Derivation of the mathematical model

1 Two-dimensional Van der Waals equation of state

To derive the relation between the number of cis isomers and the change in surface pressure we used the two-dimensional Van der Waals equation of state\(^1\):

\[
(\Pi + A)(S - B) = N_0 k_B T. \tag{1}
\]

Here, \(\Pi\) is the surface pressure in the film, \(S\) is the total surface of the film, \(N_0\) is the total number of molecules in the film, \(k_B\) is the Boltzmann constant, and \(T\) is the temperature of the system. The \(A\) and \(B\) terms account for the interactions between molecules and the finite size of the molecules, respectively.

Isolating \(\Pi\) from Eq. 1, we get:

\[
\Pi(t) = \frac{N_0 k_B T}{S - B(t)} - A(t). \tag{2}
\]

We explicitly marked the terms that are non-constant in our system as functions of time.

2 Interactions between molecules — A(t)

Assuming strictly pairwise interactions, the value of \(A\) must be proportional to the number of possible interactions between molecules. Since molecules in a dense film are constrained, we will only consider nearest neighbor interactions. The number of interactions between two molecules is proportional to the number of molecules of one type \((N_{c,t,r})\) times the probability that its neighbor is a molecule of the other type. Both values are proportional to the relative concentrations of molecules of the respective type in the film: \(x_{c,t,r} = N_{c,t,r}/N_0\). We now introduce proportionality constants which describe the strength of the interactions between molecules in our system: \(a_{cc}, a_{ct}, a_{tt}, a_{cr}, a_{tr}, a_{rr}\). Each of the two indices denotes one type of the molecule in a pair: index \(c\) stands for cis isomers of the photoactive molecules, index \(t\) for trans isomers, and index \(r\) for non-photoactive (regular molecules). The general form for \(A\) can then be written as:
\[ A = x_c^2 a_{cc} + 2x_c x_t a_{ct} + x_t^2 a_{tt} + 2x_c x_r a_{cr} + 2x_t x_r a_{tr} + x_r^2 a_{rr}. \]  

Furthermore, we introduce two more parameters \( n \) and \( m \) defined so that the total number of photoactive molecules is \( nN_0 \) and the number of photoactive molecules that are in the \textit{cis} state is \( N_c = mnN_0 \). With these parameters we can rewrite Eq. 3 as:

\[
A(m, n) = m^2n^2 a_{cc} + 2m(1-m)n^2 a_{ct} + (1-m)^2n^2 a_{tt} + 2mn(1-n)a_{cr} + 2(1-m)n(1-n)a_{tr} + (1-n)^2 a_{rr}
\]  

The change in \( \Pi \) due to the change in \( A \) is equal to:

\[
\Delta \Pi_A(m, n) = A(m, n) - A(0, n) =
\]

\[
= n^2[m^2 a_{cc} + 2m(1-m)a_{ct} + (1-m)^2 a_{tt} - a_{tt}] +
\]

\[
+ [2mn(1-n)a_{cr} + 2(1-m)n(1-n)a_{tr} - 2n(1-n)a_{tr}] =
\]

\[
= (n^2 m^2 a_{cc} + 2n^2 m(1-m)a_{ct} + n^2 m(1-n)a_{tt} - 2mn(1-n)[a_{cr} - a_{tr}])
\]

Factoring out \( m \) we get a quadratic expression:

\[
\Delta \Pi_A(t) = n^2 m^2(t)(a_{cc} - 2a_{ct} + a_{tt}) + nm(t)[2(1-n)(a_{cr} - a_{tr}) + 2n(a_{ct} - a_{tt})]
\]

If we are only interested in the total change in \( \Pi \) and assume that photostationary state contains predominantly \textit{cis} molecules, we can set \( m = 1 \) and obtain:

\[
\Delta \Pi_{A0}(n) = (a_{cc} - a_{ct})n^2 + 2n(1-n)(a_{cr} - a_{tr}).
\]

