Bouncing of charged droplets: An explanation using mean curvature flow

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Two oppositely charged droplets of (say) water in e.g. oil or air will tend to drift together under the influence of their charges. As they make contact, one might expect them to coalesce and form one large droplet, and this indeed happens when the charge difference is sufficiently small. However, Ristenpart et al discovered a remarkable physical phenomenon whereby for large enough charge differentials, the droplets bounce off each other as they make contact. Explanations based on minimisation of area under a volume constraint have been proposed based on the premise that consideration of surface energy cannot be sufficient. However, in this note we explain that on the contrary, the bouncing phenomenon can be completely explained in terms of energy, including an accurate prediction of the threshold charge differential between coalescence and bouncing.

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Droplet motion induced by electrical charges has been extensively studied at least since the 19th century (see e.g. [1]; for an overview and list of references, see [2]). Such a process occurs in a wide variety of applications such as storm cloud formation, commercial ink-jet printing, petroleum and vegetable oil dehydration, electrospray ionization for use in mass spectrometry, electrowetting and lab-on-a-chip manipulations (see e.g. [3–11]), most of which are only partially understood.

In this note, we are interested in the physics of two droplets of a conductive fluid such as water, that move within a somewhat electrically insulating immiscible fluid such as oil. The precise sizes of the droplets are not important, and we will initially consider a column of water as one of the droplets, supporting a layer of oil above, and a charged droplet of water within the oil (see the left-hand side of Figure 1). Under the influence of the charge difference the water droplet will then approach the water column until they touch, at which point one might expect the droplet to be absorbed into the water column. While this absorption does indeed occur when the droplet's charge is small enough, it is a remarkable discovery of Ristenpart et al [12] that highly charged droplets tend to *bounce off* the water column. This is illustrated in the experimental observations of Ristenpart et al that can be found in Figure 1, in which the charge arises from a voltage gradient introduced across the oil. Various explanations have been given for this phenomenon [2, 12] starting with the premise that dynamics driven by surface tension would always lead to coalescence. However, the purpose of this note is to explain that on the contrary, the bouncing/coalescing can be explained purely by postulating that after touching, when the charge difference disappears, the droplets move solely to reduce their surface area/energy as quickly as possible. We are then able to invoke some deep ideas of the so-called *mean curvature flow* as we explain below.

Our starting point is the well-understood principle that as the droplets approach each other, they deform into a conical shape (cf. *Taylor cones* [13–19]) under the influence of the differing charges, and as they touch, the droplets will look locally like a double cone with a thin connecting bridge, as illustrated in Figure 2. Experiment shows [12] – see Figure 4 – that the cone angle θ in the regime we are considering (see Figure 3) is proportional to the field strength, and that there is a critical threshold angle θ_C below which one observes coalescence, and above which one observes bouncing, independently of the choice of fluids. The diagram in Figure 4 suggests that the critical contact angle θ_C should be about 27°.

Our goal in this note is to survey the theory of *mean curvature flow from cones*, which governs how a cone can evolve in order to reduce its surface area as quickly as possible, and show that the behaviour of this flow undergoes a bifurcation at a critical cone angle of 24°. We then indicate how abstract arguments prove rigorously that evolutions of the touching droplets *must* show coalescence for cones angles below the critical angle, and *must* show bouncing for angles above the critical angle.

