rangle+(\sigma+A_n\phi)\langle\zeta\rangle\ , \quad (31)$$

$$\frac{\partial}{\partial t}\langle\eta\rangle = B_m(M-\psi)\langle\tau\rangle - A_m\psi\langle\xi\rangle - (A_m\phi+B_m\rho)\langle\eta\rangle\ , \quad (32)$$

$$\frac{\partial}{\partial t}\langle\zeta\rangle = A_n(N-\chi)\langle\xi\rangle-(\sigma+A_n\phi)\langle\zeta\rangle\ . \quad (33)$$

As one expects,

$$\frac{\partial}{\partial t}(\langle\tau\rangle+\langle\eta\rangle) = \frac{\partial}{\partial t}(\langle\xi\rangle+\langle\zeta\rangle) \quad (34)$$

and the charge conservation condition yields

$$\langle\tau\rangle+\langle\eta\rangle = \langle\xi\rangle+\langle\zeta\rangle\ . \quad (35)$$

Note that while J does not explicitly appear in (30)–(33), it does enter through its influence on the values of ρ, ϕ, ψ, and χ.

For the second-order moments, multiply in turn by $\tau^2, \tau\xi, \tau\eta, \ldots$ before integrating (27). Since τ can be replaced by $\xi+\zeta-\eta$, only the latter quantities need to be calculated. Again by partial integration the equations for $\langle\xi^2\rangle$, $\langle\eta^2\rangle$, and $\langle\zeta^2\rangle$ become

$$\frac{\partial}{\partial t}\langle\xi^2\rangle = -2[A_m\psi+A_n(N-\chi)]\langle\xi^2\rangle - 2A_m\phi\langle\xi\eta\rangle + 2(\sigma+A_n\phi)\langle\xi\zeta\rangle+\phi[A_m\psi+A_n(N-\chi)] + J+\sigma\chi\ , \quad (36)$$

$$\frac{\partial}{\partial t}\langle\eta^2\rangle = -2(B_m\rho+A_m\phi)\langle\eta^2\rangle+2B_m(M-\psi)\langle\tau\eta\rangle - 2A_m\psi\langle\xi\eta\rangle + A_m\phi\psi+B_m\rho(M-\psi)\ , \quad (37)$$

$$\frac{\partial}{\partial t}\langle\zeta^2\rangle = -2(\sigma+A_n\phi)\langle\zeta^2\rangle+2A_n(N-\chi)\langle\xi\zeta\rangle + A_n\phi(N-\chi)+\sigma\chi\ . \quad (38)$$

To obtain the cross terms, such as $\langle\xi\eta\rangle$, insert ξ into the $\langle\ \rangle$ of (32) and η into the $\langle\ \rangle$ of (31); to the sum of these add the term in $\xi\eta\partial_\xi\partial_\eta$ of (27), which becomes J times the integral over Π (which is equal to unity). Thus, by inspection of (30)–(33) one obtains

$$\frac{\partial}{\partial t}\langle\xi\eta\rangle = -A_m\psi\langle\xi^2\rangle - A_m\phi\langle\eta^2\rangle+B_m(M-\psi)\langle\tau\xi\rangle - [A_m(\phi+\psi)+A_n(N-\chi)+B_m\rho]\langle\xi\eta\rangle + (\sigma+A_n\phi)\langle\eta\zeta\rangle+A_m\phi\psi\ , \quad (39)$$

$$\frac{\partial}{\partial t}\langle\xi\zeta\rangle = A_n(N-\chi)\langle\xi^2\rangle+(\sigma+A_n\phi)\langle\zeta^2\rangle - \sigma\chi - A_n(N-\chi)\phi - [\sigma+A_n\phi+A_m\psi+A_n(N-\chi)]\langle\xi\zeta\rangle - A_m\phi\langle\eta\zeta\rangle\ , \quad (40)$$

$$\frac{\partial}{\partial t}\langle\eta\zeta\rangle = B_m(M-\psi)\langle\tau\zeta\rangle+A_n(N-\chi)\langle\xi\eta\rangle - A_m\psi\langle\xi\zeta\rangle - [\sigma+(A_n+A_m)\phi+B_m\rho]\langle\eta\zeta\rangle\ . \quad (41)$$

The covariance $\sigma^2_{\alpha\beta}$ is defined to be

$$\sigma^2_{\alpha\beta} \equiv \langle(\alpha-\langle\alpha\rangle)(\beta-\langle\beta\rangle)\rangle = \langle\alpha\beta\rangle-\langle\alpha\rangle\langle\beta\rangle \equiv \langle\langle\alpha\beta\rangle\rangle\ , \quad (42)$$

so the covariances satisfy the same kinetic equations as do the second moments (this is obvious for the cross terms from the way in which they were derived).

In an actual experiment none of these quantities would be observed directly. The statistics of interest are those of the emitted light. From the previous derivations, the model of Fig. 1 is self-contained and makes no reference to any radiation emission. The relation $I = A_m m n_c$ is imposed after m and n_c are calculated from the kinetic equations. The problem is to relate the fluctuations in

this self-contained model to the observable fluctuations in the emitted radiation intensity, and to remain consistent with the various approximations of the Ω expansion in so doing. One way to do this is to consider the more general probability $p(i,k,l,m,n|t)$, the probability that i photons have been emitted by the sample up to time t, and so on as before for the other variables. This is also the probability that a perfect detector (no internal noise and it counts all incident photons) has recorded i counts up to time t; this approach can be generalized to include detector statistics, but to illustrate the method the simplest possibility will be used. It should also be noted that i refers to the integrated number of photons emitted up to time t, not the intensity at time t; the latter is the time derivative of the former.

