Temperature Dependence of Low-Energy Electron Transport in Water

Work in Progress for Monte Carlo Simulation at the nanoscale

Notre Dame Radiation Laboratory Seminar

Ryan McClarren — June 25, 2020

Electrons passing through water undergo a variety of interactions.

- When a relativistic electron passes through liquid water, collisions with the molecules produce secondary electrons.
- The primary electron's path is negligibly affected by these interactions.
- These secondary electrons liberated are then free to interact with the water, and are characterized by their initial energy:
  - Below 100 eV these electrons form spurs where the electron does not travel far from the point of its birth and the zone of interaction (including additional electrons created) is nearly spherical.
  - Between 100 and 500 eV, a blob is a formed where the zone of interaction is not spherical.
  - Above 500 eV and below 5 keV, the electron forms a short track where additional blobs and spurs can be generated.
  - Above 5 keV the electrons produced behave similarly to a primary track.
- The interactions between the electrons and the water molecules set the stage for chemical reactions that will later take place and influence the yield of H_2, e^-_{aq}, and other products.
- The spatial distribution of the energy deposition events, the electron tracks, and the location where electrons thermalize are the quantities of interest for an electron simulation.

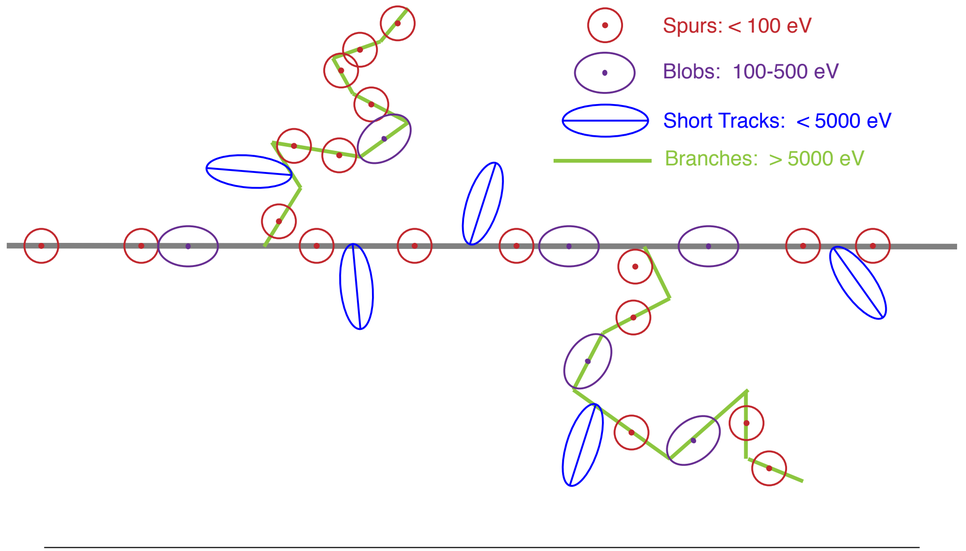


Figure Credit: M. Smith, "Computational Study of Low Energy Electrons Through Amorphous Ice and Gaseous Phase Water" (2018)

To simulate the behavior of the electrons we need cross-sections for the different interactions.

- Cross-sections, aka reaction probabilities, give the likelihood of different reactions taking place for an electron of a given energy.
  - Large value for a cross-section means that interaction is likely between an electron and the medium.
- At energies above ~100 eV cross-sections for water are fairly well known/established.
- At lower energies several factors combine to make the cross-sections not well known:
  - Quantum nature of electrons make a point description less tenable
  - Electrons interacting with a collection of water molecules in a liquid, not a single, isolated molecule.
  - Experiments are harder.

