

Homogenization of a phase-separated droplet in a polymer mixture caused by the dielectric effect of a laser

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It is found that a micrometer-sized droplet in an aqueous solution of binary polymers [water/polyethylene-glycol (PEG)/dextran] disappears upon irradiation with a focused yttrium-aluminum-garnet laser. The interface of the dextran-rich droplet broadens and disappears, and it reappears upon turning the laser off, whereas the PEG-rich droplet shrinks and disappears. These phenomena are discussed in terms of the free energy by considering the laser-induced dielectric potential.

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The spatiotemporal structures of phase separation is one of the central issues of physics. Many studies have been performed on the transition between a homogeneous phase and a phase-separated phase [1–3]. Recently it was found that local phase separation at a micrometer scale can be induced using a focused laser [4–12]. In these studies, the local phase separation—i.e., generation of a micrometer-sized droplet—was observed and discussed in relation to the generation of an attractive potential due to a dielectric interaction [13–17] by considering the two roles of a focused laser: it can induce phase separation, and it can trap a generated droplet. However, previous studies have not addressed the possible effect of laser heating.

In the present article, contrary to previous works, we report the disappearance of a micrometer-scale droplet—i.e., the transition from local phase segregation into a homogeneous state—under laser irradiation in a binary polymer solution. Such a polymer solution, a so-called aqueous-two-phase system, has been developed as a tool to partition biomolecules. Here, we used a polyethylene-glycol (PEG)/dextran aqueous solution. Due to the low interfacial tension on the order of 10^{-7} – 10^{-5} N/m [18,19], 10- μ m-sized droplets are stable in the solution.

We used a system composed of water, dextran [molecular weight (M.W.): 15 000–20 000, Nacalai] and polyethylene-glycol (PEG; M.W.: 7400–9000, Nacalai) as an aqueous-two-phase system. This system exhibits the phase diagram shown in Fig. 1; phase separation is generated with an increase in temperature at a fixed composition. The solution segregates into a PEG-rich phase (upper phase) and a dextran-rich phase (lower phase). Sample solutions were prepared as follows: We first prepared 200 mg/ml PEG and dextran aqueous solutions. Then we mixed the solutions at the ratio of 1:1, and the mixture was allowed to stand for more than 1 h. The composition of the sample solutions was chosen based on the phase-separating condition. Since an

aqueous-two-phase system has a long relaxation time, small droplets were present for at least several days. From the phase-separated solution, a PEG-rich phase or a dextran-rich phase was transferred to a thin chamber ($20\text{ mm} \times 20\text{ mm} \times 200\text{ }\mu\text{m}$). A converged laser beam (beam waist $\sim 2\text{ }\mu\text{m}$) was passed through an oil-immersed lens ($100\times$, numerical aperture=1.3) with an inverted phase-contrast microscope (TE-300, Nikon). We used an yttrium-aluminum-garnet (YAG) laser (wavelength=1064 nm, Millennia IR, Spectra Physics). The experiments were carried out under a constant temperature of 297 ± 1 K. In the PEG-rich phase, dextran-rich droplets were observed with a phase-contrast microscope, while in the dextran-rich phase, PEG-rich droplets were observed.

Figure 2(a) shows a spatiotemporal image of a gradually disappearing dextran-rich droplet in the PEG-rich phase under irradiation with a converged laser beam at a power of $P=1.5$ W. The actual shapes of the droplets are also given at

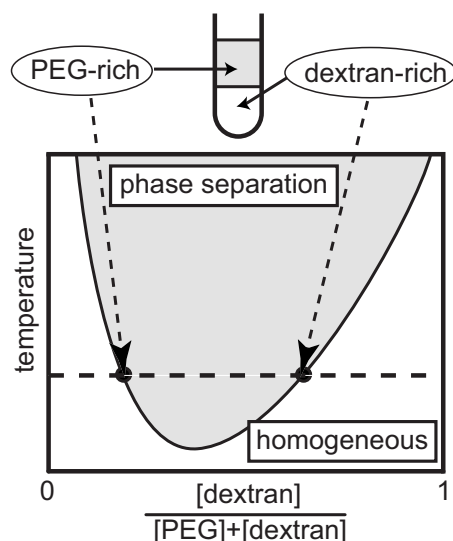


FIG. 1. Schematic phase diagram of the PEG/dextran/water system. The horizontal axis denotes the dextran concentration as a fraction of the total concentration of polymers.

