Journal of Luminescence 226 (2020) 117389

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: http://www.elsevier.com/locate/jlumin

Inherent statistics of glow curves from small samples and single grains

John L. Lawless [a,*], R. Chen [b], V. Pagonis [c]

[a] Redwood Scientific, Inc., Pacifica, CA, USA
[b] Raymond and Beverly Sackler School of Physics and Astronomy, Tel Aviv University, Tel Aviv 69978, Israel
[c] Physics Department, McDaniel College, Westminster, MD 21157, USA

ARTICLE INFO

Keywords:
Luminescence
Radiation effects
Photostimulation
Dosimetry
Thermoluminescence
Single grain
Irradiation

ABSTRACT

For measurement techniques, it is usually important to know the accuracy and detection limits. This issue is particularly important in thermoluminescence when studying either low doses or small samples, especially single grains. Our focus herein is not on instrumental measurement errors but instead on the inherent noise or uncertainty in the thermoluminescence process. To this end, we study a simple one–center, one–active-trap model that produces a first–order glow curve. A master equation is developed for the statistical noise and probability distributions for trap population during both irradiation and heating. In addition to quantifying the probability distributions, governing equations are developed for both the mean and the standard deviation of trap population during irradiation and heating.

1. Introduction

While errors and noise associated with measurement equipment have been widely investigated, there is also statistical noise inherent in thermoluminescence itself, both during the irradiation and heating stages. The noise is particularly important when dealing with either low doses or small sample sizes. We will consider a simple system with simple first–order kinetics and develop, using a master equation approach, quantitative models for the inherent noise for both irradiation and heating.

The importance of noise in thermoluminescence measurements has inspired development of new experimental techniques. One approach for handling noisy thermoluminescence signals at low doses is to increase the signal–to–noise ratio. One way to do this is to increase the heating rate such as with laser heating. CO_2 lasers can be used to generate rapid heating rates in excess of 10^4K/s[1,2]. The improved signal-to-noise ratio at these heating rates may enable non–destructive testing of ceramics [3]. Alternatively, even at high doses, the noise level is important when measuring thermoluminescence from small samples, such as a single–grain. For this purpose, specialized instruments have been developed to minimize instrumental noise when measuring luminescence from single–grains[4–8].

The inherent noise in the irradiation and heating processes of thermoluminescence can be quantified using the master equation [9]. The master equation has been applied in many fields. It was, for example, used to predict the existence of the carbon–monoxide vibrational laser [10]. It is also used for analysis of energy distributions of free electrons in both plasmas and solids [11–14]. In the field of thermoluminescence, the master equation has been used to predict autocorrelation of fluctuations in intensity [15,16].

To provide a point of comparison, the next section presents the usual (macroscopic) phenomenological model for a one–center one–active-–trap system. After this, we will use the master equation to describe the change in time of the probability distribution for trap occupation levels. This will be followed by a study of irradiation including both a model of irradiation at low dose and, for a special case, a model of irradiation at arbitrary dose. Next, a model for the glow curve during heating is developed. In all cases, governing equations are developed for not just the trap occupation probability distributions but also for the expected trap occupation and its standard deviation. This is followed by a summary of the results for standard deviation and a discussion.

2. Phenomenological model

At its simplest, we need one trap and one center to describe thermoluminescence. To obtain Randall-Wilkins behavior at low dose with finite rate constants, however, we need a second trap which may be disconnected. This is illustrated in Fig. 1 where the first electron trap has a concentration of N(cm^{-3}) with an occupation of n(cm^{-3}), the second trap has a concentration of N_D(cm^{-3}) with an occupation of n_D(cm^{-3}),

* Corresponding author.
E-mail address: lawless@alumni.princeton.edu (J.L. Lawless).

https://doi.org/10.1016/j.jlumin.2020.117389
Received 11 March 2020; Received in revised form 13 May 2020; Accepted 15 May 2020
Available online 26 May 2020

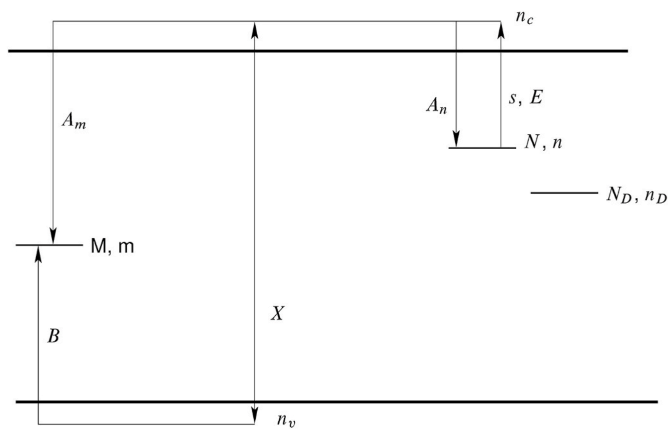

Fig. 1. Energy level diagram of the model with an active trap *N*, a disconnected trap N_D, and a hole recombination center *M*. During irradiation, electron–hole pairs are created with rate *X*. During heating, the electrons in trap *N* are thermally–excited, with a rate controlled by s, E, and recombine with the holes in *M*.

and the recombination center has a concentration of *M* (cm^{-3}) with an occupation of *m* (cm^{-3}). A_m (cm^3/s) is the rate constant for recombination of free electrons with the center. A_n (cm^3/s) is the rate constant for trapping of free electrons in the trap *N*. *B* (cm^3/s) is the rate constant for trapping of free holes in the center. The corresponding phenomenological equations are:

$$\frac{dn}{dt} = A_n(N-n)n_c - n\gamma \tag{1}$$

$$\frac{dn_D}{dt} = 0 \tag{2}$$

$$\frac{dn_c}{dt} = X + n\gamma - A_n(N-n)n_c - A_m m n_c \tag{3}$$

$$\frac{dm}{dt} = B(M-m)n_v - A_m m n_c \tag{4}$$

$$\frac{dn_v}{dt} = X - B(M-m)n_v \tag{5}$$

where *X* (cm^{-3}/s) is the production rate of electron–hole pairs due to irradiation and γ (s^{-1}) is the thermal excitation rate from a trap *N* to the conduction band:

$$\gamma = s\exp(-E/kT) \tag{6}$$

where *E* is the activation energy (eV), *k* is Boltzmann's constant (eV/ K), *T* is temperature (K), and *s* is a pre–exponential constant (s^{-1}).

