Shock Shells in Coulomb Explosions of Nanoclusters

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(Received 5 November 2002; published 3 October 2003)

We predict that Coulomb explosion of a nanoscale cluster, which is ionized by high-intensity laser radiation and has a naturally occurring spatial density profile, will invariably produce shock waves. In most typical situations, two shocks, a leading and a trailing one, form a shock shell that eventually encompasses the entire cluster. Being the first example of shock waves on the nanometer scale, this phenomenon promises interesting effects and applications, including high-rate nuclear reactions inside each individual cluster.

DOI: 10.1103/PhysRevLett.91.143401 PACS numbers: 36.40.Gk, 43.28.+h

When a cluster, a nanocorpuscule comprising tens to thousands of atoms or molecules [1], is irradiated by a high-intensity laser, it becomes very rapidly and highly ionized [2–4], and free (ionized) electrons are almost instantly swept away by the laser. The remaining ionic core is then torn apart by repulsive Coulomb forces, a so-called Coulomb explosion (CE). While the CE has been thoroughly explored by now, the possibility of a strikingly dramatic and universal phenomenon in it has apparently been overlooked. In this Letter, we show that if the outer layer of ions is less dense then the center — a typical situation — the CE must produce a spherical shock at its periphery. The shock is formed by inner ions overrunning the outer ones. Usually, there is also a trailing "antishock" moving slower. This results in an expanding double-edge shock shell, which eventually encompasses almost the entire ionic cloud. This first known nanolevel shock phenomenon may have numerous ramifications from quasi-2D dynamic crystal formation to nuclear reactions of a greatly enhanced rate inside the cluster. The shocks will also appear in CE of carbon nanotubes and thin metal wires, where they may engage billions of ions.

In the theoretical work on the CE, see, i.e., Refs. [3,4], it has usually been assumed that the ionic core is a sphere of homogeneous density of ions (a uniform, steplike model). Initially uniform, the density remains uniform (and discontinuous) during CE; see below. We show that this result does not hold even for slight nonuniformity; if the outer layers are less dense than the core center, a drastic change of CE behavior occurs. The inner ions are then moving faster, Fig. 1(a), than outer ones, displaying a shock pattern typical of the explosion of noncolliding particles. The faster ions eventually run over most of the other ions preceding them, surging together at a certain critical surface. Ion density at that surface becomes infinite, thus forming a leading shock.

By now, the CE model whereby ionized electrons are removed beyond the confines of the ionic core before the expansion starts, is well established and corroborated (see, e.g., [4]). To clarify the limitations of this model, which is also used here by us, we note that, in general, the expansion of clusters ionized by a high-intensity laser is a complicated process, which at two distinct limits is well described by either the quasineutral microplasma model, hydrodynamic model, etc., more characteristic for lower laser intensities ($\sim 10^{15}$ W/cm^2), or by the ionic core CE with free electrons swept away by the laser field, if the

