Measurement of Density, Sound Velocity, Surface Tension, and Viscosity of Freely Suspended Supercooled Liquids[1]

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Noncontact methods have been implemented in conjunction with levitation techniques to carry out the measurement of the macroscopic properties of liquids significantly cooled below their nominal melting point. Free suspension of the sample and remote methods allow the deep excursion into the metastable liquid state and the determination of its thermophysical properties. We used this approach to investigate common substances such as water, o-terphenyl, succinonitrile, as well as higher temperature melts such as molten indium, aluminum, and other metals. Although these techniques have thus far involved ultrasonic, eletromagnetic, and more recently electrostatic levitation, we restrict our attention to ultrasonic methods in this paper. The resulting magnitude of maximum thermal supercooling achieved has ranged between 10% and 15% of the absolute temperature of the melting point for the materials mentioned above. The methods for measuring the physical properties have been mostly novel approaches, and the typical accuracy achieved has not yet matched the standard equivalent techniques involving contained samples and invasive probing. They are currently being refined, however, as the levitation techniques become more widespread and as we gain a better understanding of the physics of levitated liquid samples.

KEY WORDS: density; levitation technique; supercooling; surface tension; sound velocity; viscosity.

1. INTRODUCTION

The extent of the thermodynamically metastable liquid range is comparable or even larger than that of the stable liquid range for many pure and

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multicomponent materials. Information on the temperature dependence of thermophysical properties near and below the nominal freezing point of materials is valuable for the purpose of supporting the modeling of solidification processes. Structural characteristics are also reflected in the temperature dependence of the thermodynamic and transport properties of liquids, and many cooperative structural transitions often take place in the supercooled range [1]. Finally, evidence for a thermodynamic singularity in deeply supercooled water [2] as reflected in the divergence of the temperature dependence of most physical parameters suggests that the deeply supercooled liquid state might be rich in undiscovered phenomena.

Ultrasonic techniques developed for the purpose of measuring the thermophysical properties of metastable (supercooled and superheated) liquids have been based on a contained sample and contacting probe approach [3, 4], as well as on a freely levitated sample and noninvasive technique [5–8]. In this paper we would like to concentrate on the issue of developing new methods and of refining existing ones for the remote probing of the properties of levitated supercooled liquids. We will limit our discussion to measurements at moderate temperature below and above ambient room temperature. The materials considered will therefore be restricted to ordinary water, hydrocarbons, glass-forming polyphenyls, low-melting pure metals such as indium, and transparent inorganic model materials such as succinonitrile. A summary of past results is first presented in order to allow the assessment of our current capabilities; a description of ongoing developments and more preliminary investigations will then follow. Thus, this will partially constitute a review paper as well as a status report on the development of this very small area of the thermophysical properties measurement research effort.

2. DENSITY MEASUREMENT

An obvious approach to measure the density of a freely suspended sample with a known mass is to photographically determine its volume. This is straightforward if the sample is axially symmetric or spheroidal as in the case of an ultrasonically levitated drop. For a spheroidal drop, the accuracy is dependent upon the alignment of the camera and the sample, and it would therefore be optimal for a stationary specimen with uniform backlighting and with its symmetry axis parallel to the plane of the camera detector or film. With a standard video camera and a digital frame grabber with 500×500 pixels resolution, we have obtained a relative uncertainty of about $\pm 1\%$ for the volume. If great care is taken, the uncertainty in the measurement of mass can generally be less than 1% for specimens on the order of 1 mg.

Two alternate methods based on the properties of an ultrasonically levitated sample can provide density measurement with a relative uncertainty approaching 1%, but they both require the measurement of a reference sample of known density. These approaches have been previously described and tested at ambient room temperature [9] as well as below room temperature for the measurement of the density of supercooled *o*-terphenyl [7]. The simplest of the two methods involves the measurement of the voltage input to the levitator required to suspend the specimen of interest at a specific location. The measurement of the voltage needed to levitate a sample of a *reference* material of known density at the *same location* allows the calculation of the unknown density through the simple relationship

$$\rho_1/\rho_2 = (V_1/V_2)^2 \qquad (1)$$

where the subscript 1 refers to the unknown sample and 2 to the reference sample.

