

# Variational Formula for the Relaxation Time in the Boltzmann Equation<sup>†</sup>

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The relaxation time approximation (RTA) is commonly employed in nonequilibrium statistical mechanics to approximate solutions to the Boltzmann equation in terms of an exponential relaxation to equilibrium. Despite its common use, the RTA suffers from the drawback that relaxation times commonly employed are independent of initial conditions. We derive a variational principle for solutions to the Boltzmann equation, which allows us to extend the standard RTA using relaxation times that depend on the initial distribution. Tests of the approach on a calculation of the mobility for a one-dimensional (1D) tight-binding band indicate that our analysis typically provides a better approximation than the standard RTA.

## I. Introduction

The Boltzmann equation,<sup>1</sup> the work-horse of transport calculations<sup>2</sup> in gas dynamics, solid-state physics, and related branches of investigation, is essential to the analysis of transport coefficients such as viscosity, electrical mobility, thermal conductivity, Peltier coefficients, and Lorenz numbers. The equation comes in two forms, one linear in the probability distribution (or density)  $f_k(t)$ , the other bilinear. The latter, the original form introduced by Boltzmann,<sup>1</sup> is important in gas dynamics where the elemental events involve particle–particle collisions. The former, important in solid-state physics, focuses on interaction of the particles with scattering centers or vibrations and will be the target of our study here

$$\frac{df_k(t)}{dt} = \sum_{k'} [Q_{kk'}f_k(t) - Q_{k'k}f_{k'}(t)] \quad (1)$$

Here,  $k$  represents generally a quantum mechanical state and  $Q_{kk'}$ , the transition rate from state  $k$  to state  $k'$ , is independent of the  $f$  values.

Although linear, eq 1 is not easily solved because of the summation in  $k$ -space which in the continuum limit would make eq 1 an integral equation. There is, however, an approximation, traditionally used in many, if not all, practical applications, that allows one to avoid solving eq 1 numerically: the so-called relaxation time approximation (RTA). The RTA has served as a tool throughout the last several decades to such an extent that it is often thought to be self-evident or even exact in certain nontrivial cases of carrier transport (see, e.g., refs 4–6).

Despite its widespread applications, inadequacies of the relaxation time assumption have been recognized in the past.<sup>2,8</sup> One of its main drawbacks is the absence of any dependence on the initial conditions of the probability distributions, and is the principal issue discussed in this paper. In our attempt to remove that drawback, we derive a variational principle govern-

ing solutions to the Boltzmann equation that allows us to determine relaxation times that depend on the initial state of the system.

The rest of the paper is laid out as follows. In section II, we present cases in which the relaxation time procedure is known to be valid. In section III, we explain our variational procedure and apply it to find an alternative expression for the relaxation time which depends on initial conditions. The validity of the prescription we provide to compute the relaxation time in a specific case is the subject of section IV, while the conclusions are reported in section V.

## II. The Relaxation Time Approximation

In its most common form, the RTA consists of replacing the actual evolution in eq 1 by

$$\frac{df_k(t)}{dt} + \frac{f_k(t) - f_k^{\text{th}}}{\tau_k} = 0 \quad (2)$$

where  $\tau_k$  is called the relaxation time and  $f_k^{\text{th}}$  is the thermal form to which the distribution tends at long times in the absence of driving forces. The advantage of dealing with an equation such as 2 is that it offers analytically tractable results for  $f_k(t)$  in the form

$$f_k(t) = f_k^{\text{th}} + [f_k(0) - f_k^{\text{th}}]e^{-t/\tau_k} \quad (3)$$

Although there are variants, the simplest and most common prescription for the relaxation time that one finds in the literature is (see, e.g., refs 2, 4, 5, and 7)

$$\frac{1}{\tau_k} = \sum_{k'} Q_{k'k} \quad (4)$$

Three clear cases can be cited when this approximation procedure is valid:

Case (i): If the entire system has just two states, then the relaxation time procedure is always exact. Calling the two states  $k_1$  and  $k_2$ , eq 1 takes the form

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$$\begin{aligned}\frac{df_{k_1}(t)}{dt} &= Q_{k_1 k_2} f_{k_2}(t) - Q_{k_2 k_1} f_{k_1}(t) \\ \frac{df_{k_2}(t)}{dt} &= Q_{k_2 k_1} f_{k_1}(t) - Q_{k_1 k_2} f_{k_2}(t)\end{aligned}\quad (5)$$

