Upper and Lower Bounds for Interfacial Tension using Spinning Drop Devices

D. D. Joseph, M. Arney and G. Ma[1]

In this note we show how to use spinning drop devices to determine lower and upper bounds for interfacial tension between immiscible liquids. We like the idea of upper and lower bounds because the equilibrium tension is not a robust function and depends strongly on impurities. In very viscous liquids it may be inconvenient to wait long enough to attain equilibrium values, but the bounding method is applicable. The key to lower and upper bounds for the equilibrium tension is the tension relaxation function which will be introduced after a brief review of theory which gives rise to various spinning drop devices.

A spinning drop device is a rotating container loaded with two immiscible liquids. The axis of the cylinder is rigorously perpendicular to gravity, and the constant speed of rotation of the devices is large enough so that gravity effects are negligible.

Rigid rotations of two immiscible liquids with gravity neglected are unconditionally stable when the heavy fluid is outside and the configuration of the interface minimizes a well-defined potential (Joseph and Preziosi (1)).

$$m = \int_0^L \int_0^{2\pi} T[R^2 + R_\theta^2 + R^2 R_x^2]^{1/2} - \frac{1}{8}\,[\rho]\,\Omega^2\,[R^2-\bar{R}^2]\; d\theta\, dx \quad [1]$$

where $R(\theta,x,t)$ is the radius of the bubble, $\bar{R}$ is the mean radius, L is the length of the bubble, T is the surface tension, $[\rho]$ is the density of the fluid inside minus the density of the fluid outside and W is the angular velocity. The parameter

---

[1] **Department of Aerospace Engineering and Mechanics, University of Minnesota, 107 Akerman Hall, 110 Union Street SE., Minneapolis, MN 55455, USA.**

$$J = \frac{-[\rho]\,\Omega^2\,\bar{R}^3}{T} \qquad [2]$$

is very important.

When $J > 4$ (heavy fluid outside) *m* is minimized by $R = \bar{R}$. Actually this solution can be realized only if there are end caps to restrain the expansion of the cylindrical like bubble. If the bubble is free to expand as Ω increases it will elongate with

$$J = 4 \qquad [3]$$

in an extensional flow with L increasing as $\bar{R}$ decreases. The bubble will be a long cylinder of nearly constant maximum diameter D with rounded end caps. Calculations show that when $L/D \geq 5$ we can calculate the equilibrium surface tension from [3]

$$T_{eq} = \frac{(\rho_2-\rho_1)\,\Omega^2\,D_{eq}^3(\Omega)}{32} \qquad [4]$$

where $D_{eq}(\Omega)$ is the maximum diameter of the equilibrium bubble at the given value of Ω.

Equation [4] was first derived by Vonnegut (2) and has been used for measuring interfacial tension by many authors. We own a patent on a version of the spinning drop tensiometer, which uses a central solid rod to stabilize the bubble. One of our goals is to better understand the dynamic effects which may interfere with measurement of surface tension using [4].

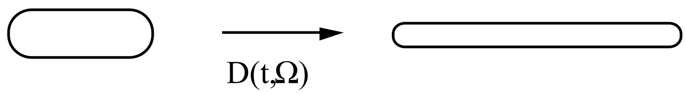
A useful *relaxation function* which can be easily measured in experiments is the maximum diameter $D(t,\Omega)$ of the evolving bubble at a fixed value of the angular velocity Ω. The value $D_{eq}(\Omega)$ which determines the equilibrium value T_{eq} of surface tension through [4] is the asymptotic value of the relaxation function

$$\lim_{t\to\infty} D(t,\Omega)\to D_{eq}(\Omega) \qquad [5]$$

The two types of relaxation, I and II below, are of special interest.

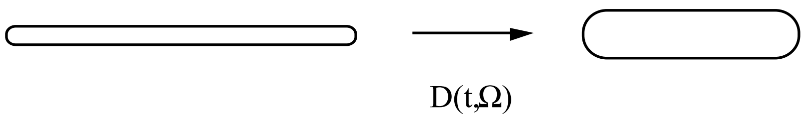
I. Overly large initial diameter

$$D(0,\Omega) > Deq(\Omega)$$



II. Overly small initial diameter

$$D(0,\Omega) < D_{eq}(\Omega)$$



To get upper and lower bounds for the equilibrium surface tension, we define a surface tension relaxation function

$$T(t,\Omega)=\frac{(\rho_2 - \rho_1)\,\Omega^2\,D^3(t,\Omega)}{32} \qquad [6]$$

The limiting value of this function as $t \to \infty$ is the equilibrium tension

$$T_{eq} = \lim_{t\to\infty} T(t,\Omega) \qquad [7]$$

independent of Ω or $D(0)$. All the relaxation functions I, for $D(0)>D_{eq}(\Omega)$, lie above T_{eq}; all those in group II, $D(0)<D_{eq}(\Omega)$, lie below T_{eq}.