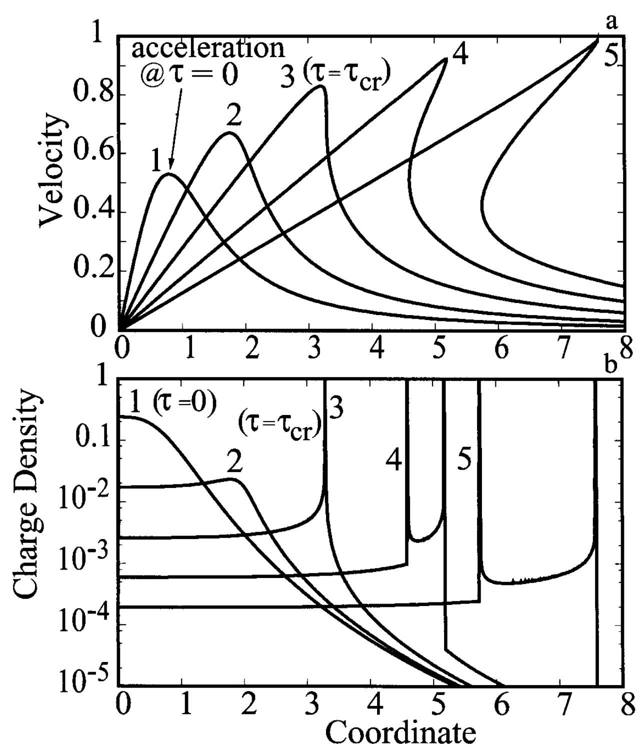

FIG. 1. Normalized profiles of velocity, $dS/d\tau$ (curves 2–5) and acceleration, $d^2S/d\tau^2$ (curve 1) in (a); and number density, ρ, in (b) of ions in the "smooth" model, Eq. (9), with $\mu = 1$, vs the normalized coordinate S for different normalized time, τ. Curve 1: $\tau = 0$; curve 2: $\tau = 2$; curve 3: $\tau = 3.783$ (critical point); curve 4: $\tau = 6$; and curve 5: $\tau = 8.5$.

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intensity is sufficiently high, usually $> 10^{17}$ W/cm^2. The force on an ion is then due only to the full ionic charges inside the sphere under it. We believe that shock waves may occur in any rapidly expanding cluster; however, the CE, with its transparent physics, presents the simplest case. Our analysis of electron trajectories taking into consideration most of the significant factors, to be published elsewhere, shows that for a circular polarization (as in a lasetron [5]), any free electron is taken away from the core by a powerful laser within the time shorter than a laser cycle. For the intensities $\gg 10^{15}$ W/cm^2 and a typical cluster size of 50 Å this time is a small fraction of a femtosecond, and the free electrons stay out of the core longer than the time of shock formation. Thus, for those intensities the electron cloud can be neglected in considering the dynamics of CE. This is consistent with the results [4] based on even tougher assumption of linear polarization. H, D, and He clusters are apparently the "cleanest" choice for observing a "pure" ionic CE and shocks. The explosion of clusters with heavier and/or mixed ions of significantly higher-Z atoms/molecules may involve, e.g., collisional ionization of deeper inner electron shells; still, they are in general expected to exhibit similar shocks for sufficiently high laser intensities. The rising time of a laser pulse before ionization reaches maximum, should also be shorter than the time scale of the CE, t_0, see Eq. (3) below. For a typical cluster above, $t_0 \sim 50$ fs; such lasers are readily available.

Our model cluster is a sphere filled by equally charged identical ions; unlike the uniform model, however, the initial ion density profile, $D(r_0)$, tapers off to the periphery [see, e.g., Eq. (9) below], such that

$$D(r_0) = (4\pi r_0^2)^{-1} dN(r_0)/dr_0 \tag{1}$$

is a decreasing function of r_0; $N(r_0)$ here is the number of ions within a sphere of a radius r_0. The acceleration of an ion at the point $r(t)$ due to Coulomb repulsion is

$$d^2r/dt^2 = (en_i)^2 N(r)/Mr^2, \tag{2}$$

where n_i is the ion charge in the units of the electron charge e, and M is the ion mass (note that for a uniform density profile, $d^2r/dt^2 \propto r$). So long as each small element of the expanding cloud consists of ions of the same momentum, the total number of ions enveloped by the sphere of radius r remains unchanged, $N[r(r_0)] = \text{const} = N(r_0)$, where $r(r_0)$ is a trajectory of an ion with $r_{t=0} = r_0$. This is a condition that no ion trajectories cross each other; its violation marks the shock formation.

For dimensionless variables, $\tau = t/t_0$, $s_0 = r_0/R_0$, $S = r/R_0$, $Q(s_0) = N(s_0)/N_\Sigma$, $\rho(S) = D(r)R_0^3/N_\Sigma$, where R_0 is the radial scale of the cluster, N_Σ is the total number of ions in the cluster, and

$$t_0 = (en_i)^{-1}\sqrt{MR_0^3/N_\Sigma} = (en_i)^{-1}\sqrt{3M/4\pi\overline{D}} \tag{3}$$

is a CE time scale [6], with $\overline{D} = 3N_\Sigma/4\pi R_0^3$ being a "mean" initial ion density, Eq. (2) is now written as

$$d^2S/d\tau^2 = Q(s_0)/S^2 \qquad [Q(\infty) = 1]. \tag{4}$$

If CE starts out with all the ions at rest, the first integral of this equation, the conservation of energy, is

