

Measuring system for complex shear modulus of liquids using torsionally vibrating quartz crystals

G J Beukema and J Mellema

Department of Applied Physics, Twente University of Technology, Enschede, The Netherlands

Received 3 July 1980, in final form 17 September 1980

Abstract In rheology torsionally vibrating quartz crystals are in use to determine dynamic shear moduli of liquids in the sonic and ultrasonic frequency range. A computer controlled measuring system using such crystals is described. The main advantages of this system are high measuring speed with respect to the manual AC bridge method and on-line data reduction.

As an illustration measurements of a solution of polystyrene in toluene in the 10–100 kHz range are presented.

1 Introduction

To determine the dynamic shear modulus of viscoelastic liquids several methods are in use. Torsionally vibrating piezoelectric quartz crystals can function as electromechanical transducers (Mason 1947). In our laboratory we use these crystals. An accurate manual AC bridge served as the measuring device.

Because of its low measuring speed, however, elaborate investigations of viscoelastic properties of liquids were time-consuming. To overcome this drawback a faster measuring system was built. The working of this system is based upon a variation on a method described by Sinclair (1938).

2 Measurement principle

The crystal can be represented by an electric circuit consisting of a resistive and a reactive component connected in parallel, $R(\omega)$ and $jX(\omega)$ respectively. The magnitude of these components change significantly in the vicinity of the crystal's mechanical torsional resonance modes. The resonance curves differ for surroundings of the crystal with different mechanical properties. If the surrounding material is well characterised (e.g. vacuo, a Newtonian liquid), the relevant electro-mechanical constants of the crystal can be calibrated. Then the mechanical properties of the liquid of interest can be

derived from a resonance curve measured in this liquid. In our procedure we always calibrate by means of a Newtonian liquid.

The resistive component $R(\omega)$ was found to be the most suitable variable to measure by means of a relatively simple method. The static inter-electrode capacitance of the crystal dominates the reactive component $jX(\omega)$ once immersion in a liquid occurs. So for the purpose of this measuring method its electric equivalent can be described by a resistance and a negative reactance connected in parallel, $R_x(\omega)$ and $-j/\omega C_x(\omega)$ respectively.

Figure 1(a) illustrates the measurement principle. The circuit can be divided into three main parts: (i) a reference resistor of known value R , (ii) the crystal components R_x and C_x and (iii) an additional circuit consisting of an inductance L , a variable capacitance C_v , and a resistor R_l representing losses in this additional circuit. The input signal is denoted by U_i , the output signal by U_o . $U_i = \hat{U}_i \sin \omega t$; $U_o = \hat{U}_o \sin(\omega t + \phi)$.

The measurement procedure for one frequency is as follows. Step 1: switch S is opened to disconnect the crystal; subsequently C_v is adjusted until phase resonance occurs ($\phi = 0$). This implies that the circuit can be represented by resistive components only (see figure 1(b)). Then U_i and U_o are measured. R_l can be deduced by using the values of U_i , U_o and R . Step 2: switch S is closed, so the crystal becomes part of the circuit. Again phase resonance is established: the addition of C_x is compensated by means of a reduction of C_v by an amount C_x . R_x can be deduced by using the values of R , R_l and the new ratio U_i/U_o .

3 System description

The crystal resistance R_x is mainly determined by the mechanical properties of the surrounding liquid. Hence the possibility of measuring the value of R_x over a wide resistance range is desirable. The use of higher harmonics would enhance the usefulness of the system. Obviously component values of the measuring circuit have to be adapted in order to cover these ranges.

We use a fixed reference resistor, one variable air capacitor, and three different coils adapted to the fundamental frequency and the lower two odd harmonics of a 18 kHz crystal. Amplitude and phase measurements are performed by a Hewlett-Packard 3042 system.

