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Taylor cones in a leaky dielectric liquid under an ac electric field

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Conical points of a leaky dielectric drop surrounded by a dielectric gas in an external ac electric field are investigated. A novel class of steady conical tips depending on the permittivity ratio and applied signal frequency is presented. It is found that conical solutions with very small angles are possible (angles much smaller than the classical Taylor cone angle 49.3° for a conducting drop in a dc field); this result can be relevant to the observations of small cone angles in Chetwani, Maheshwari, and Chang experiments [N. Chetwani, S. Maheshwari, and H.-C. Chang, Phys. Rev. Lett. **101**, 204501 (2008)].

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Introduction. It has been known from the works by Zeleny and Taylor [1,2] that liquid drops subjected to an external dc electric field, beyond some threshold, present conical singularities. In Ref. [2] a simple mathematical model was also developed to find the angle of the conical shape for a conducting drop. The relation for the cone angle $\theta_0 = \theta_0^T \approx 49.3^\circ$ readily follows from the balance of capillary and electrostatic pressure and the equipotentiality of the interface. In Refs. [3,4], Taylor's results were generalized for different electrical properties of two phases. In particular, the case of two dielectric phases was considered and an eigenvalue relation between the ratio of gas and liquid permittivities $\delta = \varepsilon_g/\varepsilon$ and cone angle θ_0 was derived and investigated; a critical value $1/\delta_* \approx 17.59$ was found. For $\delta > \delta_*$ a cone-type equilibrium becomes impossible; the cone angle at critical $\delta = \delta_*$ is $\theta_0^* \approx 30^\circ$. For $\delta < \delta_*$ there are two branches of solutions, $0 < \theta_0 < \theta_0^*$ and $\theta_0^* < \theta_0 < \theta_0^T$, which merge at δ_*. The problem of the ambiguity of the solution is resolved by the authors of Ref. [4] by a principle of less singularity of the electric field: The branch with smaller angles $0 < \theta_0 < \theta_0^*$ is found to be stable. In the case of a perfect conductor there is only one solution which corresponds to the Taylor cone with the angle $\theta_0^T \approx 49.3^\circ$ and the angle selection principle cannot be applied. It is interesting to notice that most experiments with dc fields are consistent with cone angles closed to the Taylor angle. According to the authors of Ref. [5] the existence of charged drops emitted from the apex of the cone can lead to a reduction of the cone angle because of repulsion and there have been observations of cone angles up to 32°. However, very small cone angles are not observed in experiments with dc that correspond to the dielectric limit. The possible explanation of this fact is that we never deal with perfect dielectrics and the liquid always contains ions from the dissociation of impurities or from the liquid itself. Hence, dielectrics, in fact, turn into conductors in dc, with a cone angle equal to 49.3°.

Recently, in certain experimental electrospray studies [6–9], it has been proposed to use a high-frequency ac, rather than dc, electric field. The advantages of such external fields are (1) the presence of a new control parameter, namely, the oscillation frequency, (2) the electric neutrality of liquid droplets formed during atomization, and (3) the absence of undesired electrochemical reactions accompanying the process at fairly high oscillation frequencies (greater than 10 kHz) because of the fact that the oscillation period is much less than the characteristic reaction time. In the experiments presented in Refs. [8,9] an anomalously small cone angle $\theta_0 \sim 11^\circ$ in a high-frequency (30–180 kHz) ac field is reported. A theoretical foundation to weak ac fields is offered in Ref. [10]. A preliminary analysis of conical tips in ac fields was done in Ref. [11].

In the present work, conical points of a leaky dielectric drop surrounded by a dielectric gas in an external high-frequency ac electric field are investigated. The mathematical solution for a conical shape leads to a complex eigenvalue problem connecting the signal frequency ω, the conductivity of the drop κ, the permittivity ratio δ, and the cone angle θ_0. Depending on the frequency, two limiting cases can be distinguished: at $\omega \to \infty$ the eigenvalue problem coincides with the one for the dielectric case [3] and at $\omega \to 0$ it coincides with the Taylor case of a conducting drop [2]. For a wide range of frequencies, the angles of the ac cone are found to be much smaller than the classical Taylor angle 49.3° in the dc field; this result can be relevant to the recent experimental observations [8,9].

Formulation and assumptions. The governing equations are presented in the spherical coordinate system r, θ, for the axially symmetric case. To assume that we have a given (conical) shape in the presence of ac forcing, the frequency of the applied signal ω should be much greater than the reciprocal of the typical mechanical time. For the viscous dominated case, the typical mechanical time is given by $t_m = \eta\ell/\gamma$ and for the inertial-dominated case this time is $t_m = (\rho_m \ell^3/\gamma)^{1/2}$, where η and ρ_m are the dynamic viscosity and mass density of the liquid, γ is the surface tension, and ℓ is a typical distance of the drop. Typically, this implies that the applied ac electric fields have frequencies much greater than 1 kHz for millimeter drops.

