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Photo-driven directional motion of droplets on the surface of a liquid crystal doped with photochromic azobenzene: theory

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Abstract

Recently, photo-driven directional motion of glycerol droplets on the surface of a liquid crystal doped with photochromic azobenzene derivatives has been reported. We present a theoretical model for this phenomenon. The motion of droplets is induced by a gradient in surface tension, which is produced by the combined effect of photo-isomerization and diffusion of surface azobenzenes. The theoretical relation between the surface tension and the surface concentration of *cis* isomers is proposed. The experimentally observed depletion zone of droplets can be reasonably well explained in terms of diffusion of droplets in the presence of the gradient in the surface tension.

1. Introduction

Directional motion of liquid droplets on surfaces induced by a spatial gradient in the surface free energy has been observed [1–7]. The gradient in the surface energy was induced by a diffusion-controlled process, electrochemical reactions, desorption and photochemical reactions. Most of the observations have been made on solid surfaces. For example, photo-driven directional motion of liquids has been found on a photo-responsive solid surface [4, 5]. Very recently, photo-driven directional motion of droplets on the surface of a liquid crystal doped with photochromic azobenzene derivatives has been reported [6, 7]. The directional motion of droplets is induced by a gradient in surface tension, which is produced by the photo-isomerization of surface azobenzenes. Photo-irradiation with ultraviolet (UV) light results in transformation of *trans* isomers into *cis* isomers. Photo-irradiation of *cis* isomer with visible light leads to the reverse transformation into the *trans* isomer. Ichimura *et al* observed spreading and dewetting of droplets put on a substrate surface and found that they are correlated with the concentration of *cis* isomers [4]. The polarity of *cis* isomers is larger than that of the *trans* form; therefore, the surface tension should be decreased when the fraction of *cis* isomers at the interface is increased by irradiation with UV light [4–7]. Nonuniform photo-isomerization of surface azobenzenes induces a gradient in surface tension, leading to directional motion of

a droplet [4–7]. Diffusion of azobenzene molecules modifies the concentration gradient of *cis* isomers, leading to a modification in the surface energy gradient [6, 7]. In other words, the surface energy gradient is produced by the combined effect of photo-isomerization and diffusion of azobenzene molecules. It is observed that droplets move towards the inside of the irradiated region. In the course of this motion the depletion zone of droplets appears at the periphery of the irradiated region [6, 7]. As time passes, the depletion zone of droplets spreads outward, and droplets far from the irradiated region are also gradually attracted into the irradiated region [6, 7]. When the ultraviolet light is turned off and visible light is turned on, the nonuniform distribution of droplets induced by ultraviolet light returns to the uniform distribution by simply decreasing the gradient of the distribution at any place. In this case no depletion zone of droplets appears at the periphery of the irradiated region. In this paper we investigate these phenomena theoretically and compare the results with those found from experiments.

2. Concentration profile of *cis* isomers

A driving force for the directional motion of a glycerol droplet is the surface tension gradient which is created by the concentration gradient of *cis* isomers of azobenzene in the liquid crystal. We first study the concentration profile of *cis* isomers in liquid crystals. The azobenzene doped liquid crystal is locally illuminated with UV light of radius $R = 80 \mu\text{m}$ as depicted in figure 1. The typical intensity of the light is 50 mW cm^{-2} and almost all azobenzene molecules are quickly converted into *cis* isomers. The concentrations of the *cis* form, $f_c(r, t)$, and the *trans* form, $f_t(r, t)$, satisfy

$$\begin{aligned} \frac{\partial}{\partial t} f_c(r, t) &= D_a \nabla^2 f_c(r, t) + k(r) f_t(r, t) + k_t f_i(r, t) - k_c f_c(r, t), \\ \frac{\partial}{\partial t} f_t(r, t) &= D_a \nabla^2 f_t(r, t) - k(r) f_t(r, t) - k_t f_i(r, t) + k_c f_c(r, t), \end{aligned} \quad (1)$$

