Visco-Elasticity Measurement by the Torsional Rheometer. Simple Treatment by the Application of the Four-Terminal Network

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Introduction

Some polymer and colloidal solutions, in contrast to ordinary liquids of low molecular weight, have been known to show elastic nature besides viscosity, and rheological peculiarities of these "elastic liquids"—e. g. "Fliesselastizität" (H. Freundlich, 1932), "structural viscosity" (W. Philippoff, 1935), "thread-forming ability" (H. Erbring, 1936), "Weissenberg effect" (K. Weissenberg, 1947) etc. have been studied by various workers. As it has recently become desirable to analyse such rheological behaviors of those solutions, various rheometers or elastoviscometers suitable for the measurement of their visco-elastic properties have been proposed, and among them it is thought that the rheometers in which the most rigorous treatment has been given are those of coaxial-cylinder type which provide a means of maintaining a liquid in a state of torsional oscillation in a narrow annular gap between two vertical coaxial cylinders.

In this paper, the author gives a simple general view of the rheometers of this type by the application of the four-terminal electrical network theory. The treatment by the four-terminal network is better than that by the ordinary two-terminal network from the view-point that the former can include all modifications of the rheometer by a single four-terminal circuit diagram.

It goes without saying that the treatment presented here is only approximate; the inertia of the sample liquid is neglected here. This approximation, however, is satisfactory in the measurement at very low frequencies.*

Survey of the Four-Terminal Network Theory

An electrical network which has two input and two output terminals is called a four-terminal network.

When the generalized Kirchhoff's law is applied to the four-terminal network N (Fig. 1.), the fundamental equation of the network is derived in terms of the "four-terminal

* T. Nakagawa, Third Rheological Meeting, Japan, 1953.

constants" A, B, C and D as

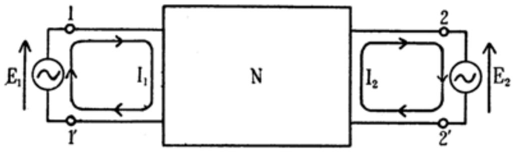

Fig. 1. Four-terminal network.

$$\begin{cases} E_1=AE_2+BI_2 & \text{(1a)} \\ I_1=CE_2+DI_2 & \text{(1b)} \end{cases}$$

or, according to the matrix expression,

$$\begin{pmatrix} E_1 \\ I_1 \end{pmatrix}=\begin{pmatrix} A & B \\ C & D \end{pmatrix}\begin{pmatrix} E_2 \\ I_2 \end{pmatrix} \qquad (2)$$

where E_1 and I_1 are the input voltage and the input current respectively; E_2 and I_2 are the quantities relating to the output. The four-terminal constants A B C D are shown to satisfy the next relation.

$$\begin{vmatrix} A & B \\ C & D \end{vmatrix}=AD-BC=1 \qquad (3)$$

According to the theory, the four-terminal constants of a circuit which has a single impedance Z as shown in Fig. 2 are

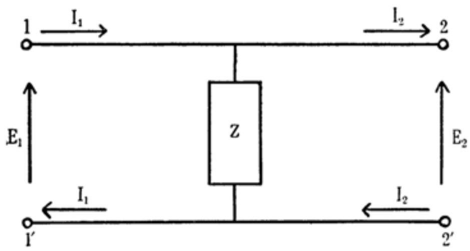

Fig. 2. Single-impedance network (I).

$$\begin{pmatrix} A & B \\ C & D \end{pmatrix}=\begin{pmatrix} 1 & 0 \\ 1/Z & 1 \end{pmatrix} \qquad (4)$$

and for a circuit of Fig. 3, they are

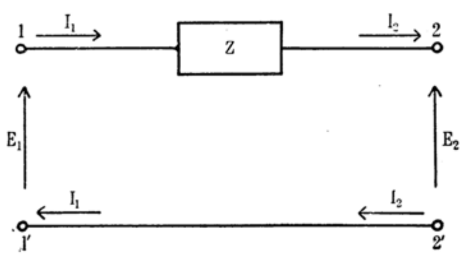

Fig. 3. Single-impedance network (II).

