Improved Understanding of Vibrating-Wire Viscometer−Densimeters

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The vibrating-wire technique has been widely applied in measurements of both viscosity and density. When tensioned by a suspended mass or sinker, the device may be used to measure these properties simultaneously. The sensitivity to density arises mainly from the effect of buoyancy on the tension and hence the resonance frequency of the vibrating wire. Earlier studies have used simplified working equations to relate the resonance frequency and the tension. In this work, we have employed the exact equations describing forced simple harmonic oscillations of a stiff wire under tension and also a second-order analytical solution of those equations. We show that the exact working equation describes the actual resonance frequency of tensioned tungsten wires with improved accuracy. This finding has been validated by means of experimental measurements of the resonance frequency at prescribed tensioning forces and at temperatures in the range (293 to 473) K. One consequence of this is that the true independently measured sinker volume may be used in preference to one obtained by calibration of the assembled sensor. The remaining parameters to be obtained are then the radius of the wire, Young's modulus *E* for the wire, and an empirical parameter that accounts for the remaining departure from the theoretical expression. The values of wire radius obtained by calibration in a liquid of known viscosity have been compared with those from independent mechanical measurements having a relative uncertainty of 0.2 %. These comparisons have been made for both drawn wires and for a centerless ground rod with a diameter of 0.15 mm, and the differences are discussed in the light of scanning electron microscopy (SEM) studies of the circularity and uniformity of the wire. Finally, we provide experimental evidence that rough drawn wires may yield inaccurate viscosity measurements when applied to fluids having viscosities very different to the one used for calibration; conversely, a centerless-ground rod gave good results even when the viscosity to be measured was 60 times that of the calibration fluid.

Introduction

Vibrating wire sensors, due to their versatility, have been used extensively to determine both viscosity and density of fluids under high pressure conditions.[1−4] The theory of such devices is well-established and relies upon working equations in which all of the parameters have a physical meaning.[5,6] In the type of device employed in this work, the vibrating wire is suspended vertically in the fluid, between the poles of a permanent magnet, and tensioned by a suspended sinker. An alternating current is passed through the wire, thereby setting it into transverse oscillation, and the voltage developed across the wire is measured by means of a lock-in amplifier. The steady-state frequency response of the oscillating wire is measured in the vicinity of the fundamental transverse resonance mode. The resonance frequency of this mode is sensitive to the density of the surrounding fluid, largely as a consequence of the buoyancy effect exerted on the sinker and the resulting changes in the tension of the wire. The width of the resonance curve is sensitive to the viscosity of the fluid. The measured voltage generally comprises two terms: the first, $V_1(f)$, arises from the electrical impedance of the stationary wire, while the second, $V_2(f)$, arises from the motion of the wire. In the analysis, we express the complex function $V_1(f)$ as

$$V_1(f) = a_0 + ia_1 + ia_2 f \tag{1}$$

where a_0, a_1, and a_2 are real constants. The second term is:

$$V_2(f) = \frac{\Lambda f i}{f_0^{\,2} - f^2(1 + \beta) + f^2(\beta' + 2\Delta_0)i} \tag{2}$$

where Λ is the amplitude, f_0 is the "buoyancy-corrected" fundamental transverse resonance frequency of the wire in vacuum, and the terms β and β' arise respectively from the added mass and the viscous damping of the fluids. In previous work,[1,2] f_0 was related to the true vacuum resonance frequency, $f_{0,\mathrm{vac}}$, as follows:

$$f_0^{\,2} = f_{0,\mathrm{vac}}^2 - \frac{gV\rho}{4\pi\rho_s R^2 L^2} \tag{3}$$

Here, g is the acceleration of gravity, V the volume of the sinker, ρ the density of the fluid, and ρ_s, R, and L are the density, radius, and length of the wire, respectively. The true vacuum frequency was approximated by that of an end-pinned rod tensioned by the sinker:[6]

$$f_{0,\mathrm{vac}} = \left(\frac{\pi^2 R^2 E}{16\rho_s L^4} + \frac{mg}{4\pi R^2 \rho_s L^2}\right)^{1/2} \tag{4}$$

Here, E is the Young's modulus of the wire material, and m is the mass of the tensioning sinker. The parameters present in eqs 2 to 4 come from a combination of direct measurements and calibration procedures.

Unfortunately, eq 4 is not exact, and the deviations observed experimentally have been attributed to the nonideal end condition of the wire; that is, a situation in which the end conditions conform to neither ideal pinned−pinned conditions nor ideal

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clamped–clamped conditions.[5,6] In an attempt to account for this, eq 4 was modified by the inclusion of an empirical parameter κ that was adjusted to fit the true vacuum resonance frequency:[1,2]

$$f_{0,\mathrm{vac}} = \kappa\left(\frac{\pi^2 R^2 E}{16\rho_s L^4}\kappa^2 + \frac{mg}{4\pi R^2 \rho_s L^2}\right)^{1/2} \qquad (5)$$

In this form, satisfactory results were obtained, enabling one to measure the viscosity and density of fluids with uncertainties of 2 % and 0.2 %, respectively.[1,3] Nevertheless, eq 5 is also not exact, and the constant κ does not generally have a full theoretical justification. To address these issues, we have revisited the theory describing the motion of a stiff wire subject to tension[6,7] and compared it with new experimental results obtained for different wires under various conditions of tension and temperature.