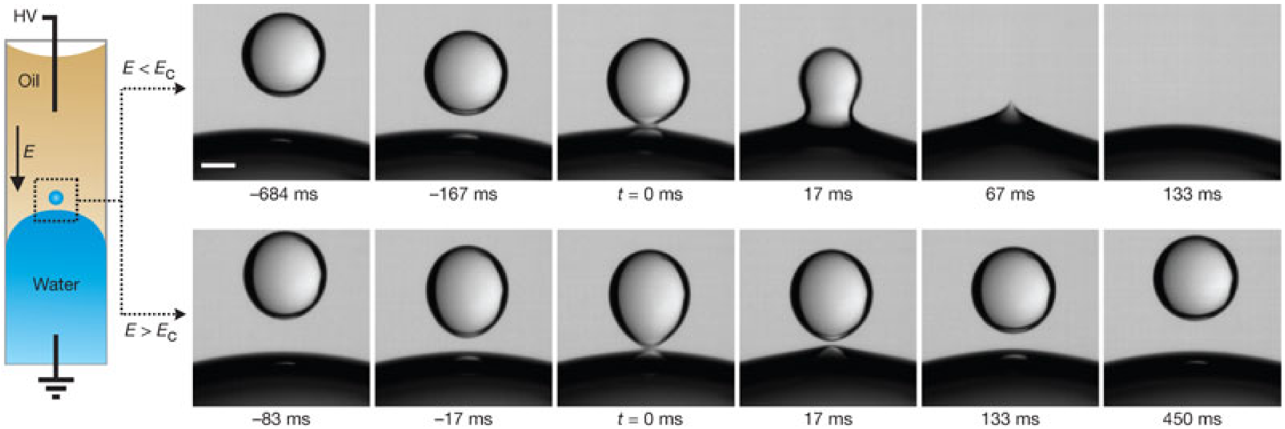
It is a feature of our approach that we need make virtually no physical assumptions or symmetry assumptions. We know from [2] that the charges are equalised at the moment of touching, and thus we postulate that after touching, the droplets evolve in order to reduce their surface area as quickly as possible. However, this evolution is occurring only *locally* in time and space, so it is irrelevant that global minimisation of surface area would always result in coalescence. Ultimately, all the subtlety of the distinction between coalescence and bouncing arises from the mathematical theory of mean curvature flow.

Consider a one-parameter family of surfaces M_t in $\mathbb{R}^3$ that can be viewed as the images of immersions $F_t : M \to \mathbb{R}^3$ from a fixed surface M. When the area A_t of these surfaces is finite, it evolves by

$$\frac{d}{dt}A_t = -\int_{M_t} \left\langle \vec{H}, \frac{\partial}{\partial t}F_t \right\rangle d\mu_{M_t} \qquad (1)$$

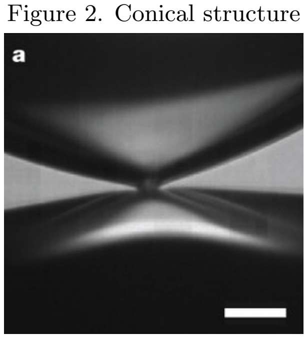
where the normal vector field $\vec{H}$ on the surface is called

Figure 1. Coalescence and bouncing of water in oil



A high-voltage (HV) provides the electric field of strength E. The top row of images shows coalescence ($E < E_C$) whereas the bottom row shows bouncing ($E > E_C$) of the water droplet. Reprinted by permission from Macmillan Publishers Ltd: Nature, WD Ristenpart et al. **461***, 377-380, ©2009, doi:10.1038/nature08294.*

Figure 2. Conical structure



As the droplets touch, they are locally conical, and form a thin connecting bridge. Reprinted by permission from Macmillan Publishers Ltd: Nature, WD Ristenpart et al. **461***, 377-380, ©2009, doi:10.1038/nature08294.*

the mean curvature (see [21, Appendix A] for a direct definition). The evolution of the surface that reduces the area as quickly as possible (more precisely the L^2-gradient flow) is then the much-studied mean curvature flow (MCF) [21] defined by the nonlinear PDE

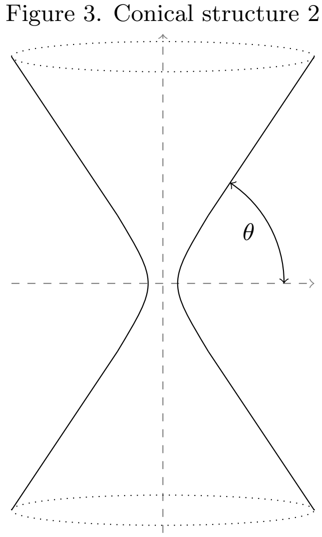
$$\frac{\partial}{\partial t} F_t = \vec{H}. \tag{2}$$

The comparison principle [21] tells us that two different solutions that are disjoint initially at time $t = 0$, will remain disjoint for later times $t > 0$.

