

Surface-controlled drop oscillations in space

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Abstract

Large liquid drops were deformed by an acoustic standing wave in a resonant air chamber called the Drop Physics Module, which was carried on Space Shuttle Columbia as part of the second United States Microgravity Laboratory mission. When this deforming force was suddenly reduced, the drops executed free oscillations about a perfect spherical equilibrium. Results are presented for pure water and for aqueous solutions of soluble surfactants. [PACS: 43.25.U, 47.55.Dz, 68.10.Cr, 83.10.-y]

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Introduction

STS-73 (October 20 - November 5, 1995) was the 17th flight of the Space Shuttle Columbia. The primary payload was the second United States Microgravity Laboratory (USML-2), a Spacelab module housing a series of fluids and materials science experiments designed to take advantage of the small ($\sim 10^{-6}g$, or "microgravity") residual acceleration afforded by low earth orbit. In the relative absence of thermal and buoyant convection and their effects, surface tension becomes the dominant fluid force, and ideal experiments can be performed to provide absolute and rigorous tests of fluid dynamic theories, which would be impossible on the ground.

In this Letter, we report the first results of liquid surface characterization experiments using the acoustic environment of a resonant chamber called the Drop Physics Module (DPM). The DPM facilitated positioning and manipulation of centimeter-radius free liquid drops in air. The aim was to study the rheological properties of liquid drop surfaces on which are adsorbed surfactant molecules, and to infer surface properties such as surface tension, Gibbs elasticity, and surface dilatational viscosity by using a theory which relies on spherical symmetry to solve the momentum and mass transport equations [1]. The technique involves the acoustic squeezing and release of the liquid drop, and the measure; ment of the complex frequency $\omega_n = 2\pi f_n + i\alpha_n$ of shape modal oscillations, which becomes a function of surfactant type and concentration. The Spacelab environment allows us to avoid undesirable nonlinear effects (acoustic streaming, drop deformation and strong acoustic field coupling) present in 1g experiments [2]. These ground experiment effects cause changes in ω_n which can dominate those due to surfactant effects, and render impossible a strict comparison with theory.

Theory

An initially non-spherical liquid drop will, when the deforming external force is removed, execute free decaying modal oscillations about its spherical equilibrium, which minimizes its configurational surface energy. Classic theoretical studies of the pure liquid problem are found in [3], the fundamental results being a family of eigenmodal frequencies ω_n^* for axisymmetric

oscillations of drop shape described by an expansion of the shape in spherical harmonics $Y_{nm}(\theta, \phi)$. The primary contribution to the damping is the presence of vorticity in the convective boundary layer.

Recently, mass transport and interracial rheology have been studied using liquid drops and soluble surfactants [1, 4]. A spherical liquid drop possessing a time-varying free surface is an ideal laboratory in which to conduct sensitive studies of surface-controlled flows. The exchange of dissolved surfactant material from the bulk to the surface is a two-step, rate-limited process. For some surfactants, the exchange is rapid: (hat is, both diffusion and sorption occur on a time scale short compared with surface disturbances. For others, especially long-chain molecules, the diffusive transfer rate can be the slowest step (*diffusion-controlled*), while for some protein molecules the adsorption/desorption step can be the limiting factor (*sorption-controlled*). The drop surface thus develops not only a reduced equilibrium surface tension and intrinsic viscoelasticity, but a dynamic viscoelasticity due to the rate-dependent mass transport effects. These changes are made manifest in changes in the dynamics of drop oscillations.

