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Strong Correlation Effects in Atmospheric Pressure Plasmas

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Motivation

Atmospheric pressure plasmas

- Increasing interest shown in atmospheric pressure plasmas
- Operational simplicity
- Low running cost (no vacuum system required)
- Promising for inactivation of pathogens in medicine, applications in food industry, agriculture, water purification, atmosphere decarbonization, among others.
- Highly non-equilibrium plasma state (Te>>Ti) which promotes chemical reactions

<u>A key science challenge is to model the main mechanisms involved in the plasma dynamics and transport of reacting species in order to improve the development of plasma sources</u>

Introduction

- The electrons are usually at much higher temperatures compared to ions and the background neutral gas.

- This highly non-equilibrium plasma state promotes chemical reactions that are either not possible or efficient in gaseous or liquid states

- The dynamics of the much hotter electrons is characterized by a weakly coupled regime, where the average Coulomb potential energy is smaller than the average electron kinetic energy

Coupling Parameter

$$\Gamma_{ss'} = \frac{\phi_{ss'}(r=a)}{k_B T_{ss'}}$$

Wigner–Seitz radius

$$a = \left(\frac{3}{4\pi n}\right)^{1/3}$$

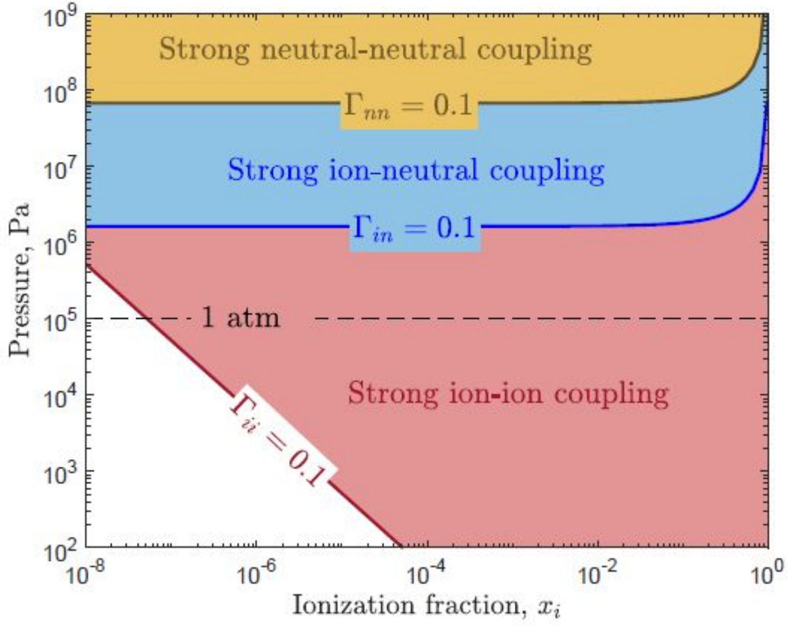
- $\Gamma < 1 \rightarrow$ Weakly Coupled
- $\Gamma > 1 \rightarrow$ Strongly Coupled

- The dynamics of the ion reactive species occurs in a regime characterized with large densities and smaller temperatures and we believe that corresponds to a strongly coupled regime

Coupling Parameter Space

Argon plasma, Z=1

T = 293 K



Coulomb Potential $$\phi(r) = \frac{q^2}{4\pi\epsilon_0}\frac{1}{r}$$

Charge Induced Dipole Potential $$\phi_{ind}(r) = -\frac{q^2}{8\pi\epsilon_0}\frac{\alpha_R a_0^3}{r^4}$$

Lennard Jones $$\phi_{LJ}(r) = 4\epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right)$$

Γin = 9.19e-4 Γii = 21.35 Γnn = 6.96e-6

- At room temperature and atmospheric pressure, **ions are expected to be strongly coupled**
- This requires a separate analysis for ion dynamics in the strongly coupled regime

