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A Vibrating-Rod Densimeter

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Measurements are reported that confirm the applicability of the theory of a vibrating-rod densimeter to a practical instrument. It is demonstrated that with such a device, liquid density measurements evaluated on an absolute basis can be made with an accuracy of ±0.2% at pressures up to 100 MPa. When the density of the liquid is evaluated on a relative basis, a precision of ±0.1% can be achieved over the same range of pressure. Future developments of the instrument that would greatly enhance its sensitivity and that rely upon the availability of a proven theory are therefore now possible.

KEY WORDS: densimeter; density; high pressure; *n*-heptane; vibrating wire.

1. INTRODUCTION

The density of a fluid or fluid mixture is a key quantity in both science and engineering. First, it is the prime variable in any statistical mechanical theory of the macroscopic properties of fluids, and second, in practical applications, it is frequently required to convert measured volumetric flow rates to mass flows. In the latter connection, it is often desirable to determine the fluid density *in situ*. While this can often be done in an environment at moderate pressures (<40 MPa), it is much more difficult at higher pressures (up to 500 MPa). Indeed, measurements of the density of liquids at pressures above 100 MPa are difficult in any event and it has rarely been possible to maintain the accuracy of measurements characteristic of lower

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pressures [1]. This is unfortunate because the interpretation of measurements of other properties of liquids, such as the thermal conductivity [2], make use of the fluid density and pressures above 100 MPa are necessary in order to achieve substantial density changes in liquids.

Most measurements of the density of liquids at elevated pressures have been carried out with bellows volumometers [3, 4]. Because these devices contain the test fluid inside a flexible surface, the deformation of the volume can be observed and related to the change in fluid density. The flexible surface is often formed in a cylindrical bellows configuration, which means that the relationship between the observed movement of one end of the bellows and the total volume change of the system must be established by calibration. The only fluids for which the density is known with a high accuracy over a wide range of pressures are water [5] and mercury [6], and they are both substantially less compressible than other fluids. Consequently, bellows volumometers are frequently used outside of their range of calibration. Other types of densimeters, such as the vibrating U-tube [7, 8] also contain the fluid inside a nominally fixed volume and determine the mass of the system in some way, by means of the resonant frequency in the case of this example. Here, the deformation of the volume under the influence of an internal pressure must be treated and this is difficult, especially when it may not be entirely elastic.

For these reasons, we have considered a different type of densimeter for use at high pressures in which the test fluid is external to all important surfaces. The principle of the densimeter then becomes that of the observation of the resonant frequency of the oscillations of a body of revolution when surrounded by the fluid. The advantages of this arrangement are that the effects of the external pressure on the dimensions of such a body are readily evaluated and that, if calibration is required, the compressibility of the fluid used for this purpose has no significance. The disadvantage of such an arrangement is that the theory of the device becomes more complicated because it is necessary to consider, in some detail, the fluid motion around the oscillating body.

This principle has been applied before to density measurements, most recently by Kestin and his collaborators [9], who have made use of a torsional oscillating-disk instrument for simultaneous density and viscosity measurements. In our work we have, in the first instance, considered the transverse vibrations of a circular section rod in the fluid since it is more readily applicable at very high pressures and the theory of the instrument has been given in detail elsewhere [10]. In this paper we consider the practical application of that theory to a prototype instrument. The present work has therefore been performed with the intention of establishing the validity of the theory. In subsequent work, it is intended to enhance the sensitivity of the instrument by making use of a direct buoyancy effect of the resonant frequency of the rod in addition to the effects of fluid motion, while relying on the same underlying theory.

2. THEORY

The principle of the present instrument is illustrated in Fig. 1, wherein a long ($L \gg R$) cylindrical-section solid body performs transverse oscillations in the fundamental mode in a fluid of infinite extent. The theory describing the motion of the solid and that of the fluid has been given in detail elsewhere [10] so that here we need only to provide the conditions to which it is subjected and the final working equation in order to permit a discussion of the design of the present instrument.