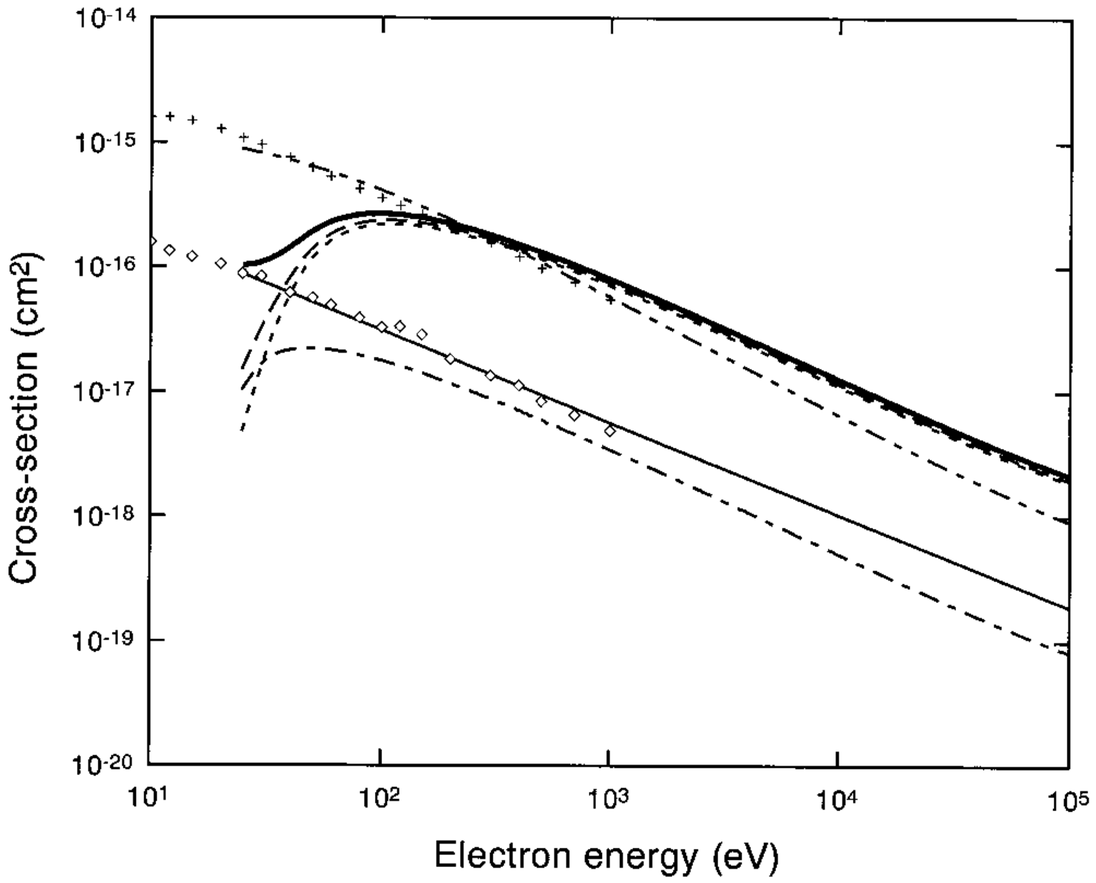


Figure 2. Dependence of the electron impact cross sections of liquid water on electron energy. Theory: (bold —) total inelastic; (— —) total electronic; (- - -) ionization; (— -) excitation; (—) vibration; (— - -) elastic. Experiment: Hayashi[36] (◇) vibration; (+) elastic.

Pimblott, S. M., LaVerne, J. A., & Mozumder, A. (1996). Monte Carlo Simulation of Range and Energy Deposition by Electrons in Gaseous and Liquid Water. The Journal of Physical Chemistry, 100(20), 8595–8606. http://doi.org/10.1021/jp9536559

In most simulations below some cutoff energy, it is assumed that a solvated electron is randomly placed near the ionization event.

- This distribution of thermalization distances has been theorized to be based on several distributions
  - Gamma distribution
  - Exponential distribution
  - Maxwell distribution (called a Gaussian in the literature)
  - Combinations of the above
- There is some debate on what the correct distance distribution is because of the uncertainties in cross-sections at these low energies.
- It has also been claimed that the thermalization distance goes down with increasing water temperature.
- This is obviously counterintuitive because the density of molecules goes down with increasing temperature.
- The question is why this might be the case…

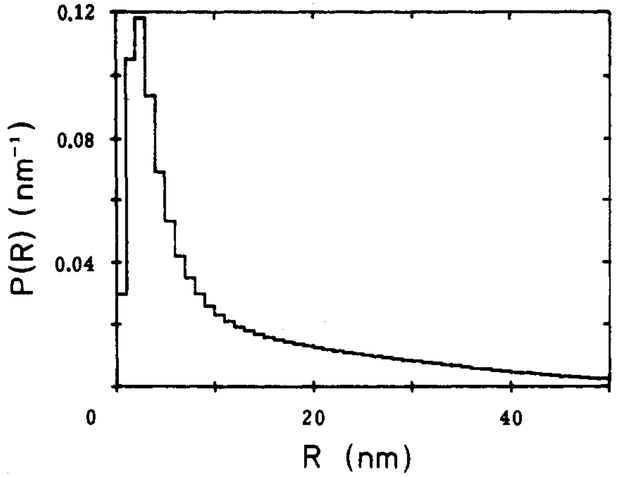


Figure 3. Distribution function $P(R)$ of radial thermalization distances for all subexcitation electrons ($E_0 \lesssim 7.4$ eV) in solid water, taking account of their energy spectrum $D(E_0)$ given by eq 2.

Goulet, T., & Jay-Gerin, J.P. Thermalization distances and times for subexcitation electrons in solid water. *The Journal of Physical Chemistry*, *92*, 6871–6874.

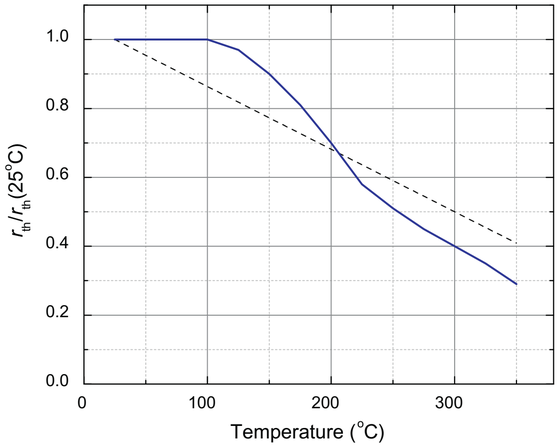
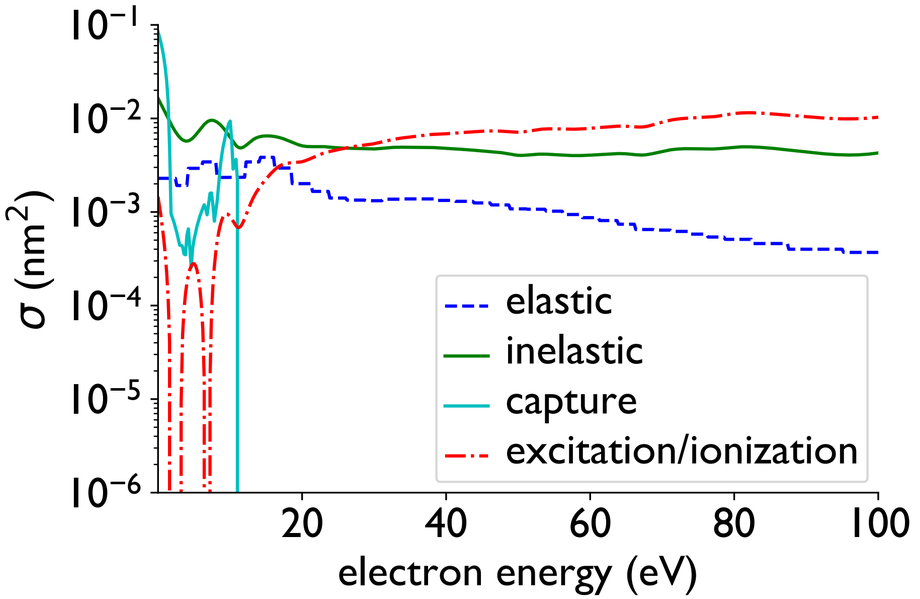