You can get many different relaxation curves, depending on $D(0,\Omega)$ and Ω. They have a common asymptote, T_{eq}, as in Figure 1. Some measured values of relaxation curves giving upper and lower bounds are exhibited in Figures 2-5.

The idea of a tension relaxation function which have introduced to from our discussion of lower and upper bounds needs further study from a theoretical point of view. The main idea here is the relaxation of a <u>system</u> which is related to the problem of stability.

References:

1. Joseph, D. D. and Preziosi, L., *J. Fluid Mech.* **285**, 323 (1987).

2. Vonnegut, B., *Rev. Sci. Instrum.* **13**, 6 (1942).

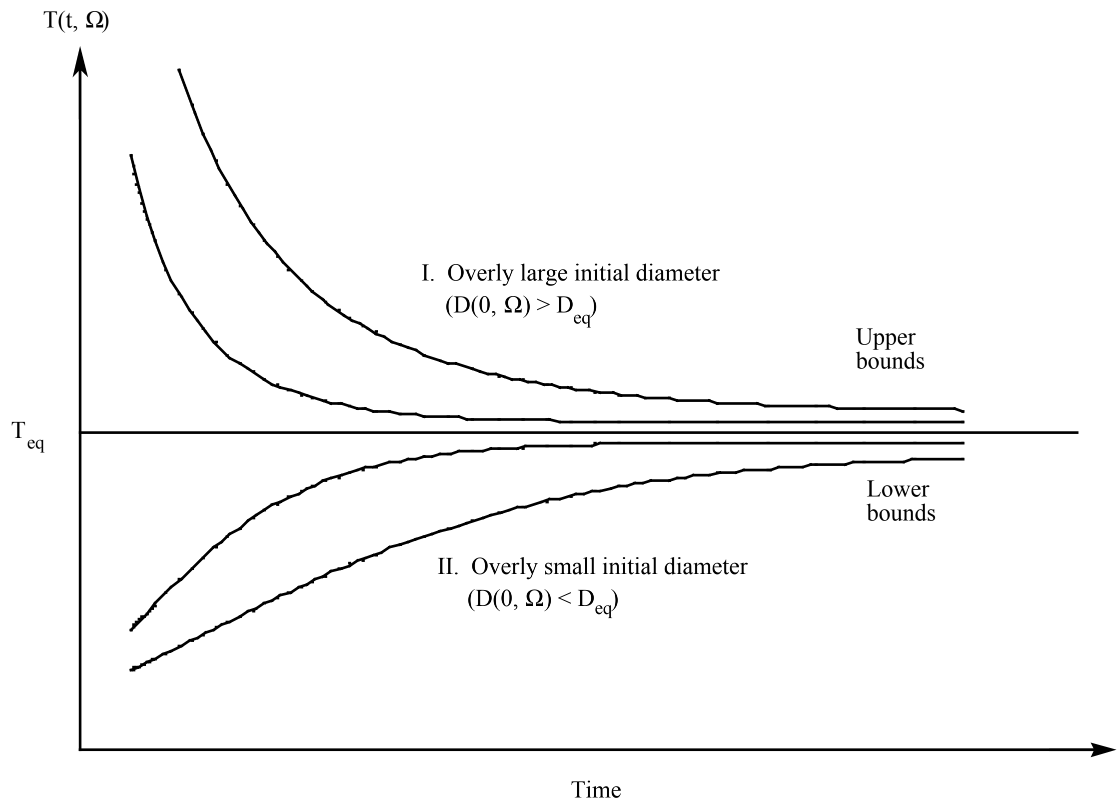


Figure 1. Surface tension relaxation function and upper and lower bounds for T_{eq}.

