Supplemental information for
Thermal Molecular Focusing: Tunable Cross effect of Phoresis and Light-driven Hydrodynamic Focusing

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I. THEORETICAL DETAILS

A. Heat conduction in polymer solution

One of fundamental novelty of this study, compared to previous studies, arises from high thermal insulation of PDMS boundary wall. Its thermal conductivity is 0.15 W/(mK) much smaller than water with 0.59 W/(mK). In this combination of materials, the heat by infrared laser focusing diffuse in an aqueous phase although PDMS wall plays a role of heat sink but it's radiation ability is low. On the other hand, when the aqueous phase is enclosed in a glass with higher thermal conductivity of 1.00 W/(mK) larger than both water and PDMS, the heat transfer is dominantly occurred from water to glass so that the heat dominantly diffuse to z axis, which means the shape of temperature distribution is insensitive to the speed of a moving laser spot. However, heat conduction in lateral direction along the traveling laser spot has to be considered for our experimental system (FIG. S1).

Suppose that the spot of heat source is built in two-dimensional space $\boldsymbol{X} = (x, y)$ and moves at constant speed u_l in x axis. The thermal field due to the moving heat spot is described by the equation of thermal conductivity

$$C_v \frac{\partial T}{\partial t} - \lambda_h \nabla^2 T = P - h\Delta T, \quad (1)$$

where C_v is heat capacity and λ_h heat conductivity, P is the source of heating spot, h the coefficient of heat sink. The equation is invariant with ΔT instead of T, we can rewrite

$$C_v \frac{\partial(\Delta T)}{\partial t} - \lambda_h \nabla^2(\Delta T) = P - h\Delta T. \quad (2)$$

In the moving frame of the heat spot, the coordinate and the derivative functions are converted as

$$x' = x - u_l t \quad (3)$$

$$\frac{\partial}{\partial t} = -u_l \frac{\partial}{\partial x'} \quad (4)$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{\partial^2}{\partial x'^2} + \frac{\partial^2}{\partial y^2} = \nabla'^2 \quad (5)$$

The shape of laser spot could be given by $P = P_0 \exp[-(x'^2 + y^2)/(2b^2)]$ with the spot radius b.

To solve thermal diffusion equation, we perform spatial Fourier transform of temperature difference ΔT and P by

$$\Delta T(x', y) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\boldsymbol{k} \hat{T}(\boldsymbol{k}) e^{i\boldsymbol{k}\cdot\boldsymbol{X'}}, \quad (6)$$

$$P(x', y) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\boldsymbol{k} P_0 \exp\left(-\frac{b^2 k^2}{2}\right) e^{i\boldsymbol{k}\cdot\boldsymbol{X'}}. \quad (7)$$

By solving thermal diffusion equation after substitution with transformed variables, $\hat{T}(k)$ is given by

$$\hat{T}(\boldsymbol{k}) = \frac{P_0}{\lambda_h k^2 - iC_v \boldsymbol{u_l} \cdot \boldsymbol{k} + h} \exp\left(-\frac{b^2 k^2}{2}\right). \quad (8)$$

We then carried out inverse Fourier transform of $\hat{T}(\boldsymbol{k})$ numerically and obtained thermal field at various u_l at the moving frame. The unsteady thermal fields are characterized by one physical parameter, the frequency of repetitive thermal stimuli $f_l = u_l/L$. FIG.S2 shows that thermal fields build by the heat spot that moves at $f_l = 0$ Hz, 10 Hz, 10^2 Hz, and 10^3 Hz. The maximal temperature difference is $\Delta T_{max} = 9.6$ K for a steady thermal field. As the speed of moving heat spot increases, the magnitude of ΔT decreases because the duration time for heating aqueous solution, which is typically $2b/u_l$, becomes shorter for larger u_l. The reduced duration time leads the reduction of heat at arbitrary position.