To implement this, replace (10) by

$$\frac{d}{dt}p(i,k,l,m,n|t)=\frac{A_m}{\Omega}(E_i^{-1}E_lE_m-1)\times lmp(i,k,l,m,n|t)+\dots , \tag{43}$$

that is, substitute the five-variable probability for the four-variable one and replace the first term of (10) by the term shown explicitly in (43); the ellipses refer to the remaining (unchanged) terms. Also set

$$i=\Omega\lambda+\Omega^{1/2}\nu , \tag{44}$$

so that $p(i,k,l,m,n,|t)\rightarrow\Pi(\nu,\tau,\xi,\eta,\zeta|t)$ and (20) becomes

$$\frac{\partial\Pi}{\partial t}-\Omega^{1/2}\left[\frac{\partial\Pi}{\partial\nu}\frac{d\lambda}{dt}+\cdots\right]=A_m\Omega^{-1}[\Omega^{-1/2}(-\partial_\nu)+\Omega^{-1}(-\partial_\nu\partial_\xi-\partial_\nu\partial_\eta+\tfrac{1}{2}\partial_\nu^2)+\cdots]\times(\Omega\phi+\Omega^{1/2}\xi)(\Omega\psi+\Omega^{1/2}\eta)\Pi+\cdots , \tag{45}$$

where the ellipses refer to all the terms on both sides of (20); they are unchanged except that Π now includes the ν dependence. The leading term, in $\Omega^{1/2}$, of (45) again must vanish, so that

$$-\frac{d\lambda}{dt}=-A_m\phi\psi . \tag{46}$$

Since the identification $\phi\rightarrow n_c$ and $\psi\rightarrow m$ has already been made, this becomes the macroscopic intensity relation if one sets

$$\frac{d\lambda}{dt}=I,\quad \lambda(t)=\lambda(0)+\int_0^t I(t')dt' . \tag{47}$$

The terms in (45) proportional to Ω^0 yield the equation

$$\frac{\partial\Pi}{\partial t}=-A_m(\phi\eta+\psi\xi)\frac{\partial\Pi}{\partial\nu}+A_m\phi\psi(-\partial_\nu\partial_\xi-\partial_\nu\partial_\eta+\tfrac{1}{2}\partial_\nu^2)\Pi+\dots , \tag{48}$$

where the ellipses refer to all the terms on the right-hand side of (27). Now

$$\Pi(\tau,\xi,\eta,\zeta|t)=\int\Pi(\nu,\tau,\xi,\eta,\zeta|t)d\nu , \tag{49}$$

so integration over ν reduces (48) to (27). The extra terms in $\partial\Pi/\partial\nu$ in (48) contribute nothing to the expected values $\langle\tau\rangle$, $\langle\xi\rangle$, $\langle\eta\rangle$, and $\langle\zeta\rangle$. Similarly, the remaining terms contribute nothing to $\langle\nu\rangle$. Consequently, (30)–(33) are recovered along with

$$\frac{\partial}{\partial t}\langle\nu\rangle=A_m(\phi\langle\eta\rangle+\psi\langle\xi\rangle) . \tag{50}$$

Equations (30)–(33) again form a self-contained system independent of the emitted radiation; the $\langle\eta\rangle$ and $\langle\xi\rangle$ derived from them [as well as ϕ and ψ from (24)] are inserted into (50) to find $\langle\nu\rangle$. Also, just as $d\lambda/dt$ was equated to the intensity I, $\partial\langle\nu\rangle/\partial t$ can be considered to be the mean value of the (first-order) fluctuations in the intensity. The second-order moments can also be readily found from (48). The pairs involving only τ, ξ, η, and ζ pick up no contribution from the $\partial\Pi/\partial\nu$ terms; the set (36)–(41) is recovered, and again a self-contained system of equations is obtained. The pairs involving ν lead to

$$\frac{\partial}{\partial t}\langle\nu^2\rangle=2A_m(\phi\langle\nu\eta\rangle+\psi\langle\nu\xi\rangle)+A_m\phi\psi , \tag{51}$$

$$\frac{\partial}{\partial t}\langle\nu\xi\rangle=-[A_m\psi+A_n(N-\chi)]\langle\nu\xi\rangle-A_m\phi\langle\nu\eta\rangle+(\sigma+A_n\phi)\langle\nu\zeta\rangle+A_m(\phi\langle\xi\eta\rangle+\psi\langle\xi^2\rangle)-A_m\phi\psi , \tag{52}$$

$$\frac{\partial}{\partial t}\langle\nu\eta\rangle=B_m(M-\psi)\langle\nu\tau\rangle-A_m\psi\langle\nu\xi\rangle-(A_m\phi+B_m\rho)\langle\nu\eta\rangle+A_m(\phi\langle\eta^2\rangle+\psi\langle\xi\eta\rangle)-A_m\phi\psi , \tag{53}$$

$$\frac{\partial}{\partial t}\langle\nu\zeta\rangle=A_n(N-\chi)\langle\nu\xi\rangle-(\sigma+A_n\phi)\langle\nu\zeta\rangle+A_m(\phi\langle\eta\zeta\rangle+\psi\langle\xi\zeta\rangle). \tag{54}$$

The second moments that do not involve ν can be found separately by solving (36)–(41) and are then inserted into (51)–(54) to yield a set of inhomogeneous differential equations for the second moments involving ν. Thus, the kinetic equations for the model of Fig. 1 can be solved by themselves; these solutions can then be inserted into the equations for the emitted intensity to find its statistics. The quantities found will be the macroscopic functions ρ, ϕ, ψ, χ, and $d\lambda/dt$ and the two lowest moments of the multivariate Gaussian probability distribution in the variables τ, ξ, η, ζ, and $\partial\nu/\partial t$. These are related to the original particle densities by, for example,

$$m_v\sim k/\Omega\sim\rho+\Omega^{-1/2}\tau , \tag{55}$$

where τ is determined by the moments $\langle\tau\rangle$ and $\langle\tau^2\rangle$.

