Free Oscillations and Surfactant Studies of Superdeformed Drops in Microgravity

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An unprecedented microgravity observation of maximal shape oscillations of a surfactant-bearing water drop the size of a ping-pong ball was observed during a mission of Space Shuttle Columbia. The goal of the research, of which this observation is a part, was to study the rheological properties of liquid drop surfaces on which are adsorbed surfactant molecules under conditions not possible at 1g. Numerical computation of the evolution of the shape of greatly deformed drops using the boundary integral method has successfully predicted the observed drop shapes over a complete cycle of oscillation, thereby permitting the calculation of the dynamic surface tension under these unique conditions. [S0031-9007(97)02484-8]

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Liquid drops have intrigued physicists for over a century. Absent any external force, the drop forms a sphere, which is conceptually elegant and mathematically tractable. Rayleigh [1] was the first to quantitatively investigate the modeling of drops, doing so from intrinsic as well as practical interest. Beginning with Kelvin, liquid drops, because of their simplicity and self containment, have also been conceived as paradigm models for other more complicated systems: the Earth, in the case of Kelvin's liquid "globes;" atomic nucleii, for those researchers interested in modeling questions of nuclear collisions and stability [2], and protostellar and stellar masses in astrophysics [3]. A body of theory has accumulated to describe the oscillations of such drops of pure liquid constituents, both in the linear normal mode limit [4] and in the limit of nonlinear, finite-amplitude, and mode-coupled oscillations [5].

The ideal interface and low-amplitude modal oscillation structure of such spherical drops is so well understood that any observed deviations from theory can be exploited to infer properties of multicomponent, nonequilibrium solutions. Specifically, the effects of introduction of very small concentrations of soluble surfactants to a pure liquid drop can now for the first time be quantitatively studied by solving the coupled convection-diffusion problem [6,7]. But the validation of such a theory requires both an ideal spherical drop equilibrium and a congruence of physical time scales (primarily those for mass diffusion and modal oscillation) such that the multiple effects of surface-active species dominate the fluid flow and hence the drop dynamics. This is impossible on Earth, and we have recently [8] completed a series of experiments which satisfy these idealized conditions by taking advantage of the minimal acceleration environment afforded by low Earth orbit aboard the Space Shuttle Columbia.

In the course of these experiments, an unprecedented maximal shape oscillation of a surfactant-bearing water drop the size of a ping-pong ball was observed (see Fig. 1) during the second United States Microgravity Laboratory, USML-2 (STS-73, 20 October–5 November, 1995). The observation was precipitated by the action of an intense sound field which produced a deforming force on the drop. When this deforming force was suddenly reduced, the drop executed nearly free and axisymmetric oscillations for several cycles, demonstrating a maximal amplitude of nonlinear motion. Interpretation of such motions over the full amplitude range could make possible the assessment of nonlinear surface rheological properties that transcend a surface equation of state approach. However, a full description of the nonlinear, nonequilibrium motion in Fig. 1 is beyond current analytical and numerical techniques.

A series of microgravity experiments with liquid drops was performed by scientists from Yale University, the Jet Propulsion Laboratory (JPL), and Vanderbilt University using the acoustic positioning/manipulation environment of the Drop Physics Module (DPM). The Yale/JPL group's objectives were to study the rheological properties of liquid drop surfaces on which are adsorbed surfactant molecules, and to infer surface properties such as surface tension, Gibb's elasticity, and surface dilatational viscosity by using a theory which relies on spherical symmetry to solve the momentum and mass transport equations [9]. The noncontact technique involves the acoustic squeezing and releasing of the liquid drop and the measurement of the subsequent free decay frequency and damping constant [10]. For small amplitude motion, it is desirable to excite only the lowest-order (energy) normal mode of the drop, the axisymmetric quadrupole mode, in which the drop oscillates between an oblate and prolate shape. In our chamber this oblate-prolate alternation is seen in the