B. Heat penetration into PDMS walls

A heated polymer solution has the finite temperature difference of $\Delta T = T - T_0$ to the PDMS wall since the temperature of a PDMS wall at the infinity is constant at T_0. The diffusion of heat occurs from the polymer solution to the PDMS wall. This heat transfer is important to estimate thermal compression of bulk polymer solution because the depth of this heat conduction decides the strain in the PDMS boundary, as shown later. For this aim, we analyze the penetration depth of transferred heat, which is described by l_0, according to thermal diffusion in a PDMS substrate. Thermal field within PDMS $\Delta T'$ is described as below

$$C_v^w \frac{\partial(\Delta T')}{\partial t} - \lambda_h^w \nabla_z^2(\Delta T') = h\Delta T', \quad (9)$$

where C_v^w is the heat capacity of PDMS, λ_h^w the heat conductivity of PDMS, and h is heat transfer coefficient
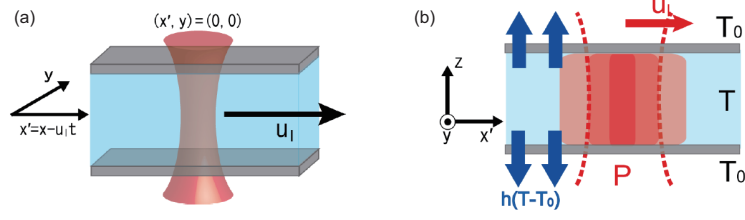
FIG. S1. Schematic illustrations of (a) the reference frame in a moving thermal gradient and (b) the thermal diffusion and sink in the reference frame.
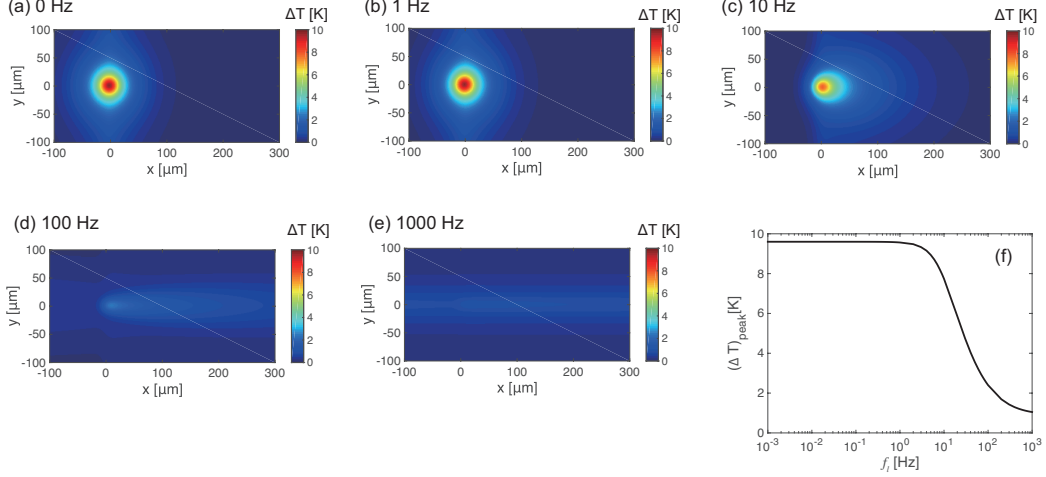

FIG. S2. Numerical simulation of temperature distribution at various speeds of heat wave propagation. Frequency of repetitive thermal stimuli is defined as $f_l = u_l/L$ with the propagation speed of heat wave u_l and the length of scanning path L. (a to e) Temperature distribution in the moving frame at f_l=(a) 0 Hz, (b) 1 Hz, (c) 10 Hz, (d) 100 Hz, (e) 1000Hz. (f) Maximal temperature difference ΔT_{max} is plotted as frequency of heat wave.

across the surface of PDMS[6][7]. The term of $h\Delta T'$ represents the transferred heat from the polymer solution, which plays a role of the heat source for PDMS. At the steady state ($\frac{\partial \Delta T'}{\partial t} = 0$), since the acquired heat from the polymer solution diffuse through the PDMS substrate, the heat diffusion of $\lambda_h^w \nabla_z^2(\Delta T')$ is comparable to $h\Delta T'$. Approximating $\nabla_z \sim 1/l_0$, we can estimate the penetration depth of heat into the PDMS wall as

$$l_0 \sim \sqrt{\frac{\lambda_h^w}{h}}. \qquad (10)$$

For PDMS, typical parameters have been known as λ_h^w=1.5×10^{-7} W/(μm·K)[6] and h=5.0×10^{-10} W/(μm^3·K)[7], and we can estimate $l_0 \simeq 17\mu m$. This penetration depth of heat is comparable to the thickness of bulk fluids (thickness of the chamber), d=25 μm.

