4. Concentric ring pattern formation in needle-plate exploding system

This chapter begins with a basic introduction to pattern formation. From a general system discussion, we move towards pattern formation in metallic systems and progress to present our findings in the exploding wire needle-plate system. We present results of concentric ring pattern formation in the needle-plate exploding system. By exploding a wire on a metallic plate, we demonstrate reorganization of the metallic surface at different length scales. While optical microscopy shows clear concentric ring patterns, atomic force microscopy (AFM) provides details of nanometre sized entities that constitute these rings. The size of these entities is shown to scale with wire dimension and applied explosion voltages. From fluctuations in the plasma current recorded during the process, the particle formation is seen to be a self-organization process.
4.1 Introduction to pattern formation

Patterns are observable macroscopic ordering in a large system arising as a result of interaction amongst its constituent microscopic elements. Nonlinearities introduced in a dynamical system are known to induce spatial patterns that are sometimes stationary, travelling or disordered in space and time. Being a universal phenomenon, pattern formation continues to draw widespread attention encompassing biological, chemical, hydrodynamical and nonlinear optical systems. These have been observed in fluid convection in Rayleigh-Bénard cells, as Turing patterns in morphogenesis, from instabilities in periodically vibrated liquids (Faraday instability), in vibrated granular media, from avalanches in electrical discharge in gases and in light intensity aggregation from nonlinear response to light passing through a medium. A brief introduction to these systems is given below.

1. Convection in Rayleigh-Bénard cell: This is a problem of Rayleigh-Bénard instability during convection inside a fluid. This instability occurs inside a fluid confined between two infinite horizontal planes at different temperatures $T_1$ and $T_2$ (figure 4.1). If $T_2 > T_1$, then the system is stable and stays stratified in temperature. But, if $T_2 < T_1$ and if a perturbation is introduced in the system, then for a critical value of the difference of temperature $(T_1 - T_2 = dT_c)$, it can appear as movements inside the fluid. Then the system becomes unstable and movements are organized in periodic rolls. These rolls, or also called cells of Rayleigh-Benard, appear when there is a coupling between the dynamic field and the thermal field. The principle behind this instability is simple. Consider a drop of fluid near the lower plane shown in figure 4.1. The drop is heated so its density decreases and it goes up inside the fluid due to the Archimede force. When the drop reaches the upper plane, which is colder, it is cooled so its density increases and it can go down inside the fluid. Rolls of Rayleigh-Benard instability are caused by this mechanism [1].
2. **Faraday patterns**: If a layer of liquid with a free upper surface is vibrated vertically with sufficient acceleration, the surface no longer remains flat but acquires what Faraday termed “crispations.” These are standing wave patterns, often with the spatial periodicity of the square lattice and having a frequency half that of the driving force. The length scale is determined by the forcing frequency, gravitational acceleration and by the ratio of the surface tension to the density of the liquid. Under certain conditions, e.g., two frequency forcing, spatially quasiperiodic patterns can arise [2]. This is depicted in figure 4.2.

3. **Turing patterns**: In 1952, Alan Turing proposed a chemical model for morphogenesis, the process by which a zygote acquires form and becomes an embryo, in which diffusion plays a counterintuitive role. The central problem of morphogenesis is that the zygote is spherically symmetrical, with identical cells, while the resulting embryo is not. As Turing puts it,
“A system which has spherical symmetry and whose state is changing because of chemical reactions and diffusion, will remain spherically symmetrical for ever..... . It certainly cannot result in an organism such as a horse, which is not spherically symmetrical.”

The solution is that a symmetrical system with a symmetrical trivial state can lose stability to a state with less symmetry. A system of chemicals which can catalyze one another’s formation and destruction is described by a set of coupled nonlinear partial differential equation for the concentration of each chemical. It may well happen that in the absence of diffusion, a uniform stable solution is present that becomes unstable upon the introduction of diffusion, producing a pattern [3]. This instability is called the Turing instability and has been first observed experimentally in 1990 in the Chlorite-Iodide-Malonic-Acid (CIMA) reaction.

