

# Analysis of a *Quasi* - Elastic Laser Scattering Spectrum Using the Maximum Entropy Method

Isao TSUYUMOTO

Department of Environmental Chemistry, Kanazawa Institute of Technology,  
7-1 Ohgigaoka, Nonoichi, Ishikawa 921-8501, Japan

We have applied the maximum entropy method (MEM) to the analysis of *quasi*-elastic laser scattering (QELS) spectra and have established a technique for determining capillary wave frequencies with a higher time resolution than that of the conventional procedure. Although the QELS method has an advantage in time resolution over mechanical methods, it requires the averaging of at least 20 – 100 power spectra for determining capillary wave frequencies. We find that the MEM analysis markedly improves the *S/N* ratio of the power spectra, and that averaging the spectra is not necessary for determining the capillary wave frequency, *i.e.*, it can be estimated from one power spectrum. The time resolution of the QELS attains the theoretical limit by using MEM analysis.

(Received August 20, 2007; Accepted October 15, 2007; Published December 10, 2007)

## Introduction

Surface tension measurements are widely used for quality control in various industrial processes, such as washing, coating, penetration, dispersion and emulsification, because they provide useful information on surfactant dynamics at liquid surfaces or liquid/liquid interfaces. The measurements are also helpful for fundamental research on interfacial thermodynamics and properties. A number of techniques, such as the Wilhelmy method, the Du Nouy method, and the spinning drop method, have been developed for surface tension measurements.<sup>1</sup> These mechanical techniques, however, are not suitable for time-resolved and remote-sensing measurements of high-temperature liquids, such as the fused silicon, the inside of a globe, and the surface of a planet.

The *quasi*-elastic laser scattering (QELS) method is used to monitor the spectrum of QELS by capillary waves (ripples), which are spontaneously generated at liquid surfaces. The surface tension is calculated from the capillary wave frequency observed in the fast Fourier transformed power spectrum. Many researchers have reported that the QELS method is appropriate for surface tension measurements, indicating that the surface tensions calculated from the capillary wave frequencies agreed with the other methods.<sup>2-8</sup> We fabricated a conventional laser heterodyne QELS measurement system using a diffraction grating as a local oscillator, and have reported on the dynamics of the mass transfer of surfactants at a liquid/liquid interface.<sup>9-13</sup> Furthermore, we devised a new principle of the QELS method using a monoluminous flux detection technique in a beam divergence, and have achieved 50 – 100 times higher *S/N* ratios than the conventional heterodyne system.<sup>14</sup> Although the *S/N* ratio was substantially improved by a new technique, averaging of 20 – 100 power spectra was necessary to estimate the capillary wave frequency.

The maximum entropy method (MEM) was first reported as a prospecting technique by Burg in 1967.<sup>15</sup> The method has been

applied to time-series analysis in various fields, such as meteorology, geophysics, economy, and biorhythm.<sup>16</sup> In the instrumental analysis area, there are also many reports<sup>17-19</sup> on the applications of MEM, such as to calculate the electron density distribution from the X-ray diffraction pattern<sup>20</sup> and to analyze the interferogram of IR spectroscopy in place of the fast Fourier transform (FFT).<sup>21</sup> The MEM provides a much higher resolution of the spectrum than the FFT. In the present study, we investigated the applicability of the MEM to the QELS method, and found that the resolution of the spectrum was substantially improved. The capillary wave frequencies were successfully estimated by the MEM without averaging the spectra.

## Principle

### *The QELS method*

The principle of the new monoluminous flux QELS methods using a beam divergence has already been reported in detail previously.<sup>14</sup> In short, the QELS method measures the capillary wave frequency of a selected wavelength, and the surface tension is calculated from the relationship between the frequency and the wavelength. A laser beam with a continuous intensity distribution in the divergence is incident normal to the surface (Fig. 1). The light intensity has a maximum at the center of the irradiated spot and decreases monotonously with the distance from the center. Because of the divergence, the angle of incidence varies as a function of the distance from the center. The strongest part of the beam is incident exactly normal to the surface, and its transmitted light is used as a local light (*F* Hz). The surrounding parts of the beam are incident obliquely and are scattered almost nondirectionally by capillary waves of various wavelengths. Some parts of the light are scattered exactly normal to the surface with a scattering angle of  $\theta$  and are mixed with the local light to generate an optical beat. By locating a photodiode at the strongest part of the transmitted light, the optical beat between the local light and the scattered