$$(1/2)(dS/d\tau)^2 = Q(s_0)\cdot(s_0^{-1} - S^{-1}), \tag{5}$$

and the trajectory $S(\tau)$ is found from the solution:

$$\sqrt{x(x-1)} + \ln(\sqrt{x} + \sqrt{x-1}) = \tau\sqrt{2Q(s_0)/s_0^3}, \tag{6}$$

where $x = S/s_0$, while the density is

$$\rho(S) = x^{-2}\rho(s_0)\cdot(ds_0/dS), \tag{7}$$

where $\rho(s_0)$ is the initial density profile. For the uniform model, $Q(s_0)/s_0^3 = 1$ for $s_0 \leq 1$ the cloud stays uniform, since for any $s_0 \leq 1$, the ratio S/s_0 is S independent. The cloud radius is then

$$S_{cl} \approx 1 + \tau^2/2 \quad \text{as} \quad \tau \ll 1, \quad \text{and} \quad \approx \tau\sqrt{2} \quad \text{as} \quad \tau \gg 1. \tag{8}$$

However, if $\rho(s_0)$ zeros out smoothly, Eq. (6) displays a dramatic change of system behavior.

Let us consider as an example a one-parameter set of smooth initial profiles

$$Q(s_0) = \frac{s_0^3}{(1 + s_0^{3\mu})^{1/\mu}}; \qquad \rho(s_0) = \frac{(3/4\pi)}{(1 + s_0^{3\mu})^{(1/\mu)+1}}. \tag{9}$$

The control parameter, $\mu = \text{const} > 1/3$, allows one to handle profiles from smooth at $\mu \approx 1/3$ to uniform but steplike at $\mu \to \infty$. In particular, for $\mu \gg 1$, the "transition" depth is as $\Delta s_{\text{tr}} \sim (4/3)\mu^{-1}$. Figure 1 depicts the dynamics of CE in time and space for $\mu = 1$ (with $\Delta s_{\text{tr}} \approx 0.82$). One can see that at $\tau = 0$, the ion acceleration peaks somewhere inside the cloud, curve 1, where ions accelerate faster than the rest of the bunch. This translates into the velocity profiles $\nu(S)$ peaking in an inner area, too, as time increases, curves 2 and 3. These profiles tell the whole story, with the peak of $\nu(S)$ being the shock predictor. As inner ions rush out faster than the outer ones, at a critical moment, τ_{cr}, both of these groups end up at the same location, S_{cr}, which marks the breaking, or critical, point of a shock, curve 3, where

$$\partial s_0/\partial S = \partial^2 s_0/\partial S^2 = \infty, \quad \text{or} \quad \partial\nu/\partial S = \partial^2\nu/\partial S^2 = \infty. \tag{10}$$

For $\mu = 1, \tau_{\text{cr}} \approx 3.8$, and $S_{\text{cr}} = 3.3$. Since $\rho(S) \propto \partial s_0/\partial S$, the density $\rho(S_{\text{cr}}) \to \infty$, too, Fig. 1(b), curve 3. From this moment on, with the fast inner ions rushing outward, and the slower outer ions falling behind, the function $\nu(S)$ assumes multivalued, or hystereticlike shape, curves 4 and 5 in Fig. 1(a) [8]. Thus, in a certain area of the cloud, at each of its points there will be now three groups of ions with different velocities. This also implies that the charge Q in Eq. (4), which acts to accelerate ions at the point S, is not a function of a single originating location

s_0 anymore, which makes Eq. (6) invalid. Instead, beyond the critical point in time, $Q(S)$ is to be evaluated as a total sum of all the ion charges enveloped by a sphere of radius $S(\tau)$, regardless of their origin and current velocities, with the density now being as

$$\rho(S) = (4\pi S^2)^{-1} dQ(S)/dS, \tag{11}$$

The "knees" of the function $\nu(S)$, i.e., the points S_{sh} at which $d\nu/dS = \infty$, correspond to infinite density, $\rho = \infty$; these are shock edges. Near the critical point, S_{cr}, the pole of density function is as $\rho \propto (S - S_{cr})^{-2/3}$, while the poles near the shock edges are as $\rho \propto |S - S_{sh}|^{-1/2}$. The fastest moving ions of the "advanced" knee form a leading shock, while the most falling-behind ions form a trailing shock, or antishock. Two of them together make a shock shell, which widens with time and finally encompasses almost the entire cloud. The singularities in the density profile will be resolved by, e.g., nonzero initial temperature of the ions. Our calculations, to be published elsewhere, show that the density shell is still strongly pronounced even at the temperature up to 10% of the highest energy of accelerated ions at $t \to \infty$ [see also below, Eq. (14) and the discussion following it].