In the bulk liquid, the electrical current $\mathbf{j}$ is given approximately by Ohm's law, $\mathbf{j} = \kappa\mathbf{E}$ (i.e., we assume the leaky dielectric model [12]). At low frequencies (<100 MHz) the electromagnetic equations reduce to the quasi-electrostatic limit [13]. In addition, we assume that the convection current can be neglected when compared to the ohmic current. Thus we assume that the electrical Reynolds number, defined as $\varepsilon v/\ell\kappa$ [14], is negligible (v is a typical velocity). Assuming that κ and ε are independent of time, the equations that govern the electric fields are

$$\nabla\cdot(\varepsilon\mathbf{E})=\rho,\quad \nabla\cdot(\kappa\mathbf{E})=-\frac{\partial\rho}{\partial t},\quad \nabla\times\mathbf{E}=0. \tag{1}$$

As the applied voltage is an ac signal of angular frequency ω, we use complex amplitudes for the electric field $\mathbf{E}(t)=\hat{\mathbf{E}}e^{i\omega t}+\text{c.c.}$ and the potential $\Phi(t)=\hat{\Phi}e^{i\omega t}+\text{c.c.}$ Combining the equations, the electric potential phasor satisfies $\nabla\cdot((\kappa+i\omega\varepsilon)\nabla\hat{\Phi})=0$. For a homogeneous liquid, we obtain the Laplace's equation. The same equation holds for the gas phase in the absence of space charge, and we have $\nabla^2\hat{\Phi}=0$, $\nabla^2\hat{\Phi}_g=0$.

The boundary conditions at the interface are (i) the continuity of potential, (ii) the difference between normal components of electric displacement is equal to the surface charge density σ, and (iii) the rate of increase of σ is equal to the net flow of charge into the interface. In complex notation, these boundary conditions at $\theta=\theta_0$ are

$$\hat{\Phi}=\hat{\Phi}_g,\quad \varepsilon\frac{\partial\hat{\Phi}}{\partial n}-\varepsilon_g\frac{\partial\hat{\Phi}_g}{\partial n}=\hat{\sigma},\quad -\kappa\frac{\partial\hat{\Phi}}{\partial n}=i\omega\hat{\sigma}, \tag{2}$$

where $\hat{\sigma}$ is the phasor of the surface charge. Combining these last two equations we get to

$$\hat{\Phi}=\hat{\Phi}_g,\quad \left(\varepsilon-\frac{i\kappa}{\omega}\right)\frac{\partial\hat{\Phi}}{\partial n}=\varepsilon_g\frac{\partial\hat{\Phi}_g}{\partial n}. \tag{3}$$

From the solution of Laplace's equation by the separation of variables, the potential near the tip is of the form $\hat{\Phi}=Br^{\nu}P_{\nu}(\cos\theta)$, $\hat{\Phi}_g=Cr^{\nu}P_{\nu}(-\cos\theta)$, where $P_{\nu}(x)$ is the Legendre function. Since we are dealing with complex numbers, the parameter ν is also complex. The electric field near the conical tip should be proportional to $r^{-1/2}$ so that the electrical pressure is proportional to r^{-1} and can balance the capillary pressure for a conical surface. This implies that the complex parameter ν should be taken as $\nu=1/2+iA$, where A is real.

From Eq. (3), we eventually obtain

$$\frac{1}{\delta}\left(1-\frac{i}{\Omega}\right)=-\frac{P_{1/2+iA}(\cos\theta_0)P'_{1/2+iA}(-\cos\theta_0)}{P'_{1/2+iA}(\cos\theta_0)P_{1/2+iA}(-\cos\theta_0)}\equiv F_{1/2+iA}. \tag{4}$$

Here $\delta=\varepsilon_g/\varepsilon$ is a permittivity ratio and $\Omega=\omega\varepsilon/\kappa$ is a nondimensional frequency. At fixed δ and Ω the complex eigenvalue problem (4) gives the cone angle $\theta=\theta_0$.

At $\Omega=\infty$ the imaginary part of Eq. (4) vanishes, $A=0$, and hence we obtain the dielectric limit [3,4]. Let us consider asymptotics $\Omega\to\infty$; expanding Eq. (4) into a series with respect to $A\to 0$ up to the second order $F_{1/2+iA}\sim F^{(0,0)}+iAF^{(1,0)}-\frac{1}{2}A^2F^{(2,0)}$, we come to the relation

$$\frac{1}{\Omega^2}=\frac{2(\delta^2F^{(0,0)}-\delta)[F^{(1,0)}]^2}{F^{(2,0)}}. \tag{5}$$

Here superscripts denote the derivative with respect to ν at $\nu=1/2$.