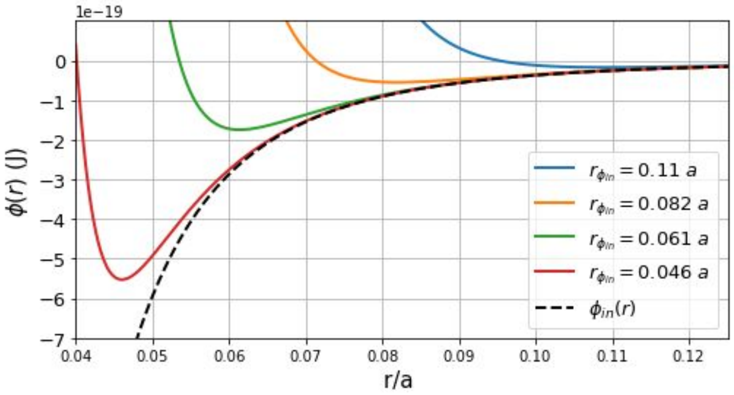
Molecular Dynamics Simulations

- LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator from Sandia National Laboratories).
- Electrons were considered as a non interacting background neutralizing species and were not included in the simulation setup.
- Partially ionized Ar plasma, **T=293 K**, **P = 1 atm**.
- Short (**neutral-neutral**), Medium (**ion - neutral**) and Large (**ion - ion**) range interactions were included..
- 3D periodic box of length ~ 25 a.
- Each simulation was performed by fixing the temperature (NVT stage) and then fixing the total energy (NVE stage). The volume and number of particles remained constant.
- Physical properties were studied in the NVE simulation once the equilibrium was reached.

Ion - Neutral Interactions: Charge Induced Dipole Potential

- Purely attractive potential → Can lead to numerical problems during a MD simulation.
- Need to add a repulsive term in order to avoid that particles get too close to each other.

$$\phi_{ind}(r) = \frac{C}{r^{12}} - \frac{q^2}{8\pi\epsilon_0}\frac{\alpha_R a_0^3}{r^4}$$

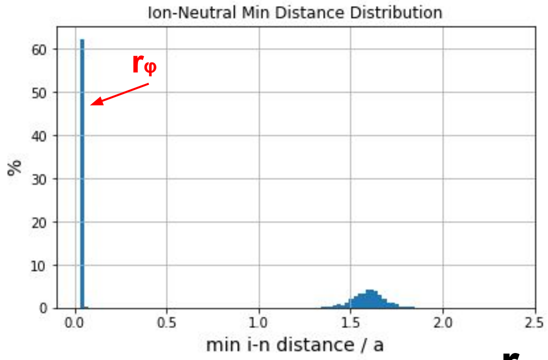


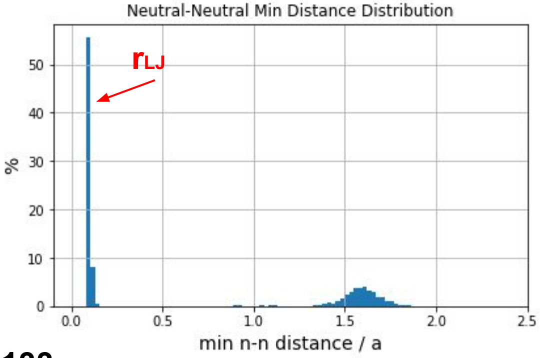
¿ How can we choose the constant C ?

- Too large → May affect the physics of the problem by changing the value of ϕ_{ind} at the average interparticle distance a.
- Too small → large computational cost associated to the requirement on a smaller timestep.

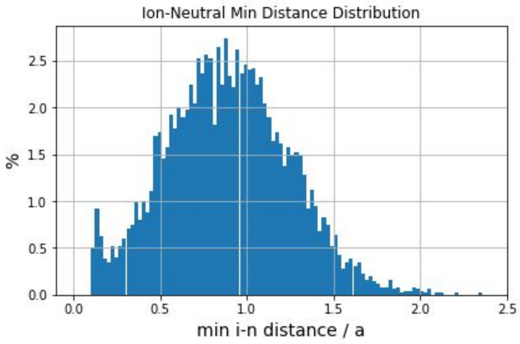
MD Simulations: Results at different r_φ values

