



## Frontiers article

# New mechanisms of macroion-induced disintegration of charged droplets



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## ABSTRACT

Molecular modeling has revealed that the presence of charged macromolecules (macroions) in liquid droplets dramatically changes the pathways of droplet fission. These mechanisms are not captured by the traditional theories such as ion-evaporation and charge-residue models. We review the general mechanisms by which macroions emerge from droplets and the factors that determine the droplet fission. These mechanisms include counter-intuitive “star” droplet formations and extrusion of linear macroions from droplets. These findings may play a direct role in determining macromolecule charge states in electrospray mass spectrometry experiments.

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## 1. Introduction

The stability of charged liquid droplets has been the subject of numerous experiments for well over a century [1–3]. The first theoretical treatment was that of Rayleigh in his concise paper on the stability of a conducting droplet with respect to small perturbations [4]. Rayleigh developed a model that finds the critical value of charge squared to volume ratio for droplet stability. This critical value is called the Rayleigh limit. The long-lasting interest on the topic arises from the principal role that highly charged droplets play in many different settings such as atmospheric aerosols [5], liquid helium droplets charged with surface-bound electrons [6,7], jets [8,9], reactivity of highly charged metal ions in small aqueous clusters [10]. This review draws its examples from one application of critical importance, namely, the use of electrospray ionization to transfer analytes from the bulk solution into the gas phase for mass spectrometry analysis. Since the discovery in the late 1960s of the electrospray ionization mass spectrometry [11] (ESI-MS) a critical question has been on how the intervening

droplet environment may affect the charge state and conformation of a macroion relative to those in the parent bulk solution [12–14]. The charge state of the macroion is intimately linked to the mechanism according to how a macroion emerges from a droplet. In order to describe the release of a macroion from a droplet two macroscopic mechanisms were developed: the charge-residue model (CRM) [11,15] and the ion-evaporation mechanism (IEM) [16,17] or a combination of those two [18]. The principles of these mechanisms will be presented later in the review. These models were developed based on intuition and indirect evidence from ESI-MS spectra [19–22]. In the last decade, the usage of molecular modeling revealed new pathways of macroion release from droplets that are not captured by the conventional aforementioned descriptions [23–29].

The review discusses the general mechanisms by which categories of macroions emerge from droplets. We distinguish the mechanisms that (a) a linear macroion may extrude from a droplet and (b) a linear or compact macroion solvated within the droplet may emerge because of solvent and solvated ion evaporation. This review provides the opportunity to collect together the mechanisms that we have identified by modeling the macroions (a) with bound charge, which is not transferred into the solvent [23,26,27,29] and (b) with transferable ions that can be exchanged between the macroion and the droplet solvent [24,25,30–33]

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under equilibrium [26,27,31] and non-equilibrium conditions [27]. Regarding the size of the droplets studied, we note that the simulated droplets have linear dimensions in the nanometer range (indicative numbers from our studies are between 7000 H<sub>2</sub>O molecule droplets with approximate radius of 4.0 nm [32,33] down to a few hundreds of H<sub>2</sub>O molecules or of other solvents [33]). On the other end, the analytical models that will be presented are not limited by the size of the systems. The simulated droplet sizes are small relative to the initially generated droplets by ESI (droplet dimensions of nanosprayed droplets are approximately 100–150 nm). However, it is the higher concentration of ions in the smaller droplets and the strong electric fields that play a critical role in the chemical and physical behaviors of the macroions, therefore, molecular simulations in the smaller droplets can provide insight into the role of the droplet environment in the charge state of a macroion.

We shall start the review with Rayleigh's model where we shall present certain aspects of the model that have not been sufficiently discussed in the literature. Following that section, the behavior of charged droplets, which are atomistically modeled above and below the Rayleigh limit will be discussed. Accumulated recent research [23–27,32] has revealed that the nature of the charge in a droplet gives rise to significant changes in the droplet properties. If the droplet charge is comprised of a number of small ions in a fluid with moderate to large dielectric constant, the corresponding droplet behaves as if it were a conductor. This is confirmed by a number of experiments [2] and numerical simulations [31,34] where Rayleigh criterion was found to predict the onset of instability closely. On the other hand if the charge is localized on a single macroion [23,26] or complexes of macromolecules [32,35] (with bound charge or transferable ions between the macroion and the droplet solvent [25–27,32,33]) the nature of the instability as well as the associated droplet dynamics differs from that predicted by the Rayleigh model [23,32]. A variety of droplet morphologies are induced by the charged macroions as it is shown in Fig. 1.

The variety of the induced droplet morphologies indicate that (1) the structure of the solvent will be distinct in a droplet relative to that of the bulk and the spherical droplets analogs therefore, it may affect the charge state and conformations of a macroion in a distinct manner; this effect cannot be captured by the CRM and the IEM. (2) New charge-induced instabilities not described by Rayleigh predictions exist that may keep a compact droplet with a macroion holding charge beyond the Rayleigh limit.

