A transfer function approach to reaction rate analysis with applications to phase-change materials and devices

M. M. Aziz and C. D. Wright

Citation: [Appl. Phys. Lett.](#) **103**, 113501 (2013); doi: 10.1063/1.4820696

View online: <http://dx.doi.org/10.1063/1.4820696>

View Table of Contents: <http://apl.aip.org/resource/1/APPLAB/v103/i11>

Published by the [AIP Publishing LLC](#).

Additional information on Appl. Phys. Lett.

Journal Homepage: <http://apl.aip.org/>

Journal Information: http://apl.aip.org/about/about_the_journal

Top downloads: http://apl.aip.org/features/most_downloaded

Information for Authors: <http://apl.aip.org/authors>

ADVERTISEMENT

**MATERIAL SCIENCE RESEARCH
AT 3K – MADE SIMPLE**

MONTANA INSTRUMENTS
COLD SCIENCE MADE SIMPLE

CLOSED CYCLE OPTICAL CRYOSTATS

A transfer function approach to reaction rate analysis with applications to phase-change materials and devices

M. M. Aziz^{a)} and C. D. Wright

College of Engineering, Mathematics & Physical Sciences, University of Exeter, North Park Road, Exeter EX4 4QF, United Kingdom

(Received 10 May 2013; accepted 23 August 2013; published online 9 September 2013)

A very good approximate, closed-form solution to the reaction rate equation with Arrhenius temperature dependence is derived, valid for activation energies $E \gg k_B T_0$ (k_B is Boltzmann constant and T_0 is room temperature) and monotonically decreasing temperatures. This solution is then used to develop a transfer function description of the reaction rate equation, enabling the bandwidth of the reaction rate to be determined and related to the kinetic and thermophysical parameters of the medium. Applications of the transfer function approach to understanding and predicting reaction (i.e., crystallization) rates in phase-change materials and devices are discussed.

© 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4820696>]

Understanding and predicting reaction rates are important in many scientific and technological fields. In phase-change materials and devices, the focus of this work, reaction rate equations are frequently used to model and predict crystallization rates.^{1,2} Understanding the factors that affect crystallization rates is most important in the design and development of phase-change memory devices, since it is the crystallization rate that is the dominant factor limiting write speeds in current-day phase-change memory devices.^{3,4}

The reaction dynamics of a mixture of two materials can be described by the n th-order nonlinear reaction rate equation with Arrhenius temperature dependence,^{1,2,5}

$$\frac{d\chi(t)}{dt} = A(1 - \chi(t))^n \exp\left(\frac{-\varepsilon}{\theta(t)}\right), \quad (1)$$

where χ is the fraction of the reactant transformed (in the case of phase-change materials the fraction of crystallized material), A is the pre-exponential frequency factor, n is the reaction order, $\varepsilon = E/k_B T_0$ is the activation energy normalized to thermal energy at room temperature T_0 , and $\theta = T/T_0$ is the normalized absolute temperature in the medium. Exact analytical solutions to the non-linear rate equation in Eq. (1) are only available for simple temperature functions including constant (isothermal) temperatures, and linearly increasing^{5,6} or decreasing⁷ temperature changes. While the use of linear temperature functions is useful for the analysis of laboratory-based calorimetry experiments, as used extensively to study the reaction dynamics of phase-change materials and to extract relevant activation energies (for example Ref. 8), in practical phase-change applications, such as optical disk systems or electrical phase-change memories, the heat sources (laser light in the case of optical disks, Joule heating in the case of electrical memories) produce more complex temperature functions with changing rate that is dependent on the heat source parameters (such as the power density) and the material/device thermal properties. In such cases, the

reaction rate equation is usually solved numerically, but such numerical solutions are complicated by rapid changes in temperature that lead to large reaction gradients, so requiring arbitrary small numerical sampling intervals or even adaptive schemes to accommodate the “stiff” conditions of the simulation to arrive at satisfactory results.^{9,10} The same difficulty arises when resorting to Fourier domain techniques to solve the reaction rate equation, as such techniques also require knowledge of the sampling resolution necessary to cover the essential bandwidth of the system. Furthermore, the correlation between the system bandwidth (or transfer function) of the reaction rate equation and the kinetic and thermophysical parameters of the medium and source parameters is not known or addressed in the literature. The determination of such a correlation would, however, be extremely beneficial not only to ensure accurate numerical evaluation and modelling of the reaction dynamics in materials and devices but also to provide a quantitative insight into the scaling of reaction times (i.e., in the phase-change case the crystallization times) with the device dimensions and the thermal and kinetic properties of the materials used in a particular device design. In this work, therefore, we develop a transfer function representation for the reaction rate equation of Eq. (1), during practical cooling/thermal relaxation schemes, that enables unambiguous identification of the reaction rate bandwidth (hence the required sampling interval for numerical simulations) along with, in the case of phase-change materials/devices, the correlation between key material/device properties and bandwidth (hence crystallization times).

