# Studying Thermal Conductivity through Equilibrium Molecular Dynamics

Nicholas Childers

[1]University of Missouri, Columbia – Missouri, United States

*Abstract –* **Transport properties describe the way mass or heat is transferred through a material, which is of particular interest to physicists wanting to study material properties. Transport properties are high interest in studies of the viscosity[1-5], diffusion, and ionic conductivity[6]; they also have applications to modelling blood plasma [7] and geophysics [8]. Physicists wanting to model the thermal conductivity of materials also concern themselves with the calculation methods of transport properties. Thermal conductivity represents the ease of heat transfer within a substance, and is thus a transport property. Modelling heat transfer quickly presents a certain problem of scale, as modelling heat transfer at even the smallest scales quickly creates large numbers of complex interactions between individual molecules. This moves our problem more towards the area of statistics, which can allow us to draw certain conclusions given a large, well described data set. In modern physics, we often find it much easier to model our physical systems with simulations, rather than with corporeal experiment. Notably, this also eliminates any physical limitations that may introduce an unwanted variable to our study. However, mathematical error may be introduced to the process in the way we attempt to calculate certain quantities from the simulated experiment. After a brief overview of thermal conductivity and how statistical autocorrelations are used in its calculation, we will concern ourselves with the errors within those calculations and the proposed methods to counteract them in simulation.**

## I. Definition of Thermal Conductivity

For our definition of thermal conductivity, consider a substance that is not in thermal equilibrium, such as in figure 1. Specifically, we consider a metal rod between two heat reservoirs. Since the substance is not in equilibrium, energy will transfer in the form of heat $\vec{q}$ from the higher temperature region to the lower temperature region. If we would like to model the current of heat from the warmer region to the cooler region, we can do so using concepts of heat flux.

Let the temperature of our warmer body be $T_1$ and the temperature of our cooler body be $T_2$. Additionally, let $\vec{l}$ be the distance from heat reservoir $T_1$ towards $T_2$. Since the temperature of our center region depends only on $l$, we can define our temperature gradient between $T_1$ and $T_2$ as: $\nabla \vec{T} = \frac{T_2 - T_1}{\vec{l}}$. This temperature gradient represents the change in temperature.

To complete our model of this system, we would like to better understand how heat flows from $T_1$ to $T_2$ across the metal rod. Ideally, we would describe how the heat flows over time, and how the cross sectional area $A$ of $L$ impacts that heat flow. Then we would like to use heat flux, or the amount of heat

crossing unit area per unit time, to model this. If we consider our heat as a current $\vec{j_q}$ running perpendicular to the plane $A$, then we could represent this current as $j_q = \frac{d\vec{q}}{dt}/A$. This heat current is proportional to our temperature gradient $\nabla \vec{T}$. Then we can add a constant of proportionality $\kappa$ and say

$$\vec{j_q} = -\kappa \nabla \vec{T} \qquad (1)$$

Note the sign of the equation: this is done to represent the way heat flows from the region of higher temperature to lower temperature. The constant $\kappa$ is dependent on the properties of the substance, and is called the coefficient of thermal conductivity. It is a measure of how much a substance allows energy flow in the form of heat. In the case of the metal rod, experience tells us that this rod will be thermally conductive (which we shorten to just say conductive) and that our substance is very permissive of heat flow.
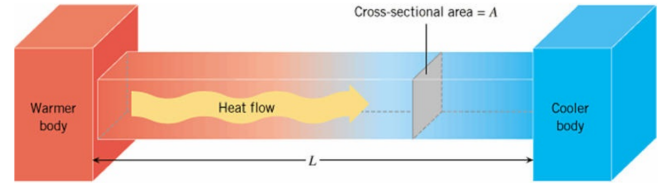


Fig. 1. Diagram of heat flow from warmer heat reservoir $T_1$ to heat reservoir $T_2$. The heat current $\vec{j_q}$ is dependent on the rate of heat flow and the cross sectional area it travels through. (Source: https://people.highline.edu/iglozman/classes/physnotes/heat$_t$rans fer.htm)

## II. Statistical Mechanics and Autocorrelation

Consider that metal bar from our definition above. If we were to attempt to model the flow of heat at a molecular level, we could do this by considering individual interactions. The molecules of the warmer end of the rod have more energy, and they transfer that energy through molecule-to-molecule interactions that resemble collisions. Calculating the effect of each individual interaction is a well defined process in physics. However, if our hypothetical rod is more than a few molecules thick, we quickly find that these interactions become so numerous that calculating them all becomes anywhere from tedious to impossible. Here lies our first problem: the scale of thermal mechanics. Early theorists attempting to study heat flow encountered this issue very quickly, and they turned to statistics to find their answer. By instead considering the fact that the thermal energy of the many interactions could be averaged as a larger temperature over a certain volume, physicists pioneered a statistical approach to physics.