General Theory. The general theory describing transverse waves on a stiff string is detailed by Morse and Ingard,[7] and here we simply recall the key expressions. We can consider the stiff string as an intermediate case between the ideal string, in which the only restoring force is that arising from tension, and the ideal bar, in which the restoring force arises only from flexure stiffness. Practical vibrating wire systems are just such an intermediate situation: the tension provides the dominant restoring force, but flexure stiffness is significant. From equilibrium considerations we can write the equation of the motion of a stiff string (or tensioned bar) of uniform cross-section as:

$$T_s\frac{\partial^2 y}{\partial x^2} - ESk^2\frac{\partial^4 y}{\partial x^4} = \rho_s S\frac{\partial^2 y}{\partial t^2} \qquad (6)$$

Here, T_s is the tension, S the cross section, and k the radius of gyration.

We are interested in simple-harmonic transverse waves on the stiff string and hence seek an harmonic solution of the form $y = C\exp[2\pi i(\mu x - ft)]$. Substituting this in eq 6, we obtain the following relation between the wavenumber μ and the frequency f:

$$\mu^4 - 2\xi^2\mu^2 - \gamma^4 = 0 \qquad (7)$$

where

$$\xi^2 = \frac{T_s}{8\pi^2 ESk^2} \quad \text{and} \quad \gamma^2 = \frac{f}{2\pi}\sqrt{\frac{\rho_s}{Ek^2}} \qquad (8)$$

This equation has two roots for μ^2 and therefore four roots for μ given by $\mu = \pm\,\mu_1$ and $\mu = \pm\, i\mu_2$, where

$${\mu_1}^2 = (\xi^4 + \gamma^4)^{1/2} + \xi^2 \quad \text{and} \quad {\mu_2}^2 = (\xi^4 + \gamma^4)^{1/2} - \xi^2 \quad \text{and} \quad \mu_1\mu_2 = \gamma^2 \qquad (9)$$

The general solution may then be written as:[7]

$$y = a\exp(2\pi\mu_1 x) + b\exp(-2\pi\mu_1 x) + c\exp(2\pi i\mu_2 x) + d\exp(-2\pi i\mu_2 x) = A\cosh(2\pi\mu_1 x) + B\sinh(2\pi\mu_1 x) + C\cos(2\pi\mu_2 x) + D\sin(2\pi\mu_2 x) \qquad (10)$$

This general solution satisfies eqs 7 to 8 for any value of the frequency f; however, the boundary conditions restrict the allowed frequencies to discrete values.

Here we consider the situation, closely approached in our practical implementation, in which a wire of circular cross-section is clamped rigidly at both ends and is subjected to an imposed tension arising from the suspended sinker. Placing the origin midway between the ends, these boundary conditions imply that

$$y = 0 \quad \text{and} \quad \mathrm{d}y/\mathrm{d}x = 0 \quad \text{at} \quad x = \pm\frac{1}{2}L \qquad (11)$$

and lead to the following relations to be solved for μ_2 for the symmetric and antisymmetric modes of oscillation:

$$\tan(\pi L\mu_2) = -\sqrt{1 + \frac{2\xi^2}{{\mu_2}^2}}\tanh\left(\pi L\sqrt{{\mu_2}^2 + 2\xi^2}\right) \qquad n = 1, 3, 5... \qquad (12)$$

$$\sqrt{1 + \frac{2\xi^2}{{\mu_2}^2}}\tan(\pi L\mu_2) = \tanh\left(\pi L\sqrt{{\mu_2}^2 + 2\xi^2}\right) \qquad n = 2, 4, 6... \qquad (13)$$

Here n denotes the order of the mode, and the corresponding allowed frequencies are given by

$$f = 2\pi\gamma^2\sqrt{\frac{Ek^2}{\rho_s}} = \sqrt{\left(\frac{{\mu_2}^4\pi^2R^2E}{\rho_s} + \frac{{\mu_2}^2 mg}{\pi R^2\rho_s}\right)} \qquad (14)$$

The exact solution for f has to be obtained numerically from eqs 12 to 14. However, in the case where $\xi \gg 1$, corresponding to the situation in which tension is the dominant restoring force, a second-order analytical approximation maybe obtained for the nth transverse mode of oscillation:[7]

$$f_n = \frac{n}{2L}\left[\sqrt{\frac{mg}{\rho_s\pi R^2}} + \sqrt{\frac{ER^2}{\rho_s L^2}} + \left(4 + \frac{n^2\pi^2}{2}\right)\cdot\sqrt{\frac{E^2\pi R^6}{16mg\rho_s L^4}}\right] \qquad n = 1, 2, 3... \qquad (15)$$