A large number of measurements have been made of rate constants for capture for free electrons or holes in traps or centers [17,18]. Typical values range from 10^{-10} cm^3/s to 10^{-5} cm^3/s. Typical trap or center concentrations of interest in TL range from $10^{12}cm^{-3}$ to $10^{17}cm^{-3}$. Consequently, the lifetime of free electrons or free holes, which is often measured in microseconds, is typically far less than the time scale over which irradiation or heating occurs. It follows that:

$$\frac{dn_c}{dt} \ll A_n(N-n)n_c \quad \text{and} \quad \frac{dn_v}{dt} \ll B(M-m)n_v \tag{7}$$

This leads to the quasi–steady approximation which allows Eq. (3) and Eq. (5) to be simplified to:

$$n_c = \frac{X + n\gamma}{A_n(N-n) + A_m m} \tag{8}$$

$$n_v = \frac{X}{B(M-m)} \tag{9}$$

Using Eq. (8) and Eq. (9), we can simplify Eq. (1) and Eq. (4) to:

$$\frac{dn}{dt} = f_n X - f_m n\gamma \tag{10}$$

$$\frac{dm}{dt} = f_n X - f_m n\gamma \tag{11}$$

where:

$$f_n = \frac{A_n(N-n)}{A_n(N-n) + A_m m} \tag{12}$$

$$f_m = \frac{A_m m}{A_n(N-n) + A_m m} \tag{13}$$

f_n has the physical meaning of being the fraction of free electrons which are captured by the trap *n* while f_m is the fraction of them which recombine with the center.

We will assume that the initial conditions before irradiation are:

$$n = 0 \tag{14}$$

$$m = n_D = m_0 \tag{15}$$

As an example, in Al_2O_3:C, values of *M* and m_0 can be inferred from optical absorption. Typical experimentally measured values of *M* and m_0 are 10^{17} and 10^{16} cm^{-3} [19].

In sum, Eq. (8) through Eq. (13) are the governing equations for the quasi–steady one–center one–active–trap model. In sections which follow, we will consider both low–dose cases, for which f_n and f_m are approximately constant, and arbitrary–dose cases, for which f_n and f_m are variable.

3. Master equation for Low–Dose

For small samples, such as single grains, or for small doses, the statistical nature of irradiation and recombination may need to be considered. In this section, we will develop equations for the probability distributions for trap populations. We will also explore how these distributions connect to the conventional phenomenological equations.

Unlike the phenomenological model, it will matter here what type of irradiation is applied. In this paper, we will assume that one irradiation event results in one electron–hole pair. This generally applies, for example, to UV irradiation but not to irradiation by high–energy sources such as X–rays or beta rays.

Let's consider a sample of volume *V* and, within this volume, it has $\mathbb{M}$ centers and $\mathbb{N}$ traps. $\mathbb{M}$ and $\mathbb{N}$ are integers and are connected to the macroscopic quantities *M* and *N* via:

$$M = \mathbb{M}/V \quad \text{and} \quad N = \mathbb{N}/V \tag{16}$$

Each of the $\mathbb{N}$ traps may or may not contain a trapped electron. Let P_i be the probability that a sample, which might be a single grain, has exactly *i* electrons in its $\mathbb{N}$ traps at some time *t*. Because P_i is a probability, we will require that:

$$\sum_{i=0}^{\mathbb{N}} P_i = 1 \tag{17}$$

It is often assumed as an initial condition in thermoluminescence problems that the traps are empty. We would express that in terms of P_i by:

$$P_i = \begin{cases} 1 & \text{for } i = 0 \text{ and } t = 0 \\ 0 & \text{for } i > 0 \text{ and } t = 0 \end{cases} \tag{18}$$

For simplicity, we will assume for the rest of Sec. 3 that the dose is sufficiently low that:

$$n \ll N \qquad \text{and} \qquad n \ll m_0 \tag{19}$$

From Eq. (19), it follows that the factors f_n and f_m are approximately constant:

$$\begin{aligned} f_n &\approx f_{n0} &= \frac{A_n N}{A_n N + A_m m_0} \\ f_m &\approx f_{m0} &= \frac{A_m m_0}{A_n N + A_m m_0} \end{aligned} \tag{20}$$

Using the factors f_{n0} and f_{m0}, the four ways that P_i may change over some small time interval, dt, are:

1. It could be that the sample has exactly $i-1$ electrons in the traps and then a radiative ionization event occurs followed by capture of the electron in the trap so that an increase in trap population occurs. For a sample of volume V that is subjected to irradiation at rate X, this causes P_i to increase by $f_{n0} VXP_{i-1} dt$.
2. It could be that the sample has exactly i electrons in the traps and then a radiative ionization event occurs followed by a capture by the trap. This causes P_i to decrease by $f_{n0} VXP_i dt$.
3. It could be that the sample has exactly i electrons in the traps and a thermal excitation event occurs followed by a recombination. For any individual occupied trap, this happens with probability $f_{m0}\gamma dt$. Since there are i occupied traps, the total probability of this happening in the sample over time interval dt is $if_{m0}\gamma dt$ and this causes P_i to decrease.
4. It could be that the sample has exactly $i+1$ electrons in the traps and a thermal excitation event occurs followed by a recombination event. This causes P_i to increase by $(i+1)f_{m0}\gamma P_{i+1} dt$

Combining these four possible events together, we have the master equation:

$$\frac{dP_i}{dt} = \begin{cases} f_{m0}\gamma(i+1)P_{i+1} - f_{n0}VXP_i & \text{for } i=0 \\ f_{m0}\gamma(i+1)P_{i+1} - f_{n0}VXP_i - f_{m0}\gamma iP_i + f_{n0}VXP_{i-1} & \text{for } i>0 \end{cases} \tag{21}$$

The equation for $i = \mathbb{N}$ is a special case but, consistent with Eq. (19), as long as the dose is low, this doesn't concern us since, as i grows, P_i will drop rapidly to zero long before i approaches $\mathbb{N}$.

In order that both Eq. (17) and Eq. (21) be obeyed at all times, it is necessary that:

$$\sum_{i=0} \frac{dP_i}{dt} = 0 \tag{22}$$

Note that every positive term in Eq. (21) for some i is balanced by an equal negative one for some other i. Consequently, Eq. (21) obeys Eq. (22) and, therefore, if the initial conditions obey Eq. (17), then Eq. (17) will also be obeyed for all subsequent times.

With Eq. (21), the probability distribution for trap population can be calculated during irradiation and/or heating. It is also interesting to know the expected value and standard deviations of the population and these can be found by taking moments of Eq. (21). At any given time, the expected value of the number of electrons in the trap is given by:

$$\mathbb{E}[i] = \sum_{i=0} iP_i \tag{23}$$

It will simplify our calculations to note that $iP_i = 0$ when $i = 0$. It follows that Eq. (23) can be written as:

$$\mathbb{E}[i] = \sum_{i=1} iP_i \tag{24}$$

Combining Eq. (21) with Eq. (24), we have:

$$\frac{d\mathbb{E}[i]}{dt} = \sum_{i=1} f_{m0}\gamma i(i+1)P_{i+1} - \sum_{i=1} f_{n0}VXiP_i - \sum_{i=1} f_{m0}\gamma i^2 P_i + \sum_{i=1} f_{n0}VXiP_{i-1} \tag{25}$$

After much math (see Appendix A), these summations reduce to:

$$\frac{d\mathbb{E}[i]}{dt} = f_{n0}VX - f_{m0}\gamma\mathbb{E}[i] \tag{26}$$

If we identify the macroscopic quantity n with the *expected value* of trap population per unit volume:

$$n = \mathbb{E}[i]/V \tag{27}$$

Eq. (26) becomes:

$$\frac{dn}{dt} = f_{n0}X - f_{m0}\gamma n \tag{28}$$

Within the low dose range, Eq. (28) agrees with Eq. (10) which shows that the n in the phenomenological equations should be interpreted as the statistical *expected value* of trap concentration.