The constraints upon the theory of the motion in a unconfined fluid are that

$$L/T \gg 1 \tag{1}$$

$$\mathrm{Ma} \equiv \omega \varepsilon R/c \ll 1 \tag{2}$$

$$\varepsilon \ll \Omega = \frac{\rho \omega R^2}{\mu} \ll 1/\varepsilon^2 \tag{3}$$

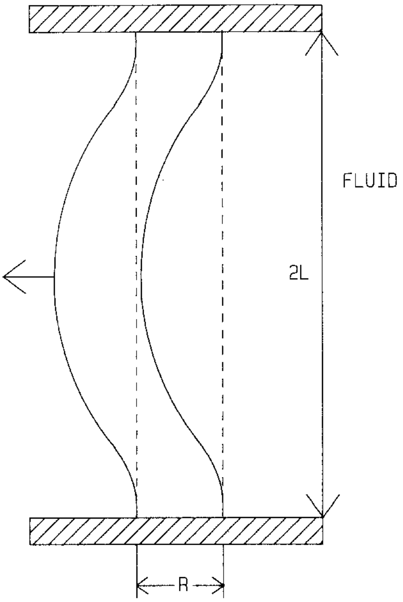

Fig. 1. The principle of the vibrating-rod densimeter.

and

$$\varepsilon \ll 10^{-2} \tag{4}$$

where ω is the angular frequency of the motion, ε the ratio of the amplitude of the motion of the rod to its radius, R, Ma the Mach number, c the velocity of sound in the fluid, ρ the fluid density, and μ its viscosity.

Provided that all of these conditions are adequately satisfied, then the resonant frequency of the rod when immersed in a fluid, ω_r, is given by the solution of the equation

$$\frac{d}{d\omega}\{[\omega^{*2}-\omega^2(1+\beta)]^2+\omega^4(\beta'+2\Delta_0)^2\}=0 \tag{5}$$

Here, ω^* is related to the resonant frequency of the rod *in vacuo* ω_0 by the equation

$$\omega_0=\frac{\omega^*}{(1+4\Delta_0^2)^{1/2}} \tag{6}$$

in which Δ_0 is a dimensionless coefficient of internal damping. The quantities β and β' contain the effects of the fluid motion on the system, and when the fluid is of infinite extent, they are defined by the equations

$$\beta=\frac{\rho}{\rho_S}k(\rho,\mu,\omega,R), \qquad \beta'=\frac{\rho}{\rho_S}k'(\rho,\mu,\omega,R) \tag{7}$$

where ρ_S is the density of the solid material. Here

$$k=-1+2\,\mathrm{Im}(A) \tag{8}$$

and

$$k'=2\,\mathrm{Re}(A) \tag{9}$$

where

$$\mathrm{Re}(A)=\mathrm{Im}(D)\,\mathrm{kei}_1(\sqrt{\Omega})-\mathrm{Re}(D)\,\mathrm{ker}_1(\sqrt{\Omega}) \tag{10}$$

$$\mathrm{Im}(A)=1-\mathrm{Re}(D)\,\mathrm{kei}_1(\sqrt{\Omega})-\mathrm{Im}(D)\,\mathrm{ker}_1(\sqrt{\Omega}) \tag{11}$$

and

$$\mathrm{Re}(D)=\left(\frac{2}{\Omega}\right)^{1/2}\left[\frac{\mathrm{ker}_0(\sqrt{\Omega})-\mathrm{kei}_0(\sqrt{\Omega})}{\mathrm{ker}_0^2(\sqrt{\Omega})+\mathrm{kei}_0^2(\sqrt{\Omega})}\right] \tag{12}$$

$$\mathrm{Im}(D)=-\left(\frac{2}{\Omega}\right)^{1/2}\left[\frac{\mathrm{ker}_0(\sqrt{\Omega})-\mathrm{kei}_0(\sqrt{\Omega})}{\mathrm{ker}_0^2(\sqrt{\Omega})+\mathrm{kei}_0^2(\sqrt{\Omega})}\right] \tag{13}$$

Here, Re( ) and Im( ) denote real and imaginary parts, respectively, and $\ker_n$ and kei_n denote Kelvin functions of order n [11].

