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Dissociation and the Development of Spatial Correlation in a Molecular Ultracold Plasma

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Penning ionization initiates the evolution of a dense molecular Rydberg gas to plasma. This process selects for pairs of excited molecules separated by a distance of two Rydberg orbital diameters or less. The deactivated Penning partners predissociate, depleting the leading edge of the distribution of nearest-neighbor distances. For certain density and orbital radii, this sequence of events can form a plasma in which large distances separate a disproportionate fraction of the ions. Experimental results and model calculations suggest that the reduced potential energy of this Penning lattice significantly affects the development of strong coupling in an ultracold plasma.

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When a gas of charged particles reaches limits of low temperature and/or high density, interactions governed by long-range interparticle potentials grow to exceed the average energy of thermal motion. Such coupling gives rise to a condition of many-body correlation that profoundly alters the collision physics and collective properties of a system, causing conventional gas-kinetic and fluid models to fail [1]. The experimental and theoretical investigation of strong coupling represents an important contemporary frontier in condensed matter and plasma physics.

One conventionally gauges the strength of ion or electron coupling in a plasma by the parameter, $\Gamma_\alpha = e^2/4\pi\varepsilon_0 a_{ws} k_B T_\alpha$, where e represents the electron charge, a_{ws} is the Wigner-Seitz radius, determined by the charge density ρ as $\sqrt[3]{3/4\pi\rho}$, and T_α denotes the corresponding singly charged ion or electron temperature.

Ultracold plasmas, in particular, offer a novel environment in which to study the properties of Coulomb systems in or near states of charged particle correlation. Formed under laboratory conditions in magneto-optical traps (MOT) [2] or supersonic molecular beams [3,4], they directly display the influence of long-range interactions on collective properties, such as density oscillations [5], ambipolar expansion [6] and recombination [7–9].

Spatially correlated ultracold plasmas can manifest liquidlike or even crystalline properties. But, interparticle forces arising from strong coupling cause disorder-induced or correlation heating, which acts intrinsically to limit the sustained development of strong coupling as a dense but randomly ordered neutral gas evolves to a plasma [10].

It has been recognized for some time that spatially precorrelating the excited gas can offer a means to overcome this limitation. For example, theorists have proposed to impose order on a gas before ionization by evolving to plasma from the spatially correlated initial state of a Fermi degenerate gas, or confining the initial atom distribution to an optical lattice [11,12].

Dipole blockade also forms strong correlations in the spatial positions of Rydberg atoms created by narrow-band laser excitation [13]. Recent models and experimental tests suggest that the ionization of a blockaded Rydberg gas could offer a means to reduce disorder-induced heating [14,15].

Here we describe a novel, highly robust method for the introduction of spatial correlations that occurs naturally in the evolution from a molecular Rydberg gas to an ultracold plasma. Recognizing the spatial selectivity of Penning ionization, we develop a model, supported by experimental results, that defines conditions for the formation of a latticelike spatial distribution of ions, which leads to a state of ion correlation that observably affects the free space expansion of the plasma.

Our experiment [3] creates a plasma by exciting nitric oxide entrained in a seeded supersonic expansion through a 0.5 mm nozzle from a stagnation pressure of 5 atm. A hydrodynamic model predicts that the 10% NO seeded in this expansion relaxes to a translational temperature on axis of $T_\parallel \approx 500$ mK. Geometric cooling reduces the transverse average velocity to a value at least ten times lower [3].

Pulsed dye laser double-resonant excitation via NO A $^2\Sigma^+ v = 0$, $N' = 0$ yields a Rydberg gas of NO molecules in a single rovibrational quantum state with a selected initial principal quantum number n_0 from 30 to 80 in the long-lived series of f Rydberg states that converges to the $N^+ = 2$ level of NO$^+$, $v = 0$, $nf(2)$. Saturating the first (ω_1) and second (ω_2) one-photon resonant transitions, forms an initial density of Rydberg molecules as high as 5×10^{12} cm^{-3}.

The Rydberg gas prepared in this way includes a fraction of excited molecules that have nearest-neighbor distances within a critical radius for prompt Penning ionization. The size of this fraction varies with the density of the Rydberg gas and the principal quantum number to which it has been promoted.

The Penning interaction between two excited NO molecules with principal quantum n_0 yields a molecular NO^+ ion and a free electron, together with a deactivated NO molecule that has the internal energy of a Rydberg state with principal quantum number $n' \leq n_0/\sqrt{2}$ [16].