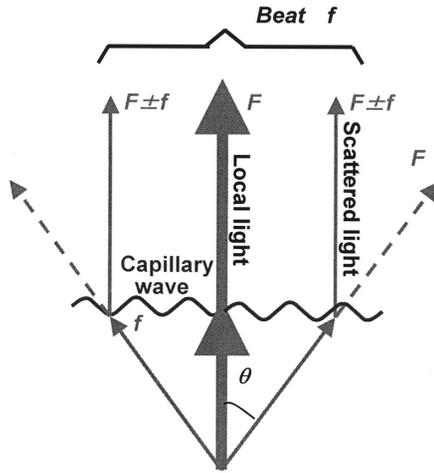


Fig. 1 Measurement principle of the QELS method of the new monoluminous flux technique utilizing beam divergence, which we have previously reported. The surrounding parts of the beam ( $F$  Hz) incident obliquely to the surface are scattered by a capillary wave ( $f$  Hz) with a Doppler shift ( $f$  Hz). An optical beat ( $f$  Hz) is generated by mixing the local light ( $F$  Hz) and the scattered light ( $F \pm f$  Hz). The beat frequency ( $f$  Hz) corresponds to the capillary wave frequency ( $f$  Hz).

light is observed in the power spectrum. Because of the continuous spatial distribution of the incident beam, the scattered beam generating the optical beat consists of multiple scattering angles. The scattering angle that generates the greatest signal intensity can be determined from the angle of the beam divergence, and it gives the wavelength of the observed capillary wave as follows.

The electric field intensity generated by all the scattered light at a distance of  $r$  from the center is approximately expressed by the following equation:

$$E(r) \propto 2\pi r \exp(-r^2/a^2). \quad (1)$$

By differentiating Eq. (1), we find the maximum at  $r = a/\sqrt{2}$ . This corresponds to a scattering angle of  $\theta_0 = 1/\sqrt{2}$ , where  $\theta_0$  is the beam divergence of the light source. In the present study, the beam divergence of the light source is 1 mrad, and thus the wavelength of the observed capillary wave is calculated to be 0.752 mm.

The surface tension,  $\gamma$  is calculated from the relationship between the capillary wave frequency,  $f$ , and the capillary wave wavenumber,  $k$ , using Lamb's equation,

$$f = \frac{1}{2\pi} \left( \frac{\gamma}{\rho} \right)^{\frac{1}{2}} k^{\frac{3}{2}}, \quad (2)$$

where  $\rho$  is the density of the liquid.

#### The MEM

The MEM is based on the idea to find the spectrum that maximizes the information entropy.<sup>15</sup> Since the theoretical details of the MEM have been reviewed in various literature, we briefly give here an outline of the MEM. When discrete time-series  $x_1, x_2, x_3, x_4, \dots, x_m$  are observed every  $\Delta t$ , the entropy,  $H$ , is expressed by

$$H = \frac{1}{2} \log(\det C_m), \quad (3)$$

where  $C_m$  is the Toeplitz matrix, consisting of an autocorrelation

functions,  $C(k)$ , of the time-series. In the MEM analysis, it is essential to find autocorrelation functions that maximize the entropy,  $H$ . We can obtain the autocorrelation functions by solving the Yule-Walker equation,

$$C(k) = a_1 C(k-1) + a_2 C(k-2) + \dots + a_m C(k-m). \quad (4)$$

Equation (4) has the same structure as the auto-regressive model of the time-series,

$$x_k = a_1 x_{k-1} + a_2 x_{k-2} + \dots + a_m x_{k-m}, \quad (5)$$

and thus we can find  $a_i$  as the least-square solutions of Eq. (5). The power spectrum is calculated from the solutions using the Wiener-Khinchine relation,

$$P(f) = \frac{P_M \Delta t}{\left| 1 + \sum_{k=1}^m a_k \exp(2\pi i f k \Delta t) \right|^2}, \quad (6)$$

where  $P_M$  and  $M$  are the prediction error and the order of the MEM, respectively. We calculated the power spectra using a self-made program according to an algorithm proposed by Burg.