Defining two new parameters \( \Delta a_{azo} = a_{cc} - a_{ct} \) and \( \Delta a_r = 2(a_{cr} - a_{tr}) \), we can finally rewrite Eq. 4 as a function of \( n \) with 2 parameters:

\[
\Delta \Pi_{A0}(n) = (\Delta a_{azo} - \Delta a_r)n^2 + \Delta a_r n.
\]

3 Finite size of the molecules — \( B(t) \)

We now move on to parameter \( B \) from the Van der Waals equation (Eq. 2). Since the value of \( B \) represents the excluded area, it must be proportional to the number of molecules in our system, which includes \( N_c \) \textit{cis} photoactive molecules, \( N_t \) \textit{trans} photoactive molecules, and \( N_r \) non-photoactive (regular) molecules. The total number of molecules \( N_0 = N_c + N_t + N_r \) remains constant in all the experiments.
described in our paper. If we ascribe each type of molecule its own proportionality constant — \(b_c\), \(b_t\), and \(b_r\) — we can write:

\[
B = N_c b_c + N_t b_t + N_r b_r. \tag{11}
\]

Rewriting this equation with parameters \(m\), \(n\), and \(N_0\), we get:

\[
B(m,n) = N_0[nmb_c + n(1-m)b_t + (1-n)b_r]. \tag{12}
\]

The corresponding change of \(\Pi\) as a function of \(m\) is:

\[
\Delta \Pi_B(m,n) = N_0 k_B T \frac{(b_c - b_t) n N_0}{S - B(m,n)} - \frac{N_0 k_B T}{S - B(0,n)}. \tag{13}
\]

Again, if we are only interested in the total change in \(\Pi\) and assume that photostationary state contains predominantly \(cis\) molecules, i.e. \(m = 1\), we can insert the expressions for \(B(1,n)\) and \(B(0,n)\) from Eq. 12 into Eq. 13 and obtain:

\[
\Delta \Pi_{B,0}(n) = N_0 k_B T \frac{(b_c - b_t) n N_0}{S - (1-n)N_0 b_r - n N_0 b_c} \frac{1}{S - (1-n)N_0 b_r - n N_0 b_t}. \tag{14}
\]

Multiplying and dividing this expression by \(S^2\) gives

\[
\Delta \Pi_{B,0}(n) = \frac{k_B T}{s} \frac{n(\hat{b}_c - \hat{b}_t)}{1 - (1-n)\hat{b}_r - n\hat{b}_c} \frac{1}{1 - (1-n)\hat{b}_r - n\hat{b}_t}, \tag{15}
\]

with \(\hat{b}_{c,t,r} = b_{c,t,r} / s\) and \(s = S / N_0\) being the mean surface area available to a molecule in the film. In the numerator, we have the difference in size between \(cis\) and \(trans\) isomers (in units of \(s\)), while in the denominator we have the product of “free area” before and after irradiation, where “free area” is the difference between mean molecular area and the average effective size of the molecules in the film.

4 Total change in surface pressure — \(\Delta \Pi\)

We can now combine the two contributions from equations 10 and 15 and write the total change in surface pressure:

\[
\Delta \Pi_0(n) = \Delta \Pi_{B,0}(n) - \Delta \Pi_{A,0}(n) = \frac{k_B T}{s} \frac{n(\hat{b}_c - \hat{b}_t)}{1 - (1-n)\hat{b}_r - n\hat{b}_c} \frac{1}{1 - (1-n)\hat{b}_r - n\hat{b}_t} - \Delta a_r n + (\Delta a_r - \Delta a_{azo}) n^2. \tag{16}
\]

For \(n = 1\), i.e. a film composed solely of photoactive molecules, we get:
\[ \Delta \Pi_0(1) = \frac{k_B T}{s} \frac{\hat{b}_c - \hat{b}_t}{(1 - \hat{b}_c)(1 - \hat{b}_t)} - \Delta a_{azo}. \]  

(17)

In other words: the change in surface pressure is proportional to the change in size of the molecules (the term in the numerator) and the effect is enhanced if the film is highly compressed — the first term diverges when either \( \hat{b}_c \) or \( \hat{b}_t \) reaches 1. The second term simply states that an increase in the strength of attractive interactions between molecules leads to a decrease in surface pressure.

