Measuring surface tension with a torsional rheometer

MEASURING SURFACE TENSION WITH A TORSIONAL RHEOMETER

M. Contant
WFW 91077

Report of internship at the department of Chemical Engineering Queensland University Australia.

Eindhoven Technical University
department Mechanical Engineering

graduation professor: Prof. Dr. Ir. H.E.H. Meijer
supervisor QU: Doctor M.E. Mackay
supervisor TUE: Dr. Ir. G.W.M. Peters

september 1991

ABSTRACT

A new device to measure surface tension with a torsional rheometer is examined. With this apparatus static and dynamic measurements of the surface tension are done. The results of the tests are promising but they are over the range of applied strains too low. This might be cased by too crude approximations in the theory used to derive the surface tension from the torque or the rheologycal properties measured by the rheometer.

CONTENTS

1 INTRODUCTION

When walking along lakes, rivers and other water containing places one can observe numerous insects walking on the water. If we take a cup of clean water we are even able to let a steel needle float on the water surface despite a difference in density of a factor eight. Another experiment is pouring more liquid in a cup than the container can hold. The liquid will bulge above the rim of the container as if it has a skin which prevents it from overflowing.

These effects are a result of the phenomenon surface tension. The surface tension is a contractive force which operates around the perimeter of the surface and tries to shrink the surface. All phase boundaries behave in this way, not just liquid surfaces. However this phenomenon is more observable for the deformable liquid surfaces.

Recently a new device to measure surface tension was developed at the department of chemical engineering of the Queensland University, Australia. After an introduction in other techniques used to measure surface tension the theory behind this new device will be discussed here followed by experiments and a comparacy with one of those other techniques.

2 BASIC THEORY

2.1 SURFACE TENSION AND SURFACE FREE ENERGY.

Although referred to as free energy per unit area, surface tension may equally well be thought of as force per unit length. An example will be given here to illustrate this. Consider a soap film stretched over a wire frame, one end of which is movable, fig.2.1. Experimentally one observes that a force is acting on the movable member in the direction opposite to that of the arrow in the diagram. If the value of this force per unit length is denoted by γ, then the work done in extending the movable member a distance dx is:

$$\text{work} = \gamma * l * dx \qquad (1)$$

Equation (1) could equally be written as:

$$\text{work} = \gamma * dA \qquad (2)$$

where $dA = l * dx$ and thus gives the change in area. In this second formulation γ appears to be an energy per unit area, [1].

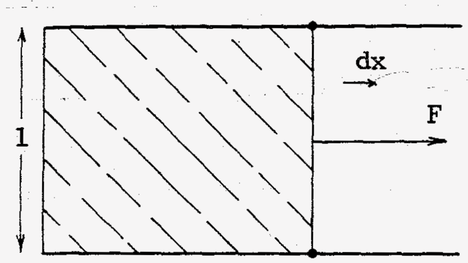


figure 2.1 A soap film streched across a wire frame with one movable side.

2.2 THE EQUATION OF YOUNG AND LAPLACE.

To describe a curved surface it is in general necessary to use two radii. A small section of a curved surface is shown in fig 2.2.

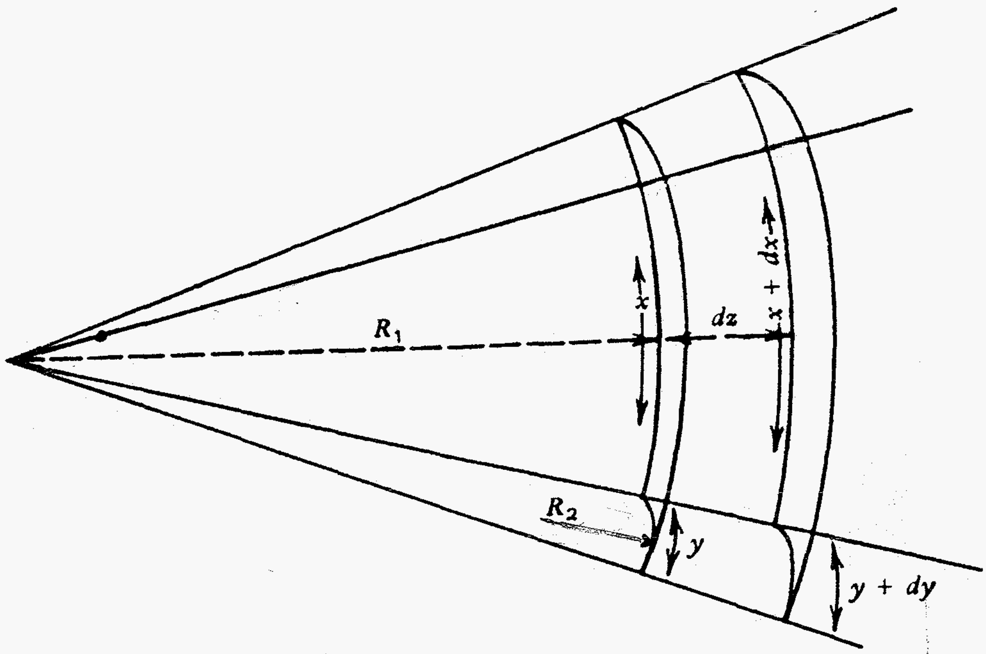


figure 2.2 curved surface.

The section of the surface is taken small enough so that R_1 and R_2 may be thought constant. Now the surface is displaced a distance dz outward, the change in area will be:

$$\Delta A = xdy + ydx \qquad (3)$$

The work done in forming this extra area is then:

$$\text{work} = \gamma(xdy + ydx) \qquad (4)$$

The displacement of the surface outward is here done by a pressure difference Δp across the surface acting on area xy through a distance dz.

$$\text{work} = \Delta p * xydz \tag{5}$$

From equality of triangles follows that:

$$\frac{x+dx}{R_1+dz} = \frac{x}{R_1} \longrightarrow dx = \frac{xdz}{R_1} \tag{6}$$

and

$$\frac{y+dy}{R_2+dz} = \frac{y}{R_2} \longrightarrow dy = \frac{ydz}{R_2} \tag{7}$$

Substitution of the last two equations in eq.(4) gives together with eq.(5) the equation of Young and Laplace.

$$\Delta p = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2}\right) \tag{8}$$

For a sphere both the radii R_1 and R_2 are equal,[8].

3 DIFFERENT TECHNIQUES TO MEASURE SURFACE TENSION

3.1 CAPILLARY RISE.

An approximate treatment of the phenomenon of capillary rise is easily made in terms of Young and Laplace equation,[1]. The liquid meets the wall at an angle θ as shown in fig 3.1. The pressure difference across the surface is given by eq.8. This pressure difference is equal to the pressure drop in the colon of liquid in the capillary. Thus $\Delta p = \Delta\rho gh$ where $\Delta\rho$ is the difference in density between liquid and gas phase. The surface is taken to be spherical in shape thus $R_1 = R_2 = \frac{r}{\cos\vartheta}$.
Equation (8) becomes:

$$\Delta\rho gh = \gamma \frac{2\cos\vartheta}{r} \qquad \gamma = \frac{\Delta\rho ghr}{2\cos\vartheta} \qquad (9)$$

For an exact solution of the capillary rise problem one must take into account that the meniscus is not a sphere everywhere. The curve must correspond to the equation $\Delta p = \Delta\rho g(h+\epsilon(r))$ at each point on the meniscus.

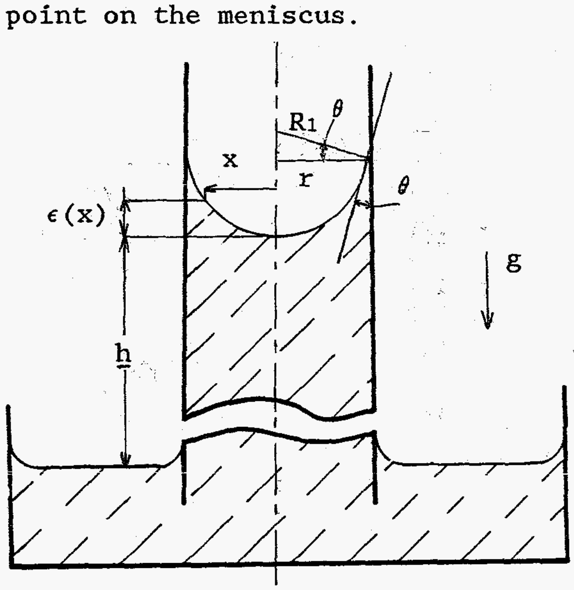


figure 3.1 capillary rise

3.2 THE MAXIMUM BUBBLE PRESSURE METHOD.

The method is, one blows slowly bubbles of an inert gas in the liquid to be examined (fig 3.2), [1]. For small tubes the shape of the bubble is always a section of a sphere. While blowing the bubble grows and its radius will reach a minimum when the bubble is half a sphere. At this point the radius of the bubble is equal to the radius of the tube. The pressure difference over the surface of the bubble will be at a maximum since the radius is at minimum.

$$\Delta p_{max} = \frac{2\gamma}{r} = p_{max} - p_0 = p_{max} - \rho g h$$

$$\gamma = \frac{r}{2}(p_{max} - \rho g h) \qquad (10)$$

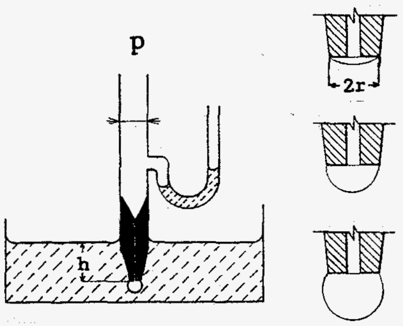


figure 3.2 maximum bubble presure method

3.3 THE DROP WEIGHT METHOD

As illustrated in fig.3.3 the procedure is to form drops of the to examine liquid at the end of a tube. The drops fall in a container until there is enough liquid collected to determine the weight per drop accurately. The weight of a drop is equal to the surface tension times the perimeter of the drop.

$$W = 2\pi r * \gamma \qquad (11)$$

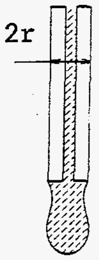


figure 3.3 drop weight method

This method needs a correction factor because the actual weight obtained is less than the ideal weight (W). The reason is that before the drop falls, it necks in and as much as 40% of the liquid may remain attached to the tube, [3].

3.4 THE RING METHOD

This method involves the determination of the force needed to detach a ring or loop of wire from the surface of a liquid.

