

Shape Oscillations and Stability of Charged Microdroplets

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(Received 22 February 2002; published 6 August 2002)

Classical Rayleigh theory predicts an instability of a surface charged liquid sphere, when the Coulomb energy E_C exceeds twice the surface energy E_S . Previously, electrified liquid droplets have been found to disintegrate at a fissility $X = E_C/2E_S$ well below one, however. We determine the stability of charged droplets in an electrodynamic levitator by observing the amplitude and phase of their quadrupolar shape oscillations as a function of the fissility. With this novel approach, which does not rely on an independent determination of the charge and surface tension of the droplets, we are able to confirm for the first time the Rayleigh limit of stability at $X = 1$ for micrometer sized droplets of ethylene glycol.

DOI: 10.1103/PhysRevLett.89.084503

PACS numbers: 47.55.Dz, 47.20.-k, 36.40.Qv

The breakup of charged microdroplets is an important process for the charge separation in electrified clouds as well as in technical applications such as electrospray ionization, fuel injection, or ink jet printing. The stability of charged droplets has been studied theoretically as early as 1882 by Lord Rayleigh [1]. He concluded that, in an incompressible charged liquid droplet, the quadrupole oscillation becomes unstable as soon as the disruptive Coulomb force is equal to the attractive cohesive force or, in terms of energies, when the Coulomb energy E_C corresponds to twice the surface energy E_S . Furthermore, Rayleigh claimed that for high charges higher multipole oscillations will become unstable and will provoke the emission of highly charged liquid in the form of fine jets. Half a century after Lord Rayleigh's publication, Bohr explained the discovery of nuclear fission [2] in terms of a classical charged droplet (here the charge is distributed uniformly through the volume) [3]. The nuclear droplet deforms through elongated shapes that, after passing a barrier, ultimately develop into two separated fragments. When the fissility ratio $X = E_C/2E_S$ becomes 1, the barrier is zero. This is the Rayleigh limit. It was immediately understood that neutron induced fission would occur for fissilities smaller than 1 through the thermal activation of the barrier. Note that the quantum nature of atomic nuclei is essential for a quantitative description of nuclear fission; nevertheless, the liquid drop feature remains qualitatively valid. Just as atomic nuclei, metal clusters can be viewed as quantum liquid drops [4]. The onset of instabilities of charged metal clusters has been studied by many groups both experimentally [5–11] and theoretically [6,12–14], and the Rayleigh model has proven to be powerful and applicable even to molecular clusters. For a review on

cluster fission, see Ref. [15]. Most often the fission of charged clusters has been observed and studied for $X < 1$ as a thermally activated process. Recently, an experimental method has allowed one to systematically approach the Rayleigh limit up to the value of 0.85 and confirmed its validity [11]. Several modern experiments addressed Rayleigh's original subject, the stability of liquid macroscopic droplets surface charged by molecular ions. In all cases, a droplet breakup below the Rayleigh limit was found [16–20]. As thermally activated fission is not effective for macroscopic droplets, it remained up to now unclear whether there exists an alternative pathway to fission which is more effective than the instability of the quadrupole oscillation.

We report here direct observations of the breakup of charged microdroplets where the amplitude and phase of forced quadrupole shape oscillations of the droplets are taken as probes for their fissility. We observe that fission occurs coincident with the divergence of the quadrupole oscillation amplitude and can therefore confirm for the first time directly the limit of Coulomb stability at $X = 1$ for charged microdroplets. Individual charged droplets of ethylene glycol with a radius of about 50 μm are produced by a homemade piezoelectric injector and are trapped in an electrodynamic levitator [21] under nitrogen atmosphere at ambient pressure and temperature. The levitator follows a well proven design [22,23] and consists of two ring electrodes (inner diameter, 10 mm; vertical distance, 2 mm) which are encapsulated in a climate chamber. The chamber has an octagonal cross section and carries the necessary ports for various optical and electrical probes as well as for a gas inlet system. In order to levitate the charged droplets, an ac voltage of about 2 kV amplitude and a frequency of