where the photo-induced *trans* to *cis* isomerization rate is given by $k(r) = k_i$ for $r \leq R$ and 0 for $r > R$. D_a is the diffusion constant of azobenzene molecules in the liquid crystal. We ignore the difference in diffusion constant between *cis* isomers and *trans* isomers. k_c is the thermal isomerization rate constant of the *cis* to *trans* transformation and k_t is the thermal isomerization rate constant of the *trans* to *cis* transformation. It is apparent that the total concentration of azobenzene, $F(r, t) = f_c(r, t) + f_t(r, t)$, is a constant in the steady state, which is denoted by F . In the steady state, the concentration of *cis* isomers is obtained as

$$f_c(r) = \frac{1}{k_c + k_t} g(r) + \frac{k_t}{k_c + k_t} F, \quad (2)$$

where

$$g(r) = \begin{cases} C_1 \frac{\alpha_1 I_1(R\alpha_1)}{\alpha_2 K_1(R\alpha_2)} K_0(r\alpha_2) & \text{for } r > R \\ -C_1 I_0(r\alpha_1) + \frac{k_i k_c}{k_i + k_c + k_t} F & \text{for } r \leq R \end{cases} \quad (3)$$

with

$$C_1 = \frac{k_i k_c F}{k_i + k_c + k_t} \frac{1}{I_0(R\alpha_1) + \frac{\alpha_1 I_1(R\alpha_1)}{\alpha_2 K_1(R\alpha_2)} K_0(R\alpha_2)}$$

and

$$\alpha_1 \equiv \sqrt{\frac{k_i + k_c + k_t}{D_a}}, \quad \alpha_2 \equiv \sqrt{\frac{k_c + k_t}{D_a}}. \quad (4)$$

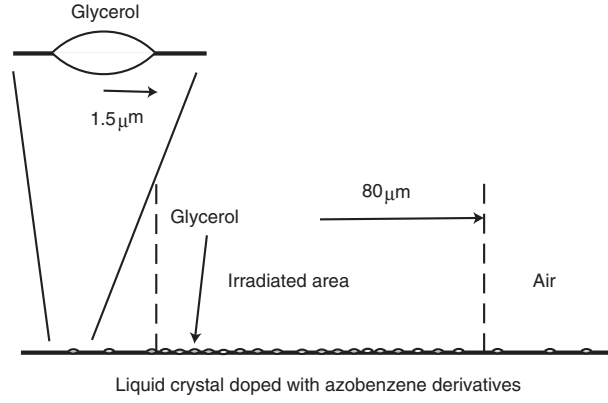


Figure 1. Schematic illustration of the experimental system.

Since the diffusion constant of the azobenzene molecules is much larger than that of the glycerol droplets, the steady state concentration of *cis* isomers is attained in a time much shorter than that needed for glycerol droplets to move distances of the order of few microns. We assume the steady state concentration of *cis* isomers when we analyse the motion of droplets on the surface of the liquid crystal.

3. Constitutive equations for distribution of droplets

In the experiments, the liquid crystal doped with azobenzene was continuously irradiated with the circular beam of UV light (365 nm, 50 mW cm⁻²) and the distribution of glycerol droplets was observed optically. The simplest relation between the interfacial energy and the concentration of *cis* isomers is a linear relation [8, 9]. By denoting the energy of the interface between glycerol and liquid crystal as $\gamma_{G,LC}$, the linear relation is written as

$$\gamma_{G,LC} = f_1^{(0)} f_c(r) + f_2^{(0)}. \quad (5)$$

$f_1^{(0)}$ is negative because the surface tension is lowered as a result of the increase of *cis* isomers. The deformation of liquid crystal due to the presence of a glycerol droplet is isotropic around the centre of the droplet in planes parallel to the surface of the liquid crystal. Orientational anisotropy of the surface tension known as anchoring energy exists in the direction perpendicular to the surface of the liquid crystal. When the concentration of *cis* isomers around the droplet becomes anisotropic after photo-irradiation, the difference in molecular shape between *cis* isomers and *trans* isomers might cause anisotropy in the anchoring energy in the direction parallel to the surface of the liquid crystal. However, such an effect seems to be small compared to the known change in the surface tension induced by photo-isomerization [4, 5] and will not be considered in this paper. The potential acting on a glycerol droplet is the surface integration of the energy of the interface between the droplet and the liquid crystal, $\gamma_{G,LC}$:

