Anomalous Atomic Hydrogen Shock Pattern in a Supersonic Plasma Jet

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A two-photon laser-induced fluorescence study on the transport of ground-state atomic hydrogen in a supersonic plasma jet, generated from an Ar-H_2 mixture, reveals an unexpected shock pattern. Whereas both the axial-velocity profile and the temperature profile of hydrogen atoms along the jet centerline can be interpreted in terms of a supersonic expansion of an Ar-H gas mixture, the H-atom density profiles do not satisfy the well established Rankine-Hugoniot relation leading to a nonconservation of the forward flux. The experimental results show that H atoms escape from the supersonic expansion by a diffusion process due to strong density gradients between the core of the jet and its vicinity.

Plasma expansion from a high pressure source region into a low pressure region is a general physical phenomenon [1–3] that covers a broad range of physical systems such as solar flares, remote plasma systems, and vacuum arc spots. Apart from the large differences in scale, those phenomena exhibit numerous similarities. For instance, they are all governed by the same set of equations, and after being accelerated the plasma flow undergoes a transition from a supersonic to a subsonic regime resulting in the formation of a shock wave structure.

From a practical viewpoint it is advantageous to study the physics of expanding plasmas on the intermediate scale as then the system is well suited for diagnostics. In this Letter, we report on the study of the dynamics of a supersonic plasma jet generated by a cascaded arc [4] from a mixture of Ar and H_2, where Ar is used as a carrier gas. We aim at an understanding of the transport of ground-state atomic hydrogen (H) from a reservoir, i.e., the plasma source, to a processed surface. From a fundamental perspective, such an investigation is unique because, contrary to commonly studied supersonic expansions, one of the components of the jet is almost absent in the background gas beyond the barrel shock. Indeed, hydrogen atoms can recombine at the wall to form molecular hydrogen, and due to the large available surface the vessel walls act as a huge sink for such a reactive light component.

The study of the transport of atomic hydrogen has also a strong technological relevance because H plays a key role as a chemical agent in many plasma processing applications such as plasma enhanced chemical vapor deposition [5,6]. In addition, remote plasma sources can be used to produce beams of neutral atomic hydrogen, and they may serve for volume production of hydrogen negative ions, both species being of importance in the field of nuclear fusion.

In spite of specific properties such as the presence of charged particles, high viscosity, high thermal conductivity, and large temperature gradients over the radius, thus far plasma expansion has been described using the adiabatic supersonic expansion theory [7] developed for the expansion of a neutral gas. This theory describes the continuum free jet shock wave structure [8,9] that results from the interaction of a supersonic flow with the ambient gas when a gas or a gas mixture expands from a reservoir into a region with a finite pressure rather than a perfect vacuum.

In the case of an expanding argon plasma, it has been demonstrated experimentally [10,11] that the expansion of the neutrals can be well described in terms of the adiabatic supersonic expansion of an ideal gas. Likewise, supersonic plasma flow created by a cascaded arc from a Ar-H_2 mixture should be understandable in terms of the adiabatic supersonic expansion of a Ar-H gas mixture leading to the formation of a well-defined free jet shock structure in the continuum regime. Only a segregation effect, the so-called mass focusing effect [9], where the heavier species is relatively more concentrated in the center of the jet, is expected in view of the mass difference between H (1 amu) and Ar (40 amu) atoms. Indeed, both the axial and radial profiles of the hydrogen atom velocity as well as the axial temperature profile are characteristic for a free jet shock structure as we will see.

In the experiments reported here, ground-state hydrogen atoms are spatially probed by using a two-photon excitation laser-induced fluorescence (LIF) technique [12,13]. A 20 Hz Nd:YAG-pumped tunable dye laser is operated around 615 nm. The output of the dye laser is frequency tripled resulting in 5 ns pulses of tunable UV light around 205 nm with a pulse energy of 2 mJ and a bandwidth of 0.2 cm^{-1}. The frequency-tripled laser light is directed into the vessel either perpendicular to the plasma expansion axis or counterpropagating with the expansion. It should be noticed that the dimensions of the detection volume that can be achieved (<1 mm^3) are smaller than the gradient sizes. Hydrogen atoms are excited with two 205 nm photons from the $1s\,^2S$ ground state to the $3d\,^2D$ and $3s\,^2S$ states. The excitation is then monitored by detection of the resulting fluorescence yield on the Balmer-α line at 656 nm. From a spectral scan with the frequency calibrated laser over the two-photon transition, the local H-atom density, temperature, and velocity along the laser beam are obtained. By applying this method for different positions in the expansion, the H distribution in the

plasma beam in terms of density, temperature, and velocity has been completely mapped.