For future use it is also worthwhile quoting the result for the two frequencies $\omega_\pm$ at which the amplitude of the motion is one-half of that at the resonant frequency ω_r because this is used later in a determination of the fluid viscosity. The result is

$$\begin{aligned} &4\{[\omega^{*2}+\omega_r^2(1+\beta)]^2+\omega_r^4(\beta'+2\Delta_0)^2\} \\ &\quad = [\omega^{*2}-\omega_\pm(1+\beta)]^2+\omega_\pm^4(\beta'+2\Delta_0)^2 \end{aligned} \tag{14}$$

From equations (5) to (13) it can be seen that given measurements of ω_0, Δ_0, ω_r, the density of the solid ρ_S, and a value for the fluid viscosity μ, it is possible to evaluate the fluid density ρ. From Eq. (14) the viscosity μ itself can be derived.

2.1. Design Criteria

In our earlier paper [10] the design procedures which enable a practical instrument to satisfy the constraints contained in inequalities (1) to (4) while maintaining a prescribed sensitivity to the fluid density and an appropriate insensitivity to the fluid viscosity were established. The dimensions of the instrument described in the next section have been selected on the basis of exactly these procedures. However, it is necessary to add to them a further constraint owing to the fact that the fluid surrounding the rod must be maintained in an enclosure of finite radius R_c. It has been shown that for a wide range of liquids, provided that $R_c/R > 25$, the effect of the outer boundary never contributes more than 0.5% to the density evaluated from an experiment. Furthermore, because an exact mathematical solution to the problem of the vibration of the rod in a finite volume of fluid is available in the limit as $\varepsilon \to 0$ [10, 12], it is possible to estimate the correction, $\delta\rho$, to be applied to the measured density to account for this effect. This evaluation cannot be exact because the true boundary of the fluid cannot be made cylindrical (Section 3); however, if the effect of the boundary is rendered sufficiently small, the error introduced will be negligible.

2.2. Measurements at Elevated Pressures

The use of measurements of the characteristics of the resonance of the rod *in vacuo* evidently removes the need for an exact knowledge of some properties and dimensions of the rod. However, if absolute measurements are to be performed over a range of conditions, then it is necessary to incorporate explicitly into the working equation the small, but significant, effects of pressure on the dimensions and properties of the rod. Those of temperature need not be included explicitly since the measurements *in vacuo* at each temperature effectively account for them. The dimensions of interest here are the rod radius and length, while the properties of concern are the density of the solid and its Young's modulus. The first three contribute to the resonant frequency both directly and indirectly through the evaluation of the quantities β and β', whereas the final one contributes only directly.

Explicit account of the effects of pressure may be taken by rewriting Eq. (5), the fundamental working equation, in the form

$$\begin{aligned}\frac{d}{d\omega}\biggl(\omega^{*2}-[\omega f_2(p)]^2\left\{1+\frac{\rho}{\rho_S}f_3(p)k[\Omega f_3(p)]\right\}^2 \\ +[\omega f_2(p)]^4\left\{\frac{\rho}{\rho_S}f_3(p)k'[\Omega f_3(p)]+2\Delta_0\right\}^2\biggr) \\ =\frac{d}{d\omega}\Theta(\omega,\rho,\mu,p;E,\rho_S,R)=0 \qquad (15)\end{aligned}$$

in which

$$f_i(p)=(1-p/E)^i \qquad (16)$$

and E is the Young's modulus of the solid material. The forms of the functions f_i are obtained from an analysis of the effects of elastic deformation on the dimensions of the rod as well as its resonant frequency. The working equation now contains the Young's modulus of the rod material as a parameter.

In order to perform absolute measurements of the fluid density at elevated pressures, it is therefore necessary to determine ω^* and Δ_0 by measurements *in vacuo* at each temperature and to have absolute values for the density of the solid material, ρ_S, its Young's modulus, E, and the rod radius, R. A value of the fluid viscosity, albeit of modest precision, is also required. Thus, given a measurement of ω_r in the test fluid at an elevated pressure, determination of the fluid density can be reduced to determination of the value of ρ, which renders the function $\Theta(\omega, \rho, \mu, p; E, \rho_S, R)$ a minimum with respect to ω at $\omega=\omega_r$.