Figure 2 shows the measuring circuit in such a way that an idea is given of geometry and screening. The left-hand compartment contains the reference resistor R and the input-output switch S_5 . The right-hand compartment contains the three coils L_1 , L_2 and L_3 together with their associated dry reed switches S_1 , S_2 and S_3 , variable capacitor C_v and switch S_4 to (dis)connect the crystal.

The assembled measuring circuit, equipped with capacitor

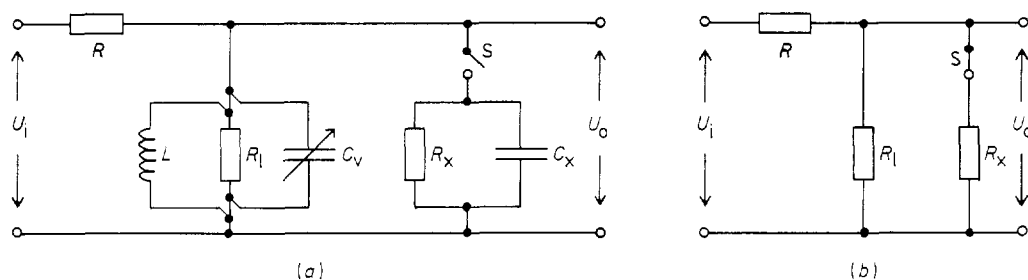


Figure 1 (a) Measurement principle. (b) Equivalent circuit at phase resonance.

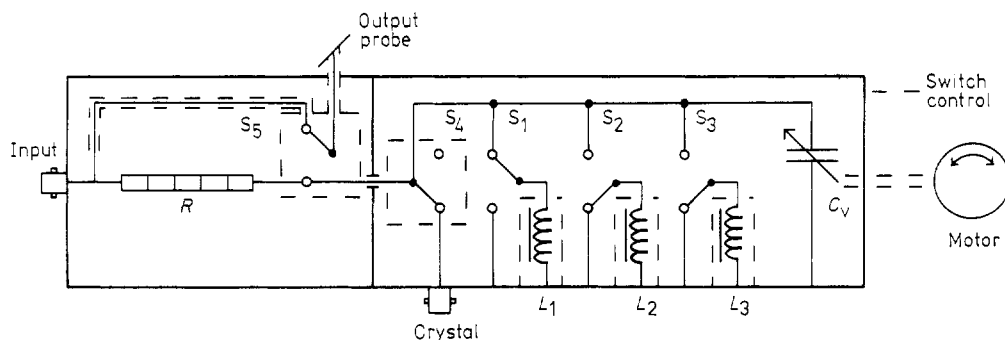


Figure 2 Measuring circuit.

drive motor, connectors for input and output signals, and motor and switch control signals, is forming a separate unit. After connection of the crystal this unit can be mounted on top of the sample holder.

Some measures were taken to reduce non-ideal component behaviour at higher frequencies:

- (i) the reference resistor R is composed of five metal film resistors connected in series. Their metal caps are soldered directly together;
- (ii) S_4 and S_5 are coaxial switches providing low open-contact capacitance (< 0.01 pF);
- (iii) coils are composed of ferrite pot-cores and low-capacitance windings of Litz wire;
- (iv) a high impedance $10\text{ M}\Omega/10$ pF probe is directly connected to the input-output switch S_5 ;
- (v) in general, connections are kept short to reduce wiring capacitance;
- (vi) to avoid changes in the self-inductance of the coils between both steps of the measuring procedure mentioned in §2 the output voltage U_o is kept at a constant level by changing the input voltage U_i accordingly.

The effective series resistance of C_v introduces an equivalent parallel loss resistance which varies with the setting of C_v . Systematic errors caused by this effect have not been observed in the frequency range used. Capacitor: Jackson Brothers, type U 102, 200 pF. Figure 3 shows the block diagram of the system. Dotted lines indicate digital control and data paths. The interface protocol is in accordance with IEEE std-488-1975. A Hewlett-Packard desk-top calculator type 9825 equipped with 24 kilobytes of read-write memory is used as the digital controller. A simple DC motor is used to drive the variable capacitor. Its control loop contains a variable-repetition pulse unit to extend the motor speed range. This

motor is disabled by the digital controller, once phase resonance occurs. Software completes the measuring system. The procedure described in §2 is carried out at the programmed frequencies. The measured resonance curves are fitted with least squares to the theoretically expected behaviour of $R_x(\omega)$. Once the system is calibrated, the dynamic moduli can be deduced from the resonance curves.

