X-ray Absorption Fine Structure Debye-Waller Factors

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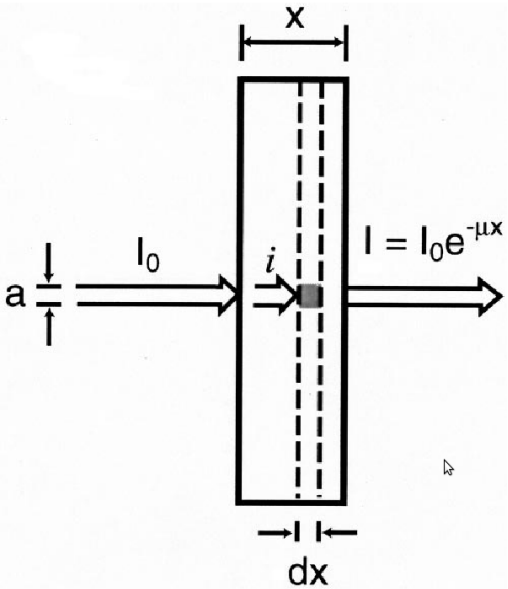
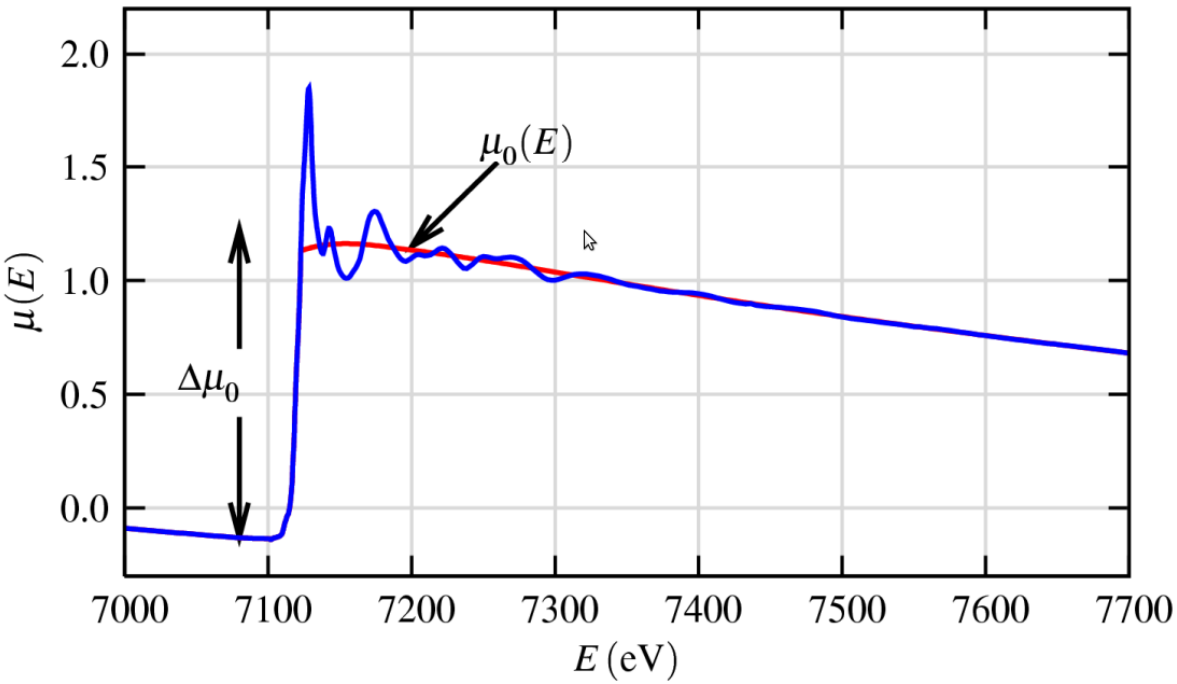
Outline

X-ray absorption fine-structure (XAFS)