Because \( m \), and consequently \( B(m) \), are relatively complicated functions of time, we will describe the time dependence of \( \Pi_B \) during irradiation by using a linear approximation of Eq. 13:

\[ \Delta \Pi_B(m, n) \equiv \left. \frac{d\Pi}{dB} \right|_{B(0, n)} [B(m, n) - B(0, n)] = \frac{k_B T}{(S - N_0 nb_t + (1 - n)b_r))^2} N_0 nm(b_c - b_t). \]  

(18)

This approximation is only valid for small changes in \( B \): in our experiments, the total change in \( \Pi \) is no more than 10%. We can once again use hatted variables by dividing by \( S^2 \) in both the numerator and denominator, which gives us the final expression:

\[ \Delta \Pi_B(t) \equiv \frac{k_B T}{S} \frac{n(\hat{b}_c - \hat{b}_t)}{(1 - nb_t - (1 - n)\hat{b}_r)^2} m(t). \]  

(19)

The full expression of the time dependence of \( \Delta \Pi \) during irradiation is the sum of contributions from \( \Delta \Pi_A \) and \( \Delta \Pi_B \):

\[ \Delta \Pi(t) = \Delta \Pi_B(t) - \Delta \Pi_A(t). \]  

(20)

Inserting the values of the terms on the right-hand side from equations 19 and 8 we obtain:

\[ \Delta \Pi(t) = \left[ \frac{k_B T (\hat{b}_c - \hat{b}_t)}{S(1 - n\hat{b}_t - (1 - n)\hat{b}_r)^2} - \Delta a_r(1 - n) - n(a_{ct} - a_{tt}) \right] nm(t) - [(a_{cc} - 2a_{ct} + a_{tt})] n^2 m^2(t). \]  

(21)

Values of \( \hat{b}_r \) and \( \Delta a_r \) are specific for each type of non-photoactive surfactant in the film, while the values of \( \hat{b}_t, \hat{b}_c, \) and \( \Delta a_{azo} \) are the same for all films.

For the purpose of fitting the data from our experiment, Eq. 21 can be written simply as

\[ \Delta \Pi(t) = c_1 m(t) - c_2 m^2(t), \]  

(22)
where \( c_1 \) and \( c_2 \) are some constants with units of \( \Pi \) and \( m(t) \) some function with values between 0 and 1.

5 Number of *cis* molecules over time — \( m(t) \)

If absorbance of the irradiated molecules is well below 1, and the rate of reverse isomerisation is much smaller than the rate of isomerisation, the time dependence of the surface number density of *trans* isomers in the film (\( \nu \)) is described by a first order differential equation with kinetic constant \( \kappa \):

\[
\frac{d \nu(x, y, t)}{dt} = -\kappa(x, y) \nu(x, y, t). \tag{23}
\]

In the case of our experimental conditions, the upper limit for absorbance of a pure GAzo film for any wavelength can be calculated to be approximately \( 7 \times 10^{-2} \). Mixed films have lower densities of photoactive molecules, so we can expect them to have lower absorbance values than the pure GAzo, therefore absorbance is indeed much smaller than 1 in all cases.

The solution to Eq. 23 is an exponential function, also known as the Beer-Lambert law:

\[
\nu(x, y, t) = \frac{nN_0}{S} \exp[-\kappa(x, y)t]. \tag{24}
\]

The product \( nN_0 \) is the total number of photoactive molecules in the film and \( S \) is total surface area of the film, making \( N_0/S \) the surface number density of photoactive molecules, which we assume to be constant across the film.