Prompt electrons produced by Penning ionization escape the Rydberg gas volume until the excess of ions grows to no more than 1%, at which point the space charge traps the electrons that remain [17]. The collisions of trapped electrons with frozen Rydberg molecules initiates an electron-impact ionization avalanche [18].

The interaction volume moves downstream with the velocity of the molecular beam to encounter the detection plane created by a perpendicularly mounted, moveable grid, G_2. This grid, together with an upstream entrance aperture, G_1, define a field-free region. As this volume of gas transits G_2, it emits electrons, a fraction of which are collected by a weak field and conveyed to a multichannel plate detector.

The ionized volume sampled by the detection grid grows with increasing flight time at a rate faster than the thermal spread of our molecular beam. In a freely expanding plasma, the ambipolar pressure of the electron gas causes a radial acceleration of the ions [6]. The expansion we observe accords with this mechanism [19,20], and we find that the ions reach a terminal velocity that varies with the initial quantum number selected in the preparation of the Rydberg gas.

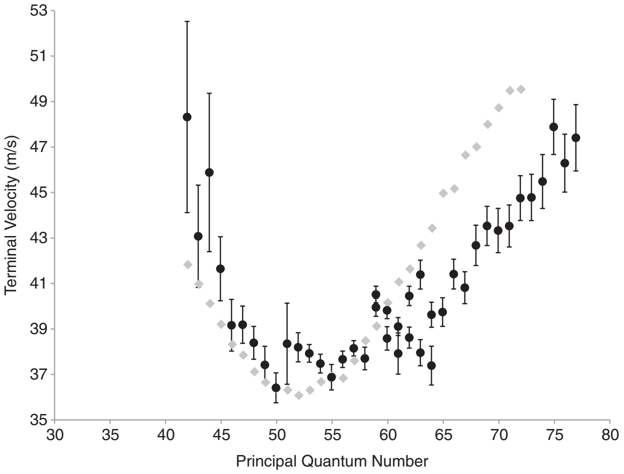

FIG. 1. Terminal radial velocities of ions measured in a long-time limit of ion expansion for ultracold plasmas created from molecular Rydberg gases of NO with initial principal quantum number, n_0. Error bars determined from the residuals of Gaussian fits to experimental waveforms produced by plasma volumes transiting G_2. Grey points represent radial expansion velocities predicted for $T_e = 9$ K by a hydrodynamical model accounting for spatial correlation calculated stochastically (see text).

Figure 1 plots terminal velocities of plasma expansion as a function of n_0. Plasmas initiated from Rydberg gases prepared by excitation to principal quantum numbers in the range from $n_0 = 45$ to 60 show the slowest rates of expansion. It remains to be said what characteristic of the plasma varies with Rydberg gas n_0 to alter its expansion velocity to such a degree.

Two properties do vary strongly with n_0 over this range: Rydberg binding energy and orbital radius. But electron-impact avalanche and evolution to plasma quasiequilibrium act quickly to redistribute population and erase memory of the initial state of the Rydberg gas.

For this reason, a selected value of n_0 can affect long-time plasma properties only by altering initiation dynamics. To explore the possibility of any such effect, we consider the initial steps of plasma formation in a molecular Rydberg gas of particular n_0 and density.

The second step of pulsed dye laser excitation from the NO A state to the $n_0 f(2)$ Rydberg state creates a Rydberg gas in which kth nearest-neighbor distances between excited molecules, r, conform with the Erlang distribution [13],

$$P_k(r) = \frac{4\pi r^2 \rho}{(1-k)!} \left(\frac{4}{3}\pi r^3 \rho\right)^{k-1} e^{-(4/3)\pi r^3 \rho}, \qquad (1)$$

where ρ represents the number density of the Rydberg gas.

Strong dipole-dipole interactions cause Rydberg molecule pairs with nearest-neighbor distances that fall within a critical radius, r_c, to undergo Penning ionization,

$$\mathrm{NO}(n_0) + \mathrm{NO}(n_0) \longrightarrow \mathrm{NO}(n' < n_0) + \mathrm{NO}^+ + e^-. \qquad (2)$$

Molecular dynamics simulations estimate that semiclassical ionization occurs with a 90% probability after 800 Rydberg periods for $r_c = 1.8 \times 2n_0^2 a_0$. This time increases with distance beyond r_c as $r^{5/2}$ [16].