in [1] relations are derived between the complex frequency of the $(n,m) = (2,0)$ (*quadrupole*) oscillation mode and the surface properties of an aqueous surfactant-bearing drop. For a wide range of conditions, a limiting form is obtained for $\omega_2^2 \approx i\omega_2^{*2} (1 + \varepsilon^1)$, where ω_2^* is the Lamb frequency for the quadrupole mode, and ε^1 is the complex first-order correction term containing the surface viscoelastic parameters and implicitly containing the diffusion/adsorption mass transport relations. The model accounts for convection/diffusion of a soluble surfactant, allowing for isothermal sorption to occur between the diffusion boundary layer and the surface. The major mechanical assumptions of the theory are the requirement of a spherical equilibrium, axisymmetric oscillation and negligible external field stress. While it is possible to simultaneously satisfy only the first two on the ground, the present space experiments satisfy all three conditions. Equally important is the fact that in ground-based experiments the oscillation time scale is much shorter than the diffusive time scale, and almost always much shorter than the sorptive time scale. For the large drops described in the present experiments, the frequencies of

oscillation are low enough that, by changing the type and concentration of surfactant, we can obtain either diffusion, sorption or mixed time-scale control of the dynamics. Thus we can test parameter ranges of the theory which are inaccessible on the ground.

Description of the measurements and techniques

The module contains a rectangular resonant chamber at one atmosphere pressure with inner dimensions (X, Y, and Z) of 12.4 cm, 12.4 cm, and 15.2 cm, respectively. Custom high-amplitude, titanium-dome acoustic loudspeakers were used to drive a superposition of the three fundamental ((001) X mode, (010) degenerate Y mode, and (001) Z mode) plane-wave modes at approximately 1350, 1350, and 1130 Hz, respectively. The intersection of the pressure nodal planes of each mode is a point at the geometrical and optical center of the chamber, towards which a drop will be forced by the acoustic radiation pressure [5]. For zero or very low (<142, dB re 20 μ Pa) acoustic pressure amplitudes, the drop shape remains spherical. Our ambient conditions ranged from 139- 142 dB, balanced on all axes.

In a typical experiment run, the spherical drop is squeezed by increasing the amplitude of the Z axis mode. Then the ambient rotation, which might be about any axis, is converted into rotation about the Z axis by appropriate duty cycle control of the phase modulation of the X-Y speakers [6]. This is a delicate procedure which is followed by a reduction of the Z rotation to a minimal level, many times identically zero. At this crucial stability point, the Z axis amplitude is lowered to its original value in a single step. This sudden relaxation of the acoustic field to the conditions for a surface-tension-dominated spherical shape produced 'ringing' oscillations of the drop about the spherical shape.

Spatio-temporal information was obtained from video. Normal speed (30 fps) video is digitally analyzed frame-by-frame to obtain the total drop shape. Shape modal distributions, and the complex frequency of each participating mode can be obtained from the free decay data.

Results and analysis

Figure 1 shows a single cycle of a free oscillation of a 2.5 cm diameter water drop in DPM. The drop equilibrium was spherical to within less than 1 percent, as was the axisymmetry. We were not always so fortunate -- oscillations for liquids with low surface viscosity were often unstable to non-axisymmetric oscillations, and a precession of the axis of symmetry of the drop was also possible. Nevertheless, many drops exhibited perfect, low amplitude (2,0) mode oscillations. Figure 2 shows the change in radius along an azimuthal vector versus time for the drop in Fig. 1. A slow 0.5 Hz rotation rate was imposed on the drop to gyro-stabilize the symmetry axis. Table 1 compares the results for frequency and damping with the theoretical results for pure water. Although the effect of the rotation on the frequency is negligible (less than 0.1 % [7]), there may be an additional damping due to enhanced vorticity induced by the Coriolis effect,

Figure 3 shows three decay curves for 2.5 cm diameter drops released from the same initial deformation. Drop a) is pure water. Drop b) is water with 1.4×10^{-4} g/ml of the non-ionic surfactant Triton-X-100 (TX 100) dissolved in the bulk, yielding an equilibrium surface tension of 31 dyn/cm². Drop c) is water containing 1.0×10^{-5} g/ml of Bovine Serum Albumin (BSA) dissolved in the bulk, yielding an equilibrium surface tension of 54 dyn/cm². The amount of surfactant in both b) and c) is too small to affect bulk properties, yet both the frequency and damping of the quadruple oscillation are very different from pure water [8].