V. THE STEADY-STATE MACROSCOPIC SOLUTION

Thermoluminescence is used to determine the radiation dose to which a sample has been exposed.[1,2] In a typical situation the sample material has a weak response to the incident radiation, that is, the production rate of electron-hole pairs is very small. After a sufficiently long exposure time there is an appreciable number of trapped electrons and holes, while the bands are essentially empty. When the sample is heated the luminescence will increase, reach a peak, and then decrease to zero as the trapped electrons are depleted. If the sample is concurrently irradiated by electron-hole pair-producing radiation and heated to a constant temperature high enough to excite trapped electrons into the conduction band, there will exist a steady state in which the particle numbers are not zero.

In the presence of constant incident radiation and constant sample temperature, after a sufficiently long time a steady state will be achieved in which the time derivatives of the macroscopic equations (21)–(24) vanish, leading to a set of algebraic equations. Since these equations are not independent, also consider the charge conservation condition (26). These functions of time are now constants, the steady-state values; thus $\rho(t)\rightarrow\rho^s$, but for convenience ρ^s will be written as ρ. First combine the stationary versions of (21) and (23) to find

$$I = A_m\phi\psi = J \ , \tag{56}$$

that is, in the steady state of this model electrons and holes recombine (and so emit radiation) at the same rate at which they are produced. The steady-state emission reveals nothing about the sample ($I=J$ independent of the model parameters), although absolute measurements of I and a knowledge of J could discern the presence of nonradiative recombination processes.

Solve in turn the stationary versions of (21), (24), and (56) to obtain

$$\rho=\frac{J}{B_m}\frac{1}{(M-\psi)}, \quad \psi=M-\frac{J}{B_m}\frac{1}{\rho} \ , \tag{57}$$

$$\phi=\frac{\sigma\chi}{A_n(N-\chi)}, \quad \chi=\frac{A_nN\phi}{\sigma+A_n\phi} \ , \tag{58}$$

$$\phi=\frac{J}{A_m}\frac{1}{\psi}, \quad \psi=\frac{J}{A_m}\frac{1}{\phi} \ . \tag{59}$$

By using these equations, one can express the functions ρ, ϕ, ψ, and χ in terms of any one of the four. Write (26) in terms of each of these in turn. For example, $\psi(\phi)+\rho(\phi)=\chi(\phi)+\phi$ becomes the fourth-order polynomial

$$\begin{aligned} A_nA_mB_mM\phi^4+[&A_mB_mM(\sigma+A_nN) \\ &-JA_n(A_m+B_m)]\phi^3 \\ -J[&\sigma(A_m+B_m)+A_nB_m(N+M)]\phi^2 \\ &-JB_m[\sigma M-J(A_n/A_m)]\phi+J^2\sigma B_m/A_m=0 \ ; \end{aligned} \tag{60}$$

similar equations are obtained for the other three variables.

One can use these polynomials to find the various steady-state electron and hole densities in the bands and traps as functions of the model parameters. When $J=0$, all four quantities have triple roots at zero, one of which is the physically correct (positive for all positive J) solution. Even if it were possible to find analytic expressions for polynomials such as these, the solutions would be quite complicated expressions involving the model parameters. To maintain simple expressions that can be interpreted in a straightforward manner, consider the special case in which J is small in some sense (which will be specified later). In the limit $J=0$, all four quantities ρ, ϕ, ψ, and χ vanish, so one would expect them to remain small for small J and in fact to be proportional to some power of J. Thus, expand all four quantities in power series in J, and retain only the first two terms in the final results. From (56), the leading term for the expansion of both ϕ and ψ is proportional to $J^{1/2}$. Hence, write

$$\phi(J)=\phi_1J^{1/2}+\phi_2J+\phi_3J^{3/2}+\cdots \ , \tag{61}$$

$$\psi(J)=\psi_1J^{1/2}+\psi_2J+\psi_3J^{3/2}+\cdots \ . \tag{62}$$

Substitute the expansion for $\phi(J)$ into the second part of (58) to find

$$\begin{aligned} \chi(J)&=\frac{A_nN}{\sigma}\{\phi_1J^{1/2}+[\phi_2-(A_n/\sigma)\phi_1^2]J+\cdots\} \\ &=\chi_1J^{1/2}+\chi_2J+\chi_3J^{3/2}+\cdots \ . \end{aligned} \tag{63}$$

Similarly substitute the expansion for $\psi(J)$ into the first part of (57) to obtain

$$\rho(J)=\frac{J}{MB_m}+\frac{J^{3/2}\psi_1}{M^2B_m}+\cdots=\rho_2J+\rho_3J^{3/2}+\cdots \ . \tag{64}$$

Multiply expansions (61) and (62) and insert into (56) to obtain

$$\psi_1=1/(A_m\phi_1) \ , \tag{65}$$

$$\psi_2=-\phi_2/(A_m\phi_1^2) \ . \tag{66}$$

Thus all first and second coefficients can be expressed in terms of ϕ_1 and ϕ_2.

Substitute the expansion (61) for $\phi(J)$ into (60), the fourth-order polynomial for ϕ; the coefficient of the lowest-order term yields

$$\phi_1=\left[\frac{\sigma}{A_m(\sigma+A_nN)}\right]^{1/2} \ . \tag{67}$$

The next term gives

$$\phi_2=\frac{\sigma A_m(\sigma+A_nN)+MNA_n^2B_m}{2MA_mB_m(\sigma+A_nN)^2} \ . \tag{68}$$

Then by (63)–(66) one obtains

$$\psi_1=\left[\frac{\sigma+A_nN}{\sigma A_m}\right]^{1/2}, \tag{69}$$

$$\psi_2=-\left[\frac{\sigma A_m(\sigma+A_nN)+MNA_n^2B_m}{2MA_mB_m\sigma(\sigma+A_nN)}\right], \tag{70}$$

$$\chi_1=\frac{A_nN}{\sigma}\left[\frac{\sigma}{A_m(\sigma+A_nN)}\right]^{1/2}, \tag{71}$$

$$\chi_2=\frac{A_nN}{2\sigma MA_mB_m(\sigma+A_nN)^2}[\sigma A_m(\sigma+A_nN) - A_nB_mM(2\sigma+A_nN)], \tag{72}$$

$$\rho_2=\frac{1}{MB_m}, \tag{73}$$

$$\rho_3=\frac{1}{M^2B_m}\left[\frac{\sigma+A_nN}{\sigma A_m}\right]^{1/2}. \tag{74}$$