## Experimental

The experimental setup is the same as what we reported previously.<sup>14</sup> The beam from a diode-pumped YAG laser (CrystaLaser, model GCL-025S, 532 nm, 25 mW) is incident normal to the liquid surface after passing through the bottom of the sample cell. An aperture (1 mm diameter) is located at the strongest part of the transmitted light, and the selected light is detected by a photodiode (Hamamatsu Photonics S1290). Data were collected by an A-D converter after amplification. The sampling frequency was 10 kHz ( $t = 0.1$  ms), and one data record consisted of 4096 data points. The collected data were transformed into the frequency region (0 - 5 kHz) by using the MEM or the FFT. Window functions were not used in the present study. The MEM spectrum consisted of 4096 data points, whereas the FFT spectrum had 2048 data points (both transformed from 4096 data points in the time region). The FFT spectrum was only averaged 100 times for the reduction of noise. Moreover, the averaged spectrum was converted to the time region again by the inverse FFT, and MEM was performed on the time region data. This procedure was performed to compare the averaged FFT spectrum with the MEM.<sup>21</sup>

We used a surfactant aqueous solution (10 mM, cetyltrimethylammonium bromide, Kanto Chemical Co., Inc.) for measurement samples. In order to monitor the surface tension change, a piece of concrete specimen containing the surfactant was immersed in distilled water.

## Results and Discussion

The FFT power spectrum of *quasi*-elastic laser scattering from surfactant aqueous solution surface with averaging of 100 times is shown in Fig. 2a, and the corresponding MEM spectrum (the order  $M = 15$ ) is shown in Fig. 2b. The broad peaks appearing at 0.6 - 0.7 kHz are the capillary wave frequencies with a wavelength of 0.752 mm. The MEM spectrum was obtained with a much higher *S/N* ratio than the FFT. The FFT spectrum was fitted with a Gaussian function, and the peak frequency was estimated at 0.684 kHz. As for the MEM spectrum, the peak frequency was estimated at 0.699 kHz from second

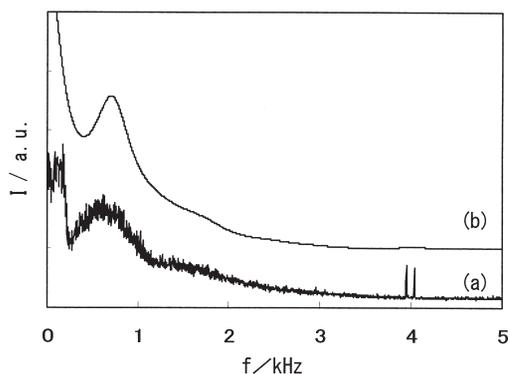


Fig. 2 (a) FFT power spectrum from a surfactant aqueous solution surface with averaging of 100 times. (b) MEM power spectrum calculated from time-series data obtained by the inverse FFT of (a). The curves are deviated for clarity.

differentiation. Substituting the frequency, the wavelength, and the density into Eq. (2), the surface tensions of surfactant aqueous solutions were calculated at 31.7 and 33.1 mN/m from the FFT and the MEM spectra, respectively. The values of the peak frequency and the surface tension agreed well with each other. We consider that a small discrepancy between the FFT and the MEM was within the experimental error. Both the FFT and the MEM power spectra were successfully used for surface tension measurements, provided they were sufficiently averaged (20 - 100 times).

Figure 3 a shows the FFT power spectrum without averaging, and Fig. 3b the corresponding MEM spectrum (the order  $M = 27$ ). The peak was not definitely observed in the FFT spectrum (depicted by an arrow), and the peak frequency could not be determined. The signals from the capillary wave seemed to be buried in noise. On the other hand, the MEM spectrum showed a definite curve, and we could calculate the peak frequency from its second differentiation. The calculated peak frequency was 0.690 kHz (surface tension 32.2 mN/m), which corresponds to the values from Fig. 2. The peak frequency of the capillary waves was successfully estimated by the MEM without averaging, whereas the peak was buried in noise in the FFT. Our result indicates that the time resolution of the QELS was improved to the theoretical limit of the present setup, 0.4096 s (4096 data points with sampling frequency of 10 kHz). We also confirmed that the surface tension change of surfactant aqueous solution can be monitored by the MEM spectra without averaging, and that the values agreed with those from the FFT spectra with averaging 100 times.