This derivation assumed one point light source at the origin — since our experiment includes multiple LED sources, Eq. 24 must be corrected to include a separate kinetic constant for each of them.

\[
\nu(x, y, t) = \frac{nN_0}{S} \exp \left[ \sum_i -\kappa(x - x_i, y - y_i) t \right] \tag{25}
\]

The point light sources in this model are positioned at points \((x_i, y_i, 0)\) and the film is at height \( h \) below them (see Figure 1).
To arrive at the expression for the number of trans molecules in the whole film \( N_t \), we must integrate \( \nu(x, y, t)dx\,dy \) from Eq. 25 over the entire surface of the film.

\[
N_t(t) = \frac{d}{S} - nN_0 \exp \left[ \sum_i -\kappa(x - x_i, y - y_i) t \right]
\]

Using \( N_c = N_0 - N_t \), we can also write the expression for the number of cis isomers over time:

\[
N_c(t) = nN_0 \left( 1 - \frac{d}{S} \exp \left[ \sum_i -\kappa(x - x_i, y - y_i) t \right] \right).
\]

Finally, since \( N_c = mnN_0 \), we obtain the expression for \( m(t) \):

\[
m(t) = 1 - \frac{d}{S} \exp \left[ \sum_i -\kappa(x - x_i, y - y_i) t \right].
\]

6.1 Kinetic constant — \( \kappa(x, y) \)

Because the film is not homogenously irradiated, both intensity and polarization of light vary across the film. Therefore, \( \kappa \) is a function of the position on the film and can be expressed as:

\[
\kappa(x, y) = \Phi \ln 10 I(x, y) 3\epsilon \cos^2 \gamma(x, y).
\]

We used \( \epsilon \) to mark the value of molar absorptivity of the photoactive molecules as measured in solution, \( \Phi \) is the quantum yield for trans-cis transition, \( I \) is the intensity of actinic light, and \( \gamma \) is the angle between the polarization of light and the dipole moment of the azobenzene moiety. The value of \( \epsilon \) has to be corrected with a factor of \( 3 \cos^2[\gamma(x, y)] \) because the molecules in a compressed film have a preferential direction, as opposed to the molecules in a solution, where their orientation is isotropic: this is shown below.

6.1 Intensity of light — \( I(x, y) \)

We set up our coordinate system so that the LED is at the origin and the film lies at height \( h \) below the LED and is perpendicular to the \( z \)-axis (see Figure 1). Note that the coordinate system is upside down — this is done so that angles \( \vartheta \) have values between 0 and \( \pi/2 \). The direction of the molecular dipole moment is described by angles \( \alpha \) and \( \beta \).
The angular distribution of intensity radiated by each of the LED sources used in the experiment is well approximated by the function:

\[ I(\varphi, \theta) = \frac{dP(\varphi, \theta)}{d\Omega} = P_0 \frac{3}{2\pi} \cos^2 \theta, \]  

(30)

where \( \varphi \) and \( \theta \) are the polar and azimuthal angles, and \( P_0 \) is the total radiative power of the LED.

If the LED is positioned at height \( h \) above the film, the distribution of intensity over the film surface can be expressed as:

\[ \frac{dP(\rho, \varphi)}{dS} = \frac{dP(\varphi, \theta)}{d\Omega} \frac{d\Omega}{dS} = \frac{dP(\varphi, \theta)}{d\Omega} \frac{d\varphi}{d\rho} \frac{d\rho}{dS} = \frac{dP(\varphi, \theta)}{d\Omega} \frac{d\varphi}{d\rho} \frac{d\rho}{dS} \frac{dS}{d\varphi} = \frac{dP(\varphi, \theta)}{d\Omega} \frac{d\varphi}{d\rho} \frac{d\rho}{dS} \frac{dS}{d\varphi} = P_0 \frac{3}{2\pi h^2} \cos^2 \theta. \]  

(31)

Here, \( \rho = \sqrt{x^2 + y^2} \). In the second-to-last step, we used the relation \( \rho = h \tan \theta \), which follows from the geometry of the problem (see Figure 1), and the result from Eq. 30.

