A Simple Method of Determining Diffusion Coefficient by Digital Laser Speckle Correlation

Giuseppe Spagnolo, Dario Ambrosini, Antonio Ponticiello, Domenica Paoletti

A Simple Method of Determining Diffusion Coefficient by Digital Laser Speckle Correlation

Giuseppe Schirripa Spagnolo (*), Dario Ambrosini, Antonio Ponticiello and Domenica Paoletti

Dipartimento di Energetica, Università di L'Aquila Località, Monteluco di Roio, 67040 Roio Poggio, Italy

(Received 5 February 1996, revised 22 April 1996, accepted 24 May 1996)

PACS.42.30.Yc – Other topics in imaging and optical processing
PACS.66.10.Cb – Diffusion and thermal diffusion

Abstract. — A laser speckle technique is proposed for the study of diffusion in transparent liquid mixtures. The diffusion constants may be deduced by a simple manipulation of the speckle patterns recorded during the diffusion process. The proposed method, checked with the LiBr-water system, gives reasonable agreement with existing *data.*

1. Introduction

The study of diffusion in liquid binary systems by optical methods based on the measurement of refractive index variation is well known [1,2]. Particularly, holographic interferometry [3–8], and ESPI (Electronic Speckle Pattern Interferometry) [9–11] have been used to evaluate the diffusion coefficient of a liquid mixture.

In this paper we report on an alternative method. The basic idea is to use the local correlation degree of speckles in the image plane (also called subjective speckles) to study the refractive index variation when two initially separated binary liquid mixtures of a solute A in solvente B, with concentration of solute c_1, and c_2, diffuse simultaneously through each other.

The principle of local correlation of laser speckles consists in the evaluation of a local parameter which estimates the correlation of the speckles after any modification of the object under test.

The proposed method can be considered to a certain extent a novel electronic version of the speckle photography of transparent objects [12]. In fact, it is based on statistical speckle properties and involves the detection of the object points not exhibiting speckle displacement.

The main advantage of the proposed method, aside from the simplicity of the optical system, is its lower sensitivity to external vibrations with respect to other interferometric techniques.

2. Experimental Set-Up

The experimental arrangement used in this work is depicted schematically in Figure 1. As a diffusion cell, we used a spectrophotometric glass cell measuring $10 \times 10 \times 45$ mm, equipped with a Teflon shutting device to avoid evaporation phenomena. The cell is filled through a capillary

(*) Author for correspondence (e-mail: schirrip@ing.univaq.it)

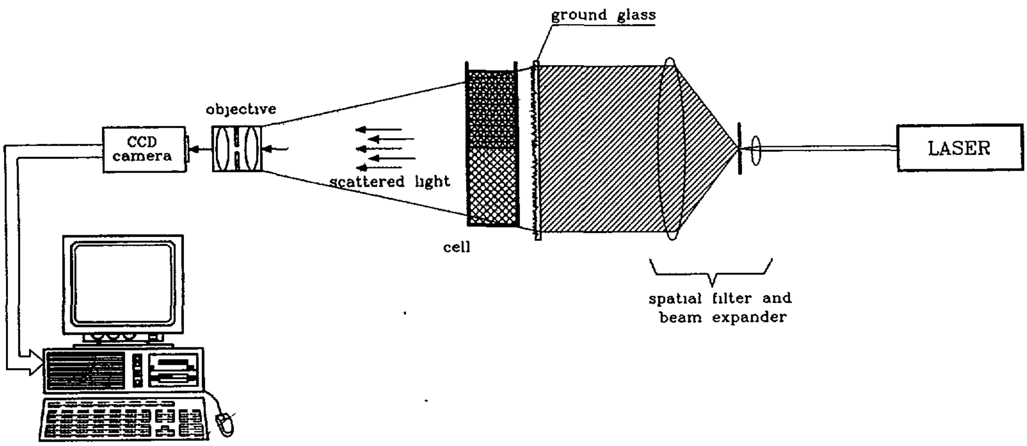

Fig. 1. — Experimental set-up for measuring the diffusivity of liquid binary mixtures by speckle local correlation.