$$\begin{pmatrix} A & B \\ C & D \end{pmatrix}=\begin{pmatrix} 1 & Z \\ 0 & 1 \end{pmatrix} \qquad (5)$$

When a four-terminal circuit N_2 is connected tandem to the right hand side of a four-terminal circuit N_1, a new four-terminal circuit N is constructed and its four-terminal constants A B C D are obtained from the product of two matrices

$$\begin{pmatrix} A & B \\ C & D \end{pmatrix}=\begin{pmatrix} A' & B' \\ C' & D' \end{pmatrix}\begin{pmatrix} A'' & B'' \\ C'' & D'' \end{pmatrix}$$
$$=\begin{pmatrix} A'A''+B'C'' & A'B''+B'D'' \\ C'A''+D'C'' & C'B''+D'D'' \end{pmatrix} \qquad (6)$$

where A' B' C' D' and A'' B'' C'' D'' are four-terminal constants of the network N_1 and N_2 respectively (Fig. 4.).

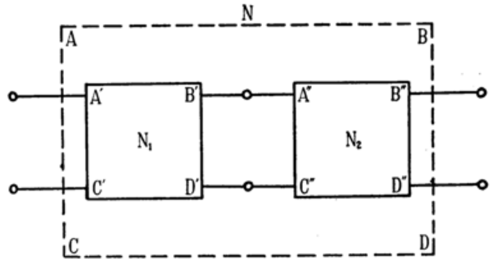

Fig. 4. Tandem connection of two four-terminal networks.

From the above-stated, the four-terminal constants of a π-type network which is composed of three impedances as shown in Fig. 5 are easily obtained as follows by the cascade connection of three circuits illustrated in Fig. 2 and 3.

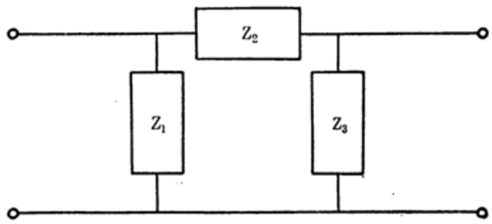

Fig. 5. π-type network.

$$\begin{pmatrix} A & B \\ C & D \end{pmatrix}=\begin{pmatrix} 1 & 0 \\ 1/Z_1 & 1 \end{pmatrix}\begin{pmatrix} 1 & Z_2 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 1/Z_3 & 1 \end{pmatrix}$$
$$=\begin{pmatrix} 1+Z_2/Z_3 & Z_2 \\ (Z_1+Z_2+Z_3)/(Z_1Z_3) & 1+Z_2/Z_1 \end{pmatrix} \qquad (7)$$

The Torsionally Oscillating Rheometer and the Four-Terminal Circuit

In this rheometer, a cylinder of radius r_1 is suspended coaxially to a depth l in a liquid contained in a cup of radius r_2. The rheometer of this type is used in two modifications. In one,[1,1',2,3,3'] the external cup is caused to oscillate through a small fixed angular amplitude Θ_0, while the top end of the suspension wire is fixed; in the other[1',4,5,6], the top end of the suspension wire is put into the torsional oscillation $\Theta=\Theta_0 e^{j\omega t}$, the cup being fixed. In both cases the rheological properties of the sample liquid are known from the analysis of the motion of the internal cylinder relative to that of the external cup or to that of the top of the suspension wire.