The cascaded arc is operated at a 40 A dc current and with a cathode-anode voltage of 100 V. A gas flow of 3.0 standard liters per minute (slm) Ar and 0.5 slm H_2 is used. The diameter of the arc channel is 3 mm, the stagnation pressure is 0.6 bar, and the opening angle of the arc nozzle is 45°. Using a 6:1 Ar-H_2 mixture, at the arc outlet the plasma jet turns into almost a gas jet composed of Ar and H atoms and of residual H_2 molecules, the electrons being consumed immediately at the outlet of the arc channel [14]. Both the amounts of H and H_2 depend on the dissociation degree of the source which is very likely to be close to unity [14].

The development of the H drift velocity along the jet centerline, shown in Fig. 1, gives unambiguous proof of a complete momentum coupling between H and Ar atoms inside the beam. First, the gas is accelerated over a few arc nozzle diameters to a maximum speed of about 4200 m s^{-1}, due to conversion of thermal energy gained in the arc into kinetic energy by means of collisions. This value is in good agreement with a theoretical value of 4000 m s^{-1} found for the terminal velocity of a 3:1 Ar-H mixture at a temperature of 1 eV that expands into vacuum [9]. Then the velocity drops because of collisions between jet particles and background particles which results in the formation of a stationary shock front whose thickness is in the order of one local mean free path for H-Ar and Ar-Ar collisions. From a comparison with the sound velocity profile (Fig. 1), determined from the measured parallel temperature $T_{\parallel}$ (associated with the velocity distribution parallel to a streamline), it can be seen that at a background pressure of 20 Pa the Mach disk is located around 100 mm from the arc nozzle in agreement with the result given by a theoretical expression for the Mach disk location [9,15]. As can be seen from Fig. 1, the deceleration of the flow in the subsonic domain depends on the background pressure (P_{back}), because

particles from the jet will lose their forward momentum more efficiently at higher pressure. The hydrogen drift velocity profile is very similar to that of argon measured in a pure argon plasma beam [16] which implies that the flow characteristics of the plasma beam are mainly determined by the argon atoms.

The axial profiles of the perpendicular temperature $T_{\perp}$ (associated with the velocity distribution perpendicular to a streamline) of atomic hydrogen, depicted in Fig. 2, clearly reveal the presence of a stationary shock front. The shape of the axial temperature profiles complies with the theory which predicts a strong cooling effect in the supersonic domain and a dependence of both the position and the thickness of the shock front on P_{back} [17]. Nevertheless, using Rankine-Hugoniot (RH) relations [18] and taking a value of 5/3 for the adiabatic exponent γ, a Mach number ahead of the normal shock front of 2.6 is deduced from the temperature jump over the shock in the 20 Pa case, in disagreement with the value of 6 deduced from the axial velocity profile. This discrepancy might be explained by heat transfer from both the source and the hot background gas into the supersonic region which partly disturbs the effect of cooling in the core of the jet. This disturbance leads to an apparent smaller γ, meaning that the expansion is not adiabatic. By taking a value of 1.3 for γ, a Mach number ahead of the shock front of 5 is found and the calculated temperature development, according to [17], agrees well with the measurements, as can be seen in Fig. 2. In the background, the gas temperature depends both on the thermal conductivity of the gas mixture and on the power input.

In contrast to the previously mentioned results, the measured H-atom density profiles along the axis of the beam, depicted in Fig. 3, are in conflict with the theory. Throughout the stationary shock front, no discontinuity (or jump) in density is observed in contrast to the Ar profile [10]. In the 20 Pa case, the density even decreases over the shock
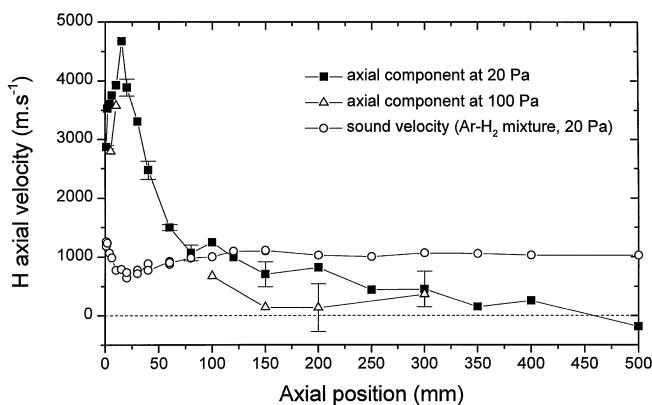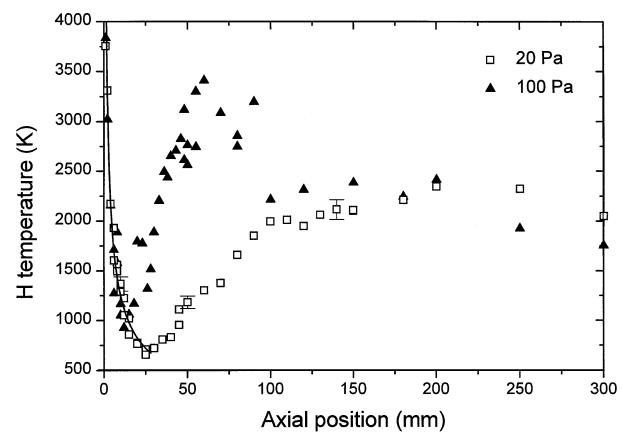

FIG. 1. Axial profile of the axial velocity component of H atoms at 20 Pa (■) and 100 Pa (Δ) background pressure. Also indicated is the velocity of sound (○), as it is determined from the parallel temperature.

