Strong Coulomb coupling influences ion and neutral temperatures in atmospheric pressure plasmas

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Abstract

Molecular dynamics simulations are used to model ion and neutral temperature evolution in partially-ionized atmospheric pressure plasma at different ionization fractions. Results show that ion–ion interactions are strongly coupled at ionization fractions as low as $10^{-5}$ and that the temperature evolution is influenced by effects associated with the strong coupling. Specifically, disorder-induced heating is found to rapidly heat ions on a timescale of the ion plasma period ($\sim 10$ s ps) after an ionization pulse. This is followed by the collisional relaxation of ions and neutrals, which cools ions and heats neutrals on a longer ($\sim$ ns) timescale. Slight heating then occurs over a much longer ($\sim 100$ s ns) timescale due to ion-neutral three-body recombination. An analytic model of the temperature evolution is developed that agrees with the simulation results. A conclusion is that strong coupling effects are important in atmospheric pressure plasmas.

Keywords: CAPP, atmospheric pressure plasmas, strong correlations, strongly coupled, fast neutral heating

(Some figures may appear in colour only in the online journal)

1. Introduction

Atmospheric pressure plasmas, in particular cold atmospheric pressure plasmas (CAPPs), have been widely tested for numerous applications including the inactivation of various pathogens in medicine [1], food industry [2], agriculture [3], and water purification [4], among others, showing promising results and an increasing interest in those industries. CAPP technology presents several advantages over other plasma technologies including operational simplicity, low running cost, and environmental friendliness, since no vacuum chamber is needed and the reactor is frequently open [1]. The increasing interest has led to an intensive effort to understand the main mechanisms responsible for plasma dynamics and its correlation with reactive species delivery [5–9]. However, still some effort should be paid to provide a deeper insight into the basic physics mechanisms, including the ones responsible for fast neutral gas heating observed at atmospheric pressure [10–18]. Here, we show an example of such a fundamental physics effect: ion–ion interactions are strongly coupled and the ion and neutral temperatures are influenced by an associated disorder-induced heating (DIH) process.

Strong coupling refers to interactions in which the average potential energy of interacting particles $\langle \phi_{ss'}(r = a_{ss'}) \rangle$, where $a_{ss'}$ is the average distance between particles of species $s$ and $s'$ exceeds their average kinetic energy $k_B T_{ss'}$, i.e. $\Gamma_{ss'} \gtrsim 1$, where $s$ and $s'$ are the species involved in the interaction and,

$$\Gamma_{ss'} = \frac{\langle \phi_{ss'}(r = a_{ss'}) \rangle}{k_B T_{ss'}},$$

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For example, the Coulomb potential for ion–ion interactions is \( \phi_{ii} = (Ze)^2 / 4 \pi \epsilon_0 a_{ii} \) and the ion–ion Coulomb coupling parameter is \( \Gamma_{ii} = (Ze)^2 / (4 \pi \epsilon_0 a_{ii} b_{ii} T) \). In most CAPPs, ions are expected to be in equilibrium with the neutral gas near room temperature, while electrons have a much higher temperature on the order of eV or several eV. A consequence is that the hotter electrons are characterized by a weakly coupled regime \( (\Gamma_{ee} \ll 1) \), while the much cooler ions can be strongly coupled \( (\Gamma_{ii} \gtrsim 1) \).

Strongly coupled plasmas are influenced by physical effects that fundamentally differ from those governing weakly coupled plasmas. An example is DIH. This arises in strongly coupled systems when the potential energy landscape changes in such a way that particles move to a lower potential energy configuration, releasing kinetic energy in the form of heat. One way that this can occur is through the ionization of a neutral gas. When short-range atomic interactions change to long-range Coulomb interactions, ions reconfigure to a more ordered state due to their mutual repulsion. The more ordered state has a lower potential energy than the initial state (immediately after ionization) because ions spread further apart from one another. The decrease in potential energy in this reconfiguration is compensated by an increase in kinetic energy. DIH is not important in weakly coupled plasmas because the kinetic energy gained in the reconfiguration is small compared to the initial kinetic energy. However, it can be a dominant effect in strongly coupled plasmas. For example, DIH caused by ionization has been measured and studied in detail in ultracold strongly coupled plasmas. For example, DIH caused by ionization can be substantial, leading to neutral gas temperatures that are elevated well above ambient room temperature [10–18]. Several mechanisms of neutral gas heating are known. Examples of the typical timescales are shown in figure 1. One is energy transfer from electron-neutral elastic collisions [23], which is typically expected to occur at timescales of 100’s of ns. Other mechanisms that can transfer energy from electrons to neutral atoms/molecules include energy transfer between vibrationally excited states in molecules [24, 25], energy transfer from vibrational to translational states [24–26], electron-ion recombination processes [14] followed by ion-neutral elastic collisions, electron impact dissociation reactions [12] and quenching of electronically excited molecules by oxygen atoms [13]. In fact, there are some examples in which one or more of these mechanisms appear to fully explain the measured neutral gas temperature. These include electron-neutral elastic heating on timescales of 100 s of nanoseconds [15] and vibrational to translational relaxation on timescales of 10 s of microseconds [16], among others [12, 13, 18].

Figure 1. Comparison of the typical timescales of the possible mechanisms of fast neutral gas heating observed. The disorder induced heating and ion-neutral temperature relaxation mechanisms affect the ion and neutral temperatures respectively in faster timescales compared to the previously studied mechanisms. The timescales here assume atmospheric pressure and typical ionization fractions.

An implication of these findings is that common approaches to modeling atmospheric pressure plasmas need to be reassessed. Most modeling techniques, including particle-in-cell (PIC) methods and solutions of multi-fluid equations, are based on solving a Boltzmann equation or approximations of it (such as multi-fluid models obtained from taking moments of the Boltzmann equation). However, the Boltzmann equation is valid only for weakly coupled systems, such as dilute gases and plasmas. At a fundamental level, it does not treat strong coupling effects that can influence dynamics of atmospheric pressure plasmas. DIH is an example of this. If strong correlations are not accounted for, the ion and neutral temperatures could be mistakenly underestimated.