Here, the first term in the square brackets, arising from the tension, is dominant; the second term is the leading correction arising from the flexure stiffness, and the third is a cross term. For the fundamental mode of a tungsten wire of a diameter of 150 μm and length of 70 mm, tensioned by a mass of 0.3 kg, these terms are approximately 664 Hz, 35 Hz, and 4 Hz, respectively. When the sinker (but not the wire) is immersed in a fluid of density ρ, we simply replace m in eq 15 by $(m - \rho V)$ to obtain the theoretical expression for f_0 in eq 2.

For purposes of comparison, we consider also the case in which both ends of the wire are pinned. The boundary conditions are:

$$y = 0 \quad \text{and} \quad \mathrm{d}^2y/\mathrm{d}x^2 = 0 \quad \text{at} \quad x = \pm\frac{1}{2}L \qquad (16)$$

and the only nonzero amplitude in eq 10 is either C, for the symmetric modes, or D for the antisymmetric modes. In either case, the solutions that satisfy eq 16 conform to $\mu_2 L = n/2$ and hence the resonance frequencies of the wire are given by

$$f_n = \left(\frac{n^4\pi^2R^2E}{16\rho_s L^4} + \frac{n^2 mg}{4\pi R^2\rho_s L^2}\right)^{1/2} \qquad (17)$$

which reduces to eq 4 for $n = 1$. The resonance frequencies of the end-pinned wire are always less than those of the corresponding end-clamped wire.

Other more complicated boundary conditions might exist. One factor, which we consider approximately in the appendix, is that the mass of the tensioning sinker is finite. Thus the

Table 1. Nominal Properties of the Wires

parameter	wire sample 1	wire sample 2	reference
$R/\mu m$	75	75	manufacturer
$\rho_s/(kg\cdot m^{-3})$	19250	19250	8
E/GPa	411	411	8
α_w/K^{-1}	$4.50\cdot10^{-6}$	$4.50\cdot10^{-6}$	8
relative eccentricity	< 2 %	0	manufacturer
coat thickness/μm	0.5	uncoated	manufacturer

transverse force acting at the bottom end of the wire must give rise to a nonzero displacement amplitude there. However, in the present case, this is estimated to cause a relative decrease in the fundamental resonance frequency amounting to less than 0.001 %, and we do not consider this effect further.

In a practical apparatus, neither the boundary conditions nor the wire properties may be known with sufficient certainty to employ a fully theoretical evaluation of the resonance frequency. Nevertheless, we expect (and our results confirm) that eq 15 is a good starting point, and we proceed by including an empirical parameter a and write the working equation for the resonance frequency of the stiff wire as:

$$f_0 = \frac{n}{2L}\left[a\sqrt{\frac{(m-\rho V)g}{\rho_s\pi R^2}} + \sqrt{\frac{ER^2}{\rho_s L^2}} + \left(4+\frac{n^2\pi^2}{2}\right)\cdot \sqrt{\frac{E^2\pi R^6}{16(m-\rho V)g\rho_s L^4}}\right] \quad (18)$$

This, of course, reduces to the theoretical expression for end-clamped conditions when a is unity. It is important to highlight the fact that eq 18, in this form, represents the resonance frequency for the hypothetical situation of the wire in vacuum with the sinker immersed in the fluid, as required in eq 2.

Experimental Procedure

To test the validity of eq 18, experimental measurements were performed on two different types of wire. Sample 1 was a gold-plated drawn tungsten wire obtained from Luma Metal (Sweden). Sample 2 was a centerless ground tungsten wire obtained from Metal Cutting Corp. (New Jersey, U.S.A.). The nominal properties of the wires are summarized in Table 1.[8] We note that the value of the Young's modulus may differ significantly from one sample of material to another, depending upon both the structure and the purity of the sample, and this is reflected in the literature where values at ambient temperature of between 355 GPa[9] and 415 GPa[8] have been reported.

The vibrating-wire apparatus used in the present study was similar to the one described previously.[1,2] One notable difference was that the current and potential leads connecting to the lower end of the vibrating wire extended all of the way to a screw terminal on the top edge of the suspended sinker, whereas previously they joined at a terminal post inside the cell, and the connection to the suspended sinker was made by a single wire.