It has been found that the differences in the character of instabilities lead to the conceptual differences between aims and methodologies for these types of charged systems. In the case of a droplet with a number of separate elementary charges the instability and the corresponding eigenmodes below the Rayleigh limit are of interest as the tentative pathways of the activated process. In that context, the IEM was developed in the mid-70s by Iribarne and Thomson [16,17]. This model states that when droplets reach a size of radius of approximately 10 nm, then simple ion ejection can occur by an activated process where a solvated ion detaches from the droplet. This process occurs when the rate of solvated ion ejection is faster than the rate of solvent evaporation. Some aspects of the IEM have been discussed in an older review by Kebarle [36] and at [22]. In the computational studies, the closest theory to the IEM is the treatment of the fragmentation process as an activated process using a collective reaction coordinate that couples the ion and solvent degrees of freedom [22,34,37–39].

In the practically important case of a charged droplet containing a single macroion one of the commonly accepted mechanisms in ESI-MS for the charging of macroions that are found in the interior of a droplet is the CRM [15]. The CRM states that single charges are released from the droplet by Rayleigh's mechanism. When the droplet shrinks to a size that is close to that of the macromolecule then

further droplet evaporation collapses the charges onto the macroion. The IEM has also been considered as a mechanism for macroion release based on the research of Fenn and co-workers [19–21]. Fenn was using the name ion-desorption mechanism (IDM) for the ejection of macroions from droplets in analogy to the IEM. The term IEM or IDM for macroions has been used so far in a qualitative manner without a theoretical basis analogous to that of IEM for single ions. The reason for this has been the fact that it has not been obvious how to extend the theory of the IEM to the macroions because of the complexity of their structures and charging mechanisms. In part of this review we present our findings on how the activation barrier in the extrusion of a macroion from a droplet can be identified.

## 2. Rayleigh model for droplet instability

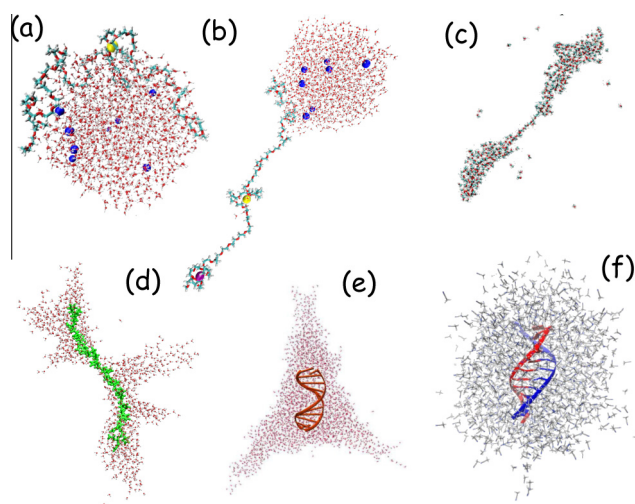
Lord Rayleigh [4] considered a model of a conducting droplet of radius  $R$  subject to small perturbations from the spherical shape. The surface of the droplet is expressed as:

$$\rho(\phi, \theta) = R + \sum_{l>0, m_l} a_{l,m} Y_{l,m}(\phi, \theta) \quad (1)$$

where,  $Y_{l,m}$  are the spherical harmonic functions,  $R$  is the  $l = 0$  term in the expansion of  $\rho(\phi, \theta)$ . Note that, in general, droplet volume conservation imposes the condition  $R < R_0$  where  $R_0$  is the radius of the unperturbed spherical droplet.  $a_{l,m}$  is the amplitude of  $Y_{l,m}$  term in the expansion of the surface in terms of the spherical harmonics.

The energy of a charged droplet ( $E$ ) is the sum of surface energy ( $E_{surf}$ ) and electrostatic energy ( $E_{coul}$ ) expressed as:

$$E = \sigma A + \frac{1}{2} Q \Phi \quad (2)$$



**Fig. 1.** Typical snapshots from molecular simulations [23,25–27,32,33] of droplets containing a macroion and complexes of macroions. Two states (a) solvated and (b) extruded solvated poly(ethylene) glycol (PEG) from an aqueous droplet with Na<sup>+</sup> ions charge carriers. The Na<sup>+</sup> ions can be transferred between the droplet solvent and the macroion [25]. The Na<sup>+</sup> ions in the aqueous droplet are represented by blue spheres, while that Na<sup>+</sup> ions captured by PEG, by a yellow and purple sphere. The extrusion of the solvated PEG occurs below the Rayleigh limit [25,33]; (c) a uniformly charged PEG in a methanol droplet induces a dumbbell shape (we call it a “pearl-necklace” shape) [27]; (d) a polyhistidine (green molecule) with bound charge in an aqueous droplet shows formation of spikes when the droplet charge is above the Rayleigh limit [23]; (e) an aqueous droplet with an embedded charged DNA shows regular formation of spikes when the charge of the droplet is above the Rayleigh limit [32]; (f) an acetonitrile droplet with an embedded charged DNA does not show as clear a formation of spikes as water when it is charged above the Rayleigh limit.

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