$$V = \oint dA \gamma_{G,LC} = \oint dA f_1^{(0)} [f_c(r') + f_2^{(0)}], \quad (6)$$

where $\oint dA$ is the surface integration over the contact surface and r' is the integration variable. A glycerol droplet undergoes diffusion with diffusion coefficient, D , under the influence of the potential, V . The distribution of glycerol droplets $P(r, t)$ obeys the Smoluchowski equation,

$$\frac{\partial}{\partial t} P(r, t) = D \nabla \cdot \left(\nabla P(r, t) + \frac{\nabla V}{k_B T} P(r, t) \right), \quad (7)$$

where r is the distance from the centre of the irradiated region, k_B is the Boltzmann constant and T is temperature. We take the integration variable in equation (6) as r' . $f_c(r')$ may be approximated as

$$f_c(r') = f_c(r) + (r' - r)\nabla f_c(r), \quad (8)$$

where r is the position of the centre of the droplet from the centre of the irradiated region. Substituting equation (8) in (6) yields

$$V(r) = f_1 f_c(r) + \nabla f_c(r) f_1^{(0)} \oint dA (r' - r) + f_2, \quad (9)$$

where $f_1 = f_1^{(0)} \oint dA$ and $f_2 = f_2^{(0)} \oint dA$. If the second term of equation (9) can be neglected compared with the first term, one obtains

$$V(r) = f_1 f_c(r) + f_2. \quad (10)$$

f_2 is a constant and is chosen such that the potential is zero at infinite distance. In figure 2, we show the potential given by equation (10). For the sake of simplicity, we introduce the following approximate potential:

$$\frac{V(r)}{k_B T} = \begin{cases} \frac{V(R/2)}{k_B T} & \text{for } r \leq R \\ \frac{V(R/2)}{k_B T} \frac{R_2 - r}{R_2 - R} & \text{for } R < r \leq R_2. \end{cases} \quad (11)$$

It is a constant, $V(R/2)$, within the irradiated region of radius R and increases linearly. The slope of the linear part is chosen such that it is equal to that of the exact potential at $r = R$; then the approximate potential becomes zero at R_2 , which is given by $R_2 = R + K_0(\alpha_2 R)/(\alpha_2 K_1(\alpha_2 R)) \sim R + 1/\alpha_2$. The approximate potential is also shown in figure 2, where $k_i = 10^5 \text{ s}^{-1}$, $k_c = 0.01 \text{ s}^{-1}$, $k_t = 0 \text{ s}^{-1}$, $D_a = 10^{-10} \text{ m}^2 \text{ s}^{-1}$ [10, 11] and $V(R)/(k_B T) = -2.8$ which is chosen to give the observed stationary distribution of droplets under the irradiation with UV light. The value of k_i is consistent with the rapid rate of transformation from *cis* to *trans* isomers and typical values are chosen for thermal isomerization rates [12]. For the particular azobenzene derivatives used in the experiments, preliminary experimental results indicate that rates of thermal isomerization from *cis* to *trans* are $\sim 10^{-5} \text{ s}^{-1}$. This value was obtained in the dark, while the experiments on glycerol droplets were performed under visible light [13]. If k_c is indeed 10^{-5} s^{-1} , the concentration of *cis* isomers does not attain the steady state on the timescale of the droplet motion, $\sim 100 \text{ s}$. Since a reliable value for k_c is not available, we tentatively take $k_c = 10^{-2} \text{ s}^{-1}$ and assume that the glycerol droplet moves under the steady concentration of *cis* isomers. As shown in figure 2, the linear potential approximation satisfactorily reproduces the exact potential. This potential is used to qualitatively explain the observed distribution of droplets.

4. Distribution of droplets

When the ultraviolet light is continuously irradiated, *trans-cis* isomerization of azobenzene molecules is induced in the irradiated region. Glycerol droplets move toward the inside of the irradiated region. As already mentioned, in the course of this motion the depletion zone of droplets appears at the periphery of the irradiated region. However, the depletion zone does not appear when the ultraviolet light is turned off and visible light is turned on. In the latter cases, the nonuniform distribution of droplets induced by the ultraviolet light returns to the uniform distribution by simply decreasing the gradient of the distribution at any place. In this section, we study these phenomena on the basis of the theoretical model given in the previous section.