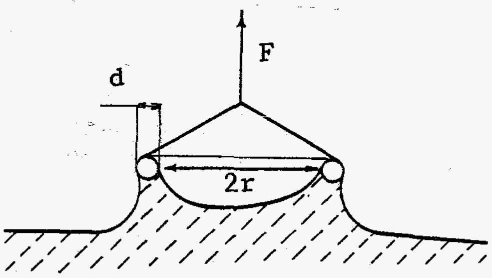


figure 3.4 The ring method: a cross section through the ring

A first approximation to detachment force is given by the surface tension times the perimeter of the ring times two. Thus:

$$F_{tot} = \text{Mass ring} * g + 2 * 2\pi r * \gamma \qquad (12)$$

Since the surface tension doesn't in general act exactly vertical a correction factor is necessary in eq.(12). More about this can be found in the literature, [1].

3.5 WILHELMY SLIDE METHOD

There is one method, attributed to Wilhelmy in 1863, that doesn't need correction factors and gives within 0.1% exact values for the surface tension, [2]. The method is that a thin plate, such as a microscope cover glass, a piece of platinum foil or a filter paper will support a meniscus. The force is very accurately given by the ideal equation (13) (assuming zero contact angle).

$$F_{tot} = \text{Mass plate} * g + \gamma * \text{perimeter plate} \qquad (13)$$

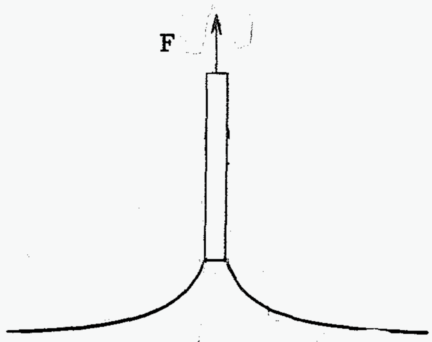


figure 3.5 wilhelmy slide method

3.6 METHODS BASED ON THE SHAPE OF STATIC DROPS OR BUBBLES

One can determine the surface tension from the shape of a drop or bubble. The bubble will tend to be spherical because surface forces depend on the area decrease as the square of the linear dimension, whereas distorsions due to gravitational effects decrease as the cube of the linear dimensions because they depend on the volume of the bubble. The procedure is to make measurements of its dimensions, for example from a photograph. The accuracy is tenths of a percent and it is possible to measure long term changes in the surface tension. For this technique only a small quantity of liquid is required, [1].

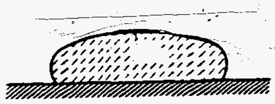


figure 3.6 shape of a drop

3.7 DYNAMIC METHODS OF MEASURING SURFACE TENSION

The above discussed methods can be used to follow the slow changes in surface tension that sometimes occurs in solutions. To study surface aging and relaxation effect on a small time scale, dynamic methods are needed, [1].

One dynamic method is the elliptical jet flow method. Here a fluid flows out of an elliptical jet. The fluid stream will be unstable. The stream prefers to have a circular cross section. Oscillations will develop when the cross section changes from elliptical to circular. This is illustrated in fig 3.7.

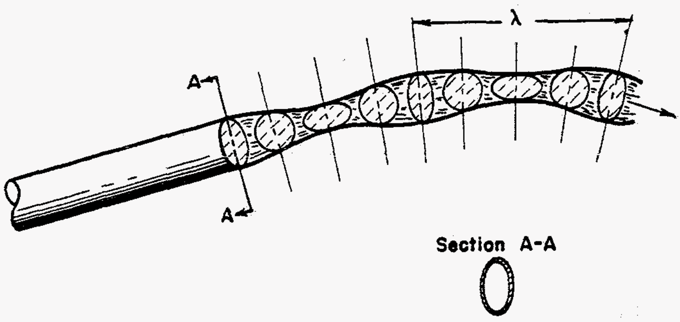


figure 3.7 oscillations in an elliptical jet.

Sutherland [5] gives the following formula

$$\gamma = \frac{4\rho\nu(1+37b^2/24r^2)}{6r\lambda^2(1+5\pi^2r^2/3\lambda^2)} \qquad (14)$$

ρ = density fluid

ν = volume velocity

λ = wave length

The sum of the minimum and maximum half diameters is called r and b is their difference.

The surface age at a given node is the distance from the orifice divided by the jet velocity. When studying surface aging of a solution of sodium di-(2-ethylhexyl)-sulfosuccinate in water one will find the following curve for the surface tension versus time.

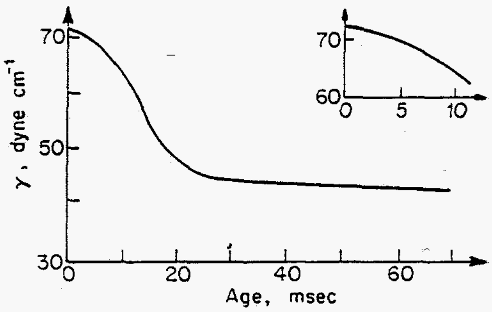


figure 3.8 Surface tension as a function of age for 0.05g/100 cm^3 of sodium di-(2-ethylhexyl)-sulfosuccinate solution

Figure 3.8 illustrates the equilibrium value of the surface tension for this solution is established after about 30 msec.

A second dynamic method is based on capillary waves. The wave length of ripples on the surface of a liquid depends on the surface tension. According to a formula given by Lord Kelvin, [1].

$$v^2 = \frac{g\lambda}{2\pi} + \frac{2\pi\gamma}{\rho\lambda}$$

$$\gamma = \frac{\lambda^3\rho}{2\pi\tau^2} - \frac{g\lambda^2\rho}{4\pi^2} \qquad (15)$$

Where v is the velocity, λ is the wave length and τ is the period of ripples.

4 SURFACE TENSION MEASUREMENTS WITH A TORSIONAL RHEOMETER

To measure the surface tension of fluids and polymers with a rheometer a new device has been developed, [6] [7]. This technique is based on the change in area. A certain amount of material is being sheared in between two steel bodies, fig 4.1. While chearing, the outer surfaces of the material are stretched. This change in area times the surface tension gives a force which is being measured via a torque on the shaft of the rheometer.

4.1 PROGRAMMING THE RHEOMETER

Because the torsional rheometer is not originally made to use this device, the rheometer has to be tricked, [6]. When using the device the geometry switch of the rheometer should be on cone and plate. In this case a cone angle and a plate radius should be provided via the terminal. The equivalent angle can be found with the following equation

$$\alpha_{cp} = \frac{h}{R_l}$$

where h is the gap between the plates, thus the thickness of the material being measured and R_l is the lever arm of the device. The equivalent disk radius can be found by assuming that the torque due to the device is the same as the torque given by a disk with the radius asked. The torque due to the device is:

$$T = \sigma_s * R_l * A \qquad (16)$$

where σ_s is the equivalent shear stress which represents the influence of the surface tension and A the surface of the device. The torque as a result of a shear stress on a disk with a radius

R_{cp} is:

$$T = \int_0^{R_{cp}} \sigma_s * 2\pi r * r dr = 2\pi\sigma_s * \frac{1}{3} R_{cp}^3 \tag{17}$$

Thus by substitution of eq.(16) in eq.(17) the equivalent cone plate radius is found.

$$R_{cp} = \sqrt[3]{\frac{3}{2\pi} * R_l * A} \tag{18}$$

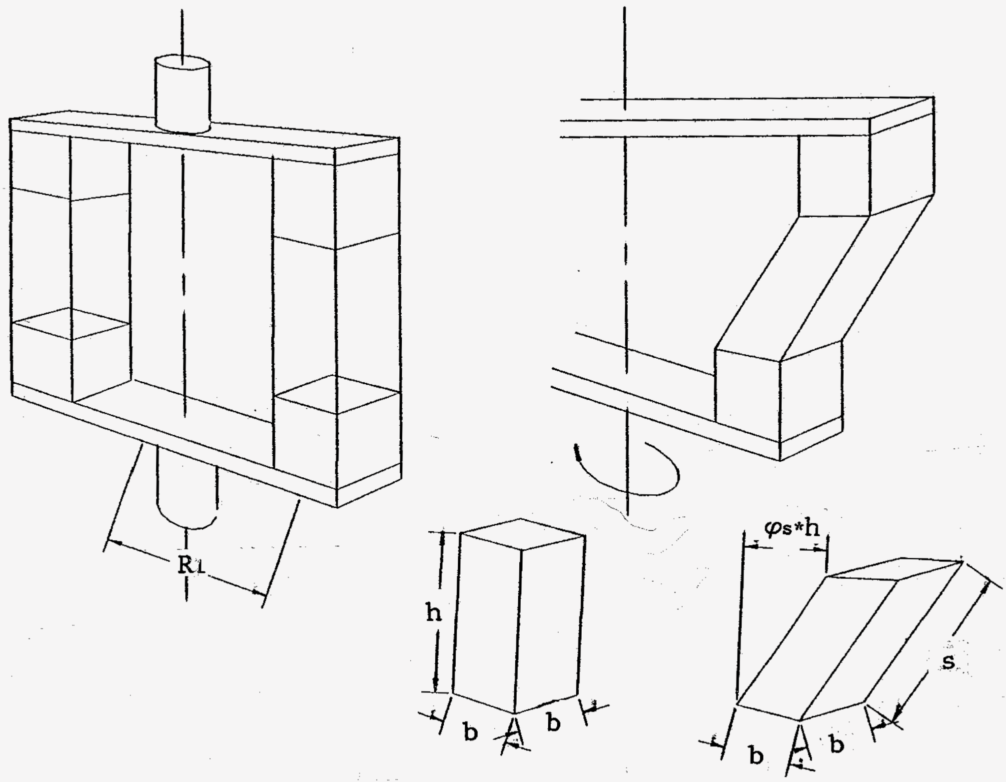


figure 4.1 device used to measure surface tension with a rheometer

4.2 TORQUE RELATED TO THE SURFACE TENSION

To calculate the surface tension equation 2 is used, [7].

$$work = \gamma * dA$$

or in this case, see fig. 4.1 and fig. 4.2:

$$F_s * ds = \gamma * dA$$

which gives:

$$F_s = \gamma * \frac{dA}{ds} \qquad (19)$$

The stretched surface is, see fig. 4.1:

$$A = 2bs + 2bh \qquad \frac{dA}{ds} = 2b$$

Then the surface force is:

$$F_s = \gamma * 2 * b \qquad (20)$$

The shear strain is the displacement of the lower body with respect to the top body divided by the gap height (or the angle θ over which the lower plate of the rheometer turns times the lever arm, divided by the gap height), (see fig. 4.2).