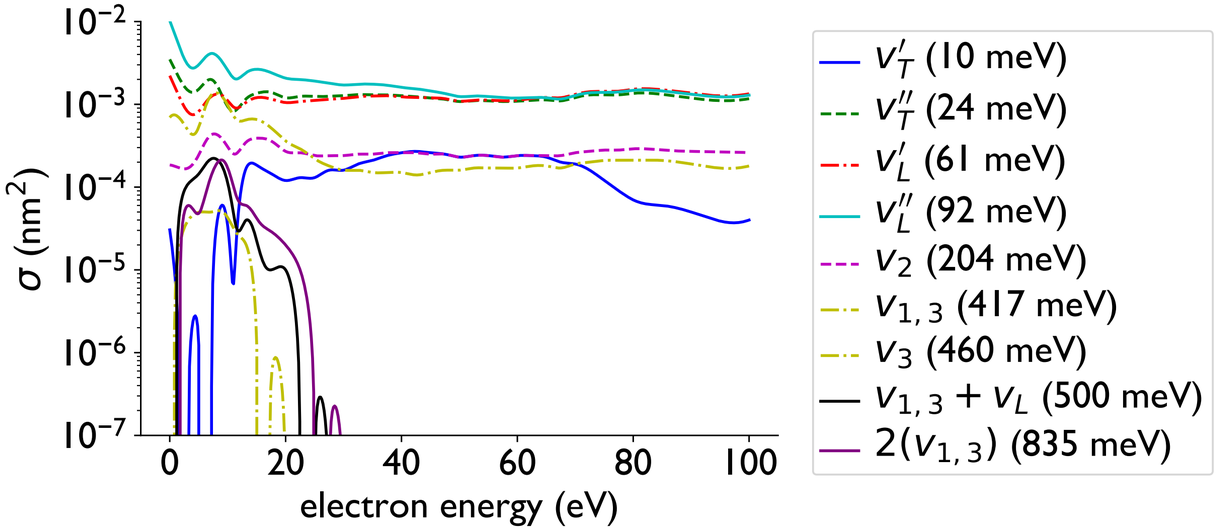
Figure 3. Temperature dependence of r_{th} over the range 25–350 °C (solid line). The average electron thermalization distance at 25 °C calculated from our simulations is $r_{th}(25\ ^{\circ}C) \sim 11.3$ nm [12]. The dashed line corresponds to the temperature dependence of r_{th} that we adopted in our previous studies on the radiolysis of water at high temperatures [7,13,33].

Sanguanmith, S., Muroya, Y., Meesungnoen, J., Lin, M., Katsumura, Y., Kohan, L. M., et al. (2011). Low-linear energy transfer radiolysis of liquid water at elevated temperatures up to 350°C: Monte-Carlo simulations. Chemical Physics Letters, 508(4-6), 224–230. http://doi.org/10.1016/j.cplett.2011.04.059