With these results it is possible to set a condition on how small "small J" must be, viz., the second term in a series must be small in comparison to the first term. For example, in the series (61), $\phi_2 J \ll \phi_1 J^{1/2}$ or $J^{1/2} \ll \phi_1/\phi_2$. From ψ, the condition is $J^{1/2} \ll \psi_1/\psi_2 = \phi_1/\phi_2$ as before. For χ, one finds

$$J^{1/2} \ll \chi_1/\chi_2 = \phi_1/(\phi_2 - A_n\phi_1^2/\sigma) \approx \phi_1/\phi_2 .$$

Finally, for ρ the condition is $J^{1/2} \ll \rho_2/\rho_3 = MA_m\phi_1$. There is also a limit on how small J can be. Terms in the fluctuations on the order of single particles, i.e., of order Ω^{-1} relative to the macroscopic values, are given by terms in the Ω expansion of higher order than the linear-noise approximation ($\Omega^{-1/2}$ relative to the macroscopic terms) of the next section. Thus, if the luminescence ($=J$) is so weak that single photons must be observed, higher-order terms of the Ω expansion must also be considered.[13]

VI. THE STEADY-STATE FLUCTUATIONS

Just as the differential equations for the deterministic quantities became algebraic equations in the steady state, so do the differential equations (36)–(41) for the covariances. One obtains the set of six equations for the steady state

$$0=-[A_m\psi+A_n(N-\chi)]\langle\xi^2\rangle - A_m\phi\langle\xi\eta\rangle + (\sigma+A_n\phi)\langle\xi\xi\rangle + J + \sigma\chi , \tag{75}$$

$$0=-[A_m\phi+B_m(M-\psi+\rho)]\langle\eta^2\rangle + [-A_m\psi+B_m(M-\psi)]\langle\xi\eta\rangle + B_m(M-\psi)\langle\eta\zeta\rangle + J , \tag{76}$$

$$0=-(\sigma+A_n\phi)\langle\xi^2\rangle + A_n(N-\chi)\langle\xi\xi\rangle + \sigma\chi , \tag{77}$$

$$0=[-A_m\psi+B_m(M-\psi)]\langle\xi^2\rangle - A_m\phi\langle\eta^2\rangle - [A_m(\phi+\psi)+A_n(N-\chi)+B_m(M-\psi+\rho)]\langle\xi\eta\rangle + B_m(M-\psi)\langle\xi\zeta\rangle + (\sigma+A_n\phi)\langle\eta\zeta\rangle + J , \tag{78}$$

$$0=A_n(N-\chi)\langle\xi^2\rangle + (\sigma+A_n\phi)\langle\zeta^2\rangle - [\sigma+A_m\psi+A_n(N-\chi+\phi)]\langle\xi\zeta\rangle - A_m\phi\langle\eta\zeta\rangle - 2\sigma\chi , \tag{79}$$

$$0=B_m(M-\psi)\langle\xi^2\rangle + A_n(N-\chi)\langle\xi\eta\rangle + [-A_m\psi+B_m(M-\psi)]\langle\xi\zeta\rangle - [\sigma+(A_m+A_n)\phi+B_m(M-\psi+\rho)]\langle\eta\zeta\rangle . \tag{80}$$

Here ξ, η, and ζ are fluctuations associated with the macroscopic quantities ϕ, ψ, and χ. Just as the macroscopic quantity $\rho(=\phi+\chi-\psi)$ was eliminated, so is its fluctuation $\tau(=\xi+\zeta-\eta)$.

For small J, it would seem appropriate to expand these equations in powers of $J^{1/2}$. The lowest-order determinant for the covariance coefficients vanishes, so the covariances cannot be determined uniquely by this power-series expansion. A convenient way to solve this system of equations (without evaluating 6×6 determinants) is to eliminate the unknown variables systematically until a set that can be solved in lowest order remains. Thus, rewrite (77) as

$$\langle\xi^2\rangle=\frac{A_n(N-\chi)\langle\xi\xi\rangle+\sigma\chi}{\sigma+A_n\phi}, \tag{81}$$

and substitute this expression for $\langle\xi^2\rangle$ into (79) and (80) to eliminate it from the equations. Similarly rewrite (76) as

$$\langle\eta^2\rangle=\frac{[-A_m\psi+B_m(M-\psi)]\langle\xi\eta\rangle+B_m(M-\psi)\langle\eta\zeta\rangle+J}{A_m\phi+B_m(M-\psi+\rho)}, \tag{82}$$

and substitute this into (78). Likewise, (79) becomes

$$\langle\xi^2\rangle=\frac{1}{A_n(N-\chi)}[(\sigma+A_n\phi+A_m\psi)\langle\xi\xi\rangle+A_m\phi\langle\eta\zeta\rangle+\sigma\chi], \tag{83}$$

which is to be substituted into (75) and (78).