Although ion temperatures are difficult to measure in atmospheric pressure plasmas, measurements have been made of neutral gas temperatures that are elevated well above ambient room temperature [10–18]. Several mechanisms of neutral gas heating are known. Examples of the typical timescales are shown in figure 1. One is energy transfer from electron-neutral elastic collisions [23], which is typically expected to occur at timescales of 100’s of ns. Other mechanisms that can transfer energy from electrons to neutral atoms/molecules include energy transfer between vibrationally excited states in molecules [24, 25], energy transfer from vibrational to translational states [24–26], electron-ion recombination processes [14] followed by ion-neutral elastic collisions, electron impact dissociation reactions [12] and quenching of electronically excited molecules by oxygen atoms [13]. In fact, there are some examples in which one or more of these mechanisms appear to fully explain the measured neutral gas temperature. These include electron-neutral elastic heating on timescales of 100 s of nanoseconds [15] and vibrational to translational relaxation on timescales of 10 s of microseconds [16], among others [12, 13, 18]. While all of these mechanisms can be present to a greater or lesser extent depending on the gas mixture and experimental setup, we propose that DIH is another mechanism that should be considered. It can considerably influence the ion temperature at large ionization fractions and has the distinguishing feature that it occurs on a much faster timescale than the other heating mechanisms.

We compare the predicted neutral gas temperature after ion and neutral reactions that occurred at timescales comparable to the cooling timescale of the neutral gas due to ion-neutral three-body recombination. In addition to the simulations, a model is developed to describe the main features of the ion and neutral temperature evolution.
close to the measured temperatures. These results are expected to be relevant to a number of plasma sources that achieve high ionization fractions at atmospheric and elevated pressures, including microdischarges [27–29], spark filaments [18, 30, 31], laser-produced plasmas [32, 33], arc filaments [34] and the anode region of electric arcs [35], among others [17, 18, 23].

In the next section the coupling parameter associated with ion–ion, ion-neutral and neutral-neutral interactions is shown in a pressure–ionization fraction space, predicting that at atmospheric pressure and over a wide range of ionization fractions ions are expected to be strongly coupled. In section 3 the MD simulation setup is described. This is followed by a discussion of the ion and neutral temperature evolution in section 4. In section 5 a theoretical model for predicting the maximum and equilibrium ion temperature as a function of the ionization fraction and pressure is described. Finally, section 6 shows a comparison of the observed heating in experiments conducted at atmospheric pressure and the prediction for the temperature using our model.

2. Coupling parameter space

For a partially ionized plasma with one gas species, neutral-neutral, ion-neutral and ion–ion interactions are modeled using the Lennard–Jones, charge induced dipole and Coulomb potentials respectively [36]

$$\phi_{\text{LJ}}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right],$$  \hspace{1cm} (2)

$$\phi_{\text{ind}}(r) = -\frac{q_{i} q_{n}}{8\pi\varepsilon_{0}} \frac{\alpha_{R} a_{\text{R}}^{3}}{r^{3}},$$  \hspace{1cm} (3)

and

$$\phi(r) = \frac{q^{2}}{4\pi\varepsilon_{0}} \frac{1}{r},$$  \hspace{1cm} (4)

where $\epsilon = 120 \, k_{B}$, $\sigma = 0.34 \, \text{nm}$, and $\alpha_{R} = 11.08$ for Ar [36] and $a_{\text{R}}$ is the Bohr radius. Considering an Ar plasma at room temperature and variable ionization fraction and pressure, the coupling parameter associated with each interaction can be computed from equations (1)–(4), using $a_{\text{ind}} = (3/4\pi n_{\text{ind}})^{1/3}$ where $n_{\text{ind}} \approx x_{i} n_{i} + x_{n} n_{n}$ to estimate the average interparticle spacing between ions and neutrals. Here, $x_{i} = n_{i}/n$ and $x_{n} = n_{n}/n$ are the ion and neutral concentrations, $n_{i}$ and $n_{n}$ are the ion and neutral densities, and $n = n_{i} + n_{n}$ is the total density. The pressure and ionization fraction at which the transition from a weakly to a strongly coupled regime occurs is estimated from the limit $\Gamma = 0.1$, which is the condition where the Boltzmann equation is known to break down [37, 38].

As shown in figure 2, at small ionization fractions and pressures below atmospheric pressure, none of the interactions are strongly coupled. However, by increasing the ionization fraction or the pressure, it is possible to find a strong ion–ion coupling region. In fact, the figure shows that ion–ion interactions at many CAPP conditions are expected to be strongly coupled. If the pressure is increased above $\approx 10 \, \text{atm}$, a strong ion-neutral coupling regime is reached. Further increases in pressure can lead to a strong neutral–neutral coupling regime at around 1000 atm.

Since the ion–ion Coulomb coupling parameter exceeds 0.1 in many CAPPs applications, the binary ion–ion collision picture and hence the Boltzmann equation are not expected to apply. In this strongly coupled regime, many-body collisions dominate the interactions between ions and a first-principles approach is required. Hence, we used MD simulations, which provide a first-principles solution of Newton’s equation of motion for the dynamics of $N$ interacting particles.

3. MD simulations

MD simulations were carried out using the open-source software LAMMPS [39]. Since electrons are much hotter than ions and are weakly coupled, they are treated as a background non-interacting species when modeling ion and neutral dynamics. Thus, they were not included in the simulation. This is similar to the one-component plasma (OCP) model [40], which is known to provide an accurate description of ions in the presence of weakly coupled (comparatively hot) electrons, such as in ultracold neutral plasmas [41]. Short (neutral–neutral), medium (ion–neutral) and long (ion–ion) range interactions were modeled using the potentials defined in equations (2)–(4).