However, it is often easier and more precise to make relative measurements, and for this purpose a calibration of the densimeter with respect to a fluid of known density must be performed. The two properties of the rod material ρ_S and E are the most difficult to measure precisely so that the calibrations should be performed so as to determine them. The solid density, ρ_S, at atmospheric pressure may be determined by the application of Eqs. (15) and (16) to a measurement of the resonant frequency made in a fluid of known density under atmospheric pressure at each temperature. For this purpose, even a crude estimate of Young's modulus is adequate. Subsequently, measurements of the resonant frequency in a fluid of known density over a range of pressure may be used to determine *E*. In practice, this is best accomplished by conducting a search to find that value of *E* securing the optimum representation of the resonant frequencies of the rod as a function of pressure.

3. EXPERIMENTAL

The practical realization of the vibrating-rod viscometer employed in this work is illustrated in Fig. 2. All elements of the assembly are supported

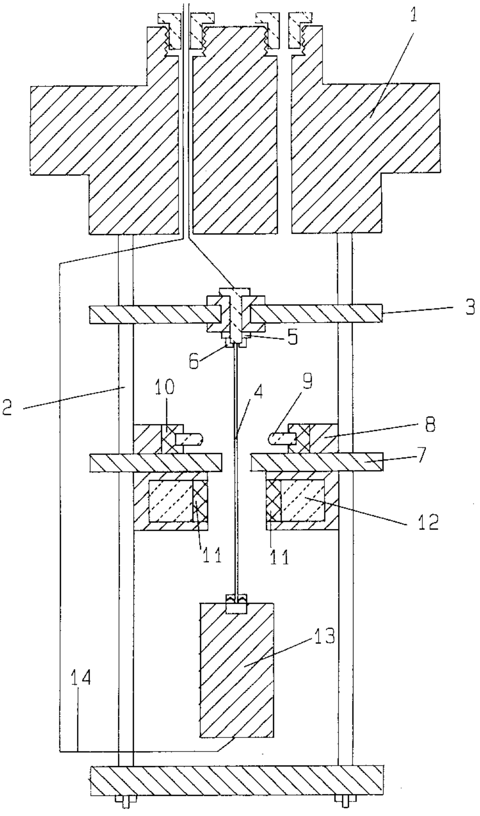

Fig. 2. The vibrating-rod densimeter assembly.

on the upper closure (1) of a 700-MPa pressure vessel (not shown). The main support is provided by three vertical pillars (2) that carry a number of horizontal plates separated by spacers in order to provide accurate alignment. The upper plate (3) has a centrally mounted, insulating ceramic bush into which is fixed the upper clamp for the vibrating stainless-steel rod (4). The clamp itself consists of a coned ferrule (5) compressed onto the rod by the action of a nut (6). An electrical connection is made to the top of the rod which passes out of the pressure vessel through a feed-through. The middle plate (7) carries on its top side an adjustable slider (8) on which are mounted a light-emitting diode (9) and a photodetector (10). The emitter and detector pair can be moved in the plane of the plate. This pair permits the vibration of the rod to be observed by means of the modulation of the light transmission between them by direct observation. An optimum adjustment of the detection system so as to secure the maximum electrical signal is made before the densimeter is inserted into the pressure vessel. It has been found that this detection system operated successfully at pressures in excess of 300 MPa and that, following suitable amplification and filtering, a resolultion of the motion of the rod of less than 0.1 μm was possible. On the lower side of the middle plate, two ceramic magnets (11) are supported, held in a soft-iron clamp (12), which serves to intensify the magnetic field in the gap between them. This field is employed in conjunction with a small, variable-frequency current flowing in the rod to excite its transverse vibrations. Obviously, the direction of the field is arranged to be such that the transverse vibrations are perpendicular to the line joint the light-emitting diode and the photodetector.