tube from the bottom, to minimize turbulence and mixing. This allows to approximate closely a step function in the initial refractive index gradient. First the lighter fluid is put into the cell. Next the denser liquid is introduced slowly from below, lifting the lighter liquid without convection movements. This filling procedure, developed by Gabelmann-Gray and Fenichel [5], is very simple and effective. The cell is illuminated by an expanded and collimated HeNe laser beam ($P = 10$ mW) by means of a diffuser (ground glass). The light rays diffracted by the ground glass, form a speckle pattern on the photosensor of a CCD video camera which images the diffuser. The video signal is finally processed by a frame grabber that allows arithmetic operations on images in real-time.

3. Basic Principles

Let us consider a free diffusion process with a diffusion coefficient (D) independent of concentration (c). Neglecting the Soret and Dufour effects, this process is ruled by Fick's second law, which can be expressed, for one-dimensional diffusion (along the x-axis), as in reference [13]

$$\frac{\partial c(x,t)}{\partial t} = D\frac{\partial^2 c(x,t)}{\partial x^2} \tag{1}$$

The solution of equation (1) for two binary liquid mixtures initially ($t = 0$) separated at $x = 0$ with concentration c_1 and c_2 is [14]

$$c(x,t) = \frac{c_1 + c_2}{2} + \frac{c_2 - c_1}{2}\operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right), \tag{2}$$

where the error function erf is defined as [15]

$$\operatorname{erf}(u) = \frac{2}{\sqrt{\pi}}\int_0^u \exp\left(-\eta^2\right)\, d\eta\ .$$

In the diffusion cell, the refractive index can be treated as a linear function of the concentration, call $c(x,t)$, especially when the concentration gradient is small. Then, as a first approximation,

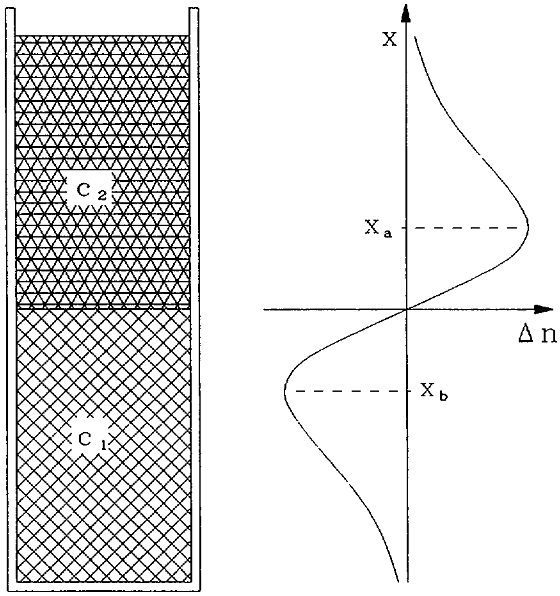

Fig. 2. — Graphic reconstruction of the refractive index variation curve.

we can write [16]

$$n(x,t) = \left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)_0 c(x,t) + n_0, \tag{3}$$

where $\left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)_0$ is the mean value of the derivative $\frac{\mathrm{d}n}{\mathrm{d}c}$ in the applied concentration range and n_0 is a constant.

The change in the index of refraction $[\Delta n(x,t_1,t_2)]$, as a function of x for two given times t_1 and $t_2 > t_1$, is

$$\begin{aligned} \Delta n(x,t_1,t_2) &= n(x,t_2) - n(x,t_1) \\ &= \left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)_0 \frac{c_2 - c_1}{2} \left[\operatorname{erf}\left(\frac{x}{2\sqrt{Dt_2}}\right) - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt_1}}\right)\right]. \end{aligned} \tag{4}$$

Equation (4) is plotted in Figure 2. The curve has two characteristic extremes. Their positions, call x_A and x_B, may be found from the condition

$$\frac{\partial}{\partial x}[\Delta n(x,t_1,t_2)] = 0. \tag{5}$$

Using equations (4) and (5), we can write

$$\frac{\partial}{\partial x}\left[\operatorname{erf}\left(\frac{x}{2\sqrt{Dt_2}}\right)\right] - \frac{\partial}{\partial x}\left[\operatorname{erf}\left(\frac{x}{2\sqrt{Dt_1}}\right)\right] = 0\,. \tag{6}$$