As $\Omega\to 0$, we can see from Eq. (3) that the normal derivative inside the liquid should go to zero and this implies that the potential is constant in the liquid, the system behaves as a conductor.

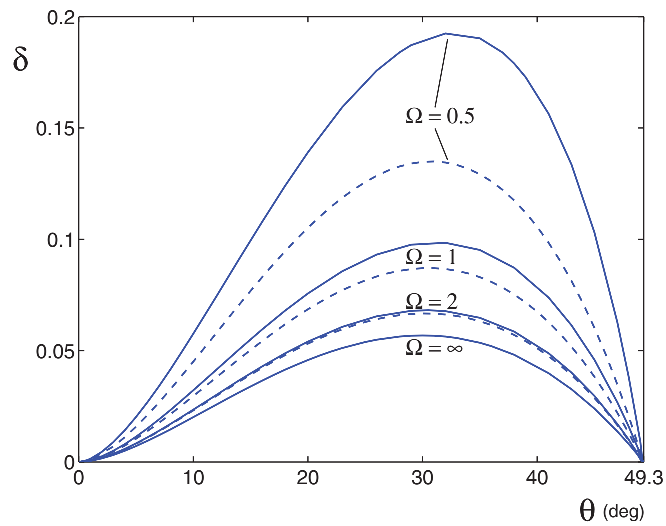

FIG. 1. (Color online) Cone angle dependence on the permittivity ratio δ with Ω taken as a parameter. Solid lines denote the exact solution of Eq. (4), dashed lines denote asymptotics (5)

Figure 1 shows the permittivity ratio δ as a function of cone angle θ_0 for different values of Ω. For a given Ω, the function $\delta=\delta(\theta)$ is zero at $\theta_0=0$ and $\theta_0=49.3$ and has a maximum value δ_m. The behavior is similar for all frequencies with increasing δ_m as Ω decreases. The perfect dielectric case [3] is re-obtained at $\Omega\to\infty$. As $\Omega\to 0$ the curve $\delta(\theta_0)$ goes to infinity, while the terminal points ($\theta_0=0$ and $\theta_0=49.3$) are "anchored" at their positions. Hence, at a finite δ and small Ω the conductor case $\theta_0=49.3$ is realized. Incidentally, the limit $\theta_0=0$ is not a limiting solution for perfect conductors, which are equipotential, since the fields near an equipotential point of a very small angle have a stronger singularity than $r^{-1/2}$ ($E\sim r^{-1+\epsilon}$, with $\epsilon\ll 1$ [15]). At $\Omega\geqslant 3$, the asymptotics (5) coincides within graphical accuracy with the exact solution.

The maximum value of the permittivity ratio δ_m is depicted as a function of Ω in Fig. 2. At small Ω it becomes unbounded

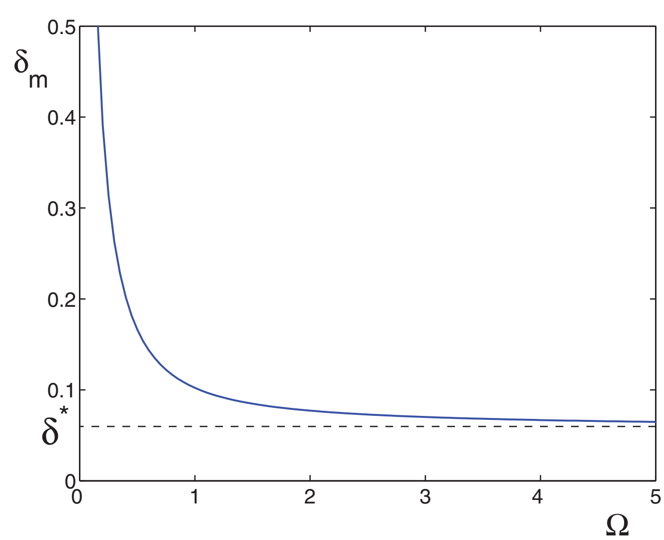

FIG. 2. (Color online) Locus of extremal points in Fig. 1. Conical solutions exist below the line $\delta_m(\Omega)$.