We begin by deriving a very good approximate closed-form solution for the reaction rate equation in Eq. (1), for the limit $\varepsilon \gg 1$ (where ε is the normalized activation energy $E/k_B T_0$) and assuming monotonically decreasing temperatures. The condition $\varepsilon \gg 1$ is satisfied by all phase-change materials of current technological importance (e.g., in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ $\varepsilon \sim 81$ —see Table I) and which form the focus of our work. Moreover, monotonically decreasing temperatures arise in practical phase-change memory devices and materials following removal of the heat source (or turn-off), from ultra-

^{a)} Author to whom correspondence should be addressed. Electronic mail: M.M.Aziz@ex.ac.uk

TABLE I. List of typical kinetic parameters for the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ material² and assumed heat source parameters used in the calculations.

Symbol	Value	Units
E	2.1	eV
A	1.5×10^{22}	s^{-1}
$\varepsilon = E/kT_0$	81	—
n	1, 3	—
T_m	894	K
T_p	850	K
t_c	5	ns

fast heating followed by thermal relaxation, or during cooling from the melting phase.¹¹ Thus, the approximate closed-form solution to Eq. (1) derived here, and the resulting reaction rate transfer function derived using Laplace transform techniques, are very well-suited to real phase-change applications.

Direct integration of the rate equation in Eq. (1) yields the solutions

$$1 - \chi(t) = \begin{cases} (1 - \chi_0)\exp(-At) & n = 1 \\ [(1 - \chi_0)^{1-n} + A(n-1)t]^{\frac{1}{1-n}} & n \neq 1. \end{cases} \quad (2)$$

The integral $I = \int_{t'=0}^t \exp(\varepsilon h(t')) dt'$ and $h(t) = -1/\theta(t)$. Exact solutions to this integral are limited to constant and linearly increasing/decreasing temperatures. A very good approximation may be derived for a monotonically decreasing temperature with maximum near $t=0$ and $\varepsilon \gg 1$ by invoking Laplace's method.¹² Under these conditions, this method stipulates that for large ε , only the immediate neighbourhood of $t=0$ contributes to the full asymptotic expansion of the integral I . Expanding $h(t)$ around this maximum to first-order $h(t) \approx h(0) + th'(0)$, where $h'(t)$ is the first derivative of $h(t)$, and integrating I yields the approximation

$$I \approx \frac{-e^{\varepsilon h(0)}}{\varepsilon h'(0)} (1 - e^{\varepsilon h'(0)t}), \quad (3)$$

where $\varepsilon \gg 1$ and $h'(0) < 0$ since the temperature is monotonically decreasing. Substituting Eq. (3) into Eq. (2) yields an approximate solution for the rate equation under these conditions. The approximation technique used to solve Eq. (1) can be applied to other systems exhibiting Arrhenius temperature dependence such as the growth velocity in interface-controlled growth.¹³

Any error in the approximate solution to Eq. (1) presented here can be estimated next by comparison with a numerical solution for Eq. (1) (or Eq. (2)). To solve (2) numerically, the integral I is re-written as a convolution with the unit-step function $U(t-t')$ in the form $\int_{t'=0}^t \exp(\varepsilon h(t')) dt' = \int_{t'=0}^\infty \exp(\varepsilon h(t')) U(t-t') dt'$, which can be integrated easily using the Fast-Fourier Transform (FFT). This choice of integration method highlights the need for knowledge of the bandwidth of the system to determine the necessary sampling interval for accurate evaluation of the Fourier transform. In this numerical example and in the analysis to follow, the normalized monotonically decreasing temperature, $\theta = T/T_0$, will be assumed to follow the exponential function:

$$\theta(t) = 1 + (\theta_p - 1)\exp(-t/t_c), \quad (4)$$

with relaxation or thermal diffusion time constant t_c (that includes the effects of the thermophysical parameters of the medium), and peak temperature $\theta_p = T_p/T_0$ (which reflects the power delivered by the heat source). The exponential temperature distribution of Eq. (4) provides a realistic model of the temperature variation/thermal diffusion in optical and electrical phase-change systems^{11,14,15} and has a temperature gradient that is not constant and is a function of the source peak temperature (unlike linear heating cases). This exponential temperature distribution also simplifies the mathematical analysis and yields closed-form expressions for the rate equation transforms. The influence of more detailed temperature histories (for example, a constant temperature preceding the exponential decay) can be easily included in this model as an initial condition χ_0 in Eq. (2) for the determination of the subsequent reaction dynamics.