Samples of the wires were mounted in the apparatus, the sinker of mass $m = 0.317$ kg was attached, and measurements of the fundamental resonance frequency in air were made. Additional measurements were made either with added masses (up to 0.3 kg) attached to the sinker, to increase the tension, or with the entire assembly immersed in liquid, to decrease the tension. The maximum load generated a longitudinal stress in the wire of 340 MPa, which is well below the yield stress of tungsten. An electronic balance with a resolution of 0.001 g was employed for all weighing, and air buoyancy corrections were applied.[10] The additional masses were fabricated from nonmagnetic stainless steel, and their volumes were computed assuming a nominal value for the density of the steel of 7850 $kg\cdot m^{-3}$.[11] Care was required when manipulating the suspended sinkers as shocks to the system sometimes resulted in significant changes in the resonance frequency.

The volume of the sinker was measured independently by means of a hydrostatic weighing technique[12] and found to be (116.14 ± 0.06) cm^3. The lengths of the wires were measured with a digital cathetometer with an expanded uncertainty of 0.05 mm at a coverage factor, k of 2. These length measurements were made with the wires tensioned by the 0.317 kg sinker; however, even under the greatest tension considered, the calculated extension of the wire did not exceed 0.02 mm and was therefore neglected. The calculated decrease in the radius of the wire under tension was also negligible.

The resonance frequency f_0 in liquid was obtained by fitting eq 2 to the raw data with β and β' calculated on the basis of reference values for the density and viscosity of the liquid under the conditions of the experiment. In the case of the measurements in air, the quality factor is quite high (approximately 200), and so the experimental frequency range is small. Consequently, β and β' could be replaced by their values at the center frequency of the scan, and f_0 could be obtained from the observed resonance frequency f_{res} (at which the imaginary part of V_2 vanishes) by means of the relation

$$f_0^{\,2} = f_{res}^{\,2}(1+\beta) \quad (19)$$

The influence of the temperature was tested at five prescribed temperatures (T/K = 298.15, 323.15, 373.15, 423.15, and 473.15). As described previously,[1,2] the temperature of the fluid was inferred from the reading of a platinum resistance thermometer that was mounted in a well in the cap of the pressure vessel. This thermometer was calibrated by comparison with a standard platinum resistance thermometer that had itself been calibrated on ITS-90 at the UK National Physical Laboratory. The expanded uncertainty of the temperature measurements was ± 0.02 K ($k = 2$). The pressure was measured by means of a Paroscientific transducer (model 40K-110) that had been calibrated against a pressure balance in the range of 0.1 MPa to 200 MPa. The expanded uncertainty of pressure was ± 0.02 MPa ($k = 2$).

The radius of the wire plays an important role both in eq 18, in the calculation of β and β', and therefore in determining the viscosity and density of a fluid. This quantity is usually obtained by calibration in a fluid of known viscosity and density, and the instrument used in a relative manner.[3] In this work, the values of R obtained by such calibrations has been compared with those from independent mechanical measurements having a relative uncertainty of about 0.2 %. In addition, scanning electron microscopy (SEM) was used to investigate the cross section and surface finish of the wire, and this proved to be a valuable tool in choosing the best samples. The results are described in the following section for each individual wire studied.

An important point to note in relation to the determination of the radius by calibration is that the only property of the wire that one needs to know is the density of the wire material; neither the length nor the elastic constants are required. For prescribed values of ρ_s and ρ, the parameters β and β' in eq 2 depend upon the dimensionless quantity $\Omega = \rho\omega R^2/\eta$,[5] and hence the relative uncertainty of R is usually dominated by that of η for the calibration fluid. A sensitivity analysis shows that the effect of small uncertainties in ρ_s cancels out in viscosity determinations provided that the value used is consistent with that assumed in the calibration experiment.

Table 2. Comparison of the Experimental Transverse Resonance Frequency, f_{exp}, with the Theoretical Value for Clamped−Clamped End Conditions, f_{th}, Obtained by Numerical Solution of Equation 12, the Approximate Analytical Solution, f_{ap}, Obtained from Equation 15, and the Theoretical Value for Pinned−Pinned End Conditions, for the *n*th Harmonic

wire	L/mm	n	m/kg	f_{exp}/Hz	f_{th}/Hz	f_{ap}/Hz	f_{pp}/Hz
sample 1	70.26	1	0.317	709.95	724.21	723.98	686.26
sample 1	70.26	1	0.494	876.14	893.74	893.59	855.71
sample 2	65.26	1	0.317	777.61	785.85	785.54	737.17
sample 2	65.26	3	0.317	2401.1	2425.2	2421.4	2276.70

Results

1. Gold-Plated As-Drawn Tungsten Wire. The radius of the wire was determined by calibration measurement in degassed and deionized water, having an electrical conductivity of <15 $\mu S \cdot cm^{-1}$, at T = 294.96 K and p = 1.02 MPa. The slightly elevated pressure was chosen to ensure complete filling of the viscometer without the possibility of bubbles forming; these might otherwise arise as a consequence of imperfect degassing. The viscosity of water under those conditions was taken to be $\eta = (0.9587 \pm 0.002)$ mPa·s and the density 998.23 $kg \cdot m^{-3}$.[13] The value of the radius obtained by this hydrodynamic calibration was $R = (74.60 \pm 0.28)$ μm.

