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Creation of large, periodic temperature gradient *via* plasmonic heating from mesoscopic planar lattice of metal domains

Ryoko Shimada [a, *], Hitomi Sakai [a], Jun Yamamoto [b], Hiroshi Watanabe [c]

[a] Department of Mathematical and Physical Sciences, Japan Women's University, 2-8-1 Mejirodai, Bunkyo-ku, Tokyo 112-8681, Japan
[b] Division of Physics and Astronomy, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan
[c] Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

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ABSTRACT

A large temperature gradient is useful for concentrating temperature-sensitive molecules having non-zero Soret coefficients. Aiming at such molecular manipulation as a final goal, this study analyzed the heat transfer equation for two types heat sources, two-dimensional lattice of metal domains and a single-spot metal domain, both being able to undergo plasmon resonance and generate heat. It turned out that the plasmonic heating from the single-spot domain can generate only a monotonic temperature profile with a single maximum associated by a gradual decay of radial gradient of temperature. In contrast, with an adequate choice of the boundary conditions, the lattice of the metal domains was found to give a profile with a large, periodic temperature gradient that is useful for the manipulation of temperature-sensitive molecules, in particular those favoring low temperatures. A preliminary experiment utilizing a lattice of silver domains confirmed creation of a large, roughly periodic temperature gradient of the order of 10^3 K/mm (being in harmony with the heat transfer analysis), which encourages a further study of temperature gradient controlled by the plasmonic heating and of the molecular manipulation utilizing this gradient.

1. Introduction

Local heating due to plasmon resonance of a metal nanoparticle is of current interest in the thermoplasmonics community [1–14]. The interaction between the metal nanoparticle/nanostructure and electric field (light), that results in the surface plasmon resonance, is well understood [15,16], and the plasmonic heating, due to enhanced absorption of the light energy by the nanoparticle in resonance, has been examined from various aspects [1–14]. The plasmonic heating is characterized by an increase of temperature in a medium embedding the nanoparticle(s), and theoretical and experimental efforts [1–7,10–14] have been made to accurately detect this temperature increase (that changes with the shape and alignment of nanoparticles [4,6,11]). The temperature increase near the nanoparticle was reported to range from a few K up to almost 100 K, depending on the concentration, size, shape, and alignment of the nanoparticles as well as the light intensity. Such a high efficiency of heating has been utilized in various applications that include medical therapy for tumor/cancer [8,17,18] and functionalization of polymeric materials [9–11]. The plasmonic heating from a single nanoparticle is efficient to supply a high heat-flux to a given point in a targeted material and thus suitable for those applications. At the same time, the heat generated from the single nanoparticle exhibits diffusion toward an edge of the material thereby unavoidably creating a monotonic and broad radial gradient of temperature, $\partial T/\partial \boldsymbol{r}$ (<0), according to the boundary conditions at the material edge.

In relation to this broad temperature gradient, we note that a planar lattice of metal domains could serve as a periodic source of heat thereby creating a periodic temperature field associated with a steep periodic gradient, given that the lattice has a small spacing (in the μm scale). This steep and periodic gradient could serve as a driving field for concentrating/manipulating temperature-sensitive molecules (having non-zero Soret coefficients [19–21]), in particular for those favoring low temperatures, given that the gradient is created in a controlled way.

* Corresponding author.
E-mail address: shimadar@fc.jwu.ac.jp (R. Shimada).

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Thus, we have conducted simple heat-transfer analysis for a lattice of metal domains to check if their plasmonic heating can create the desired, steep and periodic temperature gradient. For comparison, the gradient created by heat from a single domain was also examined. It turned out that an adequate choice of the boundary condition indeed allows the lattice of the metal domains to create the steep and periodic gradient. We also made a preliminary experiment for a model lattice of silver domains (prepared with the nanosphere lithography method [22]) to confirm the creation of such a large, roughly periodic temperature gradient of the order of 10^3 K/mm due to the plasmonic heating.

2. Heat-transfer analysis

2.1. Basic formulation

We consider the geometry of plasmonic heating shown in Fig. 1. On a top surface of a substrate at a height $z = z_h$, the plasmonic heating domains (spots) are located on a rectangular lattice of the spacing $2L$. This rectangular lattice is different from a hexagonal lattice used in the preliminary experiment (explained later), but the effect of the periodicity of the heating lattice on the temperature gradient can be clearly examined also for the former type of the lattice (that is simpler to analyze than the latter).