Since we will be integrating over a rectangular film surface, it is more practical to write the result from Eq. 31 in Cartesian coordinates:

\[ I(x, y) = P_0 \frac{3}{2\pi h^2} \left( \frac{h}{\sqrt{x^2 + y^2 + h^2}} \right)^5. \]  

(32)

6.2 Polarisation of light — 3ε

The probability for absorption of a photon is proportional to cosine squared of the angle between the polarization of light and the molecular dipole moment of the azobenzene moiety.
\[ \varepsilon = \varepsilon_\parallel \cos^2 \gamma. \] (33)

Here, \( \varepsilon_\parallel \) is the molar absorptivity for molecules whose dipole moment is aligned with the polarisation of light.

When measuring molar absorptivity in a solution, the value obtained is averaged over all angles \( \gamma \), since the directions of the molecular dipole moments \( \vec{d} \) are distributed evenly over all solid angles:

\[ \varepsilon_{sol} = \varepsilon_\parallel \langle \cos^2 \gamma \rangle = \varepsilon_\parallel \langle \vec{d} \cdot \vec{p} \rangle. \] (34)

The angled brackets indicate averaging, while the vectors \( \vec{d} \) and \( \vec{p} \) are normalised vectors describing the direction of the molecular dipole moment and polarization of light, respectively.

In contrast, the molecules in a compressed film at the air-water interface usually have a preferential orientation; if we are to use the values of \( \varepsilon_{sol} \) to describe the absorbance in the film, we must therefore first extract \( \varepsilon_\parallel \).

If the incident light is traveling along the \( z \)-axis, the two vectors \( \vec{d} \) and \( \vec{p} \) can be written out as (see Figure 2):

\[ \vec{p} = (\cos \delta, \sin \delta, 0), \] (35)
\[ \vec{d} = (\cos \tilde{\alpha} \sin \tilde{\beta}, \sin \tilde{\alpha} \sin \tilde{\beta}, \cos \tilde{\beta}). \] (36)

The tilde is used to distinguish \( \tilde{\alpha} \) and \( \tilde{\beta} \) from the \( \alpha \) and \( \beta \) angles describing the orientation of the dipole moment in the laboratory coordinate system.

![Figure 2. Illustration of a coordinate system where light from the source (marked with a white circle) travels along the z-axis.](image-url)
In a typical absorbance measurement, the light incident on the solution is unpolarised, so the averaging indicated in Eq. 34 must be done over all angles $\delta$, as well as $\tilde{\alpha}$ and $\tilde{\beta}$.

$$\varepsilon_{\text{sol}} = \varepsilon_{\parallel}(\hat{d} \cdot \hat{p}) = \varepsilon_{\parallel} \int (\cos \tilde{\alpha} \sin \tilde{\beta} \cos \delta + \sin \tilde{\alpha} \sin \tilde{\beta} \sin \delta)^2 \frac{d\delta}{2\pi} \frac{\sin \tilde{\beta} d\tilde{\alpha} d\tilde{\beta}}{4\pi}.$$ (37)

Factoring out $\sin^3 \tilde{\beta}$ we get:

$$\varepsilon_{\text{sol}} = \varepsilon_{\parallel} \int_0^\pi \sin^3 \tilde{\beta} d\tilde{\beta} \int_0^{2\pi} \frac{d\delta}{2\pi} \int_0^{2\pi} \frac{d\tilde{\alpha}}{4\pi} (\cos \tilde{\alpha} \cos \delta + \sin \tilde{\alpha} \sin \delta)^2 .$$ (38)

The first integral evaluates to $4/3$, while the squared expression can be rewritten as a cosine of the difference of angles.

$$\varepsilon_{\text{sol}} = \frac{4\varepsilon_{\parallel}}{3} \int_0^{2\pi} \frac{d\delta}{2\pi} \int_0^{2\pi} \frac{d\tilde{\alpha}}{4\pi} \cos^2(\tilde{\alpha} - \delta) \frac{d\tilde{\alpha}}{4\pi}$$ (39)

Introducing a new variable $u = \tilde{\alpha} - \delta$, it becomes obvious that the value of the integral is $1/2$, which gives us the final result

$$\varepsilon_{\text{sol}} = \frac{2\varepsilon_{\parallel}}{3} \int_0^{2\pi} \frac{d\delta}{2\pi} \int_{-\delta}^{2\pi-\delta} \cos^2(u) \frac{du}{2\pi} = \frac{\varepsilon_{\parallel}}{3},$$ (40)

which is the correction factor from Eq. 29.