Table 2 gives experimental results obtained for the fundamental mode of this wire measured in ambient air at T = 294 K under the influence of two different masses. The experimental resonance frequency may be compared with the value computed by numerical solution of eq 12 and from the analytical approximation, eq 15, based on the nominal wire properties given in Table 1 and the calibrated radius. We note that the analytical approximation gives results that are very close to those obtained with a full numerical solution. We also tabulate the theoretical resonance frequency for the case of pinned−pinned end conditions. The experimental results fall in between the theoretical values for clamped−clamped and pinned−pinned conditions, but are closer to the former.

Two different lengths of the wire, L = 67.50 mm and 70.26 mm, were investigated in detail over a range of tensioning conditions, and the results are shown in Figure 1. The values of $(m - \rho V)$ >0.317 kg relate to the cell being in ambient air, with additional masses loaded, while the smallest value of $(m - \rho V)$ was obtained with the cell filled with water. Figure 1 also shows eq 18 with the value of a fitted to the experimental data; the optimal value was found to be a = 0.9804, about 2 % different from the theoretical value of unity. In carrying out this fit, we have also treated the value of Young's modulus as

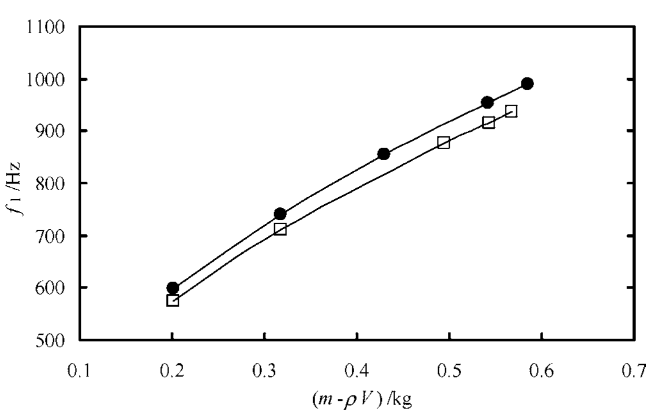

Figure 1. Experimental resonance frequency of the wire sample 1 as function of tensioning force and wire length: ●, L_1 = 67.50 mm; □, L_2 = 70.26 mm; solid line indicates eq 18.

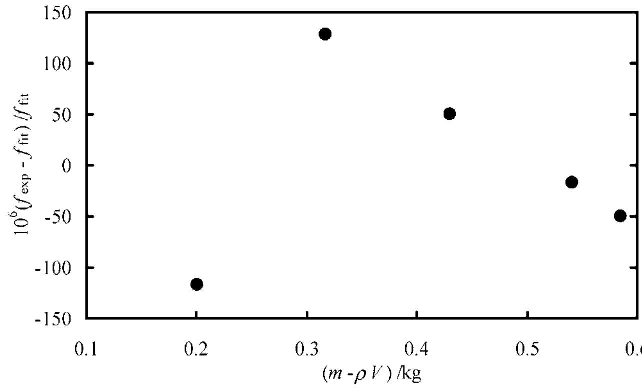

Figure 2. Fractional deviation of the experimental vacuum resonance frequency from eq 18 as a function of tensioning force (wire sample 1): ●, experimental points.

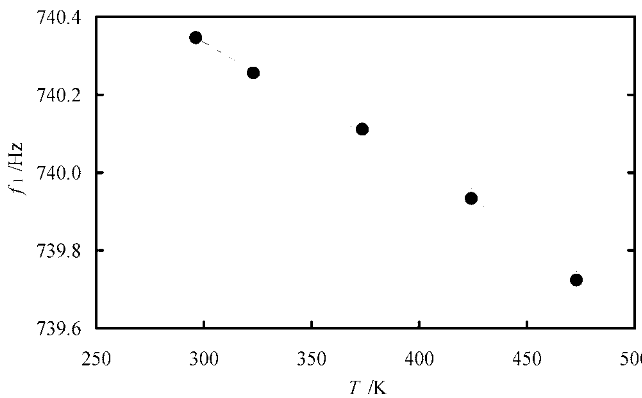

Figure 3. Vacuum resonance frequency of wire sample 1 as function of temperature: ●, experimental points; solid line indicates eq 18 with fitted ε; dashed line indicates eq 18 with ε estimated from ref 14; dash−dot−dashed line indicates eq 18 with ε estimated from ref 9.

an adjustable parameter, obtaining the value of E = 407 GPa. The goodness of fit is illustrated in Figure 2, where the fractional deviations of the experimental data from eq 18 are plotted.