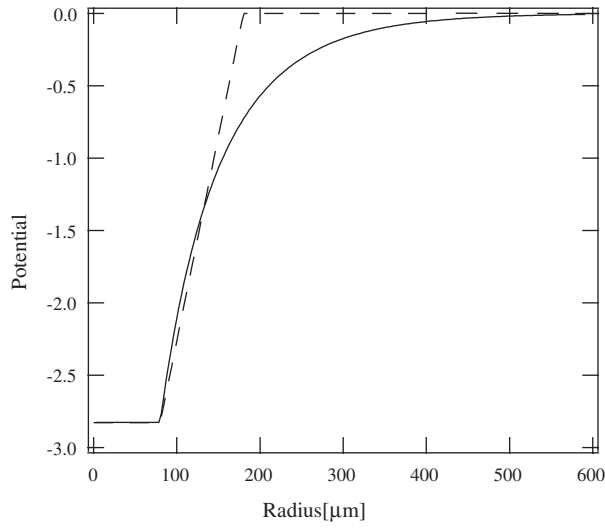


Figure 2. $V(r)/(k_B T)$ as a function of distance from the centre of the illuminated region. Parameters are given in the text. The solid line is given by equation (10) together with equations (2) and (3), where a constant term is taken such that the potential is zero at infinite distance. The dashed line is given by equation (11) with parameters given in the text.

First, we consider the process in which the nonuniform distribution of droplets is formed from the uniform distribution by irradiating with ultraviolet light. The circular beam of light with radius R creates a gradient of the concentration of *cis* isomers. An approximate form of the potential is given by equation (11). The distribution of glycerol droplets in the region between radius R and radius R_2 obeys the Smoluchowski equation, which is expressed after Laplace transformation as

$$s\hat{P}(r, s) - 1 = D \left[\frac{\partial^2}{\partial r^2} \hat{P}(r, s) + \left(\frac{1}{r} + a \right) \frac{\partial}{\partial r} \hat{P}(r, s) + \frac{a}{r} \hat{P}(r, s) \right], \quad (12)$$

where $\hat{P}(r, s) = \int_0^\infty dt \exp(-st) P(r, t)$, $a = -V(R/2)/(k_B T (R_2 - R))$ and the uniform initial condition is assumed. The homogeneous part of equation (12) is transformed into Whittaker's equation for $\sqrt{r} \exp(\frac{V(r)}{2k_B T}) \hat{P}(r, s)$ after introducing the new variable $r\sqrt{a^2 + 4s/D}$. The general solution is given by [14]:

$$\hat{P}(r, s) = \exp\left(-\frac{a + \beta}{2} r\right) [A_1 M(r) + A_2 U(r) + U(r) h_M(r) + M(r) h_U(r)], \quad (13)$$

where $\beta \equiv \sqrt{a^2 + 4s/D}$. A_1 and A_2 are two unknown coefficients to be determined from the boundary conditions. $M(r)$ and $U(r)$ are Kummer's confluent hypergeometric functions, which are written in conventional notation as [14]

$$M(r) \equiv M\left(\frac{1}{2} - \frac{a}{2\beta}, 1, r\beta\right), \quad U(r) \equiv U\left(\frac{1}{2} - \frac{a}{2\beta}, 1, r\beta\right).$$

The last two terms in equation (13) represent inhomogeneous solutions, where

$$h_M(r) \equiv \frac{\Gamma\left(\frac{1}{2} - \frac{a}{2\beta}\right)}{D} \int_R^r dr_1 r_1 \exp\left(\frac{a - \beta}{2} r_1\right) M(r_1)$$

$$h_U(r) \equiv \frac{\Gamma\left(\frac{1}{2} - \frac{a}{2\beta}\right)}{D} \int_r^{R_2} dr_1 r_1 \exp\left(\frac{a - \beta}{2} r_1\right) U(r_1).$$

The distribution of glycerol droplets in the other regions is described by the solution of the pure diffusion equation:

$$\begin{aligned} \frac{1}{s} + BI_0(r\sqrt{s/D}), & \quad r \leq R \\ \frac{1}{s} + CK_0(r\sqrt{s/D}), & \quad R_2 \leq r, \end{aligned} \quad (14)$$

where B and C are constants to be determined from the boundary conditions.