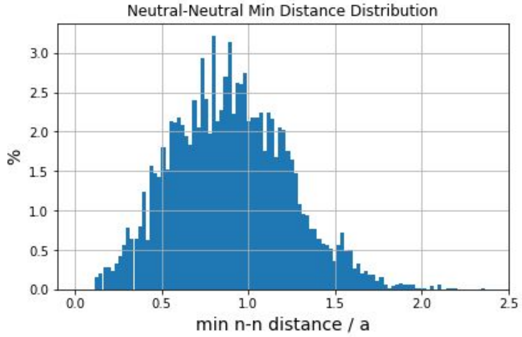
r_φ = 0.046 a





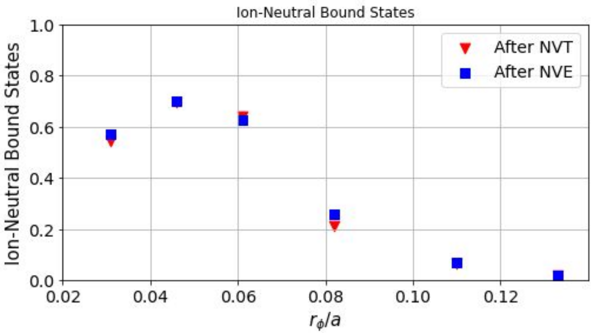
r_φ = 0.133 a

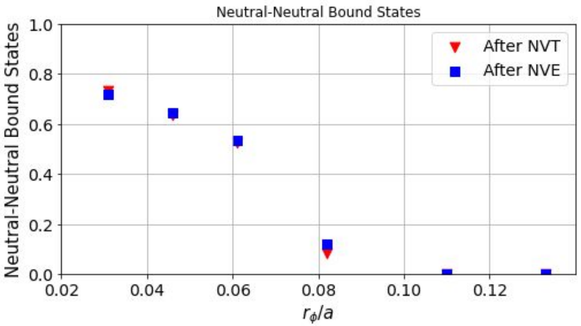




- Formation of bound states at small r_φ values
- Bound states are formed due to 3-body recombination and can be avoided by increasing r_φ

Bounds States Fraction

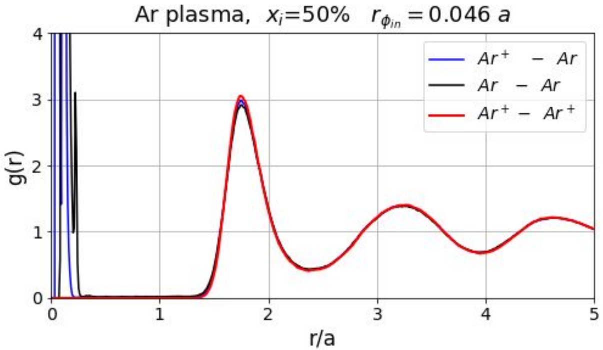


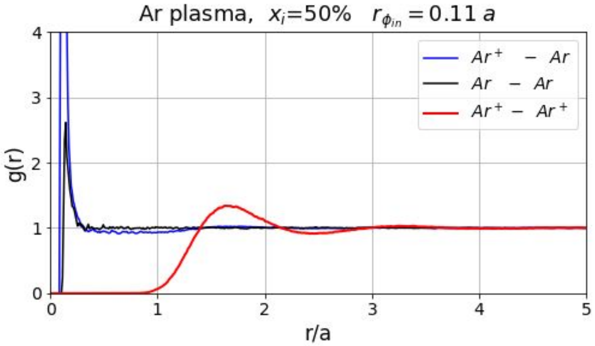


- Bound states fraction increased at smaller $\mathbf{r_\varphi}$ values.
- 3-body recombination process

Radial Distribution Functions for each interaction:

$$g(r) = \frac{N(r)}{4\pi r^2 \Delta_r n_0}$$





MD simulations: Starting with a neutral gas

Must improve the simulation setup in order to have a better physical picture of an experiment !