Figure 1 reproduces the results of the measurement of the density of supercooled *o*-terphenyl using 50 cSt silicone oil as a reference. The method is fairly insensitive to the difference in sample dimensions as long as they are both small with respect to the acoustic wavelength (the diameters of both samples were less than 10% of the acoustic wavelength in this case).
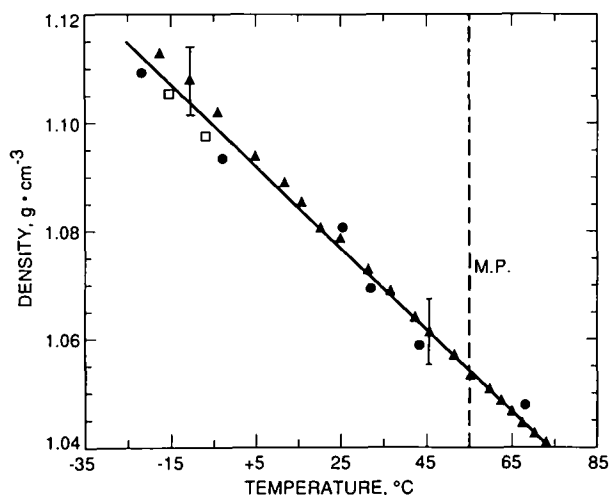

Fig. 1. Experimental results of the measurement of the density of stable and supercooled liquid *o*-terphenyl as a function of temperature. The data have been obtained by using a static levitation technique with silicone oil drops as reference samples.

The procedure consisted of first measuring the voltages for the levitated supercooled sample at specific temperatures. The same measurements were carried out for the reference sample at the same temperature. The change in the volume of the two samples was kept within 5%.

The interaction between the sample and the restoring (levitating)force generated by the acoustic field provides the basis for the second approach to density determination. The resonance frequency at which the specimen oscillates (in position) within the ultrasonic force potential depends on its density as well as on the host medium properties and the acoustic parameters. By using a reference sample with known density, one can extract the unknown specimen density by measuring the resonance frequency of very small amplitude translational oscillations of both materials and the voltages needed for levitation. For small-amplitude oscillations and for levitators operating in their linear region, the densities of the two materials are related to the acoustic drive voltage as follows [9]:

$$\frac{\rho_1}{\rho_2} = \left[\frac{\omega_2}{\omega_1}\right]^2 \left[\frac{V_1}{V_2}\right]^2 \frac{\cos(4\pi z_{01}/\lambda)}{\cos(4\pi z_{02}/\lambda)} \qquad (2)$$

where z_{01} and z_{02} are the equilibrium levitation positions of the unknown and reference samples. In 1 G, z_{01} and z_{02} will generally be different. In low gravity, however, both samples will be positioned at the pressure nodal planes of the ultrasonic standing wave, and the unknown density can be calculated directly from the measured resonance frequencies for *equal* drive voltages. A test of this approach has resulted in density values that were within 3% of those obtained by a commercial vibrating tube densitometer for normal liquids at room temperature.

3. SOUND VELOCITY MEASUREMENT

A relative technique for the measurement of the adiabatic sound velocity in liquids at 50 kHz was introduced by Apfel [10]. It was applied to the case of water supercooled to -33°C under atmospheric pressure [11]. Once again, the equations describing the interaction between the acoustic wave and the mechanical properties of the levitated drops and the host material were used to evaluate a specific property of the supercooled liquid. In this particular instance, the adiabatic sound velocity, which is related to the compressibility β_s through the formula $c_s = (1/\rho\beta_s)^{1/2}$, could only be obtained in the case of a liquid host material, because the acoustic levitation force depends on the mismatch in compressibility between the

drop and the host medium. The relationship at the basis of this method is [10]