This leaves a set of three equations in three unknowns ($\langle\xi\eta\rangle$, $\langle\xi\xi\rangle$, and $\langle\eta\zeta\rangle$),

$$0=-A_m\phi A_n(N-\chi)\langle\xi\eta\rangle-[\sigma+A_m\psi+A_n(N-\chi+\phi)]A_m\psi\langle\xi\xi\rangle - A_m\phi[A_m\psi+A_n(N-\chi)]\langle\eta\zeta\rangle+JA_n(N-\chi)-\sigma\chi A_m\psi , \tag{84}$$

$$0=-\left[A_m(\phi+\psi)+A_n(N-\chi)+B_m(M-\psi+\rho)+\frac{A_m\phi[B_m(M-\psi)-A_m\psi]}{A_m\phi+B_m(M-\psi+\rho)}\right]\langle\xi\eta\rangle$$
$$+\left[B_m(M-\psi)+\frac{[B_m(M-\psi)-A_m\psi](\sigma+A_m\psi+A_n\phi)}{A_n(N-\chi)}\right]\langle\xi\zeta\rangle$$
$$+\left[\sigma+A_n\phi-\frac{A_m\phi B_m(M-\psi)}{A_m\phi+B_m(M-\psi+\rho)}+\frac{A_m\phi[B_m(M-\psi)-A_m\psi]}{A_n(N-\chi)}\right]\langle\eta\zeta\rangle$$
$$+\frac{JB_m(M-\psi+\rho)}{A_m\phi+B_m(M-\psi+\rho)}+\frac{\sigma\chi[B_m(M-\psi)-A_m\psi]}{A_n(N-\chi)}\,, \tag{85}$$

and

$$0=A_n(N-\chi)\langle\xi\eta\rangle+\left[B_m(M-\psi)-A_m\psi+\frac{B_m(M-\psi)A_n(N-\chi)}{\sigma+A_n\phi}\right]\langle\xi\zeta\rangle$$
$$-[\sigma+(A_m+A_n)\phi+B_m(M-\psi+\rho)]\langle\eta\zeta\rangle+\frac{\sigma\chi B_m(M-\psi)}{\sigma+A_n\phi}\,. \tag{86}$$

To the lowest order in J these three equations become

$$A_nNA_m\phi_1(\langle\xi\eta\rangle_1+\langle\eta\zeta\rangle_1)+(\sigma+A_nN)A_m\psi_1\langle\xi\zeta\rangle_1=0\,, \tag{87}$$

$$A_nN\langle\xi\eta\rangle_1+(\sigma+A_nN)\frac{B_mM}{\sigma}\langle\xi\zeta\rangle_1$$
$$-(\sigma+B_mM)\langle\eta\zeta\rangle_1+B_mM\chi_1=0\,, \tag{88}$$

$$-(A_nN+B_mM)\langle\xi\eta\rangle_1+(\sigma+A_nN)\frac{B_mM}{A_nN}\langle\xi\zeta\rangle_1$$
$$+\sigma\langle\eta\zeta\rangle_1+\frac{\sigma}{A_nN}B_mM\chi_1=0\,, \tag{89}$$

which have the solution

$$\langle\xi\eta\rangle_1=\frac{\phi_1}{2}\,, \tag{90}$$

$$\langle\xi\zeta\rangle_1=-\frac{A_nN}{\sigma+A_nN}\frac{\phi_1}{2}\,, \tag{91}$$

$$\langle\eta\zeta\rangle_1=\frac{A_nN}{\sigma}\frac{\phi_1}{2}\,. \tag{92}$$

Similarly (81)–(83) yield

$$\langle\xi^2\rangle_1=\frac{\sigma+2A_nN}{\sigma+A_nN}\frac{\phi_1}{2}\,, \tag{93}$$

$$\langle\eta^2\rangle_1=\frac{\sigma+A_nN}{\sigma}\frac{\phi_1}{2}\,, \tag{94}$$

$$\langle\xi^2\rangle_1=\frac{2\sigma+A_nN}{\sigma+A_nN}\frac{A_nN}{\sigma}\frac{\phi_1}{2}\,. \tag{95}$$

The set of equations (90)–(95) are the leading terms ($\sim J^{1/2}$) of the solutions to the steady-state equations (75)–(80); the expressions for the quantities that include τ can be obtained from them.

In lowest order (31)–(33) become

$$\frac{\partial}{\partial t}\langle\xi\rangle_1=-A_nN\langle\xi\rangle_1+\sigma\langle\zeta\rangle_1, \tag{96}$$

$$\frac{\partial}{\partial t}\langle\eta\rangle_1=B_mM(\langle\xi\rangle_1-\langle\eta\rangle_1+\langle\zeta\rangle_1)\,, \tag{97}$$

$$\frac{\partial}{\partial t}\langle\zeta\rangle_1=A_nN\langle\xi\rangle_1-\sigma\langle\zeta\rangle_1\,. \tag{98}$$

The sum of (96) and (98) shows $\langle\xi\rangle_1+\langle\zeta\rangle_1$ is constant,

$$\langle\xi\rangle_1+\langle\zeta\rangle_1=\langle\xi\rangle_1(0)+\langle\zeta\rangle_1(0)\equiv\kappa\,, \tag{99}$$

so that

$$\langle\xi\rangle_1=\frac{\sigma}{\sigma+A_nN}\kappa-\left[\frac{\sigma}{\sigma+A_nN}\kappa-\langle\xi\rangle_1(0)\right]e^{-(\sigma+A_nN)t}\,, \tag{100}$$

$$\langle\zeta\rangle_1=\frac{A_nN}{\sigma+A_nN}\kappa-\left[\frac{A_nN}{\sigma+A_nN}\kappa-\langle\zeta\rangle_1(0)\right]e^{-(\sigma+A_nN)t}\,, \tag{101}$$

$$\langle\eta\rangle_1=\kappa-[\kappa-\langle\eta\rangle_1(0)]e^{-B_mMt}\,. \tag{102}$$

The autocorrelation matrix elements can be obtained by combining the kinetic solutions (100)–(102) with the steady-state values (90)–(95) for the second moments or covariances.[14] For example,

$$\langle\xi(0)\xi(t)\rangle_1=\frac{\sigma}{\sigma+A_nN}(\langle\xi^2\rangle_1+\langle\xi\zeta\rangle_1)-\left[\frac{\sigma}{\sigma+A_nN}(\langle\xi^2\rangle_1+\langle\xi\zeta\rangle_1)-\langle\xi^2\rangle_1\right]e^{-(\sigma+A_nN)t}$$
$$=\frac{\sigma+2A_nNe^{-(\sigma+A_nN)t}}{\sigma+A_nN}\frac{\phi_1}{2}\,. \tag{103}$$