When the experiment is carried out at very low frequencies (period $T=2\pi/\omega$, greater than several seconds) a simple approximate treatment seems to be permissible*. Here the inertia of the sample is assumed to be negligible and to have no effect on the motion of the inner cylinder. And moreover, the next two relations, in which viscosity η and rigidity G are related to the resistance R and the stiffness E by a simple shape factor K_0, are assumed to hold. Of the reason for employing this shape factor reference will be made in the later section on the rotational viscometer and Schwedoff's apparatus.

$$\eta=\frac{R}{4\pi l}\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right)\equiv K_0 R \quad \text{poises} \qquad (8)$$

$$G=\frac{E}{4\pi l}\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right)\equiv K_0 E \quad \text{dyn./cm}^2. \qquad (9)$$

Analogous Four-Terminal Network.—A simple consideration enables us to construct an analogous four-terminal network a in Fig. 6 corresponding to our rheometer where the electro-mechanical correspondence is as is listed in Table 1. Fig. 6 is a π-type

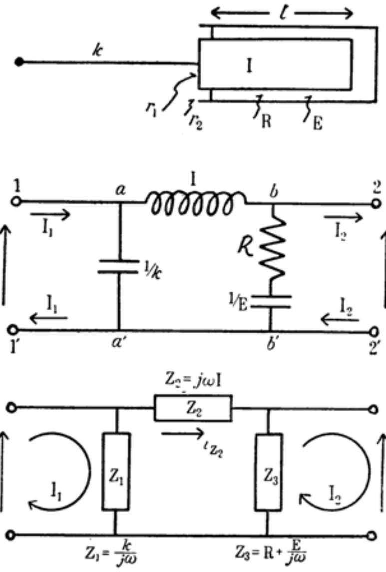

Fig. 6. Torsionally oscillating rheometer and the analogous four-terminal network.

TABLE I

ELECTRO-MECHANICAL CORRESPONDENCE

Mechanical System	Electrical System
k : Torsion constant of suspension wire	Reciprocal capacitance
I : Moment of inertia of inner cylinder	Inductance
R : Viscous resistance of sample	Resistance
E : Stiffness of sample	Reciprocal capacitance
$\dot{\theta}$: Velocity	i : Current
θ : Displacement	Q : Charge

circuit which was stated above, and since

$$\begin{cases} Z_1=\dfrac{k}{j\omega} \\ Z_2=j\omega I \\ Z_3=R+\dfrac{E}{j\omega} \end{cases} \qquad (10)$$

the four-terminal constants $A\ B\ C\ D$ are calculated by Eq. 7; and, for example,

$$C=(Z_1+Z_2+Z_3)/(Z_1Z_3) = \frac{(j\omega R-\omega^2 I+k+E)}{k\left(R+\dfrac{E}{j\omega}\right)} \qquad (11)$$

1) J. R. Van Wazer and H. Goldberg, *J. Appl. Phys.*, **18**, 207 (1947).
1') H. Goldberg and O. Sandvik, *Anal. Chem.*, **19**, 123 (1947).
2) J. R. Van Wazer, *J. Colloid Sci.*, **2**, 223 (1947).
3) H. Markovitz et al., *Rev. Sci. Instr.*, **23**, 430 (1952); H. Markovitz, *J. Appl. Phys.*, **23**, 1070 (1952).
3') J. G. Oldroyd et al., *Proc. Phys. Soc.*, B, **64**, 44 (1951); J. G. Oldroyd, *Quart. Journ. Mech. and Applied Math.* **4**, Pt. 3, 271 (1951).
4) T. Nakagawa, *J. Chem. Soc. Japan*, **72**, 759 (1951) (in Japanese).
5) T. Nakagawa, This Bulletin **24**, 191 (1951).
6) T. Nakagawa, ibid., **25**, 93 (1952).

* The exact treatment of the torsionally oscillating rheometer taking account of the inertia of the sample has recently been done by various authors; so for the cup-drive system, see for example, J. G. Oldroyd,[3'] A. A. K. Ibrahim and A. M. Kabiel, *J. Appl. Phys.*, **23**, 754 (1952), and H. Markovitz[3]; for the top-drive system, see S. Oka, *Bull. Kobayashi Inst. of Phys. Res.*, **3**, 9 and 17 (1953) (in Japanese).

where $j=\sqrt{-1}$, and ω is 2π times the frequency ν ($\omega=2\pi\nu$).