$$\left[\frac{V_1}{V_2}\right]^2 = \frac{G(\beta_{s1}/\beta_{s0}, \rho_1/\rho_0)}{G(\beta_{s2}/\beta_{s0}, \rho_2/\rho_0)} \tag{3}$$

where the subscript 0 refers to the host-liquid properties, while subscripts 1 and 2 refer to the unknown and reference material, respectively. The dimensionless function G is defined as

$$G\left(\frac{\beta_{s1}}{\beta_{s0}}, \frac{\rho_1}{\rho_0}\right) = \frac{|1 - \rho_1/\rho_0|}{\beta_{s1}/\beta_{s0} - (5\rho_1 - 2\rho_0)/(2\rho_1 + \rho_0)} \tag{4}$$

The procedure requires the acquisition of the values of the properties of the host and reference materials as well as the density of the unknown sample as a function of temperature in the range of interest. The droplet having unknown sound velocity is first injected in the liquid-filled levitation cell and trapped at a specific position at a specific temperature characteristic of a predetermined supercooling level. The levitation voltage is recorded and the sample is released from that position. This procedure is repeated for the reference droplet which is trapped at the *same* position. The sound velocity of the first droplet material is then calculated from the
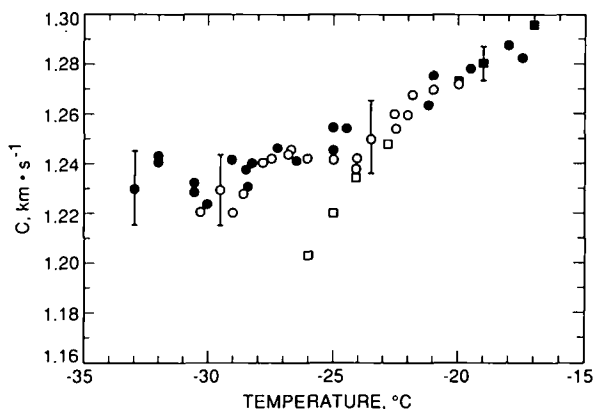
Fig. 2. Experimental results of the measurment of the sound velocity in supercooled water under atmospheric pressure as a function of temperature. The water droplets were acoustically levitated in decahydronaphthalene and the reference material was methyl cellosolve. The sound speed was obtained by levitating both the water and the reference liquid drops at the same position and by reading the voltage input to the levitator.

voltage ratio and the known properties. This is an extensive procedure, and it involves making a single measurement with each droplet.

Figure 2 reproduces the results of measurements for water supercooled to -33°C under atmospheric pressure. The host liquid was decahydronaphthalene, the reference liquid was methyl cellosolve, and the water was deionized, triply distilled, and passed through 0.5-μm Micropore filters. The other results displayed on the graph have been obtained through Brillouin scattering, and thus reflect wave propagation at much higher frequency [12, 13].
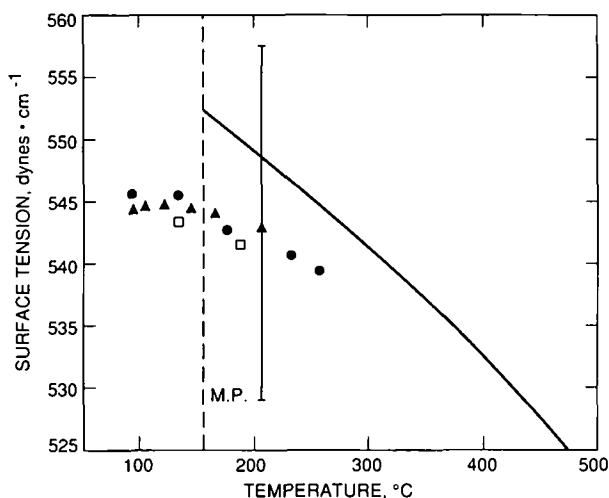
4. SURFACE TENSION MEASUREMENT