The lower end of the vibrating rod carries a stainless-steel cylinder (13) and a flexible electrical connection (14) which completes the circuit through the rod by passing through the upper closure of the pressure vessel. The mechanical coupling of the stainless-steel cylinder to the rod is accomplished in the same manner as at the upper end. The stainless-steel cylinder provides sufficient inertia that pendulum-like motions of the rod under electromagnetic forces are prevented. It was found that this arrangement was superior to one in which the rod was rigidly clamped at both ends to the support pillars because, in the latter scheme, out-of-phase differential thermal expansion of the rod and the support, in response to small temperature fluctuations within the system, led to instabilities in the resonant frequency of the rod as a result of thermally induced stresses. The configuration adopted using the cylinder was found to correspond, almost exactly, to the provision of a pinned end for the rod [10]. The assembly is completed by a lower plate (14) that secures rigidity in the entire system.

For the measurements reported here, the rod employed had a length of 133 mm and a mean radius $R = 0.7937$ mm and was constructed from

316 stainless steel. As supplied, the rod was also found to exhibit two modes of transverse vibration of slightly different frequencies owing to a lack of cylindrical symmetry. This was used to advantage by selecting the alignment of the rod so that just one mode was excited. The resonant frequency of oscillation of the rod was typically 300 Hz.

The entire densimeter assembly was mounted in a pressure vessel containing the test fluids, which could be pressurized externally with a compressor filled with water separated from the test fluid by a diaphragm or evaluated. The pressure vessel itself was suspended vertically in an oil thermostat so that the temperature of the test fluid could be maintained at a constant value to within ±0.01 K over a period of several hours.

The driving signal for excitation for the rod was derived from a high-precision frequency synthesizer through an amplifier. The synthesizer was controlled by a microcomputer in such a way that the frequency could be automatically stepped in increments of 0.01 Hz through a resonance. The signal from the optical detection system was amplified, filtered, and fed to a digital meter measuring the rms signal, which was in turn interrogated by the microcomputer. The stepping rate of the frequency synthesizer was selected empirically to provide the minimum total time of measurement while permitting stabilization of the amplitude response at each setting. A typical resonance curve obtained in this fashion is shown in Fig. 3 for an observation in *n*-heptane at 46 MPa and 298 K. It was found that in order

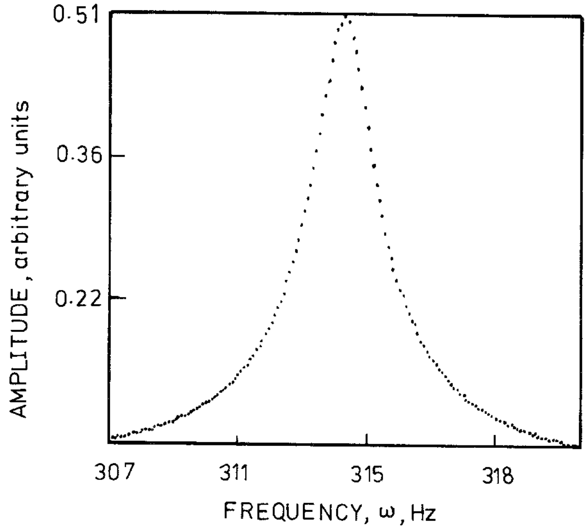

Fig. 3. A typical resonance curve in normal heptane at a pressure of 46 MPa and a temperature of 298 K.

to preserve linearity in the oscillator and, therefore, symmetry in the resonance curve, very low amplitudes ($\sim 10\,\mu$m) were necessary. Because this figure is consistent with the desire to maintain $\varepsilon \leqslant 0.01$, the driving current for the oscillator was always adjusted to ensure this magnitude of response.

In order to determine the resonant frequency of a particular oscillation, it was found that the most effective method involved a fit of the measured amplitude data near resonance to a Lorentzian function. The resonant frequency could then be determined from the maximum of the fitted function. This procedure yielded a resolution in resonant frequency of better than 0.01 Hz. Tests of the reproducibility of the resonant frequency *in vacuo* over a period of 1 month showed a stability of the same magnitude as did measurements in a fluid during four cycles of pressure to 100 MPa and a temperature cycle from room temperature to 60°C. Indeed, under pressure, at a constant temperature, a stability in resonant frequency of ± 0.005 Hz was usually attained. All of these tests confirm that a precision in the measurement of the resonant frequency of the oscillator of better than ± 0.03 Hz is possible. An error analysis, described in full elsewhere [13], demonstrates that this corresponds to an uncertainty in the fluid density of less than $\pm 0.1\%$.