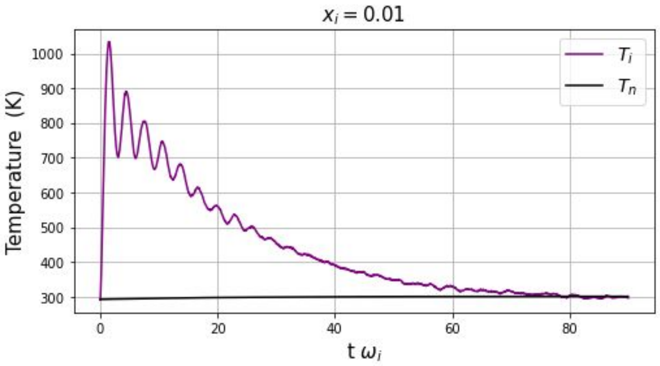
Simulation Setup:

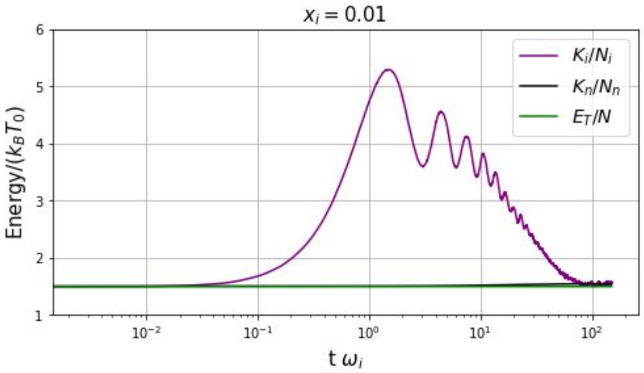
- NVT-NVE simulations for a neutral Ar gas using the LJ potential
- Instant ionization of a fraction of the particles
- NVE simulation including i-n and i-i interactions
- Study the evolution of the temperature after the ionization

MD simulations: Disorder Induced Heating

r_φ = 0.133 a

Ar gas





Characteristic regions:

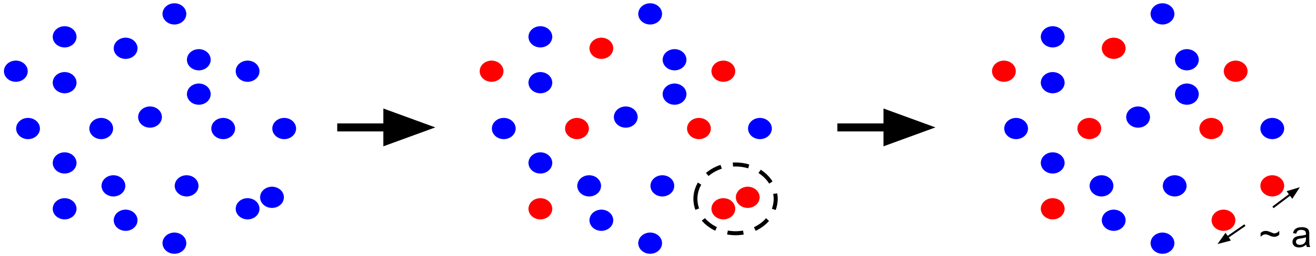
1. Disorder Induced Heating (DIH)
2. Ti fluctuations
3. Ion-Neutral temperature relaxation

- Exchange between Ki and PE during the Ti fluctuations

Neutral Gas at equilibrium

Ionization Pulse

Separation of Particles



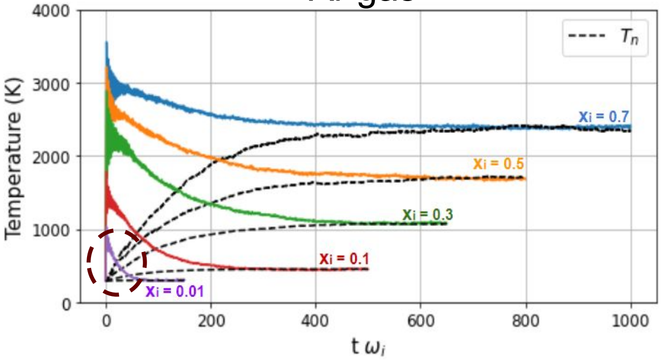
$$\Delta K_i = \Delta P \approx \frac{e^2}{4\pi\epsilon_0}\frac{1}{a_{ii}}$$