Therefore

$$\frac{\exp\left[-\left(x/\sqrt{4Dt_2}\right)^2\right]}{2\sqrt{Dt_2}} = \frac{\exp\left[-\left(x/\sqrt{4Dt_1}\right)^2\right]}{2\sqrt{Dt_1}} \tag{7}$$

Taking the logarithms of the left- and right-hand sides of equation (7) we obtain

$$-\left(\frac{x}{2\sqrt{Dt_2}}\right)^2 - \ln\left(2\sqrt{Dt_2}\right) = -\left(\frac{x}{2\sqrt{Dt_1}}\right)^2 - \ln\left(2\sqrt{Dt_1}\right), \tag{8}$$

from which

$$x^2 = \frac{2D\ln(t_2/t_1)}{(1/t_1) - (1/t_2)}. \tag{9}$$

Hence we have

$$x_{\mathrm{A}} = \left[\frac{2D\ln(t_2/t_1)}{(1/t_1) - (1/t_2)}\right]^{1/2} \quad \text{and} \quad x_{\mathrm{B}} = -\left[\frac{2D\ln(t_2/t_1)}{(1/t_1) - (1/t_2)}\right]^{1/2} \tag{10}$$

In this way we obtain the separation of the two extremes on the x axis:

$$w = x_{\mathrm{A}} - x_{\mathrm{B}} = 2\left[\frac{2D\ln(t_2/t_1)}{(1/t_1) - (1/t_2)}\right]^{1/2} \tag{11}$$

And the diffusion coefficient turns out to be

$$D = \frac{w^2\left[(1/t_1) - (1/t_2)\right]}{8\ln(t_2/t_1)} \tag{12}$$

By means of equation (12), measurement of diffusion coefficients was performed through holographic and ESPI methods [4,6,8–10].

The local correlation of laser speckle images can be used to determine w without employing interferometric techniques. This leads to a simplification of the experimental procedure.

If a transparent test object is placed in front of a laser-illuminated diffuser (as shown in Fig. 3), a speckle pattern is formed on the photosensor of a TV-camera. If the test object has a non-uniform refractive index, the rays contributing to the formation of the speckle pattern in the photosensor plane will be deflected by refraction.

If the refractive index changes, the deflection angle and the speckle pattern, formed by the ground glass, will also change. The change of the deflection angle can be seen as a local translation of the diffuser. The TV-camera should have a small aperture so that all rays contributing to a particular speckle are deflected by essentially the same amount.

For light rays defined as orthogonal trajectories to the geometrical wave-front, the equation relating the path of ray to the local index of refraction is [17]

$$\frac{\mathrm{d}}{\mathrm{d}s}\left(n\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}s}\right) = \operatorname{grad} n, \tag{13}$$

where $\mathbf{r}$ is the position vector of a typical point on a ray and s is the length of the ray measured from a fixed point on it.

In a one-dimensional diffusion process the medium is stratified, so that refractive index can be considered function of only one space variable. We assume that n varies in one direction only (x-axis), which will be perpendicular to the entering ray. As shown in Figure 3, a ray enters the medium at a location x_{p} and it is parallel to the z-axis. In this case, equation (13) can be rewritten as

$$\frac{\mathrm{d}}{\mathrm{d}s}\left[n(x,t)\frac{\mathrm{d}x}{\mathrm{d}s}\right] = \frac{\partial n(x,t)}{\partial x} \tag{14}$$