Electrons released by Penning ionization initiate an electron impact avalanche. Conditions in the Rydberg gas yield a plasma with a spatial distribution of quasistationary ions that falls between two limiting cases. An avalanche that ionizes all Rydberg molecules remaining in level n_0, as well as all Penning partners distributed over deactivated levels n', produces a plasma with a completely random distribution of ion-ion distances.

In the opposite limit, where none of the neutral Penning partners ionize, the plasma distribution of ion-ion distances contains few members spaced closer than r_c. When the conditions of n_0 and density cause the semi-classical orbital radius, $n_0^2 a_0$ to approach half the Wigner-Seitz radius, a_{ws}, such a loss of Penning partners significantly depletes the leading half of the ion-ion nearest-neighbor distance distribution function. This produces a highly correlated spatial distribution, which we term a Penning lattice.

The degree to which the system achieves such a state of spatial correlation has important consequences for ultracold plasma physics in this density range. Neglecting the effects of electron screening, the ion density (10^2 cm^{-3}) and initial temperature (< 500 mK), afforded by plasma formation in our molecular beam, yields a Γ_i greater than 50, substantially in the regime of liquidlike behavior.

However, the Coulomb repulsion in a plasma of randomly distributed ions with $\Gamma_i > 1$ represents a significant store of potential energy. In a random plasma, disorder induced heating to the correlation temperature inevitably limits Γ_i to a value of 2 or less [21,22].

Spatial correlation of the ions dramatically reduces ion-ion electrostatic correlation heating. To illustrate this, we present a simple model for spatial distributions in the plasma produced by Penning ionization and electron-impact avalanche in a molecular Rydberg gas as a function of n_0 and density. In this model, Penning ionization occurs instantaneously, and avalanche follows on a ns to sub-ns time scale.

Over time intervals as short as this, supersonically cooled ions and Rydberg molecules move a negligible fraction of the Wigner-Seitz radius. Thus, we can reasonably model the spatial consequences of Penning ionization and unimolecular dissociation by assuming a frozen Rydberg gas composed of excited molecules positioned randomly in a box with sides that are much longer than the Wigner-Seitz radius for our density. A typical simulation starts with $N = 10^6$ Rydberg molecules.

We consider the coordinates of each molecule, measuring the distance from each of its neighbors to identify pairs with nearest-neighbor spacings that fall within r_c for Penning ionization. At higher values of n_0, Rydberg molecules increasingly find multiple partners within $r < r_c$. In such cases, we choose interacting pairs at random.

For each selected pair, one molecule instantaneously ionizes, and the other relaxes to join a distribution of deactivated Penning partners in states with lower principal quantum numbers, n'. The probability of a given n' falls from a maximum at the highest accessible level, $n_0/\sqrt{2}$, as n'^5 [16]. The calculation assigns a value of n' to each primary Penning partner by sampling from this distribution.

At higher values of n_0, deactivated molecules can undergo secondary Penning interactions with n_0 molecules within the original r_c sphere. The model assumes that these also occur instantaneously whenever this secondary pair falls within the smaller critical radius figured for the combination of n_0 and a principal quantum number sampled from the distribution of n'. This process ionizes the n_0 molecule and further deactivates the n' energy donor.

The distribution of Rydberg molecules and free electrons formed by this Penning cascade undergoes an avalanche of electron-impact excitation and ionization—in competition with dissociation. The time scales for these competing processes depend on n_0, the electron density and the final distribution over n'.

Coupled rate equation simulations show that the conversion of molecular Rydberg states to ions builds in time [23,24]. The time period over which avalanche ionization occurs for a Rydberg gas density of 10^{12} cm^{-3} shortens with increasing n_0, from 50 ns for a Rydberg gas initial $n_0 = 30$, to 100 ps for $n_0 = 80$. The deactivation of Penning partners to states of lower principal quantum number retards the climb to ionization, and increases the fraction driven down by electron collisions. Results derived from our coupled rate equation calculations accord with electron avalanche onset rates extrapolated from measurements made in a rubidium atom MOT at a series of lower densities by Robert-de-Saint-Vincent, *et al.* [14]

Rydberg states of NO predissociate with a rate that falls with increasing n. A widely used model developed by Bixon and Jortner [25–27] explains this variation, and accounts well for long-time plasma decay rates that we have observed experimentally in our system [20,24]. Taking predissociation rates as a function of n from this model, the calculation computes the fraction of excited molecules lost to neutral $\mathrm{N} + \mathrm{O}$ products, by integrating n-detailed decay rates over the avalanche ionization period appropriate to the selected value of n_0.