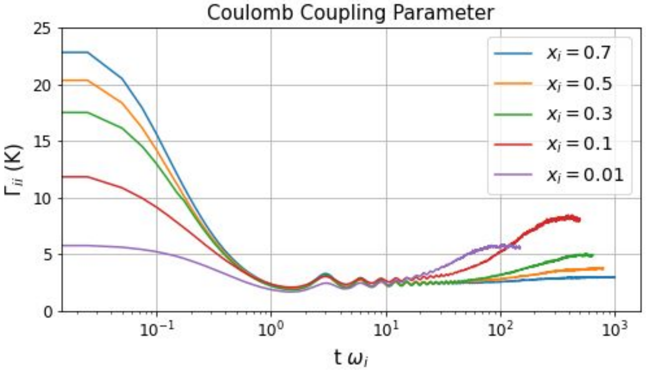
$$\rightarrow \Gamma_{ii} \approx 1$$

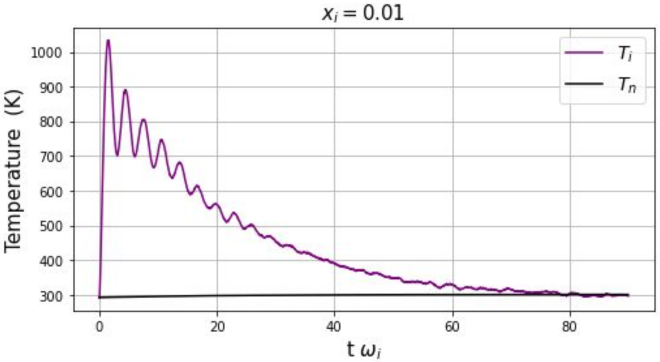
MD simulations: Evolution of Discharge

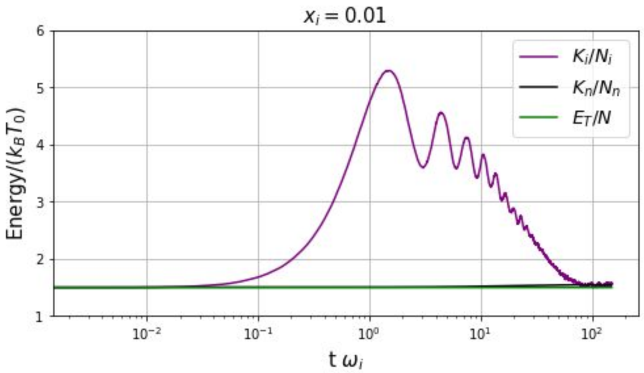
r_φ = 0.133 a

Ar gas









Characteristic regions:

1. Disorder Induced Heating (DIH)
2. Ti fluctuations
3. Ion-Neutral temperature relaxation

- Exchange between Ki and PE during the Ti fluctuations

-T_{eq} < T_0 for x_i>0.01

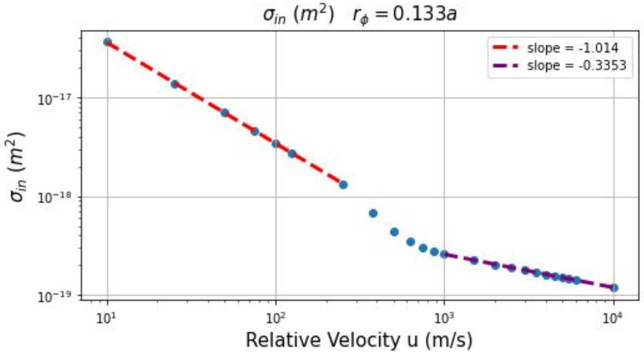
- DIH min(Γ_{ii}) ~ 2

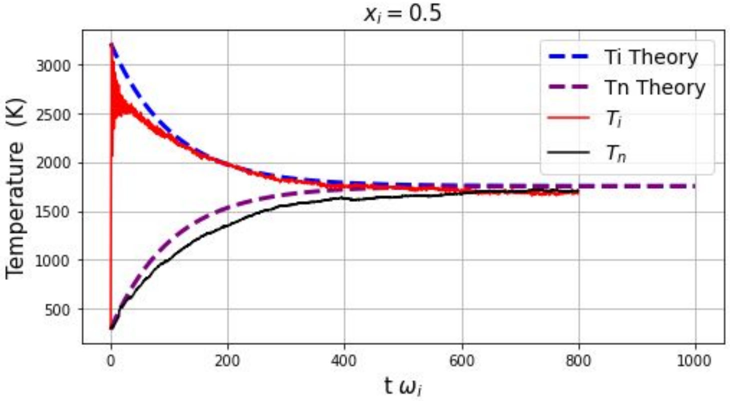
Ion-Neutral Temperature Relaxation

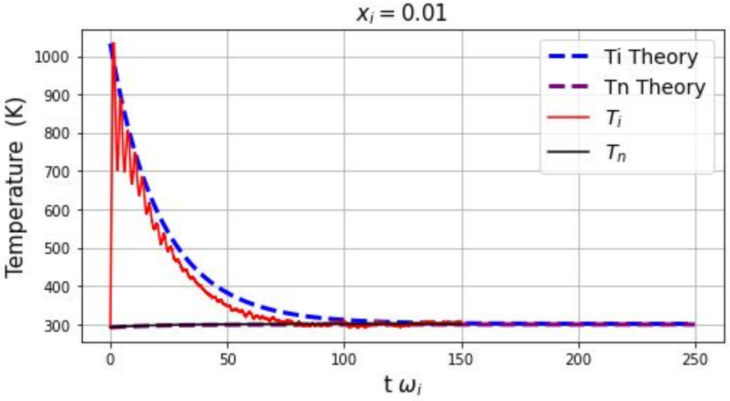
Calculation of collision frequency and temperature relaxation due to i-n collisions

$$\nu_{in} = \frac{4}{3\sqrt{\pi}} n_n \sqrt{\frac{2k_B}{m}} \sqrt{T_i + T_n} \int_0^\infty dg Q_{in}^{(1)}(g) g^5 e^{-g^2}$$

$$\frac{dT_n}{dt} = -\frac{3}{2}\nu_{ni}(T_n - T_i) \qquad \frac{dT_i}{dt} = -\frac{3}{2}\nu_{in}(T_i - T_n)$$







Theory model

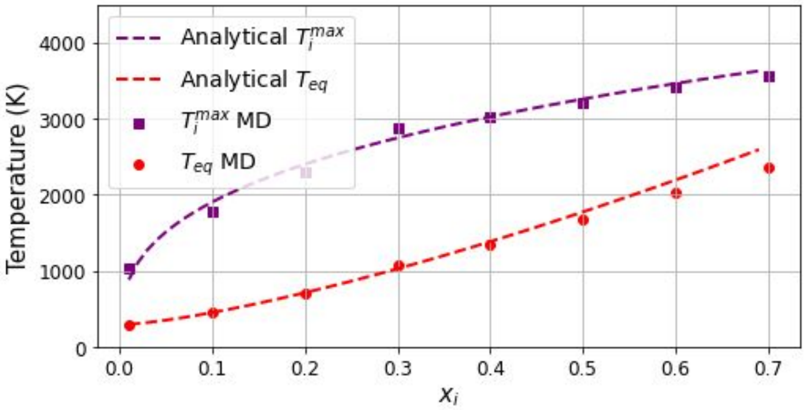
$$T^{eq} = x_i T_i^{max} + (1 - x_i) T_{n,t=0}$$

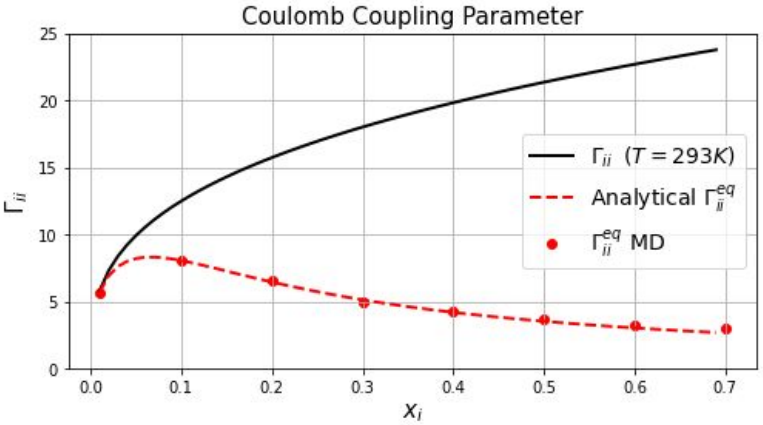
$$T_i^{max} = \left(\frac{1}{1.91}\right) \frac{Z^2 e^2}{4\pi\epsilon_0 k_B} \left(\frac{4\pi x_i n}{3}\right)^{1/3}$$

