

SURFACE TENSION AND VISCOSITY MEASUREMENT WITH SURFACE LASER LIGHT SCATTERING METHOD

by

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Measurement of thermal properties is an important topic in the thermophysics. With the developing of laser technology, laser detection technologies can be used for thermal properties measurement. Based on the laser light scattering theory and light heterodyne detection principle, an experimental system by the surface laser light scattering is developed to measure the liquid surface tension and viscosity simultaneously. The maximal experimental errors of the measured surface tension and viscosity are less than 0.5% and 4.73%, respectively.

Key words: surface tension, viscosity, surface laser light scattering, ethanol

Introduction

Surface laser light scattering (SLLS) method can be used to measure fluid thermal properties, including surface tension and dynamic viscosity. Theoretical and experimental works have been done for the surface tension and viscosity measurement of various interfaces, for example, liquid-vapor interfaces at normal temperature [1], liquid crystal surfaces [2], liquid films [3], high temperature melts [4] and other super molecular systems.

In 1969, Langevin and Bouchiat [5] firstly measured the surface tension and viscosity of carbon dioxide at 30.438 °C by applying the spectrum analysis method to the scattered light of the liquid-vapor interface, with the wave number of $3.325 \cdot 10^5 \text{ m}^{-1}$, and the fitting values were in good agreement with the experimental data. In 1987, Dorshow *et al.* [6] measured the surface tension and viscosity of ethanol, acetone and n-butanol at 22 °C using the surface laser-light scattering spectrometer, and the wave numbers were in the range of $2.5 \cdot 10^4 \sim 1.75 \cdot 10^5 \text{ m}^{-1}$. The maximal errors were 9.14%. In 1991, Sakai *et al.* [7] measured the surface tension and viscosity of methanol at 25 °C with the wave numbers range of $4 \cdot 10^4 \sim 3 \cdot 10^6 \text{ m}^{-1}$. The uncertainties were, respectively, 1% and 5% for surface tension and viscosity under smaller wave numbers and 2% and 10% under larger wave numbers. It can be seen from open literature that the best accuracy of the viscosity measurement with SLLS method is 5%, and much work is still necessary to improve this technique. Based on our previous work [1], the SLLS method of measuring surface tension and viscosity simultaneously were studied in this paper.

Principle of measurement

The liquid surface appears to be calm at thermal equilibrium state, however, in the microscopic level, there always exist thermally excited capillary waves. The capillary waves

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typically have small amplitudes (~ 1 nm) and small wavelength (~ 100 μm). The behavior of capillary waves is restored by the surface tension, and is damped by the viscosity. Because each capillary wave acts optically as a diffraction grating, as a result irradiated laser lights on the surface will be scattered. When the incident light was scattered on the liquid surface, the shift in frequency of the scattered light, due to the Doppler effect, is equal to the frequency of the capillary wave, and is obtained using the optical heterodyne technique. From ref. [8], it can be known that, for the liquid surface scattering light, the reflected light intensity of per unit solid angle can be written as:

$$\frac{dI}{d\Omega} = I \frac{q_0^4}{4\pi^2} \left(\frac{n-1}{n+1} \right)^2 \frac{k_B T}{\sigma q^2 + \rho g} \quad (1)$$

where Ω is the per unit solid angle near the reflected light, n – the liquid refractive index, σ – the liquid surface tension, q_0 – the detecting light wave number, I – the detecting light intensity, and q – liquid surface wave number.

For the liquid surface wave of the capillary wave, the liquid surface capillary wave spectrum equation can be expressed as:

$$p_q(\omega) = \frac{q k_B T \tau^2 \text{Im}[2i\omega\tau - (1 + 2i\omega\tau)^{1/2}]}{|y + (1 + i\omega\tau)^2 - [1 + 2i\omega\tau]^{1/2}|^2 \rho \pi \omega} \quad (2)$$

where $\tau = \rho/2\eta q^2$, $y = \sigma\rho/4\eta^2 q$, $\omega = 2\pi f$, K_B is the Boltzmann's constant; T – the temperature, η – the liquid viscosity, ρ – the density, ω – the angular frequency, f – the frequency. In addition, from ref. [9], the liquid surface capillary wave spectrum can also be expressed as:

$$p_q(\omega) = \frac{q^2 k_B T I_q(\omega)}{\pi \rho} \quad (3)$$

If surface adsorption force is ignored, $I_q(\omega)$ can be expressed as:

$$I_q(\omega) = \frac{1}{\omega} \text{Im} \left[\frac{-1}{\left(i\omega + \frac{2q^2\eta}{\rho} \right)^2 + \frac{\sigma q^3}{\rho} - \left(\frac{2q^2\eta}{\rho} \right)^2 \left(1 + \frac{2i\omega\rho}{2q^2\eta} \right)^{1/2}} \right] \quad (4)$$