Both the density and the flux of droplets should be continuous at $r = R$ and R_2 , which provides four equations for four unknown coefficients, i.e., A_1 , A_2 , B and C . As a result, A_1 and A_2 are obtained as

$$\begin{pmatrix} A_1 \\ A_2 \end{pmatrix} = \frac{1}{\Delta} \begin{pmatrix} T_{1,1} & T_{1,2} \\ T_{2,1} & T_{2,2} \end{pmatrix} \begin{pmatrix} \frac{\exp(\frac{a+\beta}{2}R)}{s} - h_U(R)T_{2,2} \\ \frac{\exp(\frac{a+\beta}{2}R_2)}{s} - h_M(R_2)T_{1,1} \end{pmatrix}. \quad (15)$$

The usual definition of a determinant is used, $\Delta = T_{1,1}T_{2,2} - T_{1,2}T_{2,1}$, together with the components

$$\begin{aligned} T_{1,1} &= U(R_2) \left(1 - \frac{K_0}{K'_0} \frac{a-\beta}{2} \right) - \frac{K_0}{K'_0} U'(R_2), \\ T_{1,2} &= -U(R) \left(1 - \frac{I_0}{I'_0} \frac{a-\beta}{2} \right) + \frac{I_0}{I'_0} U'(R) \\ T_{2,1} &= -M(R_2) \left(1 - \frac{K_0}{K'_0} \frac{a-\beta}{2} \right) + \frac{K_0}{K'_0} M'(R_2), \\ T_{2,2} &= M(R) \left(1 - \frac{I_0}{I'_0} \frac{a-\beta}{2} \right) - \frac{I_0}{I'_0} M'(R) \end{aligned}$$

where the abbreviated notation $I_0 \equiv I_0(R\sqrt{s/D})$, $K_0 \equiv K_0(R_2\sqrt{s/D})$, $I'_0 \equiv \sqrt{\frac{s}{D}} I_1(R\sqrt{s/D})$ and $K'_0 \equiv -\sqrt{\frac{s}{D}} K_1(R_2\sqrt{s/D})$ is introduced, together with

$$\begin{aligned} M'(r) &\equiv \frac{\partial}{\partial r} M(r\beta) = \beta \left(\frac{1}{2} - \frac{a}{2\beta} \right) M \left(\frac{3}{2} - \frac{a}{2\beta}, 2, r\beta \right) \\ U'(r) &\equiv \frac{\partial}{\partial r} U(r\beta) = -\beta \left(\frac{1}{2} - \frac{a}{2\beta} \right) U \left(\frac{3}{2} - \frac{a}{2\beta}, 2, r\beta \right). \end{aligned}$$

The other coefficients, B and C , are written as

$$B = \frac{e^{-\frac{a+\beta}{2}R}}{I'_0} \left[(A_1 + h_U(R)) \left(\frac{a-\beta}{2} M(R) + M'(R) \right) + A_2 \left(\frac{a-\beta}{2} U(R) + U'(R) \right) \right] \quad (16)$$

$$C = \frac{e^{-\frac{a+\beta}{2}R_2}}{K'_0} \left[A_1 \left(\frac{a-\beta}{2} M(R_2) + M'(R_2) \right) + (A_2 + h_M(R_2)) \left(\frac{a-\beta}{2} U(R_2) + U'(R_2) \right) \right]. \quad (17)$$

The distribution of glycerol droplets is calculated through numerical Laplace inversion by the Stehfest algorithm [15]. The number of droplets inside the illuminated region increases monotonically with time, exhibiting a sublinear curve as shown in figure 3, where $D = 10 \mu\text{m}^2 \text{s}^{-1}$ and the other values of the parameters are the same as those in figure 2. The straight line portion is increased when the diffusion constant is decreased because a longer period is needed to attain the steady state distribution. In contrast, the sublinearity of the curve is greatly enhanced for higher values of the diffusion constant. A sublinear curve similar to that shown in figure 3 is indeed observed in the recent experiments [7]. The value of the diffusion constant