If we instead consider the macroscopic temperature of the substance, rather than the microscopic thermal energies, than we can make accurate estimates about the physical qualities

of a substance. We have, however, added a certain amount of error. By not being the proper accountants for every interaction in our system, there could hypothetically be microscopic fluctuations in thermal energy. This is, thankfully, unlikely to be of any real significance if the conclusions are made with sufficient data.

### A. Time Series Analysis and Stochastic Process

Equilibrium Molecular Dynamics (EMD) simulations model large, complex systems of molecules based on a set of predetermined parameters, so we require a theoretical framework that fits. Time series analysis is a statistical field allows us to examine EMD as a stochastic process in more detail.

Our EMD is a realization of the stochastic processes of a molecule set of our choosing (crystals, gases, etc.), which means we would like to understand the probabilistic properties of our system. If we allow our time series to be deterministic, then we can see that our future values will be determined by some mathematical function $z_t$. This could be periodic, exponential, logarithmic, or anything else in theory, but we will be focusing on stationary stochastic processes. In a stationary process, the joint probability distribution associated with $m$ observations of $z_t$ is the same as the probability distribution associated with $m$ observations of $z_{t+k}$, where $k$ is an integer. In other words, our joint probability distribution is identical no matter how we shift our time origin by some integer $k$.

Next, we would like to understand the mean and variance of a stationary process. Since our probability distribution is identical, we can write $p(z_t) = p(z)$. This implies that our stochastic process has a constant mean:

$$\mu = E[z_t] = \int_{-\infty}^{\infty} zp(z)dz \qquad (2)$$

Which we can estimate in simulation by:

$$\mu = \bar{z} = \frac{1}{N}\sum_{t=1}^{N} z_t \qquad (3)$$

Similarly, we find that we have a constant variance:

$$\sigma_z^2 = E[(z_t - \mu)^2] = \int_{-\infty}^{\infty} (z - \mu)^2 p(z)dz \qquad (4)$$

Which we can estimate in simulation by:

$$\sigma_z^2 = \frac{1}{N}\sum_{t=1}^{N} (z_t - \bar{z})^2 \qquad (5)$$

We can now begin to unpack the concepts of autocovariance and autocorrelation coefficients. Our stationary process tells us that our covariance between values $z_t$ and $z_{t+k}$ separated by lag $k$ must be the same for all $t$. This stationary covariance is called autocovariance, and we model it as:

$$\gamma_k = cov[z_t, z_{t+k}] = E[(z_t - \mu)(z_{t+k} - \mu)] \qquad (6)$$

The autocorrelation at lag $k$ also describes a stationary process. If we would like to find the correlation between $z_t$ and $z_{t+k}$:

$$\rho_k = \frac{E[(z_t - \mu)(z_{t+k} - \mu)]}{\sigma_z^2} = \frac{\gamma_k}{\gamma_0} \qquad (7)$$

### B. Autocorrelation Functions

We can represent the covariance matrix of a stationary process with observations $(z_1, z_2, ..., z_n)$ made at $n$ successive times is:

$$\Gamma_n = \begin{bmatrix} \gamma_0 & \gamma_1 & \gamma_2 & \cdots & \gamma_{n-1} \\ \gamma_1 & \gamma_0 & \gamma_1 & \cdots & \gamma_{n-2} \\ \gamma_2 & \gamma_1 & \gamma_0 & \cdots & \gamma_{n-3} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \gamma_{n-1} & \gamma_{n-2} & \gamma_{n-3} & \cdots & \gamma_0 \end{bmatrix} \qquad (8)$$

and we construct our autocorrelation matrix $P_n$ as:

$$\Gamma_n = \sigma_z^2 P_n = \sigma_z^2 \begin{bmatrix} 1 & \rho_1 & \rho_2 & \cdots & \rho_{n-1} \\ \rho_1 & 1 & \rho_1 & \cdots & \rho_{n-2} \\ \rho_2 & \rho_1 & 1 & \cdots & \rho_{n-3} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \rho_{n-1} & \rho_{n-2} & \rho_{n-3} & \cdots & 1 \end{bmatrix} \qquad (9)$$