$$\varphi_s = \frac{\theta * R_L}{h}$$

The output of the rheometer is the torque. Equation 20 gives in terms of torque and surface tension, (see fig 4.2).

$$T = F_t * R_L * 2 = F_s * \frac{\varphi_s}{\sqrt{1+\varphi_s^2}} * R_L * 2 \qquad (21)$$

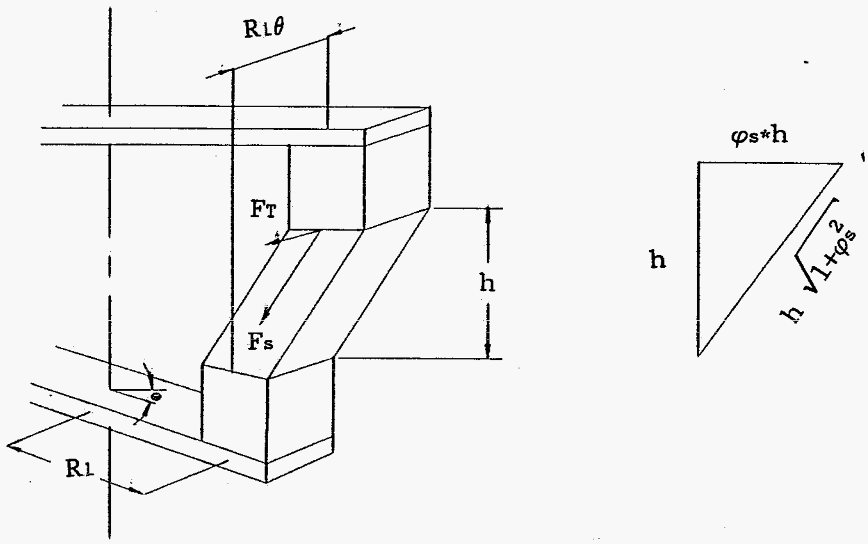


figure 4.2

Note the device has two cubes of material which are being stretched, thus:

$$T = 4*b*R_L*\gamma * \frac{\varphi_s}{\sqrt{1+\varphi_s^2}} \tag{22}$$

Another device uses disks in stead of squares to hold the sample in between, fig 4.3.

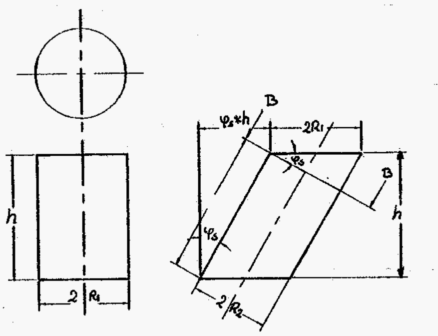


figure 4.3 disks

Plane B-B is an ellipse with the short axes is R_2 and the long axes is R_1 whereas:

$$R_2 = R_1*\frac{h}{s}$$

The perimeter of the ellipse is approximately:

$$\sqrt{2} * \pi * R_1 * \frac{1}{s} * \sqrt{s^2 + h^2}$$

The elliptical cylinder has an outer surface so as:

$$A = \sqrt{2} * \pi * R_1 * \sqrt{s^2 + h^2}$$

This gives together with eq.19 a surface force of:

$$F_s = \gamma * \sqrt{2} * \pi * R_1 \frac{\sqrt{1+\varphi_s^2}}{\sqrt{2+\varphi_s^2}}$$

Substitution of the last equation in equation (21) gives:

$$T = \gamma * \sqrt{2} * \pi * R_1 * R_1 \frac{\varphi_s}{\sqrt{2+\varphi_s^2}} * 2 \qquad (23)$$

Note, the device has two cylinders of material which are being stretched.

5 THE USED TESTS

5.1 DYNAMIC TESTS

Dynamic measurements are made by applying a sinusoidale strain to the fluid for a range of frequencies and measure the torque response on the shaft of the rheometer. The strain is:

$$\varphi_s = \overset{o}{\varphi}_s \sin(\omega t) \tag{24}$$

The shear stress of the viscous newtonian fluid is approximately zero because the storage modulus is zero and the loss modulus is very small. The only stress of any importance is the stress caused by the surface tension. This is the torque divided by two times the lever arm and the top surface of the square or circle.

$$\sigma_s = \frac{T}{2R_1 * A}$$

Where $A=b^2$ for the squares, fig.4.2.
and $A=\pi R_1^2$ for the disks, fig.4.3.
This gives together with eq.(22) for the squares:

$$\sigma_s = 2\,\frac{\gamma}{b}\,\frac{\varphi_s}{\sqrt{1+\varphi_s^2}} \tag{25}$$

With eq.(23) this results for the disks in:

$$\sigma_s = \sqrt{2}\,\frac{\gamma}{R_1}\,\frac{\varphi_s}{\sqrt{2+\varphi_s^2}} \tag{26}$$

Normally the stress in a linear viscoelastic material is described by:

$$\sigma_s = \overset{o}{\varphi}_s * G(t)$$

where

$$G(t)=G'\sin(\omega t)+G''\cos(\omega t)$$

thus

$$\sigma_s=\overset{o}{\varphi}_s(G'\sin(\omega t)+G''\cos(\omega t)) \qquad (27)$$

To substitute eq.(24) in eq.(25) and (26) first develop a Taylor range for the last two equations.

$$\sigma_s(\varphi_s) = \sigma_s(0) + \varphi_s\sigma_s'(0) + \frac{\varphi_s^2}{2!}\sigma_s''(0) + \frac{\varphi_s^3}{3!}\sigma_s'''(0) + o\varphi_s^4$$

This gives for the squares:

$$\sigma_s = \frac{2\gamma}{b}\left\{\varphi_s - \frac{\varphi_s^3}{2} + o\varphi_s^4\right\} \qquad (28)$$

Substitution of eq.24 in eq 28 results in:

$$\sigma_s = \frac{2\gamma_o}{b}\varphi_s\left\{ \sin(\omega t) - \frac{1}{2}\overset{o2}{\varphi_s}\sin(\omega t) + \frac{1}{2}\overset{o2}{\varphi_s}\sin(\omega t)\cos(\omega t) \right\} \qquad (29)$$

Based on the fact that the last term in this equation is smaller compared to the others, it is neglected. Thus eq.(29) gives together with eq.(27):

$$\overset{o}{\varphi}_s(G'\sin(\omega t)+G''\cos(\omega t)) = \frac{2\gamma_o}{b}\varphi_s{*}\sin(\omega t)\left\{ 1 - \frac{1}{2}\overset{o2}{\varphi_s}\right\} \qquad (30)$$

The same derivation gives for the disks the following equation

$$\overset{o}{\varphi}_s(G'\sin(\omega t)+G''\cos(\omega t)) = \frac{\sqrt{2}}{R_1}\gamma\overset{o}{\varphi}_s \sin(\omega t)\left\{ \frac{1}{\sqrt{2}} - \frac{1}{4\sqrt{2}}\overset{o2}{\varphi_s} \right\} (31)$$

The equations (30) and (31) will be used to calculate the surface tension from dynamic measurements for the diverse fluids. For fluids the storage modulus (G′) is zero and the loss modulus is very small for low frequencies. Doing dynamic measurements, we measure a very small loss modulus and a relatively high storage modulus. The storage modulus we measure here is in fact the elasticity due to the surface tension. Neglecting the loss modulus in the equations (30) and (31) gives for the surface tension:

$$\gamma = \frac{G'*b}{2-\overset{o}{\varphi}^2} \qquad (32)$$

for the squares and:

$$\gamma = \frac{G'*R_1}{1-\frac{1}{4}\overset{o}{\varphi}^2} \qquad (33)$$

for the disks

5.2 STEP-STRAIN TESTS.

In this case an instantaneously strain is applied to the material at time t=0 which is then held constant. The relaxation of the torque and strain is measured. The surface tension can be calculated with equations (22) and (23).

This gives for the squares:

$$\gamma = \frac{T*\sqrt{1+\varphi_s^2}}{4*b*R_1*\varphi_s} \qquad (32)$$

and for the disks:

$$\gamma = \frac{T*\sqrt{2+\varphi_s^2}}{2\sqrt{2}*\pi*R_1*R_1*\varphi_s} \qquad (33)$$

6 RESULTS

Dynamic and step-strain tests have been done for glycerol and dibutyl phthalate (dph). The tests have been done with the disks and the squares. The strain was varied for 20% to 120%. Al tests were done at room temperature.

6.1 DYNAMIC TESTS

The storage and loss modulus and the viscosity against the frequency for the diverse strains are plotted in appendix 1 for glycerol and in appendix 2 for dbp.

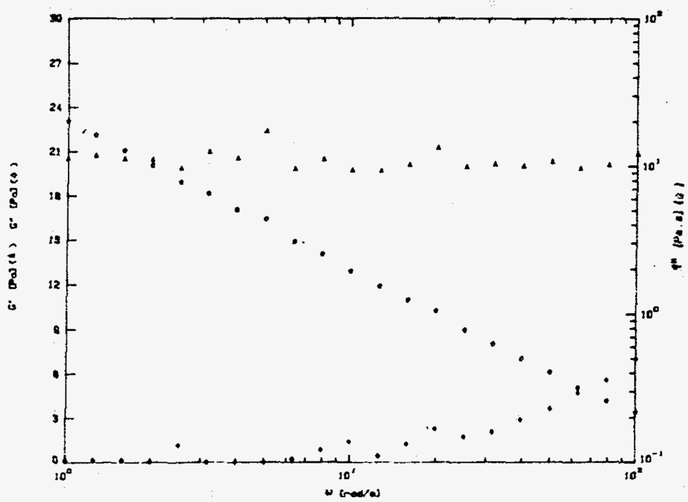


figure 6.1 G',G'' and η^* versus frequency, glycerol, 20% strain, disks

Table 6.1 gives the calculated values of the surface tension based on the average measured values of the storage modulus.

	glycerol				dbp			
	disks		squares		disks		squares	
φ_0 %	G' N/m^2	γ mN/m	G' N/m^2	γ mN/m	G' N/m^2	γ mN/m	G' N/m^2	γ mN/m
20	20.5	51.8	17.9	45.7	8.34	21.1	7.04	18.0
40	21.1	54.9	17.8	48.4	8.31	21.6	6.87	18.7
60	20.2	55.5	17.0	51.8	7.66	21.0	6.40	19.5
80	19.1	56.8	15.7	57.7	7.41	22.1	5.91	21.7
100	18.0	60.0	11.7	58.5	6.70	22.3	5.36	26.8
120	14.1	55.1						

tabel 6.1 Results dynamic tests gap height 0.5mm

For glycerol, the disks and a strain of 100% the dynamic tests are also done for different gap heights. Gap heights of 0.3, 0.4, 0.5 and 0.6 mm are compared. The results are given in table 6.2

h mm	G' N/m^2	γ mN/m
0.3	12.8	42.7
0.4	14.3	47.7
0.5	18.0	60.0
0.6	15.0	50.0

table 6.2 result dynamic tests strain=100%

6.2 STEP-STRAIN TESTS

In appendix 3 - 6 the results of the step strain tests are given. The torque, measured on the shaft of the rheometer, is plotted against the time for different values of the strain. Appendix 3 and 4 gives this for glycerol for the disks and squares and in appendix 5 and 6 the values for dbp are given. Table 6.2 gives the values of the surface tension calculated from the torque.