Since the charge induced dipole potential is attractive, particles can interact at short spatial scales. In order to avoid the rare occurrence of close interactions that require a very short timestep to resolve, a repulsive core term was added to the charge-induced dipole potential from expression (3)

$$\phi_{\text{ind}}(r) = -\frac{q^{2}}{8\pi\varepsilon_{0}} \frac{\alpha_{R} a_{\text{R}}^{3}}{r^{3}} \left( \frac{r_{\text{R}}^{3}}{r^{3}} \right),$$  \hspace{1cm} (5)
The number of particles was varied such that the minimum number of particles was 2500 and the number of particles in the range was varied. The NVE simulation was run until the equilibrium was reached. The NVT ensemble was applied for the stage of the simulation was run with a Nosé-Hoover thermostat. Pressure was simulated until equilibrium was reached. This shows that the ion and neutral temperature at the end of the simulation was independent of $r_\phi$. The effect of the repulsive core also depends on the simulation setup. For simulations conducted at thermodynamic equilibrium, we found that the value of $r_\phi$ sets the number of ions that attach to neutrals; as shown in the appendix. However, this work concentrates on non-equilibrium simulations where $r_\phi$ is only a numerical convergence parameter needed to avoid closely orbiting particles. The reason why $r_\phi$ is important in the non-equilibrium simulations is that ion-neutral three-body recombination is slow compared to the DIH and ion-neutral relaxation timescales that we focus on. For the non-equilibrium simulations we chose $r_\phi = 0.133a_{in}$ (here $a_{in}$ was estimated as $a_{in} = \frac{x_i}{N}$ for $x_i < 0.5$ and $a_{in} = \frac{x_i}{N}$ for $x_i > 0.5$). This is the smallest value at which we can avoid closely orbiting particles and non-physical force values; see appendix and figure 3. A convergence test was conducted varying $r_\phi$ from 0.133$a_{in}$ to 0.5$a_{in}$ at an ionization fraction of $x_i = 0.5$ (figure 3) showing that the ion and neutral temperature at the end of the simulation (after ion-neutral relaxation) is independent of $r_\phi$ when $r_\phi < 0.25a_{in}$.

In order to study the evolution of a non-equilibrium discharge, a neutral Ar gas at room temperature and atmospheric pressure was simulated until equilibrium was reached. This stage of the simulation was run with a Nosé-Hoover thermostat (NVT ensemble) applied [44]. Then, a fraction of the particles were instantly ionized and a NVE (microcanonical) simulation was run including the ion-neutral, neutral-neutral and ion–ion interactions. This simulation setup was repeated for different ionization fractions. The timestep used was $5 \times 10^{-4}\omega_{pi}$ and the NVE simulation was run until the equilibrium was reached. The number of particles was varied such that the minimum number of ions in the system was 2500 and the number of neutral atoms was scaled in order to achieve the desired ionization fraction in each simulation. The simulation domain size was scaled with the total number of particles in order to maintain the desired gas density. The simulation domain was a three-dimensional box with periodic boundary conditions. The ionization fraction, total number of particles, time step and length of simulation used for each simulation are specified in table 1.

| Ionization fraction ($x_i$) | Number of particles | Plasma frequency ($\omega_{pi}) \times 10^{12}$ (rad s$^{-1}$) | Length of simulation ($t_f \times \omega_{pi}$) |
|---------------------------|---------------------|-------------------------------------------------|----------------------------------|
| 0.01                      | 250000              | 0.1046                                          | 150                              |
| 0.1                       | 25000               | 0.3308                                          | 500                              |
| 0.3                       | 10000               | 0.5731                                          | 650                              |
| 0.5                       | 10000               | 0.7398                                          | 800                              |
| 0.7                       | 10000               | 0.8754                                          | 1000                             |

4. MD results

As shown in figure 4, the evolution of the ion temperature can be divided into three stages. First, a rapid increase in the ion temperature was observed over the first ion plasma period of the simulation. This is thought to be due to disorder induced heating. This stage generates fluctuations in the ion temperature that persist for several plasma periods; as shown in figures 4 and 8. Secondly, ion-neutral temperature relaxation was observed with a timescale characterized by the ion-neutral collision frequency. Finally, a gradual heating of both ions and neutrals is observed over a much longer timescale due to three-body recombination of ions and neutrals (this is difficult to view in figure 4, but is demonstrated more clearly below).

4.1. Disorder induced heating

Before the ionization pulse is applied, the initial distribution of positions of neutral atoms corresponds to the equilibrium state of a gas interacting via the short-range Lennard–Jones potential. Therefore, ionization creates many ions separated by distances that are much smaller than the average distance between ions $a_{ni} = (3/4\pi n_i)^{1/3}$ where $n_i$ is the ion density. Since the interaction between ions is governed by the Coulomb potential, which is a long range potential, this leads to a large repulsion force between ion pairs that brings ions apart, as illustrated in figure 5.

The separation of ions corresponds to the formation of a correlated state. This can be quantified by the radial distribution function $g(r)$, which is defined by setting $n_o g(r) 4\pi r^2 dr = N(r)$, where $N(r)$ is the total number of particles in a spherical shell of radius $r$ and thickness $dr$ centered on a chosen particle. Here, $n_o = N/V$ is the average number of particles ($N$) in a volume ($V$); i.e. it is the uniform background number density. When $g(r) = 1$ for all distances $r$, where $r_\phi$ is the radius at which the repulsive core acts. It was desired to choose $r_\phi$ to be small enough to minimize the occurrence of non-physical force values, but large enough to decrease the computational cost due to the smaller timestep requirement. This is similar to what has been done in MD simulations of ultracold neutral plasmas [42, 43]. The ion and neutral final temperatures for different ion-neutral, neutral-neutral and ion–ion interaction are shown in figure 3.
the system is in an uncorrelated state. Figure 6 shows that just after ionization the ion positions correspond to the weakly correlated state of the neutral gas they were formed from. Correlations quickly develop as ions spread apart over the timescale of an ion plasma period. This is indicated by the void of particles that forms from distances \( r = 0 \) to approximately \( r = a_i \). Such a void, which is sometimes referred to a Coulomb hole in plasmas, is a characteristic property of a strongly coupled system. Another characteristic is a peak near the average nearest neighbor distance \( a_i \), which is also observed at times later than one ion plasma period.