Using conservation of probability,  $f_{k_2}(t) = 1 - f_{k_1}(t)$ , we see that this is identical to

$$\begin{aligned}\frac{df_{k_1}(t)}{dt} + (Q_{k_2 k_1} + Q_{k_1 k_2}) f_{k_1}(t) &= Q_{k_1 k_2} \\ \frac{df_{k_2}(t)}{dt} + (Q_{k_1 k_2} + Q_{k_2 k_1}) f_{k_2}(t) &= Q_{k_2 k_1}\end{aligned}\quad (6)$$

which is in the RTA form (eq 2) with  $1/\tau_k = Q_{k_1 k_2} + Q_{k_2 k_1}$  and  $f_k^{\text{th}} = Q_{k_1 k_2} / (Q_{k_2 k_1} + Q_{k_1 k_2})$  and  $f_{k_2}^{\text{th}} = Q_{k_2 k_1} / (Q_{k_1 k_2} + Q_{k_2 k_1})$  as is required by detailed balance.

Case (ii). If the transition rates are not dependent on the label  $k$  or  $k'$ , in a system of an arbitrarily large number of states  $N$ , then eq 1 takes the form

$$\frac{df_k(t)}{dt} = Q \sum_{k'} [f_{k'}(t) - f_k(t)] = Q - NQf_k(t)\quad (7)$$

which is also of the exact form (eq 2) with  $1/\tau_k = NQ$ ,  $f_k^{\text{th}}$  being the infinite temperature limit  $1/N$  as imposed by detailed balance in light of the  $k$  independence of the transition rates.

Case (iii). If one recasts eq 1 in the form of a matrix equation

$$\frac{df_k(t)}{dt} + \sum_{k'} A_{kk'} f_{k'}(t) = 0\quad (8)$$

where  $A_{kk'} = -Q_{kk'} + \delta_{k,k'} \sum_q Q_{qk}$ , one can formally consider the matrix  $A$ , diagonalize it, and write the solution in terms of eigenvalues  $\lambda_i$  of the  $A$  matrix as

$$f_k(t) = \sum_i a_k^i e^{-\lambda_i t}\quad (9)$$

where the coefficients  $a_k^i$  are obtained by the overlap of the initial distribution  $f_k(0)$  with the eigenvectors of the  $A$  matrix. There is always an eigenvalue zero, with the corresponding  $a_k^i$  being the thermal distribution function  $f_k^{\text{th}}$ . If we arrange the terms in the above expansion in ascending order of the values of  $\lambda_i$ , we notice that for large times, specifically for times much larger than the reciprocal of the difference between the third-smallest and the second-smallest (dominant) eigenvalues of the  $A$  matrix, the distribution function can be written approximately as

$$f_k(t) \approx f_k^{\text{th}} + a_k^1 e^{-\lambda_1 t}\quad (10)$$

Equation 10 is in the RTA form since it satisfies eq 2 with  $\lambda_1$  as  $1/\tau_k$ .

In all these three cases, the rate  $1/\tau_k$  turns out to be *not* dependent on  $k$ . This fact ensures that probability is conserved at all times. On the contrary, solutions of eq 2 will not generally conserve probability (except when  $t = 0$  or  $t \rightarrow \infty$ ) if the relaxation rate depends explicitly on  $k$ . This can be easily verified by summing the solution (eq 3) over  $k$ . This failure to conserve probability is not only repugnant in itself but is also known to lead to practical inaccuracies as in the case of the

Rayleigh problem.<sup>8</sup> That problem deals with the motion of a light particle harmonically bound to a fixed point and colliding with a gas of heavy particles in thermal equilibrium. When the ratio of the masses of the bound particle to the heavy particles is very small, the assumption of the existence of a relaxation time does not allow conservation of the number of particles in a collision. This, in turn, leads to the paradoxical result that the average position of the light particle does not change in time as would be expected in terms of its average velocity.

The other important shortcoming of the standard RTA is concerned with the fact that the relaxation time, as traditionally computed (see, e.g., eq 4), is independent of the initial conditions of the system. There is no way to have changes in those conditions reflected in the subsequent evolution of the system as described by the RTA. In an attempt to remove these limitations associated with the standard implementation (eq 4) of the RTA, we develop below a variational principle and obtain a relaxation time prescription which *does* depend on initial conditions and conserves probability at all times.