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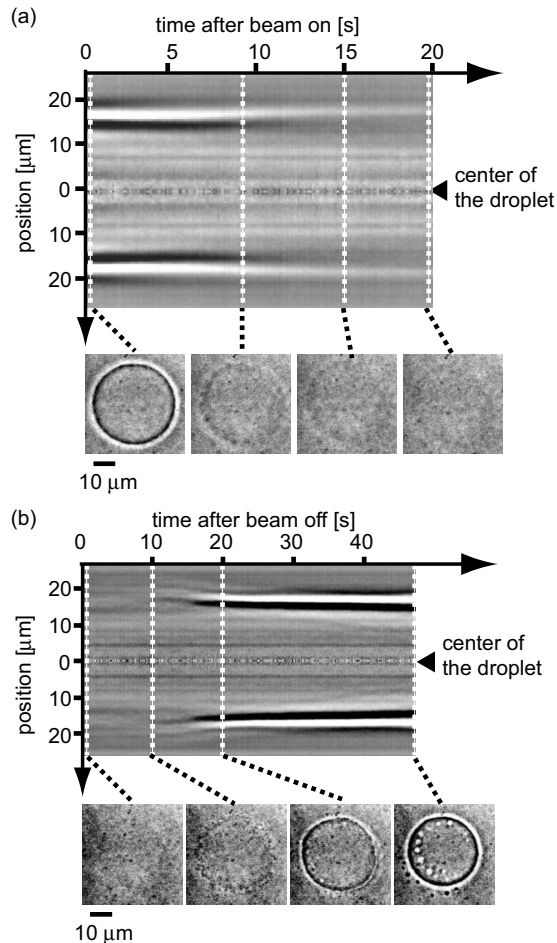


FIG. 2. (a) Spatiotemporal image of a gradually disappearing dextran-rich droplet around the focus of a YAG laser ($\lambda=1064$ nm) in the PEG-rich phase at a laser power of 1.5 W, reconstructed from time-successive video frames. Actual pictures of the droplets are shown at the bottom. (b) Spatiotemporal image of a reappearing dextran-rich droplet after laser irradiation was discontinued, reconstructed from successive video frames. Actual pictures of the droplets are also shown at the bottom. Micrometer-sized droplets are generated both inside and outside the original dextran-rich droplet. The origin of the time axis corresponds to when the laser was switched (a) on or (b) off.

the bottom. A straight line in the real pictures that passes through the center of the droplet was picked up and aligned in sequence to make the spatiotemporal image. The interface of the droplet disappeared gradually. When the laser was turned off, the dextran-rich droplet reappeared in the same region, followed by the formation of multiple smaller droplets both inside and outside the original dextran-rich droplet, to form a nested structure. Figure 2(b) shows a spatiotemporal image together with pictures of the reappearing dextran-rich droplet.

On the other hand, Fig. 3 shows a spatiotemporal image and actual pictures of a disappearing PEG-rich droplet in the dextran-rich phase under irradiation with a converged laser at a power of $P=1.5$ W. The diameter of the dextran-rich droplet decreased linearly with time. The PEG-rich droplet did not reappear after laser irradiation was stopped.

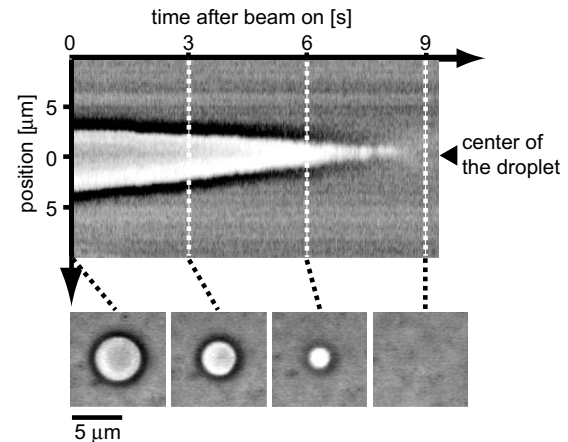


FIG. 3. Spatiotemporal image of a shrinking PEG-rich droplet around the laser focus at a laser power of $P=1.5$ W, reconstructed from time-successive video frames. The diameter of the droplet decreased linearly with time. The origin of the time axis corresponds to when the laser was switched on.

In order to investigate the heating effect by laser irradiation, the same experiments were conducted with a D_2O /dextran/PEG system, in which H_2O was replaced with D_2O . Since D_2O absorbs light at a wavelength of 1064 nm only 1/100 as much as H_2O [20], heating due to laser irradiation can be neglected in the experiments with D_2O . We confirmed that there was no essential difference in the experimental trends regarding the disappearance of droplets if H_2O was replaced by D_2O . Thus, the disappearance of droplets is attributed to the laser potential, at least as the main driving force.

As shown in Fig. 1, this system tends to exhibit phase separation with increasing temperature; i.e., heating should induce phase separation. In the above experiments shown in Figs. 2 and 3, however, the droplets disappear when the laser beam is turned on. This fact clarified that the transition between the homogeneous state and phase-separated state is induced by electromagnetic interaction with the focused laser, not by local heating due to laser irradiation.