Generally speaking, for low-n_0 conditions, where r_c is much smaller than a_{ws}, Penning ionization occurs for a very small fraction of molecules in the Rydberg gas. For example, in a model Rydberg gas at $n_0 = 30$, fewer than 1% of the molecules undergo a Penning interaction. All of the deactivated Penning partners dissociate within the 50 ns period for avalanche ionization. This depletes the leading edge of the nearest-neighbor distribution slightly, but otherwise yields a plasma with a random distribution of ion-ion distances.

At very high principal quantum number, where r_c is greater than a_{ws}, all Rydberg molecules undergo a Penning interaction. The electron avalanche proceeds on a sub-ns time scale, converting nearly all Rydberg molecules to ions. Any dissociation specific to Penning partners affects molecules with interaction distances distributed over the entire range of r, and thus causes no change in the final ion-ion distribution

For intermediate values of n_0, a significant fraction of molecules Penning ionize and, on the avalanche time scale, a significant fraction of these dissociate. Figure 2 shows simulation results describing final distributions of ion-ion distances for initial Rydberg gas densities of 10^{12} cm^{-3} with initial principal quantum numbers from $n_0 = 30$ to 80.

For $n = 30$, we see that very little Penning ionization occurs, while dissociation of initial Rydberg molecules yields a plasma with only 3% of the starting density of the Rydberg gas. The resulting ion-ion distances thus conform with a low-density Erlang distribution. Dissociation similarly reduces the overall density of the plasma formed by a

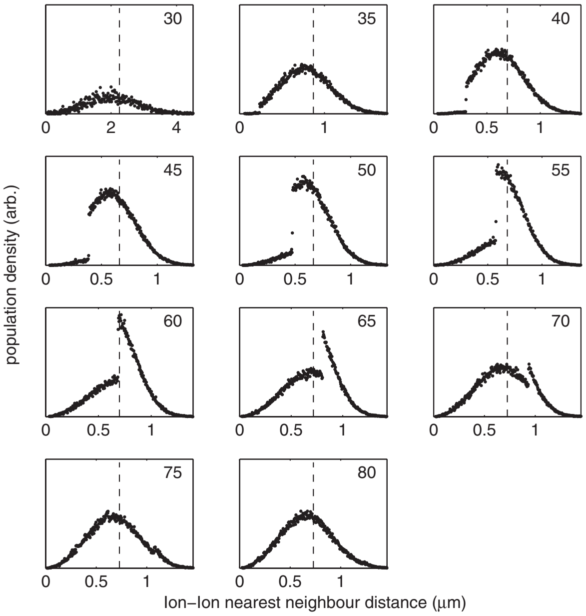

FIG. 2. Distributions of ion-ion nearest neighbors following Penning ionization and electron-impact avalanche in a predissociating molecular Rydberg gas of initial principal quantum number, n_0, from 30 to 80. Dashed lines mark corresponding values of a_{ws}. Calculated by counting ion distances after relaxation to plasma in 10^6-particle stochastic simulations. Integrated areas proportional to populations surviving neutral dissociation.

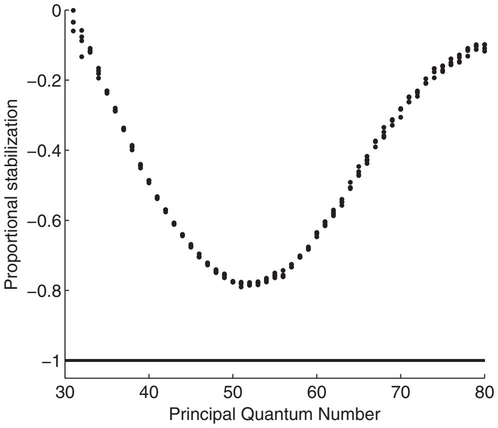

FIG. 3. Reduction of average ion-ion repulsion energy in Penning lattices formed by Rydberg gases of initial density, 10^{12} cm^{-3} and principal quantum number from 30 to 80, plotted as a fraction of the pairwise repulsion energy difference between a gas of random ions and a perfect lattice. Data points at each value of n_0 taken from the results of four simulations.