Next, let's consider the standard deviation of the trap population. At any given time, the standard deviation, σ, of i is given by:

$$\sigma^2 = \sum_{i=0} (i - \mathbb{E}[i])^2 P_i \tag{29}$$

Using Eq. (23), Eq. (29) simplifies to:

$$\sigma^2 = \sum_{i=0} i^2 P_i - \mathbb{E}[i]^2 \tag{30}$$

or, using expected value notation:

$$\sigma^2 = \mathbb{E}[i^2] - \mathbb{E}[i]^2 \tag{31}$$

We can determine how the variance changes in time by combining Eq. (30) with Eq. (21) and Eq. (26):

$$\frac{d\sigma^2}{dt} = \sum_{i=0} i^2 \frac{dP_i}{dt} - 2\mathbb{E}[i]\frac{d\mathbb{E}[i]}{dt} \tag{32}$$

After the use of Eq. (21), Eq. (26), and Eq. (31) and after much math (see Appendix A), the governing equation for variance of the trap population i is:

$$\frac{d\sigma^2}{dt} = f_{n0}VX + f_{m0}\gamma\left[\mathbb{E}[i] - 2\sigma^2\right] \tag{33}$$

Note that irradiation, X, always acts to increase the standard deviation of trap population while recombination, γ, can increase or decrease it depending on whether $\mathbb{E}[i]$ is larger or smaller than $2\sigma^2$.

In sum, in this section, the dose was assumed low enough that f_{n0} and f_{m0} could be considered constants as per Eq. (20). The master equation governing this process, during either irradiation and/or heating, is given by Eq. (21). This equation allows the probability distribution for the number of electrons in the trap to be computed. By taking the first and second moments of the master equation, the governing equations for the expected value of trap population, Eq. (28), and its standard deviation, Eq. (33), were found. Eq. (28) corresponds to macroscopic Eq. (10) and shows that the macroscopic trap population n corresponds to the statistical *expected value* of trap population as in Eq. (27). Eq. (33) provides new information: there is no analog for it in the macroscopic phenomenological model. Note also that Eq. (28) and Eq. (33) apply regardless of the initial conditions for P_i.

4. Irradiation

The statistics of irradiation of a sample with a thermally–stable trap will be examined for two cases. The first is that of low dose. The second case will produce results over the full range of dose but for a special case of the rate constants.

4.1. Low–dose

Consider irradiation at low dose of a solid with thermally–stable traps of a single kind. As long as the traps are thermally stable, $\gamma \approx 0$, the master equation of Eq. (21) simplifies to:

$$\frac{dP_i}{dt} = \begin{cases} -f_{n0}VXP_i & \text{for } i = 0 \\ -f_{n0}VXP_i + f_{n0}VXP_{i-1} & \text{for } i > 0 \end{cases} \tag{34}$$

where P_i is the probability at time t that the traps contain i electrons and f_{n0} and f_{m0} are as defined in Eq. (12) and Eq. (13), respectively. For the remainder of this subsection, we will assume that the traps are initially empty as per Eq. (18).

Even before we solve Eq. (34), we can obtain useful results from Eq. (26) and Eq. (31). With a thermally–stable trap, $\gamma = 0$, both equations are readily integrated to find:

$$\mathbb{E}[i] = f_{n0}VD \tag{35}$$

and,

$$\sigma = \sqrt{f_{n0}VD} = \sqrt{\mathbb{E}[i]} \tag{36}$$

where D is the dose, measured in ionizations per unit volume (cm^{-3}), is given by:

$$D = \int_0^t X(t')dt' \tag{37}$$

where t is the time over which the sample of volume V is exposed to the irradiation X. X may be constant or it may be a function of time. t' is a variable of integration. As an example, Eq. (36) states that, if the expected value for the trap population was 1,000, then the standard deviation of that population would be ~32.

The complete solution of Eq. (34), subject to initial conditions Eq. (18), as can be verified by substitution, is given by:

$$P_i = \frac{(f_{n0}VD)^i}{i!}\exp(-f_{n0}VD) \tag{38}$$

Eq. (34) describes a Poisson process and Eq. (38) is the probability distribution of that process. Its mean and standard deviation are given by Eq. (35) and Eq. (36). For large enough $f_{n0}VD$, the Poisson distribution asymptotically approaches a Gaussian distribution.

Note that the results Eq. (35) through Eq. (38) do not depend on X except through its integral D. This means that, under our assumptions, Eq. (7) in particular, the same results are found for any dose rate as long as the total dose is held constant.

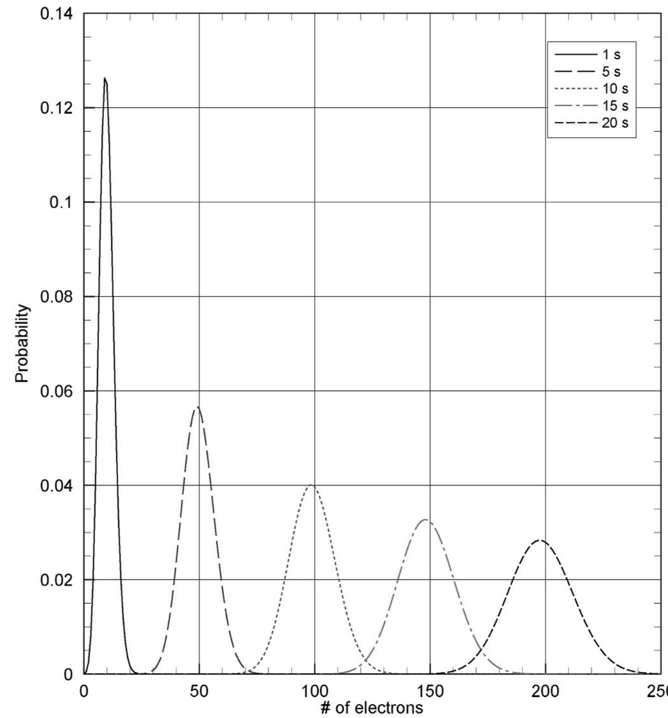

Fig. 2. For a sample of volume $V = 10^{-9}cm^3$, the probability distribution for the number of electrons in the trap during irradiation, given by Eq. (38) is shown for various times. Because the trap is assumed initially empty as per Eq. (18), the distribution starts with a sharp peak around $i = 0$. As time progresses, the distribution broadens and moves to higher populations.

$$\frac{dP_i}{dt} = \begin{cases} -\frac{A_n(\mathbb{N}-i)}{A_n(\mathbb{N}-i)+A_m(i_m+i)}VXP_i & \text{for } i = 0 \\ -\frac{A_n(\mathbb{N}-i)}{A_n(\mathbb{N}-i)+A_m(i_m+i)}VXP_i + \frac{A_n(\mathbb{N}+1-i)}{A_n(\mathbb{N}+1-i)+A_m(i_m+i-1)}VXP_{i-1} & \text{for} 1 \le i \le \mathbb{N} \end{cases} \tag{39}$$

If we were to consider high dose, then the rate at which the trap population increases, say from i to $i+1$, would be $A_n(N-i)VX/[A_n(N-i)+A_m(i_m+i)]$. Since, through i, this rate depends on past history, the Poisson distribution ceases to apply. With a properly modified master equation, though, the problem could still be solved as will be shown in the next subsection.