The material parameters used in this paper are for the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ phase-change material frequently used in optical recording and phase-change memory devices (PCMs). This material experiences temperature distributions in the form of Eq. (4) during turn-off of laser and voltage pulse operations that determine the final crystalline fraction transformed from the starting amorphous phase. Typical kinetic and thermodynamic parameters for $\text{Ge}_2\text{Sb}_2\text{Te}_5$ are listed in Table I along with the assumed heat source parameters.

Thus, the predicted crystalline fraction as a function of time for a $\text{Ge}_2\text{Sb}_2\text{Te}_5$ material subjected to the temperature distribution of Eq. (4) and calculated using the approximate analytical solutions from Eqs. (2) and (3) is shown in Fig. 1, for the reaction orders of $n=1$ and $n=3$. Also shown in the same figure are the results from the convolution based numerical approach; excellent agreement between the analytical and numerical approaches is achieved (maximum root-mean-square error is 0.4%) and therefore the approximate solutions in Eqs. (2) and (3) are used below to derive the reaction rate transfer function. Note that the sampling time for the numerical integration was chosen by progressively reducing it from a starting value of $1/\varepsilon h'(0) \sim 270$ ps (rise time constant of I in Eq. (3)) until further reductions caused negligible changes to the numerical solution (at which point

FIG. 1. Crystalline fraction versus time calculated using the analytical approximation in Eqs. (2) and (3), compared to a solution using the convolution based numerical technique.

the sampling interval was 10 ps, a choice that is confirmed directly using the reaction rate bandwidth expression derived later).

We now derive the reaction rate transfer function, and therefore the system frequency response, via the Laplace transform of Eq. (2). For first-order reactions ($n = 1$), evaluating the Laplace transform of Eq. (2) (after substituting Eq. (3)) yields

$$\chi(s) = \frac{1}{s} + \frac{(1 - \chi_0)}{\varepsilon h'(0)} e^{\eta} \eta^a \gamma(-a, \eta), \quad (5)$$

where $a = s/\varepsilon h'(0)$, $\eta = A e^{\varepsilon h(0)}/\varepsilon h'(0)$, and γ is the incomplete Gamma function defined by the integral $\gamma(a, z) = \int_0^z e^{-t} t^{a-1} dt$.¹⁶ For $n \neq 1$, the Laplace transform of Eq. (2), again using the approximation in Eq. (3), was found to be

$$\chi(s) = \frac{1}{s} + \frac{(1 - \chi_0)}{s} {}_2F_1\left(\frac{1}{n-1}, 1; 1-a; \frac{n-1}{(1-\chi_0)^{(1-n)}} \eta\right), \quad (6)$$

where ${}_2F_1(\cdot)$ is the Hypergeometric function.¹⁶ The Laplace transform of the exponential temperature distribution, which is needed for the determination of the transfer function (which is defined as the ratio of the Laplace transform of the fraction transformed to the Laplace transform of the input temperature) is given by

$$\theta(s) = \frac{\theta_p s + 1/t_c}{s(s + 1/t_c)}. \quad (7)$$

Thus, for $n = 1$, the reaction rate transfer function ($\chi(s)/\theta(s)$) is given by dividing Eq. (5) by Eq. (7) and simplifying

$$\frac{\chi(s)}{\theta(s)} = \frac{(s + 1/t_c) \left(1 + s e^{\eta} \eta^a \gamma(-a, \eta) / \varepsilon h'(0)\right)}{(\theta_p s + 1/t_c)}. \quad (8)$$

Since the focus of the analysis is on the sinusoidal frequency response at steady-state, the initial condition of the transformed fraction is assumed zero (i.e., $\chi_0 = 0$) in the transfer function evaluation. For higher order reactions ($n \neq 1$), the transfer function is derived from Eqs. (6) and (7) and is given by

$$\frac{\chi(s)}{\theta(s)} = \frac{(s + 1/t_c) \left(1 - {}_2F_1\left(\frac{1}{n-1}, 1; 1-a; \frac{n-1}{(1-\chi_0)^{(1-n)}} \eta\right)\right)}{(\theta_p s + 1/t_c)}. \quad (9)$$

The gain of the transfer functions (or frequency responses) in Eqs. (8) and (9) is plotted in Fig. 2 as a function of angular frequency ω (with $s = j\omega$). The frequency responses in Fig. 2 exhibit a low pass filter effect and a reduction in the low frequency gain for an increased reaction order. At high frequencies, the effect of the reaction order becomes negligible and the gain rolls off at a rate of approximately 20 dB per decade.