A simple estimate for the magnitude and timescale of DIH can be obtained by considering the motion of a typical ion. In the limit that the initial configuration is random in space, and the final distribution is perfectly ordered (a lattice), ions will move an average distance of approximately \( a_i/2 \). The electrostatic potential change in moving from a position \( r_1 = a_i/2 \) to \( r_2 = a_i \) is \( \Delta \phi = \phi_2 - \phi_1 = -eZ/(4\pi\epsilon_0a_i) \). This will decrease the total potential energy of the ions by a factor of \( \Delta U \approx -Z^2e^2/(4\pi\epsilon_0a_i) \). Since energy is conserved during the NVE simulation, this leads to a corresponding increase in the ion kinetic energy \( \Delta K = -\Delta U \approx Z^2e^2/(4\pi\epsilon_0a_i) \). For ionization fractions above approximately \( 10^{-4} \), the initial value of \( \Gamma_i \) based on room temperature (when the ionization pulse is applied) is considerably larger than 1, so the change in the ion kinetic energy due to DIH is much greater than the kinetic energy before the pulse. Estimating the temperature after DIH as \( k_B T \approx \Delta K \), the Coulomb coupling parameter from equation (1) is \( \Gamma_i \approx 1.5 \). In all cases simulated, DIH is observed to increase the ion temperature until a critical value of approximately \( \Gamma_i = 1.9 \) is reached; see figure 7. This is quite close to the estimate of 1.5. The value of the temperature directly after DIH is the maximum value observed, \( T_i^{\text{max}} \), as ions subsequently cool due to collisional relaxation with neutrals.

The timescale for DIH can be estimated from the time it takes an ion to move from a position \( r_1 = a_i/2 \) to \( r_2 = a_i \) due to the Coulomb repulsion of a nearby ion. Considering Newton’s equation of motion, \( m\ddot{x}/dt^2 = eE \) and approximating \( d^2x/dt^2 \approx \Delta x/\Delta t \approx (a_i/2)/\Delta t^2 \), and \( eE \sim e^2/(4\pi\epsilon_0a_i^2) \), the characteristic timescale for this process is the ion plasma period \( \Delta t \approx \omega^{-1}_p \). This also agrees well with the simulations, where the maximum ion temperature is reached approximately \( 1.5\omega^{-1}_p \) after the ionization pulse; see figure 7.

Disorder induced heating has been previously observed in ultracold neutral plasmas formed by photionizing laser-cooled atoms [19]. Immediately after ionization ions have a very small kinetic energy since the neutral gas they are formed from was at millikelvin temperature. However, they have significant excess potential energy since the ionization has changed the potential energy landscape to that associated with long-range interactions. As the excess potential energy is converted into kinetic energy the ions heat to a state where \( \Gamma_i \approx 1 \) over a timescale of \( 1/\omega_{p}^{-1} \), just as described above. The process observed here is essentially the same. One important difference is that the ionization pulse in an atmospheric pressure environment is applied) is considerably larger than 1, so the change in ion kinetic energy before the pulse. Estimating the temperature...
plasma typically only partially ionizes the gas, whereas near total ionization is common in an ultracold neutral plasma.

An implication is that DIH is only expected to be important if the ionization fraction is high enough. Heating occurs only when the initial ion state (just after ionization) satisfies $\Gamma_{ii} > 1$. Otherwise, the kinetic energy gained by DIH is small compared to the initial kinetic energy. Furthermore, the basic mechanism is not expected to apply since the ions remain in a weakly coupled disordered state even after ionization. Assuming ions are born from neutral gas at room temperature, $\Gamma_{ii} > 1$ requires that $x_i \gtrsim 10^{-4}$. Thus, at room temperature atmospheric pressure gas conditions, DIH is expected to occur only if the ionization fraction is larger than one part in ten thousand $x_i \gtrsim 10^{-5}$.

After DIH, ions overshoot their equilibrium positions leading to oscillations of the Coulomb potential energy near the ion plasma frequency. Since the total energy is conserved during the NVE simulation and the ions are strongly coupled after the DIH, those oscillations translate to observable kinetic energy fluctuations. This is shown in figure 8 from the simulation with an ionization fraction of 0.01. Such fluctuations are only noticeable in the strongly coupled regime, where the ion kinetic energy is comparable to the Coulomb potential energy ($\Gamma \approx 1$). These fluctuations were observed to damp over a period of time between $2\nu_{pi}^{-1}$ and $50\omega_p^{-1}$ depending on the ionization fraction; see figure 4. The presence of large fluctuations in the ion temperature after DIH has also been observed in ultracold neutral plasmas experiments [19] and MD simulations [42].

4.2. Ion-neutral temperature relaxation

After DIH, ion and neutral temperatures equilibrate due to ion-neutral collisions. This causes the ions to cool and the neutrals to heat by an amount and at a rate that depends on the ionization fraction.

Ion cooling increases the ion–ion coupling strength, as shown in figure 7. This leads to an ion–ion coupling strength that is larger than one, $\Gamma_{ii} > 1$, after the ion and neutral temperatures relax for all ionization fractions simulated. It is also noteworthy that fast neutral heating can be significant, especially when the ionization fraction is high. Neutral heating is a common observation in atmospheric pressure plasma experiments [10, 12–14].

Ion-neutral temperature relaxation was modeled using standard methods based on the Boltzmann equation [45]. The cross section for ion-neutral interactions was computed based on two-body collisions interacting through the charge-induced dipole potential from equation (5). The Boltzmann-based approach is expected to be valid since the ion-neutral interaction is in a weakly coupled regime; see figure 2. The resulting temperature relaxation rate is described by

$$\frac{dT_i}{dt} = -\frac{3}{2} \nu_{in}(T_i - T_n), \quad (6)$$

$$\frac{dT_n}{dt} = \frac{3}{2} \nu_{in}(T_i - T_n), \quad (7)$$

and

$$\nu_{st} = \frac{4n_t \nu_{st}'}{3} \int_0^\infty dg \frac{Q_{st}^{(1)}(g) g^5 e^{-g^2}}. \quad (8)$$

Here, $T_i$ and $T_n$ are ion and neutral temperatures respectively, $\nu_{st}$ is the energy transfer collision frequency between the species $s$ and $s'$, $g = u/\nu_{st}$, where $u$ is the relative velocity and
\[ v_{st}^2 = 2k_B T_s/m_s + 2k_B T_i/m_i, \]

where \( m_s \) and \( m_i \) are both the Ar mass, and \( Q_{st}^{(1)} \) is the momentum transfer cross section

\[
Q_{st}^{(1)} = 2\pi \int_0^{\infty} [1 - \cos(\chi)] bdb, \tag{9}
\]

where

\[
\chi = \pi - 2b \int_{r_0}^{\infty} \frac{dr/r^2}{\sqrt{1 - \frac{b^2 - \frac{2m_s m_i}{m_i + m_s}}{m_i + m_s}}}; \tag{10}
\]

is the scattering angle. Here, \( b \) is the impact parameter, \( r_0 \) is the distance of closest approach obtained from the largest root of the denominator in equation (10), \( r \) is the radial distance, \( m_{st} \) is the reduced mass, \( u \) is the relative velocity and \( \phi_{in} \) is the charge induced dipole potential from equation (5) with \( r_0 = 0.133a_{in} \) computed from equation (9). The ion-neutral momentum transfer cross section obtained is shown in figure 9.