The MEM was found to afford a higher  $S/N$  spectra of the *quasi*-elastic laser scattering method, and it successfully enhanced the time resolution of the QELS by reducing the averaging times. We should note the following points in practical applications of the MEM. In the MEM analysis, the order  $M$ , which is the counterpart of the maximum lag of the autocorrelation function in Eq. (4) or of the order in the autoregressive model in Eq. (5), is the only free parameter. Inappropriate  $M$  values give no peaks or disproportionate curves in the spectra, which can be regarded as being incorrect in every respect, and thus it is of great significance to find an appropriate  $M$  value. Although some procedures have been reported to find the optimum order  $M$ , such as the final prediction error (FPE) and Akaike's information criterion (AIC),<sup>22</sup> such determined  $M$  values brought about disproportionate spectral curves. We found empirically that the appropriate  $M$  value for the QELS

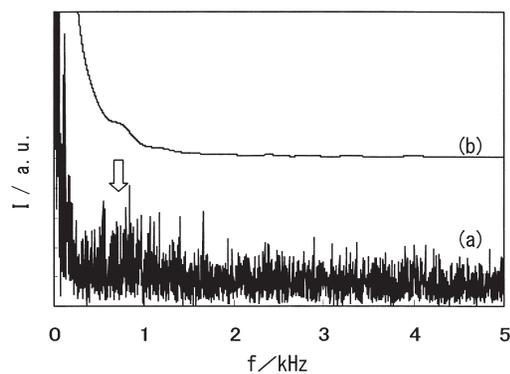


Fig. 3 (a) FFT power spectrum from a surfactant aqueous solution surface without averaging. A broad peak due to the capillary wave is indicated by an arrow. (b) MEM power spectrum calculated from raw time-series data of 4096 sampling points without averaging. The curves are deviated for clarity.

method was in the range of 6 to 30, which was dependent on the sampling conditions. We used  $M = 15$  for the time-series data without averaging (Fig. 3), and  $M = 27$  for the data from the averaged spectra (Fig. 2). The data above were all obtained by the new monoluminous flux QELS method, but additionally, the MEM can also analyze the data of the conventional heterodyne QELS method using the diffraction grating similarly ( $M = 7$ , 1024 data points with sampling frequency 100 kHz). On the other hand, Sasaki *et al.* have reported that the adequate  $M$  lies within the range of  $N/3 < M < N/2$ , as for the interferograms of IR data, where  $N$  is the number of the sample points.<sup>21</sup> We can say that the appropriate order  $M$  is dependent on the type of peaks that we want to be enhanced. For example, two small sharp peaks appearing at around 4 kHz in the FFT spectrum (Fig. 2a) disappeared in the MEM spectrum (Fig. 2b). This is due to the choice of the appropriate order,  $M = 15$ . If the spectrum is analyzed by MEM of order,  $M = 1500$ , the broad capillary wave peak becomes discrete, and the two small sharp peaks are enhanced. Once the appropriate order  $M$  was determined, we could use the same  $M$  value as long as the experimental conditions, such as the data points, sampling frequency, and observable peaks were the same. MEM analysis takes a rather longer computation time than the FFT, but owing to the recent rapid progress in information processing technology, we can carry out MEM analysis in real-time measurements. The procedures of MEM and FFT were completed within 1 and 0.1 s using a standard personal computer, respectively.

The theoretical limit of the time resolution was 0.4 s because of the sampling frequency of 10 kHz and the sample point number, 4096. This is because the peak frequency of the capillary wave ( $\lambda = 0.752$  mm) was 0.6 - 0.7 kHz. We can increase the sampling frequency, *i. e.*, the observable capillary wave frequency by decreasing the wavelength of the waves. This can be easily done by increasing the divergence angle of the incident light. It is possible to achieve a time resolution of 1 ms by increasing the sampling frequency to 1 MHz.