Rydberg gas with $n = 35$. For initial principal quantum numbers from $n = 40$ to 60, deactivated Penning partners dissociate disproportionately, and this produces a striking deficiency of smaller nearest-neighbor distances. Above $n_0 = 60$, the increased range of Penning ionization combines with slower dissociation and faster avalanche to produce a plasma with random ion-ion nearest-neighbor distances.

Following avalanche ionization, we gauge the effect of spatial correlation by calculating the average ion-ion pairwise electrostatic repulsion energy as, $\sum E(r)/2N$, where $E(r) = e^2/4\pi\epsilon_0 r$

In a perfect lattice of ions, all distances, r, equal a_{ws}, and this unscreened average repulsion energy is $E_{a_{ws}} = e^2/4\pi\epsilon_0 a_{ws}$. For a random ionized gas under the same conditions, we compute the average repulsion energy, as the integral of $E(r)$ over Eq. (1) for $k = 1$. The result, E_{random}, equals the pairwise repulsion energy of the perfect lattice multiplied by the gamma function, $\Gamma(2/3)$. Figure 3 compares these limits to the average ion-ion repulsion energy, calculated stochastically for the Penning lattice, and plotted as a fraction of the difference between the repulsion energy of a random ion gas and that of a perfect lattice.

Inspection of Fig. 3 shows that the distribution of ion-ion distances shown in Fig. 2 for $n_0 = 55$ reduces the average ion-ion repulsion energy by an amount equal to more than 80% of the potential energy removed in a rearrangement from the random gas to a perfect lattice. We take this quantity as a relative measure of the ion spatial correlation immediately after the electron avalanche.

This plasma evolves on the time scale of the ion plasma frequency to approach a local equilibrium in which the relaxation of ion-ion repulsive forces drives disorder-induced heating. Here, a state variable, U_{ii}, describes the correlation energy of a system of locally repelling ions in the mean field of the electron background. Charbrier and Potekhin (*CP*) have developed an analytic expression for the correlation energy of such an electron-screened ionic fluid that extends to Γ of 100 or more [28].

Pohl *et al.* (PPR) show that the thermal energy added by the relaxation of ions from an initially random spatial distribution gives rise to a local equilibrium in which little correlation energy remains [21]. A perfectly ordered ion gas has no such initial displacement from local equilibrium.

Between these limits, we estimate the effect of an intermediate degree of spatial order on correlation energy, by defining an effective initial $U_{ii}(0) = \alpha\, U_{ii}^{\mathrm{eq}}(0)$. The term, α describes the fractional extent to which short-range order reduces the average ion-ion pairwise repulsion energy to that of a perfect lattice. We assume that such a partial ordering at $t = 0$ permits the plasma to reach a quasiequilibrium state with a fraction, α, of the reference correlation energy, $U_{ii}^{\mathrm{eq}}(0)$, determined by the *CP* expression for the initial ion temperature and density of the plasma. We calculate α from the results of the simulation model by, $\alpha = (E_{\mathrm{random}} - E_{\mathrm{Penning}})/(E_{\mathrm{random}} - E_{a_{ws}})$.

To predict terminal expansion velocities as a function of n_0, we apply the hydrodynamical model developed by PPR [21], using an electron temperature of 9 K, determined experimentally from a measured rate of expansion in the uncorrelated regime of n_0. This yields a result shown by grey points plotted in Fig. 1.

The model presented here presumes a quasineutral plasma that undergoes a normal ambipolar expansion driven by the thermal pressure of an electron gas. We regard this plasma as unconventional only by virtue of the spatial correlation created in the distribution of ion-ion nearest-neighbor distances by Penning ionization in Rydberg gases of certain selected initial principal quantum numbers and density. At its maximum, this spatial correlation reduces the electrostatic potential energy of the ions to a value near that of ions in a perfect lattice. This stabilization dissipates with falling density, giving rise to the force we observe opposing expansion.

Thus, much like the evolution suggested for an ion distribution that has been spatially ordered by dipole blockade [14,15], spatial correlation produced by the short-range interaction of Rydberg states that forms a Penning lattice enables the ultracold plasma to sustain a low ion temperature and reveal the effects of Γ_i on the hydrodynamics of expansion.

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