200 Hz is applied to both ring electrodes. The resultant electrical quadrupole field is rotationally symmetric around the vertical axis. A superimposed dc voltage U_{dc} between the upper and the lower ring electrode is used to balance the gravitational force on the droplet via a feedback regulator which keeps the particle centered. From this dc voltage, the mass to charge ratio of the droplets can be determined with a time resolution of 100 ms. The levitated droplets are illuminated horizontally by a HeNe laser ($\lambda = 632.8$ nm), and two types of light scattering measurements are performed: (I) The angular dependence of the scattered light intensity is recorded by a CCD camera in a range from 80° to 100° with respect to the incoming laser beam. Here both directions of polarization, parallel and perpendicular to the horizontal plane of scattering, are recorded simultaneously (phase function measurements). (II) The integrated light intensity in the same angular range is monitored continuously using a fast photodiode and a digital oscilloscope connected to a computer. While the analysis of the phase function allows us to determine the size of the droplet with high accuracy, it is limited to low time resolution due to the acquisition rate of the CCD camera (12.5 Hz). In contrast, the photodiode signal monitors the scattered light intensity in real time (rise time $\tau = 0.5$ ms) and is used for the detection and analysis of shape oscillations of the droplets, which occur with the frequency of the ac field and are discussed in more detail below. Figure 1 shows a representative measurement of the size and charge of an evaporating glycol droplet as a function of time. Size and charge have been obtained from the phase function measurements and from the balance voltage U_{dc} . It is clearly evident that initially the droplet charge remains constant while the droplet shrinks through evaporation. Then it drops instantaneously to about 75% of its original value. This implies that about 10^5 elementary charges are expelled in a single collective process. The mass loss associated with this Coulomb instability is so small that it could not be determined by our phase function measure-

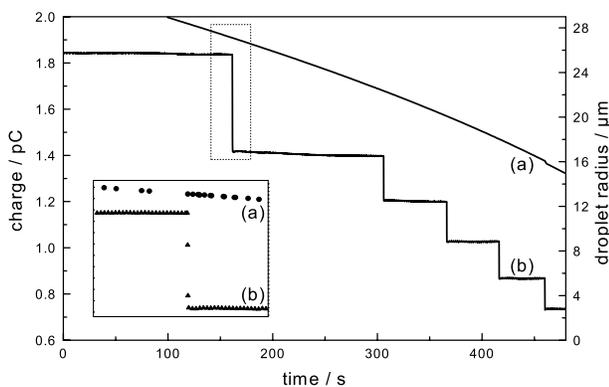


FIG. 1. Size (a) and charge (b) of an evaporating glycol droplet. The dotted region around the first Coulomb instability is enlarged in the inset.

ments (cf. inset in Fig. 1). The Coulomb instabilities repeat themselves whenever the droplet has evaporated sufficiently to reach the limit of stability again. There are no size data points given in the inset of Fig. 1 at times slightly before the instability because the analysis of the phase function becomes increasingly difficult as the droplet approaches its stability limit. This effect has been observed before [19] and we attribute it to quadrupolar shape oscillations of the highly charged droplet which are driven by the ac field of the levitator. The slow CCD camera averages over many periods of oscillation and the phase function appears distorted. In the fast light detection channel, however, the shape oscillations can be clearly resolved.

The existence and analysis of the shape oscillations is crucial for the interpretation of our measurements, and they are therefore described here in some detail. A charged sphere in a quadrupolar ac potential $\Phi(r, t) = A(x^2 + y^2 - 2z^2) \sin(\omega t)$ is driven into forced oscillations, which are conveniently described in spherical coordinates (r, θ, ϕ) by a time dependent droplet shape $r(\theta, t) = a_0[1 + \beta Y_{20} \cos(\theta)] \sin(\omega t + \phi)$, where a_0 is the radius of the spherical droplet, Y_{20} is the spherical harmonic function with $l = 2$ and $m = 0$, β is the amplitude of the quadrupole oscillation, and ϕ is the phase shift between driving field and droplet oscillation. The z axis of symmetry coincides with the vertical direction in our experiment. The equation of motion resembles that of a classical driven harmonic oscillator and was solved analytically for a vibrating, surface charged, viscous droplet [24] in the limit of small excursions. The resulting resonance curves for the amplitude and phase of the oscillation are plotted in Fig. 2 for an evaporating glycol droplet as a function of the fissility. It is important to note that a sharp increase of the oscillation amplitude together with a phase shift of $\frac{\pi}{2}$ does occur only for X values very close to 1, which is in fact Rayleigh's result. The analysis of resonance curves of that kind allows us to determine the fissility X of the vibrating droplets at the time of disintegration without having to resort to additional determination of droplet charge and surface tension.