In conclusion, we applied MEM to calculations of the power spectra for the *quasi*-elastic laser scattering from liquid surfaces in place of FFT, and found that the  $S/N$  ratio of the spectra were greatly improved. Although the averaging of 20 - 100 spectra was necessary to estimate the peak frequency in the FFT power spectra, the MEM spectra provided the correct peak frequency without averaging. We also found empirically that the appropriate order  $M$  for the MEM analysis of the QELS spectra

was in the range of 6 to 30. MEM has a great advantage in time-resolution, and it will be possible to achieve a time-resolution of 1 ms by increasing the sampling frequency to 1 MHz. In addition, there is also a possibility of further improvements of FFT as well, like for MEM, by combining with the other data processing methods, such as nonlinear optimization methods, such as the auto-regressive model.

## References

1. J. Mingins, J. A. G. Taylor, B. A. Pethica, C. M. Jackson, and B. Y. T. Yue, *J. Chem. Soc., Faraday Trans. 1*, **1982**, 78, 323.
  2. K. Sakai, H. Tanaka, and K. Takagi, *Jpn. J. Appl. Phys.*, **1990**, 29, L2247.
  3. B. B. Sauer, Y. L. Chen, G. Zografis, and H. Yu, *Langmuir*, **1988**, 4, 111.
  4. M. Sano, M. Kawaguchi, Y.-L. Chen, R. J. Skarlupka, T. Cheng, G. Zografis, and H. Yu, *Rev. Sci. Instrum.*, **1986**, 57, 1158.
  5. S. Härd, Y. Hamnerius, and O. Nilsson, *J. Appl. Phys.*, **1976**, 47, 2433.
  6. R. H. Katyl and U. Ingard, *Phys. Rev. Lett.*, **1968**, 20, 248.
  7. H. Yui and T. Sawada, *Bunseki Kagaku*, **2005**, 54, 427.
  8. D. Byrne and J. C. Earnshaw, *J. Colloid Interface Sci.*, **1980**, 74, 467.
  9. Y. Uchiyama, T. Kitamori, and T. Sawada, and I. Tsuyumoto, *Langmuir*, **2000**, 16, 6597.
  10. Y. Uchiyama, M. Fujinami, T. Sawada, and I. Tsuyumoto, *J. Phys. Chem. B*, **2000**, 104, 4699.
  11. Y. Uchiyama, I. Tsuyumoto, T. Kitamori, and T. Sawada, *J. Phys. Chem. B*, **1999**, 103, 4663.
  12. Z. H. Zhang, I. Tsuyumoto, T. Kitamori, and T. Sawada, *J. Phys. Chem. B*, **1998**, 102, 10284.
  13. Z. H. Zhang, I. Tsuyumoto, S. Takahashi, T. Kitamori, and T. Sawada, *J. Phys. Chem. A*, **1997**, 101, 4163.
  14. I. Tsuyumoto and H. Uchikawa, *Anal. Chem.*, **2001**, 73, 2366.
  15. J. P. Burg, in Proceedings of the 37th Meeting of the Society of Exploration Geophysicists, 1967; (reprinted in "Modern Spectrum Analysis" ed. D. G. Childers, IEEE Press, New York, **1978**, 34 - 39.)
  16. N. Ohtomo, S. Terachi, Y. Tanaka, K. Tokiwano, and N. Kaneko, *Jpn. J. Appl. Phys.*, **1994**, 33, 2821.
  17. Y. He and L. Geng, *Anal. Chem.*, **2001**, 73, 5564.
  18. M. A. Delsuc and T. E. Malliavin, *Anal. Chem.*, **1998**, 70, 2146.
  19. Y. Sasanuma, R. V. Law, Y. Kobayashi, and K. Sasaki, *Anal. Chem.*, **1997**, 69, 794.
  20. M. Sakata, R. Mori, S. Kumazawa, M. Takata, and H. Toraya, *J. Appl. Crystallogr.*, **1990**, 23, 526.
  21. K. Sasaki, S. Kawata, and S. Minami, *Appl. Opt.*, **1983**, 22, 3599.
  22. H. Akaike, *Annals of Institute Statistical Mathematics*, **1969**, 21, 203.
-