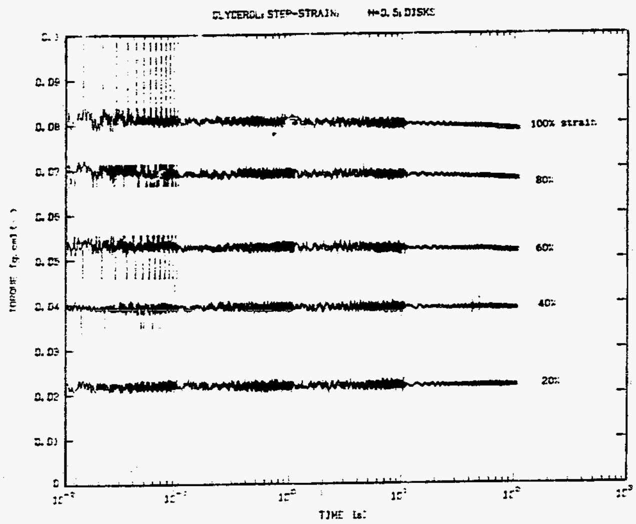


figure 6.2 torque versus time, glycerol, disks

	glycerol				dbp			
	disks		squares		disks		squares	
φ %	T g*cm *10^2	γ mN/m	T g*cm *10^2	γ mN/m	T g*cm *10^2	γ mN/m	T g*cm *10^2	γ mN/m
20	2.17	50.7	3.45	63.9	0.87	20.3	1.07	19.8
40	3.91	47.0	4.44	43.4	1.51	18.1	1.77	17.3
60	5.16	43.2	6.24	44.0	2.21	18.5	2.57	18.1
80	6.75	44.8	7.65	44.4	2.88	19.1	3.13	18.2
100	7.88	44.6	8.34	42.8	3.49	19.8	3.56	18.3

tabel 6.3 Results step-strain tests

6.3 WILHELMY SLIDE TESTS

The surface tension for both fluids is also measured with the Wilhelmy Slide technic (§3.5). For glycerol it appeared to be 61.8 mN/m and for dbp the surface tension turned out to be 32.1 mN/m which is very close to values found in the literature, (9).

7 CONCLUSIONS

The first thing we notice from table 6.1 and 6.2 is that, compared with the results of the Wilhelmy Slide method and those found in literature, the surface tension measured with the new devices is too low. Over the whole range of strains the dynamic technique gives for glycerol values which are more or less 10% to low. For dbp this is 30%. The step strain measurements give 12% lower values than the Wilhelmy Slide technique for glycerol and 15% for dbp.

Because the difference in comparison with the Wilhelmy slide technique is very constant there might be a error in the theoretical model. For example the model is based on linear shear but in fact the fluid is also twisted by rotating the bottom plate of the rheometer. This error could be diminished by using devices with longer lever arms so the approximation to the linear movement becomes more accurate. Another reason is probably that the cleanness of the surfaces is more important than was expected in the first case.

The reason that the measurements are less accurate for dbp is probably because the torque is in this case very low. The measured torque is on the lower side of the range of the rheometer so the values are less accurate than in the case of the glycerol which gives a higher torque. Also here longer lever arms will provide better results because of a higher torque.

Especially for dynamic measurements of the surface tension the disks turned out to give better results. The surface of the fluid has problems with following the perimeter of the squares because there are four very sharp corners. The surface tension causes the fluid to go around a corner in a bigger radius than the corner is itself.

A strain of 20% gives a very low torque which causes inaccuracy. At the step strain tests a strain of 100% causes the fluid not to stick any more to the disks or squares perfectly. The same effect occurs at a strain of 120% at the dynamic tests.

When we compare the effect of the different gap heights it appears that there is an optimum gap height. This is very strange if we look at the theory. According to the theoretical model the gap height should not have any influence. This also gives reason to think that the theoretical model is not fully correct. For example we assumed that the fluid in between the two bodies doesn't neck-in when stretched. In reality the cross section of the fluid in the middle in between the bodies will tend to be a circle in stead of a square or ellipse.

The conclusion is that working with the disks gives better results than working with the squares. The results of the dynamic tests are closer to those obtained from the Wilhelmy Slide tests and from the literature [9] than the results of the step strain tests. The optimum strain is for the dynamic tests 100% and for the step strain tests 80% . The optimum gap height seems to be 0.5 mm. Longer lever arms will improve the accuracy of the measurements. The influence of strange elements (dirt) on the surface should be examined. Also the theoretical model can be improved.

REFERENCES

1 Adamson, A.W., "Physical Chemistry of Surfaces". John Wiley and Sons, New York, (1990).

2 Hiemenz P.C., "Principles of Colloid and Surface Chemistry". Marcel Dekker,Inc., New York, (1986).

3 Davies J.T.; Rideal E.K., "Interfacial Phenomena". Academic Press, New York, (1961).

4 Hansen R.S.; Ahmord J., "Progress in Surface and Membrane Science", Vol 4. Academic press, New York, (1971).

5 Sutherland K.L., Australian J. Chem., Vol 7, p 319 (1954).

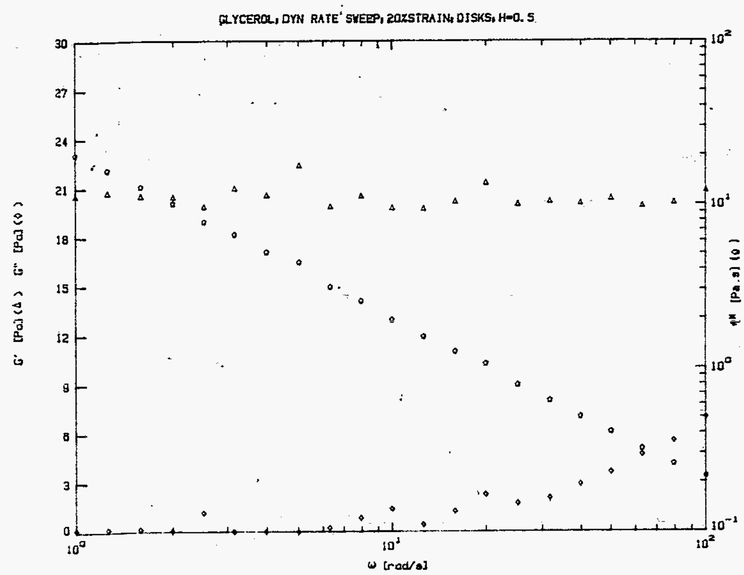
6 Mackay M.E.;Cathey C.A., J. Rheol., Vol 2, (1991).

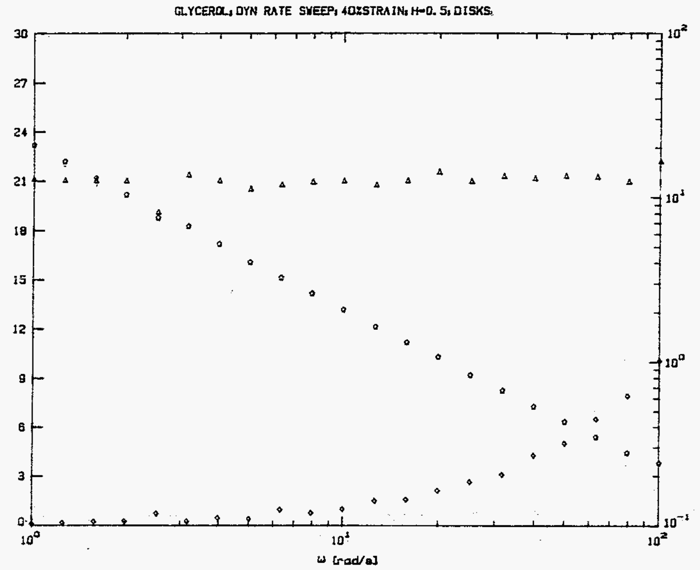
7 Mackay M.E., Intern communication.

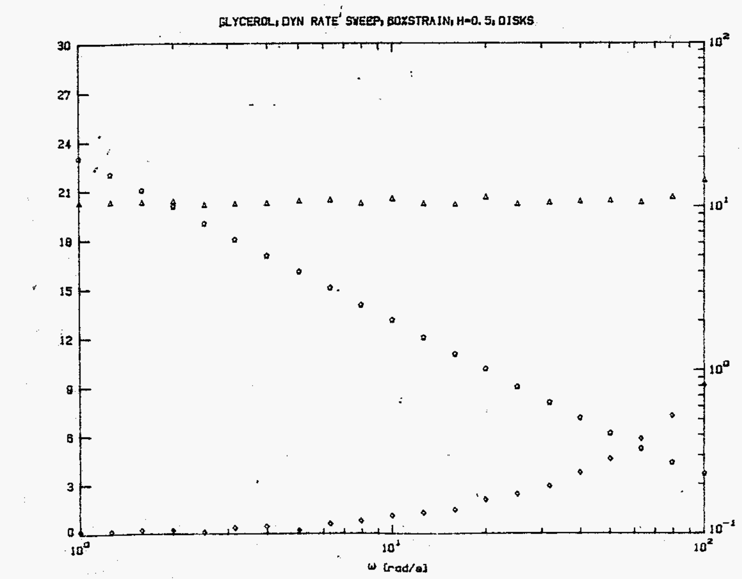
8 Jaycock M.J.; Parfitt G.D., "Chemistry of Interfaces". John Wiley and Sons, New York.

