報 文 3

Size Measurement of Microparticles in Liquids Using Photoacoustic Spectroscopy

Takehiko KITAMORI, Kazumichi SUZUKI, Tsuguo SAWADA*
and Yohichi GOHSHI*

Energy Research Laboratory, Hitachi, Ltd., 1168
Moriyama, Hitachi, Ibaraki 316, JAPAN

* Department of Industrial Chemistry, Faculty of
Engineering, University of Tokyo, 7-3-1 Hongo,
Bunkyo, Tokyo 113, JAPAN

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北森 武彦・藤井 正昭・沢田 嗣郎・合志 陽一

日立製作所エネルギー研究所 日立市森山町 1168 (〒316)
東京大学工学部工業化学科 文京区本郷 7-3-1 (〒113)

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The size measurement method for microparticles in liquids using the phase shift of photoacoustic signals theorized in our earlier paper [J. Appl. Phys., 58, 1456 (1985)] was verified using polystyrene turbid solutions. The experimental values for polystyrene microparticles, radii 0.4–5.2 μm , agreed with the theoretical values within the experimental accuracy of ± 0.2 deg. The physical meaning of the phase shift was clarified as representing the delay angle of the photoacoustic signal generation determined by the ratio of the heat release time from the microparticles to the modulation period of the excitation beam. Applications of photoacoustic spectroscopy for sizing and determination of microparticles in liquids by proper use of modulation frequency are discussed.

1. Introduction

Photoacoustic spectroscopy (PAS) has been applied to liquid phase samples as a direct coupling method, in which a piezoelectric signal detector is directly contacted with the liquid sample^{1,2)}. Using a laser as the beam source, the method is quite sensitive, and it has been applied as a weak absorption detector³⁾. The lower limit for a detectable absorption coefficient is on the order of 10^{-8} cm^{-1} , utilizing an optimized cylindrical cell⁴⁾. Thus PAS has been effectively applied to ultrasensitive colorimetric analysis in ppt (pg/mL) regions^{5–9)}. These applications are based on measurement

of the photoacoustic (PA) signal amplitude. However, the phase of the PA signal has not been applied to characterization of liquid samples.

In our previous papers, the phase of the PA signal in liquids was analyzed using linear response theory, and the relationship between the phase and energy migration in liquid was clarified^{10,11)}. This generalized theory was applied to the phase due to heat transfer from microparticle to the liquid medium, and the possibilities of sizing and thermal characterizations for suspended microparticles by phase measurements were indicated. Part of this characterization method, i.e. measurement of

heat transfer coefficients, was proved¹¹⁾. In this paper, the sizing method is verified for sub-micron to micron particles, and the relationships between the PA signals, heat migration time from microparticles to the medium, and modulation frequency of the excitation beam are discussed. Analytical applications of PAS for sizing and determination of microparticles in liquids are also introduced.

2. Experimental

2.1 Outline of the method

The basic relationships between the phase of PA signals and the size of microparticles in liquids was obtained from analysis of rigorous thermal and acoustic coupling equations for the following process:^{10, 11)} the temperature of the particles rises with the heat caused by absorption of the excitation beam; heat in the particles is released to the medium as a heat flux along the temperature field; the heat distribution in the medium fluctuates due to intensity modulation of the excitation beam; an acoustic wave is generated by the fluctuation of the heat distribution in the medium. The thermal process, in which the photoenergy of the excitation beam is converted to the heat distribution in the medium, is described by thermal equations for the particles and the medium. The acoustic process in which the PA signal is generated by fluctuation of the heat distribution is described by the wave equation for which the source term is the fluctuation of the heat distribution. The phase of the PA signal can be obtained from the frequency domain solutions of these coupling equations using linear response theory, and the phase ϕ_D due to the thermal process is described as follows;^{10, 11)}

$$\phi_D = \tan^{-1} \frac{\sigma_s C_{ps} V}{Sh} \omega_0 \quad (1)$$

$$= \tan^{-1} \frac{\sigma_s C_{ps} d^2}{3\kappa} \omega_0 \quad (2)$$

(for spherical particles)

where σ_s , C_{ps} and d are the density, specific heat, and the radius of the particles, respectively; κ is the heat conductance of the medium; h is the heat transfer coefficient from the

particles to the medium; and ω_0 is the angular frequency of the beam modulation. S and V represent the surface area and the volume of the particle, respectively. The physical meaning of ϕ_D is discussed later.

In addition to the phase ϕ_D , the measured phase ϕ_m has other phase components ϕ_Q and ϕ_R due to propagation of the PA signal and response of the PAS equipment, respectively. The phase ϕ_Q can be obtained from the analysis of the acoustic process, and it corresponds to the phase of the PA signals generated in a solvent itself¹²⁾. Therefore, in the experiment, the value of the additional phase $\phi_Q + \phi_R$ can be obtained as the background phase ϕ_B by measuring the PA signal phase of the solvent. Hence, the measured phase ϕ_m for a turbid solution and background phase ϕ_B are written as follows,

$$\phi_m = \phi_D + \phi_Q + \phi_R,$$

$$\phi_B = \phi_Q + \phi_R.$$

Then, ϕ_D can be obtained as $\phi_m - \phi_B$.