FIG. 2. Gain versus frequency for the transfer functions in Eqs. (8) and (9). The dashed lines indicate the low and high frequency limits derived in Eqs. (10) and (11), respectively.

The bandwidth of the reaction rate equation can now be estimated, from the frequency at which the high frequency response reduces to a given fraction of the low frequency limit. Evaluating the low frequency limit of the transfer functions in Eqs. (9) and (10) by setting $s \rightarrow 0$ yields

$$L_n = \begin{cases} 1 - \exp(\eta) & n = 1 \\ 1 - (1 - (n-1)\eta)^{-1/(n-1)} & n \neq 1, \end{cases} \quad (10)$$

indicating a decrease in the low frequency gain with increasing reaction order as indicated in Fig. 2 (which corresponds to reduction in χ at steady-state as indicated in Fig. 1). At high frequencies, the incomplete Gamma function in Eq. (8) and the Hypergeometric function in Eq. (9) can be expanded to second-order for $s \rightarrow \infty$ with both yielding the high frequency limit

$$H(s) \approx \frac{\eta \varepsilon h'(0)}{\theta_p s}, \quad (11)$$

with a slope of -20 dB per decade as shown by the dashed line at high frequency in Fig. 2. The bandwidth ω_B of the reaction rate equation is now determined at the frequency at which the high frequency response reduces to a fraction r of the low frequency limit by solving $rL_n = H(s)$, where $r < 1$, and setting $s = j\omega$ to yield:

$$\omega_B = \frac{\eta \varepsilon h'(0)}{\theta_p r L_n}. \quad (12)$$

In the remainder of this paper, the system bandwidth is determined for $r = 0.1$. Equation (12) explicitly illustrates the dependence of the essential bandwidth, and therefore the achievable crystallization time (or switching time in phase-change devices) on the kinetic and thermophysical parameters of the medium and on the heat source parameters. It also gives direct quantitative values for the required sampling frequency ω_s , and therefore sampling interval t_s , necessary to properly sample the reaction dynamics according to the sampling theorem, i.e., $\omega_s = 2\pi/t_s > 2\omega_B$.

FIG. 3. Reaction rate bandwidth (for $r=0.1$) as a function of the normalized activation energy ε for different frequency factors using Eq. (12). The activation energies for $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (from Table I) and AgInSbTe (Ref. 18) are shown for comparison. The dashed lines are for $n=1$, while the solid lines are for $n=3$. The heat source parameters are fixed to the values shown in Table I.

The effect of the kinetic material parameters, including activation energy ε , frequency factor A , and reaction order n on ω_B is plotted in Fig. 3. As ε increases, ω_B initially decreases logarithmically, reflecting the slower reaction rate expected with increasing ε and meaning that the sampling time (for accurate numerical simulation) is getting larger. Increasing the factor A (the probability of a molecule or “monomer” at energy E to be involved in the reaction) in this region increases ω_B by the same proportion to correctly follow the fast transients in the system. Figure 3 also reveals that ω_B reaches a minimum and then increases linearly with further increases in ε (and independent of A). This is due to abrupt increases in reaction rate that can take place at high temperatures or over prolonged heating for large ε , thus increasing ω_B to encompass these dynamics. The transition between the logarithmic and linear dependance of ω_B (minima in Fig. 3) happen approximately at $\varepsilon \approx -W(Ah(0)/h'(0))/h(0)$ where $W(\cdot)$ is the Lambert function.¹⁷ Increasing the reaction order n appears to cause negligible increases in ω_B for the parameters used here. The values of ε for both $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and AgInSbTe (common phase-change materials in use today) and their essential bandwidths are also shown in Fig. 3 for comparison.

The influence, on the reaction rate bandwidth, of the thermal parameters of the medium (e.g., the dimensions, thermal conductivity and specific heat of the material and/or device structure) and the heat source power are included in the parameters t_c and θ_p , respectively. Thus, Fig. 4 illustrates the variation in ω_B for $\text{Ge}_2\text{Sb}_2\text{Te}_5$ as a function of t_c for a number of peak temperatures θ_p . Fig. 4 shows that ω_B increases with reductions in t_c due to the consequent increase in the rate of χ in response to larger temperature gradients. For large t_c , however, the reaction rate is slow leading to reductions in ω_B . For sufficiently large peak temperatures ($\theta_p = 2.8, 3$ in Fig. 4), ω_B does not decrease indefinitely with increasing t_c but remains constant at a minimum level to accurately sample the temperature gradients induced in the material by the high peak temperatures. Fig. 4 also illustrates the correlation between t_c and the thickness of the phase-