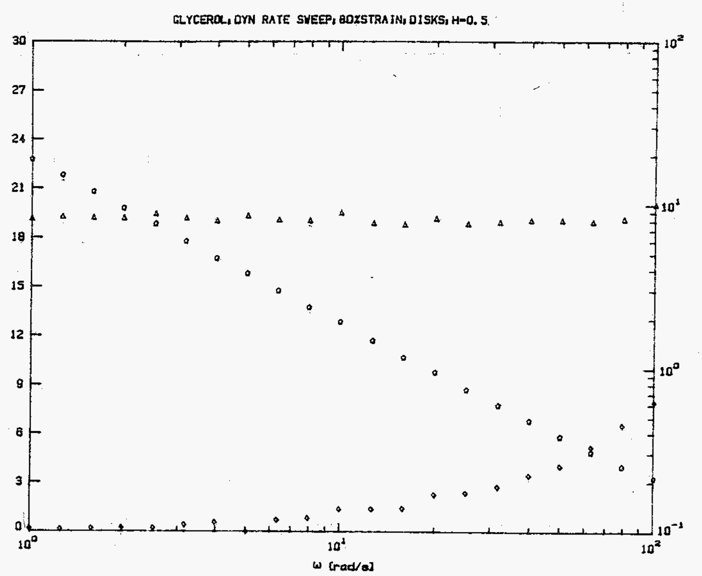
9 Creemers M.R.; Leyendeckers P.H.H., "Polytechnisch Zakboekje". 42th edition, Koninklijke PBNA bv, Arnhem.

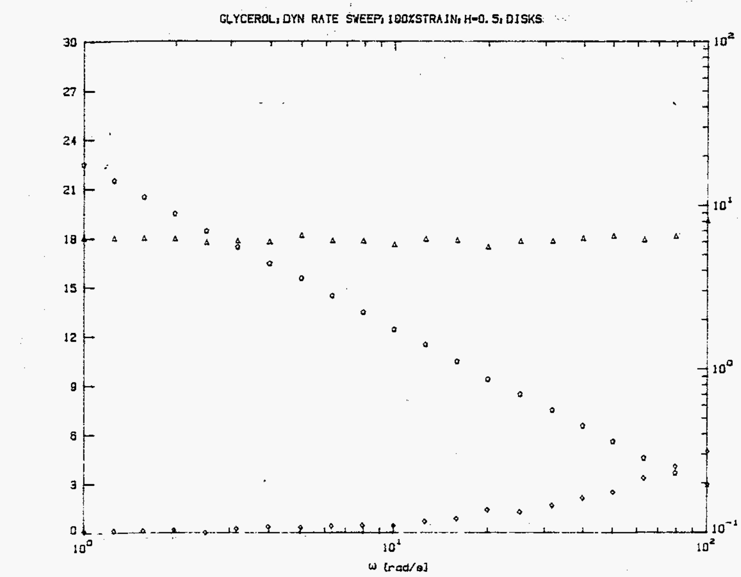
APPENDIX 1

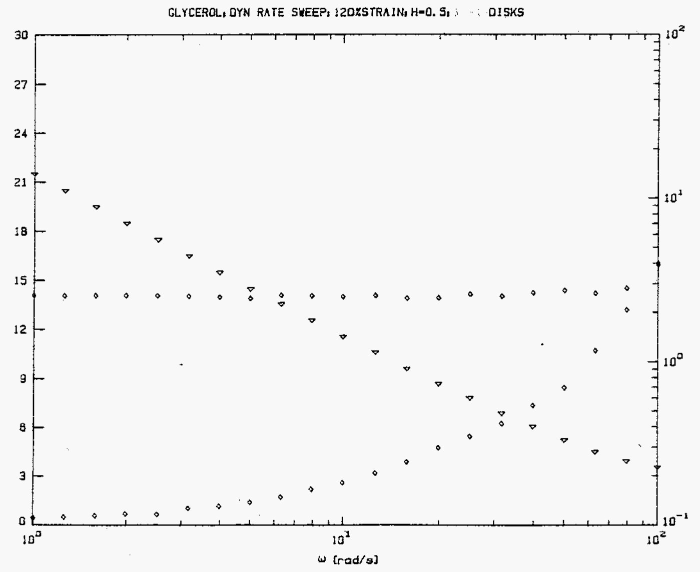

GLYCEROL; DYN RATE SWEEP; 20%STRAIN; DISKS; H=0.5
G' [Pa] (Δ) G" [Pa] (◇)
η* [Pa.s] (○)
ω [rad/s]


GLYCEROL; DYN RATE SWEEP; 40%STRAIN; H=0.5; DISKS
ω [rad/s]

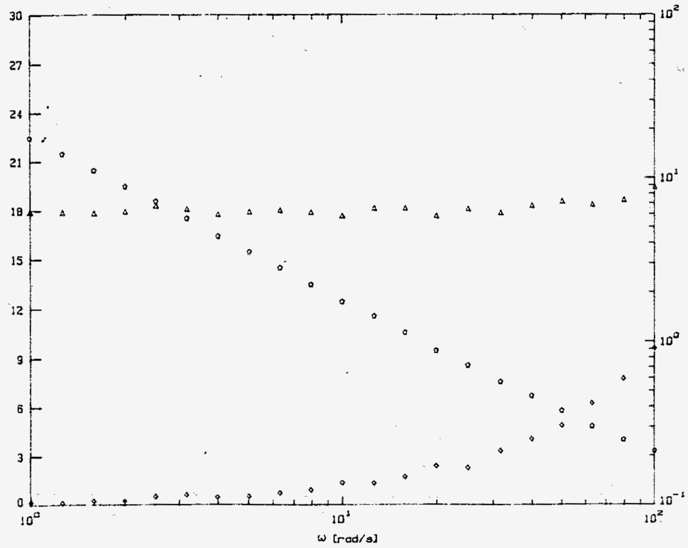

GLYCEROL; DYN RATE SWEEP; 60%STRAIN; H=0.5; DISKS
ω [rad/s]


GLYCEROL; DYN RATE SWEEP; 80%STRAIN; DISKS; H=0.5
ω [rad/s]

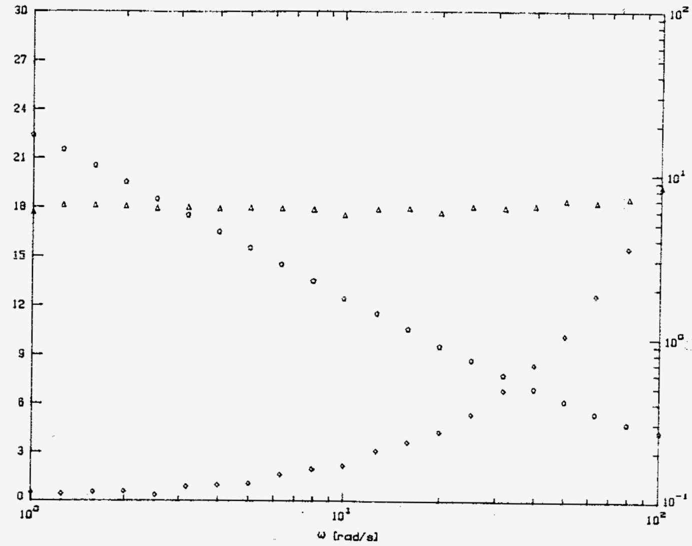

GLYCEROL; DYN RATE SWEEP; 100%STRAIN; H=0.5; DISKS
ω [rad/s]


GLYCEROL; DYN RATE SWEEP; 120%STRAIN; H=0.5; DISKS
ω [rad/s]

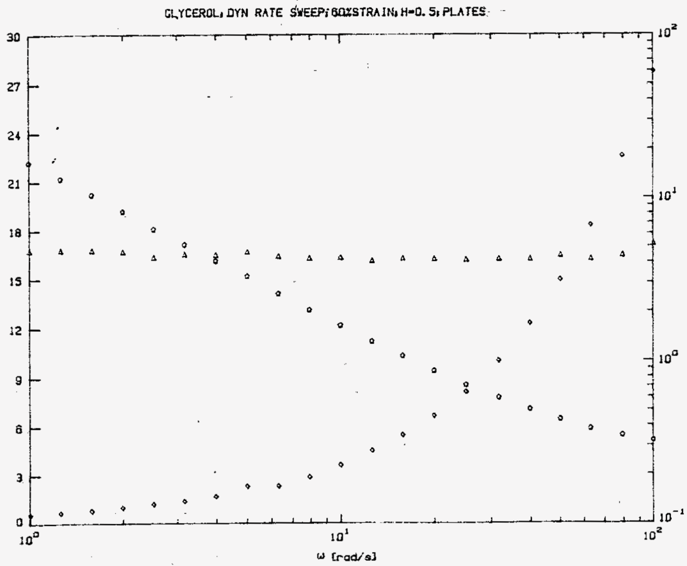
GLYCEROL; DYN RATE SWEEP; 20%STRAIN; H=0.5; PLATES.



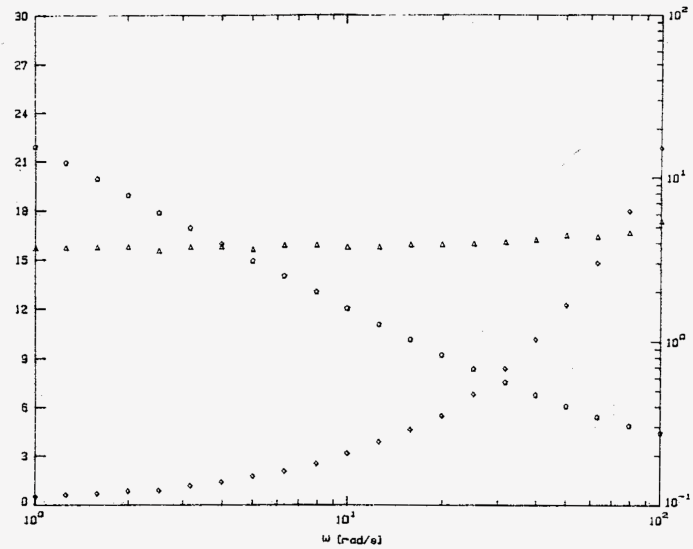
GLYCEROL; DYN RATE SWEEP; 40%STRAIN; H=0.5; PLATES.