4. **Vibrated granular layers**: If instead of a liquid, a layer of sand is vibrated vertically, many of the same qualitative features appear as for the Faraday instability, including square and hexagonal structures with frequency half that of the driving force. However many other features also appear, including localized “oscillons”. These appear to be completely stable. These oscillons interact with one another through a short range force and can connect to form long chains nicknamed “molecules” [4].

5. **Nonlinear optics**: Many optical media exhibit a non-linear response to light passing through them. For example, in the case of self-focusing, the medium has an increased index of refraction in regions of high light intensity. Therefore, a beam whose intensity profile is high at the centre and decreases toward the periphery causes the medium to turn into a focusing lens which further intensifies the beam. Thus, in the two-dimensional cross-section of the beam, there is a tendency for intensity to aggregate, and in some experiments periodic patterns can arise [5].

6. **Electric discharge avalanches**: Take a pair of flat and uniform electrodes, with a gaseous medium filling the space between them. For applied high enough voltage between the electrodes, electrons spill across the gap and illuminate it, but not uniformly.
To quote Breazeal et al. [6], “For appropriate ranges of the experimental control parameters, regions of high and low current density form in the gas and arrange themselves into a number of different light-emitting two-dimensional patterns.”

These patterns include concentric ring pattern (figure 4.3), rolls, positive and negative hexagons, and a pair of sets of rolls that alternate between two orientations 120° apart. In a circular domain, roll patterns as a set of concentric rings have only been reported in Rayleigh-Bénard cells, in vertically oscillated fluids and a planar barrier gas discharge system [7].

![Figure 4.3: Time averaged concentric ring pattern in a dielectric barrier discharge system.](image)

4.2 Pattern formation in metals
Pattern formation in metals is rare. Patterns have however been seen in ion irradiation and sputtered surfaces [8], dendritic growth [9] and electrochemical dissolution of metals [10].

**Dendritic growth:** It is both a common form of solidification in metals and alloys and an archetypal problem in pattern formation far from equilibrium. When a volume of liquid is frozen starting at one end, a solidification front propagates from that end to the other, warmer end. The simplest solution is a uniformly flat solid-liquid interface, but in general this solution is unstable. A small portion of the interface may proceed in advance of the rest and thereby affect the rate of freezing, so as to increase its own growth. The result is often a form of dendritic growth, with branches extending far ahead of the rest of the
front and sprouting branches of their own. At this point the system is well beyond the purview of a weakly nonlinear approach and is deep into the nonlinear regime.

**Ion beam irradiation:** Self-organization of surface morphological features to produce structures of potential use in nanotechnology is in its infancy. Sputtering by collimated low energy beams can spontaneously create periodic structures on many surfaces. Ripple structure is produced on Si (001) surface by bombardment with 750 eV Ar$^+$ ions at 600° C and a flux of 0.7 mA/cm$^2$. Ion bombardment acts as a driving force to roughen the surface and surface diffusion acts to restore the surface to its flat equilibrium state. The competition between two processes results in selection of a preferred wavelength that grows faster than any other [8].

![Incident ion beam](image)

**Figure 4.4:** Ripple structure on sputtered silicon surface.

**Electro-chemical dissolution of metals:** Pattern formation also occurs in electrochemical systems where it has attracted considerable interest. Electrochemistry is an ideal playground for the study of dynamic instabilities since here most experiments are carried out under conditions far from thermodynamic equilibrium. It is therefore not surprising that the majority of known bistable, oscillating and chaotic reactions are found in electrochemistry. In addition, spatial coupling is intrinsic to most processes that occur on the surface of electrodes because local changes in the double-layer potential induce migration currents that can affect significantly the dynamics at other locations. The range and the strength of this spatial coupling are determined by parameters such as the cell
geometry, external resistance and the conductivity of the electrolyte. In many standard electrochemical applications, the set-up creates strong, long-range coupling through the electrolyte, which hampers the formation of pronounced spatial patterns.