Our autocorrelation matrix's diagonals all correspond to a specific lag time after our original signal, with $\rho_0 = 1$ for the entire diagonal, by definition. The correlations between a signal its later self provides important stochastic insight into problems. For instance, if we would like to observe how a stationary system reacts to an outside perturbation, the autocorrelation of the heat current could be used to model thermal energy flow. That is precisely the kind of autocorrelation we are interested in, describing heat flow, and therefore, thermal conductivity.
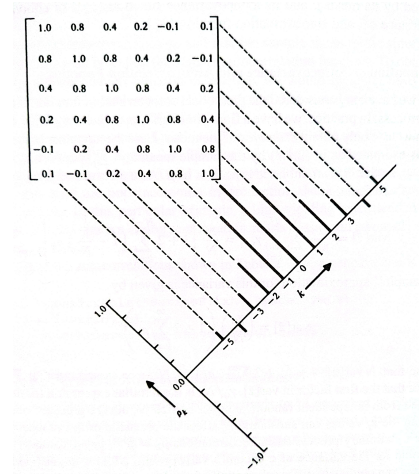
We would like to describe autocorrelation as a function

Fig. 2. A representation of the autocorrelation function as the diagonals of the autocorrelation matrix. As the lag time $k$ increases, the autocorrelation value decays towards 0. Credit: Time Series Analysis 2016

of the time $t$ the function was measured at. Let our initial observations $(z_0, z_1, ... z_n)$ stand, but let $n = t$ approach infinity, so we take infinite observations. At $t = 0$ our autocorrelation $\rho_0 = \frac{\gamma_0}{\gamma_0} = 1$. We continue from there, with our function decaying from 1 to 0 as $t$ approaches infinity. Think of imposing our autocorrelation matrix onto a graph, using the diagonals as our independent variable and our autocorrelation value as our dependent variable. Figure 2 shows an example of what this may look like, although we only use positive $t$ values in practice, as $\rho_k = \rho_{-k}$.

Physically, what does this mean? It means that the further our observation $z_t$ is from $t = 0$, the lagged signal correlates less strongly with the original observation. This error accumulates over time, meaning that our signals correlate less strongly over time.

## III. Thermal Conductivity and Green-Kubo Relations

With a proper foundation for statistics, we can now consider heat flow as a stochastic process more directly. In the physical flow of heat, Fourier's law of heat conduction tells us that the heat flux between two bodies maintained at different temperatures is proportional to the temperature gradient. The constant of proportionality, thermal conductivity $\kappa$, is a linear transport coefficient for the linear transport of heat. The relation between our thermal dynamic force $F$ and the heat flux is a linear constitutive relation:

$$j = \kappa F \qquad (10)$$

We are concerned with many interactions, so this must be represented using a linear transport coefficient matrix which must be symmetric in most cases. In the mid 20th century, physicists Green and Kubo proved an exact equation for general linear transport coefficients [11,12]. Specifically, they used the time dependence of equilibrium fluctuations in our system. In the case of thermal conductivity:

$$\kappa = \frac{V}{kT} \int_0^\infty dt < j(0)j(t) > \qquad (11)$$

Where $V$ is the volume of our system of interest, $k$ is the Boltzmann constant, and $T$ is the temperature. We now see why it was necessary to understand the nature of autocorrelation functions to calculate thermal conductivity, as we use a heat current autocorrelation function (HCACF) in the process. The Green-Kubo relation for thermal conductivity uses the correlations between our initial heat current and a calculated future value of the current. Integrating this HCACF over infinite time, we calculate an exact value of thermal conductivity.

Of course, integrating an autocorrelation over an infinite amount of time is impossible in experiment, so physicists take advantage of the convergence of the HCACF to truncate the function at some maximum time $M$. This introduces error into an otherwise exact relation. The remainder of our discussion of thermal conductivity is concerned primarily with such error. In a simulation where we are able to predict exact, deterministic trajectories, we would like to find a way to eliminate this error with existing knowledge.