6.3 Polarisation of light — $\cos^2 \gamma(x, y)$

The light in our experiment is unpolarised, just as in the case of the absorption measurement, the molecules, however, are not oriented isotropically. We will now repeat the same calculation, with the assumption that all molecular dipole moments are pointing in the same direction. In this case, averaging is only necessary over the angles $\delta$.

$$\langle \cos^2(\gamma) \rangle = \int_0^{2\pi} (\hat{d} \cdot \hat{p})^2 \frac{d\delta}{2\pi} = \int_0^{2\pi} (\cos \delta \cos \tilde{\alpha} \sin \tilde{\beta} + \sin \delta \sin \tilde{\alpha} \sin \tilde{\beta})^2 \frac{d\delta}{2\pi} =$$ (41)

$$= \sin^2 \tilde{\beta} \int_0^{2\pi} (\cos \delta \cos \tilde{\alpha} + \sin \delta \sin \tilde{\alpha})^2 \frac{d\delta}{2\pi}$$ (42)

From the previous calculation (Eq. 38), we know that integral in the second line evaluates to $1/2$, while $\sin^2 \tilde{\beta}$ can be written as $1 - \cos^2 \tilde{\beta}$:
\[
\frac{1}{2} (1 - \cos^2 \beta) = \frac{1}{2} \left[ 1 - \left( \frac{\vec{d} \cdot \vec{r}}{|\vec{r}|} \right)^2 \right]. \tag{43}
\]

The result in line 43 is expressed independently of a coordinate system and can therefore be used in the laboratory system as well, where vectors \( \vec{d} \) and \( \vec{r} \) can be written as:

\[
\vec{d} = (\cos \alpha \sin \beta, \sin \alpha \sin \beta, \cos \beta) \tag{44}
\]

and

\[
\vec{r} = (x, y, h). \tag{45}
\]

Written out explicitly, the result from Eq. 43 is:

\[
\langle \cos^2 (\gamma) \rangle = \frac{1}{2} \left[ 1 - \left( \frac{x \cos \alpha \sin \beta + y \sin \alpha \sin \beta + h \cos \beta}{\sqrt{x^2 + y^2 + h^2}} \right)^2 \right]. \tag{46}
\]

We can now insert the results for \( I(x, y) \) (Eq. 32) and \( \langle \cos^2 (\gamma) \rangle \) (Eq. 46) into the expression for \( \kappa(x, y) \) from Eq. 29:

\[
\kappa(x, y) = \Phi \kappa_0 f(x, y, \alpha, \beta). \tag{47}
\]

We defined the constant \( \kappa_0 \) as,

\[
\kappa_0 = \frac{9P_0 \varepsilon_{\text{sol}} \ln 10}{2\pi h^2} \frac{1}{E_{\gamma} N_A}, \tag{48}
\]

and the dimensionless function \( f(x, y, \alpha, \beta) \):

\[
f(x, y, \alpha, \beta) = \frac{1}{2} \sum_i \frac{h^5}{[(x - x_i)^2 + (y - y_i)^2 + h^2]^{5/2}} \left\{ 1 - \left[ \frac{((x - x_i) \cos \alpha + (y - y_i) \sin \alpha) \sin \beta + h \cos \beta}{(x - x_i)^2 + (y - y_i)^2 + h^2} \right]^2 \right\}. \tag{49}
\]

The value of \( \kappa_0 \) can easily be calculated from the known total power of the LEDs and measured molar absorptivity of the molecules in the film. The factor \( 1/E_{\gamma} N_A \) (\( E_{\gamma} \) is the energy of an incident photon, \( N_A \) is Avogadro’s constant) is added so that quantum yield is expressed as “the probability for a molecule to change conformation per absorbed photon” instead of “moles of molecules that change conformation per unit of absorbed energy”.