If we consider a small volume of the liquid, the electromagnetic potential by a laser is given as

$$U = -\frac{1}{2} \epsilon \langle |\vec{E}|^2 \rangle, \quad (1)$$

where \vec{E} is the electric field generated by a focused laser and ϵ is the permittivity of the liquid, which is almost proportional to the difference between the square of the refractive index and that of the surrounding medium. When the refractive index of the object is greater than that of the surrounding medium, a focused laser can trap an object in the vicinity of the focal point. We measured the refractive indices of various solutions: $n_{\text{dextran}}=1.365$, $n_{\text{PEG}}=1.363$, and $n_{\text{water}}=1.332$, where n_{dextran} , n_{PEG} , and n_{water} are the refractive indices of dextran solution (200 mg/ml), PEG solution (200 mg/ml), and pure water, respectively; i.e., $n_{\text{dextran}} \geq n_{\text{PEG}} > n_{\text{water}}$. Consequently, the trapping potential is on the order of $U_{\text{dextran}} \approx U_{\text{PEG}} < U_{\text{water}}$.

Therefore, we can discuss the two different patterns of droplet disappearance in terms of a free-energy model that includes the laser potential. We introduce two order parameters

$$\rho = ([\text{dextran}] - [\text{PEG}]) / ([\text{dextran}] + [\text{PEG}]), \quad (2)$$

$$\sigma = [\text{dextran}] + [\text{PEG}] (= 1 - [\text{water}]), \quad (3)$$

where $[\text{dextran}]$, $[\text{PEG}]$, and $[\text{water}]$ indicate the volume fractions of dextran, PEG, and water, respectively, in the total system. Local free energy can be defined as

$$f_{\text{local}}(\rho, \sigma) = a\rho^4 - b(\sigma - \sigma_0)\rho^2, \quad (4)$$

where a and b are positive constants, and σ_0 indicates the threshold value of σ ; i.e., when σ is smaller than σ_0 , $f_{\text{local}}(\rho, \sigma)$ has only one minimum value, and when σ is larger than σ_0 , $f_{\text{local}}(\rho, \sigma)$ has two local-minimum values, which corresponds to the fact that the system is homogeneous with a lower polymer concentration and undergoes phase separation with a higher polymer concentration.

The total free energy including the laser potential, $F(\rho; \sigma, I(r))$, can be written as

$$F(\rho; \sigma, I(r)) = \int [f_{\text{local}}(\rho, \sigma) - \epsilon_1 \rho I(r) - \epsilon_2 \sigma I(r) + \gamma_1 |\nabla \rho|^2 / 2 + \gamma_2 |\nabla \sigma|^2 / 2] d\vec{r}, \quad (5)$$

where ϵ_1 , ϵ_2 , γ_1 , and γ_2 are constants, and $I(r) = P \exp(-r^2/r_0^2)$ indicates the laser potential of the Gaussian beam, where P , r_0 , and r are laser power, beam waist, and distance from the focus, respectively. The terms $-\epsilon_1 \rho I(r)$ and $-\epsilon_2 \sigma I(r)$ show the effects of the laser potential, which indicate that dextran is attracted to the laser field more than PEG and that polymers are stabilized under the laser potential compared to water, respectively. γ_1 and γ_2 correspond to the interfacial tension if the phase separation is induced.

Due to the relationship among n_{PEG} , n_{dextran} , and n_{water} , the trapping potentials show the same relationship as $U_{\text{dextran}} \lesssim U_{\text{PEG}} < U_{\text{water}}$. The characteristic time scale of change in ρ and σ is proportional to $|U_{\text{PEG}} - U_{\text{dextran}}|$ and $|U_{\text{water}} - U_{\text{PEG}}|$, respectively. Since $|U_{\text{PEG}} - U_{\text{dextran}}| \ll |U_{\text{water}} - U_{\text{PEG}}|$, σ changes much faster than ρ . If we consider that both ρ and σ are conservative, the evolution equations for ρ and σ can be derived from Eq. (5):

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= L_1 \nabla^2 \left(\frac{\delta F}{\delta \rho} \right) \\ &= L_1 \nabla^2 [4a\rho^3 - 2b(\sigma - \sigma_0)\rho - \epsilon_1 I(r) - \gamma_1 \nabla^2 \rho], \end{aligned} \quad (6)$$

$$\frac{\partial \sigma}{\partial t} = L_2 \nabla^2 \left(\frac{\delta F}{\delta \sigma} \right) = L_2 \nabla^2 [-b\rho^2 - \epsilon_2 I(r) - \gamma_2 \nabla^2 \sigma], \quad (7)$$

where L_1 and L_2 are the inverse of the characteristic time scales for changes in ρ and σ , respectively. It is also noted that the difference in permittivity is small enough for us to ignore the effect of the spatial difference in permittivity on the beam intensity.