C. Thermal expansion of boundary walls by heat spot propagation

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The aqueous polymer solution was enclosed with the flexible boundary walls whose substrate is polydimethyl siloxane (PDMS) being deformed upon the exposure of a thermal stimuli. The moving laser spot, that moves at a constant speed $\boldsymbol{u_l} = u_l\boldsymbol{e_x} = (u_l, 0)$ in x axis, heats water solvent and the temperature of polymer solution $\Delta T(x, y)$ is increased locally. In this occasion, thermal expansion of the solution of $5.0wt\%$ PEG is negligible because of the incompressibility of fluids. The conducted heat thereafter reaches the boundary walls at bottom and ceil and the PDMS substrates thermally expands. increase the temperature of PDMS walls. Thus, the expansion of the flexible boundaries subject to laser heating generates the mechanical force to drive the fluid flow. The continuum equation for the volume of aqueous solution $V(x, t)$ is

$$\frac{\partial V}{\partial t} + \boldsymbol{\nabla} \cdot (V\boldsymbol{u}) = 0, \qquad (11)$$

where $\boldsymbol{\nabla} = \frac{\partial}{\partial x}\boldsymbol{e_x} + \frac{\partial}{\partial y}\boldsymbol{e_y}$ and $\boldsymbol{u} = (u, v)$ is the flow induced by thermal expansion of the wall. At the reference frame of the heat spot, we can rewrite the coordinate as $(x', y) = (x - u_l t, y)$ and the time-derivative can be rewritten as $\frac{\partial}{\partial t} = \frac{\partial x'}{\partial t}\frac{\partial}{\partial x'} = -u_l\frac{\partial}{\partial x'} = -u_l\frac{\partial}{\partial T}\frac{\partial T}{\partial x'}$. By using this derivative of T, the continuum equation of the local volume V in x axis is given by

$$-u_l\frac{\partial V}{\partial T}\frac{\partial T}{\partial x'} + \nabla' \cdot (V(u + u_l)) = 0, \qquad (12)$$
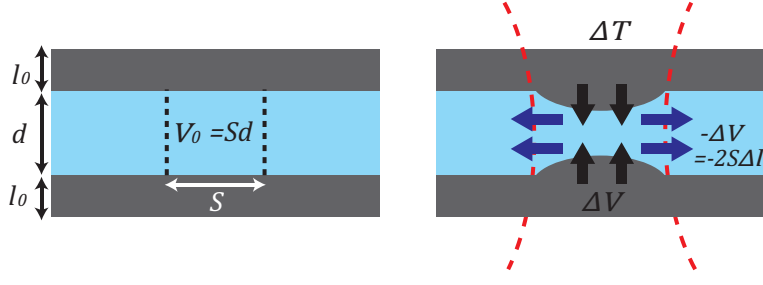
FIG. S3. Schematic illustration of thermal expansion of boundary wall and the compression of enclosed solution.

where ∇' is $\frac{\partial}{\partial x'}$. Because the motion of a hot spot is symmetric across $x = 0$, one can suppose that the change of local volume in y axis does not depend on time and we thus get $V\partial v/\partial y = 0$ in order to satisfy the conservation of mass. Accordingly,

$$-u_l \frac{\partial V}{\partial T}\frac{\partial T}{\partial x'} + V\frac{\partial u}{\partial x'} = 0. \tag{13}$$

After the exchange of x variable from x' ($\because \partial/\partial x' = \partial x/\partial x' \cdot \partial/\partial x = \partial/\partial x$), we obtain

$$\frac{\partial u}{\partial x} = u_l \frac{\partial(\ln V)}{\partial T}\frac{\partial T}{\partial x}. \tag{14}$$

Next, to find the explicit form of thermal expansion coefficient of γ for polymer solution, we consider thermal expansion of the PDMS substrate, through the effect of viscoelastic deformation. Suppose that the polymer solution is locally heated by focused infrared laser, the transferred heat from bulk solution induces thermal expansion of soft deformable wall of PDMS. The length of thermal expansion in z axis is assumed to

$$\Delta l = l_0 \gamma^w \Delta T, \tag{15}$$

where l_0 is the penetration depth of transferred heat (Eq.(10)), and γ^w is thermal expansion coefficient of PDMS defined as $\gamma^w = (1/V^w)(\partial V^w/\partial T)$. Because of this thermal expansion, the change of volume in a PDMS channel is $\Delta V^w = 2S\Delta l = 2Sl_0\gamma^w\Delta T$ with the area of S (FIG.S3).