The angular velocity $\dot{\theta}$ of the inner cylinder corresponds to the current i_{Z2} which flows through the inductance I, and to know the angular displacement of the inner bob it is enough to compute the charge Q_{Z2}

$$Q_{Z2}=\frac{i_{Z2}}{j\omega} \tag{12}$$

(1) **Top-Drive System.**—First is discussed the case in which the cup is fixed and the top end of the suspension wire is subjected to oscillational displacement

$$\Theta=\Theta_0\, e^{j\omega t}$$

This situation is electrically as follows (Fig. 7). The input current at the terminal 1—1′ is

$$I_1=j\omega\Theta_0\, e^{j\omega t},$$

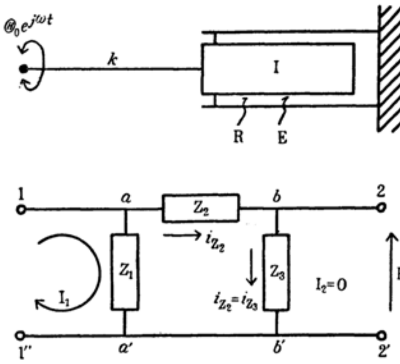

Fig. 7. Top-drive rheometer.

and the velocity of the cup is zero, that is, the terminal 2—2′ is opened

$$I_2=0$$

From Eq. (1b) of the four-terminal equation

$$E_2=\frac{I_1}{C}$$

The angular velocity of the inner cylinder $\dot{\theta}$ corresponds to i_{Z2}, and

$$i_{Z2}=i_{Z3}=\frac{E_2}{Z_3}=\frac{I_1}{CZ_3}$$

$$=\frac{k\Theta_0\, e^{j\omega t}}{R+j\left(\omega I-\frac{k+E}{\omega}\right)}$$

So that

$$\theta=\frac{\dot{\theta}}{j\omega}=\frac{k\Theta_0\, e^{j\omega t}}{[(k+E)-\omega^2 I]+j\omega R}$$

$$\therefore\ \theta=\frac{k\Theta_0}{\sqrt{(k+E-\omega^2 I)^2+\omega^2R^2}}e^{j(\omega t-\phi)}\equiv Ae^{j(\omega t-\phi)}$$

where
$$\tan\phi=\frac{\omega R}{(k+E-\omega^2 I)} \tag{13}$$

This result of course agrees with that obtained by the direct solution of the equation of motion of the inner cylinder

$$I\ddot{\theta}=k(\Theta-\theta)-R\dot{\theta}-E\theta$$

If m, the amplitude ratio A/Θ_0 and ϕ, the phase angle are observed, R and E are known from Eq. 13 or from

$$\begin{cases} R=\dfrac{kT\sin\phi}{2\pi m} \\ E=k\left(\dfrac{\cos\phi}{m}-1\right)+\dfrac{4\pi^2 I}{T^2} \end{cases} \tag{14}$$

where $T=2\pi/\omega$, and consequently η and G can be calculated from Eqs. 8 and 9. Or the observation of the amplitude resonance enables us to calculate η and G[4,6),**] from

$$\begin{cases} \omega_{res}=2\pi\nu_{res}=\sqrt{n_e^2-2\epsilon^2} \\ A_{res}=L/\sqrt{4\epsilon^4+4\epsilon^2\omega^2_{res}} \end{cases}$$

where ν_{res} and A_{res} are the resonance frequency and the resonance amplitude respectively, and

$$2\epsilon=R/I,\quad n_e^2=(k+E)/I,\quad L=k\Theta_0/I.$$

(2) **Cup-Drive System.**—In this case the external cup is put into sinusoidal oscillation, and the top end of the suspension wire is fixed (Fig. 8.). This condition corresponds electrically to the case in which, contrary to that of the top-drive system,