Electro-explosion is a non-equilibrium process. We know that non-equilibrium processes lead to pattern formation. Various experimental and theoretical investigations of this phenomenon exist [11-20]. A study of the literature shows that wire explosion and fragmentation generally tend to proceed in the following manner [19,20]: a) Heating of wire and wire melting; b) Wire evaporation and formation of a high density core surrounded by low density ionized corona; c) Coronal compression by self-induced magnetic fields and d) Fast expansion of explosion products resulting in shock wave generation. Shock waves generated during explosion can be used to introduce nonlinearity in any system. In chapter 2, we have established electro-explosion in the needle-plate geometry. In comparison with traditional electro-explosion geometry, our needle-plate geometry provides us an opportunity to capture shock wave in the metal plate. Various experimental details pertaining to SWSE experiment are already explained in chapter 2.

4.3 Concentric ring pattern via electro-explosion

In chapter 2, we have explained that a metal plate roughness is very important for a good experiment. We have also shown AFM images of a polished metal plate surface before the explosion. After the explosion, the metal plate surface stands modified and can be observed under an optical microscope. Figure 4.5 shows an optical micrograph of an exploded plate in an experiment of exploding iron needle (tip diameter = 30 μm) on an iron plate while holding the plate at positive polarity compared to needle at 48 V (Fe/Fe_{30p,48w} system, current plot for this experiment is shown in figure 2.8). The figure clearly shows rings emanating from the point of contact made by the tip with the iron plate.
Figure 4.5: Optical micrograph shows result from explosion in the needle-plate configuration for the Fe/Fe$_{30p_{.48w}}$ system.

4.3.1 Origin of ring formation

As this ring pattern is incorporated by transformation of an otherwise flat metal surface (in the order of a few nanometres as measured by AFM), melting of the metal is a prerequisite to its formation. The melting is initiated at the point of needle-plate contact, as the high current density through the metal plate melts the metal with circular symmetry when electrons travel from tip to plate. The spatial extent of the molten disc will then be determined by the power dissipated by the metal plate. Despite the lack of symmetry in our system, we assume a similarity with the exploding wire phenomena, whereby the molten metal (in step a as indicated in section 4.2) is finally subjected to a shock wave (step d). The pattern could be a result of a series of shock wave fronts travelling through the molten metal and freezing at the boundary, or due to standing wave formation.

To verify this, we have measured the width of the bands formed within the ring. In case of a disturbance starting from the centre and proceeding outwards, the width of a single band would widen due to dispersion through the molten metal plate. However, the measured values of selected bands at the explosion centre and periphery indicates that these are reasonably constant with a value of $(4.77 \pm 0.01) \mu m$. Hence we can say that
these are standing waves formed following the shock wave generation in the molten metal, which can now be visualized as a vibrating liquid surface.

4.3.2 System studied for the scaling behaviour

1. Fe/Fe\textsubscript{370p,48w} system: Exploding $370\,\mu$m iron wire (needle electrode) on an iron plate (plate electrode).

2. Fe/Fe\textsubscript{30p,48w} system: Exploding $30\,\mu$m iron wire (needle electrode) on an iron plate (plate electrode).

3. Fe/Fe\textsubscript{25p,36w} system: Exploding $25\,\mu$m iron wire (needle electrode) on an iron plate (plate electrode).

The experiments have been done in these systems while holding the plate at positive polarity compared to the needle at $48\,V$ for Fe/Fe\textsubscript{370p,48w} and Fe/Fe\textsubscript{30p,48w} systems and $36\,V$ for the Fe/Fe\textsubscript{25p,36w} system. In figure 4.6, we show optical micrographs of SWSE results for Fe/Fe\textsubscript{370p,48w} and Fe/Fe\textsubscript{25p,36w} systems. Optical micrograph for the Fe/Fe\textsubscript{30p,48w} system has already been shown in figure 4.5.