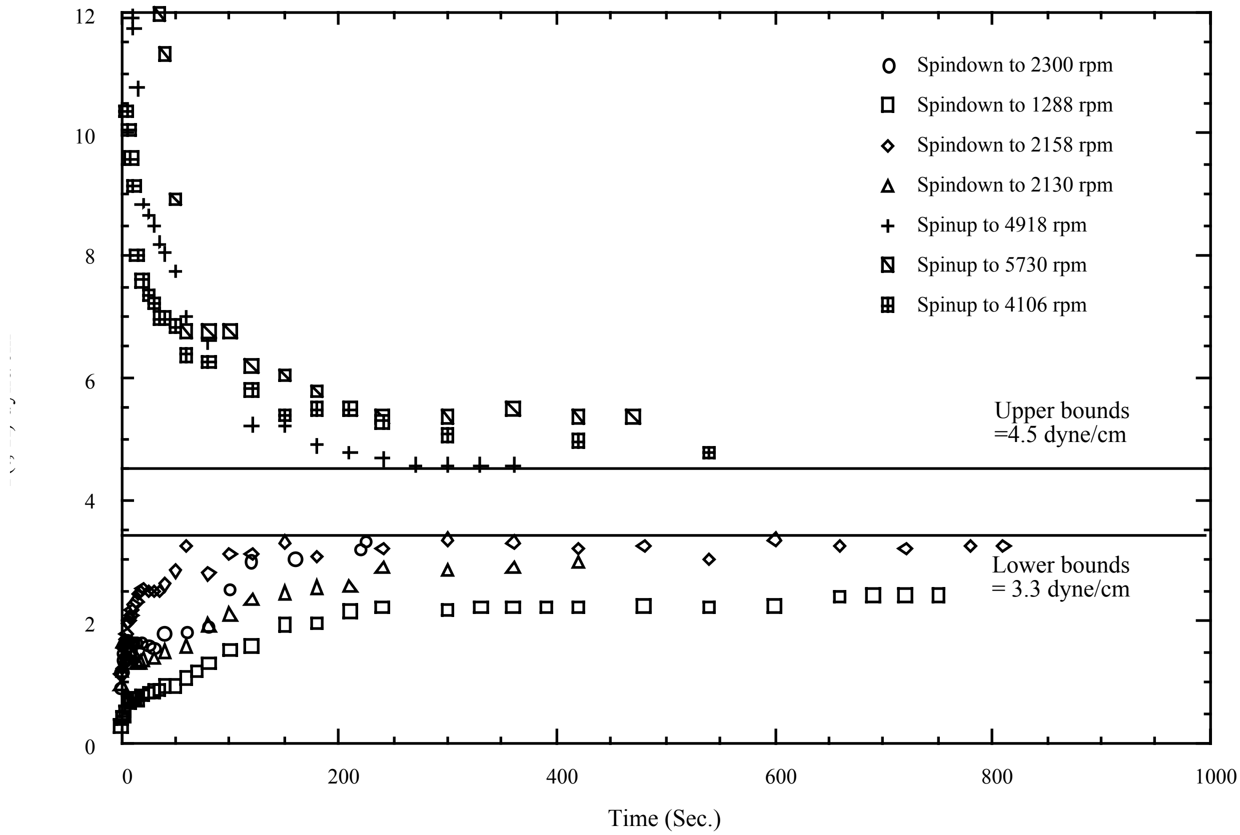


Figure 2. Surface tension relaxation function for STP in glycerol. The asymptotic value $T(t,\Omega)$ for large time is the equilibrium tension T_{eq}, a material parameter, independent of Ω or D, whose value lies between the lower bound of 3.3 dyne/cm and the upper bound of 4.5 dyne/cm.