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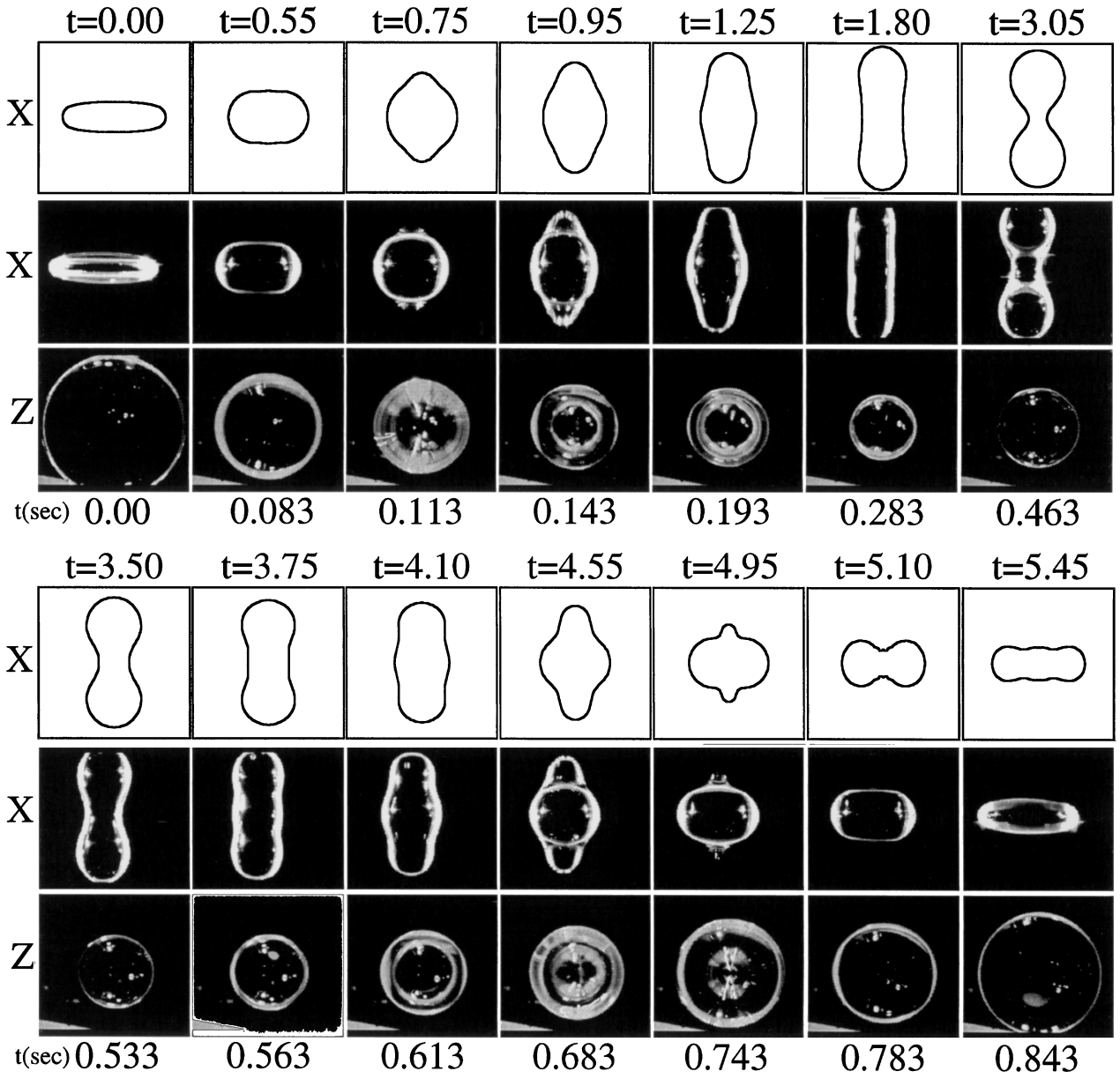