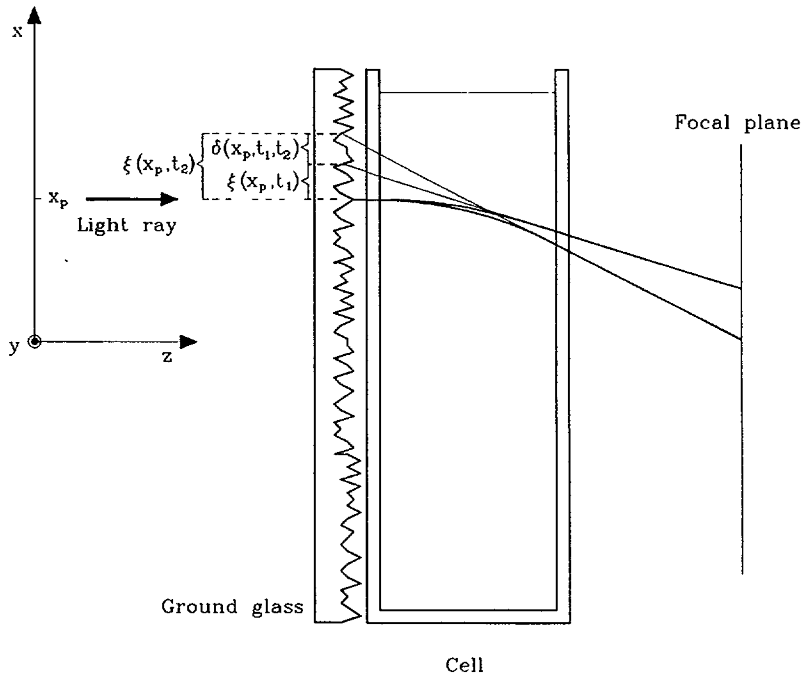

Fig. 3. — Schematic illustration of local speckle pattern shift.

If the bending of the light ray is small $\mathrm{d}s \simeq \mathrm{d}z$, the equation (14) can be simplified as

$$\frac{\mathrm{d}}{\mathrm{d}z}\left[n(x,t)\frac{\mathrm{d}x}{\mathrm{d}z}\right] = \frac{\partial n(x,t)}{\partial x} \tag{15}$$

If the ray enters at $z = 0$ and $x = x_\mathrm{p}$, so that $n(x_\mathrm{p}, t) = n_\mathrm{p}$, equation (15) can be integrated, with respect to z, and we obtain

$$\frac{\mathrm{d}x}{\mathrm{d}z} = \frac{1}{n_\mathrm{p}}\int_0^\ell \frac{\partial n(x,t)}{\partial x}\mathrm{d}z = \frac{\ell}{n_\mathrm{p}}\frac{\partial n(x,t)}{\partial x}, \tag{16}$$

where ℓ represents the thickness of the diffusion cell.
Therefore, the angle of refraction of a ray passing through the diffusion cell is [18–20]

$$\phi = \frac{\mathrm{d}x}{\mathrm{d}z} = \frac{\ell}{n_\mathrm{p}}\frac{\partial n(x,t)}{\partial x} \tag{17}$$

The corresponding local shift of the speckle pattern results

$$\xi(x_\mathrm{p}, t) = \ell \tan\phi \simeq \frac{\ell^2}{n_\mathrm{p}}\frac{\partial n(x,t)}{\partial x}, \tag{18}$$

where, as the bending of the ray is small, we consider $\tan\phi \simeq \phi$. If we record two speckle patterns at different times (*i.e.* t_1 and t_2), we have two different local shifts, that is

$$\xi(x_\mathrm{p}, t_1) = \frac{\ell^2}{n_\mathrm{p}}\left.\frac{\partial n(x,t_1)}{\partial x}\right|_{x_\mathrm{p}} \qquad \text{and} \qquad \xi(x_\mathrm{p}, t_2) = \frac{\ell^2}{n_\mathrm{p}}\left.\frac{\partial n(x,t_2)}{\partial x}\right|_{x_\mathrm{p}} \tag{19}$$

If we consider a diffusion process with a small concentration gradient, the value of n_{p} can be considered constant between t_1 and t_2.
Therefore, the shift of the individual speckle, during a time $\Delta t = t_2 - t_1$ is

$$\delta\left(x_{\mathrm{p}}, t_1, t_2\right) = \xi\left(x_{\mathrm{p}}, t_2\right) - \xi\left(x_{\mathrm{p}}, t_1\right) = \frac{\ell^2}{n_{\mathrm{p}}}\left[\left.\frac{\partial n\left(x, t_2\right)}{\partial x}\right|_{x_{\mathrm{p}}} - \left.\frac{\partial n\left(x, t_1\right)}{\partial x}\right|_{x_{\mathrm{p}}}\right]. \tag{20}$$