Sample results for irradiation at low dose is shown in Fig. 2. Since we assume that the trap is initially empty, Eq. (18), the probability distribution starts out narrow and peaks around $i = 0$. As time progresses, the distribution moves to higher populations and broadens. The calculation assumed: $V = 10^{-9}cm^3$, $N = 10^{14}cm^{-3}$, $m_0 = 10^{16}cm^{-3}$, $A_m = 10^{-9}cm^3/s$, $A_n = 10^{-9}cm^3/s$, and $X = 10^{14}cm^{-3}/s$.

4.2. Arbitrary dose

The statistics of the irradiation process are quite different at high doses than they are at low doses. In this subsection, we will, for the special case of $A_n = A_m$, develop equations for the probability distribution P_i for arbitrary radiation dose.

At low doses, the factors f_{n0} and f_{m0} in Eq. (34) were constant and independent of i. For higher doses, this is not true. The master equation that applies to the one–center one–active–trap model at arbitrary levels of dose is:

where $i_m = m_0V$. To simplify Eq. (39), we will consider the special case of equal rate constants:

$$A_n = A_m \tag{40}$$

Applying Eq. (40) to Eq. (39), we have:

$$\frac{dP_i}{dt} = \begin{cases} -\frac{\mathbb{N}-i}{\mathbb{N}+i_m}VXP_i & \text{for } i=0 \\ -\frac{\mathbb{N}-i}{\mathbb{N}+i_m}VXP_i + \frac{\mathbb{N}+1-i}{\mathbb{N}+i_m}VXP_{i-1} & \text{for } 1 \le i \le \mathbb{N} \end{cases} \tag{41}$$

Combining Eq. (23) with Eq. (41) and using the same techniques as before, we can derive the governing equation for the expected value of trap population:

$$\frac{d\mathbb{E}[i]}{dt} = \frac{X}{N+m_0}(\mathbb{N}-\mathbb{E}[i]) \tag{42}$$

Similarly, the governing equation for the expected value of the square of the population is found to be:

$$\frac{d\mathbb{E}[i^2]}{dt} = \frac{X}{N+m_0}\left(\mathbb{N}+(2\mathbb{N}-1)\mathbb{E}[i]-2\mathbb{E}[i^2]\right) \tag{43}$$

Combining Eq. (42) and Eq. (43) with Eq. (31), we find the equation governing the change in variance with time:

$$\frac{d\sigma^2}{dt} = \frac{X}{N+m_0}\left(\mathbb{N}-\mathbb{E}[i]-2\sigma^2\right) \tag{44}$$

Eq. (42) through Eq. (44) apply regardless of the initial distribution of P_i. If we assume that the traps are initially empty, as in Eq. (18), then Eq. (42) can be integrated to find:

$$\mathbb{E}[i] = \mathbb{N}\left[1-\exp\left(-\frac{D}{N+m_0}\right)\right] \tag{45}$$

where D is the dose (Eq. (37)).

We can substitute Eq. (45) into Eq. (44) and integrate to find:

$$\sigma^2 = \mathbb{N}\left[\exp\left(\frac{-D}{N+m_0}\right) - \exp\left(\frac{-2D}{N+m_0}\right)\right] \tag{46}$$

Eq. (46) shows that, consistent with the initial condition Eq. (18), σ, the standard deviation of the trap population, starts at zero, it climbs to a peak, and then drops back to zero as the trap saturates. Using Eq. (45), we can rewrite Eq. (46) as:

$$\sigma = \sqrt{\mathbb{E}[i]}\exp\left(\frac{-D}{2(N+m_0)}\right) \tag{47}$$

At low doses, Eq. (47) shows that σ initially rises as the square root of the expected trap population, the same as the low dose (Poisson process) result of Eq. (36). This ceases to be true at higher doses when the exponential term in Eq. (47) becomes important and, instead of growing, σ will decline toward zero. If we apply Eq. (45) again, Eq. (47) can also be written as:

$$\sigma = \sqrt{\frac{\mathbb{E}[i](\mathbb{N}-\mathbb{E}[i])}{\mathbb{N}}} \tag{48}$$

Eq. (45) and Eq. (48) characterize the overall behavior of the probability distribution P_i for this case. The distribution in detail is given by:

$$P_i = \binom{\mathbb{N}}{i}\exp\left(\frac{-(\mathbb{N}-i)D}{N+m_0}\right)\left[1-\exp\left(\frac{-D}{N+m_0}\right)\right]^i \tag{49}$$

The validity of Eq. (49) can be verified by substitution into Eq. (41).

A plot of P_i vs i is shown in Fig. 3. Just like the low–dose case of Figs. 2 and 3 shows, initially at least, a distribution that is narrow and broadens as irradiation proceeds. Unlike the low dose case, however, Fig. 3 shows that, as irradiation proceeds further, the distribution narrows again. To show this more clearly, the standard deviations of the distributions in Figs. 2 and 3 are plotted against $\mathbb{E}[i]$ in Fig. 4. The standard deviation for the $V = 10^{-9}\text{cm}^{-3}$ case are computed from Eq. (36) and, for the $V = 10^{-12}\text{cm}^{-3}$ case, they are computed from Eq. (48).