### III. Variational Prescription for the Relaxation Time

Using techniques from the calculus of variations (see, e.g. ref 9), we derive in this section a variational principle for the Boltzmann equation and use it to find an expression for the relaxation time, alternative to eq 4, that better approximates the exact solutions of the Boltzmann equation. It is well known that any function  $f(t)$  which satisfies the following variational condition

$$\delta J = \delta \int_{t_1}^{t_2} dt' F(f', f, t') = 0\quad (11)$$

where  $t_1$  and  $t_2$  are the endpoints of the evolution chosen according to the specific problem,  $f' = df/dt$  and  $\delta$  means a functional derivative of the action  $J$  with respect to  $f$ , is also a solution to an associated Euler's equation

$$\frac{\partial F}{\partial f} - \frac{d}{dt} \left( \frac{\partial F}{\partial f'} \right) = 0\quad (12)$$

generated by the functional  $F(f', f, t)$ . We are here interested in applying this variational principle to situations in which eq 12 is of the form

$$\frac{df}{dt} + Rf = 0\quad (13)$$

where, in general,  $f$  may be a vector and  $R$  a matrix. Differentiating eq 13 once with respect to  $t$ , we have

$$\frac{d^2 f}{dt^2} = R^2 f\quad (14)$$

If  $R$  is a symmetric matrix, it then follows from mechanical analogues and Lagrangian insights that a functional  $F$  that generates the appropriate equation of motion is given by the expression

$$F = f^2 + R^2 f^2\quad (15)$$

To identify eq 13 with the Boltzmann eq 1 and write the functional in the form of eq 15, it is necessary to rewrite eq 8 in terms of a symmetric matrix instead of the generally asymmetric matrix  $A_{kk'}$ . After  $g_k = f_k (f_k^{\text{th}})^{-1/2}$  is defined, eq 8 can be recast in the form

$$\frac{dg_k(t)}{dt} + \sum_{k'} W_{kk'} g_{k'}(t) = 0 \quad (16)$$

in which the detailed balance relation  $Q_{kk'} f_k^{\text{th}} = Q_{k'k} f_{k'}^{\text{th}}$  ensures symmetry of the matrix  $W_{kk'} = A_{kk'} (f_k^{\text{th}} f_{k'}^{\text{th}})^{1/2}$ . By calculating the time derivative of eq 16 it is then possible to express the functional  $F$  in terms of the quantities  $g_k$  and  $g_{k'}$  through the relation

$$F(g'_k, g_{k'}(t)) = \sum_k \left\{ (g'_k)^2 + \sum_{p,r} W_{kp} g_p(t) W_{kr} g_r(t) \right\} \quad (17)$$

which is thus of the form of eq 15. The Boltzmann equation of motion (eq 1) now appears as a consequence of the Euler eq 12 obtained directly from the functional  $F$  defined in eq 17. We emphasize at this point that with the definition (eq 17) of the relevant functional, the *exact* solutions to the Boltzmann equation obey the variational principle (eq 11), that is, they extremize the effective action  $J$ .

We now use this variational principle obeyed by the exact solutions as a guide to find “optimal” approximate solutions to the Boltzmann equation, by postulating a family of trial solutions of simple form and then directly solving the associated Euler–Lagrange equation, thus minimizing the effective action  $J$  associated with them. To this end, we build into our ansatz the fact that the distribution becomes thermal at long times by considering a family of trial solutions of the form

$$f_k(t) = f_k^{\text{th}} + a_k f(t) \quad (18)$$

where the endpoint conditions require that  $f(\infty) = 0$  and  $f(0) = 1$ . Since  $f(t)$  does not depend on  $k$ , conservation of probability is guaranteed by the condition

$$\sum_k a_k = 0 \quad (19)$$

where  $a_k = f_k(0) - f_k^{\text{th}}$  is the deviation of the initial distribution from the thermal distribution. Our ansatz for  $g_k(t)$  is thus given by the functional form

$$g_k(t) = \sqrt{f_k^{\text{th}}} + \frac{a_k}{\sqrt{f_k^{\text{th}}}} f(t) = g_k^{\text{th}} + \tilde{a}_k f(t) \quad (20)$$

Taking into account the detailed balance condition  $\sum_s W_{ks} (f_s^{\text{th}})^{1/2} = 0$ , the functional (eq 17) simplifies to

$$F = \sum_k \left\{ \tilde{a}_k^2 \left( \frac{df(t)}{dt} \right)^2 + \sum_{p,r} W_{kp} W_{kr} \tilde{a}_p \tilde{a}_r f^2(t) \right\} \quad (21)$$