We use data from amorphous ice for low energy cross-sections

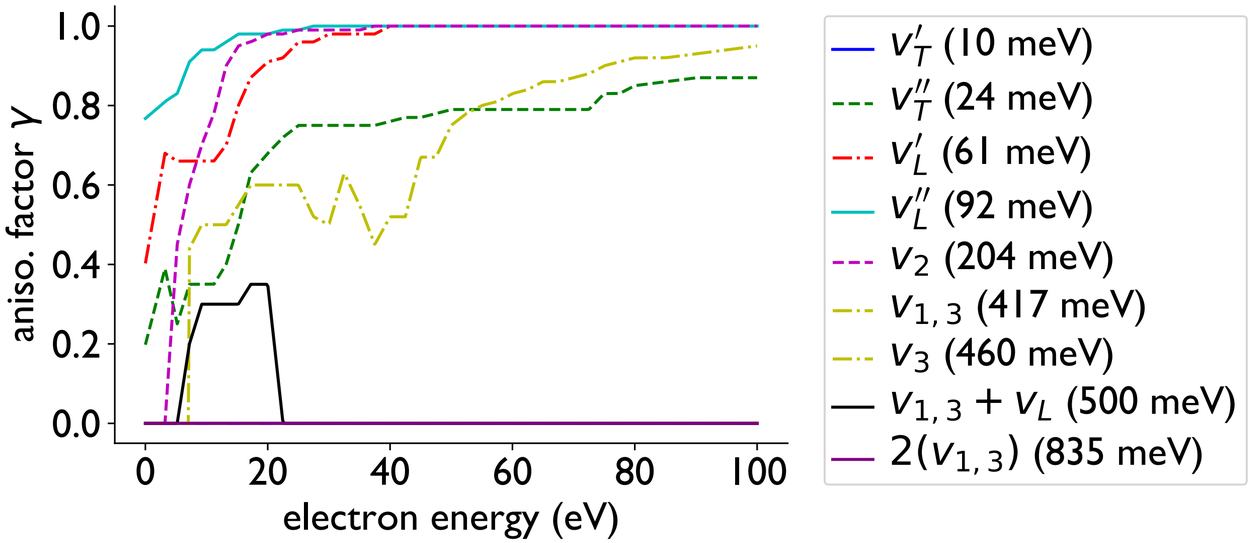
- We use cross-sections for amorphous ice as given by Michaud and Sanche (2000) for our simulations.
- For low (<25 eV) electrons, inelastic scattering is the dominant scattering mechanism.
- The inferior inelastic scattering modes correspond to translations, librations, bending, and stretching of the water molecule.
  - Each of these interactions results in a loss of energy less than 1 eV for the electron.
- At higher energies excitation/ionization (particularly ionization) is the dominant interaction.
- The capture cross-sections are taken from Smith (2018)
  - This is the sum of low-energy capture and into a pre-solvated or solvated state or energetic capture into a resonance state.
  - Near 10 eV there is a peak corresponding to the transient negative anion (TNA) resonance.





Anisotropy in Scattering is also a function of energy.

- When an electron inelastically scatters, we use the anisotropy factor ɣ reported my Michaud and Sanche (2000) to determine the exiting direction of the electron.
- ɣ is the fraction of scatters that *do not* change direction,
- (1-ɣ) is the fraction of scattering events where the electron exits isotropically.
- Some inelastic scattering events are isotropic over the energy range we consider
- Others transition from isotropic to anisotropic.



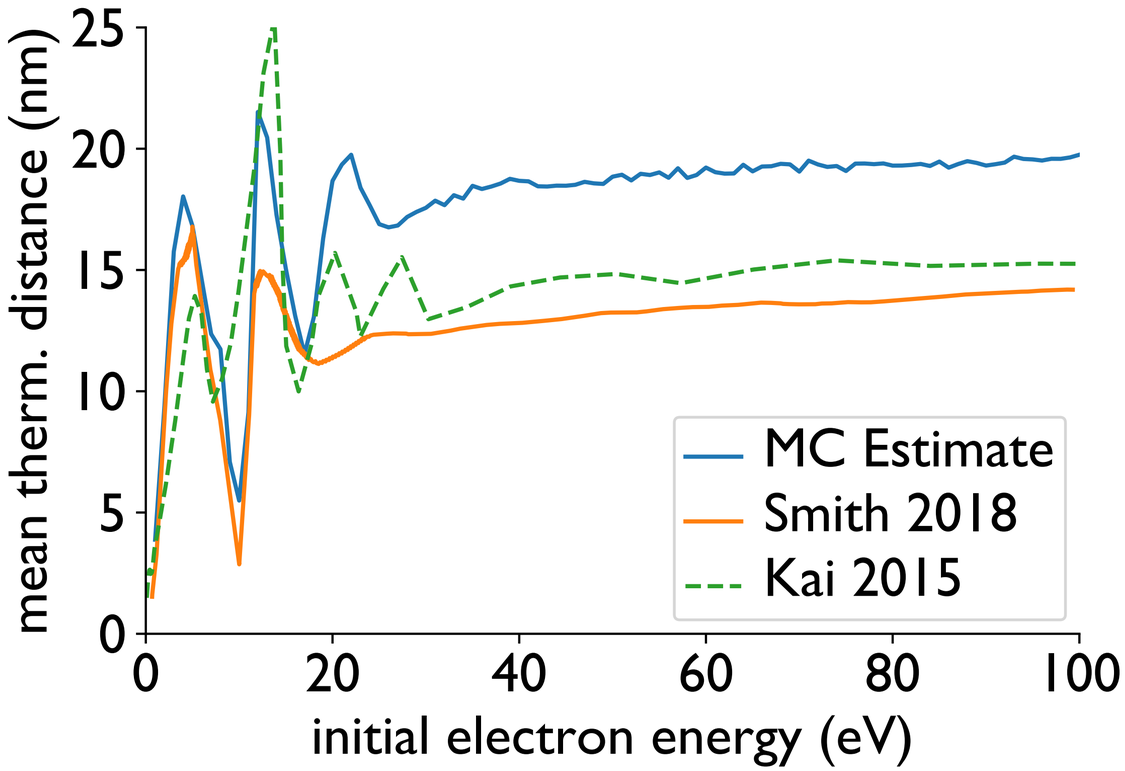
We perform Monte Carlo simulations for low-energy electrons using the following procedure