In sum, for irradiation at arbitrary dose but restricted to the case $A_n = A_m$, we developed governing differential equations for expected trap population (Eq. (42)) and σ (Eq. (44)). For the case of an initially

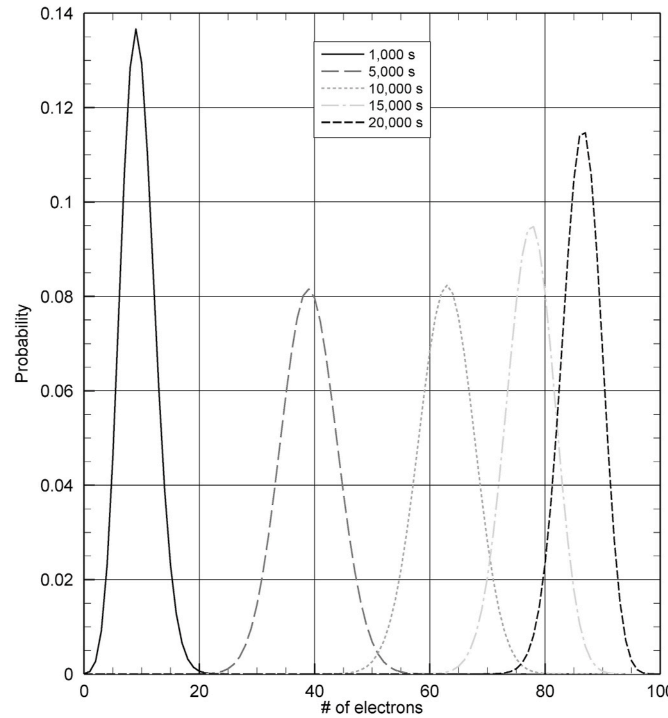

Fig. 3. The behavior of a material irradiated toward saturation, as given by Eq. (49), is plotted. The parameters are the same as in Fig. 2 except for a smaller volume: $V = 10^{-12}\text{cm}^{-3}$. Because the volume is smaller, it takes a longer time to reach the same trap population i. Also, at this volume, $\mathbb{N} = VN = 100$ so that the trap population saturates at $i = 100$. As saturation is approached, the distribution narrows instead of broadens. Eq. (49) is the result of solving master equation Eq. (41) subject to initial condition Eq. (18) and the assumption $A_n = A_m$ (Eq. (40)).

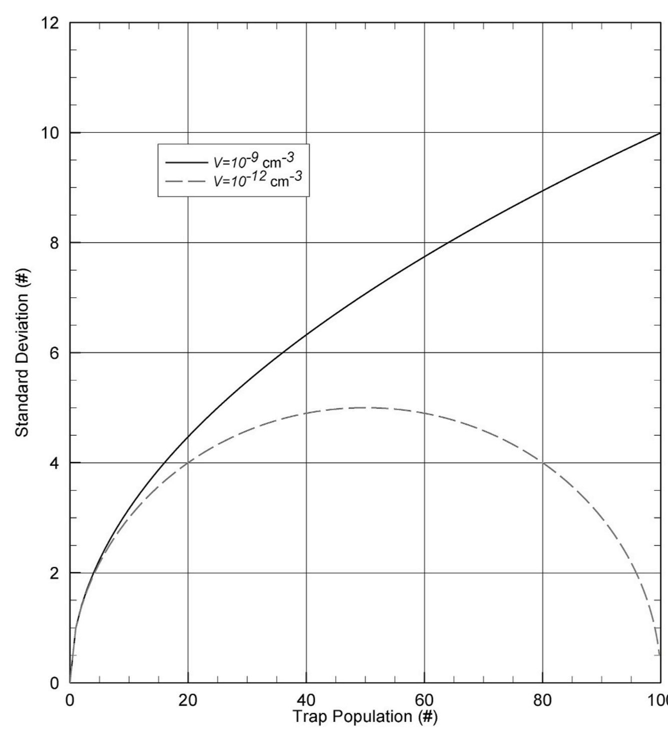

Fig. 4. The standard deviations of the probability distributions shown in Fig. 2 ($V = 10^{-9}$ cm^{-3}) and Fig. 3 ($V = 10^{-12}$ cm^{-3}) are plotted against expected trap population using Eq. (36) for the large volume and Eq. (48) for the small.

empty trap, the solutions to these are given by Eq. (45) and Eq. (48). These agree with the conventional Poisson model only at low doses ($n \ll N$).

5. Heating stage

The process of a trap emptying during heating also changes the noise level. Depending on conditions, we will see that heating can either increase or decrease the standard deviation of trap population. We will consider a simple system with first–order kinetics. The governing equations will be developed for the mean of the trap population, its standard deviation, and probability distribution for trap occupation. We will consider the governing equations in general and then develop particular solutions for two initial conditions of interest.

To obtain a first–order glow curve, we need f_m, but *not* necessarily f_n, to be approximately constant. This will be true for low dose if the inequalities in Eq. (19) hold. It will also be true even at high dose if:

$$A_n N \ll A_m m_0 \qquad \text{and} \qquad N \ll m_0 \tag{50}$$

In either case, as long as f_n remains approximately constant and there is no irradiation, $X = 0$, the results of Sec. 3 can be applied to the heating stage. The master equation during heating reduces to:

$$\frac{dP_i}{dt} = \begin{cases} f_{m0}\gamma(i+1)P_{i+1} & \text{for} \quad i = 0 \\ f_{m0}\gamma(i+1)P_{i+1} - f_{m0}\gamma i P_i & \text{for} \quad i > 0 \end{cases} \tag{51}$$

Before we solve Eq. (51), we can obtain useful information from Eq. (26) and Eq. (33). Without irradiation, $X = 0$, Eq. (26) is readily integrated to find:

$$\mathbb{E}[i] = n_o V \exp\left(-f_{m0}\int_0^t \gamma(t')dt'\right) \tag{52}$$

where t' is a variable of integration. Combining Eq. (33) with Eq. (52) and integrating, we find:

$$\sigma^2 = n_o V \exp\left(-f_{m0}\int_0^t \gamma(t')dt'\right) + \left(\sigma_0^2 - n_o V\right)\exp\left(-2f_{m0}\int_0^t \gamma(t')dt'\right) \tag{53}$$

where σ_0 is the initial standard deviation of trap population at $t = 0$ before the heating begins. Two initial conditions are of particular interest. The first is the value of σ_0 that results from irradiation at low dose. Substituting Eq. (36) into Eq. (53), we find:

$$\sigma^2 = n_o V \exp\left(-f_{m0}\int_0^t \gamma(t')dt' \int_0^t\right) \tag{54}$$

or, using Eq. (52):

$$\sigma = \sqrt{\mathbb{E}[i]} \tag{55}$$

This shows that the standard deviation of the trap population, σ declines in time as heating progresses. For this initial condition, an exact solution of Eq. (51) is available:

$$P_i = \frac{\left(n_o \exp\left(-f_{m0}\int_0^t \gamma(t')dt'\right)\right)^i}{i!} \exp\left(-n_o \exp\left(-f_{m0}\int_0^t \gamma(t')dt'\right)\right) \tag{56}$$

This provides the probability distribution for trap population as a function of time during heating. Eq. (56) can be verified by substitution into Eq. (51).

Alternatively, after irradiation, we may have some way of measuring the trap population. This might, for example, be an optical absorption method. Assuming the measurement method is accurate and determines that the trap population is, say, i_0, then our initial condition is:

$$P_i|_{t=0} = \begin{cases} 1 & \text{for} \quad i = i_0 \\ 0 & \text{for} \quad i \neq i_0 \end{cases} \tag{57}$$

A consequence of Eq. (57) is that the standard deviation of the population at $t = 0$ is $\sigma_0 = 0$.