Experimentally, we obtain the amplitude and phase of the droplet oscillation by analyzing the time resolved intensity of the scattered light. During one period of the quadrupole drive field, the droplet shape varies from spherical over prolate to oblate and back to spherical. During this motion, the rotational symmetry of the shape around the vertical axis is maintained. As the droplet is illuminated horizontally, the angular distribution of the light scattered in horizontal directions can be described in the limit of ray optics as an interference pattern between all possible rays which are reflected or refracted by the droplet within its equatorial plane. This plane remains circular even if the droplet assumes the shape of a rotational ellipsoid. Therefore, the droplet scatters the light

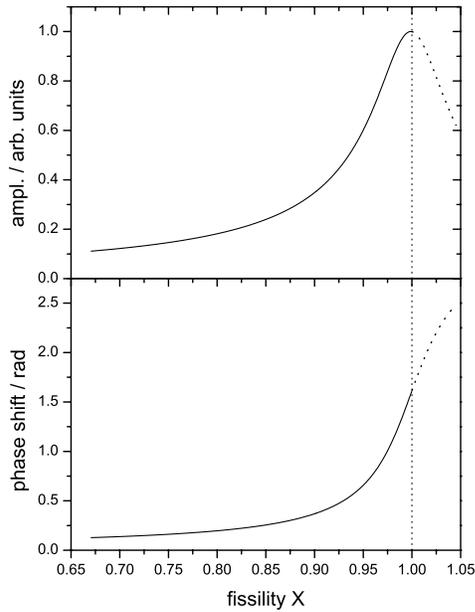


FIG. 2. Calculated amplitude and phase shift to the driving force of quadrupolar shape oscillations of a surface charged evaporating glycol droplet as a function of droplet fissility. ($a_0 = 35 \mu\text{m}$ at $X = 1$, calculation based on the work of Hasse [24].)

in the equatorial plane very much like a sphere of the same equatorial radius. This assumption, the “equivalent sphere model,” was tested theoretically for some representative configurations by ray tracing calculations and integral equation methods [25] and was found to hold very well in the size and deformation range under question. The equivalent sphere model allows one to analyze the droplet vibration with conventional Mie theory. The main features in the time dependent light scattering patterns of an oscillating droplet are intensity maxima and minima which are distributed equidistantly along the equatorial radius $r(\theta = \frac{\pi}{2}, t)$.

By analyzing the number of light scattering maxima and minima between the prolate and oblate droplet geometry, the amplitude of the quadrupole oscillation can be derived. This is illustrated in Fig. 3, which shows time resolved light scattering data from a glycol droplet approaching the Coulomb instability. At early times [Fig. 3(b)], the vibrating droplet modulates the scattered light with the drive frequency of the trap [Fig. 3(a)], while closer to the instability [Figs. 3(c) and 3(d)], the droplet undergoes several light scattering maxima and minima during one period of the drive field, as it oscillates between oblate and prolate geometry. Under these conditions, the phase shift between the drive field and the droplet oscillation is clearly visible and can be obtained quantitatively by comparison with the drive field [Fig. 3(a)]. At larger amplitude, the droplet vibration becomes increasingly anharmonic [Fig. 3(d)]. The moment of Coulomb instability is finally marked by