The evolution of the ion temperature obtained using equations (6)–(8) is shown in figure 10 for the discharge at an ionization fraction of 0.01. Here, the initial temperature used in the model was taken from the value of the MD simulations after DIH. The predictions show good agreement with the MD simulations in both the equilibrium temperature as well as the relaxation time. At other ionization fractions, the equilibrium temperature increases with ionization fraction due to smaller neutral atom densities and due to the larger ion temperature achieved due to the DIH. The equilibrium temperature was higher than room temperature and the corresponding coupling parameter was smaller compared to the initial value of \( \Gamma_{ii} \) with the exception of the smallest ionization fraction of 0.01, where the large neutral density led to an equilibrium temperature similar to room temperature; see figure 4.

4.3. Three-body recombination

As described in section 3, \( r_0 \) was used as a numerical convergence parameter in the non-equilibrium simulations and the temperature evolution over the timescale of DIH and ion-neutral equilibration was independent of \( r_0 \). However, as shown in the appendix, for \( r_0/a_{in} < 0.133 \) neutral particles start to orbit ions, which forms bound states that can cause heating over a much longer timescale than the DIH or ion-neutral relaxation. In order to compare these time scales, we repeated the non-equilibrium simulation on a longer time scale with different values of \( r_0/a_{in} \). Simulations at an ionization fraction of \( x_i = 0.01 \) and \( r_0/a_{in} \) values of 0.100 and 0.090 were carried out with a total simulation time of \( t \times \omega_{pi} = 4000 \) and compared with a simulation at the same ionization fraction but using \( r_0/a_{in} = 0.133 \). As shown in figure 11, the simulations show a similar ion temperature evolution immediately after the ionization pulse, including DIH followed by ion-neutral temperature relaxation through collisions. However, at \( t \times \omega_{pi} \approx 50 \), bound states start to form when \( r_0/a_{in} < 0.133 \), which increases the ion temperature when compared to the same simulation with \( r_0/a_{in} = 0.133 \). This is due to particles becoming trapped in the potential well of the charge-induced dipole potential, which exchanges a reduction in the potential energy with an increase in the kinetic energy. The increase of the fraction of ion-neutral bound states over time is shown in figure 12 for both \( r_0/a_{in} \) values. The recombination fraction was determined from a histogram of nearest neighbor positions, as described in appendix. The additional heating due to the ion-neutral three-body recombination causes the temperature to increase by approximately 75 and 125 K, reaching a value near 375 and 425 K at \( t \times \omega_{pi} = 4000 \) for \( r_0/a_{in} \) values of 0.100 and 0.090 respectively. This corresponds to a time at which 97% of ions have at least one neutral atom orbiting them. It was observed that the timescale of the ion-neutral three-body recombination is much longer than...
4.4. Radial distribution function

The radial distribution gives information of how the density varies with the distance from a reference particle and it can be used to look for signatures of strong correlations. It also determines the non-ideal components of thermodynamic parameters [46]. Figure 6 shows that the radial distribution for the interactions between ions corresponds to that of the OCP at the same equilibrium coupling parameter. Here, the ionization fraction was 0.01. This result shows that the ion–ion interactions are in a strongly coupled regime and the radial distribution function shows signatures of these strong correlations. Since the radial distribution function corresponds to an OCP at the same $\Gamma_{ii}$ the ion–ion interactions are not screened by the presence of neutral atoms. This behavior was observed for all the ionization fractions simulated. The ion–ion radial distribution function also exhibits a Coulomb hole and correlation peak, which are common features of strongly coupled plasmas [47].

5. Model for maximum and equilibrium ion temperature

The maximum and equilibrium ion temperatures can be estimated using simple energy conservation arguments. Since the increase in the ion temperature is due to DIH, where the ions travel a distance $\sim a_{ii}$ over a plasma period $\omega_{pi}^{-1}$, the maximum ion temperature corresponds to that which makes the ion–ion coupling parameter approximately unity. Utilizing the simulation result that $\Gamma_{ii} \approx 1.91$ at the peak temperature and equation (1), the maximum ion temperature is estimated to be

$$T_{i,\text{max}} = \frac{1}{1.91} \frac{Z^2 e^2}{4\pi\epsilon_0 k_B a_{ii}}$$

where $a_{ii} = (3/4\pi x_i n)^{1/3}$ is the average interparticle spacing between ions. The maximum ion temperature estimated with the equation (11) shows good agreement with the results obtained from the MD simulations, as shown in figure 13.

If we assume that the total kinetic energy is conserved after DIH until thermodynamic equilibrium is reached, it is possible to write a simple energy equation to obtain the equilibrium temperature $T_{eq}$, i.e. the temperature after ion-neutral thermal equilibration,

$$T_{eq} = x_i T_{i,\text{max}} + (1-x_i) T_n(t=0)$$

where $T_n$ is the neutral atom temperature at the beginning of the simulation, $x_i$ is the ionization fraction and $T_{i,\text{max}}$ is the maximum ion temperature obtained with equation (11). As shown in figure 13, the values of $T_{eq}$ and $T_{i,\text{max}}$ obtained using the model show good agreement with the results from the MD simulations over a broad range of ionization fractions. Furthermore, the expected coupling parameter with and without accounting for the DIH can be calculated by using the correct equilibrium temperature and the room temperature respectively, as shown in figure 14. The values predicted for $\Gamma_{ii}^{\text{eq}}$ show good agreement with the results from the MD simulations. It is noticeable how the coupling parameter at equilibrium is smaller than what would be predicted using room temperature, since the DIH increases the equilibrium temperature of the system at large ionization fractions. However, at small ionization fractions the values for $\Gamma_{ii}(T_0, x_i)$ and $\Gamma_{ii}^{\text{eq}}(T_{eq}, x_i)$ match due to the large neutral density compared to the ion density.
Figure 13. Variation of the maximum ion temperature and equilibrium temperature with the ionization fraction from the MD simulations and the model.