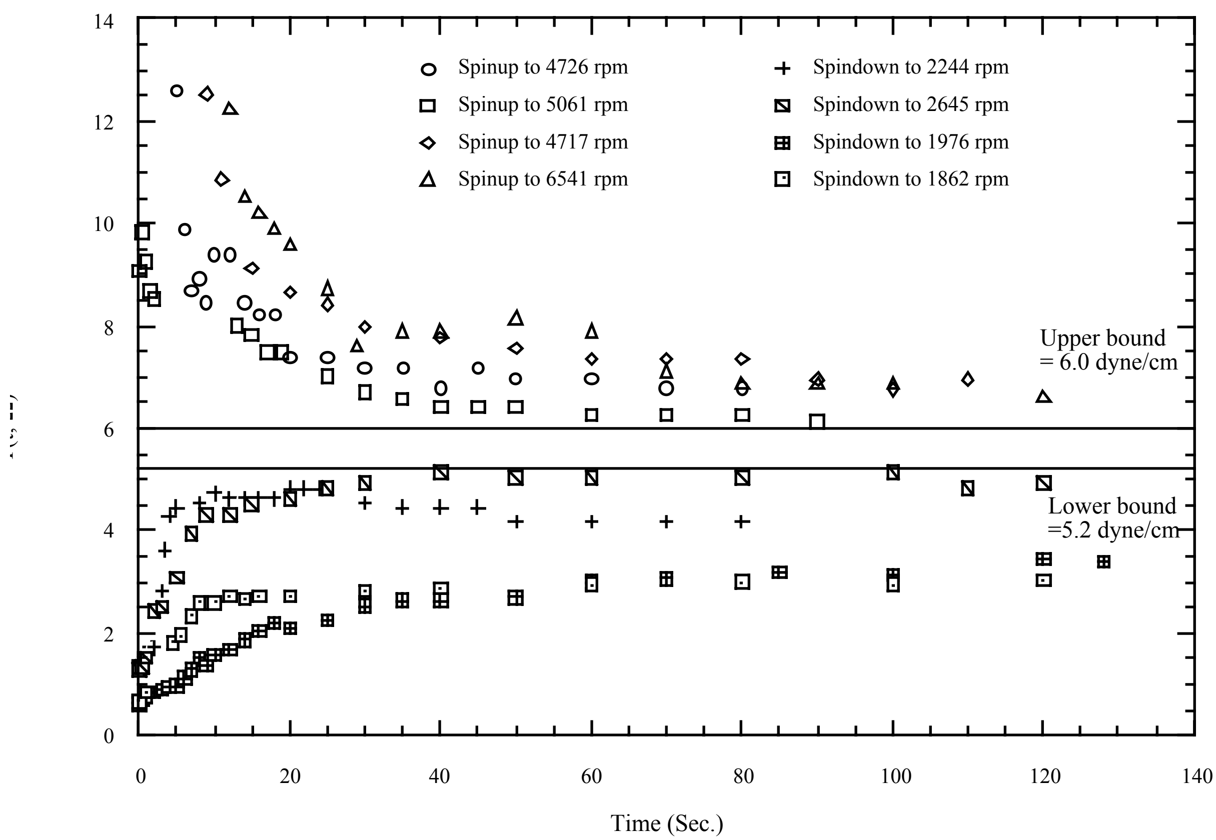


Figure 3. Surface tension relaxation function for STP in water. The value of Teq lies between the lower bound of 5.2 dyne/cm and the upper bound of 6.0 dyne/cm.