2.2 Measurements

The dependence of the phase ϕ_D on the radius of the microparticles was measured with polystyrene turbid solutions of different particle radii. The radii were 0.4, 0.5, 1.2, 3.2 and 5.2 μm . Turbid solutions with 1 ppm solid were prepared by stepwise dilutions of standard stock solutions of 10% solid using distilled and demineralized water filtered

Fig. 1 A block diagram of the PAS apparatus.

Table 1 Experimental parameters for measurement of the phase shifts.

Parameter	Value
Cell	
Cell radius	4.5 mm
Cell length	100 mm
Excitation beam	
Wavelength	514.5 nm
Beam power	200 mW
Beam radius	2.0 mm
Modulation frequency	6.5 kHz
Modulation function	Sinusoidal

through $0.1\text{ }\mu\text{m}$ membrane filters. A portion of each turbid solution was filtered through the $0.1\text{ }\mu\text{m}$ membrane filter, and the particle radii were measured by observation with a scanning electron microscope.

A block diagram of the PAS equipment is shown in Fig. 1, and the experimental parameters are listed in Table 1. A cylindrical direct coupling cell for which the signal detector was a cylindrical piezoelectric transducer (PZT) was used⁽⁴⁾. The excitation beam was sinusoidally modulated at 6.5 kHz by the acousto-optic modulator. The beam power was 200 mW, which was low enough to avoid generation of PA signals on PZT surface due to the direct exposure to the scattered beam.

The background phase ϕ_B was measured with the water subjected to the following ultrapurification steps: distillation in a glass apparatus, two demineralizations with a resin ion exchanger, and filtration through an activated carbon filter and a membrane filter. The resistivity of the obtained water was about $18\text{ M}\Omega/\text{cm}$, and particulate impurities above $0.1\text{ }\mu\text{m}$ were almost completely removed, hence the PA signal generated from any impurities was negligibly small in comparison with that of the water. The phase ϕ_m for each polystyrene turbid solution and the background phase ϕ_B for the water were measured. The phase ϕ_D for each radius was calculated as $\phi_m - \phi_B$. The results obtained are plotted in Fig. 2.

3. Discussion

The theoretical values of the phase shift for the polystyrene microparticle are calculated

Fig. 2 Dependence of the phase shift on the radius of polystyrene microparticles in liquids. The solid line is the theoretical values calculated with eq. (2), and the dashed line is the regression line for the measured values. The experimental parameters are listed in Table 1, and the material constants for the calculation are listed in Table 2.

Table 2 Material constants.

Parameter	Value
Polystyrene	
Specific heat; C_{p_s}	$1.22 \times 10^3 \text{ J/kgK}$
Density; σ_s	$1.05 \times 10^3 \text{ kg/m}^3$
Water	
Heat conductance; κ	$6.3 \times 10^{-1} \text{ J/msK}$
BaSO ₄	
Specific heat; C_{p_s}	$4.36 \times 10^2 \text{ J/kgK}$
Density; σ_s	$4.49 \times 10^3 \text{ kg/m}^3$

with eq. (2) using the parameters listed in Table 2, and the values are indicated in Fig. 2 by the solid line. The experimental results agree well with the theoretical values within the experimental accuracy and the size distributions of each solution. Hence the relationship between the phase shift of PA signals and the radius of the microparticles in liquids,

expressed in eq. (2), is confirmed, and the size measurement based on the relationship is verified. However, the slope of the regression line in the graph is smaller than that of the theoretical values. This seems to be due to approximating the heat transfer coefficient $h = \kappa/d$ in eq. (1), in which additional terms with respect to the particle radius d originating in the Grashof number are neglected^{10, 13)}.

The phase measurement accuracy of the present PAS equipment is ± 0.2 deg, hence the lower limit of the size measurement defined as twice the experimental accuracy is calculated as $d = 0.48 \mu\text{m}$ using eq. (2). In Fig. 2, the experimental values at $d = 0.4$ and $0.5 \mu\text{m}$, including their error bars are overlapped, and closely approach the lower sizing limit. Equation (2) shows that the tangent of the phase shift ϕ_D is proportional to the modulation frequency ω_0 , as was also verified previously¹⁰⁾. According to this relationship, the phase shift can be enlarged by using a higher modulation frequency, and the size measurement limit can be lowered. However, a more sensitive PAS system is required for using higher modulation frequency than 6.5 kHz at which the present experiment was carried out. Because the PA signal magnitude decreases with increased modulation frequency,¹²⁾ and the signal magnitude became insufficient for the phase measurement over 6.5 kHz modulation frequency region with the present PAS system.