X-ray absorption



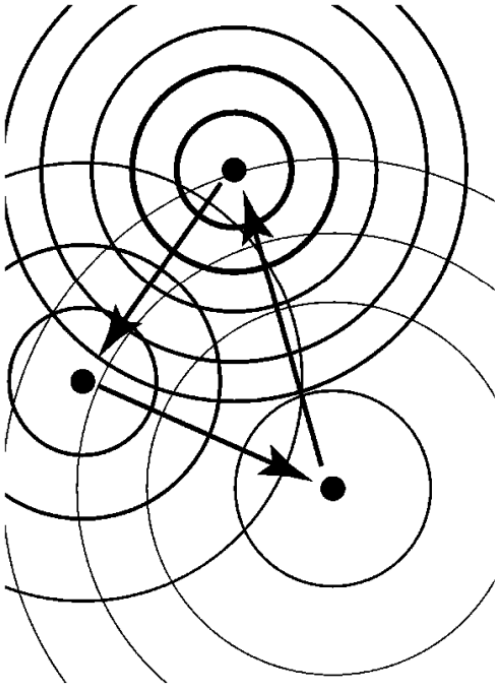


The XAFS spectrum is defined as the normalized oscillatory part of the x-ray absorption coefficent μ:

$$\chi \stackrel{\text{def}}{=} \frac{(\mu - \mu_0)}{\Delta\mu_0} \tag{1}$$

X-ray absorption fine-structure (XAFS)

Photoelectron scattering of neighboring atoms



$$\gamma + e^-_{core} \longrightarrow e^-_{photo} + h_{core} \tag{2}$$

According to Fermi's Golden Rule:

$$\mu \propto \left|\langle f|H_{trans}|i\rangle\right|^2 \tag{3}$$

- Scattering of neighboring atoms produces an **energy dependent interference pattern**, which modulates the matrix element.
  $\Rightarrow$ oscillations in $\mu(E) \Leftrightarrow$ fine structure, χ.
- For highly localized core electrons: χ is proportional to the amplitude of the photo electron at the absorbing atom $\Leftrightarrow$ acts as a **probe of local structure**.

X-ray absorption fine-structure (XAFS)

The standard (E)XAFS equation

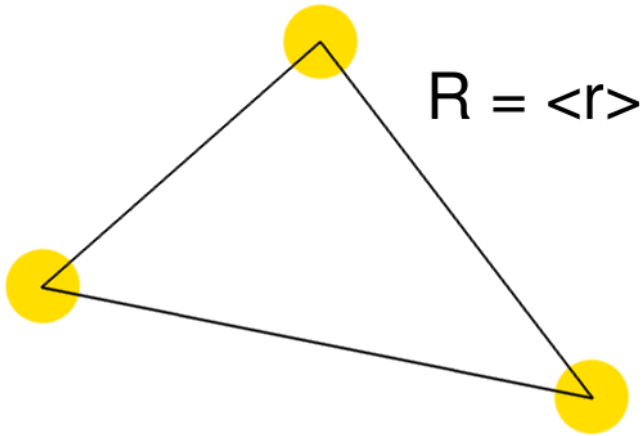
$$\chi(k) = \sum_j \frac{N_j S_0^2}{kR_j^2} |f_j^{eff}(k, R_j)| sin\big(2kR_j + \phi_j(k)\big) e^{-2R_j/\lambda} e^{-2\sigma_j^2 k^2} \quad (4)$$

- Sum is over all unique scattering paths j with degeneracy N_j
- f_j^{eff} is the effective backscattering amplitude for scattering path j.
- $sin\big(2kR_j + \phi_j(k)\big)$ reflects the oscillatory dependence on interatomic distances and energy.
- $e^{-2R_j/\lambda}$ accounts for the finite lifetime of both photoelectron and the core-hole.
- $e^{-2\sigma_j^2 k^2}$ is the **Debye-Waller factor**, which accounts for thermal and structural disorder of the atoms.

The Debye-Waller (DW) factor

More general form: e^{-W}. This reduces in the harmonic approximation to a Gaussian with W = $2\sigma_j^2 k^2$, where

$$\sigma_j^2 = \langle (r_j - R_j)^2 \rangle \qquad (5)$$



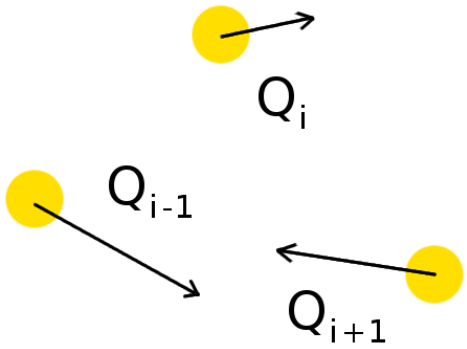
is the variance of the half scattering path length r_j.