The shock phenomenon is universally inherent in any initial density profile with "sloping down" nonuniformity, regardless of the specific model or the spatial depth of the transient layer. Certain details, however, are model specific. While "smooth" models such as (9) always produce double-shock shell, the relative density in both shocks may change. For example, for the "tanh" model, $Q(s_0) = [\tanh(s_0^{3\mu})]^{1/\mu}$ or super-Gaussian model, $\rho(s_0) \propto \exp(-s_0^{2\mu})$, the intensity of the trailing shock quickly diminishes as μ increases. Furthermore, in a "cut-off" model: $\rho(s_0) \propto 1 - s_0^{\mu}$ if $s_0 < 1$, and $\rho(s_0) = 0$ otherwise, the trailing shock disappears, being replaced by the discontinuity of the gradient of density, $d\rho/dS$. The velocity profile here has only two branches. In fact, the initial profiles $\rho(s_0)$ can be constructed that produce a multiple (> 3) number of solutions in the hystereticlike area. This is the case of "hetero" clusters consisting of different ionic species, e.g., heteronuclear molecular clusters, or mixed clusters [9] formed by depositing layers of atoms upon a cluster initially made of different atoms; multishocks are well pronounced for all of them.

Common features of the homonuclear CE behavior for any model in the area of the central core remaining inside the shock shell as time increases, see Fig. 1, are that $\nu(S) \propto S$, while the density $\rho(S)$ is becoming flat, similar to the big-bang distribution. Essentially, in this limit they reproduce features of the uniform model with

$$dS/d\tau \approx S/\tau \quad \text{and} \quad \rho \approx (3/4\pi)/(\tau\sqrt{2})^3. \tag{12}$$

When an initial profile approaches the uniform one ($\mu \to \infty$), the width of a shock shell in smooth models or the double-solution area in a cut-off model, is narrowing as expected. Amazingly, however, neither the critical point of the shock formation moves infinitesimally close to the edge of the cluster, $S \approx 1$, nor critical time zeros out. Instead, these parameters remain finite, $S - 1 \approx 0.635$ and $\tau \approx 1.237$, respectively. Being roots of equations

$$\sqrt{S(S-1)} + \ln(\sqrt{S} + \sqrt{S-1}) = 2S^{3/2}/3\sqrt{S-1} = \tau\sqrt{2}, \tag{13}$$

they are universal and model independent. So, even a slight perturbation of a uniform model results in a shock with nonvanishing formation parameters.

So far we have assumed that all ions are initially at rest. Will the initial motion be able to suppress the shock? For an arbitrary initial velocity profile, $\nu_0(s_0)$, the conservation of energy reads as:

$$(dS/d\tau)^2 = 2Q(s_0)(s_0^{-1} - S^{-1}) + \nu_0^2(s_0). \tag{14}$$

Let us assume the worst-case scenario with "big bang" connotations, whereby the initial velocity is proportional to the distance, $\nu_0(s_0) = H_{CE} s_0$, where H_{CE} is a "nano-Hubble" constant. Our calculations show that if H_{CE} is higher than some critical value, $H_{CE} > H_{cr}$, the shocks will be suppressed; e.g., for the profile (9) with $\mu = 1$, we have $H_{cr} = 1/2\sqrt{3} \sim 0.3$. However, we found that H_{cr} increases rapidly as the transition depth Δs_{cr} decreases; in most cases of interest, the initial thermal velocity of ions would be insufficient to suppress the shock.