![305\mu m](a)  ![305\mu m](b)

Figure 4.6: Optical micrographs show results from explosions in the needle-plate configuration for Fe/Fe systems (plate-positive) (a) Fe/Fe\textsubscript{370p,48w} system and (b) Fe/Fe\textsubscript{25p,36w} system.

The figures 4.5 and 4.6 clearly show rings emanating from the point of contact made by the respective tips with the iron plate. The rings die out at the extreme of a circle whose
diameter for the studied Fe/Fe systems are $1425 \mu m$ (Fe/Fe$_{370p_{-}48w}$), $1091 \mu m$ (Fe/Fe$_{30p_{-}48w}$) and $856 \mu m$ (Fe/Fe$_{25p_{-}36w}$). The following observations are common for all the tips exploded: (a) evolution of concentric rings emanating from the point of contact where the wire explodes and (b) presence of internal structure in all the rings. The lateral extent of the rings on the plate surface, as measured by the diameter of the rings, scales with the tip diameter.

4.3.3 Time evolution of current during explosion

We show in figure 4.7, plots of the current flowing through the needle-plate configuration during the explosion event for all the Fe/Fe systems studied. These plots are a real-time map of the SWSE event and their behaviour is already explained in detail in chapter 2. Here vertical arrows in the current plot represents first and second current peak in time evolution of current during explosion.

Figure 4.7: Time evolution of current through the needle-plate configuration during explosion in Fe/Fe systems (plate-positive). (a) Fe/Fe$_{370p_{-}48w}$ system (same as figure 3.2d), (b) Fe/Fe$_{30p_{-}48w}$ system (same as figure 2.8) and (c) Fe/Fe$_{25p_{-}36w}$ system. Vertical arrows in each plot identify the first and second peak in time evolution of current during explosion. The regions marked by a line having double-sided arrows have been employed to study spectral density.
For the Fe/Fe$_{370p\_48w}$, Fe/Fe$_{30p\_48w}$ and Fe/Fe$_{25p\_36w}$ systems, we find that the total time during which the current passes through the needle-plate system is approximately 8.25 ms, 2 ms and 1.2 ms respectively. Comparing figures 4.7a, 4.7b and 4.7c, we can see that the inherent process remains the same in all experiments, however, the entire process is scaled down in time for reduced tip diameters.

Comparing figures 4.7a, 4.7b and 4.7c we can conclude that the energy deposited is likewise reduced resulting in a total connect time of 8.25 ms for the 370 µm wire and 2 ms for 30 µm wire at 48V and 1.2 ms for 25 µm wire at 36 V. This scaling behaviour in the energy deposition and dissipation allows us to confirm the basic process steps as well. From this we conclude that energy deposition and dissipation increases with increase in tip diameter and applied voltage.

4.3.4 Atomic force microscopy

To get the microscopic details of these rings we have taken AFM images. In figure 4.7, we show details of each ring with nanometre resolution, employing an AFM working in the non-contact mode (AFM is discussed in detail in the appendix). This mode is chosen so as not to have contact with a topologically non-uniform surface.

Figure 4.8: Atomic force microscopy of Fe/Fe systems (plate-positive) (a) Fe/Fe$_{370p\_48w}$ system, (b) Fe/Fe$_{30p\_48w}$ system and (c) Fe/Fe$_{25p\_36w}$ system. These 3D images show the various grain sizes obtained under various exploding conditions.
Each ring is seen to consist of smaller particles whose size distribution could provide microscopic details of the processes leading to their formation. Evidence of shock waves producing small (nano-sized) particles is indeed there in the literature [18].