7 Final equation and \( f(x, y) \)

The results from Eq. 48 can now be inserted into the expression for \( m(t) \) from Eq. 28:
\[ m(t) = 1 - \int \frac{dx dy}{S} \exp[-\Phi k_0 f(x,y,\alpha,\beta)t]. \] (50)

In the general case, angles \( \alpha \) and \( \beta \) are distributed according to some distribution function \( \chi \), which can itself be a function of coordinates \( x \) and \( y \): \( \chi(x,y,\alpha,\beta) \).

\[ m(t) = 1 - \int \frac{dx dy}{S} \int \chi(x,y,\alpha,\beta) \exp[-\Phi k_0 f(x,y,\alpha,\beta)t] \, d\alpha \, d(cos \beta) \] (51)

Here, we will consider just the simple limiting case where all the molecules are oriented in the same direction; this means that \( \chi(x,y,\alpha,\beta) = \delta(\alpha - \alpha_0) \delta(cos \beta - cos \beta_0) \), where \( \delta(x) \) is the Dirac delta function, and the integration over all angles gives the original expression for \( m(t) \) from Eq. 50.

For convenience, we introduce two dimensionless variables \( \hat{x}_i = (x - x_i)/h \) and \( \hat{y}_i = (y - y_i)/h \); with these variables, function \( f(x,y,\alpha,\beta) \) is written as:

\[
f(x,y,\alpha,\beta) = \frac{1}{2} \sum_i \frac{1}{[1 + \hat{x}_i^2 + \hat{y}_i^2]^{s/2}} \left\{ 1 - \frac{[(\hat{x}_i \cos \alpha + \hat{y}_i \sin \alpha) \sin \beta + \cos \beta]^2}{1 + \hat{x}_i^2 + \hat{y}_i^2} \right\}. \] (52)

8 Initial rate of change of surface pressure — \( d\Pi(t)/dt \)|t=0

The rate of change of \( \Pi(t) \) at the start of irradiation is described by the time derivative of \( \Pi(t) \):

\[
\frac{d \Delta \Pi(t)}{dt} \bigg|_{t=0} = \frac{d}{dt} \Delta \Pi_B(t) \bigg|_{t=0} - \frac{d}{dt} \Delta \Pi_A(t) \bigg|_{t=0}. \] (53)

We will again tackle each term separately. The time derivative of the first term is:

\[
\frac{d}{dt} \Delta \Pi_B(t) \bigg|_{t=0} = \frac{N_0 k_B T}{[S - B(t = 0)]^2} \frac{d}{dt} B(t) = \frac{N_0^2 k_B T}{[S - B(t = 0)]^2} \frac{d}{dt} (nm(t)b_c + n(1 - m(t))b_t + (1 - n)b_r) \bigg|_{t=0}. \] (54)

We arrived at the expression on the right hand side by inserting the expression for \( B \) from Eq. 12.

Using the expression for \( m(t) \) from Eq. 50, the time derivative of \( m(t) \) is:

\[
\frac{d}{dt} m(t) \bigg|_{t=0} = \frac{d}{dt} \left\{ 1 - \int \frac{dx dy}{S} \exp[-\Phi k_0 f(x,y)t] \right\} = \] (55)

\[
\int \frac{dx dy}{S} \frac{d}{dt} \left\{ -\exp[-\Phi k_0 f(x,y)t] \right\} \bigg|_{t=0} = \] (56)

\[
\int \frac{dx dy}{S} \Phi k_0 f(x,y) \exp[-\Phi k_0 f(x,y)t] \bigg|_{t=0} = \] (57)

\[
\Phi k_0 \int \frac{dx dy}{S} f(x,y). \] (58)
Using the expression for the function \( f(x,y) \) from Eq. 52, we can see that it can only have values between 0 and 2: the factor \( [1 + \hat{x}_i^2 + \hat{y}_i^2]^{-5/2} \) clearly has values between 0 and 1, while the rest was the result of averaging of a \( \cos^2 \gamma \) function (Eq. 46), which is also constrained between 0 and 1. In our case, we have 4 light sources so the value of any \( f(x,y) \) function is between 0 and 2. The integral in Eq. 58 represents the average value of \( f(x,y) \) across the entire surface of the film so that is constrained between 0 and 2 as well. We will therefore replace the integral with some unknown constant \( \sigma \) whose values lie between 0 and the half the number of light sources.