1. For an electron at energy *E* moving in direction (Θ,ϕ) we first compute the total cross-section as the sum of the inelastic, excitation/ionization, elastic, and capture cross-sections.
2. We then sample a distance to collision, *d*, from an exponential distribution with a mean-free path corresponding to the total cross-section
3. We move the electron a distance *d* along its current trajectory.
4. Decide what type of interaction based on the ratio of the inelastic, excitation/ionization, elastic, and capture cross-sections to the total cross-section.
    - If the interaction is elastic scattering, we sample a new direction (Θ,ϕ) uniformly on the unit sphere and go back to step 1.
    - If the interaction is capture, we stop following the electron. If the capture is between 7 and 12 eV, we label it as TNA
    - If the interaction is an inelastic scatter, we sample what kind of scatter it is based on the relative sizes of the cross-sections for each interaction.
        - Then using the anisotropic factor we sample whether the electron does not change direction or needs a new, random direction (Θ,ϕ)
        - The electron energy is decreased by the mean energy of the mode excited by the scatter and we return to step 1.
    - If the interaction is excitation/ionization, we then decide if the interaction is excitation or ionization based on the ionization efficiency
        - The ionization efficiency is considered to be 1 above 20 eV and linearly extended down to 0.3 at 9.2 eV (Pimblott, LaVerne, & Mozumder 1996)
        - If the interaction is an ionization, we sample the energy lost uniformly from 6 eV to 0.5*E*
        - If the interaction is an excitation, we sample the excitation energy based on the valence transitions at 8.5, 10.4, 14.5, and 28 eV. The maximum the electron can lose is 0.5*E* in the interaction.
        - Ionization/Excitation does not alter the electron trajectory, and we go back to step 1.

- The electron is followed until it is captured or it slows down to an energy below 0.1 eV.

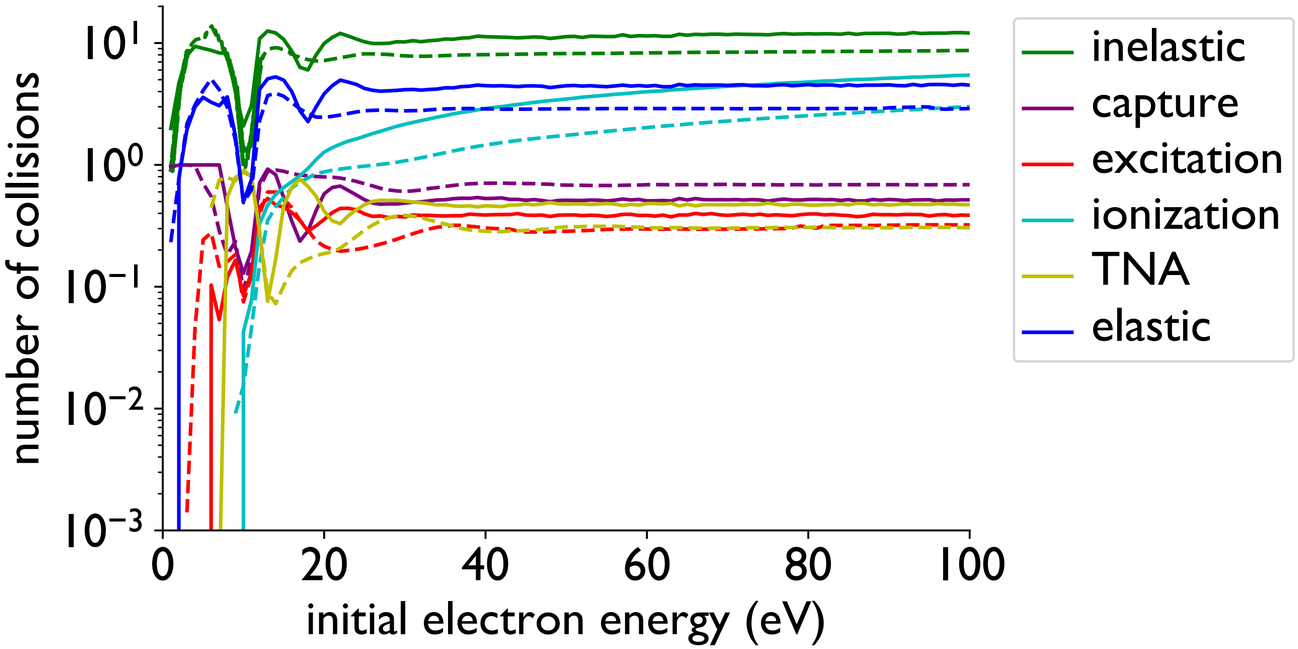
We compare at room temperature with previous results.

- We take 10^4 electrons at a given energy and compute their distance to thermalization.
- During the electron simulation we count all of the different processes that occur.
- We compare our results with Smith 2018 and Kai 2015
  - Exact agreement is not expected because it is not known how all of the energy losses and scattering angle changes were computed.
- At low energies all methods predict a peak in the thermalization distance (ours is the highest).
- Both our calculation and Kai predict a peak at 13-14 eV.
  - This peak is much smaller in the Smith calculation.
- We are higher than the other two calculations above 20 eV.