Discussion

The phenomena shown in Fig. 3 can be explained by an analysis of the time scales in the problem. During a quarter cycle of the oscillation, the deviation from spherical equilibrium creates fresh surface locally. Since this will cause a surface gradient in surfactant concentration, there will be a retarding Marangoni stress or surface tension gradient opposing the motion. The resultant damping will be increased. Surfactant mass transfer from the sublayer to the surface can mitigate this damping if a) both diffusion and sorption occur more rapidly than the convection; and b) if there is a high enough concentration of surfactant present in the sublayer (and the bulk) to replenish the surface [9].

For BSA, surface tension relaxation measurements yield a (concentration dependent) relaxation time $t_{1/2}$ of about 100 seconds for 1.0 CMC [8, 10], much longer than the period of shape oscillations. Thus, for these drop sizes and oscillation frequencies, we expect the interface to exhibit a higher damping rate. For the drop in Fig. 3c, the damping was 15 times that of pure water. We see qualitatively different behavior for TX100, which possesses short diffusion/sorption times ($t_{1/2}$ is on the order of a second, compared with t_{osc} -0.5 sec). Even though the surface tension is much less than that for BSA (as evidenced by the lower frequency), the damping is not much different than water (about 1.7 times that of water). This is because TX 100 at 1 CMC is not only a rapid diffuser, but suffers no sorption barrier such as BSA. At these frequencies, the surface concentration remains nearly uniform, able to be replenished rapidly by molecules in the diffusion boundary layer. The details of the analysis, and a comparison with the theory in [1] will be published elsewhere.

The research described in this paper was carried out under contract with the National Aeronautics and Space Administration. The authors gratefully acknowledge the efforts of the crew of S1'S-73 (K. Bowersox, C. Coleman, F. Leslie, M. Lopez-Alegria, D. Matthiesen, K. Rominger, A. Sacco and K. Thornton) in acquiring the data. We also acknowledge invaluable discussions with A. Croonquist, P. Marston, J. Reimer, K. Stebe and E. Trinh, and D.B. Thiessen for setting up a pendant drop apparatus.

Footnotes

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10. Unpublished results using a pendant drop method; see also F. MacRitchie and A.E. Alexander, *J. Colloid Interface Sci.* **18**, 458 (1963); D.E. Graham and M.C. Phillips, *J. Colloid Interface Sci.* **70**, 403 (1979); *J. Colloid Interface Sci.* **76**, 227 (1980). It is important to note that BSA, due to a reversible denaturation upon adsorption, exhibits a resistance to resorption, and this will induce a nonlinear element into the dynamics.

Table 1

Water drop diameter (cm)	Rotation Hz	$f_{measured}$ (Hz)	$f_{theoretical}$ (Hz)	$\alpha_{measured}$ s ⁻¹	$\alpha_{theoretical}$ s ⁻¹
2.07 ± 0.01	<0.1 \hat{x}	3.64 ± 0.01	3.63	0.051 ± 0.001	0.047
2.50 ± 0.01	0.5 \hat{z}	2.78 ± 0.01	2.73	0.053 ± 0.001	0.032

Table 1

Comparison of the measured frequency and damping for two different pure water drops (the 2.5 cm drop is the same as that depicted in Figs. 1 and 2) to the theoretical values for water at 20° C. The theoretical values are the classic results [3].

Figure Captions

Figure 1: Simultaneous side (above) and top view (below) of a single cycle of a quadrupole (2,0) free oscillation of a pure water drop. Time is increasing left to right. The equilibrium diameter is 2.5 cm, and the ambient sound pressure level is 142 dB (re 20 μ Pa) on all axes.