4.3.5 Grain formation
The exploding needle-plate system brings the plate surface instantaneously to its melting point (typically after 140 $\mu$sec, as can be seen from close-up pictures of the plots in figure 4.7). The shock wave generated after the explosion then travels through the melt. In a situation somewhat similar, there is proof of shock wave generation as nonlinear pressure waves, following explosion of single wires in water [18]. In our experiment, the shock waves transform the melt into micron-sized particles as our AFM measurements show. Assuming that the shock waves travel with the velocity of sound in Fe (5130 m sec$^{-1}$), it would typically take 500 nsec to cover the region modified as a result. This is $\sim$ 3 orders of magnitude smaller than the time for which the melt exists (as measured by us, figure 4.7). From theoretical estimates of resolidification time available in literature [20], we likewise conclude that sufficient time exists for the shock waves to travel while the melt survives. The melt however solidifies starting from the region farthest from the needle-plate contact point providing a natural boundary that confines the melt. The ring patterns are a result of stationary waves set up in the melt, emanating obviously with cylindrical symmetry from the centre of the figure, which resembles now a vibrating liquid surface.

4.3.6 Histogram analysis
In order to further establish the scaling of the generated particles with tip diameter, we have done a grain size analysis of the AFM data. This is presented in figure 4.9. Errors due to large variation in the background height of the sampled area are avoided by a height threshold (or Z-threshold) selection, which tagged all the grains to be analysed. Individual grains are then selected and their areas are determined. The area analysis is presented in figure 4.9 as a histogram. Area analysis has been chosen as a parameter and not volume analysis, to negate any erroneous estimate in volume from a contribution to
the grain height from the system background. The background is not stripped during these estimates.

Figure 4.9: Histogram shows number of grains ($N$) vs. area ($\mu m^2$) for Fe/Fe systems (plate-positive) for (a) Fe/Fe$_{370p_48w}$ system, (b) Fe/Fe$_{30p_48w}$ system and (c) Fe/Fe$_{25p_36w}$ system. Grain size variation with diameter and their distribution profile can be seen.

It is clear from figure 4.9 that the particle sizes are largest for the Fe/Fe$_{370p_48w}$ system. Grains are formed from reorganization in the melt in all the cases studied and shows scaling with tip diameter. While the influence of applied electro explosion voltage does not appear to have any major influence on the grain size (compare figures 4.9b and 4.9c). The other significant result here is the distribution of grain sizes. The smaller exploding tips have produced a reasonably normal grain size distribution while the size distribution obtained with the large tip is skewed, with a long exponential tail.

The formation of these particles is a result of the dissipation of energy following the needle-plate explosion, whereby the molten metal surface has re-crystallized in this form, allowing the shock waves to reconfigure the molten metal plate. The enhanced surface area (and hence formation of interfaces/defects) of the small metal particles is a result of the energy released by the shock waves, which gets stored in this manner. As this process takes place far away from equilibrium, the configuration gets frozen in a time scale shorter than the time available for the individual particles to coalesce into a single mass.
again. While sizing down of materials as a result of shock waves are known, it is also established that resolidification of Fe at high pressures and temperatures induces pressure-temperature zones in the liquid with short range nano-scale local structures [22]. As an outcome of this experiment, we indeed collect nanoparticles of Fe in the water medium whose size is less than 15 nm as indicated by disappearance of the ferromagnetic Mössbauer signal [23].

The histogram analysis and the time evolution of current during the electro explosion process allow us to understand the scaling behaviour of observed grain sizes with tip diameter. From figure 4.7, current connect time is seen to be largest for the wire with largest diameter, dissipating the largest amount of heat for the longest time. Hence it can be easily deduced that the melt survives longest. During this time, any small particle produced due to the shock waves would coalesce, leading to larger particle size. This is a possible explanation for scaling of particle size with tip diameter.

4.3.7 Plasma current fluctuations study
In order to further analyse the current data, we have identified the fluctuating part of the current in all the current plots of figure 4.7 with a line having double-sided arrows. This current is a result of plasma formation after restrike or reignition. The ionized plasma carries the current here. This is expected to be a random process during its existence between the tip and the plate. Hence, we have tried to analyse this data using time series analysis.