Γ_{min}^{avg}

- Total Energy is conserved → Teq
- Γii ≅ 1 (DIH) → Ti max

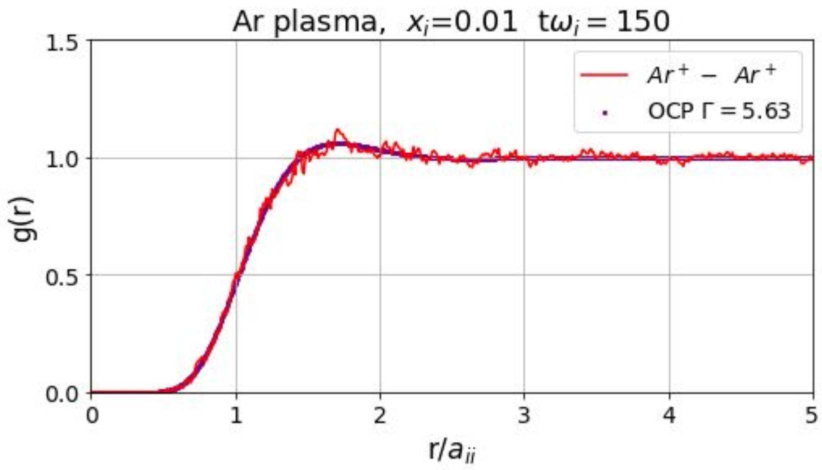
$$\Gamma_{ii}^{eq}(x_i, T^{eq}(x_i))$$

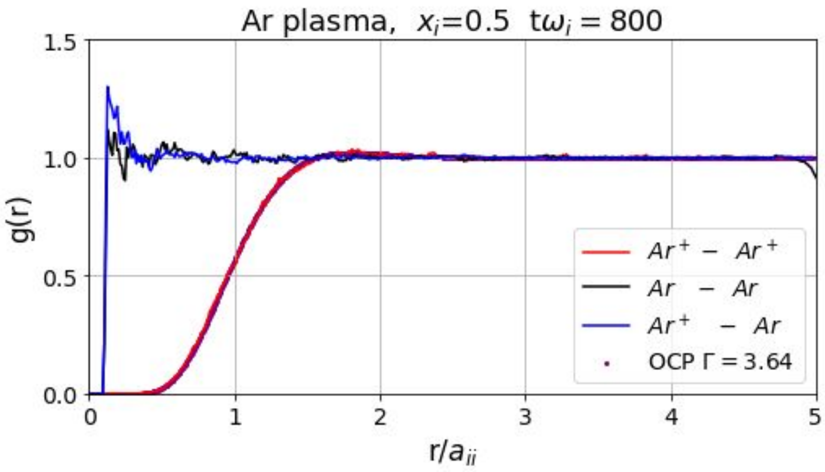




Radial Distribution Function

- Coupling parameter Γ > 1 → ions are strongly coupled at equilibrium
- Equilibrium i-i radial distribution function corresponds to an OCP at the same coupling parameter





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Conclusions

- The equilibrium temperature is set by different processes:
    - Disorder Induced Heating
    - Ion-neutral temperature relaxation through collisions
    - 3-body recombination

- Ions are strongly coupled at equilibrium ($\Gamma > 1$) in atmospheric pressure plasmas

- Equilibrium i-i radial distribution function corresponds to an OCP at the same coupling parameter