\[
\frac{d}{dt} \left. m(t) \right|_{t=0} = \Phi \kappa_0 \sigma \quad (59)
\]

With this result, we can simplify the expression from Eq. 54 and obtain the final expression:

\[
\frac{d \Delta \Pi_B(t)}{dt} \bigg|_{t=0} = \frac{N_B^2 k_B T}{[S - B(t = 0)]^2} \Phi \kappa_0 \sigma (b_c - b_t)n = \frac{s\Pi_{B,0}^2}{k_B T} \Phi \kappa_0 \sigma (\hat{b}_c - \hat{b}_t)n. \quad (60)
\]

In the last step we used \( \Pi_{B,0} = N_0 k_B T/[S - B(0)] \) and the definition of hatted variables: \( \hat{b}_{c,r,t} = s^{-1} b_{c,r,t} \).

The expression for \( A(t) \) (Eq. 4), and consequently \( \Delta \Pi_A(t) \), includes both \( m(t) \) and \( m^2(t) \) terms. The time derivative of \( m^2(t) \) is equal to 0 because \( m(t = 0) = 0 \):

\[
\frac{dm^2(t)}{dt} \bigg|_{t=0} = 2m(t = 0) \frac{dm(t)}{dt} = 0. \quad (61)
\]

Using the expression from Eq. 8 and omitting the \( m^2(t) \) term, since its time derivative is 0, we can write:

\[
\frac{dA(t)}{dt} \bigg|_{t=0} = 2n[(1 - n)(a_{cr} - a_{tr}) + n(a_{ct} - a_{tt})] \frac{dm(t)}{dt} \bigg|_{t=0}. \quad (62)
\]

We can simplify this expression by using the previously defined \( \Delta a_r = 2(a_{cr} - a_{tr}) \) and introducing a new variable: \( \Delta \hat{a}_{azo} = 2(a_{ct} - a_{tt}) \). Inserting the value of the derivative \( dm(t)/dt \) from Eq. 59 we can write:
\[
\frac{dA(t)}{dt}\bigg|_{t=0} = [n\Delta a_r - n^2(\Delta a_r - \Delta a_{azo})]\Phi \kappa_0 \sigma. \quad (63)
\]

Bringing the results from equations 60 and 63 together we get:

\[
\frac{d\Delta \Pi(t)}{dt}\bigg|_{t=0} = \left\{\left[\frac{s \Pi_{B,0}}{k_B T} (\tilde{b}_c - \tilde{b}_t) - \Delta a_r \right] n + (\Delta a_r - \Delta a_{azo})n^2\right\}\Phi \kappa_0 \sigma. \quad (64)
\]

9 Comment on two additional assumptions

Two implicit assumptions were made during this derivation. First, we neglect the diffusion of molecules in the film. In order for diffusion to be important in our model, the molecules would have to travel far enough that the difference in \(\kappa\) is appreciable. By using \(10^{-7}\text{cm}^2\text{s}^{-1}\) as an estimate for the diffusion constant\(^3\), we can estimate the average distance travelled by a molecule to be 0.5 mm. At this distance, the relative change in \(f(x,y)\) can be at most 6\% for our setup.

Second: when a molecule switches from \textit{trans} to \textit{cis} conformation, the new shape of the molecule has to reorient itself into a new energetically favourable position\(^4,5\) — for the purposes of this derivation, this process is assumed to be much faster than the rate of isomerisation and is therefore neglected.

10 References

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