4 Discussion and results

Losses in the additional circuit, represented by R_1 , must be kept low in order to do accurate measurements at the higher harmonics as R_x increases with frequency. R_1 decreases as frequency increases, however, mainly due to coil losses. The value of R_1 is about 6, 4 and 3 M Ω at 18, 54 and 90 kHz respectively. The value of the reference resistor R is 1.8 M Ω .

The performance of the complete system was investigated with the aid of Newtonian liquids having a low dielectric constant.

The accuracy of the viscosity measurements appeared to be about 0.5% if $R_x \ll R_1$. If $R_x = R_1$, the accuracy decreased to about 1% and the maximum viscosity was 1.0, 0.15, and 0.05 Pa s at 18, 54 and 90 kHz respectively. The accuracy obtained is comparable with the accuracy of other systems used in this field. See survey by Oosterbroek *et al* (1980).

During measurements the voltage across the crystal is kept at a constant level of 0.1 V RMS. The system is in use for the determination of linear viscoelastic behaviour of liquids and no attempts were made to change this voltage level.

The time needed to measure one resonance curve depends

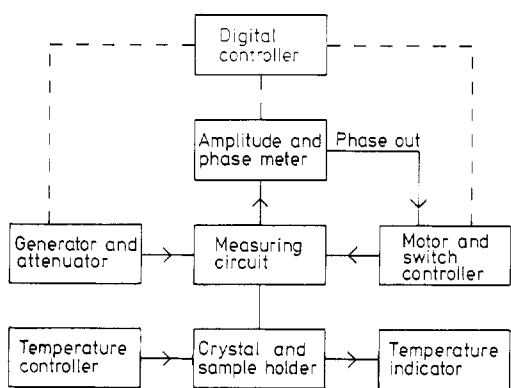


Figure 3 Block diagram of the measuring system.

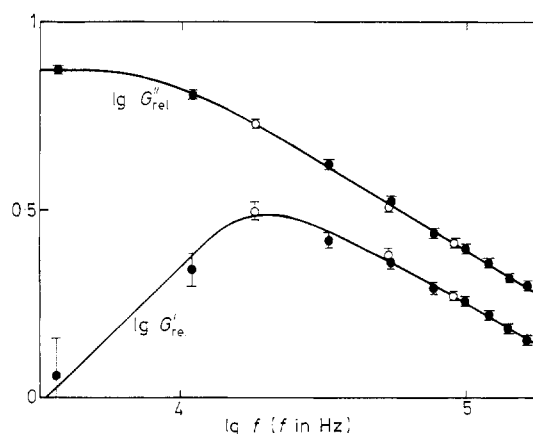


Figure 4 Dimensionless dynamic modulus of 3.8 g of polystyrene ($M = 254\ 000$) in 100 ml toluene as a function of frequency, measured with the crystal method (open circles) and the nickel-tube method (closed circles).

mainly on the settling time of the closed-loop capacitor drive system. This settling time has a maximum value at the lowest frequency. At this frequency less than 5 min are needed to complete the measurement of one resonance curve consisting of 15 discrete frequencies. The same measurement performed by means of our manual AC bridge (General Radio 1621 system) required about 20 min.

As an illustration of the quality of the described measuring system a set of measurements of a 3.8 g polystyrene in 100 ml toluene solution is presented. The weight average molecular weight of the polystyrene is 254 000. The dynamic shear moduli, shown in figure 4, are made dimensionless with the aid of the solvent viscosity η_0 according to $G_{rel}' = G'/\omega\eta_0$ and $G_{rel}'' = G''/\omega\eta_0$.