FIG. 1. Sequence of 14 frames showing single complete oscillation of a 6.6 cm^3 drop that begins in a highly deformed (oblate) shape owing to a high intensity acoustic field, and which then oscillates after the acoustic field intensity is suddenly reduced. The top images in each row are the *X* (side) view, and the bottom images are the *Z* (top) view demonstrating the axisymmetric nature of the oscillation. The time of each frame is marked. Shown above the *X* view observations is a sequence of frames computed using the boundary integral method, assuming a Reynolds number of 600. The nondimensional time *T* shown with each frame is defined in the text. Note that the last two frames of the predictions differ from the observations, because the predictions are showing the center plane of the drop (which is dimpled in), whereas the observations are showing the front view image which cannot show the inward dimpling effect.

X view of the DPM, while in the *Z* view one observes a simple circular shape.

The DPM-2 facility was designed by the Jet Propulsion Laboratory, in conjunction with the science teams at Yale and Vanderbilt, and built by Loral Corporation's electro-optical sensors division. The test section of the DPM facility is an air-filled acoustic resonator at ambient (atmospheric) pressure with inner dimensions (*X*, *Y*, and *Z*) of 12.4, 12.4, and 15.2 cm, respectively. Four custom high-amplitude, titanium-dome acoustic loudspeakers were placed in the box along the intersections of the bottom and side panels. A pair of stepper-motor-controlled injectors is used to inject and retrieve drops, ranging from 1–14 cm^3 in our experiments. A common configuration for drop manipulation consists of opposing driving speakers 1 and 3 in the (100) *X* mode, speakers 2 and 4 in the degenerate (010) *Y* mode, and all four speakers in the (001) *Z* mode, typically 1350, 1350, and 1130 Hz, respectively.

The payload crew scientists on board Columbia operated the DPM via an interactive software interface, allowing the alteration of the acoustical environment by changing speaker drive voltages, frequencies, and phases. They were supported on the ground by the payload operations team of the Marshall Space Flight Center (Huntsville, Alabama) and the DPM Science Team, which included the scientific investigators, development engineers, and support personnel. Almost continuous real-time communication between the Spacelab team and the ground team via voice, telemetry, and video was available. These links enabled results to be immediately evaluated, allowing for parameter adjustments over the course of the experiments which could not be defined before the mission, and which were absolutely essential for the carefully timed sequences that led to our observations.

From that oscillation data both the time dependent frequency of oscillation and decay constant can be retrieved. The oscillation is considered a "good one" if the Z view of the oscillation displays a circular outline for the drop which changes in size during the oscillation. This confirms the axisymmetric character of the oscillation. It is well known from both theory [11] and 1g laboratory practice [12] that pure liquid drops can be unstable to nonaxisymmetric perturbations; the asymptotic behavior of such drops is a difficult-to-analyze mixture of nearly degenerate modes (or resonantly coupled modes). Therefore, special drop handling techniques, both planned and improvised, were an essential element in retrieving "good" data. The axisymmetric character, along with the idealized spherical shape made possible by microgravity, makes data analysis straightforward.

During the Yale experiments with the DPM, we observed 82 oscillation sequences of drops of pure water or solutions of either of two surfactant materials. Drops were manipulated into a variety of static shapes and motions. The drop oscillation sequence reviewed here involved the oscillation of a 6.6 cm^3 drop (2.33 cm diam) water drop containing the nonionic surfactant Triton X-100, which is commonly used in detergents and mixing agents. The chemical formula is $CH_3C(CH_3)_2CH_2C(CH_3)_2C_6H_4E_{(n)}OH$, where $E = OCH_2CH_2$, and ranges from 9 to 10. It was saturated in the water at the critical micelle concentration (CMC)—that is, the concentration beyond which small aggregates of the material will form in the bulk of the liquid and negligible lowering of the surface tension will occur. The CMC for Triton is a minuscule 1.4×10^{-4} g/ml, at which the approximate static surface tension of this aqueous solution is 0.03 N/m (less than half that of pure water). It is thus readily apparent why these types of materials are of interest to scientists and engineers—tiny concentrations leave bulk properties unchanged, but result in marked surface viscoelastic properties, and thus alter the surface and bulk motion dramatically. The development of rational models of the behavior of surfactants is the ultimate goal of this research.