Based on the above equations, we performed numerical calculations in a two-dimensional system. The initial value

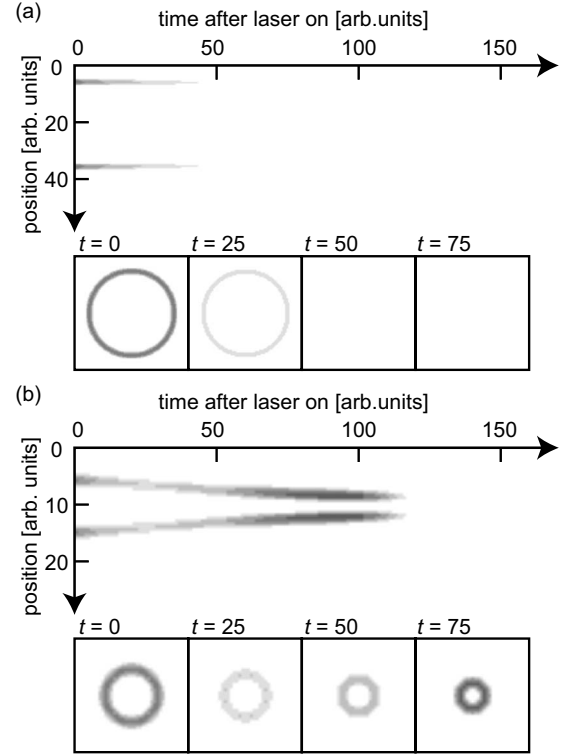


FIG. 4. Numerical results based on Eqs. (6) and (7). Spatiotemporal image and snapshots of the time development are shown. The numerical results are colored depending on $|\nabla \rho|$, which corresponds to the phase-contrast observation. (a) Numerical results for a dextran-rich droplet in the PEG-rich phase as shown in Fig. 2. (b) Numerical results for a PEG-rich droplet in a dextran-rich phase as shown in Fig. 3.

of ρ for the dextran-rich phase is given as $+\rho_{\text{ini}}$, while that for the PEG-rich phase is $-\rho_{\text{ini}}$, where ρ_{ini} is a positive constant. The initial value of σ is given as σ_{ini} . The ratio of the beam waist and the sizes of the droplets is the same order as that in the experiments. We fixed the parameters as follows: $a=1$, $b=1$, $\rho_{\text{ini}}=0.22$, $\sigma_{\text{ini}}=0.11$, $\sigma_0=0.1$, $\epsilon_1=0.03$, $\epsilon_2=1$, $L_1=1$, $L_2=0.01$, $\gamma_1=0.1$, $\gamma_2=10.0$, and $r_0=10$. The initial radius of the droplet, R , is set as $R=15$ for (a) and $R=5$ for (b).

Figure 4(a) shows a numerical result for the dextran-rich droplet in a PEG-rich phase. Since the experiments were conducted with a phase-contrast microscope, the interface of the observed droplet roughly corresponds to $|\nabla \rho|$. After laser irradiation begins, σ begins to have a nonuniform profile, with larger values around the laser focus and smaller values near the interface of the droplet, which means that polymers aggregate due to the laser potential, while water is repelled from the focal point. As a consequence, the profile of $|\nabla \rho|$ at the boundary becomes smoother.

Figure 4(b) shows a numerical result for the PEG-rich droplet in a dextran-rich phase. As soon as irradiation starts, the PEG-rich droplet begins to shrink, since the PEG-rich state becomes metastable. The diameter of the droplet decreases linearly with time. These results reproduce well the experimental results.

From the numerical calculation based on the free energy,

the mechanism of the disappearance of the droplets can be summarized as follows: Under local laser irradiation, both PEG and dextran are attracted to the laser focus. Due to this attractive force, the fraction of polymers at a certain distance from the focus decreases. For a dextran-rich droplet in a PEG-rich phase, it is found that the droplet size is larger than the beam waist and the fraction of polymers decreases near the interface of the droplet. Therefore, the interface of the droplet becomes broad and the droplet disappears. For a PEG-rich droplet in a dextran-rich phase, it is found that the droplet size is on the same order of the beam waist and the fraction of polymer does not decrease near the interface. Due to the small difference in the attractive force between PEG and dextran, the PEG-rich droplet becomes unstable and shrinks.

In the present study, when a focused laser was used to

irradiate a mixed polymer system, the interface of the droplets disappeared due to a laser-induced potential. We found two different processes for this disappearance. These phenomena were described in terms of the phenomenological free-energy model, which included a laser potential term based on a relational expression of the refractive indices of the compounds.

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