Figure 14. The Coulomb coupling parameter at equilibrium is smaller than the coupling parameter at room temperature without accounting for DIH. At small ionization fractions \( \Gamma_{ii}^{eq}(T_{eq}, x_i) \) converges to \( \Gamma_{ii}(T_0, x_i) \) where \( T_0 \) is the room temperature.

6. Comparison with experiments

Previous measurements have observed considerable neutral gas heating in ns pulsed spark discharges at atmospheric pressure. For example van der Horst et al measured a neutral gas temperature of 750 K at time 1 \( \mu \)s after ignition in a \( \text{N}_2/\text{H}_2\text{O} \) mixture [23]. They also showed that the pressure due to elastic collisions between electrons and \( \text{N}_2 \). For the conditions of this experiment, the energy transfer time due to elastic collisions is approximately 0.5 \( \mu \)s, which is near the time at which the temperature was measured. Measurements at a shorter timescale might reveal the degree to which DIH may contribute to the observed heating.

DHI is predicted to occur over the first 13 ps after ignition for the pressure and ionization fraction measured in [23]. The subsequent ion-neutral temperature relaxation occurs over 2.6 ns after the ignition. The noticeable separation of timescales shows that a better time resolution for experiments could help to identify the responsible heating mechanisms.

Lo et al showed that in pulsed discharges in air at atmospheric pressure [17] the neutral gas temperature at the end of the streamer phase in the center of the discharge was approximately 1200 K and the electron density at the same time and location was \( 9.2 \times 10^{19} \) cm\(^{-3} \). Assuming quasi neutrality and using our model for an initial temperature of 300 K and the corresponding total ion density, the gas temperature after the DHI and ion-neutral temperature relaxation (which occurs in a timescale smaller than the duration of the streamer phase) is predicted to be 1250 K. This agrees well with the experimental measurement.

Finally, we note that not all measurements of neutral gas heating appear to be explained solely by DHI and additional heating mechanisms might contribute significantly to the heating observed in some cases. Minesi et al [18] studied a fully ionized atmospheric pressure plasma in a thermal spark with an electron density of \( \sim 4 \times 10^{19} \) cm\(^{-3} \). These measured a neutral gas temperature of 48 000 K from the relative emission intensity of \( \text{N}^+ \) excited states, after 10 ns. Using our model for an initial temperature of 300 K and the measured density the predicted neutral gas temperature is only 5000 K, which does not agree with the observed increase in the temperature. This suggests that the DHI is not a dominant effect and other mechanisms are responsible for the very large neutral gas heating in this experiment. It is also possible that the experimentally derived temperature from the relative emission intensity, which assumes a Saha-Boltzmann distribution in equilibrium with the electrons, significantly overestimates the actual electron temperature as the excited states are often not in equilibrium with the electron temperature in gas discharges [48].

Table 2 summarizes these comparisons between the model and experiments. The results presented here suggest that the DHI and subsequent ion-neutral relaxation should be considered as a possible mechanism for the observed neutral measurement. The original reference suggested that the gas heating may be due to elastic collisions between electrons and \( \text{N}_2 \). For the conditions of this experiment, the energy transfer time due to elastic collisions is approximately 0.5 \( \mu \)s, which is near the time at which the temperature was measured. Measurements at a shorter timescale might reveal the degree to which DIH may contribute to the observed heating.

\[
\begin{array}{|c|c|c|c|}
\hline
\text{Total ion density} & \text{Measured gas} & \text{Predicted gas} & \text{Reference} \\
\text{(m}^{-3}\text{)} & \text{temperature (K)} & \text{temperature (K)} & \\
\hline
4 \times 10^{24} & 750 & 765 & [23] \\
9.2 \times 10^{24} & 1200 & 1250 & [17] \\
4 \times 10^{25} & 48 000 & 5000 & [18] \\
\hline
\end{array}
\]
heating in multiple experiments where high ionization fractions are achieved.

7. Conclusions

This work demonstrates that ions are strongly coupled in atmospheric pressure plasmas and that strong correlations influence ion and neutral temperature evolution. First-principles MD simulations reveal that the ion and neutral temperatures in CAPPs are influenced by an associated disorder induced heating process. DIH is not important in weakly coupled plasmas, but can be a dominant effect for strongly coupled plasmas. It causes ions to rapidly heat to temperatures that can reach several times the background neutral gas temperature. After DIH, ions thermally equilibrate with neutrals causing them to cool and the neutrals to heat by an amount and at a rate that depends on the ionization fraction. The cooling causes ions to return to a more strongly coupled state. Due to DIH and ion-neutral temperature relaxation, the final neutral gas temperature depends on the ionization degree achieved at plasma formation. We show that at atmospheric pressure, DIH is significant for ionization fractions larger than $x_i \gtrsim 10^{-4}$ and thus, it could be important for experiments that involve spark discharges, laser-produced plasmas, or other sources that achieve high ionization fractions. In parallel with these comparatively fast processes, a weaker heating of both ions and neutrals was observed over a much longer timescale due to ion-neutral three-body recombination. A model is presented to describe the main features of the ion and neutral temperature evolution, showing a good agreement with the neutral gas temperature measured in experiments at atmospheric pressure [17, 23]. Therefore, we show that DIH is an additional heating mechanism that can occur in CAPP applications and must be accounted for.