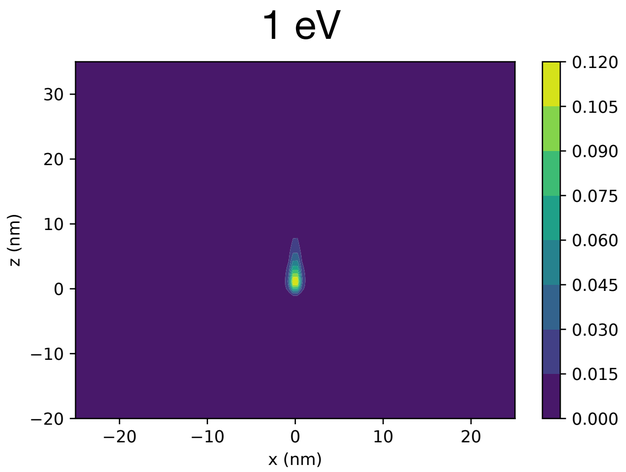


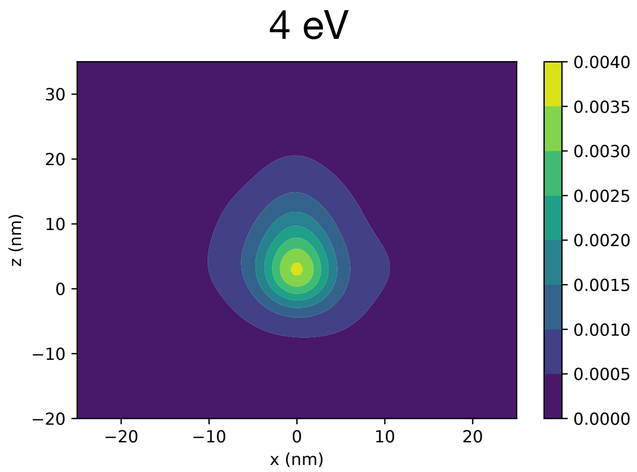
The number of collisions by type will help illustrate the differences.

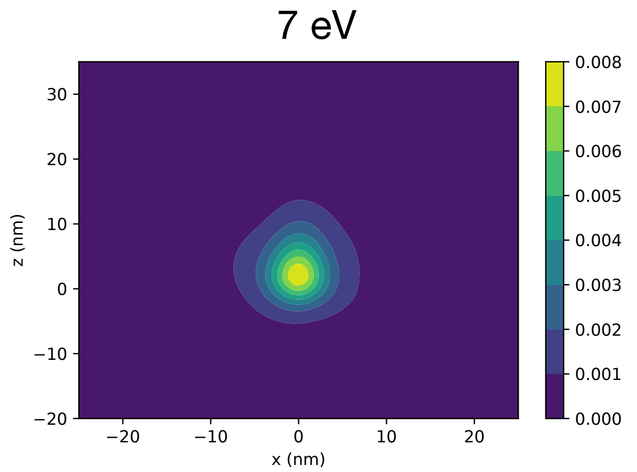
- In the figure at right the solid lines are from our MC code, and the dashed line are from Smith.
- At low energies the number of inelastic and scattering collisions are the same in both calculations.
- At higher energies we predict that the number of collisions needed is higher.
- In particular several more inelastic and ionization collisions occur during thermalization.
- The greater number of collisions could be due to our calculation not removing as much energy from the electron per collision at these higher energies.

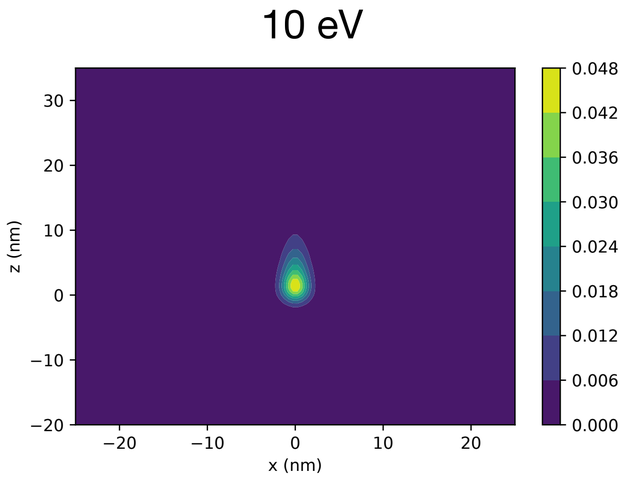


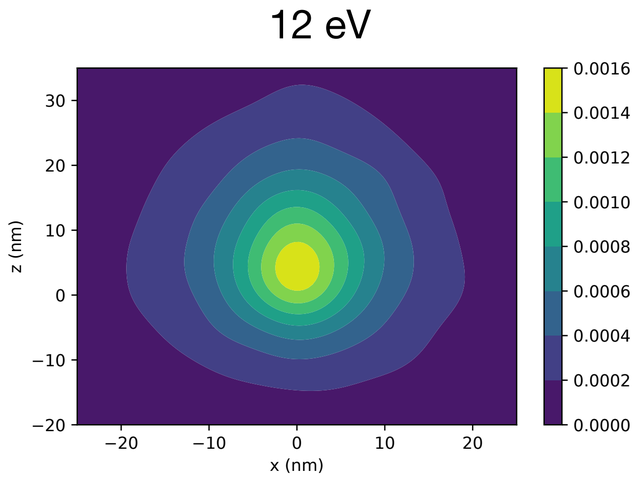
At different initial energies the distribution of thermalized electrons have different shapes.