The microgravity sequence (black background) shown in Fig. 1 involved a drop that was slowly squeezed so that in the Z view the circular outline grew and the X view appeared initially as a narrow ellipse of aspect ratio of 4.5. One complete cycle is shown here, both in X and Z views, although the complete video shows about 20 cycles (in about 17 sec) before the oscillation reverts to the lowest energy quadrupole mode [13]. The cigar-shaped image of the 6th frame has an aspect ratio approaching 3, which, in the parlance of nuclear modeling is called "hyperdeformed" [14]. A second remarkable feature is that the drop did not fission. The lower surface tension that allowed for the large deformations and the surface damping afforded by the presence of the surfactant probably prevented the elongated sections from pinching off.

The oscillation in Fig. 1 is beyond the reach of analysis via methods based on small-amplitude motion found in Refs. [7] and [8]. In a preliminary attempt to determine how closely the dynamics adhered to pure fluid motion, we have performed numerical computations of the evolution of the shape of greatly deformed drops using the boundary integral method. Our version of this method [15,16] includes the external acoustic field stress, and thereby permits the study of large free or forced shape oscillations of axisymmetric drops. Surface tension is considered spatially constant in the model. Damping is including by modeling a simple bulk viscosity whose effects are primarily due to vorticity in the boundary layer. Such a lumped-element approach ignores the diffusion of the surfactant component and cannot distinguish the enhanced vorticity due to resultant surface nonuniformities in surface tension present in high-amplitude motion. Nonetheless, we wondered whether such an analysis would produce drop shapes comparable to our observations. If so, they would permit us to extract descriptive parameters such as the dynamic surface tension, which can differ from the statically measured value. Such differences, when they occur, indicate departures from pure-fluid behavior, and in the case cited would clearly indicate the presence of surface tension nonuniformities due to the nonequilibrium distribution of surfactant molecules.

Figure 1 also shows the predictions of the shape oscillations using the boundary integral method (X view). These frames are displayed above the corresponding observations. The numbers indicated in each frame show the nondimensional time given by the ratio of the real time to the factor $T = a_0/v_0$, where $v_0 = (2\sigma/\rho a_0)^{1/2}$, which is the capillary wave speed. Here σ is the surface tension, ρ is the liquid density, and a_0 is the drop radius. The computation was carried out for a Reynolds number $(\rho v_0 a_0/\mu)$ of 600, where μ is the shear viscosity, taken to be about 1.5 times that of water to account for the presence of the surfactant which increases the surface layer damping. The procedure for introducing

damping, which assumes that it occurs only near the surface, follows the work of Lundgren and Mansour [17]. The capillary wave speed is taken to be about 7.5 cm/s, which is estimated from the surface tension of Triton X-100 at this concentration. Interestingly, when the same calculation is carried out for infinite Reynolds number, the drop fissions. Thus, our calculation can inform future detailed investigations by fixing the correct value for the spatially averaged energy dissipation. That the shape can be fit so well indicates that inertia dominates nonuniformities in the bulk flow, an implicit vindication for the boundary-layer approach.