We locally model the touching fluid droplets as follows (Figure 5 shows the construction). We rotate the function $u_\theta(x_1) := |x_1|/\tan\theta$ around the x_1 axis in $\mathbb{R}^3$ to get a double cone M_0^θ, and model the fluid bridge with an arbitrary one-sheeted surface M_0 that smooths out M_0^θ as in Figure 5.

We can solve the mean curvature flow starting with this M_0, and it will either flow for all time (corresponding to coalescence) or will develop a singularity at finite time

Figure 3. Conical structure 2

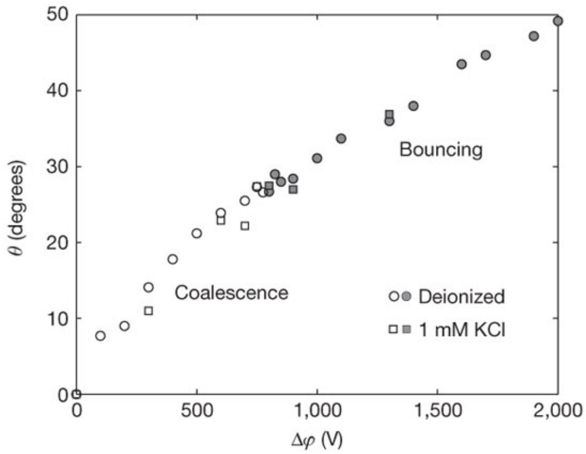


The double cone angle θ is proportional to the field strength and determines the behaviour of the system.

as the thin neck shrinks to nothing (meaning the bridge between the droplets breaks apart and we get bouncing) [24].

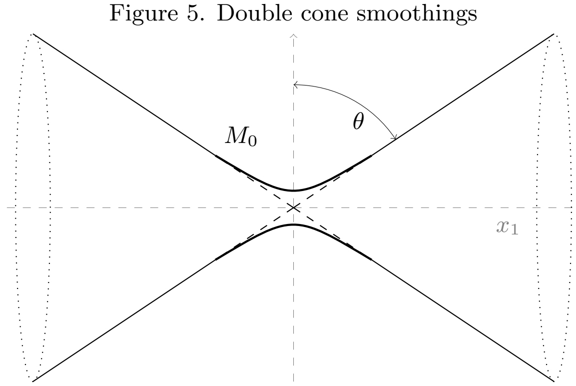
To understand which of these occurs for each θ, we consider *self-similar* solutions of the mean curvature flow starting at the double cone of angle θ, i.e. solutions M_t of the form $\sqrt{t}M_1^\theta$ where M_1^θ asymptotically approaches the double cone M_0^θ. In general, there will be many solutions of this form with the same cone as the initial surface, but if we impose the ansatz that the solution should be symmetric under rotations about the x_1-axis, and under reflections $x_1 \mapsto -x_1$, then all solutions can be classified up to the solution of a simple ODE [24, 25]. It turns out that for θ smaller than some critical value, which can be computed numerically [25] to be $\theta_C^* \sim 23.96°$, there

Figure 4. Double cone angle and potential



The contact angle θ of the double cone for water droplets in air with applied potential $\triangle\varphi$. Open symbols denote coalescence, filled symbols denote bouncing. Reprinted by permission from Macmillan Publishers Ltd: Nature, WD Ristenpart et al. **461***, 377-380, ©2009, doi:10.1038/nature08294.*