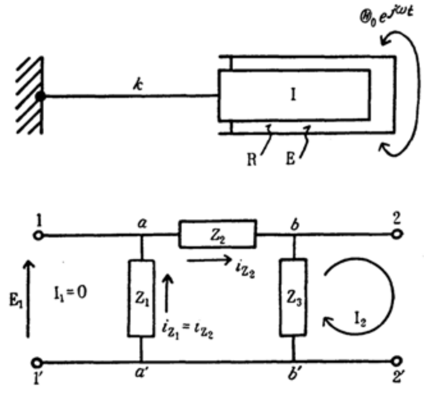

Fig. 8. Cup-drive rheometer.

$$I_1=0$$
$$I_2=j\omega\Theta_0\, e^{j\omega t}$$

** The resonance method starting from Eq. (13) which implies the neglect of the inertia of the sample, however, seems to be doubtful, for in this case the observation is ordinarily made at the frequencies several cycles per second or more, and then the inertia of the liquid can not be neglected. With the phase angle method, on the other hand, very low frequencies can be adopted and then Eq. 13 is satisfactory.

and the four-terminal equation is

$$\begin{cases} E_1 = AE_2 + BI_2 & \text{(1a)} \\ I_1 = 0 = CE_2 + DI_2 & \text{(1b)} \end{cases}$$

From (1a), (1b) and (3)

$$E_1 = \left(B - \frac{AD}{C}\right) I_2 = \frac{(BC-AD)}{C} I_2 = \frac{-1}{C} I_2$$

$$= -\frac{Z_1 Z_3}{(Z_1+Z_2+Z_3)} \cdot j\omega\Theta_0 \, e^{j\omega t}$$

$\dot{\theta}$ corresponds to i_{Z2}, and

$$i_{Z2} = i_{Z1} = -\frac{E_1}{Z_1}$$

So that

$$\theta = \int \dot{\theta} dt = \frac{\dot{\theta}}{j\omega} = \frac{(E+j\omega R)\Theta_0}{[(k+E-\omega^2 I)+j\omega R]} e^{j\omega t}$$

or $$\theta = \frac{\sqrt{E^2+\omega^2 R^2} \cdot \Theta_0}{\sqrt{(k+E-\omega^2 I)^2+\omega^2 R^2}} e^{j(\omega t-\phi)} \qquad (15)$$

$$\tan\phi = \frac{\omega R(\omega^2 I - k)}{E(k+E-\omega^2 I)+\omega^2 R^2}$$

This is somewhat complicated in comparison with Eq. 13. It is not possible to obtain a relation as simple as Eq. 14 for the calculation of R and E from the observed m and ϕ***.

(3) **Impedance-Less Suspension** In the rheometer which was used by J. R. Van Wazer and H. Goldberg[1] the internal cylinder is suspended from a thin thread whose mechanical loss and elastance are both assumed to be negligible in comparison with those of the liquid under study. The external cup is set into oscillation. This situation corresponds to Fig. 9 in which the terminals a and a' are short-circuited and

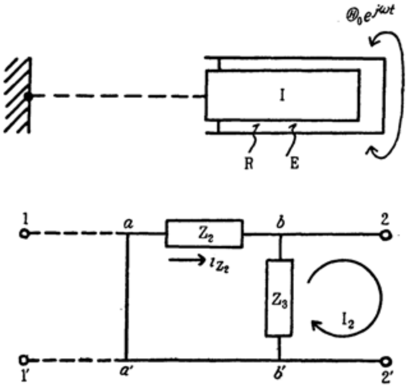

Fig. 9. Impedance-less suspension rheometer.