## IV. Errors in Equilibrium Molecular Dynamics

### A. Equilibrium Molecular Dynamics

When attempting to study heat transfer in a physical experiment, we find that it is difficult to limit outside variables, and we also have a very limited selection of information available: We may be able to measure temperature in regions, but measuring thermal energy of individual molecules becomes impossible. It is far more efficient to simulate these situations, where we can carry out far more extensive control over our systems.

We are interested in a specific kind of simulation pertaining to Equilibrium Molecular Dynamics (EMD). There are two main methods of EMD: modelling the heat flow of a system in equilibrium, or perturbing a system that was in equilibrium. This equilibrium is vital, as it allows our processes to be time reversible and deterministic, as physical models require. Once the trajectories of each individual molecule has been calculated, we should be able to reverse any time steps and end up with the original setup at $t = 0$. By studying the transfer of heat energy through the system, we can calculate our coefficient of thermal conductivity.

However, in actual practice, inconsistencies have been spotted. Experiments done by Chen et al.[13] and Sousa et al.[14], among many others have noted that after running their EMD programs, we encounter some sort of noise signal that accumulates over time into significant error for our calculations of thermal conductivity. This noise is still being studied by those in the field, mainly in how to counteract the noise and achieve accurate measurements of thermal conductivity despite the errors [13]. To understand this noise, we turn to study where this noise could originate from. Figures 2 and 3 show examples of how this noise has appeared in practice. Although we should see slow decay as $t$ approaches the end of our simulation, we instead see this error term dominate the measurements. This is troubling, as there are processes that occur later in the simulation which may be of physical interest to us. In crystalline materials, our linear heat transport is often analyzed in terms of the propagation of quantized lattice vibrations, or phonons. Long term phonon decay has been largely overshadowed in these experiments, and the physicists are forced to account for errors in an attempt to compensate [13,14].

Where this error originates from is the focus of our research here. We will consider where errors appear in the calculation methods of EMD, as well as discuss their convergence over time or lack thereof. The goal is to better understand where this error comes from so that we may better counteract or account for it. Solutions have been proposed, but we first need to better understand how thermal conductivity is calculated in experiment.

### B. Errors in Numerical Integration: Velocity Verlet

The first place our error might appear is in the integration of Newton's equations of motion. As heat moves through our system, this can be understood as the movement of kinetic energy between molecules. If we know the initial conditions of our system, as well as any possible perturbations to the system, then we can integrate Newton's equations of motion over the course of our experiment to find positions and velocities
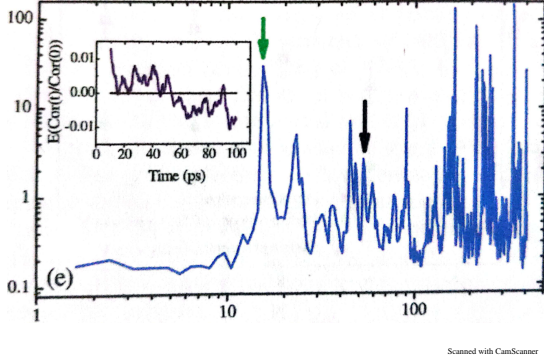
Fig. 3. Measure of Fluctuation in Heat Current Autocorrelation against time done by Chen et al. Higher values mean a fast deviations previous values for the heat current autocorrelation, suggesting statistical errors in the computation.
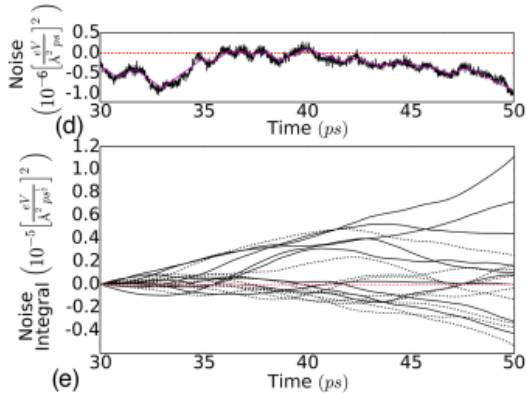


Fig. 4. Noise integral over time by Sousa et al.; Panel (d) corresponds to the tail of a Heat Current Autocorrelation Function, depicting the noise fluctuations that integrate to a large error akin to a random walk, shown in panel (e).

of each individual molecule at any time $t + \Delta t$, where $\Delta t$ is our discrete time step chosen for the simulated model. Our goal is to use the following equation to solve for our thermal conductivity:

$$m\left(\frac{d^2 r_i}{dt^2}\right) = F_i(t) \qquad (12)$$

With mass $m$, positions of each molecule $r_i$, time $t$, and the force on the molecule $F_i$. To calculate the positions and velocities of particles, the velocity Verlet is often used as our numerical integrator. The velocity Verlet algorithm holds good numerical stability, time reversibility, and symplectic form on the phase space. This is all done for a relatively low computational cost, despite the benefits it offers as an integrator.