The quintessential method for the measurement of liquid surface tension and even viscosity involves the noncontact laser heterodyne detection of thermally induced capillary waves in the tens of kHz frequency range and with several microns in amplitude (see, for example Refs. 14 and 15). Current commercially available laser vibrometers have extended the displacement amplitude to an even larger range (to $100\,\mu$m). The critical optical alignment inherent in this approach makes it complicated, however, to adapt it to thermally controlled enclosures around levitated samples that are supercooled at lower or higher than ambient temperature. For this reason we have resorted to the measurement of low-frequency surface waves, the resonant shape oscillation modes that are controlled by surface tension and viscosity. Originally introduced for liquid–liquid levitation systems [16], the drop shape oscillations driven by modulated acoustic radiation pressure were applied to the measurement of liquid–gas surface tension [17]. The basis for the technique is the *inviscid linear* theory of drop shape oscillations derived by Rayleigh [18]. The angular resonance frequencies of *axisymmetric* shape oscillations of a spherical drop are given by the well-known relation

$$\omega_L^2 = \frac{L(L+2)(L-1)\sigma}{\rho R^3} \tag{5}$$

where L is the mode number, σ is the surface tension, R is the drop radius, and ρ is the drop density. For moderately viscous liquids levitated in air, the resonance frequencies are very weakly dependent on the liquid viscosity. In practice, the use of ultrasonic levitators on Earth inevitably introduces a slight oblate axisymmetric distortion of the drop [19–21] which slightly shifts the resonance frequencies downward [17]. Rotation of the levitated drop, on the other hand, shifts these frequencies upward [22, 23]. In addition, both static drop shape distortion and rotation split

the degeneracy of the resonance frequencies of the non-axisymmetric modes of shape oscillations, rendering the measurement of the appropriate resonant frequency more difficult. The experimental challenge thus consists not only in levitating supercooled droplets and measuring their temperature, but also measuring the resonance frequency of the fundamental axisymmetric mode of shape oscillation while the drop is not rotating and has a small oblate distortion which can be accurately measured.

Attempts to implement this approach using molten and supercooled 99.9% pure indium produced the data displayed in Fig. 3. In this case, the host gas in which the indium droplet was levitated was scrubbed high-purity argon. These results are the highest values obtained for three different samples. A large number of other data points were discarded on the basis of the likelihood of surface contamination. The resonance frequencies were measured by amplitude modulation of the acoustic force at a level which corresponded to shape oscillations with amplitude on the order of 1–2% of the drop diameter. The mass of the sample was determined prior to processing while in the solid state. The initially solid specimen was

Fig. 3. Experimental data obtained for the surface tension of high-purity indium (99.9%) in argon as a function of temperature. The surface tension was obtained by measuring the resonance frequency of the fundamental mode of shape oscillations. The solid curve is based on Ref. 24, where the sessile drop method was used in the stable liquid range. The error bar represents the overall estimated experimental uncertainty including contributions from mass, oscillation frequency, and sample geometry (a/b ratio) measurements.

levitated and subsequently melted as the temperature of the furnace was slowly increased. The sample temperature was inferred by a proximity thermocouple placed 2 mm away from the drop. The static distortion of the indium samples was characterized by a/b ratios (a being the major and b the minor axis of the oblate profile of the axisymmetric drop) in the 1.2–1.25 range, and the rotation of the sample was less than 0.1 rmp during the measurements. These results are in agreement with *some* of the literature values when values above the melting point are compared. The solid line shown in Fig. 3 is based on the experimental data reported by White [24].