Both of the two kinds of theories power spectrum model can be used to fitting experimental data, but the theoretical model should be chosen according to the actual fitting results. Due to the finite instrumental resolution, the light we obtained is not scattered by the uniform surface waves with the wavelength of q but the surface waves with a wavelength distribution of $q \pm \Delta q$. The liquid surface scattering light spectrum is widened due to the instrument broaden effect [6, 10]. Therefore, the power spectrum measured at the detector was represented as:

$$p(\omega; q, \Delta q) = A \sum_{-\infty}^{+\infty} p_q(\omega; q + N\Delta\delta) \exp \left[-\frac{2\delta^2}{(\Delta q)^2} \right] \Delta\delta + B \quad (5)$$

where A is the amplitude, B – the baseline, δ – the optical path in F ($\Delta q/\delta$) width, N – the fitting steps, $\Delta\delta$ – the seasonable step length, and Δq – the instrument resolution. In our experiments, it was found that better fitting result can be got at step length of $\Delta\delta = \Delta q/50$.

Experimental system

The surface laser light scattering system that was used to measure the liquid surface tension and viscosity simultaneously is shown in fig. 1, which includes a laser, an optical wedge, three mirrors, a photomultiplier tube, a spectrum analyzer, a thermostat, a digital multimeter and a computer. All the optical components are fixed in an optical platform to reduce the external vibration of the experiment. An optical wedge is chosen to split the laser beam so that the scattered light and reflected light have the same polarization state. More details about the optical interference technique can be found in ref. [11].

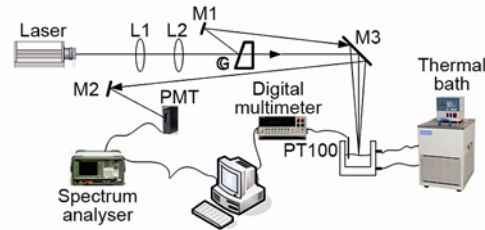


Figure 1. Schematic diagram of SLLS experimental system;
L1, L2 – convex lens, M1-M3 – optically flat reflector, G – optical wedge, PMT – photomultiplier tube

Results and discussion

We measured the surface tension and viscosity of ethanol with the mass fraction of 99.95% at 29.15 °C, at which the density is 781.28 kg/m³, the surface tension is 0.02141 N/m [12], viscosity is 0.0010026 Pa·s [13]. The experiment is measured under two different scattering angle, which are, respectively, $\theta_1 = 19.68$, and $\theta_2 = 22.80$. The corresponding surface wave numbers are, respectively, $q_1 = 67612 \text{ m}^{-1}$, and $q_2 = 78324 \text{ m}^{-1}$.

The fitting results using equation sets of (2) and (5) or (3) and (5) are shown in figs. 2 and 3. Δq of 12851 m⁻¹ and 12031 m⁻¹ are used in the fitting of for the experimental data with wave numbers of q_1 and q_2 . As a contrast, for each wave number of the experimental data, different Δq is tested to fit the experimental data, and the results are listed in tab. 1 and fig. 4. The measurements were repeated for ten times at different scattering angles, and the relative standard deviations were calculated as:

$$s = \frac{\sqrt{\frac{\sum \left(x_n - \frac{\sum_{1}^n x_n}{n} \right)^2}{n-1}}}{\left(\frac{\sum_{1}^n x_n}{n} \right)} \cdot 100 \quad (6)$$

The surface tension, viscosity, and relative standard deviation are shown in tab 2.

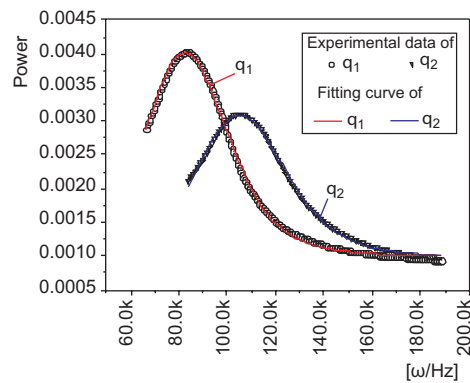


Figure 2. The fitting curve of the experimental data using eqs. (2) and (5)
 (for color image see journal web site)

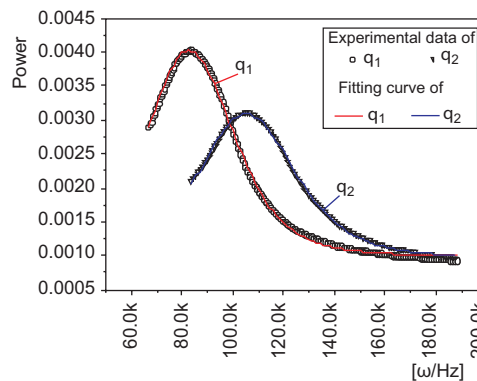
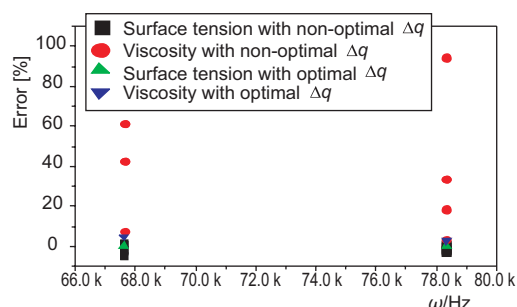