We describe the local volume of bulk fluid at rest as $V_0 = Sd$ with the area of S and the thickness of d. This bulk fluid is subject to the compression owing to the expanded PDMS wall. Then volume pushed out by PDMS expansion is assumed as $\Delta V = 2S\Delta l$. The strain of ϵ is defined as $\epsilon = -(V - V_0)/V_0 = -\Delta V/V_0$. This expression leads $\gamma = (1/V)(\partial V/\partial T) = -(2l_0/d)(1/\epsilon_\tau)(\partial\epsilon_\tau/\partial T) \equiv -(2l_0/d)\gamma^w$

To describe the mechanics of local thermal expansion, we employed Voigt model consisted of one spring and one dash-pot. The dynamics of strain relaxation is given by

$$\eta^w \frac{d\epsilon_\tau}{dt} + E\epsilon_\tau = \sigma, \tag{16}$$

ϵ_τ is strain, E is the elastic constant, η^w is the viscosity of the dash-pot (PDMS substrate), σ the stress due to

thermal expansion. Because the mechanical stress arises from thermal expansion in the exposure of ΔT, one can yield $\sigma = E\gamma^w\Delta T$ with thermal expansion coefficient of PDMS γ^w and Eq. (16) is rewritten as

$$\frac{d\epsilon_\tau}{dt} + \frac{1}{\tau}\epsilon_\tau = \frac{1}{\tau}\gamma^w\Delta T. \tag{17}$$

$\tau = \eta^w/E$ is the characteristic times for viscoelastic relaxation. By solving this differential equation within the frame of one cycle, $t = [n/f_l, (n+1)/f_l]$ ($n = 0, 1, 2, \cdots$), the ratio of volume change of solution under compression by expanded walls is

$$\frac{\Delta V}{V_0} = -\gamma\Delta T(1 - e^{-\frac{1}{f_l\tau}}), \tag{18}$$

where $\Delta V = V - V_0$ and $\gamma = -(2l_0/d)\gamma^w$. The typical penetration depth l_0 of PDMS is $17\,\mu\text{m}$ while the depth of microchannel of d is $25\,\mu\text{m}$ in this experiment. We assume that the ratio $2l_0/d$ is close to 1 ($\gamma \approx -\gamma^w$).

D. Reduced viscosity in temperature and solute gradients

In a solution of polymer such as polyethylene glycol (PEG), the viscosity of solution η depends on both temperature T and the concentration of PEG c^p. According to the previous studies, the empirical relation of the viscosity is given by

$$\eta = C\exp\left[\frac{B(c^p)}{T - T_c}\right], \tag{19}$$

where C and T_c are the constants independent of thermodynamic variables T and c^p but $B(c^p)$ is the function showing monotonic increase for c^p. This empirical relation has been independently obtained from the study using molecular dynamics simulation[2], such that $\eta = C'\exp[E/(RT)]$ where C' is the constant while E is the variable depending on c^p. Given that the small deviations of temperature ΔT and polymer concentration Δc^p, the change of viscosity $\Delta\eta$ is described as

$$\Delta\eta = \left(\frac{\partial\eta}{\partial T}\right)_{c^p}\Delta T + \left(\frac{\partial\eta}{\partial c^p}\right)_T\Delta c^p \tag{20}$$

$$= \left[-\frac{B}{(T - T_c)^2}\Delta T + \frac{1}{T - T_c}\frac{dB}{dc^p}\Delta c^p\right]\eta. \tag{21}$$

Then we need to consider how large $1/(T - T_c)$ changes around at room temperature. The previous studies has reported $T_c \approx 180$ K, suggesting that $1/(T - T_c)$ assumed to be constant at room temperature $T=300$ K. We therefore replace the coefficients of ΔT and Δc^p as constants β_0 and β_1 respectively. Eventually, the general form of viscosity change yields

$$\frac{\Delta \eta}{\eta} = \beta_0 \Delta T - \beta_1 \Delta c^p. \tag{22}$$

This expression indicates that one needs to consider both temperature and the concentration of polymer in order to capture the change of viscosity in a temperature gradient. To find the explicit form of concentration gradient of polymer, the balance of density flux is considered. Local thermal gradient ∇T induces the transport of molecules, which named as thermophroesis or the Soret effect. For typical polymer or colloidal particles whose density is heavier than water, thermophoresis depletes these solutes from hot region. The flux of solute due to thermophoresis is described by $J_{Tp}^p = -c^p D_T^p \nabla T$. The spatial distribution of solute concentration is determined by the balance of solute fluxes between thermal diffusion of J_{Tp}^p and normal diffusion $J_{diff}^p = -D^p \nabla c^p$. The phenomenological equation for the net flux $J^p = J_{diff}^p + J_{Tp}^p$ is