A material of our interest (that is, in our final goal, solutions of temperature-sensitive molecules in adequate solvents) occupies the volume between the top surface of the substrate (at $z = z_h$) and a thin, upper wall placed at $z = z_b$. Time (t) evolution of the local temperature $T(\boldsymbol{r}, t)$ at a spatial position $\boldsymbol{r}(= (x, y, z)^+)$ is described by a standard heat transfer equation containing the heat source term $\Theta(\boldsymbol{r})$,

$$C(\boldsymbol{r})\frac{\partial T(\boldsymbol{r},t)}{\partial t} = \frac{\partial}{\partial \boldsymbol{r}}\{\kappa(\boldsymbol{r})\frac{\partial T(\boldsymbol{r},t)}{\partial \boldsymbol{r}}\} + \Theta(\boldsymbol{r}) \quad (-\infty < x,\ y < \infty,\ 0 < z < z_b) \tag{1}$$

$C(\boldsymbol{r})$ and $\kappa(\boldsymbol{r})$, respectively, denote the heat capacity *per* unit volume and the thermal conductivity at the position $\boldsymbol{r}$. For simplicity, we hereafter assume that C and κ are the same in the entire space of $-\infty < x,\ y < \infty$ and $0 < z < z_b$, that is, the same for the material of our interest and the substrate. The analysis can be refined by introducing $\boldsymbol{r}$ dependence for $C(\boldsymbol{r})$ and $\kappa(\boldsymbol{r})$ [1], if necessary. This refinement is discussed in Appendix I: It turned out that the difference of κ between the substrate and material *formally* serves a hypothetical, "extra" heat source and this extra source tends to reduce the temperature gradient *if* κ is larger in the substrate. However, even for such cases, the large temperature gradient can be still created by increasing the domain spacing, as shown in Appendix I.

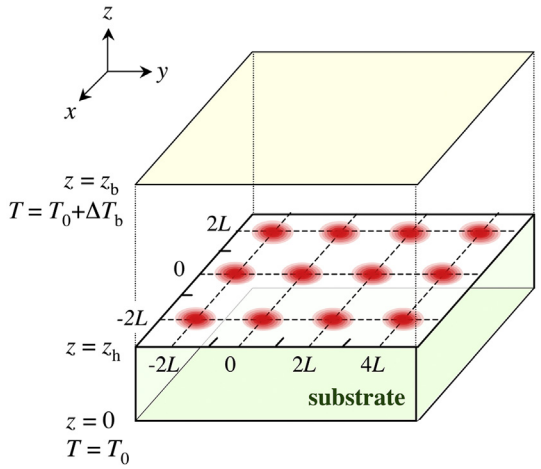

Fig. 1. Geometry of plasmonic heating lattice.

The plasmonic heating domain in our model occupies a certain area in the x-y plane (not a point), as is the case for an actual lattice explained later. Considering this area but neglecting the domain height ($<< z_b - z_h$), we model the heat source term as

$$\Theta(\boldsymbol{r}) = 0 \ \text{(no plasmonic heating) at } t \le 0 \tag{2a}$$

$$\Theta(\boldsymbol{r}) = \theta\delta(z - z_h)Q(x,y) \quad \text{(constant flux heating) at } t > 0 \tag{2b}$$

$Q(x, y)$ indicates the plasmonic heating power distribution (*i.e.*, domain shape), and θ represents a heat-flux density from unit area of the domain at $t > 0$: For the case of plasmonic heating, θ is a parameter that includes an effect of interference of the electric fields emerging at surfaces of the neighboring domains; θ is proportional to the light power (UV light power in our experiment explained later) and adsorption cross-section of the metal in the domain unless the light power is too large, as suggested from a linear relationship experimentally observed between the light intensity and the increase of temperature [12–14]. (This increase of temperature is proportional to θ; cf. Eqs. (12b), (13b) and (18) combined with Eq. (24d) shown later.) If the light power is too large, the plasmonic resonance efficiency is saturated to induce downward deviation of the increase of temperature from this linear relationship, as also noted from experiments [13,14].

At $t > 0$, we keep the temperatures at the substrate bottom and the top wall (material surface) at T_0 and $T_0+\Delta T_b$, respectively. This gives the boundary conditions for Eq. (1),

$$T(x,y,0,t) = T_0 \ \ (t > 0) \tag{3a}$$

$$T(x,y,z_b,t) = T_0 + \Delta T_b \ \ (t > 0) \tag{3b}$$

In addition, we assume that the temperature in the system at $t \le 0$ is uniform and kept at T_0. This gives the initial condition,

$$T(\boldsymbol{r}, 0) = T_0 \tag{4}$$

2.2. Calculation

As can be clearly noted from Fig. 1, the system of our interest has the translational symmetry in the x and y directions with the periodicity of $2L$ to satisfy the zero-gradient conditions,

$$\frac{\partial T}{\partial x} = 0 \ \text{at}\ x = \alpha L, \quad \frac{\partial T}{\partial y} = 0 \ \text{at}\ y = \alpha L \quad (\alpha = \text{integer}) \tag{5}$$

Thus, $T(\boldsymbol{r},t)$ can be Fourier-expanded with respect to cosine functions, $\cos(p\pi x/L)$ and $\cos(q\pi y/L)$, so as to simplify the calculation. Specifically, we focus on a deviation of the temperature from the bottom of the substrate, $\Delta T(r,t) \equiv T(r,t) - T_0$, and expand it as

$$\Delta T(\boldsymbol{r},t) = \sum_{p,q\ge 0} A_{pq}(t,z)\cos\left(\frac{p\pi x}{L}\right)\cos\left(\frac{q\pi y}{L}\right) \tag{6}$$

Combining Eqs. (1) and (2) with Eq. (3) and making Fourier cosine integral in the range of $0 < x, y < 2L$, we can easily find the time evolution equation for the expansion coefficients A_{pq} appearing in Eq. (6):