First, how does the velocity Verlet work? We start with our initial conditions, including initial positions $r_i(0)$ and velocities $v_i(0)$. We then take a Taylor series expansion of $r_i(t + \Delta t)$ and $r_i(t - \Delta t)$ using the basic equations of motion:

$$r_i(t + \Delta t) = r_i(t) + v_i(t)(\Delta t) + \frac{a_i(t)}{2}(\Delta t)^2 \qquad (13)$$

$$r_i(t - \Delta t) = r_i(t) - v_i(t)(\Delta t) + \frac{a_i(t)}{2}(\Delta t)^2 \qquad (14)$$

Taking the sum of the equations above, we find:

$$r_i(t + \Delta t) = 2r_i(t) + a_i(t)(\Delta t)^2 - r_i(t - \Delta t) \qquad (15)$$

Taking the difference of the first two equations, we find:

$$r_i(t + \Delta t) - r_i(t - \Delta t) = 2v_i(t)(\Delta t) \qquad (16)$$

Rearranging to solve for $v_i(t)$:

$$v_i(t) = \frac{r_i(t + \Delta t) - r_i(t - \Delta t)}{2\Delta t} \qquad (17)$$

Finally, we use our force to solve for the expected velocity after our time step:

$$v_i(t + \Delta t) = v_i(t) + \frac{\Delta t}{2}\left(\frac{F_i(t) + F_i(t + \Delta t)}{m}\right) \qquad (18)$$

Using the velocity Verlet method, we have a memory efficient method of integrating the equations of motion and determining heat flow $j_q$ by understanding how kinetic energy is moving through our simulation. The velocity Verlet is time reversible, meaning that using our new value $v(t + \Delta t)$, we would calculate $v((t + \Delta t) - \Delta t) = v(t)$. That is, calculating our heat flow in reverse holds a consistent answer with calculating it in normal time steps. It's also a symplectic integrator, with answers that consistently conserve energy in our system. We will not lose or gain energy, as this is an isolated system.

The global error of our velocity Verlet is of the order $O(\Delta t^2)$. This means our error depends on the size of our time step $\Delta t$, and increases as a quadratic over time. However, in simulation, global error is not what we are calculating with. Instead, we are forced to truncate our simulation at some maximum time. Thus, we must use the velocity Verlet's truncation error: $O(\Delta t^3)$. As we increase our time step size, we will also see that cutting off the simulation earlier will have a notable effect on the outcome. There is some global error to our algorithm, but the truncation error will eventually dominate our simulation and impact our data. In simulation, this can create situations in which the error from truncation is so significant that it creates appreciable error in our calculations of thermal conductivity, as was found by physicists studying the phenomenon [13,14].

## V. Experimental Methods to Counteract Error

### A. First Avalanche Method

We now turn to current attempts within the field to counteract the error that dominates the HCACF at large time $t$. A natural reaction to this constraint is to attempt to determine if there exists some hypothetical cutoff time $\tau_c$. Chen et al. attempted to determine an experimentally consistent cutoff time, as well as optimize a double exponential fitting approach to the HCACF.

Chen et al. suggests a truncated HCACF as the solution. Before describing the simulation itself, we will note that the results of the simulations show that our HCACF decays to approximately zero at a time much shorter than a time in the function which is dominated by noise. However, Chen et al. only prove this for Silicon and Germanium. Although it is likely that many materials have this property, it will be an

insurmountable obstacle to this method if the material does not.