A second way that initial condition Eq. (57) could be realized is if the traps were irradiated to saturation. In this case, we know that $i_0 = \mathbb{N}$, and initial condition Eq. (57) again applies.

In either case, if i_0 is known and $\sigma_0 = 0$, Eq. (53) simplifies to:

$$\sigma^2 = i_0\left[\exp\left(-f_{m0}\int_0^t \gamma(t')dt'\right) - \exp\left(-2f_{m0}\int_0^t \gamma(t')dt'\right)\right] \tag{58}$$

and, Eq. (52) becomes:

$$\mathbb{E}[i] = i_0 \exp\left(-f_{m0}\int_0^t \gamma(t')dt'\right) \tag{59}$$

Combining Eq. (58) with Eq. (59), we have:

$$\sigma^2 = \mathbb{E}[i]\left[1 - \exp\left(-f_{m0}\int_0^t \gamma(t')dt'\right)\right] \tag{60}$$

or,

$$\sigma = \sqrt{\frac{\mathbb{E}[i](i_0 - \mathbb{E}[i])}{i_0}} \tag{61}$$

While Eq. (59) and Eq. (61) provide an overview of the heating process, the detailed probability distribution during heating, subject to initial condition Eq. (57), is given by:

$$P_i = \binom{\mathbb{N}}{i}\exp\left(-if_{m0}\int_0^t \gamma(t')dt'\right)\left[1 - \exp\left(-f_{m0}\int_0^t \gamma(t')dt'\right)\right]^{\mathbb{N}-i} \tag{62}$$

This can be verified by substitution into Eq. (51).

Several equations above require integrals over the thermal excitation coefficient γ. In thermoluminescence, it is most common to use a constant heating rate:

$$T = T_0 + \beta t \tag{63}$$

where β is a constant. In this case, the integral over γ reduces to:

$$\int_0^t \gamma(t')dt' = \frac{Es}{k\beta}\left(\Gamma(-1, E/kT) - \Gamma(-1, E/kT_0)\right) \tag{64}$$

where $\Gamma(-1, E/kT)$ is the incomplete gamma function as defined by Ref. [20]:

$$\Gamma(a, x) = \int_x^\infty e^{-t} t^{a-1} dt \tag{65}$$

This incomplete gamma function, or its equivalent exponential integral, are widely supported by current scientific software packages. With this integral, for example, the expected value of the trap population when heated at a constant rate becomes:

$$\mathbb{E}[i] = i_0 \exp\left(f_{m0}\frac{Es}{k\beta}\left(\Gamma(-1, E/kT) - \Gamma(-1, E/kT_0)\right)\right) \tag{66}$$

Analytical integrals over γ are also available for other heating rate profiles [21].

For a given heating rate and trap parameters, Eq. (66) allows the expected trap population, Eq. (59), to be computed as a function of time. Using Eq. (66), the standard deviation of the trap population distribution can be computed with Eq. (61).

To illustrate, consider a trap with binding energy $E = 1\text{eV}$ and pre-exponential factor $s = 10^{10}\ \text{s}^{-1}$ with the material heated at a rate of $\beta = 1\text{K/s}$ and other parameters as described previously. If the trap is irradiated to a low dose and consequently starts from a Poisson distribution, as per Eq. (38), the probability distribution for trap occupation varies as shown in Fig. 5. The distribution is initially broad but gets narrower as the temperature increases. Alternatively, if the trap was

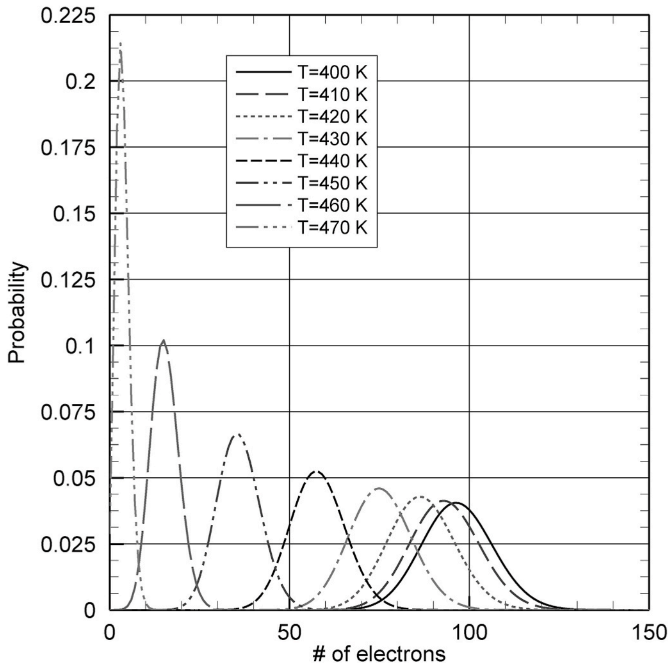

Fig. 5. Using Eq. (56) with Eq. (64), the probability distribution for trap population is plotted for various temperatures during heating. The calculation was performed assuming an initial ($T = 300$ K) Poisson distribution from Eq. (38) centered around $i = 100$. As the temperature rises, the trap population declines and the distribution narrows and moves to the left.

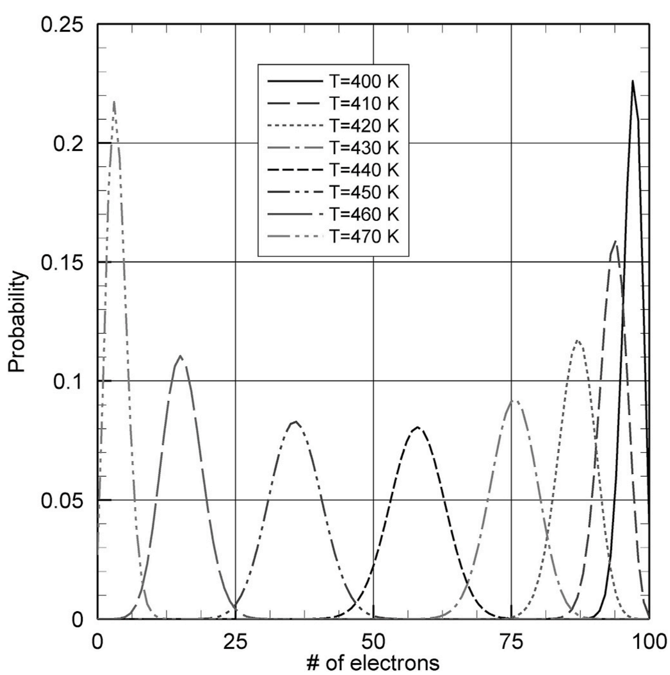

Fig. 6. The probability distribution, as given by Eq. (62) with Eq. (64), for trap population is plotted for various temperatures during heating just as in Fig. 5 except that initial condition Eq. (57) was used.