Other elements that will be needed are

$$\langle \eta(0)\eta(t)\rangle_1 = \frac{\sigma + A_n N}{\sigma}\frac{\phi_1}{2} , \tag{104}$$

$$\langle \xi(0)\eta(t)\rangle_1 = \frac{\phi_1}{2} , \tag{105}$$

$$\langle \eta(0)\xi(t)\rangle_1 = \frac{\phi_1}{2} . \tag{106}$$

Now the stochastic quantities of interest are those associated with the observable intensity of radiation emitted from the sample. By (47)

$$\Omega\frac{d\lambda}{dt} + \Omega^{1/2}\frac{d\nu}{dt} \to \Omega I + \Omega^{1/2} i \tag{107}$$

and (50) becomes to lowest order

$$\frac{\partial}{\partial t}\langle \nu\rangle_1 = \langle i\rangle_1 = A_m(\phi_1\langle \eta\rangle_1 + \psi_1\langle \xi\rangle_1) . \tag{108}$$

This leads to the autocorrelation function

$$\begin{aligned}\langle i(0)i(t)\rangle &= A_m^2\{\phi^2\langle \eta(0)\eta(t)\rangle + \phi\psi[\langle \eta(0)\xi(t)\rangle + \langle \xi(0)\eta(t)\rangle] + \psi^2\langle \xi(0)\xi(t)\rangle\} \\ &= A_m\phi_1\left[2 + \frac{A_n N}{\sigma}e^{-(\sigma + A_n N)t}\right]J^{3/2} + \cdots .\end{aligned} \tag{109}$$

This is the central result of the paper, since it relates the observable intensity autocorrelation function to the model parameters. Another way to derive this result is to express the variation of the relation $I = A_m\phi\psi$, $I + \delta I = A_m(\phi + \delta\phi)(\psi + \delta\psi)$, in the form

$$\Omega I + \Omega^{1/2} i = \frac{A_m}{\Omega}(\Omega\phi + \Omega^{1/2}\xi)(\Omega\psi + \Omega^{1/2}\eta) , \tag{110}$$

from which one obtains $i = A_m(\phi\eta + \psi\xi)$ and the autocorrelation function (109) for the observed radiation. In the limiting case $t \to 0$, one recovers the covariance

$$\langle i^2\rangle = A_m\phi_1\left[2 + \frac{A_n N}{\sigma}\right]J^{3/2} + \cdots . \tag{111}$$

Now one expects that as $t \to \infty$ the correlations will vanish,[15] $\langle i(0)i(t)\rangle_2 \to 0$ and similarly for (103)–(106). The constant terms that contradict this are only approximations; to the next order in J they also decay exponentially. The system of equations (31)–(33) is given to lowest order by (96)–(98). The characteristic equation of the latter yields the eigenvalues (again to lowest order) $\lambda_0 = \{0, -B_m M, -(\sigma + A_n N)\}$. To the next order, the eigenvalues $\lambda = \lambda_0 + \lambda_1 J^{1/2}$ must satisfy

$$\begin{vmatrix} -A_n N + (A_n\chi_1 - A_m\psi_1)J^{1/2} - \lambda & -A_m\phi_1 J^{1/2} & \sigma + A_n\phi_1 J^{1/2} \\ B_m M - (A_m + B_m)\psi_1 J^{1/2} & -B_m M + [B_m(\psi_1 - \rho_1) - A_m\phi_1]J^{1/2} - \lambda & B_m M - B_m\psi_1 J^{1/2} \\ A_n N - A_n\chi_1 J^{1/2} & 0 & -\sigma - A_n\phi_1 J^{1/2} - \lambda \end{vmatrix} = 0 , \tag{112}$$

so

$$\lambda_1 = \{-2A_m\phi_1, B_m\psi_1, (A_n/\sigma)\phi_1[(A_n - A_m)N - \sigma]\} . \tag{113}$$

Thus, the "constant" term decays very slowly, $\sim \exp(-2A_m\phi_1 J^{1/2}t)$. In lowest order, (109) does not include a term that decays like $\exp(-B_m M t)$; to the next order in J it does, so to measure all three relaxation times one may need to exceed some minimum value for J. One could then extrapolate from such measurements to find the relaxation times for small J, from which the model parameters will be derived.

VII. DEDUCTION OF MODEL PARAMETERS

In the previous sections a stochastic formulation was developed for a simple thermally stimulated system. There are several model parameters and of the particle densities only the luminescence from the recombination of conduction electrons and trapped holes is observable. By combining various measurements one can obtain estimates for at least some of these parameters.[4] The purpose of the stochastic approach is to relate the fluctuations in the observed luminescence to the underlying physical processes in the sample. In this section will be shown how to use these additional fluctuation measurements to determine the model parameters.

The first question is what can be determined, at least in principle, from the results such as (109). The observed intensity consists of a macroscopic part $Y(t)$, which is constant in the steady-state case, and a fluctuation about this value, $\delta Y(t)$. Since Y is an observed intensity while I and J are intensities per unit volume of the source, one has for the steady state

$$Y + \delta Y = \Omega(I + \Omega^{-1/2} i) = \Omega(J + \Omega^{-1/2} i), \tag{114}$$

so that

$$\langle Y\rangle = \Omega J . \tag{115}$$

Thus, the average of the observed intensity immediately yields the electron-hole production rate in the sample. The covariance of the autocorrelation for the observed

intensity becomes

$$\langle\langle (Y+\delta Y)_0 (Y+\delta Y)_t \rangle\rangle = \Omega \langle i(0) i(t) \rangle = \Omega \langle i(0) i(t) \rangle_1 J^{3/2} + \cdots . \tag{116}$$