Because of this exponential damping the XAFS, χ is smeared. Determining accurate structure (e.g. coordination number and interatomic distances) from XAFS experiment requires understanding of the DW-factors from first principles.

The Equation-of-Motion Method

- Start with the 3N coupled Newton's equations of motion for the system of N atoms:

$$\frac{d^2 Q_{i\alpha}(t)}{dt^2} = -\sum_{k\beta} D_{i\alpha,k\beta} Q_{k\beta} \qquad (6)$$



- Look for oscillatory solutions of the displacement vector $Q_{i\alpha}$, $Q_{i\alpha}(t) \sim e^{-i\omega t}$
  $\Rightarrow$ an eigenvalue problem for the 3N normal modes (eigenvectors) $|\lambda\rangle$ of the dynamical matrix $D_{i\alpha,k\beta}$, each with eigenvalue ω_λ.

The Equation-of-Motion Method

- Since $\sigma^2 = \sigma^2(Q_{i\alpha})$, we can now expand the displacements $Q_{i\alpha}$ in terms of the normal modes and get (...)

$$\boxed{\sigma_j^2(T) = \frac{\hbar}{2\mu_j} \int_0^{\omega_{max}} \frac{d\omega}{\omega} \rho_j(\omega) \coth\left(\frac{\beta\hbar\omega}{2}\right)} \tag{7}$$

$\rho_j(\omega)$ is the **projected density of normal modes** for scattering path j

$$\rho_j(\omega) \stackrel{\text{def}}{=} \sum_\lambda |\langle\lambda|Q_j(0)\rangle|^2 \delta_\Delta(\omega - \omega_\lambda) \tag{8}$$

where the sum is over all normal modes λ. The initial displacement vector $|Q_j(0)\rangle$ is given uniquely by the scattering path j.

The Equation-of-Motion Method

- Conventionally, we would have to get all the normal modes of the system - potential computational bottleneck. But, we can also be express $\rho_j(\omega)$ in terms of the Fourier transform of the **correlation function** $\langle Q_j(t)|Q_j(0)\rangle$:

$$\rho_j(\omega) = \frac{2}{\pi}\int_0^{t_{max}} \langle Q_j(t)|Q_j(0)\rangle e^{-\epsilon t^2} cos(\omega t) dt \tag{9}$$

  The correlation function reflects how the entire atomic system is oscillating in time and **contains the same information** as the normal modes.

- Can be obtained using Density Functional Theory, e.g. via implementations such as VASP or SIESTA. Allows us to extract the DW factors without using experimental fitting or semi-empirical formulas for getting the force constants.

The Equation-of-Motion Method

Conventional vs. correlation function approach

Conventional approach

Frequency space

$$\omega_\lambda^2 |\lambda\rangle = D|\lambda\rangle$$

$$\rho_j(\omega) = \sum_\lambda |\langle\lambda|Q_j(0)\rangle|^2 \delta_\Delta(\omega - \omega_\lambda)$$

Normal modes required

Impractical for complex systems.

Correlation function approach

Real-time

$$\frac{d^2}{dt^2}|Q(t)\rangle = -D|Q(t)\rangle$$

$$\rho_j(\omega) = \text{FT}\,\langle Q_j(t)|Q_j(0)\rangle$$

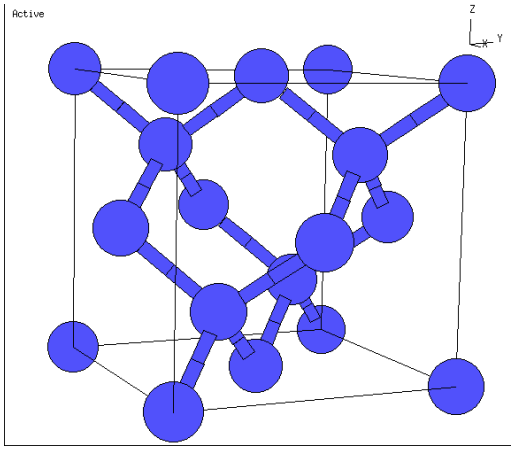
Normal modes not required

Applicable to complex systems

Germanium

Setup and results

- 64-atom cluster of Ge, diamond space group. Periodic boundary conditions.
- Calculations made for a single-scattering nearest neighbor path.
- Correlation function calculated using atomic trajectory output from VASP.
- Calculated σ^2 using the Equation of Motion Method: 3.23 10^{-3}Å^2.
  Experimental value: 3.50 10^{-3}Å^2.
- Accuracy requirements for DW factors $\sim 10 - 20\%$.