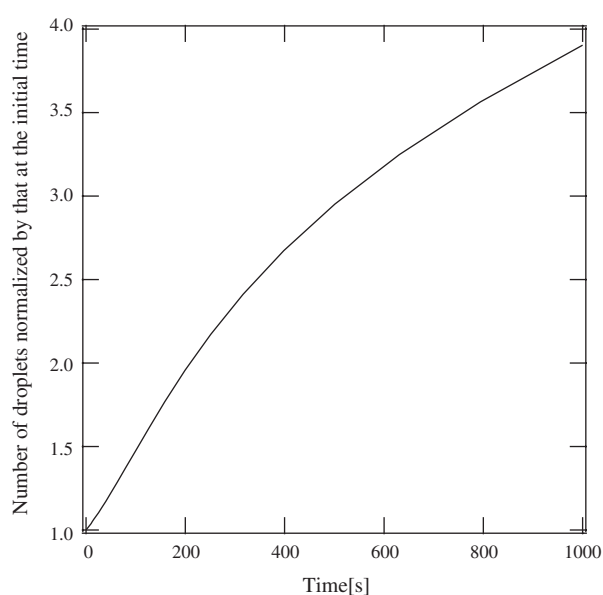


Figure 3. Number of glycerol droplets inside the illuminated region as a function of irradiation time. Parameters are given in the text.

used is larger than $0.02 \mu\text{m}^2 \text{s}^{-1}$ estimated from the Stokes–Einstein law assuming spherical particles of radius $1.5 \mu\text{m}$. In the experiments, the glycerol droplets are on the surface of the liquid crystal and are not completely embedded in the liquid crystal. Furthermore, the shape is greatly deformed from the sphere. Therefore, the frictional force should be reduced from the value predicted from the Stokes law and a larger value of the diffusion constant is expected compared to that predicted from the Stokes–Einstein law. Unfortunately, the diffusion constant is not measured. In the dense region of glycerol droplets, there is an interaction between droplets due to the deformation of an elastic field for the director [16–18]. If we include the repulsive interaction, the steady state is reached earlier and the curve shows more sublinearity. Although there is some ambiguity in the value of the diffusion coefficient used, our model explains a monotonic increase of the glycerol droplets in the illuminated region reasonably well in terms of diffusion under the potential gradient caused by *trans* to *cis* isomerization of azobenzene derivatives.

Now, we investigate why the depletion zone of glycerol droplets appears at the periphery of the illuminated region. In figures 4 and 5, the density of glycerol droplets is plotted as a function of the distance from the centre of the irradiated region for various time periods after the light irradiation. In figure 4, the density of glycerol droplets at the periphery of the illuminated region is lowered as time proceeds. Both the width and the depth of the depletion zone increase during the periods shown. In the later times, as shown in figure 5, the depth gets less while the depletion zone still increases. The appearance of the depletion zone and its time evolution are consistent with experimental findings [7]. At long times, 10^4 s , the distribution of glycerol droplets approaches that of the steady state, $\propto \exp[-V/(k_B T)]$.

In the reverse process, where the ultraviolet light is turned off and visible light is turned on, the potential gradient quickly disappears. Droplets diffuse in the absence of a potential and the density of glycerol droplets returns to the uniform distribution as observed in experiments [7].