Figure 5. Double cone smoothings

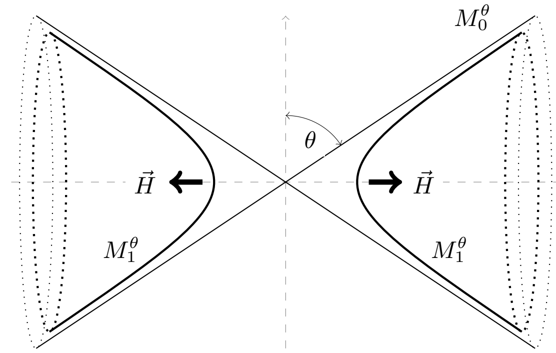


We smooth out the double cone M_0^θ in order to obtain a rotationally symmetric surface M_0, locally modeling the touching fluid droplets.

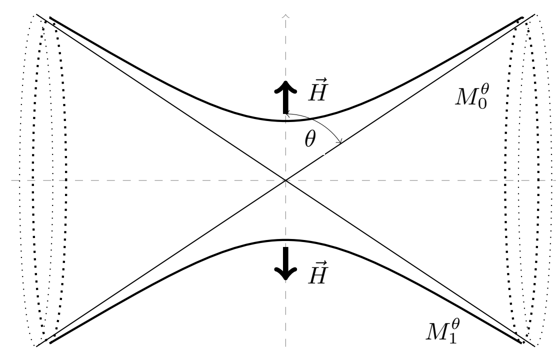
are at least two such solutions that are one-sheeted (see Figure 6b), but as θ increases to θ_C^*, these two solutions merge into one, a bifurcation occurs, and for $\theta > \theta_C^*$, there is *no* such one-sheeted solution, only a two-sheeted solution which corresponds to bouncing (see Figure 6a).

Meanwhile, a simple application of a suitable comparison principle (see [20]) *proves* that for cone angles less than θ_C^*, *any* solution of MCF starting at the smoothed cone M_0 *must* evolve as a one-sheeted solution that corresponds to coalescence (see Figure 6b.). A more subtle argument [24, 25] tells us that for cone angles greater than θ_C^*, any solution of MCF starting at M_0^θ *must* evolve as a two-sheeted solution that corresponds to bouncing (see Figure 6a.). For this latter case, one imagines an envelope of all possible solutions emanating from the cone,

Figure 6. One-sheeted and two-sheeted evolutions of double cones



a. *The two-sheeted evolution of M_0^θ exists for any angle θ. It is the unique evolution of M_0^θ for $\theta > \theta_C^*$ and corresponds to the droplets bouncing off each other.*



b. *For $\theta < \theta_C^*$ at least two one-sheeted evolutions of M_0^θ exist. These can be used as pinching barriers and therefore imply coalescence of the droplets.*

whether rotationally symmetric or not, and argues that this envelope itself must be a new, regular solution that is now necessarily rotationally symmetric. If there exists any non-bouncing solution starting at a cone, then this envelope solution must be a one-sheeted solution of the type classified above, which does not exist for cone angles greater than θ_C^* [24, 25].

Our theory therefore predicts a transition between coalescence and bouncing at a critical angle which is within a few degrees of the experimentally observed value.

Finally we want to compare our approach to the one from [2]. There it is assumed that the bridge between the touching droplets minimizes area under a volume constraint which leads to constant mean curvature surfaces of revolution (Delaunay surfaces). Similarly to our definition of double cone smoothings such a bridge is then fitted to a linear double cone and it is assumed that the sign of the mean curvature H (respectively capillary pressure) determines the behaviour. The construction is not differentiable and therefore there are several ways to fit a given Delaunay surface to a given double cone, leading to different predictions of θ_C. The way the fitting is done in [2] leads to a prediction of $\theta_C = 30.8°$.