Results obtained at fixed tension but at different temperatures are shown in Figure 3 in comparison with eq 18 with the value of a equal to that determined at ambient temperature. In making this comparison, ρ_s, L, V, E, and ρ were all treated as temperature-dependent parameters, assuming for the wire and sinker isotropic thermal expansion with the temperature-independent expansivities given in Table 1. For Young's modulus, we assumed a linear dependence upon temperature of the form $E = E_0\{1 - \varepsilon(T - T_0)\}$ with E_0 = 407 GPa and T_0 = 294 K. The temperature coefficient ε was estimated both from the available literature data and by fitting to the experimental resonance frequencies. Unfortunately, the literature data for $E(T)$ have large relative uncertainties, of the order of 3 % to 5 %,[9,14] and we prefer the fitted result, $\varepsilon = 0.98 \cdot 10^{-4}$ K^{-1}. With ε adjusted in this way, the agreement with eq 18 is excellent, and the absolute relative deviations are never greater than $1.5 \cdot 10^{-4}$. This demonstrates that a is independent of temperature and that eq 18 is an excellent working equation for the buoyancy-corrected fundamental vacuum resonance frequency of the wire.

We next commissioned the UK National Physical Laboratory to make an independent mechanical measurement of the radius of one of the two pieces of wire sample 1 used in our experiments. The measurements were made by means of a contact technique at five equally spaced positions around the circumference and at various positions along the length. They

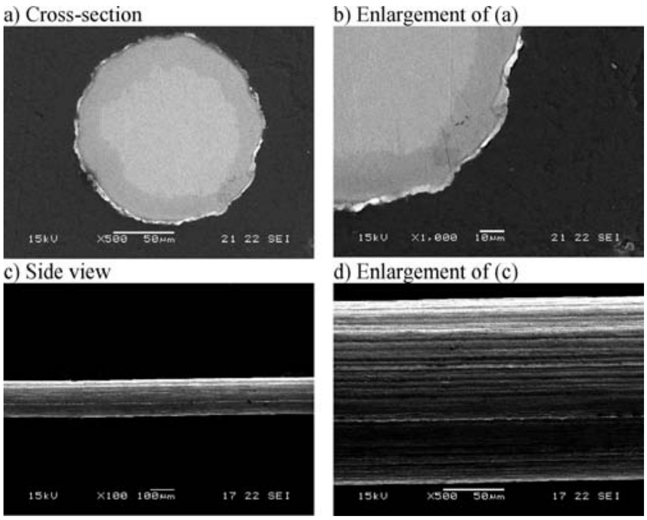

Figure 4. SEM images of wire sample 1 (gold-plated tungsten wire).

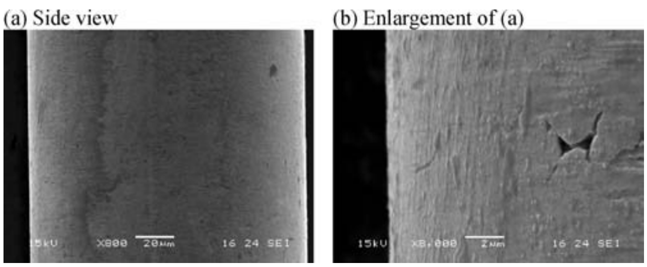

Figure 5. SEM images of wire sample 2 (centerless ground tungsten wire).

gave a mean radius of (75.94 ± 0.06) μm at T = 293.15 K, with a mean eccentricity of 0.9 μm.

This measurement of R is relatively 1.7 % greater than the hydrodynamic radius determined by calibration in water, clearly indicating that calibration is required to keep the relative uncertainty in viscosity measurements below 2 %.

The SEM images obtained, (Figure 4), show that the surface of the wire is irregular with marked longitudinal grooves and significant deviations from circular cross section, both presumably resulting from the manufacturing process. Thus the difference between the values of the effective radius obtained by mechanical and hydrodynamic means are not surprising and we attribute it to the observed deviations from the ideal cylindrical form.

2. Centerless Ground Tungsten Wire. Similar experiments were repeated on sample 2. As shown in Figure 5, this wire exhibited an excellent surface finish and a regular section along the length, with only some sporadic micro cracks of the order of 1 μm long. In this case, the radius of the wire was determined by calibration in octane (Fluka, mass fraction purity >0.995) at T = 298.15 K and p = 1.0 MPa. The viscosity of octane under those conditions was taken to be η = (0.514 ± 0.002) mPa·s, on the basis of the value at T = 298.15 K and p = 0.1 MPa, and the associated relative uncertainty of ± 0.3 %, recommended by Dymond and Øye[15] and the pressure dependence given by the correlation of Huber et al.[16] The density of octane at T = 298.15 K and p = 1.0 MPa was taken to be ρ = 699.1 kg·m^{-3} from the equation of state of Span and Wagner.[17] Octane was preferred to water which had led to some corrosion in a previous test. The value of the radius obtained by calibration was (74.18 ± 0.45) μm.