Germanium

The damped correlation function, $\langle Q_j(t)|Q_j(0)\rangle e^{-\epsilon t^2}$

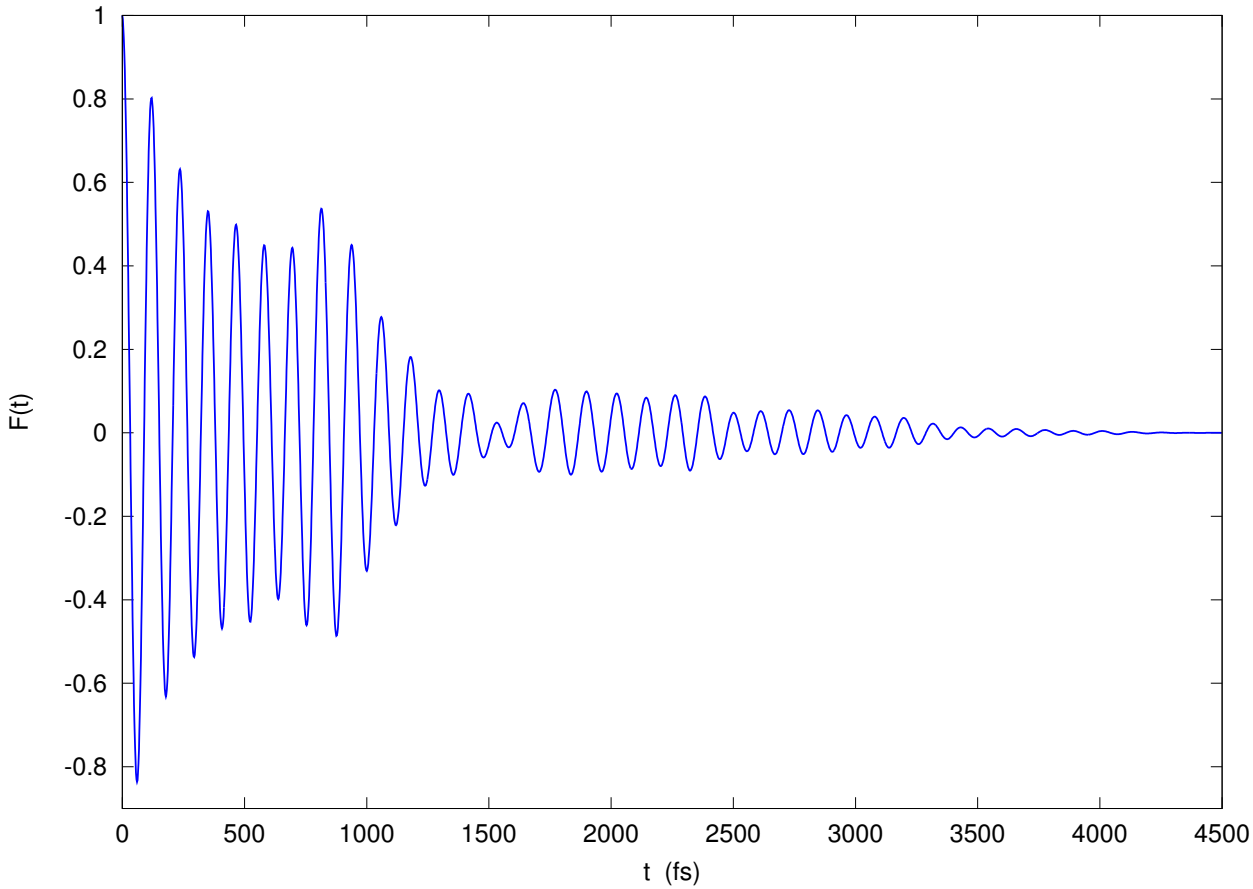


Figure: Damped correlation function for nearest neighbor single scattering.