There is no translation when

$$\left.\frac{\partial n\left(x, t_2\right)}{\partial x}\right|_{x_{\mathrm{p}}} - \left.\frac{\partial n\left(x, t_1\right)}{\partial x}\right|_{x_{\mathrm{p}}} = 0. \tag{21}$$

Equation (21) is equal to equation (5), therefore at the extremes x_{A} and x_{B} there is no local shift of the speckle pattern, that is

$$\delta(x_{\mathrm{A}}, t_1, t_2) = 0 \qquad \text{and} \qquad \delta\left(x_{\mathrm{B}}, t_1, t_2\right) = 0. \tag{22}$$

The dependence of subjective speckle correlation on speckle displacement has been studied by Owner-Petersen [21]. The correlation of the speckle intensity corresponding to a surface resolution element ΔS has been evaluated theoretically by considering the local shift in image plane and the global shift in the pupil plane of the speckle pattern. This second effect alters the microstructure of the speckle pattern.
When we have no local shift and no microstructural change of the speckle pattern, the local coefficients calculated in x_{A} and x_{B} relative to the speckle patterns recorded at the time t_1 and t_2 are

$$\rho\left(x_{\mathrm{A}}, t_1, t_2\right) = 1 \qquad \text{and} \qquad \rho\left(x_{\mathrm{B}}, t_1, t_2\right) = 1. \tag{23}$$

The correlation coefficient can be deduced, in real-time, by squaring and averaging the arithmetic difference between two digital speckle images.
We indicate with $I\left(x, y, t_1\right)$ and $I\left(x, y, t_2\right)$ the intensity values, for a single point in the image plane of the viewing lens, at two different instants t_1 and t_2 respectively. As the system is stratified along the x direction, for the sake of simplicity we can neglect the dependence upon y. The light intensity of the speckle pattern is converted to an electrical video signal by a TV camera. We assume that the video signals from the TV camera are proportional to the light intensities. Commercial CCDs with typical nonlinearity about 5% are usable. The video signal is converted to a digital picture by a frame grabber. If we subtract the two digital pictures and if the signal after subtraction is square-law detected, the expected brightness is

$$\begin{aligned} Q(x, t_1, t_2) &\propto \left\langle \left[I\left(x, t_1\right) - I\left(x, t_2\right)\right]^2 \right\rangle \\ &= \left\langle I^2\left(x, t_1\right)\right\rangle + \left\langle I^2\left(x, t_2\right)\right\rangle - 2\left\langle I\left(x, t_1\right) I\left(x, t_2\right)\right\rangle, \end{aligned} \tag{24}$$

where $\langle \ldots \rangle$ denotes a spatial average over an area that contains many speckles [22]. The last term in equation (24) is a cross correlation between the two light intensities. Usually, the light amplitude scattered from an optically rough surface, illuminated by coherent light, can be treated as a circular complex random Gaussian statistics process. The cross correlation term in equation (24) is then expressed as [23]

$$\left\langle I\left(x, t_1\right) I\left(x, t_2\right)\right\rangle = \left\langle I\left(x, t_1\right)\right\rangle \left\langle I\left(x, t_2\right)\right\rangle \left[1 + \rho\left(x, t_1, t_2\right)\right]. \tag{25}$$

Assuming that the light amplitudes are stationary signals with respect to the spatial coordinates we have $\left\langle I\left(x, t_1\right)\right\rangle = \left\langle I\left(x, t_2\right)\right\rangle = \left\langle I\left(x, t\right)\right\rangle$ (*i.e.* the spatial average intensities over an area that contains many speckles, at any time, are equal). Furthermore, taking into account the negative exponential statistics of speckle patterns, we have

$$\left\langle I^2(x,t)\right\rangle = 2\left\langle I(x,t)\right\rangle^2 \tag{26}$$

