SAND2022-7772C

Sandia National Laboratories

Strong Correlation Effects in Atmospheric Pressure Plasmas

Acciarri M. D. [1] , Baalrud S. [1], Moore C. [1, 2]

1. University of Michigan
2. Sandia National Laboratories

UNIVERSITY OF MICHIGAN

Atmospheric Pressure Plasmas are used for multiple applications

- **Operational Simplicity (no vacuum system required) and low running cost**
- **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**

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

Ions are strongly coupled in atmospheric pressure plasmas

This leads to strongly correlated effects that currently are not accounted for in standard modeling techniques

Coupling Parameter

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

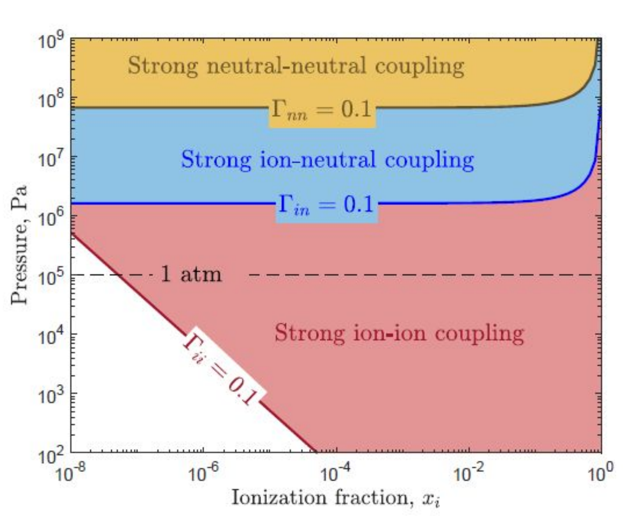
Wigner–Seitz radius

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

- **Γ < 1 → Weakly Coupled**
- **Γ > 1 → Strongly Coupled**

s,s´ → species (i,n), (i,i), (n,n), (e,e), etc

Argon plasma, Z=1, T = 293 K



Ti = 293 K, Te = 2 eV, P = 1 atm:

x_i	Γ_{ee}	Γ_{ii}
0.01	0.07	5.80
0.5	0.27	21.35

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

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

At room temperature and atmospheric pressure, ions are expected to be strongly coupled

Strongly Coupled Plasmas do not obey the Boltzmann Equation

- **The collision operator used in the Boltzmann equation only accounts for binary collisions.**
  This only applies to the weakly coupled regime (Γ < 0.1) !
- **PIC codes solve the Boltzmann equation**
  → By using PIC you will totally miss the strongly coupled effects in the ion dynamics

In order to account for all the relevant physics we can use Molecular Dynamics (MD) Simulations

- LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator)
- Electrons were considered as a non interacting background neutralizing species and are not included
- 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.

Starting with a neutral gas and applying an instant ionization pulse

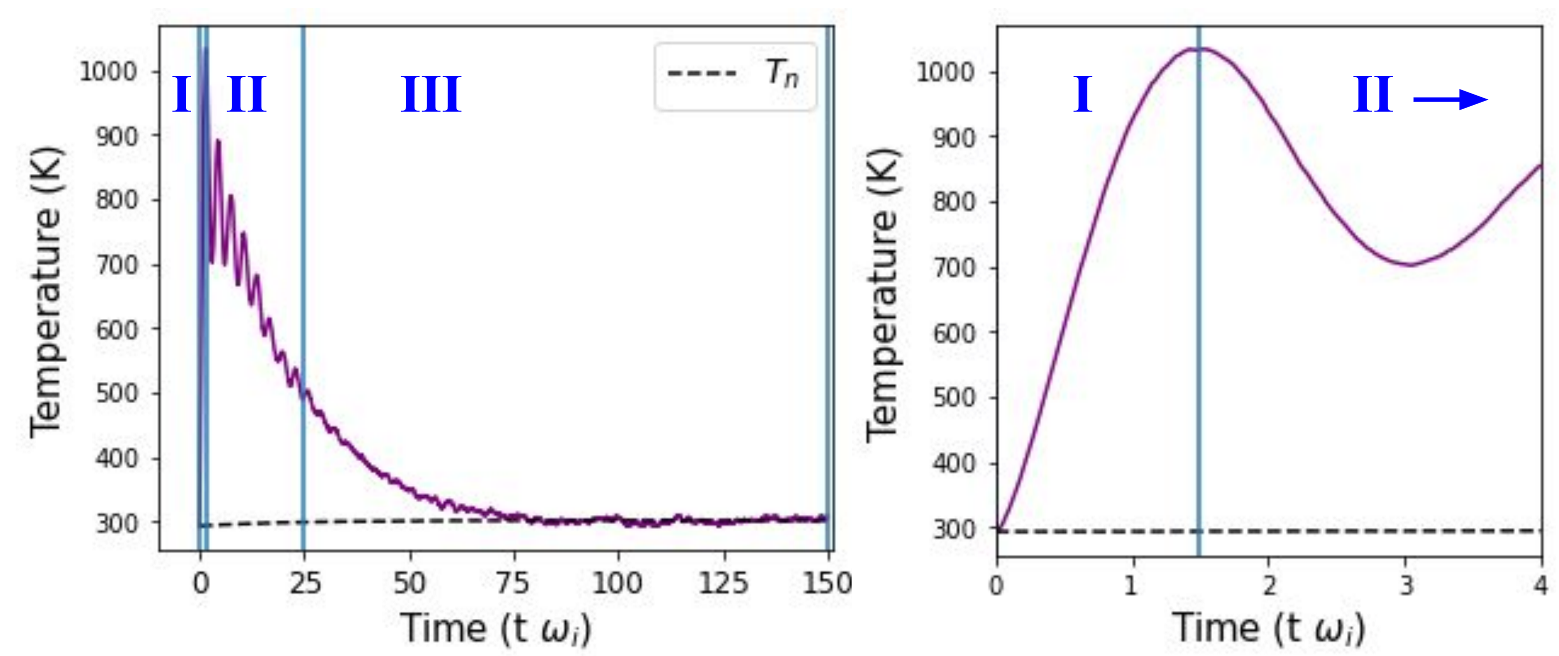
Evolution of Neutral Ar to equilibrium → **Instant Ionization of a fraction of the particles** → **NVE simulation including interactions between: i-n, n-n and i-i**