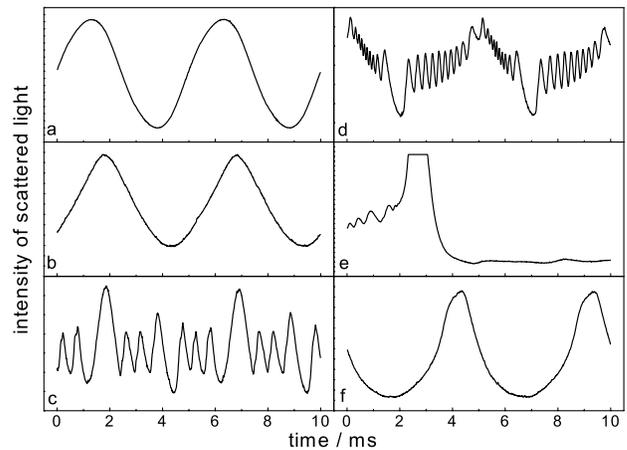


FIG. 3. Light scattering intensity during two periods of the drive field at various times before and after a Coulomb instability. (a) Drive field; for comparison, (b) $t = -268$ s, (c) $t = -55$ s, (d) $t = -2$ s, (e) $t = 0$ s, and (f) $t = 2$ s. (Times are given relative to the moment of disintegration.)

a pronounced increase in scattering intensity [Fig. 3(e)]. After this, the droplet oscillates at low amplitude again [Fig. 3(f)]. The amplitude and phase of the fundamental droplet oscillation is given in Fig. 4 as a function of time, i.e., the decreasing size of the evaporating droplet. We observe a pronounced resonance maximum which is accompanied by a phase shift of almost $\frac{\pi}{2}$ before the droplet disintegrates. By comparison with Fig. 2, we can conclude that, indeed, the droplets disintegrate exactly at or very close to 1, as was predicted by Lord

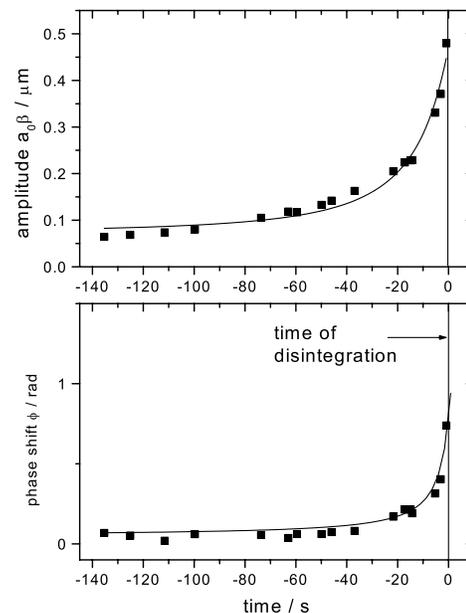


FIG. 4. Amplitude and phase of the droplet oscillation as a function of time before the moment of disintegration.

Rayleigh. For all of the droplets investigated, the instability was found to occur at X values above $X = 0.95$, independent of the size of the droplet at the moment of instability. This is in clear contrast to the previous investigations [17–20] which report a critical fissility between 0.5 and 0.7. If we evaluate our own microbalance data (compare Fig. 1) using the tabulated value for the surface tension of glycol, we find an “apparent” critical fissility of X around 0.7 as well. This implies that the surface tension of the droplets is lowered compared to the bulk liquid by the same factor. In principle, the surface tension depends on the curvature of the droplet surface and possibly on the influence of the charges on the intermolecular forces. Under our experimental conditions, however, both effects seem to be too weak to account for the observed change in surface tension. Experimentally, we find that the apparent X decreases with subsequent instabilities of the same droplet and, therefore, tentatively attribute the reduced surface tension to surface active contaminants which become more concentrated as the droplet shrinks.

We have presented a novel method for the stability analysis of charged microdroplets by driving them into quadrupolar shape oscillations. By analyzing their light scattering properties, we find that the microdroplets undergo large amplitude quadrupolar shape oscillations before they reach the Rayleigh stability limit. This is a direct proof of the Rayleigh model for charged droplets. Additionally, the method allows to determine the surface tension and viscosity of levitated liquids. This might have important applications, e.g., for the investigation of supersaturated solutions and supercooled liquids which are common in planetary atmospheres.

We thank H.J. Krappe and D. Bouche for valuable discussions and L. Wöste for his support in early stages of the project. This work has been supported by the French-German program PROCOPE (Dossier No: 00353XC).

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