initially at saturation or the trap population was known by measurement, then the probability distribution during heating is shown in Fig. 6. In this case, the distribution is initially sharply peaked and, as temperature increases, it broadens and then later narrows again. The behavior of the standard deviation for both cases in shown in Fig. 7. For the case of initial condition Eq. (57), the standard deviation starts out at zero,

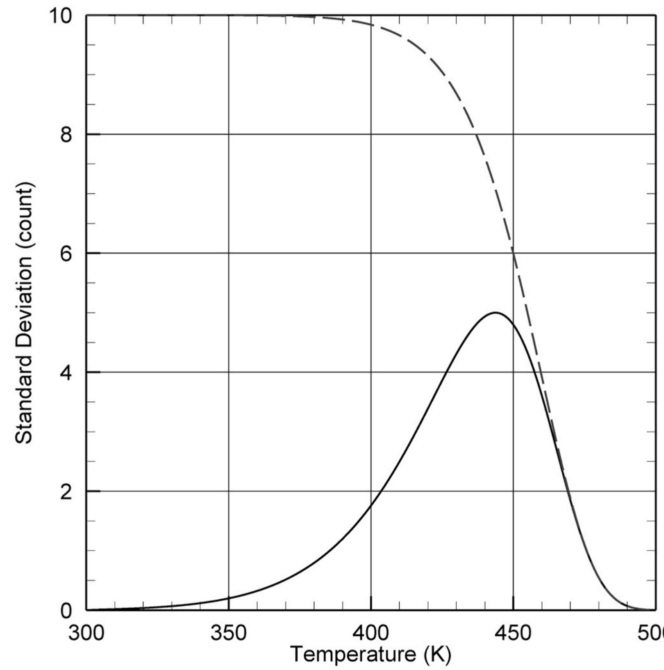

Fig. 7. The standard deviations of the trap occupation probability distribution from Figs. 5 and 6 are plotted against temperature during heating. The solid curve is for initial condition Eq. (57) and is computed using Eq. (61) and Eq. (52). The dashed curve is for initial condition Eq. (38) and is computed using Eq. (55) and Eq. (52).

slowly rises to a peak around 440 K and then rapidly declines again to zero. For initial condition Eq. (38) by contrast, the standard deviation starts out at its peak and begins to decline at about 400 K as the trap starts to empty.

To summarize, we found that, during heating and subject to either Eq. (19) or Eq. (50), the standard deviation of the trap population i varied with time according to Eq. (53). Subject to initial condition Eq. (36), we find that σ declines monotonically during heating as shown in Eq. (55). Alternatively, with initial condition $\sigma_0 = 0$, the standard deviation of trap population, σ, first grows then declines as shown in Eq. (61).

6. Standard deviation at the macroscopic level

The σ is the standard deviation of the occupation number i. This is related to the standard deviation of the trap concentration i/V via:

$$\sigma_n = \frac{\sigma}{V} \tag{67}$$

This section will summarize the results of the preceding sections in terms of σ_n.

The simplest result for σ_n is for irradiation at low dose (Eq. (36)):

$$\sigma_n = \sqrt{n/V} \tag{68}$$

This is the usual result one expects from a Poisson process. Note that, while the standard deviation in i increases with sample volume V, σ_n, Eq. (68), decreases with increasing sample volume. At higher dose, and subject to the $A_n = A_m$ assumption, Eq. (47) shows that the irradiation process ceases to follow Poisson statistics and instead we have:

$$\sigma_n = \sqrt{\frac{n(N-n)}{NV}} \tag{69}$$

If heating follows irradiation at low dose, with σ_n after irradiation given by Eq. (68), then, during heating as per Eq. (55) and Eq. (67), σ_n behaves as:

$$\sigma_n = \sqrt{n/V} \tag{70}$$

During heating, because n declines with time, σ_n also declines with time. By contrast, after a high dose radiation leaving a saturated trap, $n = N$ and $\sigma_n = 0$, then, from Eq. (61) and Eq. (67), a very different behavior is observed:

$$\sigma_n = \sqrt{\frac{n(N-n)}{NV}} \tag{71}$$

σ_n reaches a peak when n has declined to $N/2$.

7. Discussion

Although not captured by phenomenological equations such as Eq. (1) through Eq. (5), thermoluminescence is inherently a statistical process. The models herein quantify the statistical behavior for a one–center one–active-trap model with a first–order glow curve. For the simple cases discussed here, the expected value of trap population behaved the same as one would expect from the phenomenological equations. The actual trap population would vary from run to run with a probability distribution as described by the master equation.

For a binomial or Poisson process, a measurement that averages k independent events is associated with a standard deviation of $\sqrt{k}$ and this square–root law is widely used. As we have seen herein, the physics of thermoluminescence is sometimes such a process with irradiation at low dose being an example. At other times, such as shown in Eq. (47) or Eq. (61), it is not.

The model herein assumed that a single irradiation event produces a single electron-hole pair. This may apply to UV irradiation but is unlikely to apply to other higher–energy forms of irradiation.

The models herein address the inherent statistical noise in thermoluminescence processes for a particular simple model. A real thermoluminescence experiment will generally involve more complex physics and additional statistical processes associated with the laboratory measurement instrumentation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix. A

The derivations of Eq. (26) and Eq. (33) require careful manipulation of sums. As the techniques used are quite useful, the derivations will be presented here.

To obtain Eq. (26), we start from Eq. (25) and manipulate the sums as follows:

$$\begin{aligned}
\frac{d\mathbb{E}[i]}{dt} &= \sum_{i=1} f_{m0}\gamma i(i+1)P_{i+1} - \sum_{i=1} f_{n0}VXiP_i - \sum_{i=1} f_{m0}\gamma i^2 P_i + \sum_{i=1} f_{n0}VXiP_{i-1} \\
&= \sum_{i=2} f_{m0}\gamma (i-1)iP_i - \sum_{i=0} f_{n0}VXiP_i - \sum_{i=0} f_{m0}\gamma i^2 P_i + \sum_{i=0} f_{n0}VX(i+1)P_i \\
&= \sum_{i=0} f_{m0}\gamma (i-1)iP_i - \sum_{i=0} f_{n0}VXiP_i - \sum_{i=0} f_{m0}\gamma i^2 P_i + \sum_{i=0} f_{n0}VX(i+1)P_i \\
&= f_{n0}VX\sum_{i=0}[(i+1)P_i - iP_i] + f_{m0}\gamma\sum_{i=0}[(i-1)iP_i - i^2P_i] \\
&= f_{n0}VX\sum_{i=0}P_i - f_{m0}\gamma\sum_{i=0}iP_i
\end{aligned} \tag{A.1}$$

Using Eq. (17) and Eq. (23), Eq. (A.1) reduces to:

$$\frac{d\mathbb{E}[i]}{dt} = f_{n0}VX - f_{m0}\gamma\mathbb{E}[i] \tag{A.2}$$

which provides the desired result, Eq. (26).