FIG. 2. Perpendicular temperature $T_{\perp}$ of H atoms as a function of the distance from the nozzle at 20 Pa (□) and at 100 Pa (▲) background pressure. Also shown is the theoretical temperature profile in the supersonic region derived from [17] with $\gamma = 1.3$ (−).
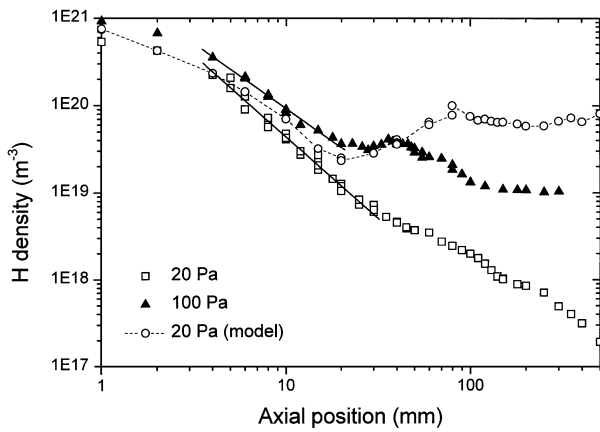
FIG. 3. Axial density profile of H at 20 Pa ($\square$) and at 100 Pa ($\blacktriangle$) background pressure. The lines are drawn to guide the eye. Also shown is the model density profile at 20 Pa ($- \bigcirc -$) based on the axial velocity data of Fig. 1.

front (Fig. 3), whereas the drop in drift velocity should be accompanied by a density jump with a factor of 3.7 according to the RH relation (and as shown by the calculated profile). At 100 Pa, the density is almost constant over the shock.

The theoretical H-atom density profile $n_H(z)$ along the jet centerline can be calculated from the measured H axial velocity profile $w_H(z)$ (Fig. 1), which is imposed by Ar atoms ($w_H \approx w_{Ar}$), using a simple model for $n_H(z)$ derived from the conservation of the forward H flux. When assuming a perfect 45° expansion ($r = z$), the injected H flux ϕ_H^0 in the supersonic domain and at some distance from the source is given by $n_H w_H \pi z^2 = \phi_H^0$ [17]. Throughout the stationary shock front, the diameter of the plasma jet is constant. In the subsonic domain, the gas flows at a constant pressure and no recombination effects at the wall are taken into account. The expansion of a pure Ar plasma can be satisfactorily described by this simple model [10]. The result of the calculation for $P_{back} = 20$ Pa is also depicted in Fig. 3.

The observed density profile leads to a nonconservation of the forward flux of atomic hydrogen. Such effects cannot be explained by volume recombination of atomic hydrogen because of the too low reaction rates [19,20]. Therefore the only explanation to this anomalous shock pattern is to consider the fact that H atoms radially escape the supersonic expansion. From measured radial profiles of H-atom density, temperature, and velocity components at $z = 8, 20, 50, 80$, and 100 mm, several fluxes can be estimated in order to clarify the situation. From an integration of the product $n_H \times w_H$ over the shock front radius, we determined the forward flux of H atoms entering the shock front ϕ_H^{in} as well as the flux behind the shock front ϕ_H^{out}. We found that $\phi_H^{in} = 4.9 \times 10^{19}$ s^{-1} and $\phi_H^{out} = 3.9 \times 10^{18}$ s^{-1} which means a 1 order of magnitude radial loss of H flux. The mass focusing effect [9] cannot explain this H outflow. The key of the

problem is the following: There is a significant density gradient between the interior of the plasma jet and the surroundings, caused by the (quasi)absence of H in the ambient gas, which drives a radial diffusion of atomic hydrogen. In contrast, when the plasma jet turns from underexpanded into overexpanded, this gradient for Ar is opposite (nonreactive species). From radial profiles, an averaged H-atom radial flux ϕ_H^{rad} over the shock front can be estimated. We found $\phi_H^{rad} = 1.9 \times 10^{19}$ s^{-1} which is in quite good agreement with the loss of forward flux inside the stationary shock front. In addition, an estimate of the same flux can be obtained using Fick's diffusion law. This gives 1.7×10^{19} s^{-1} which strongly encourages the idea of radial outflow induced by a density gradient. The determination of both fluxes is not straightforward and will be explained in detail in a subsequent paper.