Therefore the equation (24) turns out to be

$$Q(x,t_1,t_2) \propto \left\langle \left[I(x,t_1) - I(x,t_2)\right]^2\right\rangle = \left\langle I^2(x,t)\right\rangle\left[1-\rho(x,t_1,t_2)\right], \tag{27}$$

hence

$$\rho(x,t_1,t_2) = 1 - \frac{\left\langle \left[I(x,t_1) - I(x,t_2)\right]^2\right\rangle}{\left\langle I^2(x,t)\right\rangle} = 1 - \frac{Q(x,t_1,t_2)}{B(x,t)}, \tag{28}$$

where $B(x,t)$ represents the expected digital picture after squaring and averaging, *i.e.* $B(x,t) \propto \left\langle I^2(x,t)\right\rangle$.

This demonstrates that the correlation coefficient can be deduced by squaring and averaging the arithmetic difference between the speckle images $I(x,t_1)$ and $I(x,t_2)$.

In practice, two speckle pattern images at two different instants t_1 and t_2 are acquired and stored in the frame grabber memory during the diffusion process. A digital subtraction, between the speckle images $I(x,t_1)$ and $I(x,t_2)$, is performed and displayed, after a square-law, on a monitor in real-time. Thereby, the ensemble average $\langle\ldots\rangle$ is effected by a local average [22]. Where there is no shift, $\rho(x,t_1,t_2) = 1$. Therefore, according to equation (27), we have

$$\left\langle \left[I(x,t_1) - I(x,t_2)\right]^2\right\rangle = 0 \tag{29}$$

so that in correspondence with x_{A}, and x_{B}, dark fringes appear.

4. Results

Some measurements of a LiBr-water system (0.1 M) at 25 °C were carried out to check the technique described above. Figure 4 shows an example of correlation pattern obtained with $t_1 = 600$ s and $t_2 = 1272$ s. The dark fringes located at x_{A} and x_{B} are indicated by the white lines.

A set of correlation patterns, like Figure 4, was performed during a particular diffusion experiment. From each correlation pattern a value of the diffusion coefficient D was deduced from parameters t_1, t_2, w by equation (12).

The mean value of independent measurements was $D = 1.25 \pm 0.04 \times 10^{-5}$ cm^2 s^{-1}. The uncertainty represents the standard deviation of the measurements. It compares reasonably to the value reported in literature [16] that is 1.279×10^{-5} cm^2 s^{-1}

5. Conclusion

We proposed a new method to evaluate the diffusion coefficient in liquid binary mixtures. The experimental examples clearly demonstrate the potentialities of the local correlation technique for the study of diffusion.

The local correlation method can be considered less sensitive than holographic or ESPI techniques, but it is relatively simple to construct and more straight to align. Furthermore, it presents a remarkable simplicity in experimental procedure. Therefore, the local speckle laser correlation can be used as an alternative method for routine measures of the diffusivity of liquid binary mixtures.

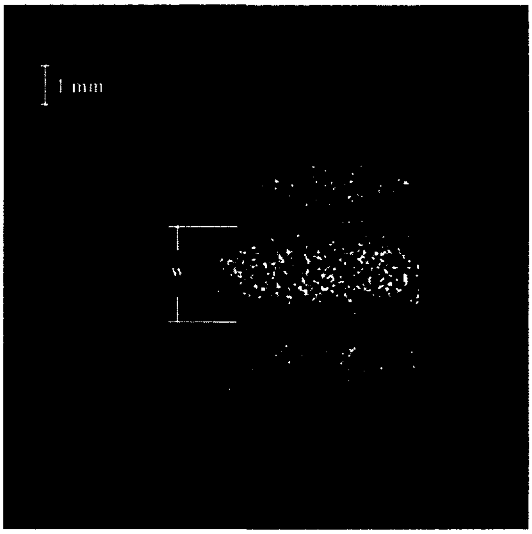

Fig. 4. — Correlation speckle pattern relative to an isothermal diffusion of LiBr-water system (0.1 M): ($t_1 = 600$ s; $t_2 = 1272$ s; $w = 2.93$ mm; $D = 1.258 \times 10^{-5}$ cm^2 s^{-1}).