$$J^p = -D^p(\nabla c^p + c^p S_T^p \nabla T), \tag{23}$$

where D^p is the diffusion coefficient, c^p the local concentration of the solute and S_T^p the Soret coefficient. One can solve this equation in steady state ($J^p = 0$), the concentration of the solute yields

$$c^p(r) = c_0^p \exp[-S_T^p \Delta T] \tag{24}$$

with the Soret coefficient of $S_T^p = D_T^p/D^p$ and c_0^p is the solute concentration at infinity (FIG.S4). For small ΔT, we can assume $\Delta c^p \approx -c_0^p S_T^p \Delta T$. By substituting this form in Eq.(22), the change of viscosity reads

$$\frac{\Delta \eta}{\eta} = (\beta_0 + \beta_1 c_0^p S_T^p)\Delta T. \tag{25}$$

E. Thermal molecular focusing

Next, we show theoretical details for the derivation of Eq. (6) in the main text by considering the transport equation of DNA molecules that are subject to thermophoresis, diffusiophoresis, and hydrodynamic focusing. The equation of density flux of DNA reads

$$\boldsymbol{J} = -D(\boldsymbol{\nabla} c + c S_T \boldsymbol{\nabla} T) + c\boldsymbol{u}_{Dp} + c\boldsymbol{u}_{hf} \tag{26}$$

where the diffusiophoretic velocity is $\boldsymbol{u}_{Dp} = (u_{Dp}, v_{Dp})$ and $v_{Dp} = \frac{k_B T}{3\eta}\lambda^2 c^p(S_T^p - 1/T)\nabla_y T$ with the thickness of depletion layer λ[3][4], and the microflow of local hydrodynamic focusing $\boldsymbol{u}_{hf} = (u_{hf}, v_{hf})$. Because v_{hf} is

10 times smaller than u_{hf} in our experiment, we assume that v_{hf} in the equation above is negligible. Hence, as shown in Eq. (2) in the main text, light-driven hydrodynamic focusing (LHF) of $\boldsymbol{u}_{hf} = u_{hf}\boldsymbol{e}_x$ along the path of laser scanning (x axis) is given by

$$\boldsymbol{u}_{hf}(x) = -\boldsymbol{u_l} \sinh\left[\frac{2x}{u_l\tau}\right](\beta_0 + \beta_1 c_0^p S_T^p)(\gamma - \Gamma_\tau)(\Delta T)^2 \tag{27}$$

where $f_l=u_l/2L$, defined as $1/f_l=(\Delta t_f + \Delta t_r)/2$. The $\beta(\gamma - \Gamma_\tau)(\Delta T)^2$ means the multiplicative interplay of thermal viscosity and thermal viscoelastic compression under $\gamma > \Gamma_\tau$. Since the magnitude of v_{hf} is 0.1 μm/sec while the typical length of normal diffusion is $\sqrt{D/f_l} \approx$ 1 μm. Thus the diffusion is relatively faster than the induced flow, meaning that the steady state can be present. By solving the equation in the steady state ($J = 0$), the spatial distribution of DNA in x axis yields

$$c(x,y) = c_0 \exp\left[-S_T\Delta T + V'\Delta c^p + \frac{1}{D}\left(\int_{-\infty}^x dx' u_{hf}(x')\right)\right], \tag{28}$$

where $V' = 2\pi a\lambda^2$ with the radius of gyration of DNA of a. We can renormalize the DNA concentration relative to the accumulated amount in the absence of the microflow as

$$\frac{c(x)}{c_0 \exp[-S_T\Delta T + V'\Delta c^p]} = \exp\left[\frac{1}{D}\left(\int_{-\infty}^x dx' u_{hf}(x')\right)\right]. \tag{29}$$

We define this expression as $A(x)$ in order to examine the index of molecular focusing.

