SUPPORTING INFORMATION

Tracking Molecular Aggregates at a Liquid Interface by Non-Linear Correlation Spectroscopy

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Theoretical framework

As mentioned in the text of the article, the general framework has been developed in order to analyze the autocorrelation traces obtained with a fluctuant surface SHG intensity. This theoretical model only takes into account the case where the fluctuation in the SHG signal comes from the density fluctuation under the laser spot. The two main phenomena are introduced: the 2D diffusion and a global flow. In the general case, $C(\vec{r},t)$ is assumed to be the surface

concentration of the species, which generates the SHG signal at the position $\vec{r} = u_x\vec{e}_x + u_y\vec{e}_y$ (for a 2 dimensional system). A fluctuation in this concentration is given by:

$$\delta C(\vec{r},t) = C(\vec{r},t) - \langle C \rangle \tag{1}$$

where <C> is the average concentration in space and time. We suppose a global flow in the y direction: $\vec{V} = V\vec{e}_y$. The intensity profile of the laser beam is supposed to be Gaussian: $w(\vec{r})=I_0\exp[-2(\vec{r}/r_0)^2]$ where r_0 is the laser waist. Using Geissbuehler's et al work, the SHG intensity is given by[1]:

$$I_{SHG}(t) = K\left|\int \chi^{(2)}(\vec{r},t)w(\vec{r})d\vec{r}\right|^2 \tag{2}$$

Where K is a global constant, which contains the fundamental constant and the optical characteristic of the medium. $\chi^{(2)}$ is the second order electric susceptibility tensor which depends *a priori* of r and t. If we assume that the individual response of each molecule does not change, it means that we do not consider any change in the molecular orientation onto the surface, the $\chi^{(2)}$ term can be written as:

$$\chi^{(2)}(\vec{r},t) = \frac{1}{\varepsilon_0}C(\vec{r},t)\beta_L \tag{3}$$

where β_L is the hyperpolarisability tensor of the molecule in the laboratory frame. This last assumption means that the model will not consider that the fluctuation of the SHG signal comes from the orientational variation of the molecules. Those fluctuations are likely present but certainly too fast to be observed. The equation (2) becomes:

$$I_{SHG}(t) = K\left|\beta_L\right|^2\left(\int C(\vec{r},t)w(\vec{r})d\vec{r}\right)^2 \tag{4}$$

A temporal fluctuation of the SHG intensity is thus given by:

$$\begin{aligned}\delta I_{SHG}(t) &= 2K\left|\beta_L\right|^2 \times \int C(\vec{r},t)w(\vec{r})d\vec{r} \times \delta\left(\int C(\vec{r}\,',t)w(\vec{r}\,')d\vec{r}\,'\right)\\ \delta I_{SHG}(t) &= 2K\left|\beta_L\right|^2 \times \iint C(\vec{r},t)w(\vec{r})\delta C(\vec{r}\,',t)w(\vec{r}\,')d\vec{r}\,d\vec{r}\,'\end{aligned} \tag{5}$$

The following definition of the normalized autocorrelation function G is used:

$$G_{SHG}(\tau) = \frac{\left\langle I_{SHG}(t+\tau)I_{SHG}(t)\right\rangle}{\left\langle I_{SHG}(t)\right\rangle^2} = 1 + \frac{\left\langle \delta I_{SHG}(\tau)\delta I_{SHG}(0)\right\rangle}{\left\langle I_{SHG}(t)\right\rangle^2} \tag{6}$$

We will evaluate this autocorrelation function G under the assumption explained before. The first step in the calculus is to determine the numerator

$$\left\langle \delta I_{SHG}(\tau)\delta I_{SHG}(0)\right\rangle = 4K^2\left|\beta_L\right|^4 \int\int\int\int \left\langle C(\vec{r}_1,\tau)\delta C(\vec{r}_2,\tau)C(\vec{r}_3,0)\delta C(\vec{r}_4,0)\right\rangle w(\vec{r}_1)w(\vec{r}_2)w(\vec{r}_3)w(\vec{r}_4)d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 d\vec{r}_4 \tag{7}$$

We note $\phi(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4,\tau) = \left\langle C(\vec{r}_1,\tau)\delta C(\vec{r}_2,\tau)C(\vec{r}_3,0)\delta C(\vec{r}_4,0)\right\rangle$

By applying the relation (1), we get

$$\begin{aligned}\phi(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4,\tau) = &\left\langle \delta C(\vec{r}_1,\tau)\delta C(\vec{r}_2,\tau)\delta C(\vec{r}_3,0)\delta C(\vec{r}_4,0)\right\rangle\\ &+\left\langle C\right\rangle\left\langle \delta C(\vec{r}_2,\tau)\delta C(\vec{r}_3,0)\delta C(\vec{r}_4,0)\right\rangle\\ &+\left\langle C\right\rangle\left\langle \delta C(\vec{r}_1,\tau)\delta C(\vec{r}_2,0)\delta C(\vec{r}_4,0)\right\rangle\\ &+\left\langle C\right\rangle^2\left\langle \delta C(\vec{r}_2,\tau)\delta C(\vec{r}_4,0)\right\rangle\end{aligned} \tag{8}$$