*** In this case the rigorous analysis[3,3'] is rather convenient to use.

$$Z_1 = \frac{k}{j\omega} = 0$$

When we put $k=0$ in Eq. 15, motion of the internal cylinder in the case of the impedance-less suspension is obtained as

$$\theta = \frac{\sqrt{E^2+\omega^2 R^2} \cdot \Theta_0}{\sqrt{(E-\omega^2 I)^2+\omega^2 R^2}} e^{j(\omega t-\phi)} \equiv A_0 e^{j(\omega t-\phi)}$$

$$\tan\phi = \frac{\omega^3 R I}{E(E-\omega^2 I)+\omega^2 R^2}$$

If we differentiate A_0 and set $\partial A_0/\partial\omega$ equal to zero, the condition for a maximum, or for the amplitude resonance, is fulfilled and we find that

$$\omega^2_{res} = \frac{-n_e^4 + n_e^4 \cdot \sqrt{1+8\varepsilon^2/n_e^2}}{4\varepsilon^2}$$

at resonance, where $2\varepsilon = R/I$ and $n_e^2 = E/I$. When $\varepsilon^2 \ll n_e^2$, or when the elastic nature is very strong in the liquid under study,

$$\omega^2_{res} = \frac{-n_e^4 + n_e^4(1+4\varepsilon^2/n_e^2)}{4\varepsilon^2} = n_e^2 = \frac{E}{I}$$

So that it is possible to know the elastic constant of an elastic liquid approximately from

$$G = \frac{I}{4\pi l}\left(\frac{1}{r_1^2} - \frac{1}{r_2^2}\right)\omega^2_{res}$$

(It is of course possible to calculate the true shear modulus and the damping viscosity by the appropriate correctional procedure[1].)

The resonance method, however, as was mentioned previously, seems to be incorrect from the point that the inertia of the sample can not be neglected in the frequency range usually adopted.

(4) **Rotational Viscometer and Schwedoff Apparatus** Apart from the oscillating devices, two simple rheometers will be mentioned; one of them is the rotational viscometer and the other is the apparatus which was used by Th. Schwedoff[7] and others[8] to measure the shear modulus of gel-like matter.

Rotational Viscometer.—In the ordinary type rotational viscometer (Couette-Hatschek apparatus) the external cylinder rotates with a constant angular velocity Ω, while the top end of the suspension wire is kept in position. The stationary state is reached after the inner cylinder is deflected to a certain extent θ.

The electrical analog is illustrated in Fig. 10; the input terminals $1-1'$ are opened and the output direct current $I_2 = \Omega$ (D.C.). In

7) Th. Schwedoff, *J. de Phys.*, [2] **8**, 341 (1889).
8) E. Hatschek and R. S. Jane, *Koll. Z.*, **39**, 300 (1926); H. J. Poole, *Trans. Farad. Soc.*, **22**, 82 (1926).

the stationary state the inductance I is inactive because no current flows in it, and counter-electromotive force at the resistor part balances with that of the capacitor

$$R\Omega = \frac{\theta}{1/k}$$

or

$$R\Omega = k\theta$$

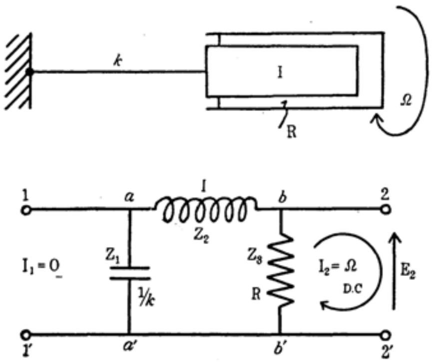

Fig. 10. Rotational viscometer.

The well-known Couette-Hatschek formula of the rotational viscometer is

$$\frac{4\pi l}{\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right)}\eta\Omega = k\theta$$

and then

$$\eta = \frac{R}{4\pi l}\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right) \equiv K_0 R \qquad (8)$$

It has simply been assumed in the present discussion that the relation 8 holds in the oscillatory case too.