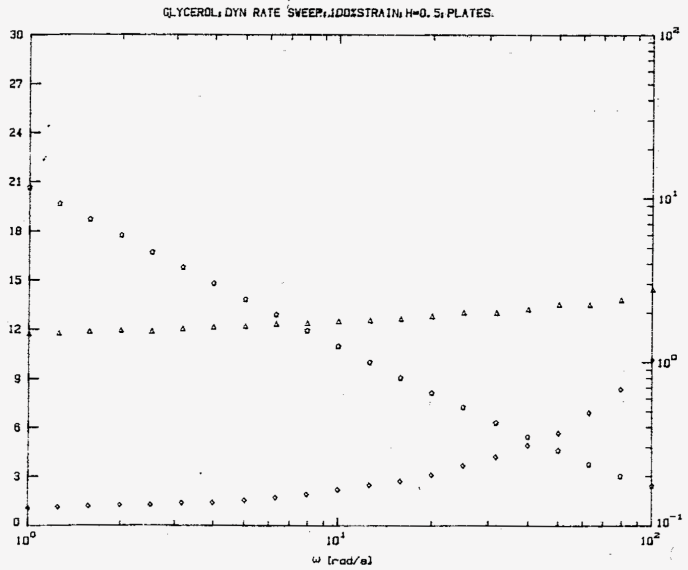
GLYCEROL; DYN RATE SWEEP; 60%STRAIN; H=0.5; PLATES.



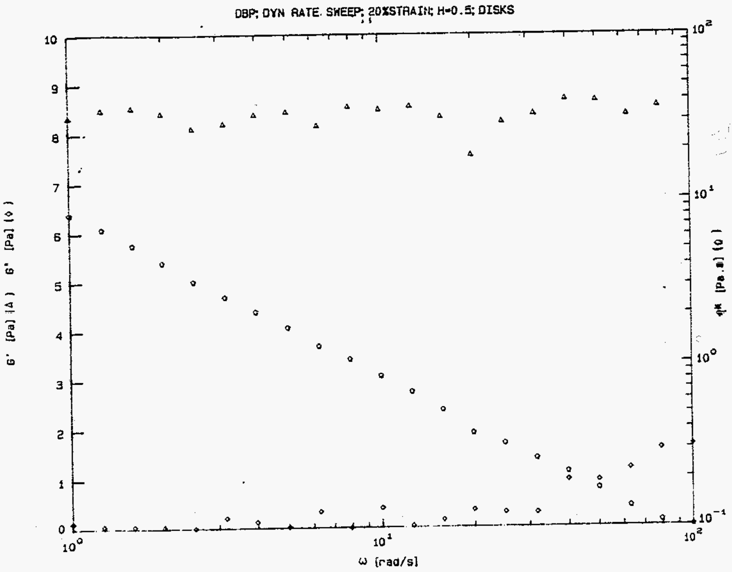
GLYCEROL; DYN RATE SWEEP; 80%STRAIN; H=0.5; PLATES.

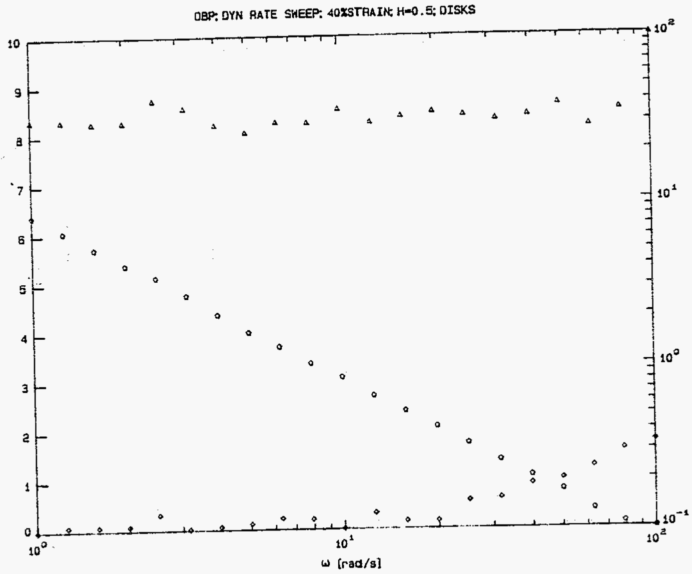


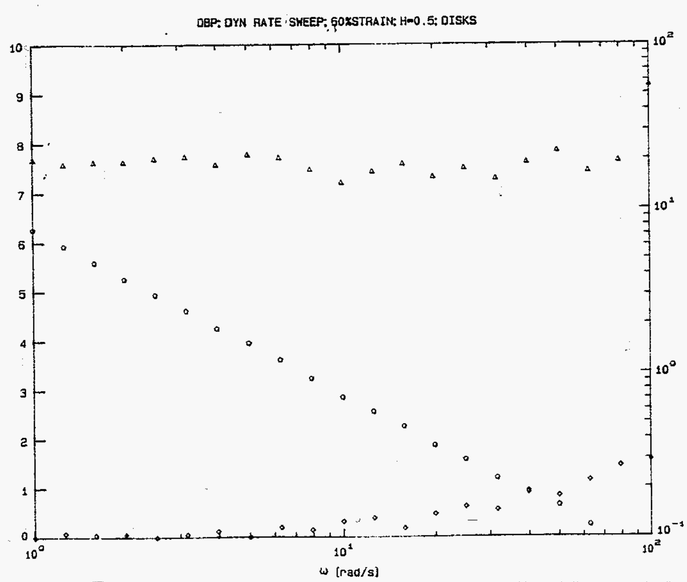
GLYCEROL; DYN RATE SWEEP; 100%STRAIN; H=0.5; PLATES.

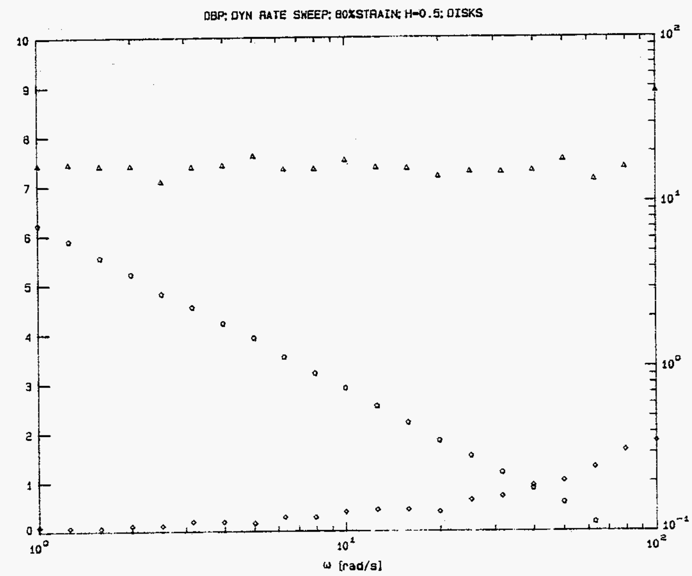


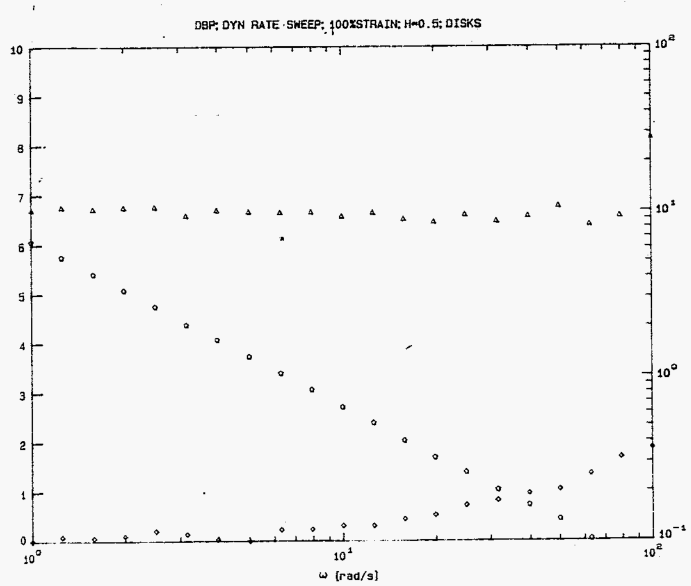
APPENDIX 2

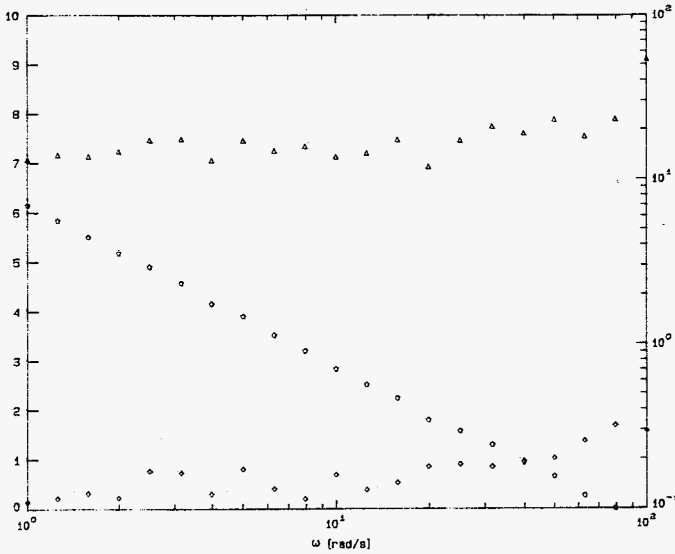

DBP: DYN RATE SWEEP: 20%STRAIN; H=0.5; DISKS
G' [Pa] (Δ) G'' [Pa] (◊)
η* [Pa.s] (o)
ω [rad/s]


DBP: DYN RATE SWEEP: 40%STRAIN; H=0.5; DISKS
ω [rad/s]

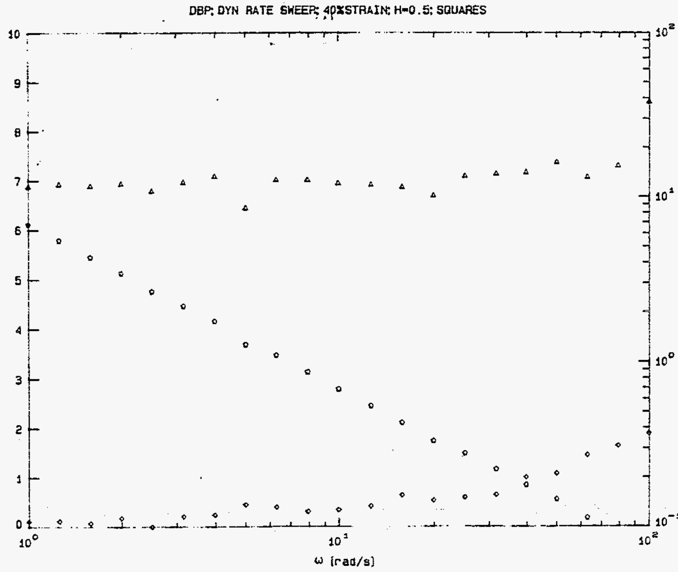

DBP: DYN RATE SWEEP: 60%STRAIN; H=0.5; DISKS
ω [rad/s]