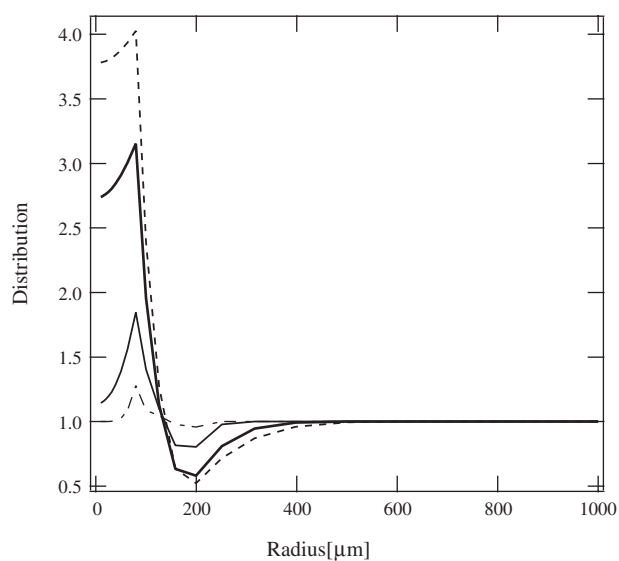


Figure 4. Distribution of glycerol droplets as a function of distance from the centre of the illuminated region for various irradiation times. The dash-dotted line, the thin solid line, the thick solid line and the dashed line represent the distributions for 20, 100, 500 and 1000 s, respectively.

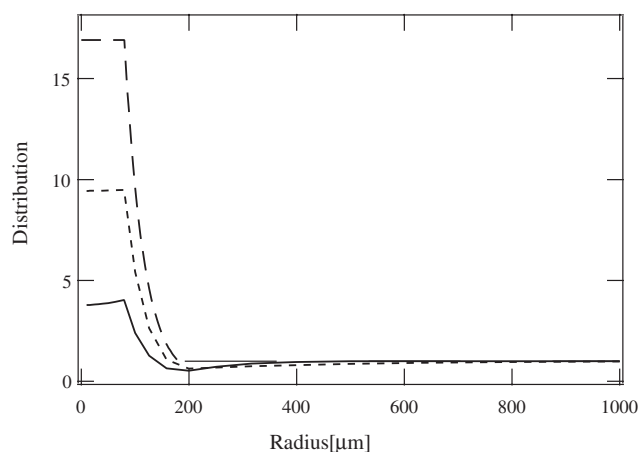


Figure 5. Distribution of glycerol droplets as a function of distance from the centre of the illuminated region for various irradiation times. The solid line and the short-dashed line represent the distributions for 1000 and 10^4 s, respectively. The long-dashed line is the steady state distribution.

5. Summary and conclusions

We have studied photo-induced condensation and dispersion of glycerol micro-droplets on the surface of liquid crystals doped with azobenzene derivatives. Photo-induced *trans* to *cis* isomerization of the azobenzene derivatives is induced in the region irradiated with the ultraviolet light, while it is not induced outside that region. The combined effect of photo-isomerization and diffusion of azobenzene derivatives produces a concentration gradient of *cis* isomers which leads to the formation of a gradient of interfacial energy between glycerol

droplets and the liquid crystal. Glycerol droplets move toward the region where the surface tension is smaller. The surface tension gradient is large at the periphery of the illuminated region. The motion of glycerol droplets is faster there compared to the case in the other region where the surface tension gradient is small. As a consequence, the density of glycerol droplets is lowered at the periphery of the illuminated region. The density gradient induces diffusive flow of glycerol droplets and the droplets far from the irradiated region are gradually attracted. Glycerol droplets diffuse under the influence of the surface tension gradient and the distribution approaches the steady state. The number of droplets inside the illuminated region increases with time first linearly, then sublinearly. This behaviour is observed in recent experiments [7]. The depletion zone of glycerol droplets appears at the periphery of the illuminated region. This is also consistent with the result of recent experiments [7]. We assumed a fast approach to the steady state concentration of *cis* isomers. Our estimate of the surface tension may be oversimplified. However, our model reproduces the appearance of the depletion zone of glycerol droplets observed experimentally and explained it reasonably well in terms of the diffusion of droplets in the presence of the gradient in the surface tension associated with photo-induced *trans* to *cis* isomerization of azobenzene derivatives.

In order to make our work more quantitative, we need to know the exact values of the diffusion constants of both droplets and azobenzene molecules, isomerization rates and the rate of exchange of *cis* isomers between the bulk and the interface. The theoretical analysis would be much more simplified if a stripe region was irradiated instead of the circular one. Such experiments will stimulate further quantitative theoretical analysis.

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