The CE shock is not limited to spherical clusters. Calculations show that all our results hold for a cylindrical geometry. This tremendously broadens the scope of conditions and systems to observe and use this phenomenon. For example, instead of clusters, one can use much better defined and designable carbon nanotubes, or well engineerable wires of nm- to μm diameter (similar to the ones proposed for a lasetron source [5]), that would produce a huge amount of ions injected into CE and shock when irradiated by laser. A gold wire of 2.0 nm diameter positioned normally to the laser beam in the focal spot of $\sim$5 μm size, would eject $\sim 2 \times 10^9$ ions with the huge total charge of up to $10^{10} - 10^{11}$ $|e|$. The shocks could also be generated on larger scales of ion energy (MeV instead of keV), as a laser pulse expels almost all the electrons from the cluster of heavy ions.

The CE shocks can manifest themselves through, or be used for quite a few physical effects. Thin shock edges are basically 2D spherical surfaces, within which the ions may form a dynamic yet well organized structure akin to a 2D crystal with a near-space ordering, whose "order range" depends on how long individual ions remain near that surface. This "shock crystal," and the shock edges in general, could be detected and studied via scattering of electrons or x-rays, in particular, using x-ray pulses in subfemtosecond domain [10]. Other ways to observe CE shocks may include neutron burst detection (see below), and a modification of visualization technique [11].

One of the most rapidly growing research fields related to laser-irradiated clusters and ensuing CE [7], as well as in other nanostructures [12], is the nuclear reactions, in particular, the production of neutrons due to collisions of sufficiently high energy ions in deuterium. To estimate the energy scale of those collisions, we note that the maximal velocity and energy of an ion corresponding to $(dS/d\tau)_{\tau=\infty}$, are, respectively,

$$v_{\max} = en_i\sqrt{2N_\Sigma/MR_0}, \qquad E_{\max} = (en_i)^2 N_\Sigma/R_0, \quad (15)$$

so that the energy of collision between two ions in cluster due to shock can be large [13]. Thus, another, and perhaps most spectacular, effect due to CE shock could be that these reactions may occur mostly inside the cluster due to collisions between the ions of the same cluster, e.g., fast ions at the leading shock and slow-moving ions of the lower branch of velocity profiles in Fig. 1(a). The ratio of reaction-generating collisions per "hot" ion inside and outside a cluster is $\sim O(1) \cdot \rho_{\rm cl}/\rho_{\rm pl}$, where $\rho_{\rm cl}$ and $\rho_{\rm pl}$ are number densities of ions in a cluster and in plasma, respectively. The resulting enhancement for the reaction rate compared to conventionally expected plasma collisions is a few orders of magnitude, which could be consistent with most recent experimental data [14]. This effect may also be instrumental in detection and verification of CE shocks: a neutron burst at the initial stages of CE when expanding clusters have not yet interacted with surrounding gas could be a signature of the shock.

The shocks discussed here are so generic, it is tempting to relate them to a broader and bigger picture. Any explosion, be it Coulomb, thermal, nuclear, or supernova, and other stellar or galactic explosions [15], regardless of the nature of forces that set it in motion, is prone to generating shocks. The defining factor (in essence the shock predictor) here is whether, usually due to radial nonuniformity of initial conditions, the velocity profile at some moment peaks inside the cloud. In view of that, it is amazing that Universe-scale shocks have not showed up in the big-bang model of the Universe. The initial (and ensuing) uniform profile in CE is an analogy to the uniform Hubble expansion in the big-bang model. Any perturbation of that idealized profile might have brought about a "big shock," whose primordial remnants might still be found in the Universe. An example would be the existence of far-remote areas that expand slower than predicted by the Hubble constant, and furthermore, those that are seen as running toward us, similarly to the slow front tail of CE velocity profile seen by the faster emerging ions. Another connection can be found at the opposite, subnucleus scale, where a shock could be expected in the expanding quark plasma [16].

In conclusion, we showed that rapid photoionization and ensuing Coulomb explosion of clusters can lead to the shocks formation due to the hystereticlike velocity profiles produced by the nonuniformity of initial conditions. This phenomenon may result in many effects, in particular, fast collisions of ions with different velocities and ensuing nuclear reactions inside the cloud.

This work is supported by AFOSR.

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