By measuring the autocorrelation of the observed intensity for various delay times t, one can construct $F(t)$, the autocorrelation function defined to be the left-hand side of (116). It has the form

$$F(t) = \sum_{i=1}^{n} G_i e^{-t/\tau_i} , \tag{117}$$

where the amplitudes G_i and the relaxation times τ_i are functions of the sample temperature T and of the generation rate J, as well as of the model parameters. The number of such quantities n is determined by how many physical processes occur [in the model for n (theory) and in the sample material for n (experiment)]; this helps one to decide if the model used is appropriate for the material under investigation. By standard methods[16-18] one can extract the G_i and τ_i from an observed $F(t)$. For small J in the simple model considered here, one can find the three inverse relaxation times $B_m M$, $\sigma + A_n N$, and $2 A_m \phi_1 J^{1/2}$. The last inverse relaxation time is the smallest and is the one that will vary the most as the incident intensity is varied; call it τ_3^{-1}. If the measurements are made for different temperatures T, only $B_m M$ will not vary; call it τ_2^{-1}. The remaining inverse relaxation time can also be identified by its having the largest change with temperature; call it τ_1^{-1}. Thus, the three observed relaxation times can be identified with those of the model,

$$\tau_1^{-1} = \sigma + A_n N, \quad \tau_2^{-1} = B_m M, \quad \tau_3^{-1} = \left[\frac{4\sigma A_m J}{\sigma + A_n N} \right]^{1/2} , \tag{118}$$

where the τ's are obtained from measurements of the intensity fluctuations.

The quantity $B_m M$ can be obtained immediately from its identification with τ_2^{-1}. Since the product $\tau_1^{-1}\tau_3^{-2} = 4\sigma A_m J$, by performing the measurements at two different temperatures T_1 and T_2 and by taking the ratio

$$D_{12} = \frac{\tau_1^{-1}(T_1)\tau_3^{-2}(T_1)}{\tau_1^{-1}(T_2)\tau_3^{-2}(T_2)} = \frac{\sigma(T_1)}{\sigma(T_2)} \tag{119}$$

as well as the difference

$$\tau_1^{-1}(T_1) - \tau_1^{-1}(T_2) = \sigma(T_1) - \sigma(T_2) , \tag{120}$$

one obtains two equations for the two unknowns $\sigma(T_1)$ and $\sigma(T_2)$. Hence

$$\sigma(T_2) = \frac{\tau_1^{-1}(T_2)\tau_3^{-2}(T_2)[\tau_1^{-1}(T_1) - \tau_1^{-1}(T_2)]}{\tau_1^{-1}(T_1)\tau_3^{-2}(T_1) - \tau_1^{-1}(T_2)\tau_3^{-2}(T_2)} , \tag{121}$$

and since $A_n N = \tau_1^{-1}(T_2) - \sigma(T_2)$,

$$A_n N = \frac{\tau_1^{-1}(T_1)\tau_1^{-1}(T_2)[\tau_3^{-2}(T_1) - \tau_3^{-2}(T_2)]}{\tau_1^{-1}(T_1)\tau_3^{-2}(T_1) - \tau_1^{-1}(T_2)\tau_3^{-2}(T_2)} . \tag{122}$$

Similarly, one has

$$A_m = \tau_1^{-1}(T_2)\tau_3^{-2}(T_2)/4\sigma(T_2)J$$

so that

$$A_m = \frac{\tau_1^{-1}(T_1)\tau_3^{-2}(T_1) - \tau_1^{-1}(T_2)\tau_3^{-2}(T_2)}{4J[\tau_1^{-1}(T_1) - \tau_1^{-1}(T_2)]} . \tag{123}$$

Now $\sigma = s \exp(-E/k_B T)$, so this quantity depends on two model parameters. Suppose $s = s_0$, a constant independent of temperature. Then (119) leads to

$$E = \frac{-\ln D_{12}}{\frac{1}{k_B T_1} - \frac{1}{k_B T_2}} , \tag{124}$$

so that

$$s_0 = \sigma(T_2) \left[\frac{1}{D_{12}} \right]^{T_1/(T_2 - T_1)} . \tag{125}$$

If the frequency factor s has some power-law dependence on the temperature, $s(T) = s_\alpha T^\alpha$, (124) is replaced by

$$E = \frac{-\ln D_{12} + \alpha \ln(T_1/T_2)}{\frac{1}{k_B T_1} - \frac{1}{k_B T_2}} , \tag{126}$$

while (125) becomes

$$s_\alpha = \frac{\sigma(T_2)}{T_2^\alpha} \left[\left[\frac{T_1}{T_2} \right]^\alpha \frac{1}{D_{12}} \right]^{T_1/(T_2 - T_1)} . \tag{127}$$

From the luminescence autocorrelation relaxation times in the steady state one can thus obtain values for the model parameters s, E, A_m, and the products $B_m M$ and $A_n N$. From (67)-(74) it is also possible to obtain the electron and hole densities, at least to lowest order in J. The coefficients G_i in front of the exponentials in (109) will not provide any additional information, but they can serve to confirm the values found from the relaxation times τ_i. The trap and recombination center densities N and M occur only in products because only the lowest-order (in J) solutions have been used. If the production rate J can be increased enough to make the corrections of (113) large enough to be observed, both B_m and A_n can be determined along with all the other parameters solely by a suitable set of measurements of the autocorrelation relaxation times. The $J^{1/2}$ term of τ_2^{-1} is $B_m \psi_1$; since all the quantities in ψ_1 are known from (121)-(123), B_m is immediately determined. The J^0 term of τ_2^{-1} is $B_m M$, so M is also found. Similarly, the $J^{1/2}$ term of τ_1^{-1}, $[(A_n - A_m)N - \sigma] A_n \phi_1 / \sigma$, can be expressed as known quantities except for A_n. Hence A_n is found and from (122) so is N. Thus, the initial rise of the relaxation times as functions of $J^{1/2}$ should be determined along with the relaxation times themselves.