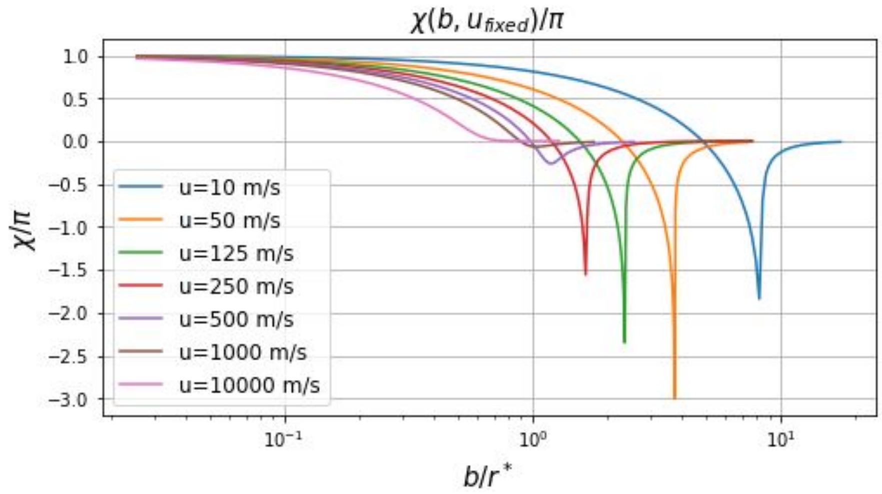
- Using energy conservation arguments and the concept of DIH the maximum temperature and equilibrium can be correctly predicted.

Thank you !

Ion-Neutral Scattering Angle and Cross Section

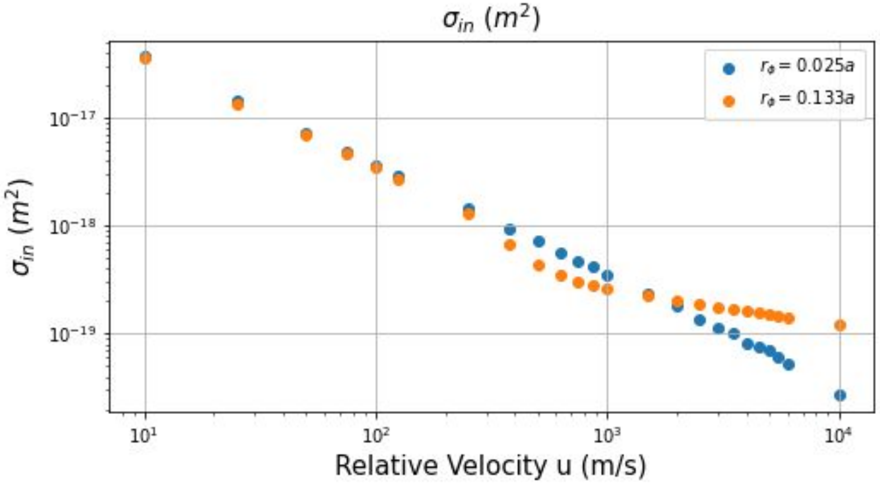
Scattering Angle

$$\chi = \pi - 2b \int_{r_0}^{\infty} \frac{dr/r^2}{\sqrt{1 - \frac{b^2}{r^2} - \frac{2\phi_{in}(r))}{mu^2}}}$$



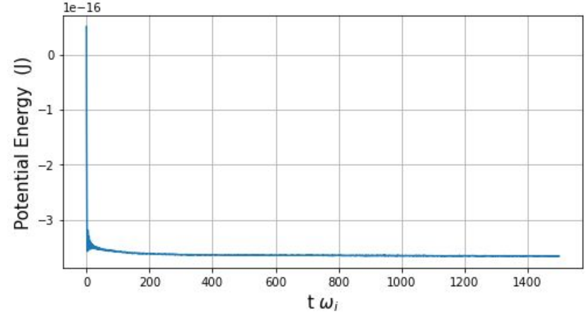
Cross Section

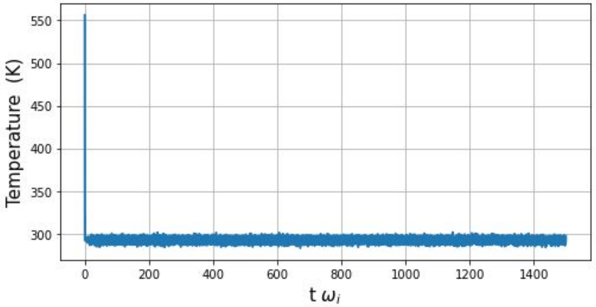
$$Q_{in}^{(1)} = 2\pi \int_0^{\infty} (1 - cos(\chi))b\ db$$



MD Simulations: Temperature and Energy evolution

Example of Simulation result, r_{φ} = 0.11 a





NVT simulation

The temperature was fixed and the Noose Hover algorithm was used to reach the desired room temperature

NVE simulation