Schwedoff Apparatus.— In the Schwedoff method for measuring the elasticity of typical elastic gels—e.g. gelatin gel, agar-agar gel and so on, the top end of the suspension wire is twisted to an angle θ_1 and the equilibrium deflection θ_2 of the internal cylinder is observed.

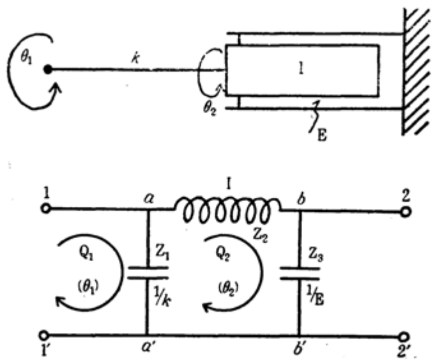

Fig. 11. Schwedoff apparatus.

The situation is that at the equilibrium the inductance is inactive and the voltage Q (charge)/C (capacitance) of the one capacitor is equal to that of the other (cf. Fig. 11 and Table I).

$$\frac{(\theta_1-\theta_2)}{1/k} = \frac{\theta_2}{1/E}$$

or

$$E = k\frac{(\theta_1-\theta_2)}{\theta_2}$$

The exact formula derived by Schwedoff is

$$G = \frac{k}{4\pi l}\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right)\cdot\frac{(\theta_1-\theta_2)}{\theta_2}$$

Then

$$G = \frac{E}{4\pi l}\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right) \equiv K_0 E \qquad (9)$$

The author has extended this shape factor K_0 to the case of the dynamic elasticity throughout the discussion.

As to the time effect of the elastic deformation of gels, (a) the elastic after-effect (retarded elasticity or parallel visco-elasticity) is described by a resistor element inserted in series to the capacitor of Z_3, and (b) flow (relaxed elasticity or series visco-elasticity) is analogized by a leakage resistance inserted in parallel in Z_3.

(5). **More Complicated Cases.**—When the cup and the upper end of the wire are both driven, the general case must be solved in

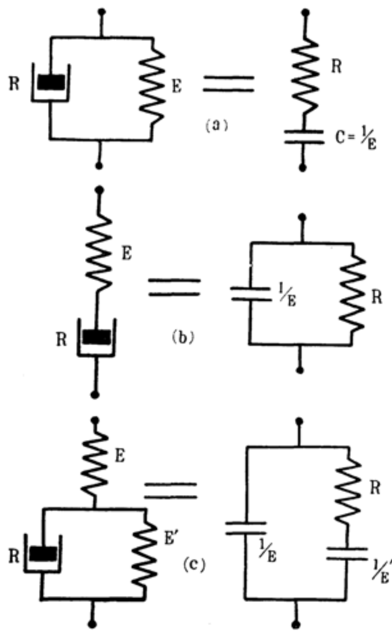

Fig. 12. Mechanical models and corresponding networks.

which $I_1 \neq 0$, $I_2 \neq 0$ and they are in some phase difference.

Throughout the discussion the $R-C$ series circuit was assumed as to the components of Z_3, corresponding to the parallel mechanical model (Voigt model) as is shown in Fig. 12 a, in which $Z_3 = R + E/(j\omega)$. If necessary, however, other impedance functions may be adopted—e.g. R—C parallel circuit corresponding to Maxwell model (Fig. 12 b), or three-element model (Fig. 12 c) in which

$$Z_3 = \frac{1}{\dfrac{1}{E/(j\omega)} + \dfrac{1}{R + E'/(j\omega)}}$$

Summary

(1) The four-terminal electrical network is shown to be useful in the schematic representation of various mechanical systems.

(2) A simple review on various types of torsionally oscillating rheometers is given according to the theory of four-terminal networks.

(3) It is shown that complicated viscoelastic systems are easily solved so far as their formalistic treatment is concerned.

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