Open circles indicate measurements of the described system, closed circles are results derived from the nickel-tube method (Waterman *et al* 1979, Oosterbroek *et al* 1980). Considering the indicated error boundaries, the results of both methods are in good agreement.

Acknowledgment

The authors wish to thank E G Altena and J Labrie for their contribution to the construction of the system.

References

- Mason W P 1947 Measurement of the viscosity and shear elasticity of liquids by means of a torsionally vibrating crystal
Trans. ASME **69** 359–70
- Oosterbroek M, Waterman H A, Wiseall S S, Altena E G, Mellema J and Kip G A M 1980 Automatic apparatus, based upon a nickel-tube resonator, for measuring the complex shear modulus of liquids in the kHz region
Rheol. Acta **19** 497–506
- Sinclair D B 1938 Parallel-resonance methods for precise measurements of high impedances at radio frequencies and a comparison with the ordinary series-resonance methods
Proc. IRE **26** 1466–97
- Waterman H A, Oosterbroek M, Beukema G J and Altena E G 1979 On the use of a nickel-tube resonator for measuring the complex shear modulus of liquids in the kHz range
Rheol. Acta **18** 585–92

A new technique for the determination of vapour pressures by the Knudsen effusion method

Josef Tomiska

Institut für Physikalische Chemie der Universität Wien, Austria

Received 15 July 1980, in final form 7 October 1980

Abstract A description of a new technique – PENKER (Pendulum electronically balanced Knudsen-effusion recoil) – for vapour pressure measurements based on the Knudsen effusion method is given. The determination of vapour pressures by means of the suggested method is based on the recoil momentum of the evaporating species: the displacement of a pendulum, caused by the recoil of the escaping molecular beam, is automatically counteracted by an electromagnetic compensation system which is electronically controlled. The suggested method has clear advantages over the TORRER technique. It shows better mechanical stability, no oscillations, symmetrical furnace – cell configurations are possible, and there are no problems with electromagnetically induced cell rotations.

1 Introduction

The molecular effusion method (after Knudsen 1909a, b) has become a standard tool of experimental thermodynamics applied to vapour pressure measurements of condensed samples (Knudsen 1950, Margrave 1967, Komarek 1973, Rapp 1970, Kubaschewski and Alcock 1979). The method is based on the kinetic theory of dilute gases by which the molecular flux at a boundary can be calculated for a gas at equilibrium (Knudsen 1909a, b, 1950). Knudsen (1909a, b) showed that the equation for steady-state effusion of a dilute gas, derived by Hertz (1882),

$$p = \frac{dm}{dt} \frac{1}{A_0} \sqrt{\frac{2\pi k_B T}{M}} \quad (1)$$

where p = equilibrium vapour pressure, dm/dt = mass rate of effusion, A_0 = orifice area, k_B = Boltzmann constant, T = temperature, M = mass of a molecule in the vapour, can be used successfully for the determination of small vapour pressures (Knudsen 1909a, b, 1950, Margrave 1967, Komarek 1973, Rapp 1970, Kubaschewski and Alcock 1979).

Vapour pressure measurements based on the Knudsen effusion can be made in three different ways:

- (i) *The mass-loss technique* If the mass M of the molecules in the vapour is known, the direct determination of the mass rate of effusion dm/dt from the crucible, called the 'Knudsen cell', allows the evaluation of the equilibrium vapour pressures of the considered sample by means of equation (1).
- (ii) *The Knudsen-effusion method in combination with a mass spectrometer* (Margrave 1967, Komarek 1973, Rapp 1970, Kubaschewski and Alcock 1979). The composition of the molecular beam escaping the 'Knudsen cell' is analysed by means of a mass spectrometer. But direct determination of the absolute values of the partial and/or integral vapour pressures are beset with difficulties associated with indeterminate