Figure 3. The fitting curve of the experimental data using eqs. (3) and (5)
 (for color image see journal web site)

Table 1. Viscosities and surface tension of ethanol obtained under different q and Δq

| Equations | q [m^{-1}] | Δq [m^{-1}] | ω [Hz] | σ [Nm^{-1}] | η [Pa·s] |
|-----------|-------------------------|--------------------------------|---------------|-------------------------------|---------------|
| (2), (5) | 67612 | 12851 | 83720 | 0.02142 | 0.00101 |
| (2), (5) | 67612 | 11000 | 83451 | 0.02051 | 0.00084 |
| (2), (5) | 67612 | 10000 | 83364 | 0.02004 | 0.00077 |
| (2), (5) | 78324 | 12031 | 106068 | 0.02143 | 0.00102 |
| (2), (5) | 78324 | 11000 | 105991 | 0.02092 | 0.00091 |
| (2), (5) | 78324 | 10000 | 105939 | 0.02046 | 0.00081 |
| (3), (5) | 67612 | 12851 | 80665 | 0.02042 | 0.00108 |
| (3), (5) | 67612 | 11000 | 81019 | 0.02096 | 0.00147 |
| (3), (5) | 67612 | 10000 | 81202 | 0.02059 | 0.00084 |
| (3), (5) | 78324 | 12031 | 103411 | 0.02149 | 0.00104 |
| (3), (5) | 78324 | 11000 | 103634 | 0.02095 | 0.00095 |
| (3), (5) | 78324 | 10000 | 103843 | 0.02114 | 0.00084 |

**Figure 4. Relative deviations between fitting and experimental data***(for color image see journal web site)*

it can be seen that the surface tension and viscosity of relative standard deviation were 0.425% and 2.067%, respectively, which means the random error is very small.

Table 2. Surface tension, viscosities, and the relative standard deviation (S) of ethanol obtained under different q and Δq

| | Equation | q [m^{-1}] | 1 | 2 | 3 | 4 | 5 | S |
|----------------------------------|----------|-------------------------|---------|---------|---------|---------|---------|--------|
| σ [Nm^{-1}] | (2), (5) | 67612 | 0.02142 | 0.02134 | 0.02152 | 0.02133 | 0.02151 | 0.425% |
| | (2), (5) | 78324 | 0.02143 | 0.02152 | 0.02132 | 0.02131 | 0.02152 | |
| η [Pa·s] | (3), (5) | 67612 | 0.00101 | 0.00099 | 0.00105 | 0.00103 | 0.00105 | 2.067% |
| | (3), (5) | 78324 | 0.00102 | 0.00101 | 0.00099 | 0.00103 | 0.00102 | |

Conclusions

In this paper, based on the laser light scattering theory and light heterodyne detection principle, we developed the experimental light path and surface laser light scattering

From tab. 1 and fig. 4, it can be known that, for certain wave number q , there is a best instrument resolution Δq to get the best fitting results, and the maximum deviation of the surface tension and viscosity compared with the reference value are less than 0.5% and 4.73%, respectively. In theory, the center frequency and bandwidth of the power spectrum are determined by the liquid surface tension and viscosity. Instruments broaden effect lead to a larger bandwidth of the power spectral, but the center frequency remains unchanged. So, the surface tension measurement results are better than the viscosity results. From ref. [8], it is known that the instrument broaden effect can be reduced through the power spectrum fitting analysis.

From tab. 1, better result can be obtained when $q = 78324 \text{ m}^{-1}$. This is because the contribution of the wave with the wave number q to the power spectral bandwidth is proportional to q^2 , while the contribution of the wave with the wave number of $q \pm \Delta q$ to the power spectral bandwidth is proportional to $q^{1/2}$. But, the signal-to-noise ratio could be worse at the higher wave numbers. So, we have to balance between instrument border effect and signal-to-noise ratio. In this paper, larger wave number was chosen. From tab. 2,

(SLLS) system, which can be used to measure the liquid surface tension and viscosity simultaneously. To test the experimental system, ethanol was used as a standard sample, and two power spectrum equations were used to fit the experimental. Compared with the direct measurement of spectrum, this method can improve the accuracy of measurement. The best instrument resolution, fitting step length and the number of fitting were determined for certain wave numbers through the experiments. Based on the analysis of ten groups of experimental data, the maximum measurement error of the surface tension and viscosity were less than 0.5% and 4.73%, respectively; the relative standard deviation were 0.425% and 2.067%, respectively, which can satisfy the requirements of engineering applications.

Acknowledgments

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