The ansatz (eq 18) that best approximates the evolution of the Boltzmann equation can now be obtained by simply solving the associated Euler’s eq 12 for the relaxation function  $f(t)$ , that is

$$\frac{d^2 f(t)}{dt^2} = \sum_{k,p,r} \frac{A_{kp} A_{kr} a_p a_r}{f_k^{\text{th}}} \left[ \sum_k \frac{a_k^2}{f_k^{\text{th}}} \right]^{-1} f(t) \quad (22)$$

where we have rewritten the matrix  $W_{k'k}$  and  $\tilde{a}_k$  elements in terms of the original  $A_{k'k}$  and  $a_k$  elements. Since the coefficient on the right-hand side of eq 22 is always positive, the only physical solution is a single exponential of the form

$$f(t) = e^{-t/\tau} \quad (23)$$

Expressing the elements  $A_{k'k}$  in terms of the rates  $Q_{k'k}$ , we obtain the initial condition-dependent decay rate

$$1/\tau = \sqrt{\frac{\sum_k \left( \sum_{k' \neq k} Q_{k'k} f_k(0) - \sum_{k' \neq k} Q_{kk'} f_{k'}(0) \right)^2 / f_k^{\text{th}}}{\sum_k (f_k(0) - f_k^{\text{th}})^2 / f_k^{\text{th}}}} \quad (24)$$

We thus have found a variational approximation to the solution of the Boltzmann equation in the form of eq 18 where  $f(t)$  is exponential and with a relaxation rate which does depend on the initial conditions as well as the rates  $Q_{k'k}$ . Generally, it carries information about the initial conditions of the system through  $f_k(0)$  as can be seen in eq 24. For cases (i) and (ii) explained in section II, it is a straightforward exercise to show that this initial condition effect disappears and that eq 24 reduces to the standard relaxation approximation. Specifically, the exercise proceeds by restricting the  $k$  sum to two states in case (i) and writing  $Q_{kk'} = Q$  in case (ii).

To be noted is the fact that the variational procedure itself has determined the exponential time dependence of the function  $f(t)$  in eq 18, the functional form of which was not assumed at the outset.

#### IV. Study of the Validity of Our Prescription

To assess the validity of our prescription

$$f_k(t) = f_k^{\text{th}} + a_k e^{-t/\tau} \quad (25)$$

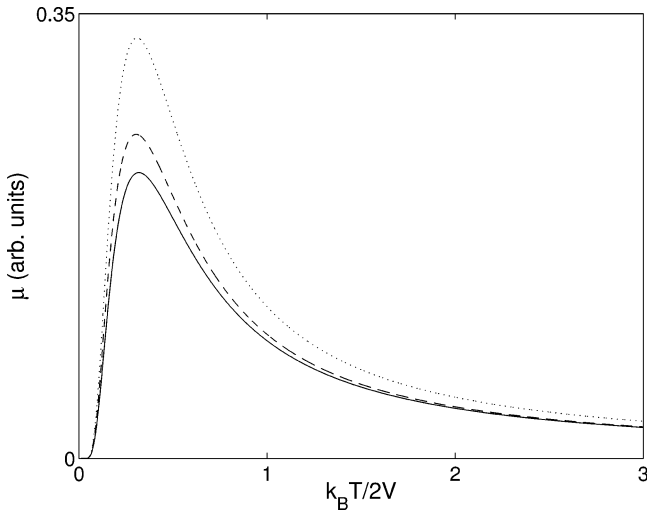
when the relaxation rate is determined through our variational procedure (eq 24), we compare the mobility when evaluated through the use of the approximate solutions in eqs 25 and 3 to the exact mobility calculated numerically. We will do so for a specific system.

We are interested in evaluating the diffusion coefficient and thus the mobility through the Einstein relation  $\mu = qD/k_B T$ , where  $q$  is the charge carrier,  $D$  is the diffusion coefficient,  $T$  is the temperature, and  $k_B$  is the Boltzmann constant. The diffusion coefficient can be evaluated from the Kubo relation<sup>10</sup>

$$D = \int_0^\infty dt \langle v(t)v(0) \rangle \quad (26)$$

where  $v(t)$  is the speed of the particle. The velocity autocorrelation function in eq 26 is obtained as the  $\text{Tr}\{\rho(v(t)v + vv(t))/2\}$  with  $\rho$  being the system density matrix. As is well-known,<sup>11</sup> and as can be verified by cyclic permutation within the trace, the autocorrelation function can be recast as the average velocity  $\text{Tr}(vK(t))$  computed for a specific initial condition on the density matrix  $K$ , namely,  $K(0) = (v\rho_{\text{th}} + \rho_{\text{th}}v)/2$ . While  $K(0)$  is the initial density matrix used in this computation,  $\rho_{\text{th}}$  is the thermal (equilibrium) density matrix of the *system*. These considerations which apply equally well for classical and quantum systems are detailed in ref 11.