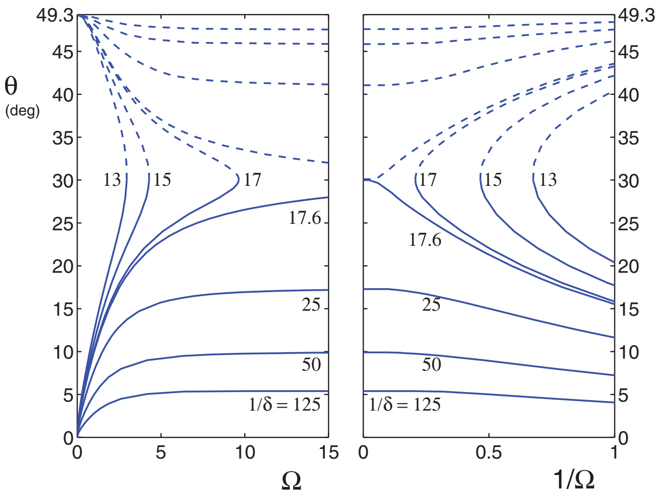

FIG. 3. (Color online) Cone angle dependence on the frequency Ω with permittivity ratio taken as a parameter. Solid and dashed lines refer, respectively, to stable and unstable solutions

while at large Ω it tends to the asymptotic value δ_*. Thus, for a given value of Ω, conical solutions are only possible for $\delta < \delta_m$, which opens the possibility of experimental research on the transition to conical shape using Ω as a parameter.

It is instructive to depict the cone angle dependence on frequency for a given δ (see Fig. 3). For $1/\delta < 1/\delta_* \approx 17.6$ the domain of existence is finite, for $1/\delta > 1/\delta_*$ it is infinite. There are two branches of conical solutions for a given δ. To evaluate the stability of these solutions, let us apply the arguments presented in ref. [4]. The larger angles correspond to an unstable equilibrium because a small disturbance decreasing the angle will cause a more singular electric field ($E \propto r^{\nu-1}$ with $\nu < 1/2$), which implies a greater electrical pressure at the tip, and eventually the disturbance will grow. Similarly, a disturbance which increases the angle will cause a less singular electric field and eventually the disturbance will also grow. The branch with a smaller angle is stable with respect to small angle disturbances [4]. The solid and dashed lines in Fig. 3 refer, respectively, to stable and unstable solutions. As observed in Ref. [16], this argument is rather puzzling because it predicts that the static Taylor cone is unstable, which is the angle observed in experiments in dc. However, it is true that very close to the cone tip an emitted jet is almost always observed with dielectric liquids and so Taylor cones are not entirely static. The arguments were applied to the case of a perfect dielectric in a dc field with a prediction of the realization of the smaller angles. Interestingly, parallel experiments on ferrofluid drops in static magnetic fields seem to show these small cone angles [17]. Static dielectric cones should be difficult to observe in dc fields because any dielectric liquid always contains a small amount of impurities that tend to dissociate into ions to some degree and the liquid acquires a certain conductivity. Therefore, dielectrics are leaky dielectrics, in general, and behave as conductors in dc. On the other hand, in the ac case ions do not have time to charge the interface if the frequency is much higher than the reciprocal charge relaxation time of the liquid ε/σ and very small angles can be realized experimentally [8,9]. In other words, in the ac case there is a control parameter, the frequency Ω, which allows variation of the cone angle.

Comparison with experiments. Experiments [8,9] seem to support the theoretical finding that conical surfaces with much smaller angles than the Taylor cone angle can be obtained. In Ref. [9], three organic liquids were used: acetonitrile ($1/\delta = 37.5$), ethanol ($1/\delta = 24.5$), and isopropanol ($1/\delta = 18.3$). The frequency of the applied signal was changed from 80 to 180 kHz and the observed cone angles were from 8° to 11°. To observe the dc Taylor cone, the conductivity of isopropanol and acetonitril was increased from 7×10^{-4} S/m up to $\kappa = 40 \times 10^{-4}$ S/m by adding an NaCl salt solution. If we look at the theoretical curves of Figs. 1 and 3, there are steady solutions with angles around 10° for nondimensional frequency $\Omega \sim 1$ for these permittivity ratios. For instance, $1/\delta = 18.3$ shows a solution of the cone angle equal to 10° at $\Omega \approx 0.5$. Taking a signal frequency of 120 kHz, this implies that the conductivity of the liquid should be 2.4×10^{-4} S/m, which is not far from the value of 7×10^{-4} S/m. The corresponding theoretical cone angles for infinite frequency (the dielectric limit) are 12° for $1/\delta = 37.5$, 16° for $1/\delta = 24.5$, and 23° for $1/\delta = 18.3$. For finite values of frequency smaller angles can be realized and, therefore, these steady conical solutions can correspond to the experimental observations in ac. Although the existence of charged drops emitted from the apex of the cone can lead to a reduction of the cone angle [5], and cone angles have been observed from 49.3° to 32° in experiments in dc, this angle range is still far from the observations in ac around 10°. We claim that the novel class of steady conical solutions presented in this work can be relevant to the observations of small cone angles in ac fields.

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