DBP: DYN RATE SWEEP: 80%STRAIN; H=0.5; DISKS
ω [rad/s]

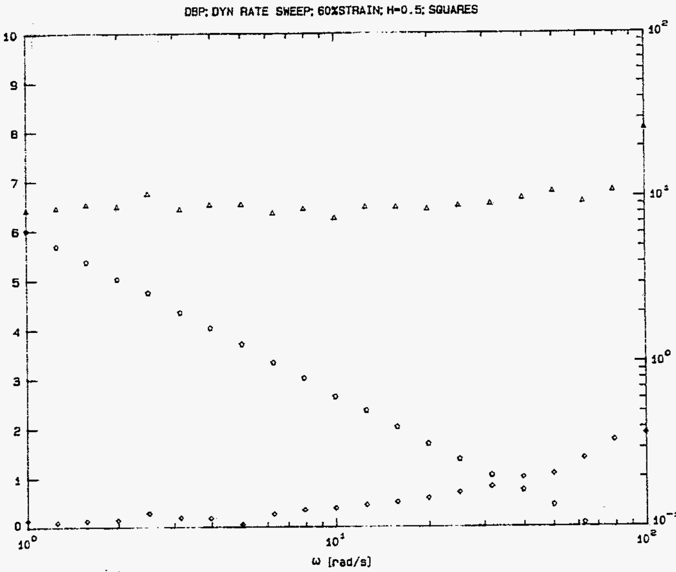

DBP: DYN RATE SWEEP: 100%STRAIN; H=0.5; DISKS
ω [rad/s]