The system under consideration is a charge carrier undergoing diffusive motion in the presence of scattering in a 1D tight-binding band. It is of considerable physical interest in the theory of quasi-particle transport in organic materials.<sup>12,13</sup> In the  $k$ -state representation, we have  $v_k = \hbar^{-1} d\epsilon_k/dk$ , with the band energy  $\epsilon_k$  being given by  $2V[1 - \cos(ka)]$  with  $a$  being the lattice constant. We consider for simplicity transition rates  $Q_{k'k}$  equal to  $\tau_0^{-1}$  if  $k'$  is a state with lower or equal energy to that of  $k$ .



**Figure 1.** Comparative examination of the validity of our prescription and of the standard relaxation time approximation (RTA). Plotted is the temperature dependence of the mobility for a carrier in a 1D band obtained exactly (solid line), via our prescription (dashed line), and via the standard RTA (dotted line). Temperature is expressed in units of half the carrier bandwidth divided by the Boltzmann constant. It is significant that our prescription is always more accurate than the standard RTA.

The corresponding downward rate, that is, when  $k'$  is a state with higher energy than  $k$ , is obtained through the detailed balance relation. For this form of the rates, the diffusion constant can be evaluated irrespective of the number of  $k$  states considered. We display below the case of a Brillouin zone with 7 states,  $k = 0, \pm(\pi/3a), \pm(2/3)(\pi/a), \pm(\pi/a)$ , whose thermal distribution are  $f_{1,7}^{\text{th}} = \exp(-2\Delta)/Z, f_{2,6}^{\text{th}} = \exp(-3\Delta/2)/Z, f_{3,5}^{\text{th}} = \exp(-\Delta/2)/Z, f_4^{\text{th}} = 1/Z$  with  $Z = 1 + \exp(-\Delta/2) + \exp(-3\Delta/2) + \exp(-2\Delta)$ , and  $\Delta = 2V/k_B T$

$$\frac{D_{\text{exact}}}{v_0^2 \tau_0} = \frac{3(2 + 2e^{\Delta/2} + 3e^{3\Delta/2} + 2e^{2\Delta} + 5e^{5\Delta/2})}{2(8 + 36e^{\Delta/2} + 48e^{\Delta} + 40e^{3\Delta/2} + 74e^{2\Delta} + 64e^{5\Delta/2} + 22e^{3\Delta} + 36e^{7\Delta/2} + 15e^{4\Delta})} \quad (27)$$

where  $v_0 = 2Va\hbar^{-1}$ . It is straightforward to compare the exact analytic expression (eq 27) with the corresponding analytic expressions for the diffusion constant obtained through our variational prescription and through the standard RTA. We have done so in Figure 1 where we have plotted the temperature dependence of the mobility  $\mu$  for each case. A larger number of  $k$ -states do not qualitatively change the plot in Figure 1: our variational approximation overestimates the exact solution at all temperatures but, in turn, the standard RTA overestimates the variational solution at all temperatures. A detailed study with rates that satisfy detailed balance but drop off exponentially in  $k$ -space, as represented by  $Q_{k'k}$  that contains a factor  $\exp(-|k' - k|/\sigma)$ , also shows no qualitative difference from the result in Figure 1. The value of the mobility for any given temperature increases in the three cases as  $\sigma$  decreases. Our variational

approximation gets better as  $\sigma$  increases, that is, as the scattering range gets smaller. We thus conclude that it is definitely more accurate to evaluate the temperature dependence of the mobility via the variational implementation of the RTA that we have presented in this paper rather than the traditional version for any temperature and for any  $\sigma$ . Surely, the conclusion we draw is specific to the system we have considered and does not apply universally. Nevertheless, confidence in the applicability of our prescription is strengthened by the fact that our illustrative choice addresses one of the most natural systems to which the RTA is applied in the literature.

## V. Conclusions

We have derived a (probability-preserving) relaxation time prescription for the solution of the linear Boltzmann equation used in transport theory that accommodates initial condition effects. The relaxation time  $\tau$  we compute depends explicitly on initial conditions as shown in eq 24. Our procedure is based on the implementation of a variational technique.

We have tested our formula (eq 24) by analyzing the mobility of a carrier in a 1D tight-binding band. We have found that our procedure provides a more accurate representation of the mobility than the standard relaxation time procedure used in the literature and that this is true for the system considered for any temperature and any scattering range. This conclusion is surely not universal but provides support to the prescription. It is hoped that the prescription will find use in practical computations in transport calculations.

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