Conclusion: We propose a new model to explain the remarkable phenomenon of bouncing and coalescence of charged fluid droplets. Our model assumes that the system after touching moves according to the mean curvature flow, which means its area decreases as fast as possible. Analyzing the flow in this setting leads to a prediction of about 24° for the critical angle, which is in good agreement with experiments. Therefore minimization of energy can, contrary to general belief, explain the phenomenon. One advantage of our approach compared to existing ones is that we do not make strong assumptions on the precise shape of the bridge between the touching fluid droplets.

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[1] Lord Rayleigh, Proc. R. Soc. Lond. 28, 405-409 (1879).
[2] W.D. Ristenpart, J.C. Bird, A. Belmonte, H.A. Stone, Phys. Rev. Lett. 103 (2009).
[3] M. Trau, N. Yao, E. Kim, Y. Xia, G.M. Whitesides, I.A. Aksay, Nature, 390(6661), 674676 (1997).
[4] M.E. Leunissen, C.G. Christova, A.P. Hynninen, C.P. Royall, A.I. Campbell, A. Imhof, M. Dijkstra, R. Van Roij, A. Van Blaaderen, Nature, 437(7056), 235240 (2005).
[5] J.C. Baygents, D.A. Saville, J. Chem. Soc., Far. Tr., 87(12), 18831898 (1991).
[6] H.T. Ochs, R.R. Czys, Nature, 327(1038), 606608 (1987).
[7] J.S. Eow., M. Ghadiri, A.O. Sharif, T.J. Williams, Eng. J., 84(3), 173192 (2001).
[8] J.B. Fenn, M. Mann, C.K. Meng, S.F. Wong, C.M. Whitehouse, Science, 246(4926), 6471 (1989).
[9] J.C. Baret, F. Mugele, Phys. Rev. Let., 96(1), 16106 (2006).
[10] D.R. Link, E.A. Grasland-Mongrain, F. Sarrazin, Z. Cheng, G. Cristobal, M. Marquez, D.A. Weitz, Ang. Chem. Int. Ed., 45(16), 25562560 (2006).
[11] P. Calvert, Chem. Mater. 13, 32993305 (2001).
[12] W. D. Ristenpart, J. C. Bird, A. Belmonte, F. Dollar, H. A. Stone, Nature 461, 377-380 (2009).
[13] G. Taylor, Proc. R. Soc. A 280, 383 (1964).
[14] D. A. Saville, Annu. Rev. Fluid. Mech. 29, 27 (1997).
[15] H.A. Stone, J. R. Lister, M. P. Brenner, Proc. R. Soc. A 455, 329 (1999).
[16] L. Oddershede, S. R. Nagel, Phys. Rev. Lett. 85, 1234 (2000).
[17] R.T. Collins, J. J. Jones, M. T. Harris, O. A. Basaran, Nature. Phys. 4, 149 (2008).
[18] J. R. Melcher, G. I. Taylor, Annu. Rev. Fluid Mech. 1, 111 (1969).
[19] J. F. de la Mora, Annu. Rev. Fluid Mech 39, 217 (2007).
[20] G. Barles, S. Biton, M. Bourgoing, and O. Ley, Calc. Var., 18,159-179 (2003).
[21] K. Ecker, 'Regularity Theory for Mean Curvature Flow.' Progr. Nonl. Diff. Equ. Appl., Birkhauser (2004).
[22] O. A. Ladyženskaja, V. A. Solonnikov, N. N. Uralceva, 'Linear and Quasilinear equations of parabolic type.' Am. Math. Soc. (1968).
[23] M. Simon, Honours thesis, ANU Canberra (1990).
[24] S. Helmensdorfer, SIAM J. Mat. An., 44, 1359-1371 (2012).
[25] S. Angenent, D.L. Chopp, T. Ilmanen, Comm. Part. Diff. Equ. 20, 1937-1958 (1995).
[26] G. Barles, S. Biton, M. Bourgoing, O. Ley, Calc. Var. 18, 159-179 (2003).