We used the formalism developed by Palmer et al.[2], where they define the $f_{m,n}$ function :

$$
\begin{aligned}
f_{1,1}(\vec{r}_1,\vec{r}_2,t) &= \langle \delta C(\vec{r}_1,t)\delta C(\vec{r}_2,0)\rangle - \langle \delta C(\vec{r}_1,t)\rangle\langle \delta C(\vec{r}_2,0)\rangle \\
f_{1,2}(\vec{r}_1,\vec{r}_2,\vec{r}_3,t) &= \langle \delta C(\vec{r}_1,t)\delta C(\vec{r}_2,0)\delta C(\vec{r}_3,0)\rangle - \langle \delta C(\vec{r}_1,t)\rangle\langle \delta C(\vec{r}_2,0)\delta C(\vec{r}_3,0)\rangle \\
f_{2,1}(\vec{r}_1,\vec{r}_2,\vec{r}_3,t) &= \langle \delta C(\vec{r}_1,t)\delta C(\vec{r}_2,t)\delta C(\vec{r}_3,0)\rangle - \langle \delta C(\vec{r}_1,t)\delta C(\vec{r}_2,t)\rangle\langle \delta C(\vec{r}_3,0)\rangle \\
f_{2,2}(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4,t) &= \langle \delta C(\vec{r}_1,t)\delta C(\vec{r}_2,t)\delta C(\vec{r}_3,0)\delta C(\vec{r}_4,0)\rangle - \langle \delta C(\vec{r}_1,t)\delta C(\vec{r}_2,t)\rangle\langle \delta C(\vec{r}_3,0)\delta C(\vec{r}_4,0)\rangle
\end{aligned}
\tag{9}
$$

So, we can express ϕ with those functions

$$
\phi(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4,\tau) = f_{2,2}(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4,\tau) + \langle C\rangle \times f_{1,2}(\vec{r}_2,\vec{r}_3,\vec{r}_4,\tau) + \langle C\rangle \times f_{2,1}(\vec{r}_1,\vec{r}_2,\vec{r}_4,\tau) + \langle C\rangle^2 f_{1,1}(\vec{r}_2,\vec{r}_4,\tau)
\tag{10}
$$

By using the solution[2] for the $f_{m,n}$, we find that

$$
\phi(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4,\tau) = \phi_A + \phi_B + \phi_C + \phi_D + \phi_E + \phi_F
\tag{11}
$$

$$\phi_A = \frac{\langle C \rangle^3}{4\pi D\tau} \mathrm{Exp}\left[-\frac{\left(\vec{r}_2 - \vec{r}_4 + V\tau\vec{e}_y\right)^2}{4D\tau} \right]$$

$$\phi_B = \frac{\langle C \rangle^2 \delta(\vec{r}_2 - \vec{r}_4)}{4\pi D\tau} \mathrm{Exp}\left[-\frac{\left(\vec{r}_1 - \vec{r}_2 + V\tau\vec{e}_y\right)^2}{4D\tau} \right]$$

$$\phi_C = \frac{\langle C \rangle^2 \delta(\vec{r}_3 - \vec{r}_4)}{4\pi D\tau} \mathrm{Exp}\left[-\frac{\left(\vec{r}_3 - \vec{r}_2 + V\tau\vec{e}_y\right)^2}{4D\tau} \right]$$

$$\phi_D = \frac{\langle C \rangle \delta(\vec{r}_1 - \vec{r}_2)\delta(\vec{r}_3 - \vec{r}_4)}{4\pi D\tau} \mathrm{Exp}\left[-\frac{\left(\vec{r}_1 - \vec{r}_3 + V\tau\vec{e}_y\right)^2}{4D\tau} \right] \tag{12}$$

$$\phi_E = \frac{\langle C \rangle^2}{\left(4\pi D\tau\right)^2} \mathrm{Exp}\left[-\frac{\left(\vec{r}_1 - \vec{r}_3 + V\tau\vec{e}_y\right)^2}{4D\tau} \right] \times \mathrm{Exp}\left[-\frac{\left(\vec{r}_2 - \vec{r}_4 + V\tau\vec{e}_y\right)^2}{4D\tau} \right]$$

$$\phi_F = \frac{\langle C \rangle^2}{\left(4\pi D\tau\right)^2} \mathrm{Exp}\left[-\frac{\left(\vec{r}_1 - \vec{r}_4 + V\tau\vec{e}_y\right)^2}{4D\tau} \right] \times \mathrm{Exp}\left[-\frac{\left(\vec{r}_2 - \vec{r}_3 + V\tau\vec{e}_y\right)^2}{4D\tau} \right]$$