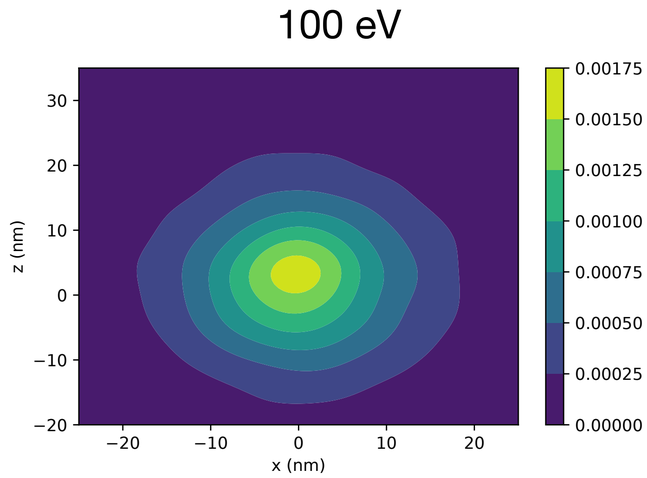








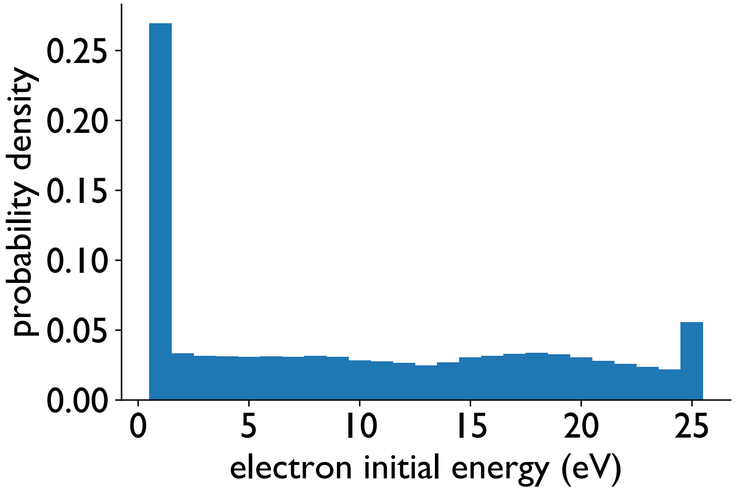




In these simulations all electrons started in the z direction. The plots project the electron's final positions into the xz plane and compute the probability density.

We estimate the distribution of thermalization distances by sampling initial electron velocities.

- Smith 2008 gives a distribution (at right) of the energy of electrons produced in a spur.
- Note that 1 eV is the most common energy of the electrons.
- We sample an electron energy from this distribution and then compute via MC the thermalization distance.
- This will give us the distribution of thermalization lengths expected to be observed in a spur.
- Smith's calculated distribution and a Maxwell distribution matching the mean are shown at left.
- Despite having the same mean, the character of the distributions are very different.
    - The Maxwell distribution underestimates the number of electrons with a very small thermalization distance.



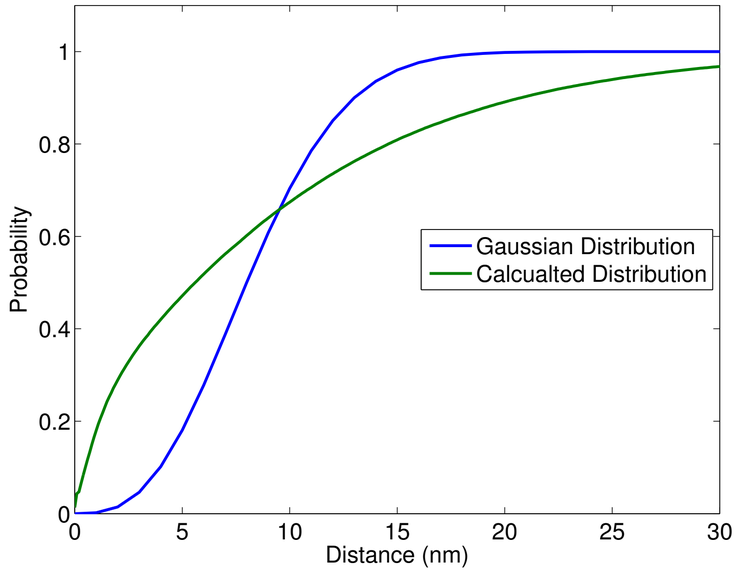
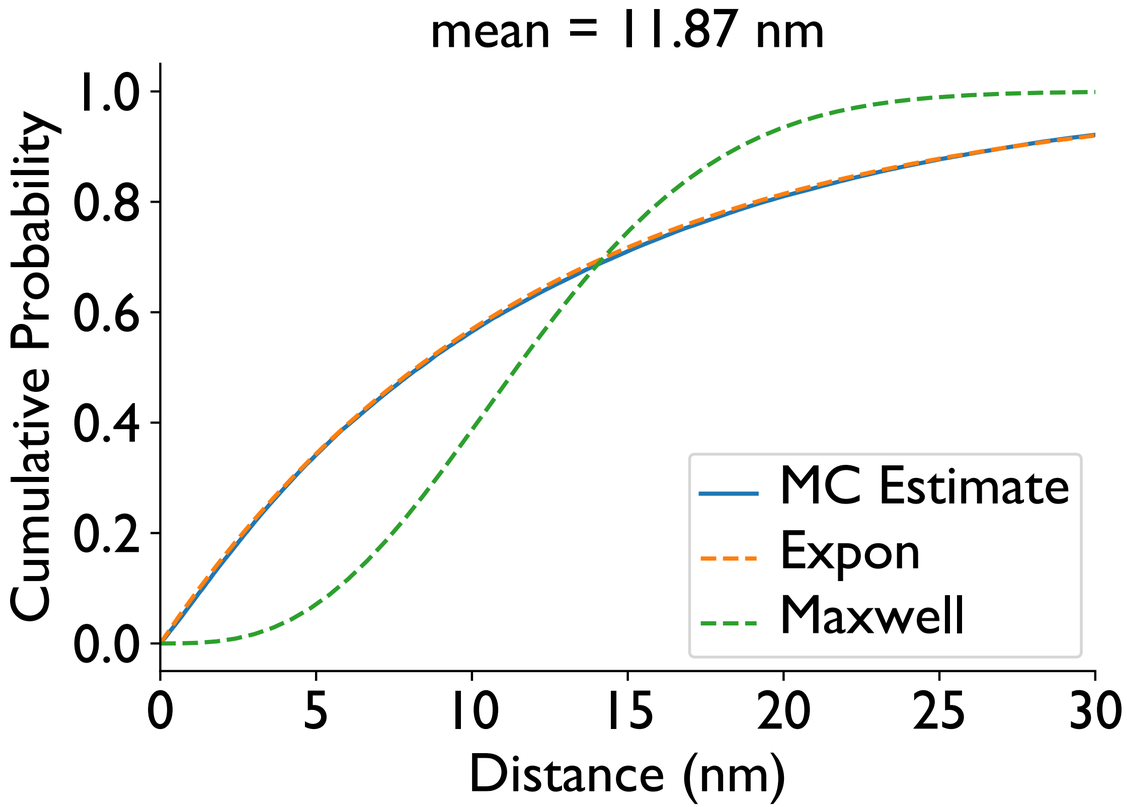