Figure 2: The decay of the normalized azimuthal radius of the drop in Fig.1 as a function of time. The data is sampled at 1/30 s. The results of fitting the data to a decay functional $Ae^{-\alpha t} \cos(2\pi ft)$ (where A is the amplitude, α the damping constant, and f the frequency) are $\alpha = 0.053 \pm 0.001$ s⁻¹, and $f = 2.78 \pm 0.01117$.

Figure 3: Decay of the azimuthal radius for 2.5 cm diameter aqueous drops with an initial deformation of approximately 20%: a), pure water; b), water with 1.4×10^{-4} g/ml Triton-X-100 dissolved in the bulk; c), water with 1.0×10^{-5} g/ml Bovine Serum Albumin (BSA) dissolved in the bulk.

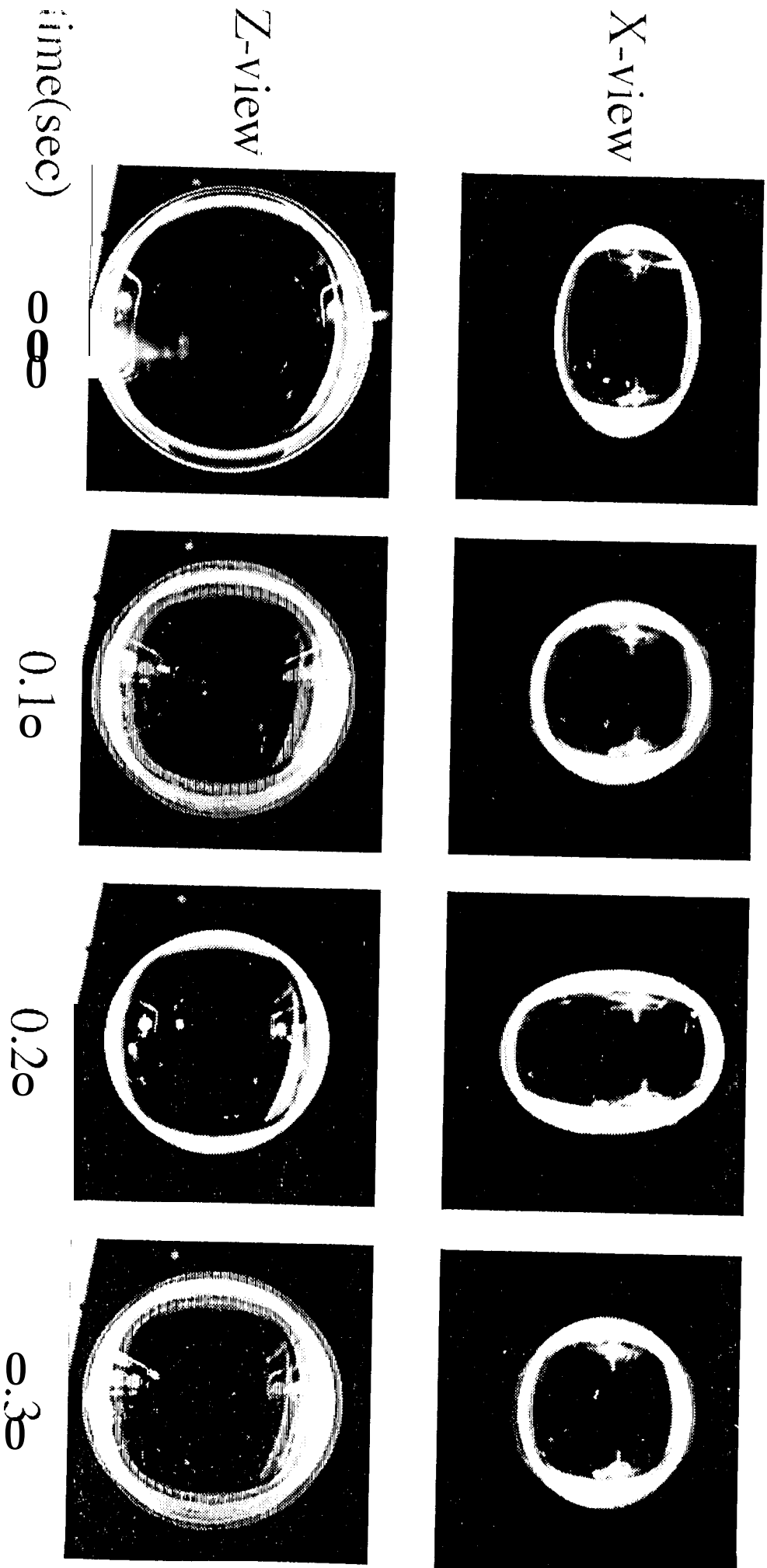


Fig. 1

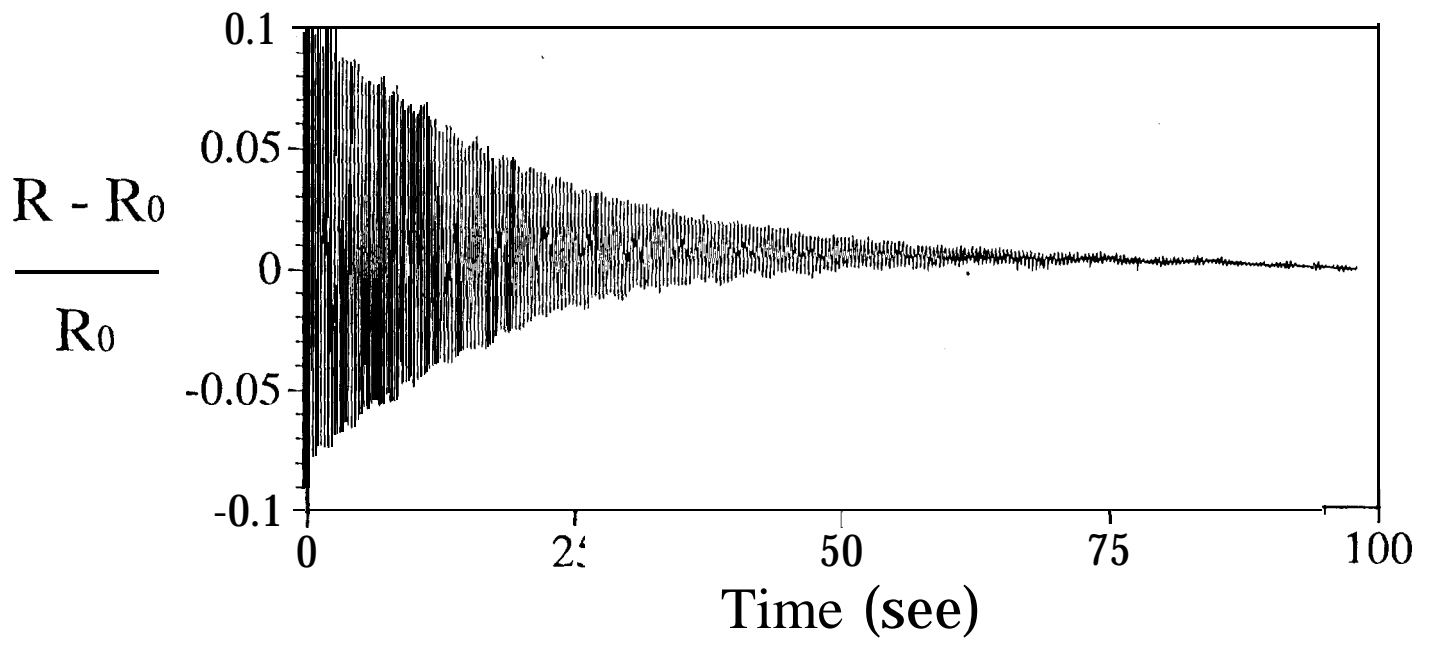


Fig. 2

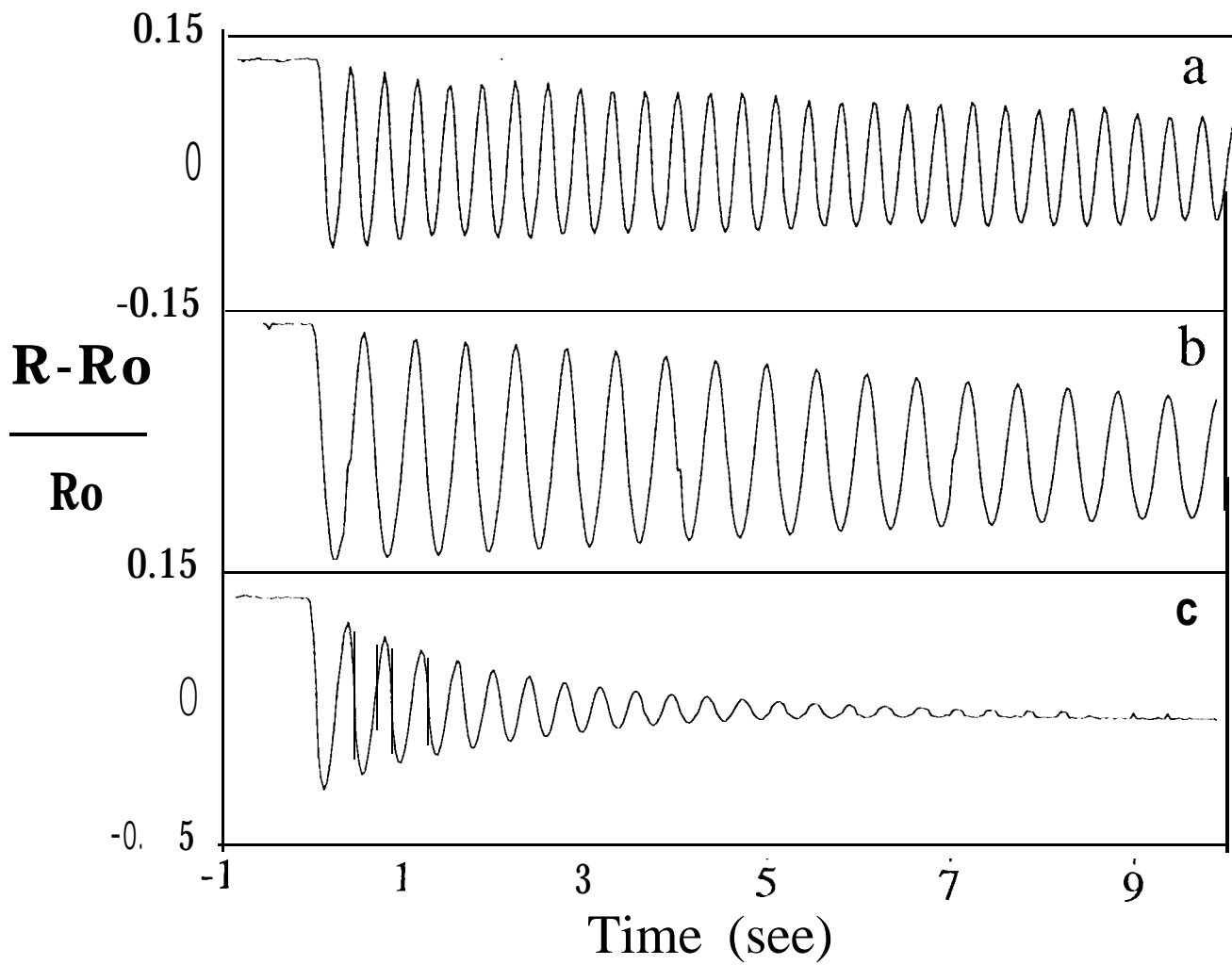


Fig. 3