As indicated earlier, the viscosity of the fluid can be derived from measurements of the width of the resonance curves at one-half of their height, by means of Eq. (14). Generally, the viscosity determined in this way was found to lie within $\pm 2\%$ of standard values tabulated in the literature. Although the level of accuracy is not adequate for primary measurements of the viscosity, it is certainty sufficient for establishing a value of the viscosity to be used in the evaluation of the fluid density.

4. RESULTS

It was mentioned in Section 1 that the principal purpose of the present experimental work is to confirm the validity of the theory of the densimeter, particularly in relation to the description of the fluid flow around the vibrating rod. Accordingly, two sets of measurements have been carried out of the density of normal heptane at pressures up to 100 MPa. In the first set the density of normal heptane has been determined by means of the absolute evaluation discussed earlier. In the second set, the instrument has been calibrated by means of measurements with water and the evaluation of the density of normal heptane determined according to the relative method.

In either case the first essential step is the determination of the solid material density ρ_S from measurements of the resonant frequency at a temperature of 29.86°C *in vacuo* and in *n*-heptane at atmospheric pressure. For this purpose, the most accurate values of the density and viscosity of *n*-heptane were taken from the literature [14, 15]. The value determined in this way as

$$\rho_S = 7453.5\ \mathrm{kg \cdot m^{-3}}$$

which differs by less than 0.5% from values quoted in the literature for the same nominal material.

In order to implement the scheme for the absolute evaluation of the density of *n*-heptane at the same temperature over a range of pressure, a value for the Young's modulus of the solid material, $E = 1.93 \times 10^{11}\ \mathrm{N \cdot m^{-2}}$, was taken from the literature. The viscosity of *n*-heptance has been taken from the results of Kashiwagi and Makita [15]. Table I lists the measured resonant frequencies and the density derived from them on an absolute basis over a range of pressures from 0.1 to 95 MPa. Figure 4 compares these values with accurate data reported by Muringer et al. [1]. It can be seen that the maximum deviation amounts to only ±0.2% but that the densities determined in this work are systematically below the literature data. Nevertheless, the results indicate that the instrument is capable of absolute density measurements over a range of pressure with an accuracy of ±0.2% and thereby confirm the applicability of the theory of the instrument.

From a series of measurements of the resonant frequency of the vibrating rod in triply distilled, deionized water, a more appropriate value

Table I. The Results of the Measurements of the Density of *n*-Heptane at $T = 29.36°\mathrm{C}$ in the Pressure Range 0.1 to 95 MPa

Pressure P (MPa)	Resonant frequency ω_r (Hz)	Density ρ ($\mathrm{kg \cdot m^{-3}}$) Absolute evaluation	Density ρ ($\mathrm{kg \cdot m^{-3}}$) Relative evaluation
0	382.635	—	—
0.1	365.557	675.4	675.4
15.5	365.238	689.0	689.2
20.3	365.171	691.8	692.1
32.7	364.925	702.4	702.9
35.5	364.892	703.9	704.4
50.0	364.657	714.0	714.7
56.1	364.603	716.4	717.2
74.9	364.344	727.6	727.7
94.9	364.128	737.2	738.5