Strongly Coupled Effects set the ion Temperature

Characteristic regions:

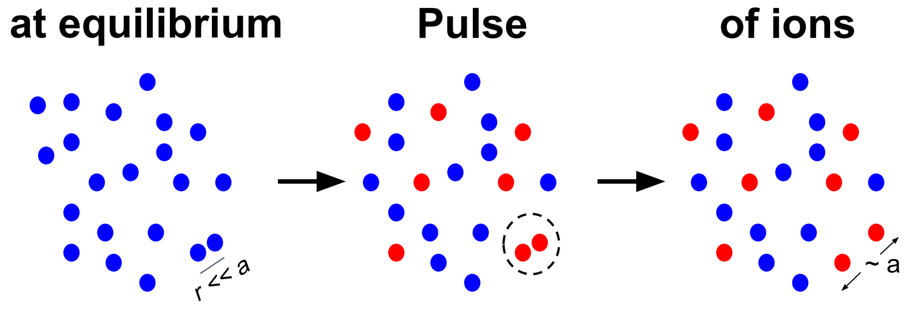
I. **Disorder Induced Heating (DIH)**
II. **Large fluctuations in the ion temperature**
III. **Ion - Neutral temperature relaxation**

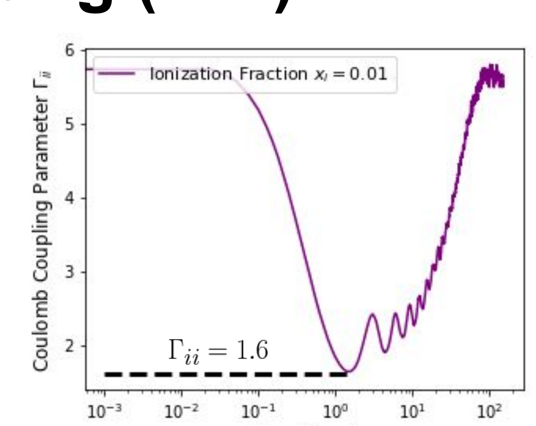
Ionization fraction xi = 0.01



I. Disorder Induced Heating (DIH)

Neutral Gas at equilibrium → **Ionization Pulse** → **Separation of ions**



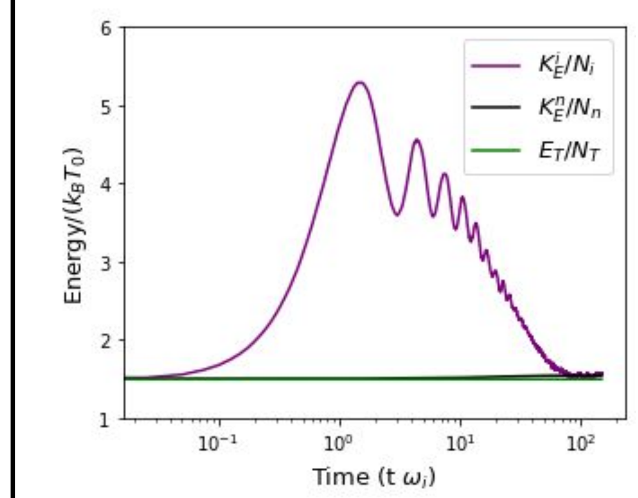


Ionization causes: $\varphi^{short\ range} \rightarrow \varphi^{long\ range}$

Total energy is conserved $\Delta E = \Delta K_i + \Delta P_e = 0$

Ions move to lowest potential configuration $\Delta K_i = -\Delta P_e \approx \frac{e^2}{4\pi\epsilon_0}\frac{1}{a_{ii}} \rightarrow \Gamma_{ii} \approx 1$