To find when error overtakes the HCACF, Chen et al. worked to quantify the fluctuation of the HCACF. Using the standard deviation and the mean of $Cor(t)$,

$$F(t) = |\frac{\sigma(Cor(t))}{E(Cor(t))}| \qquad (19)$$

Until some later time, fluctuation $F(t)$ remain nearly zero. When numerical error begins to dominate the HCACF, our fluctuation will increase rapidly. We are interested in the time at which fluctuation dominates the signal, and Chen et al. suggested that we consider $\tau_c$ be the time when our fluctuation first reaches $F(t) = 1$. They call this point the first avalanche, or *FA*. After FA, values at all other times $t$ are discarded and the direct integration process is used solely on the simulation up to FA.

Notably, some factors contribute to this cutoff time. Because variations of the initial conditions can represent different thermodynamic ensembles with slightly differing properties, the finite, direct integration causes some amount of fluctuation of the cutoff time (additionally, longer wavelength phonons are underrepresented by a finite direct integration, by nature). To remedy this, Chen et al. suggest that the experimenter take a case by case basis, carefully using direct integration multiple times for a substance and making conclusions only for that substance. In their work, Chen et al. do show that their methods of direct integration are very well in agreement with experimental values, giving confidence in their choice of FA for $\tau_c$. How can we fit this HCACF? With no satisfactory answer in literature, Chen et al. decided to modify earlier attempts at a double exponential fitting approach. They determine that the decay of the HCACF must be exponential, due to the macroscopic law of relaxation and Onsager's postulate for microscopic thermal fluctuation. They chose double exponential to fit both the contribution from short wavelength phonons and long wavelength phonons. They also added in a constant to help fit the model, which represents the missing long wavelength phonon contributions.

$$\frac{Cor(t)}{Cor(0)} = A_1 e^{\frac{-t}{\tau_1}} + A_2 e^{\frac{-t}{\tau_2}} + Y_0 \qquad (20)$$

$A_1$, $A_2$, $\tau_1$, $\tau_2$, and $Y_0$ are fitting parameters. $\tau_1$ and $\tau_2$ represent the relaxation time of short wavelength and long wavelength phonons, respectively. As we've stated, long wavelength phonons are underrepresented in EMD because we are force to use a finite integration in simulation. Thus, we require a correction in the form of a constant $Y_0$. Below, the derived equations for accumulative thermal conductivity are given, one with the correction and one without.

$$\kappa_C(t) = \frac{Cor(0)}{3k_B T^2 V}(A_1 \tau_1 + A_2 \tau_2) \qquad (21)$$

$$\kappa_F(t) = \frac{Cor(0)}{3k_B T^2 V}(A_1 \tau_1 + A_2 \tau_2 + Y_0 \tau_c) \qquad (22)$$

$\tau_c$ is the cutoff time determined by the experimenter, which Chen et al. endorses the FA as a consistent cutoff time. Using the above equations, Chen et al. found that $\kappa_F(t)$, which uses the FA cutoff, was much more accurate for calculating the thermal conductivity of silicon and germanium. $\kappa_C(t)$ has much more significant error, and it represents the previous attempts at double exponential integration.

This approach succeeds at its approach, which is to create a quantitative method to truncate our HCACF. However, while this approach does allow an experimental way of quantifying fluctuation and eliminating the noise, it also eliminates the contributions of long wavelength phonons. The double exponential fitting attempts to add a constant to account for this, but this isn't a complete, mathematical understanding of our system, but a correction meant to allow us to work around the statistical noise.

## VI. Discussion

Computation of thermal conductivity through heat-current autocorrelation has shown much promise to the diverse applications of materials science, and there exist several methods to reduce the error in previous methods of calculation. We find that the accuracy of the our velocity Verlet's Taylor series and the nature of the stoichiometry involved in autocorrelation create a significant amount of error for the experimenter. However, careful selection of initial conditions of the system like time step size can reduce the error by some amount. It can be reduced further by attempting to find the best time to truncate the function as done with Chen et al. in their work [13]. Other physicists like Olivera et al. have suggested modelling the error of the HCACF as a random walk and filtering out the random noise [14].

Returning to the physics of interest, it is inherently unsatisfying to have calculation methods with intrinsic error. Since we have calculated each individual trajectory of each individual molecule, we have an interest in understanding thermal conductivity from just this information. There is quite possibly an existing solution to this problem, where the error terms may be used to cancel each other or we can more accurately predict the error of truncating our HCACF. Until that solution is found however, we are forced to rely on current methods for estimation of errors.

## ACKNOWLEDGEMENTS

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