Figures 6 and 7 show the effects of tension and temperature on f_0 for the fundamental mode in comparison with eq 18 after fitting the values of a and E to the data in Figure 6. As with sample 1, we considered both the temperature dependence of Young's modulus obtained from the literature data and also a value fitted to our results. With the latter approach, the deviations from eq 18 were found to be smaller than for sample 1, and the maximum absolute relative deviation was $0.7 \cdot 10^{-4}$. Interestingly, the value of a remained about the same, a = 0.9832, and this parameter was again independent of temperature, but we obtained a significantly higher value of Young's modulus and a larger temperature coefficient: E = 488 GPa and ε = $1.24 \cdot 10^{-4}$ K^{-1}. The mean radius of sample 2, as measured by the supplier, was (74.29 ± 0.06 μm), and this agrees to well within the combined uncertainties with the value obtained by hydrodynamic calibration in octane. This suggests that the surface finish is of some importance. Furthermore, it suggests that it is possible to use the viscometer in an absolute way and with relative uncertainties in viscosity and density less than 1 % and 0.2 %, respectively, provided that a precision centerless ground wire is used.

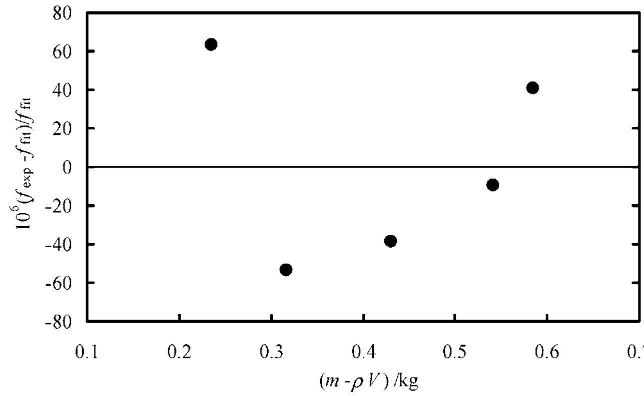

Figure 6. Fractional deviation of the experimental vacuum resonance frequency from eq 18 as a function of tensioning force (wire sample 2). ●, experimental points.

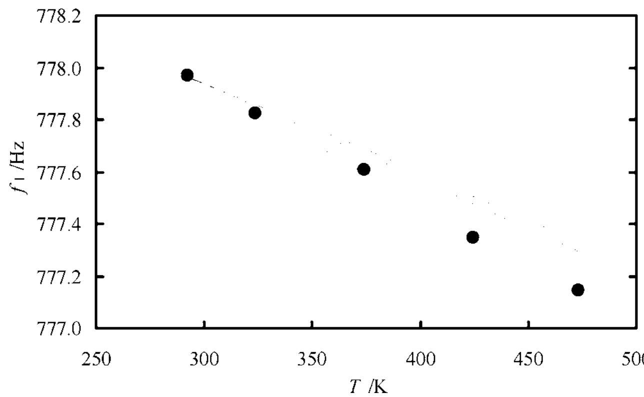

Figure 7. Vacuum resonance frequency of wire sample 2 as function of temperature: ●, experimental points; solid line indicates eq 18 with fitted ε; dashed line indicates eq 18 with ε estimated from ref 14; dash−dot−dashed line indicates eq 18 with ε estimated from ref 9.

Table 2 compares the experimental resonance frequency in ambient air with the theoretical values for both the fundamental mode (n = 1) and the third harmonic (n = 3) on the basis of the nominal wire properties given in Table 1 and the calibrated radius. We note that the analytical approximation, eq 15, differs from the exact solutions, eq 12, slightly more in the case of the third mode, but the difference remains smaller than the deviation of the experimental value. For the n = 3 mode, the experimental resonance frequency is much closer to the theoretical value for clamped−clamped end conditions than it is to the value for

Table 3. Viscosity Results on S20 Standard Fluid at T = 298.15 K and p = 0.1 MPa

source	wire sample 1	wire sample 2	calibration report
η/mPa·s	28.28	29.08	29.23
relative deviation	3 %	0.5 %	

pinned–pinned conditions. The resonance frequency for that mode predicted by eq 18, on the basis of the values of a and E fitted to the data for the n = 1 mode, is 2409.7 Hz, which is fractionally 0.36 % greater than the experimental value.