Analysis of the real-time measurements from USML-2 and the nondimensional time from the predictions of the boundary integral method allows one to compute a dynamic surface tension of approximately 33.5 ± 1.0 dyn/cm (0.0335 N/m), which is slightly higher than the statically measured value for a 1 CMC solution of Triton X-100 of 31 dyn/cm. A higher dynamic surface tension might be expected, because surfactant transport to the surface is a rate-limited process, and the equilibrium concentration of surfactant is not fully achieved during the period of oscillation. While surfactant molecules in a thin boundary layer near the surface can reach the surface as it rapidly expands, diffusion from the bulk will be too slow to fully replenish the boundary layer. The drop in Fig. 1 was allowed to equilibrate at the highly deformed static shape shown in frame 1, which represents a maximum surface area. Thus, an excess surface concentration of surfactant was present beyond that which would be present at spherical equilibrium. This would have the effect of mitigating any Marangoni stresses developing on the surface via surface diffusion, which occurs on a faster time scale than diffusion from the bulk. Nevertheless, the fact that the apparent dynamic surface tension differs from the static value indicates that even surface diffusion cannot compensate.

We can thus see that such an extremely nonlinear motion as that recorded in Fig. 1 is a wellspring of new information. Only with a proper model of surfactant behavior will a one-to-one correspondence between observation and prediction be possible, if at all. The maximal oscillation data set therefore becomes a standard of comparison for surfactant models. It can also be related to work with small drops (and higher oscillation frequencies) performed at 1g so that the models can be tested over at least 2 orders of magnitude in the relevant time constants of the process [7].

Finally, it should be noted that the observed maximal oscillations may provide insights into similar processes occurring in other sciences and at other scales, such as the behavior of hyperdeformed atomic nuclei or the explosion of stars. Moreover, the images of these oscillations may be viewed by some as aesthetically pleasing, reinforcing connections between motivations underlying those who contribute in science and in art.

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[1] J. W. S. Rayleigh, Proc. R. Soc. Lond. **29**, 71 (1879).
[2] A. A. Amsden *et al.*, Phys. Rev. Lett. **35**, 905 (1975); J. A. Zingman *et al.*, Phys. Rev. C **38**, 760 (1988).
[3] R. H. Durisen *et al.*, Astrophys. J. **305**, 281 (1986).
[4] W. H. Reid, Q. Appl. Math. **18**, 18 (1960); P. L. Marston and S. G. Goosby, Phys. Fluids **28**, 1233 (1985).
[5] A. Prosperetti, J. Fluid Mech. **100**, 333 (1980); T. S. Lundgren and N. N. Mansour, J. Fluid Mech. **194**, 479 (1988); O. A. Basaran, J. Fluid Mech. **241**, 169 (1992).
[6] Y. Tian, R. G. Holt, and R. E. Apfel, Phys. Fluids **7**, 2938 (1995).
[7] Y. Tian, R. G. Holt, and R. E. Apfel, "Investigation of Liquid Surface Rheology of Surfactant Solutions by Droplet Shape Oscillations: Experiments" (to be published).
[8] R. G. Holt *et al.*, J. Acoust. Soc. Am. (to be published).
[9] Y. Tian, R. G. Holt, and R. E. Apfel, Phys. Fluids **7**, 2938 (1995).
[10] H. L. Lu and R. E. Apfel, J. Fluid Mech. **222**, 351 (1991).
[11] N. Natarajan and R. A. Brown, Phys. Fluids **29**, 2788 (1986); J. Fluid Mech. **183**, 95 (1987).
[12] E. H. Trinh, P. L. Marston, and J. L. Robey, J. Colloid Interface Sci. **124**, 95 (1988); E. H. Trinh, R. G. Holt, and D. B. Thiessen, Phys. Fluids **8**, 43 (1996).
[13] A World Wide Web animated video sequence can be found at http://www.yale.edu/engineering/fac-info/apfel-data/drop.mpg.
[14] B. Schwarzschild, in "Search and Discovery," Phys. Today **48**, No. 11, 17–19 (1995).
[15] W. T. Shi and R. E. Apfel, Phys. Fluids **7**, 1545 (1995).
[16] W. T. Shi, R. E. Apfel, and R. G. Holt, Phys. Fluids **7**, 2601 (1995).
[17] T. S. Lundgren and N. N. Mansour, J. Fluid Mech. **194**, 479 (1988).