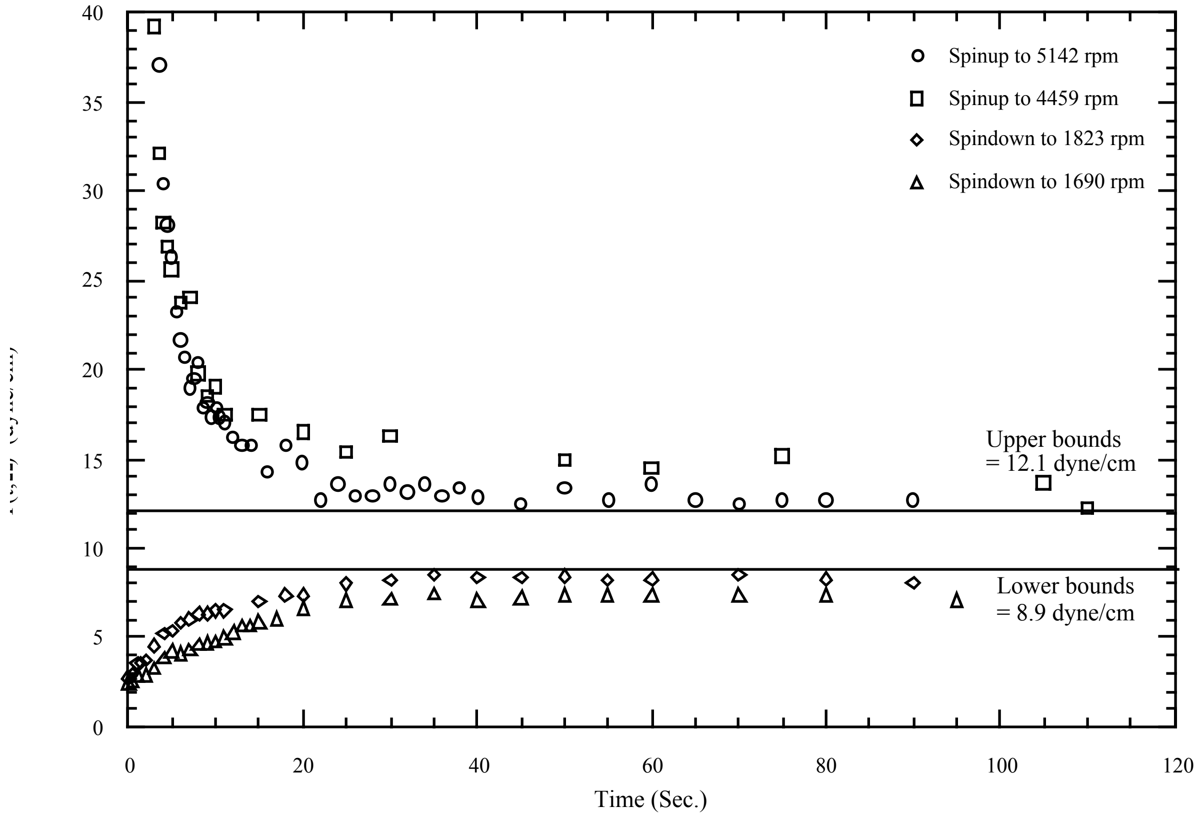


Figure 4. Surface tension relaxation function for Safflower oil in glycerol. The value of Teq lies between the lower bound of 8.9 dyne/cm and the upper bound of 12.1 dyne/cm.

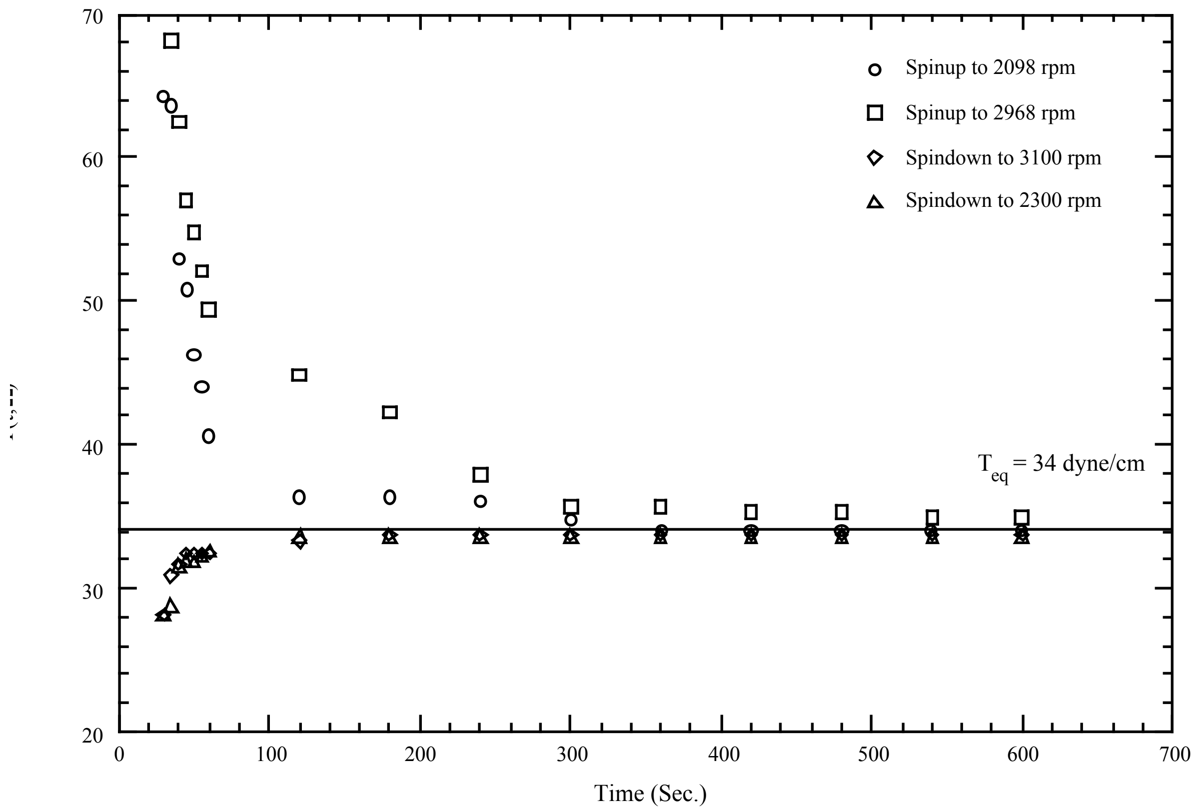


Figure 5. Surface tension relaxation function for 20 cs poly(dimethyl-siloxane) in water. In this case, the asymptotic value of $T(t,\Omega)$ for large time was achieved. This value is the equilibrium tension T_{eq}=34 dyne/cm.