Results of the measurement of the surface tension of supercooled water levitated in air are reproduced in Fig. 4. In this case, the lowest temperature attained in the metastable range was $-21°C$, and the sample size had to be determined photographically by measuring the major and minor axes of the oblate profile of the backlit sample. The static oblate distortion was relatively small with a/b values between 1.5 and 1.1. The water droplet shrank significantly during the time needed for supercooling to the desired temperature. At the highest supercooling, the size of the drop was generally down to 1.5 mm in diameter. The uncertainty is estimated to be less than $\pm 1\%$ for the surface tension.
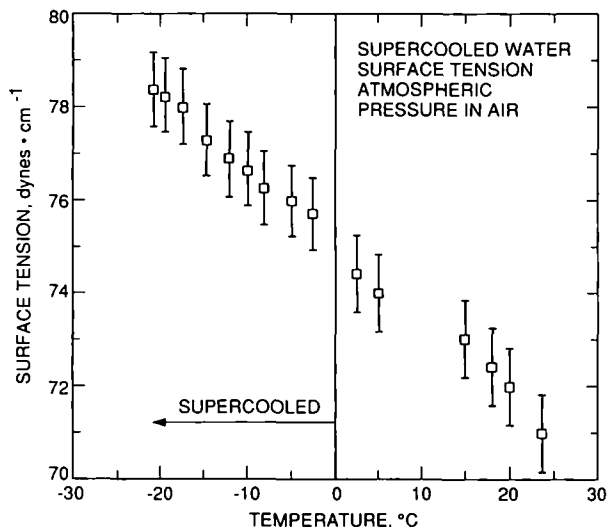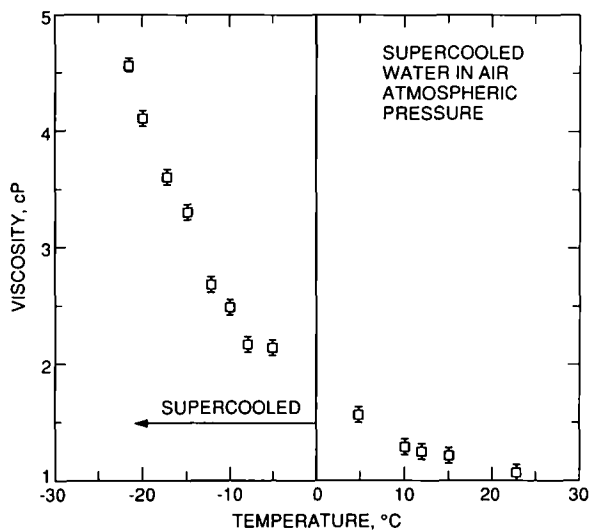

Fig. 4. Experimental results for the measurement of the surface tension of supercooled water in air as a function of temperature. The driven shape oscillation frequency method was used together with the measurement of the drop volume.

5. VISCOSITY MEASUREMENT

For low- and moderate-viscosity liquids (less than 50 cP), the characteristic time scale for damping of the shape oscillations can be used to calculate the viscosity of the specimen. For *spherical* drops with low viscosity, the damping time constant τ for shape oscillations is given by the well-known Lamb [25] relation $1/\tau = 5\nu/R^2$, where ν is the kinematic viscosity and R is the drop radius. The application of this formula to non-spherical drops is not theoretically sound, but experimental investigations of the effect of static oblate distortion on the decay time constant have not revealed a significant and reproducible change in the measured values for a/b ratio less than 1.15.

The decay time constant for levitated drops oscillating in the fundamental shape mode was measured by the pseudoextinction optical technique introduced by Trinh et al. [17]. The time dependence of the oscillations was recorded on a storage oscilloscope after the termination of the modulation of the acoustic force. The initial amplitude of oscillation was never more than 10% of the vertical dimension of the oblate drop. An alternate method involved the use of the high-speed video system (Spin

Fig. 5. Experimental results for the measurement of the viscosity of supercooled water as a function of temperature. The viscosity was calculated from the measured decay time constant for initially oscillating drops in the driven fundamental mode.

Physics) capable of providing 6000 frames per second, but used only at 2000 frames per second. The resulting video sequence was digitized, and both the frequency of free decay and the time constant could be obtained. The experimental uncertainty is estimated to be at most ± 0.05 cP. The principal contribution to the error in viscosity is possible contamination of the droplet from the deployment system. The uncertainty in the linear dimension of the oblate spheroidal drop is less than 0.2%.