Germanium

Density of modes normal modes, $\rho(\omega)$

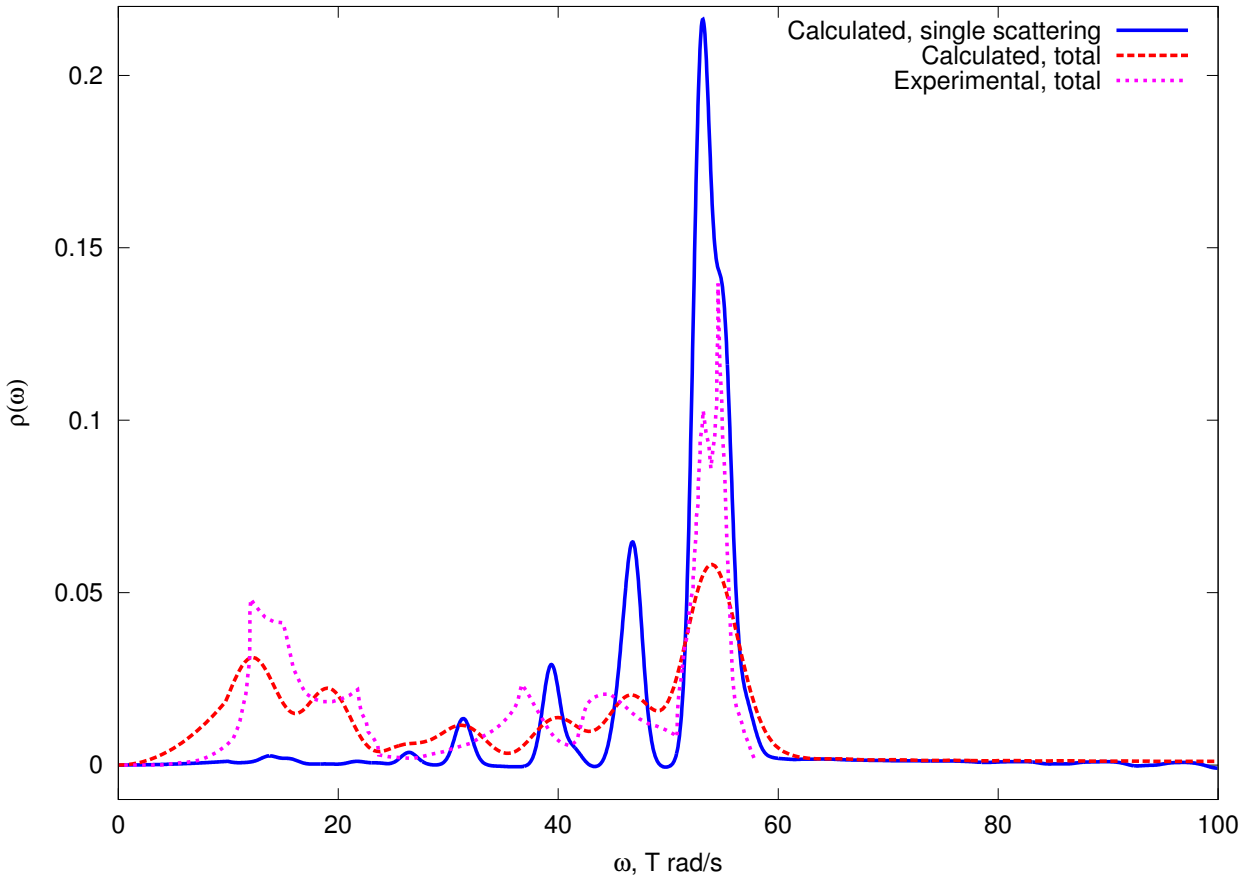


Figure: Density of modes, $\rho(\omega)$, for projected single scattering (blue), calculated total (red) and experimental total (magenta).