The numerator in equation (6) can be re-written as

$$\left\langle \delta I_{SHG}(\tau)\delta I_{SHG}(0) \right\rangle = 4\left|\beta^{(2)}\right|^4 \int\int\int\int \left(\phi_A + \phi_B + \phi_C + \phi_D + \phi_E + \phi_F\right) \prod_{i=1}^{4} I(\vec{r}_i)\, d\vec{r}_i \tag{13}$$

If we define

$$G_A = \frac{4K^2 \left|\beta_L\right|^4 \int\int\int\int \left(\phi_A\right) \prod_{i=1}^{4} w(\vec{r}_i) d\vec{r}_i}{\left\langle I_{SHG}(t)\right\rangle^2}$$

$$G_B = \frac{4K^2 \left|\beta_L\right|^4 \int\int\int\int \left(\phi_B\right) \prod_{i=1}^{4} w(\vec{r}_i) d\vec{r}_i}{\left\langle I_{SHG}(t)\right\rangle^2} \tag{14}$$

...

$$G_F = \frac{4K^2 \left|\beta_L\right|^4 \int\int\int\int \left(\phi_F\right) \prod_{i=1}^{4} w(\vec{r}_i) d\vec{r}_i}{\left\langle I_{SHG}(t)\right\rangle^2}$$

Then the SHG autocorrelation function can now be expressed as

$$G_{SHG}(\tau) = 1 + G_A + G_B + G_C + G_D + G_E + G_F \tag{15}$$

We define the following characteristic quantity: firstly, the diffusion time

$$\tau_D = \frac{r_0^2}{4D} \tag{16}$$

where D is the diffusion coefficient of the specie. Secondly, the flow time

$$\tau_f = \frac{r_0}{V} \tag{17}$$

and finally the characteristic size of the beam

$$S_{eff} = \pi \times r_0^2 \tag{18}$$

We also define N as the number of aggregates in the spot size

$$N = \langle C \rangle \times S_{eff} \tag{19}$$

The final calculation gives the following expression for the autocorrelation function:

$$G_{SHG}(\tau)=1+\frac{4\times e^{-\left(\frac{\tau}{\tau_f}\right)^2\frac{1}{\left(1+\frac{\tau}{\tau_D}\right)}}}{N\times\left(1+\frac{\tau}{\tau_D}\right)}+\frac{8\times e^{-2\left(\frac{\tau}{\tau_f}\right)^2\frac{1}{\left(1+\frac{\tau}{\tau_D}\right)}}}{N^2\left(1+\frac{\tau}{\tau_D}\right)^2}+\frac{8\times e^{-2\left(\frac{\tau}{\tau_f}\right)^2\frac{1}{\left(1+2\frac{\tau}{\tau_f}\right)}}}{N^3\left(1+2\frac{\tau}{\tau_D}\right)}+\frac{32\times e^{-\frac{4}{3}\left(\frac{\tau}{\tau_f}\right)^2\frac{1}{\left(1+\frac{4}{3}\frac{\tau}{\tau_f}\right)}}}{3N^2\times\left(1+\frac{4\tau}{3\tau_D}\right)} \quad (20)$$

Extracted parameters

The three parameters N, τ_D and τ_F have been extracted from the autocorrelation traces by a fit procedure using equation (Eq. 20). Table 1 presents the values of theses parameters for the experiment performed on a DiA film formed at the air-water interface using chloroform as solvent for DiA. Table 2 presents the same parameters when methanol was used as solvent for the DiA solution.

Table 1: N, τ_D and τ_F values obtained from the adjustment of the experimental SHG autocorrelation traces (chloroform was used as solvent for DiA solution)

Molecular Area [Å^2] when the stop was performed	Surface pressure [mN/m]	N	τ_D [s]	τ_f [s]
102	5	0.93	0.21	0.22
85	10	1.51	0.34	0.24
73	15	1.4	0.62	0.48
56	25	3	0.14	10
47	30	3.8	0.35	10
41	35	3.6	0.53	10
35	40	4.5	1.1	10
30	43	5.8	2.5	10

Table 2 : Value for the parameters N, τ_D and τ_f obtained by the adjustement of the experimental autocorrelation traces (methanol was used as solvent for DiA solution)

Molecular Area [Å^2] when the stop was performed	Surface pressure [mN/m]	N	τ_D [s]	τ_f [s]
50	0	10	600	39
35	10	20	3000	80
25	25	5000	100	500

REFERENCES

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