Figure Credit: M. Smith, "Computational Study of Low Energy Electrons Through Amorphous Ice and Gaseous Phase Water" (2018)

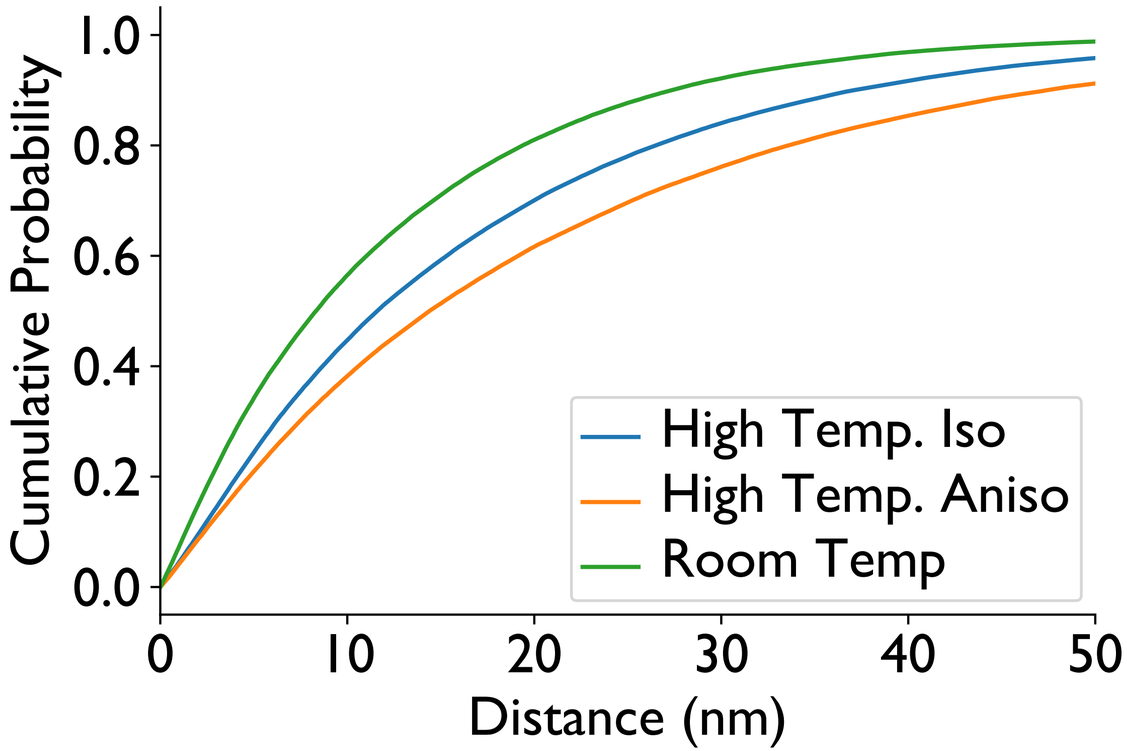
Our MC results give an exponential distribution for the thermalization distance.

- Using our MC calculations we get a larger mean distance than Smith (11.9 compared to 8.4 nm).
- On this plot we show an exponential distribution and a Maxwell distribution with the same mean.
- The exponential distribution matches the calculated results closely.



Changing the temperature will affect the distribution of thermalization distances.

- Before we noted that it has been suggested that the thermalization distance goes down at high temperatures by as much as factor of 2.
- This is counterintuitive because the density of scatters (molecules) goes down at high temperatures.
- Here we compare room temperature density water (0.997 g/cc) and pressurized water at 350 ºC (0.575 g/cc).
- If we just change the density the thermalization distance increases from 11.9 nm at room temperature to 20.6 nm.
- However, if we make all of the inelastic scatters isotropic at this high temperature we decrease the distance to 16.35 nm.
- This adjustment is not enough to explain the decrease in the thermalization distance, but it is pushing the distribution in the right direction.
- We will need another affect to explain that finding.



There are several other potential adjustments that could reduce the thermalization distance in the direction that is suggested by previous studies.

- The decrease in the dielectric constant with higher temperatures, would decrease the dielectric screening and increase the cross-sections.
- The magnitude of this effect is something we plan on looking at.
- We also would like to include the recent data from the Signorell group at ETH in our simulations.
- Also, we can look into simulating the microjet simulations of the Suzuki group with our capability.