One implication of this work is that modeling techniques for CAPPs may need to be reassessed. Current methods are largely based on solutions of a Boltzmann equation, such as PIC, or moments of the Boltzmann equation, such as multi-fluid models. These implicitly assume that the plasma is weakly coupled, since the Boltzmann equation only treats weakly coupled gases and plasmas. This may be limiting in the context of CAPPs, because fundamentally different physical behaviors arise in strongly coupled fluids. For instance, DIH could not be obtained by solving the Boltzmann equation, as in PIC simulations. Using such models may lead to a significant underestimation of the ion and neutral temperatures. This motivates the need for further development of theory and computational models that can account for strong coupling effects in CAPPs.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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Appendix. Equilibrium MD simulations

An analysis was realized varying the radius $r_\phi$ of the charge induced dipole potential. For this analysis the simulation setup consisted of an NVT (canonical) simulation using the Nosé–Hoover thermostat, where the temperature was set to 293 K, over 1500 plasma periods. This was followed by an NVE (microcanonical) simulation for 1500 plasma periods. The timestep used varied with $r_\phi$ since smaller $r_\phi$ led to larger attractive forces and smaller timesteps were required. The timesteps used varied from $5 \times 10^{-4} \omega_p^{-1}$ to $1 \times 10^{-4} \omega_p^{-1}$ where $\omega_p^{-1}$ is the ion plasma period. The total number of particles was 10000 for all the simulations. Since the numerical charge induced dipole potential has both a repulsive and an attractive part, it presented a potential well, as shown in the figure 15. Different radius and, therefore, minimum values of the charge induced dipole potential were explored. Once the equilibrium was reached in the NVE simulation, the distribution of minimum distances between ion-neutral and neutral–neutral pairs of particles was computed in order to study the presence of bound states. These bound states consisted of ion-neutral molecules with a spatial scale characterized by $r_\phi$ and $r_{1J} \approx 21/6 \sigma$ which corresponds to the minimum of the charge induced dipole and the Lennard Jones potentials respectively.

It was observed that for relatively small values of $r_\phi$ the formation of bound states was more prominent. As it is shown in the distributions of minimum distances between ion-neutral and neutral–neutral pairs of particles after 1500 plasma periods in figure 16, for $r_\phi \approx 0.046a_{in}$ and a ionization fraction of 0.5, large peaks were observed corresponding to the distances $r_\phi$ and $r_{1J}$.

As the radius of the charge induced dipole potential was increased, the population of ion-neutral and neutral–neutral bound states decreased until it was negligible for $r_\phi \approx 0.133a_{in}$ as shown in figure 17. The observed behavior suggests that in order to avoid the formation of bound states an $r_\phi \approx 0.133a$ must be used.
Figure 15. Numerical charge induced dipole potential for different values of $r_\phi$ compared to the charge induced dipole potential.

Figure 16. (a) Ion-neutral and (b) neutral-neutral minimum distance distribution for $r_\phi = 0.046a_n$ at an ionization fraction of 0.5.

Figure 17. Fraction of ion-neutral and neutral–neutral bound states for different $r_\phi$ values.
References

[1] Domonkos Maria, Tichá P, Trejbal J and Demo P 2021 Applications of cold atmospheric pressure plasma technology in medicine, agriculture and food industry Appl. Sci. 11 4809

[2] Cullen P J, Lalor J, Scally L, Boehm D, Milosavljević V, Bourke P and Keener K 2018 Translation of plasma technology from the lab to the food industry Plasma Process. Polym. 15 1700085

[3] Misra N N, Schlüter O and Cullen P J (eds) 2016 Cold Plasma in Food and Agriculture: Fundamentals and Applications (Amsterdam, Boston: Elsevier, Academic) OCLC: ocn934606423

[4] Adamovich I et al 2022 The 2022 plasma roadmap: low temperature plasma science and technology J. Phys. D: Appl. Phys. 55 373001

[5] Xiong Z and Kushner M J 2012 Atmospheric pressure ionization waves propagating through a flexible high aspect ratio capillary channel and impinging upon a target Plasma Sources Sci. Technol. 21 034001

[6] Robert E, Sarron V, Riës D, Dozias S, Vandamme M and Pouvesle J-M 2012 Characterization of pulsed atmospheric-pressure plasma streams (paps) generated by a plasma gun Plasma Sources Sci. Technol. 21 034017

[7] Darby T, Pouvesle J-M, Fontane J, Joly L, Dozias S and Robert E 2017 Plasma action on helium flow in cold atmospheric pressure plasma jet experiments Plasma Sources Sci. Technol. 26 105001

[8] Neys E C and Bogaerts A 2014 Understanding plasma catalysis through modelling and simulation—a review J. Phys. D: Appl. Phys. 47 224010

[9] Bogaerts A et al 2020 The 2020 plasma catalysis roadmap J. Phys. D: Appl. Phys. 53 443001

[10] Pai D Z, Lacoste D A and Laux C O 2010 Nanosecond repetitively pulsed discharges in air at atmospheric pressure—the spark regime Plasma Sources Sci. Technol. 19 065015

[11] Rusterholtz D L, Lacoste D A, Stancu G D, Pai D Z and Laux C O 2013 Ultrafast heating and oxygen dissociation in atmospheric pressure air by nanosecond repetitively pulsed discharges J. Phys. D: Appl. Phys. 46 464010

[12] Popov N A 2011 Fast gas heating in a nitrogen–oxygen discharge plasma: I. Kinetic mechanism J. Phys. D: Appl. Phys. 44 285020

[13] Popov N A 2016 Pulsed nanosecond discharge in air at high specific deposited energy: fast gas heating and active particle production Plasma Sources Sci. Technol. 25 044003

[14] Mintoussou E I, Pendleton S J, Gerbault F G, Popov N A and Starikovskaja S M 2011 Fast gas heating in nitrogen–oxygen discharge plasma: II. Energy exchange in the afterflow of a volume nanosecond discharge at moderate pressures J. Phys. D: Appl. Phys. 44 285202

[15] Yue Y, Kondeti V S S K, Sadeghi N and Bruggeman P J 2022 Plasma dynamics, instabilities and oh generation in a pulsed atmospheric pressure plasma with liquid cathode: a diagnostic study Plasma Sources Sci. Technol. 31 025008