To analytically solve $A(x)$, we need to derive the explicit form of $u_{hf}(x)$. For a heat spot that moves in the path $-L \leq x \leq L$ at $y = 0$, the spatial distribution of temperature increase, $\Delta T(x,y)$, follow $\Delta T(x,0) \exp\left(-\frac{y^2}{2w^2}\right)$, with the width of temperature distribution w. We then consider the microflow on the path of the moving heat spot ($y = 0$). On the one hand, the temperature gradient that moves in forward direction drives the microflow u_{ve}^f at the position x ($-L \leq x \leq L$) as

$$u_{ve}^f(x) = -\frac{u_l}{2}(\beta_0 + \beta_1 c_0^p S_T^p)\gamma(1 - e^{-\frac{L+x}{f_l\tau L}})(\Delta T(x,0))^2. \tag{30}$$

On the other hand, when the heat spot moves in opposite direction (backward), the microflow u_{ve}^b at the position x reads

$$u_{ve}^b(x) = +\frac{u_l}{2}(\beta_0 + \beta_1 c_0^p S_T^p)\gamma(1 - e^{-\frac{L-x}{f_l\tau L}})(\Delta T(x,0))^2. \tag{31}$$

By summing reciprocal microflows of Eqs. (30) and (31), we obtain the expression of LHF as

$$u_{hf}(x) = -u_l e^{-\frac{1}{f_l\tau}} \sinh\left[\frac{2x}{u_l\tau}\right](\beta_0 + \beta_1 c_0^p S_T^p)\gamma(\Delta T(x,0))^2. \tag{32}$$
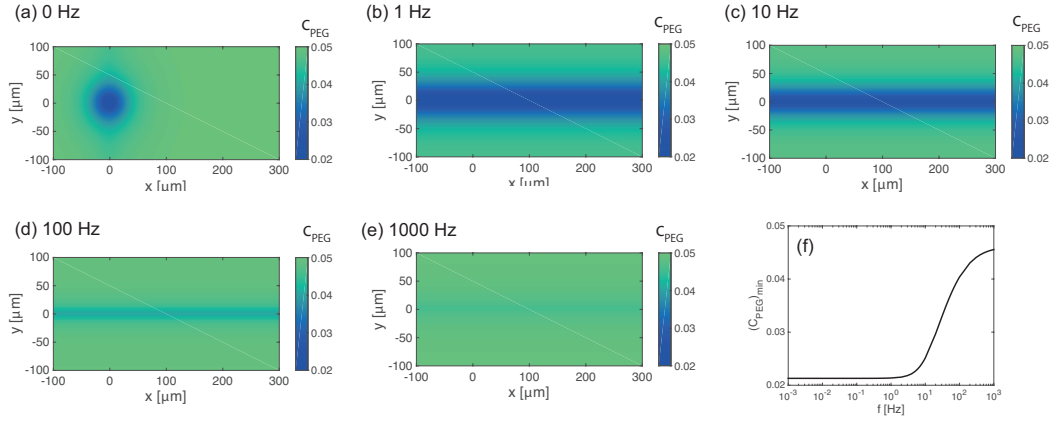
FIG. S4. Numerical simulation of the concentration of PEG, c^p, under a moving temperature gradient. The color map of depleted solute from hot region is shown in moving frame of heat wave at various propagation speeds. (a to e) $c^p(x)$ in the moving frame. f_l=(a) 0 Hz, (b) 1 Hz, (c) 10 Hz, (d) 100 Hz, (e) 1000 Hz. (f) the minimal concentration of solute versus frequency f_l is plotted.

Parameter	Symbol	Value
Half of the length of laser scanning line	L	80 µm
Relaxation time constant of PDMS	τ	1.2 sec [5]
Heat capacity of water	C_v	4.2×10^{-12} J/(µm³·K)[6]
Heat conductivity of water	λ_h	6.1×10^{-7} W/(µm·K)[6]
Heat conductivity of PDMS	λ_h^w	1.5×10^{-7} W/(µm·K)[6][11]
Heat transfer coefficient	h	5.0×10^{-10} W/(µm³·K) [7]
Thermo-viscous coefficient of water	β_0	- 2.2×10^{-2} 1/K [9]
The rate of viscosity change by PEG conc.	β_1	- 27.7 ml/g [2]
Thermo-expansion coefficient of PDMS	γ	- 3.1×10^{-4} 1/K [10]
The size of a moving heat spot	b	7.5 µm
Soret coefficient of PEG20000	S_T^p	8.89×10^{-2} 1/K [8]
Soret coefficient of DNA	S_T	3.80×10^{-1} 1/K [4]
The depth of depletion layer	λ	2.5 nm
The gyration radius of DNA	a	0.1 µm
Diffusion coefficient of PEG20000	D^p	58 µm²/s
Diffusion coefficient of DNA under the heat spot	D	2.89 µm²/s

TABLE S1. The list of parameters used in this study for numerical simulation

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