Within the supersonic domain of the jet, the density decays slightly faster than predicted by the model, which means that it is not only geometrically determined [9,17]. Moreover, the steepness of the density decay depends on P_{back} in contrast with the prediction by the expansion theory. Again these effects can be explained by H atoms radially escaping the expansion by a diffusion process. A study of the beam cross section at a distance $z = 8$ mm from the arc outlet, of which the results are shown in Fig. 4, reveals that the hydrogen diffusion phenomenon is strong and that
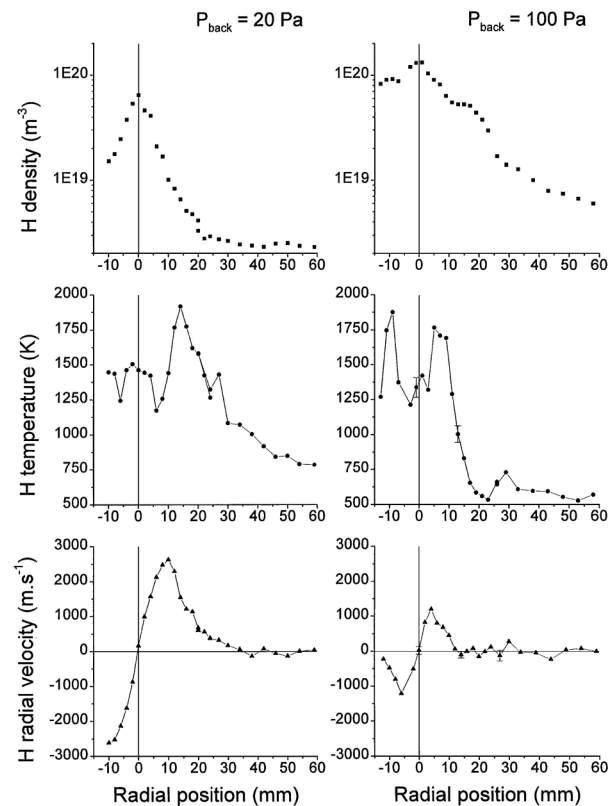

FIG. 4. Radial profiles of the density ($\blacksquare$), perpendicular temperature ($\bullet$), and radial velocity ($\blacktriangle$) of H atoms at $z = 8$ mm for a background pressure of 20 Pa (left) and for 100 Pa (right).

it occurs already at the beginning of the mixture expansion. The radial profile of both the radial velocity component and the perpendicular temperature reveals the barrel shock structure of the expansion, and they show the influence of the background pressure on both the dimension of the jet and on the shock wave structure. The lower absolute H density in the 20 Pa case compared to the 100 Pa case, visible in both Figs. 3 and 4, can mean only that in between the nozzle and the measurement position already more H is lost from the plasma jet than in the 100 Pa case. At low pressure, the outward diffusion phenomenon is strong because of the large local mean free path for momentum exchange which creates a diffuse shock structure [21]. The higher density in the wings of the 100 Pa profile (Fig. 4), as well as the plateau in the axial density profile at 100 Pa (Fig. 3), can then be explained by a slower outward diffusion of H. It just takes more collisions for H to pass the barrel shock in the 100 Pa case than in the 20 Pa case. This means that H atoms are poorly confined within the supersonic domain of the plasma beam, the efficiency of the confinement depending on P_{back}, i.e., on the permeability of the shock structure.

In the subsonic domain, the H density is still decreasing. After diffusing out of the jet, H atoms travel towards the vessel wall where they can recombine to form molecular hydrogen. Even if the recombination probability at the wall is low, the large available wall area causes H to almost vanish from the residual gas. This is confirmed by the measurement of the dissociation degree at 300 mm from the arc outlet (i.e., in the background) which equals to 0.2% for $P_{back} = 20$ Pa and to 1% at 100 Pa. This creates very specific boundary conditions for the H density and results in the formation of large radial H density gradients all over the expansion which are responsible for the diffusion process of H out of the beam.

In conclusion, we experimentally demonstrated that the expansion of atomic hydrogen when seeded in Ar cannot be entirely described in terms of the adiabatic supersonic expansion theory. First, heat transfer leads to an apparent smaller adiabatic exponent. Second, the striking absence of a H density jump across the shock front comes from a strong outward diffusion of H atoms. This process is driven by large radial density gradients induced by the loss of H atoms from the background gas by wall recombination. The Ar shock structure is partially transparent to H leading to a poor confinement of H atoms even at high pressure and therefore to a nonefficient transport mechanism. This leads to a less than optimal use of the chemical potential of the plasma source. The loss of H atoms at the vessel wall should therefore be taken into account in the design of reactors using remote plasmas as an atomic hydrogen source.

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