Acknowledgments

Special thanks are due to Mr. A. Colagrande and Mr. G. Pasqualoni for technical assistance. The authors would like to thanks the referees for the valuable suggestions on some aspects of this work.

References

[1] Thyrrell H.J.K., Diffusion and Heat Flow in liquids (Butterworth, Great Britain, 1961).
[2] Cussler E.L., Diffusion: Mass Transfer in Fluids System (Cambridge University Press, Cambridge, 1984).
[3] Durou C., Une installation d'interférométrie holographique destinée à l'étude des phénoménes de diffusion dans les liquides, *J. Phys. E: Scien. Instrum.* **6** (1973) 1116-1120.
[4] Bochner N. and Pipman J., A simple method of determining diffusion constants by holographic interferometry, *J. Phys. D: Appl. Phys.* **9** (1976) 1825-1830.
[5] Gabelmann-Gray L. and Fenichel H., Holographic interferometric study of liquid diffusion, *Appl. Opt.* **18** (1979) 343-345.
[6] Szydlowska J. and Janowska B., Holographic measurement of diffusion coefficients, *J. Phys. D: Appl. Phys.* **15** (1982) 1385-1393.
[7] Ruiz-Bevia F., Celdran-Mallol A., Santos-Garcia C. and Fernandez Sempere J., Holographic interferometric study of free diffusion: a new mathematical treatment, *Appl. Opt.* **24** (1985) 1481-1484.
[8] Paoletti D., Schirripa Spagnolo G., Laurenti L. and Ponticiello D., Automated fringe analysis in diffusivity measurements by sandwich holography, *J. Phys. III France* **2** (1992) 1835-1842.

[9] Paoletti D. and Schirripa Spagnolo G., Fiber optics speckle interferometer for diffusivity measurements, *J. Phys. III France* **3** (1993) 911-914.

[10] Paoletti D., Schirripa Spagnolo G., Bagini V. and Santarsiero M., A new method for measuring the diffusivity of liquid binary mixtures using DSPI, *Pure Appl. Opt.* **2** (1993) 489-498.

[11] Schirripa Spagnolo G., Ambrosini D., Ponticiello A. and Paoletti D., Evaluation of diffusion in liquids by digital speckle pattern interferometry: computer simulation and experiments, *Eur. J. Phys.* **17** (1996) 51-59.

[12] Vest C.M., Holographic interferometry (John Wiley & Sons, New York, 1979).

[13] Hansen J.P. and McDonald I.R., Theory of simple liquids (Academic Press, London, 1990).

[14] Crank J., The mathematics of Diffusion (Oxford University Press, Oxford, 1972).

[15] Abramowitz M. and Stegun I.A., Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables (Dover, New York, 1972).

[16] Weast R.C., Handbook of Chemistry and Physics (Chemical Rubber Co. Press, Cleveland, 1972).

[17] Born M. and Wolf E., Principles of Optics (Pergamon Press, Oxford, 1980).

[18] Kopf U., Application of speckling for measuring the deflection of light by phase object, *Opt. Comm.* **5** (1972) 347-350.

[19] Debrus S., Francon M.,Grover C.P., May M. and Roblin M.L., Ground Glass Differential Interferometer, *Appl. Opt.* **11** (1972) 853-857.

[20] Nirala A.K. and Shakher C., Measurement of temperature profile of a two-dimensional slot Burner (pre-mixed Laminar) flame using laser speckle photography and laser speckle shearing interferometry, *J. Optics (Paris)* **26** (1995) 215-223.

[21] Owner-Petersen M., Decorrelation and fringe visibility: on the limiting behaviour of various electronic speckle-pattern correlation interferometers, *J. Opt. Soc. Am.* **8** (1991) 1082-1089.

[22] Hofling R. and Osten W., Displacement by image-processed speckle patterns, *J. Mod. Opt.* **34** (1987) 607-617.

[23] Goodman J.W., Statistical Properties of Laser Speckle Pattern, in "Laser Speckle and related Phenomena" (J.C. Dainty, Ed., Springer-Verlag, Berlin, 1975) pp. 9-75.