Germanium

Temperature dependence of σ^2

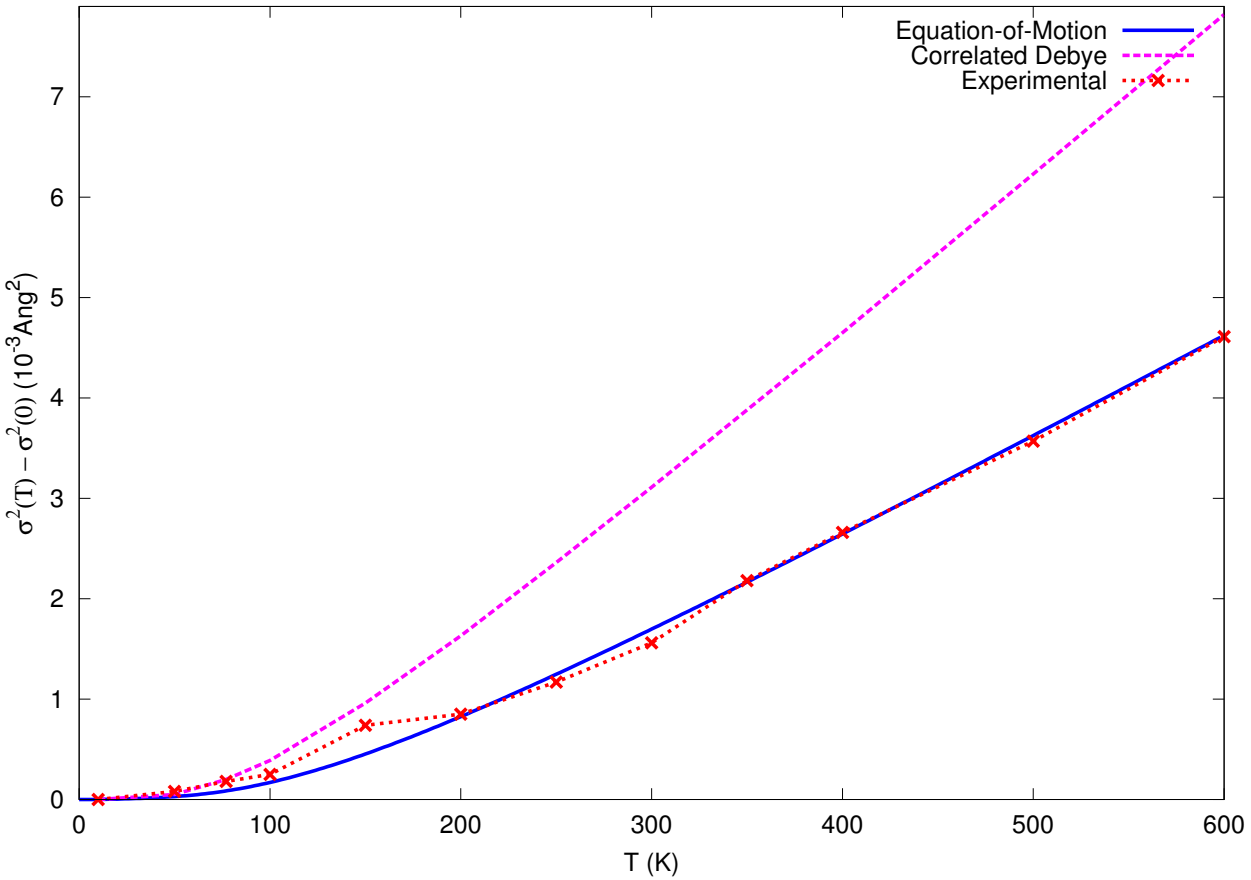
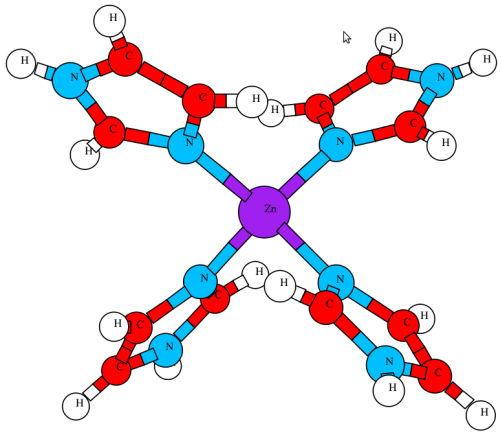


Figure: Calculated (blue) and experimental (red) σ^2 (single-scattering) as a function of temperature, T. Also, calculations for the correlated Debye method (magenta).

Future work

- Currently working on the organic compound Zn-tetraimidazole.
- Apply the Equation-of-Motion method to other structures.
- Validate the method for multiple scattering paths.
- Investigate further how time length, time step length and other computational factors effect the final result for σ^2.



Thank You!

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