[16] Cheng L, Barleon N, Cuenot B, Vermorel O and Bourdon A 2022 Plasma assisted combustion of methane-air mixtures: validation and reduction Combust. Flame 240 111990

[17] Lo A, Cessou A, Lacour C, Lecordier B, Boubert P, Xu D A, Laux C O and Vervisch P 2017 Streamer-to-spark transition initiated by a nanosecond overvoltage pulsed discharge in air Plasma Sources Sci. Technol. 26 045012

[18] Minesi N, Stepanyan S, Mariotto P, Stancu G D and Laux C O 2020 Fully ionized nanosecond discharges in air: the thermal spark Plasma Sources Sci. Technol. 29 085003

[19] Killian T C and Rolston S L 2010 Ultracold neutral plasmas Phys. Today 63 46–51

[20] Pohl T, Pattard T and Rost J M 2005 Relaxation to nonequilibrium in expanding ultracold neutral plasmas Phys. Rev. Lett. 94 205003

[21] Gericke D O and Murillo M S 2003 Disorder-induced heating of ultracold plasmas Contrib. Plasma Phys. 43 298–301

[22] Kuzmin S G and O’Neill T M 2002 Numerical simulation of ultracold plasmas Plasma Phys. 9 3743–51

[23] van der Horst R M, Verreycken T, van Veldhuizen E M and Bruggeman P J 2012 Time-resolved optical emission spectroscopy of nanosecond pulsed discharges in atmospheric-pressure N2 and N2/H2O mixtures J. Phys. D: Appl. Phys. 45 345021

[24] Adamovich I V 2001 Three-dimensional analytic model of vibrational energy transfer in molecule-molecule collisions AIAA J. 39 1916–25

[25] Guerra V, Caz A T del, Pintassilgo C D and Alves Lis L 2019 Modelling N2–O2 plasmas: volume and surface kinetics Plasma Sources Sci. Technol. 28 073001

[26] Ono R and Oda T 2008 Measurement of gas temperature and OH density in the afterflow of pulsed positive corona discharge J. Phys. D: Appl. Phys. 41 035204

[27] Dong L, Ran J and Mao Z 2005 Direct measurement of electron density in microdischarge at atmospheric pressure by stark broadening Appl. Phys. Lett. 86 161501

[28] Belei D, Mohr S, Luggenhölscher D and Czarnetzki U 2011 An atmospheric pressure self-pulsing micro thin-cathode discharge J. Phys. D: Appl. Phys. 44 125204

[29] Miclea M, Kunze K, Heitmann U, Florek S, Franzke J and Niemax K 2005 Diagnostics and application of the microhollow cathode discharge as an analytical plasma J. Phys. D: Appl. Phys. 38 1709

[30] Parkevich E V, Medvedev M A, Ivanenkov G V, Khirianova A I, Selyukov A S, Agafonov A V, Korneev P A, Guskov S Y and Mingaleev A R 2019 Fast fine-scale spark filamentation and its effect on the spark resistance Plasma Sources Sci. Technol. 28 095003

[31] Bataller A, Putterman S, Pree S and Koulatkis J 2016 Observation of shell structure, electronic screening and energetic limiting in sparks Phys. Rev. Lett. 117 085001

[32] Bataller A, Plateau G R, Kappus B and Putterman S 2014 Blackbody emission from laser breakdown in high-pressure gases Phys. Rev. Lett. 113 075001

[33] Bataller A, Latshaw A, Koulatkis J P and Putterman S 2019 Dynamics of strongly coupled two-component plasma via ultrafast spectroscopy Opt. Lett. 44 5832–5

[34] Verreycken T, van der Horst R M, Baede A H F M, Van Veldhuizen E M and Bruggeman P J 2012 Time and spatially resolved LIF of OH in a plasma filament in atmospheric pressure He–H2O J. Phys. D: Appl. Phys. 45 045205

[35] Heberlein J, Mentel J and Pfenzer E 2009 The anode region of electric arcs: a survey J. Phys. D: Appl. Phys. 43 023001

[36] Lieberman M A and Lichtenberg A J 2005 Atomic Collisions (New York: Wiley) ch 3, pp 43–85

[37] Scheiner B and Baalrud S D 2020 Mean force kinetic theory applied to self-diffusion in supercritical Lennard–Jones fluids J. Chem. Phys. 152 174102
[38] Daligault Jöme 2012 Diffusion in ionic mixtures across coupling regimes Phys. Rev. Lett. 108 225004
[39] Thompson A P et al 2022 LAMMPS—a flexible simulation tool for particle-based materials modeling at the atomic, meso and continuum scales Comp. Phys. Comm. 271 108171
[40] Baus M and Hansen J-P 1980 Statistical mechanics of simple Coulomb systems Phys. Rep. 59 1–94
[41] Killian T C, Pattard T, Pohl T and Rost J M 2007 Ultracold neutral plasmas Phys. Rep. 449 77–130
[42] Kuzmin S G and O’Neil T M 2002 Numerical simulation of ultracold plasmas: how rapid intrinsic heating limits the development of correlation Phys. Rev. Lett. 88 065003
[43] Tiwari S K, Shaffer N R and Baalrud S D 2017 Thermodynamic state variables in quasiequilibrium ultracold neutral plasma Phys. Rev. E 95 043204
[44] Frenkel D and Smit B 2002 Molecular dynamics in various ensembles Understanding Molecular Simulation 2nd edn, ed D Frenkel and B Smit (San Diego: Academic) ch 6, pp 139–63
[45] Ferziger J H, Kaper H G and Gross E P 1973 Mathematical theory of transport processes in gases Am. J. Phys. 41 601–3
[46] Hansen J-P and McDonald I R 2013 Statistical mechanics Theory of Simple Liquids 4th edn, ed J-P Hansen and I R McDonald (Oxford: Academic) ch 2, pp 13–59
[47] Ott T, Bonitz M, Stanton L G and Murillo M S 2014 Coupling strength in Coulomb and Yukawa one-component plasmas Phys. Plasmas 21 113704
[48] Fierro A, Barnat E, Moore C, Hopkins M and Clem P 2019 Kinetic simulation of a low-pressure helium discharge with comparison to experimental measurements Plasma Sources Sci. Technol. 28 055012