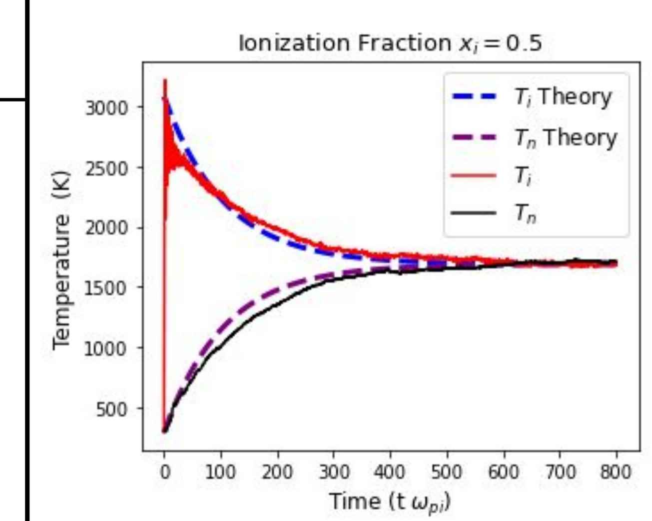
II. Large fluctuations in the ion temperature



K^i_E: Ions total Kinetic Energy
K^n_E: Neutral atoms total Kinetic Energy
E_T: Total Energy

Oscillations in ions positions after DIH
→ Exchange between K_E and P_E
→ ion Temperature fluctuations due to the strong coupling between ions (Γ_{ii} > 1 → Avg. Potential Energy > Avg. Kinetic Energy)

III. The Ion-Neutral temperature relaxation through collisions lowers the ion temperature increasing Γ_{ii}



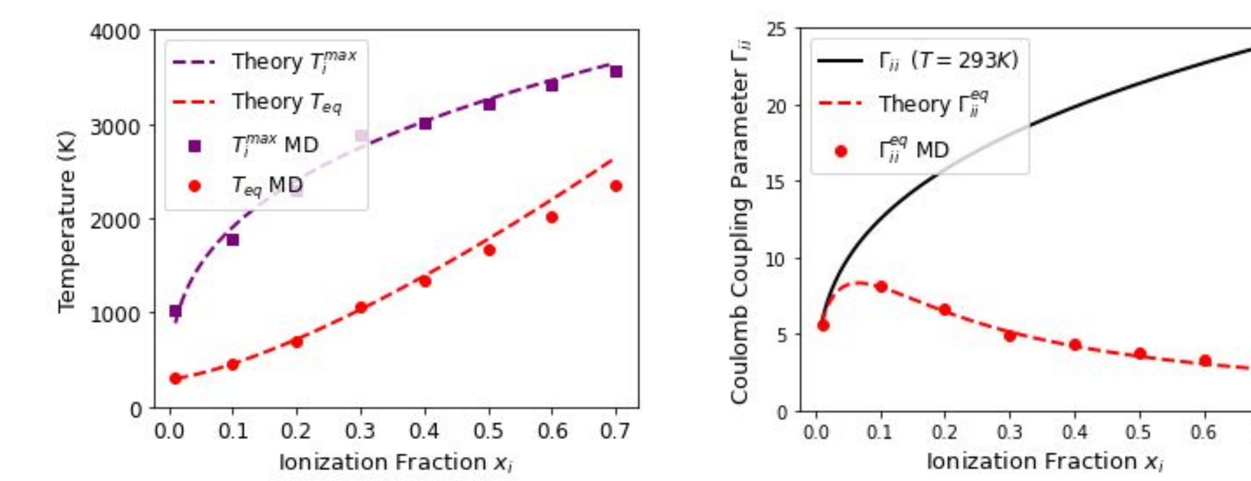
Ion neutral collision frequency can be computed from the charge induced dipole cross section

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

Ion-Neutral temperature relaxation through collisions

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

T^{eq} and Ti^{max} can be modeled using energy conservation arguments



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

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

$$\Gamma_{ii}^{eq} = \frac{Z^2 e^2}{4\pi\epsilon_0}\left(\frac{4\pi x_i n}{3}\right)^{1/3}\frac{1}{k_B T^{eq}(x_i)}$$

Conclusions

- **Ions are strongly coupled in atmospheric pressure plasmas**
- The equilibrium temperature is set by the DIH, Ion-Neutral temperature relaxation through collisions and 3-body recombination
- **The DIH and ion temperature fluctuations could not be obtained by solving the Boltzmann equation or using PIC simulations since they only apply to weakly coupled plasmas**
- **i-i interactions are not screened by the presence of neutral atoms**
- **The strongly coupled effects are not negligible and you need models to capture this important physics**

Acknowledgments

This work is supported by DOE FES grant No. DE-SC0022201, and the LDRD program at Sandia National Laboratories under contract DE-NA-0003525.