Time series is an ordered sequence of values of a variable at equally spaced time intervals. Time series analysis accounts for the fact that data points taken over time may have an internal structure (such as autocorrelation, trend or seasonal variation). It is used to obtain an understanding of the underlying forces and structure that produced the observed data. 1/f noise is a signal or process with a frequency spectrum such that the spectral energy density is proportional to the reciprocal of the frequency. 1/f noise, sometimes pronounced as one over f noise, is also called pink noise or flicker noise. There are many ways of characterising different noise sources, one is to consider the
spectral density, that is, the mean square fluctuation at any particular frequency and how that varies with frequency. Consider a process with a power spectrum of the form

\[ S(f) = \text{const.} / \left| f \right|^n, \quad \text{(4.1)} \]

With \( 0 < n < 2 \), when \( n = 1 \), a stochastic process characterised by a spectral density as in equation 4.1 is called \( 1/f \) noise. When \( n = 0 \) the noise is referred to white noise, when it is 2 it is referred to as Brownian motion.

Starting from the current data taken during explosion (as defined by the double-sided arrow), we have calculated the spectral density dependence on frequency employing the following steps:

1. We select a region of current where the shock wave propagates through the plasma.
2. The natural slope is eliminated by background subtraction using curve fitting. The background is not expected to originate from any physical processes.

The pure fluctuations left after the above procedure are now employed to calculate its autocorrelation plot. In this plot, the vertical axis is the autocorrelation coefficient \( R_h \) and horizontal axis is time lag \( (h) \). These terms are defined as given below:

\[ R_h = \frac{C_h}{C_0}, \quad \text{where } C_h \text{ is the autocovariance function and } C_0 \text{ is the variance function.} \]

\[ C_h = \frac{1}{n} \sum_{i=1}^{n-h} (y_i - y_m)(y_{i+h} - y_m) \]

\[ C_0 = \frac{1}{n} \sum_{i=1}^{n} (y_i - y_m)^2, \quad y_m \text{ is the mean value and } h=1,2,3,\ldots,n. \]

Fourier transform of the autocorrelation plot gives the spectral density. We find out the spectral density dependence on frequency by the way of fitting a curve to the spectral plot using the formula

\[ S(f) = \frac{1}{f^a}, \]
Figure 4.10: Spectral density dependence is shown by plotting $\log_{10}(S_f)$ vs. $\log_{10} f$ (represented by a solid line) for (a) random numbers, (b) Fe/Fe370p_48w system, (c) Fe/Fe30p_48w system and (d) Fe/Fe25p_36w system. Dashed line shows the best fit of power law $S(f) = \frac{1}{f^a}$ to solid curve, whose exponent is recorded in the respective figures.

In figures 4.10a – 4.10d, we show $\log_{10} S(f)$ vs. $\log_{10} f$ plots starting with a random test data in figure 4.10a. This data is generated employing a random number generator. As expected the random data returns a value of $a = 0$ for the exponent of the frequency $f$. The other values of the exponent are $a = 0.57$ for Fe/Fe370p_48w system, $a = 0.605$ for Fe/Fe30p_48w system and $0.576$ for Fe/Fe25p_36w system. Thus the fluctuations in the current data reflect some self-organization process and are not strictly random processes.

4.4 Conclusion

Pattern formations in metals are rare, while concentric ring patterns in metallic systems have never been observed before. We are able to generate these due to uniqueness of the
non-equilibrium process in the exploding needle-plate geometry. In this geometry, a plate electrode is capable to capture shock waves generated during the process and freeze the standing wave pattern, as soon as contact between electrodes breaks. Our AFM study allows us to show modifications introduced in a metallic surface as a result of electro-explosion. The explosion transforms the region under consideration to consist of microscopic entities that arrange due to instabilities introduced by the process. The microscopic elements themselves are a result of shock wave propagation and resolidification of the melt. In this regard, although a metal, the system described here belongs to a new universal class whereby the microscopic elements can be large micron-sized objects. Thus the patterns formed can be equated to those in vibrated granular media with inter-granular contact forces similar to van der Waals forces.
References