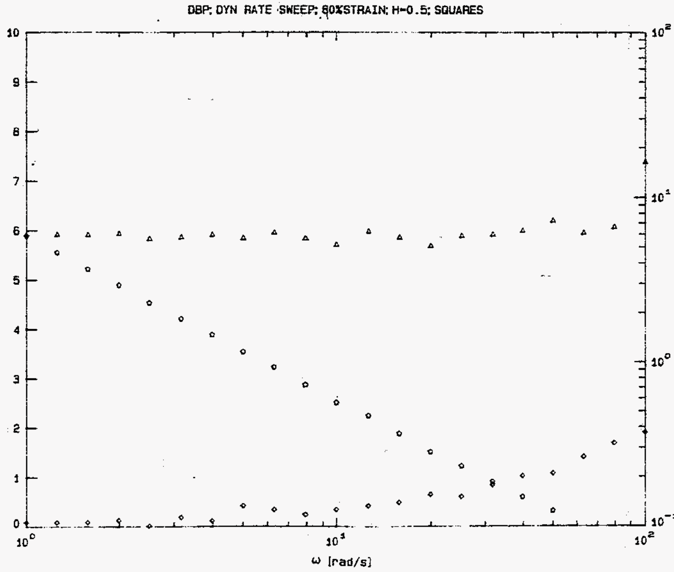
DBP; DYN RATE SWEEP; 20%STRAIN; H=0.5; SQUARES



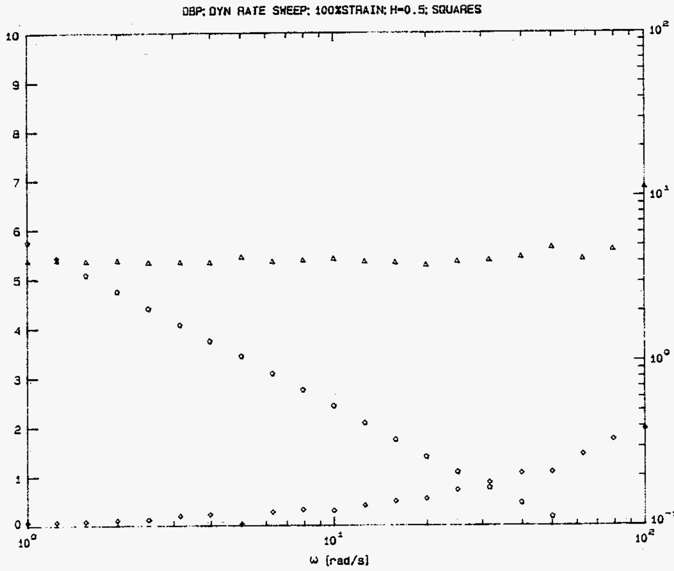
DBP; DYN RATE SWEEP; 40%STRAIN; H=0.5; SQUARES



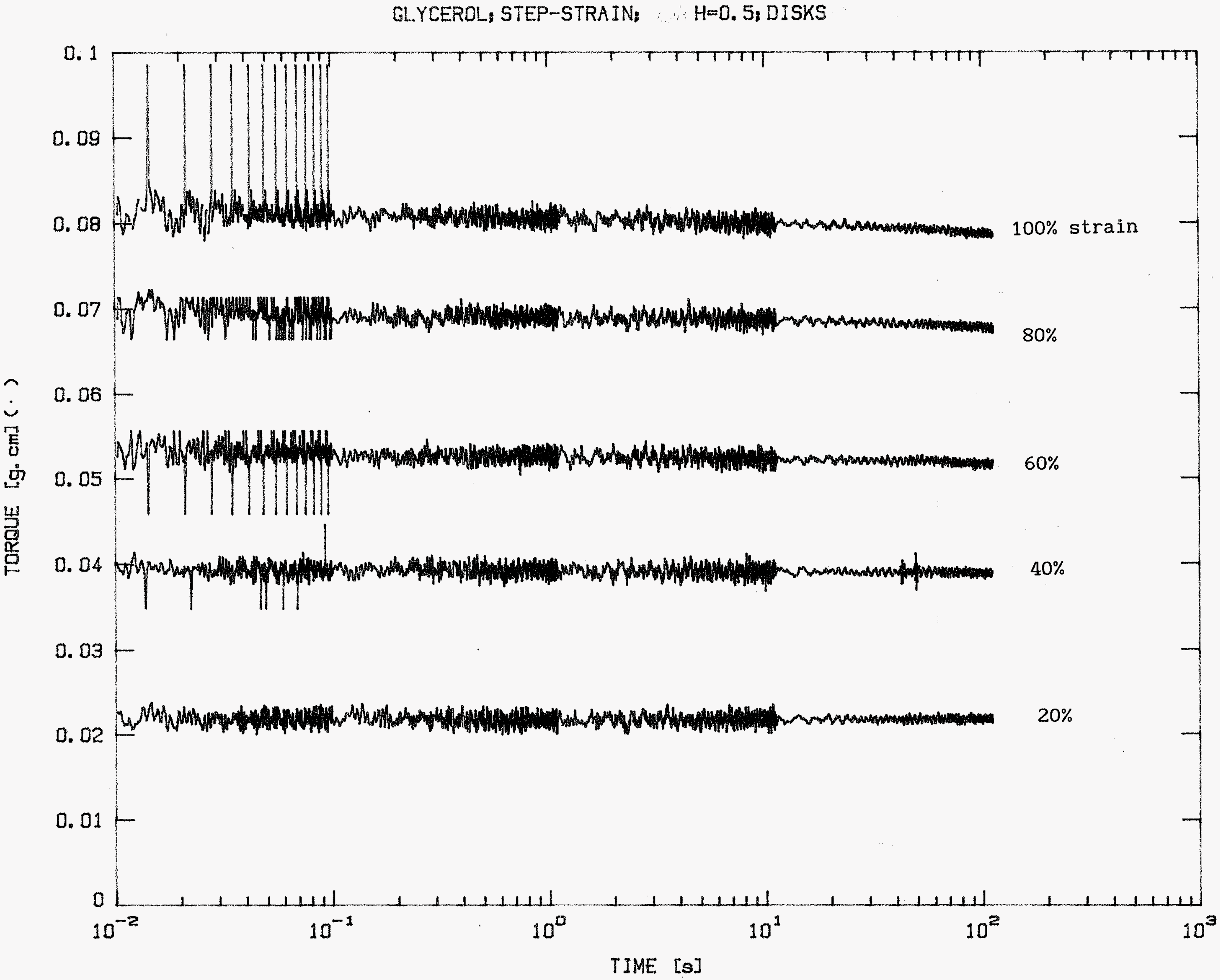
DBP; DYN RATE SWEEP; 60%STRAIN; H=0.5; SQUARES



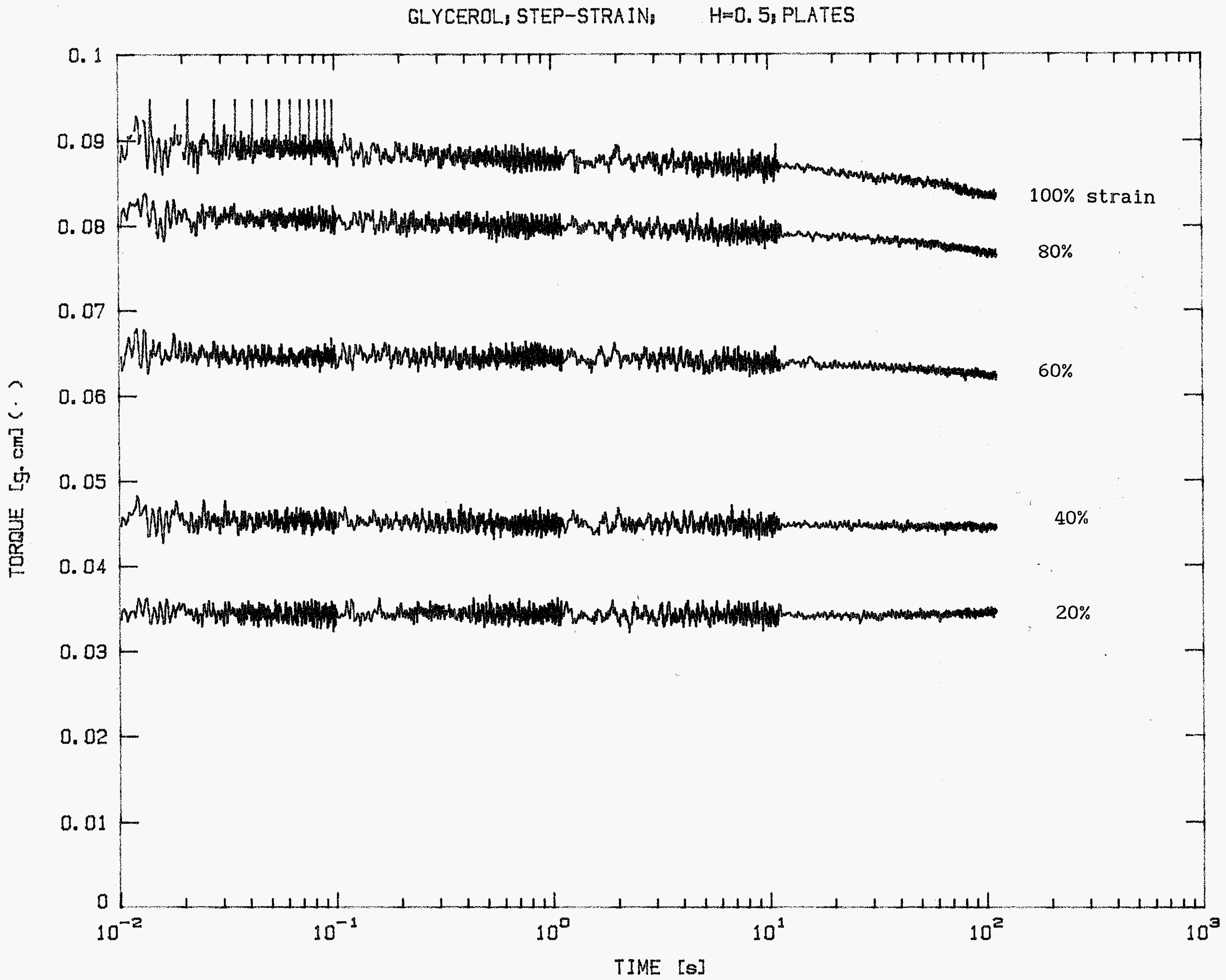
DBP; DYN RATE SWEEP; 80%STRAIN; H=0.5; SQUARES

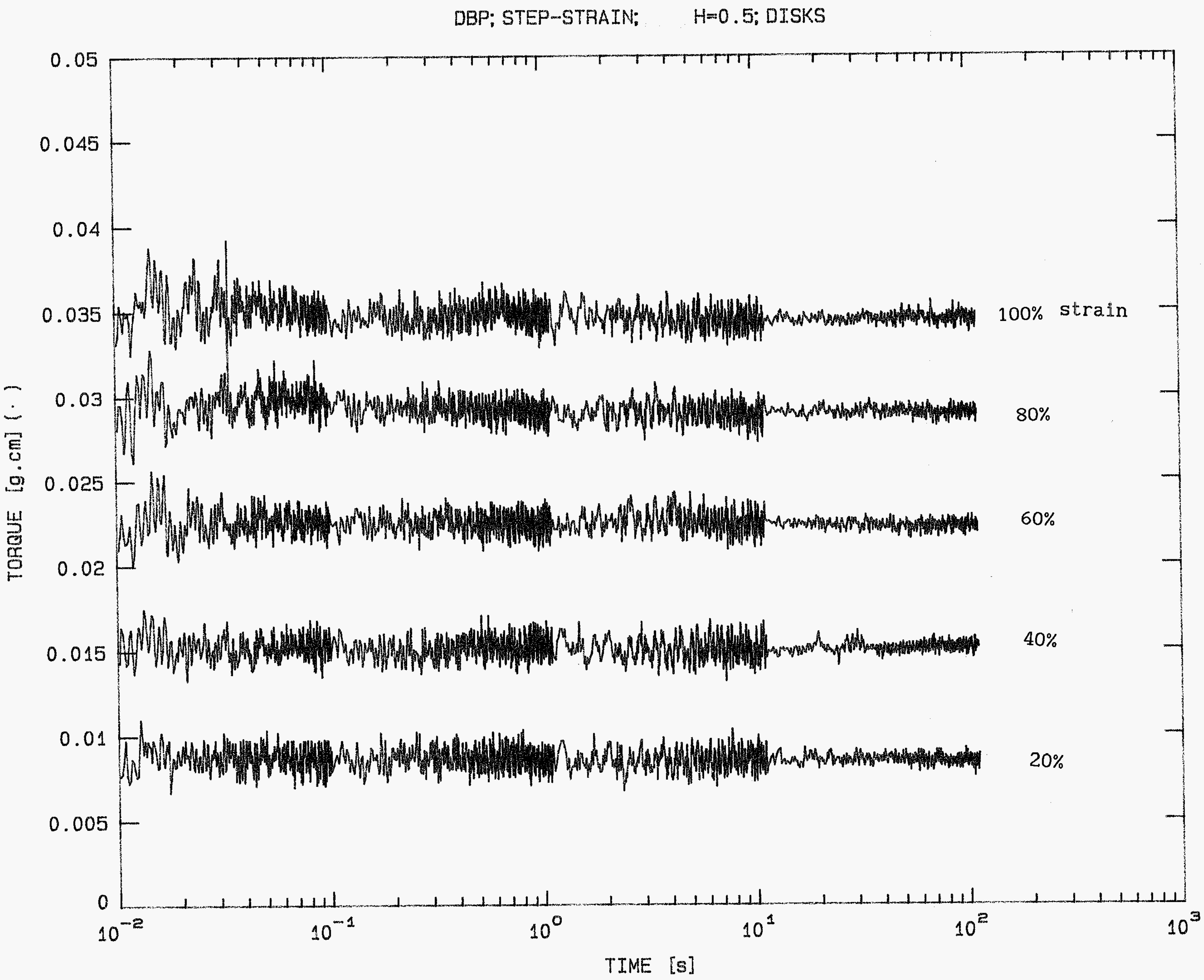


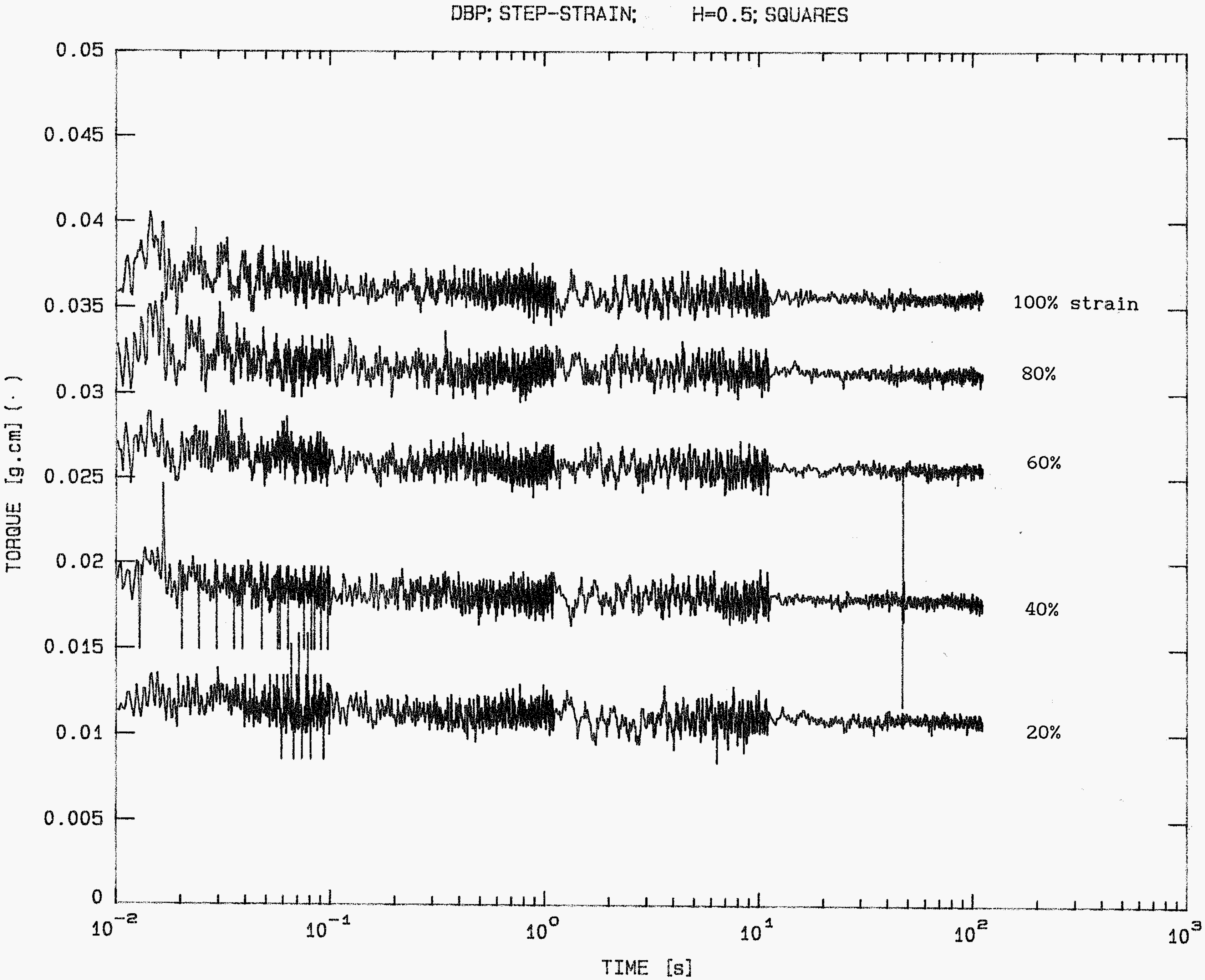
DBP; DYN RATE SWEEP; 100%STRAIN; H=0.5; SQUARES


GLYCEROL; STEP-STRAIN; H=0.5; DISKS
TORQUE [g. cm] (·)
TIME [s]
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
100% strain
80%
60%
40%
20%

APPENDIX 4


GLYCEROL; STEP-STRAIN; H=0.5; PLATES
TORQUE [g.cm] (·)
TIME [s]
100% strain
80%
60%
40%
20%
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}


DBP; STEP-STRAIN; H=0.5; DISKS
TORQUE [g.cm] (·)
0.05
0.045
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
100% strain
80%
60%
40%
20%
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
TIME [s]


DBP; STEP-STRAIN; H=0.5; SQUARES
TORQUE [g.cm] (·)
0.05
0.045
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
TIME [s]
100% strain
80%
60%
40%
20%