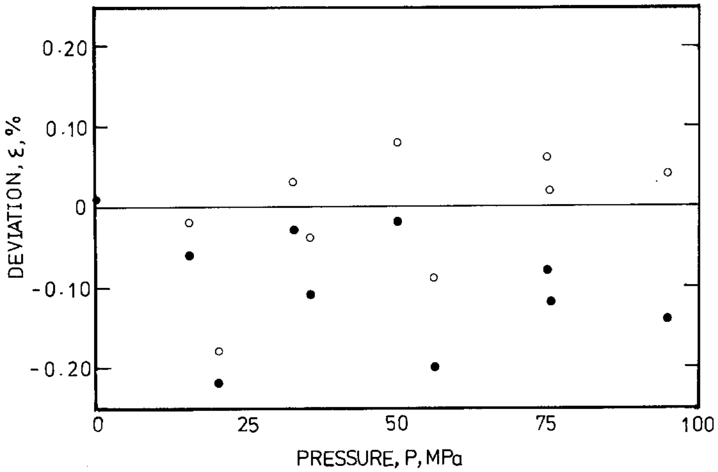

Fig. 4. A comparison between values of the density of *n*-heptane determined with the vibrating-rod densimeter and other measurements [1]. (●) Absolute method of evaluation; (○) relative method of evaluation.

of the Young's modulus of the actual sample of material employed has been determined as outlined earlier. This measured value of E is

$$E = 1.79 \times 10^{11}\ \mathrm{N \cdot m^{-2}}$$

This value has then been employed in a relative evaluation of the density of *n*-heptane over the same pressure range and the results are included in Table I. The deviations of these relative densities from the work of Muringer et al. [1] are included in Fig. 4. As should be expected, the agreement with the measurements of Muringer et al. is now better and is generally within ±0.1%, and in particular, there is no evidence of systematic discrepancies. Again, this is taken as proof of the validity of the theoretical description of the instrument.

5. CONCLUSIONS

The theory of a vibrating-rod densimeter has been validated by means of a series of measurements under elevated pressures on normal heptane. In particular, it has been shown that, when operated in a relative manner, such an instrument is capable of a precision in liquid density measurement of better than ±0.1%. For a device of this type the change of the resonant frequency with fluid density is small, amounting to only 1.4 Hz in 360 over the pressure 0.1 to 100 MPa. However, this may be increased substantially (by a factor of about 30) by utilizing the changing buoyancy of a tensioning weight on the resonant frequency of a thinner suspension rod. In such a case the theoretical description of the effect of this fluid motion around the vibrating element becomes a small part of the total effect, and the present work demonstrates conclusively that the available theory is entirely appropriate for its analysis. These further developments of the instrument, which should significantly improve the precision of the measurements, will be reported subsequently.

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REFERENCES

1. M. J. P. Muringer, N. J. Trappeniers, and S. Biswas, *Phys. Chem. Liq.* **14**:273 (1987).
2. S. F. Y. Li, R. D. Trengove, W. A. Wakeham, and M. Zalaf, *Int. J. Thermophys.* **7**:273 (1986).
3. N. Glen, NEL Report D1/582, National Engineering Laboratory.
4. P. J. Back, A. J. Easteal, R. L. Hurle, and L. A. Woolf, *J. Phys. E Sci. Instrum.* **15**:360 (1982).
5. G. S. Kell and E. Whalley, *J. Chem. Phys.* **62**:3496 (1975).
6. L. A. Davis and R. B. Gordon, *J. Chem. Phys.* **46**:2650 (1967).
7. O. Kratky, H. Leopold, and H. Statinger, *Z. angew. Phys.* **27**:273 (1969).
8. H. J. Albert and R. H. Wood, *Rev. Sci. Instrum.* **55**:589 (1984).
9. A. H. Krall, J. C. Niewoudt, J. V. Sengers, and J. Kestin, *Fluid Phase Equil.* **36**:207 (1987).
10. T. Retsina, S. M. Richardson, and W. A. Wakeham, *Appl. Sci. Res.* **43**:127 (1986).
11. M. Abramowitz and I. Stegun (eds.), *Handbook of Mathematical Functions with Formulas, Graphs and Mathematical Tables*, Appl. Math. Ser. 55 (U.S. Government Printing Office, Washington, D.C., 1964).
12. S. S. Chen, M. W. Wambsganass, and J. A. Jendrzejczyk, *Trans. ASME J. Appl. Mech.* **43**:325 (1976).
13. T. Retsina, Ph.D. thesis (University of London, London, 1987).
14. Q. K. Doolittle, *J. Chem. Eng. Data* **9**:275 (1964).
15. H. Kashiwagi and T. Makita, *Int. J. Thermophys.* **3**:289 (1982).