FIG. 4. Effect of the heat source parameters including thermal relaxation time t_c and normalized peak temperature θ_p on ω_B determined using Eq. (12). The kinetic parameters were fixed at the values in Table I for $n=1$. The dashed lines indicate how changes in thermal diffusion time t_c correlate and scale with changes in thickness of an amorphous phase-change material stack with composition $\text{ZnS-SiO}_2/\text{Ge}_2\text{Sb}_2\text{Te}_5/\text{ZnS-SiO}_2/\text{Si}$ substrate from Ref. 11 heated by a femtosecond laser source with 20mJ/cm^2 peak fluence (corresponding to peak temperature of 850 K in the top of the phase-change layer in the material stack).

change layer in a practical phase-change optical disk stack¹¹ consisting of $\text{ZnS-SiO}_2/\text{Ge}_2\text{Sb}_2\text{Te}_5/\text{ZnS-SiO}_2/\text{Si}$ excited by a femtosecond laser. This illustrates that Eq. (13) can be used study the correlation and therefore scaling of ω_B (and hence crystallization/switching time) in a phase-change medium with the dimensions of the active layer, and/or with the thermal parameters of the medium in general.

Finally, we note that for the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ parameters listed in Table I, Eq. (12) predicts bandwidths $\omega_B = 2.5 \times 10^{10}$ and 4×10^{10} rad/s for $n=1$ and $n=3$, respectively. The 10 ps sampling interval used for the correct numerical evaluation of the integral I satisfies these bandwidth requirements therefore illustrating the validity of Eq. (12) in predicting the essential bandwidth for the reaction rate equation. The approximate theory presented here therefore provides a general understanding and foundation for more complex simulations of reaction dynamics in materials (involving nucleation and growth for example). It is important to note that the theory presented here is valid for any class of monotonically decreasing temperatures with arbitrary relaxation time constant (not necessarily in the nanosecond range used in this paper) provided that $\varepsilon \gg 1$.

¹A. Redaelli, A. Pirovano, A. Benvenuti, and A. L. Lacaita, *J. Appl. Phys.* **103**, 111101 (2008).

²S. Senkader and C. D. Wright, *J. Appl. Phys.* **95**, 504 (2004).

³J. Orava, A. L. Greer, B. Gholipour, D. W. Hewak, and C. E. Smith, *Nature Mater.* **11**, 279 (2012).

⁴D. Loke, T. H. Lee, W. J. Wang, L. P. Shi, R. Zhao, Y. C. Yeo, T. C. Chong, and S. R. Elliott, *Science* **336**, 1566 (2012).

⁵H. E. Kissinger, *Anal. Chem.* **29**, 1702 (1957).

⁶J. Farjas and P. Roura, *AIChE J.* **54**, 2145 (2008).

⁷M. M. Aziz, M. R. Belmont, and C. D. Wright, *J. Appl. Phys.* **104**, 104912 (2008).

⁸J. Kalb, E. Spaepen, and M. Wuttig, *J. Appl. Phys.* **93**, 2389 (2003).

⁹C. David Wright, K. Blyuss, and P. Ashwin, *Appl. Phys. Lett.* **90**, 063113 (2007).

¹⁰P. Ashwin, B. S. V. Patnaik, and C. David Wright, *J. Appl. Phys.* **104**, 084901 (2008).

- ¹¹Y. Liu, M. M. Aziz, A. Shalini, C. D. Wright, and R. J. Hicken, *J. Appl. Phys.* **112**, 123526 (2012).
- ¹²C. M. Bender and S. A. Orszag, *Advanced Mathematical Methods for Scientists and Engineers* (McGraw-Hill, Singapore, 1978), Chap. 6, p. 261.
- ¹³J. W. Christian, *The Theory of Transformations in Metals and Alloys* (Pergamon, Oxford, 1975), Chap 11, p. 480.
- ¹⁴C. Peng, L. Cheng, and M. Mansuripur, *J. Appl. Phys.* **82**, 4183 (1997).
- ¹⁵D. Kim, F. Merget, M. Först, and H. Kurz, *J. Appl. Phys.* **101**, 064512 (2007).
- ¹⁶M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (National Bureau of Standards, 1972), Chap. 6, p. 260, Tenth Printing 1972.
- ¹⁷R. M. Corless, G. H. Gonnet, D. E. G. Hare, D. J. Jeffrey, and D. E. Knuth, *Adv. Comput. Math.* **5**, 329 (1996).
- ¹⁸W. K. Njoroge and M. Wuttig, *J. Appl. Phys.* **90**, 3816 (2001).