To develop the governing equation for variance, Eq. (33), we start by substituting the master equation, Eq. (21), into Eq. (32) and then manipulate the sums:

$$\begin{aligned}
\frac{d\sigma^2}{dt} &= \sum_{i=1} f_{m0}\gamma i^2(i+1)P_{i+1} - \sum_{i=1}\left[f_{n0}VXi^2P_i - f_{m0}\gamma i^3 P_i\right] + \sum_{i=1} f_{n0}VXi^2P_{i-1} - 2\mathbb{E}[i]\frac{d\mathbb{E}[i]}{dt} \\
&= \sum_{i=2} f_{m0}\gamma (i-1)^2 iP_i - \sum_{i=1}\left[f_{n0}VXi^2P_i - f_{m0}\gamma i^3 P_i\right] + \sum_{i=0} f_{n0}VX(i+1)^2P_i - 2\mathbb{E}[i]\frac{d\mathbb{E}[i]}{dt} \\
&= \sum_{i=0} f_{m0}\gamma (i-1)^2 iP_i - \sum_{i=0}\left[f_{n0}VXi^2P_i - f_{m0}\gamma i^3 P_i\right] + \sum_{i=0} f_{n0}VX(i+1)^2P_i - 2\mathbb{E}[i]\frac{d\mathbb{E}[i]}{dt} \\
&= f_{n0}VX\sum_{i=0}\left[(i+1)^2 - i^2\right]P_i + f_{m0}\gamma\sum_{i=0}\left[(i-1)^2 i - i^3\right]P_i - 2\mathbb{E}[i]\frac{d\mathbb{E}[i]}{dt} \\
&= f_{n0}VX\sum_{i=0}(2i+1)P_i + f_{m0}\gamma\sum_{i=0}\left[-2i^2 + i\right]P_i - 2\mathbb{E}[i]\frac{d\mathbb{E}[i]}{dt} \\
&= f_{n0}VX(2\mathbb{E}[i]+1) + f_{m0}\gamma\left[-2\mathbb{E}\left[i^2\right] + \mathbb{E}[i]\right] - 2\mathbb{E}[i]\frac{d\mathbb{E}[i]}{dt}
\end{aligned} \tag{A.3}$$

Substituting Eq. (A.2) into Eq. (A.3), we find:

$$\frac{d\sigma^2}{dt} = f_{n0}VX + f_{m0}\gamma\left[\mathbb{E}[i] + 2\mathbb{E}[i]^2 - 2\mathbb{E}\left[i^2\right]\right] \tag{A.4}$$

Applying Eq. (31)to Eq. (A.4), the governing equation for variance of the trap population *i* is:

$$\frac{d\sigma^2}{dt} = f_{n0}VX + f_{m0}\gamma\left[\mathbb{E}[i] - 2\sigma^2\right] \tag{A.5}$$

This concludes the derivation of Eq. (33).

References

[1] J. Gasiot, P. Bräunlich, J.P. Fillard, Laser heating in thermoluminescence dosimetry, J. Appl. Phys. 53 (7) (1982) 5200–5209.
[2] P. Bräunlich, Present state and future of TLD laser heating, Radiat. Protect. Dosim. 34 (1990) 345–351.
[3] J. Lawless, S. Lam, D. Lo, Nondestructive in situ thermoluminescence using CO_2 laser heating, Optics Express 10 (2002) 291–296.
[4] G. Duller, L. Bøtter-Jensen, A. Murray, A.J. Truscott, Single grain luminescence (SGLL)measurements using a novel automated reader, Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms 155 (1999) 506–514.
[5] L. Bøtter-Jensen, E. Bulur, G. Duller, A. Murray, Advances in luminescence instrumentation, Radiat. Meas. 32 (2000) 523–528.
[6] G.A.T. Duller, Luminescence dating of quaternary sediments: recent advances, J. Quat. Sci. 19 (2) (2004) 183–192. https://onlinelibrary.wiley.com/doi/abs/10.1002/jqs.809.
[7] Z. Jacobs, G.A.T. Duller, A.G. Wintle, Interpretation of single grain D_e distributions and calculation of D_e, Radiat. Meas. 41 (3) (2006) 264–277. http://www.sciencedirect.com/science/article/pii/S1350448705002404.
[8] Z. Jacobs, R.G. Roberts, Advances in optically stimulated luminescence dating of individual grains of quartz from archeological deposits, Evol. Anthropol. Issues News Rev. 16 (6) (2007) 210–223. https://onlinelibrary.wiley.com/doi/abs/10.1002/evan.20150.
[9] N.G. van Kampen, Stochastic Processes in Physics and Chemistry, Elsevier Science, Amsterdam, 1992.
[10] J.W. Rich, C.E. Treanor, Vibrational relaxation in gas-dynamic flows, Annu. Rev. Fluid Mech. 2 (1970) 355–396.
[11] A.D. Fokker, Die mittlere Energie rotierender elektrischer Dipole im Strahlungsfeld, Ann. Phys. 348 (5) (1914) 810–820. https://onlinelibrary.wiley.com/doi/abs/10.1002/andp.19143480507.
[12] M. Planck, Über einen Satz der statistischen Dynamik und seine Erweiterung in der Quantentheorie, Sitzungsber. Preuss. Akad. Wiss. 24 (1917) 324–341.
[13] R.O. Dendy, Plasma Dynamics, Oxford Science Publications. Clarendon Press, 1990. https://books.google.com/books?id=rCm3QgAACAAJ.
[14] V. Kolobov, Fokker-â€"Planck modeling of electron kinetics in plasmas and semiconductors, Comput. Mater. Sci. 28 (2003) 302–320.
[15] J.R. Swandic, Stochastic approach to recombination luminescence with retrapping in the steady state, Phys. Rev. B 45 (1992) 622–634.
[16] J.R. Swandic, Stochastic analysis of multiple-level recombination luminescence and retrapping in the steady state, Phys. Rev. B 53 (1996) 2352–2366.
[17] A. Rose, Recombination processes in insulators and semiconductors, Phys. Rev. 97 (1955) 322–333.
[18] M. Lax, Cascade capture of electrons in solids, Phys. Rev. 119 (5) (1960) 1502–1523.
[19] E.G. Yukihara, V.H. Whitley, J.C. Polf, D.M. Klein, S.W.S. McKeever, A.E. Akselrod, M.S. Akselrod, The effects of deep trap population on the thermoluminescence of Al_2O_3:C, Radiat. Meas. 37 (6) (2003) 627–638, https://doi.org/10.1016/S1350-4487(03)00077-5.
[20] M. Abramowitz, I.A. Stegun (Eds.), Handbook of Mathematical Functions, U.S. Government Printing Office, Washington, D. C, 1970.
[21] J. Lawless, D. Lo, Thermoluminescence for nonlinear heating profiles with application to laser heated emissions, J. Appl. Phys. 89 (2001) 6145–6152.