Figure 5 shows the results of the measurement of the viscosity of supercooled water down to approximately $-21°C$ using levitaed oscillating droplets of 1-2 mm in diameter. Comparison with results obtained by Hallett [26] with a tube viscometer reveals a reasonably good agreement: the current measurements are consistently lower than those of Hallett with a mean deviation of -4%.

6. SUMMARY

The results obtained thus far provide a reasonably favorable assessment of the capability of ultrasonic levitation techniques for providing data on common physical properties in the supercooled state. The few cases mentioned above deal with a restricted set of materials, and they must be considered as test cases for the purpose of demonstrating the feasibility of the methods. Although this paper has been limited to relatively low temperature measurements, such techniques can be adapted to other levitation techniques (electrostatic and electromagnetic) and to higher temperature environments. Further development currently pursued are the measurement of the refraction index of transparent droplets and of the thermal diffusivity.

ACKNOWLEDGMENTS

REFERENCES

1. A. R. Ubbelohde, *The Molten State of Matter* (Wiley, New York, 1978), pp. 343–372.
2. C. A. Angell, *Nature* **331**:206 (1988).
3. D. J. McClements, M. J. W. Povey, and E. Dickinson, *Ultrasonics* **31**:433 (1993).
4. E. Trinh and R. E. Apfel, *J. Acoust. Soc. Am.* **63**:777 (1978).
5. E. Trinh and R. E. Apfel, *J. Chem. Phys.* **72**:6731 (1980).
6. C. Hsu and R. E. Apfel, *J. Colloid Interface Sci.* **107**:467 (1985).
7. E. H. Trinh, in *Proceedings VII European Symposium on Materials and Fluid Science in Microgravity* (ESA SP-295, 1990), p. 503.

8. K. Ohsaka, E. H. Trinh, and M. E. Glicksman, *J. Cryst. Growth* **106**:191 (1990).
9. E. H. Trinh and C. J. Hsu, *J. Acoust. Soc. Am.* **80**:1757 (1986).
10. R. E. Apfel, *J. Acoust. Soc. Am.* **59**:339 (1976).
11. E. Trinh and R. E. Apfel, *J. Chem. Phys.* **72**:6731 (1980).
12. J. Teixeira and J. Leblond, *J. Phys. Lett. (Paris)* **39**:L83 (1978).
13. J. C. Bacri and R. Rajaonarison, *J. Phys. Lett. (Paris)* **41**:L403 (1979).
14. S. Hard, Y. Hamnerius, and O. Nilsson, *J. Appl. Phys.* **47**:2433 (1976).
15. M. Sano, M. Kawaguchi, Y. L. Chen, R. J. Skarlupka, T. Chang, G. Zografi, and H. Yu, *Rev. Sci. Instrum.* **57**:1158 (1986).
16. P. L. Marston and R. E. Apfel, *J. Colloid Interface Sci.* **68**:280 (1979).
17. E. H. Trinh, P. L. Marston, and J. L. Robey, *J. Colloid Interface Sci.* **124**:95 (1988).
18. Lord Rayleigh, *The Theory of Sound* (Dover, New York, 1945), p. 371.
19. P. L. Marston, S. E. Lo Porto Arione, and G. L. Pullen, *J. Acoust. Soc. Am.* **69**:1499 (1981).
20. E. H. Trinh and C. J. Hsu, *J. Acoust. Soc. Am.* **79**:1335 (1986).
21. Y. Tien, R. G. Holt, and R. E. Apfel, *J. Acoust. Soc. Am.* **93**:3096 (1993).
22. F. H. Busse, *J. Fluid Mech.* **142**:1 (1984).
23. P. Annamalai, E. Trinh, and T. G. Wang, *J. Fluid Mech.* **158**:317 (1985).
24. R. White, *Met. Trans.* **3**:1933 (1972).
25. H. Lamb, *Hydrodynamics*, 6th ed. (Cambridge University Press, Cambridge, 1932), p. 473.
26. J. Hallett, *Proc. Phys. Soc.* **82**:1046 (1963).