To clarify the physical meanings of the phase shift, eq. (1) is rewritten as

$$\phi_D = \tan^{-1} \frac{\tau}{\tau_f} 2\pi \quad (3)$$

where

$$\tau = \frac{\sigma_s C_p V}{Sh}, \quad (4)$$

$$\tau_f = \frac{1}{f}, \quad (5)$$

and f ($\omega_0 = 2\pi f$) is modulation frequency. The denominator of eq. (4) means the heat release quantity per unit time and unit temperature difference between the particles and the medium, while the numerator is the heat capacity of the particles. Hence τ means the time re-

quired for heat release from the particles to the medium. The phase shift means the delay angle of the PA signal generation determined by the ratio between the heat release time τ and the modulation period τ_f . The PA signals $P(\vec{r}, t)$ from the microparticles in liquids are written as follows¹¹⁾ using τ and τ_f ,

$$P(\vec{r}, t) = \eta I_0 \tilde{D}(\tau) Q(\vec{r}, t) \quad (6)$$

$$\eta = \frac{\beta}{C_p} \frac{\kappa}{\kappa_s} \alpha_s V N_s$$

$$= \frac{\beta}{C_p} \frac{\kappa}{\kappa_s} \alpha_s \frac{C_s}{\sigma_s}, \quad (7)$$

$$Q(\vec{r}, t) = e^{i\omega_0 t} i\omega_0 \int_{\vec{r}'} R(\vec{r}') G_{\omega_0}(\vec{r}|\vec{r}') d\vec{r}', \quad (8)$$

$$\tilde{D}(\tau) = \frac{1}{\frac{\tau}{\tau_f} i + 1}, \quad (9)$$

where C_p is the specific heat; β is the isothermal expansion coefficient; α is the absorption coefficient; N is the number density; and C is the concentration. The subscript s identifies the material constants for microparticles. I_0 is the excitation beam power and the function $R(\vec{r})$ is its distribution, and $G_{\omega_0}(\vec{r}|\vec{r}')$ is the propagator. Hence the function $Q(\vec{r}, t)$ means the PA signal generation and propagation in the medium. On the other hands, $\tilde{D}(\tau)$ is the Fourier image of the impulse response concerned with formation of the heat distribution in the medium, and it expresses the influence of the heat migration process on the signal generation. The phases ϕ_D and ϕ_Q can be obtained as the argument of $\tilde{D}(\tau)$ and $Q(\vec{r}, t)$ respectively. When the modulation frequency is low enough and τ_f is sufficiently larger than τ , the value of $\tilde{D}(\tau)$ becomes 1, and eq. (6) shows that the magnitude of the PA signal does not depend on the particle radius. Therefore, when the modulation period τ_f is sufficiently larger than τ , the PA signal is proportional to the concentration as shown in eq. (7), and the calibration curve does not depend on the particle size. Oda et al.¹⁴⁾ give experimental evidence for these theoretical conclusions in their measurements of the calibration curves for BaSO_4 (particle radii: $0.3\text{--}11 \mu\text{m}$; modulation frequency: 33 Hz). Using eq. (4) and the parameters listed in Table 2, τ for

these BaSO_4 particles is calculated to be 0.1–139.2 μs , and the value of τ_f is 3.0×10^{-2} s. Hence, in their experiments τ was small enough for the approximation $\tilde{D}(\tau) \simeq 1$ to be valid.

In summarizing the above discussion, PAS can size microparticles in liquids and determine their concentrations, by properly selecting a modulation frequency with regard to the heat release time of the microparticles. Therefore, PAS is expected to be a useful tool for study of colloidal and turbid solutions.

4. Conclusion

A size measurement method for microparticles in liquids using the phase shift of the PA signals, which is caused by the time required for heat release from the microparticles to the medium, was proved. The phase shifts were measured at the modulation frequency of 6.5 kHz, with polystyrene turbid solutions having particle radii of 0.4–5.2 μm . The experimental results agreed well with the theoretical values. The phase measurement accuracy of the present PAS equipment was $\pm 0.2^\circ$, and the lower limit of this sizing method, defined by doubling the accuracy value was 0.48 μm of radius for the present conditions. However, the tangent of the phase shift is proportional to the modulation frequency, and the limitation can be improved by using higher modulation frequencies.

The physical meaning of the phase shift was shown to represent the delay angle of PA signal generation determined by the ratio between the heat release time and the modulation period of the excitation beam. When the modulation frequency was low enough, the

delay angle of the PA signal generation was negligibly small and the PA signal magnitude was proportional to the concentration of the microparticles independent of their sizes. Therefore, PAS can size microparticles in liquids and determine their concentrations, by properly selecting the modulation frequency with regard to their heat release time.

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