To illustrate the method, attention has been directed to the sample material and the stochastic nature of the processes that occur in it. In a real experiment one must also deal with the stochastic nature of the source term J and with the statistics of the detector. In a typical case a

large number of incident particles must impinge on the sample to produce even a weak generation rate J. This is consistent with assuming no spatial dependence in the electron-hole pair-production rate ($\sim\Omega J$). If J were time varying, no steady state could exist. Now because of the statistical nature of the incident particle beam and of the particle-sample interactions that produce the electron-hole pairs, even a macroscopically constant J will have some fluctuations in time [so consider $J+\delta J(t)$]. If the incoming particles have random arrival times that are independent, there will be a constant probability per unit time for electron-hole pair production.[19] The particle-sample interaction fluctuations will have an $\Omega^{1/2}$ relative decrease as the sample volume Ω increases ($\Omega J+\Omega^{1/2}\gamma$, for example). The stochastic nature of the source itself can be represented as an external fluctuation acting on the sample. The kinetic equation for the sample will now have a random coefficient J, whose effect on the system can be studied by the use of stochastic differential equations.[20] The detector will similarly introduce fluctuations into the measurements. It may not detect all the emitted photons that it receives (detector efficiency $<100\%$); also, internal noise may cause spurious counts. This can be incorporated into the system of equations by considering the probability $p(i_c,i_e,k,l,\ldots|t)$, where i_c is the number of photon counts recorded by the detector and i_e is the number of photons emitted by the sample, both up to time t. Presumably both source and detector statistics can be determined independently of any thermoluminescence experiments, so they can be taken as a known complication to experimental measurements and data analysis.

VIII. CONCLUSION

In this paper van Kampen's Ω-expansion method has been applied to a simple model for recombination luminescence in the presence of retrapping and continuous irradiation. In the lowest order of this expansion, one recovers the deterministic macroscopic kinetic equations. The next order yields the Fokker-Planck equation governing the fluctuations in the linear-noise approximation. From this equation one derives the evolution equations for the two lowest moments of the fluctuations. The kinetic equations (21)–(24) cannot in general be solved analytically, so the more complicated moment equations (30)–(33) and (36)–(41) must certainly be solved numerically. A special case in which this is not so is the steady state, in which the macroscopic differential equations are replaced by algebraic equations ($\partial/\partial t=0$), and the differential equations for the moments now have constant coefficients. Further, the steady state with a weak electron-hole production rate leads to fairly simple analytic expressions, which in principle can be used to determine the model parameters from measurements of the relaxation times of the luminescence autocorrelation function. To carry out this scheme, of course, one must be able to measure with high enough accuracy and time resolution the fluctuations of the possibly weak steady-state luminescence.

There are several features that must be considered if this method is to be used in actual experiments. To obtain simple expressions from which the model parameters can be easily found, one imposes the restriction of a weak electron-hole production rate J; this is physically realistic in most experiments. To obtain all the parameters, however, one must have J large enough that the second terms in the various series expansions can be measured. Thus, J must be small, but not too small. If it is too large, the expressions become more involved and interpretation of them more difficult; if it is too small, not all the parameters can be found and more terms in the Ω expansion may be required.

A second point is the form of (121)–(123), from which the model parameters are found in terms of the autocorrelation relaxation times (which are themselves obtained from an analysis of directly observable quantities). The denominators of these equations involve the difference between two almost equal quantities (as do the numerators); the uncertainties in these quantities must be much smaller than the difference between them if one wants to obtain sensible values for the model parameters. This sets a requirement on the accuracy of the measurements.

Finally, the model considered here contains a single trapping level and recombination center; generalization to the more realistic case of multiple traps and centers is straightforward. The algebraic expressions are more involved and the large number of relaxation times (including those from cross correlations) will require more analysis before one can use them to find the model parameters. There are several special cases of some interest. Not observing a luminescence level is equivalent to having a nonradiative decay channel. A large number of closely spaced traps leads to a continuum distribution of traps. Multiple traps and a single recombination center would place a heavy burden on the extraction of information from luminescence. On the other hand, a large number of recombination centers would lead to many redundant equations. If the energy separation of the traps is large compared to the thermal energy k_BT, two special cases can arise. If the temperature is high enough to cause the normal electron escape from the lower traps ($\sim se^{-E/k_BT}$), the upper traps will be almost completely devoid of electrons due to the much higher escape rate. On the other hand, at a temperature low enough to cause normal escape from the upper traps, there will be hardly any electron escape from the lower traps; eventually this would lead to filled lower traps. Generalization of the model formalism to include multiple traps and recombination centers and its application to some special cases will be discussed in a future publication.

[1]L. A. DeWerd, in *Thermally Stimulated Relaxation in Solids*, edited by P. Braunlich (Springer-Verlag, Berlin, 1979), pp. 275–299.

[2]R. Chen and Y. Kirsh, *Analysis of Thermally Stimulated Processes* (Pergamon, Oxford, 1981), pp. 296–321.

[3]P. Braunlich, in *Thermally Stimulated Relaxation in Solids* (Ref. 1), p. 1.

[4]Reference 2, pp. 183–268.

[5]N. G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1981), pp. 253–283.
[6]E. I. Adirovitch, J. Phys. Radium **17**, 705 (1956).
[7]A. Halperin and A. A. Braner, Phys. Rev. **117**, 408 (1960).
[8]R. Chen, S. W. S. McKeever, and S. A. Durrani, Phys. Rev. B **24**, 4931 (1981).
[9]See Ref. 5.
[10]Reference 5, pp. 185–187.
[11]Reference 5, p. 260.
[12]Reference 5, pp. 228–230.
[13]Reference 5, pp. 278–283.
[14]Reference 5, pp. 269 and 277.
[15]L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley, Reading, 1969), p. 370.
[16]V. V. Apanasovich and E. G. Novikov, Opt. Commun. **78**, 279 (1990).
[17]Louis G. Kelly, *Handbook of Numerical Methods and Applications* (Addison-Wesley, Reading, 1967), pp. 80–82.
[18]N. Link, S. Bauer, and B. Ploss, J. Appl. Phys. **69**, 2759 (1991).
[19]Reference 5, p. 372.
[20]Reference 5, pp. 381–412.