3. Viscosity Measurements. The fact that the quality of the surface of the wire plays a certain role is also suggested by viscosity measurements made with both wires on a viscosity standard fluid (Cannon, S20). In this case, both wires were calibrated in octane at T = 298.15 K. Measurements were then made on S20 at ambient pressure and various temperatures using wire sample 1, the gold-plated drawn tungsten wire. At higher temperatures such that η <20 mPa·s, the results agreed with the data provided by the supplier to within 0.01·η. However, at T = 298.15 K, where the viscosity was 29 mPa·s (approximately 60 times the value used in calibration of the wire), we obtained the result reported in Table 3, which has a relative deviation of 3 %. This discrepancy was not present when using sample 2, the centerless ground wire. Use of a centerless ground tungsten wire for measurements of the viscosity of S20 has been reported previously by Sopkow et al.[18] However, their results at ambient pressure agree with earlier measurements[19] made with an as-drawn tungsten wire of the same diameter to within approximately 0.01η. Although larger relative differences were found at higher pressures, these might be attributed to differences between the two batches of S20 used, and so these results do not provide clear evidence of the effect of surface roughness. We also note that the importance of a good surface finish has been discussed by Wilhelm et al.[20] in the context of viscosity measurements on gases made with a vibrating-wire instrument.

Conclusions

An equation describing the buoyancy-corrected vacuum resonance frequency of a vibrating wire sensor has been tested over a wide range of tension and at temperatures up to 473 K. The equation gives significant improvements compared with previous models, leading to a more rigorous approach in determining the density of the fluids. Knowing all of the physical properties of the wire, the new working equation requires only one adjustable parameter, a, to obtain the resonance frequency. However, the present study also highlights the significant role of Young's modulus and the fact that this property is sample-dependent. Accordingly, $E(T)$ should be determined for the wire sample in question. Measurements of the resonance frequency of the wire in both air or vacuum and in a fluid of known density and viscosity are sufficient to determine both a and the value of E at the calibration temperature. The temperature dependence of E may be obtained by extending the calibration measurements in air or vacuum over the working temperature range of the instrument. It is likely that $E(T)$ will be the same for a given lot of wire, so that a simplified calibration procedure at a single temperature may be followed for subsequent pieces cut from the same batch.

Centerless ground tungsten wires give more accurate and consistent results and, combined with a precise mechanical measurements of the radius, permit absolute measurement of viscosity with a relative uncertainty below 1 %. Drawn tungsten wires appear to be adequate for relative viscosity measurements within 2 % for a range of viscosities extending up to approximately 40 times the value at which the radius was calibrated. At higher viscosities, slightly larger errors are to be expected depending upon the imperfections of the wire surface.

Appendix: Inertial End Condition for a Flexible String

We consider transverse oscillations of a flexible string of a circular cross-section fixed to a rigid support at its upper end and tensioned by a suspended mass m. Since, for the wires considered in the present work, tension is by far the dominant restoring force, this approximation should suffice for determining the effect of the finite inertial of the sinker. The equation of motion is

$$(\partial^2 y/\partial t^2) = c^2(\partial^2 y/\partial x^2) \tag{A1}$$

where y is the transverse displacement, x is the vertical coordinate, t is time, $c = [T_s/(\pi R^2 \rho_s)]^{1/2}$, and T_s is the tension. For simple harmonic oscillation at angular frequency ω, the displacement may be written as $y = \mathrm{f}(x)\exp(i\omega t)$ and $\mathrm{f}(x)$ obeys the equation

$$(d^2\mathrm{f}/dx^2) + k^2\mathrm{f} = 0 \tag{A2}$$

with $k = \omega/c$. In this case, we place the origin at the top end of the string. The solution of eq A2 satisfying the boundary condition $y = 0$ at $x = 0$ is $\mathrm{f}(x) = A\sin(\omega t)$, and if the lower end of the string at $x = L$ were also rigidly clamped, then the allowed values of k would satisfy:

$$kL = n\pi \tag{A3}$$

where n is a positive integer. However, in the present case the end condition at $x = L$ is an inertial one:

$$T_s(\partial y/\partial x) = m(\partial^2 y/\partial t^2) \tag{A4}$$

For simple harmonic motion eq A4 requires that

$$T_s(d\mathrm{f}/dx) = -\omega^2 m\mathrm{f} \tag{A5}$$

and with $T_s = mg$, the allowed values of k are the solutions of

$$\tan(kL) = -g/(kc^2) \tag{A6}$$

Since $g/(kc^2) \ll 1$, we write the solution in the form $kL = n\pi(1 - \delta)$ and solve eq A6 correct to first order in δ with the result

$$\delta = \rho_s R^2 L/(n^2 \pi m) \tag{A7}$$

This quantity is the fractional decrease in the nth transverse resonance frequency resulting from changing the lower end condition from a rigid support to one determined by the inertia of the sinker under conditions of constant tension. For the examples considered above, this perturbation is very small, amounting to just $8\cdot10^{-6}$ for the fundamental mode of wire 1.

Note Added in Proof: It has been reported recently[21] that the effect of stiffness on the fundamental resonance frequency of a wire with pinned–pinned end conditions was considered in some detail by the physicist Richard Feynman in a letter to his piano tuner dated July 3, 1961. Feynman's result may be obtained from eq 4 by expanding the square root and retaining the two leading terms.

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