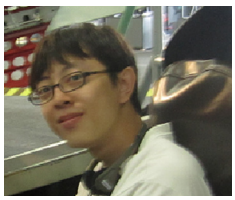
Science Progress (2013), 96(1), 1–18
Doi: 10.3184/003685013X13592844053451

Optical trapping of nanoparticles by ultrashort laser pulses

ANWAR USMAN, WEI-YI CHIANG and HIROSHI MASUHARA

Dr Anwar Usman gained his PhD from Tohoku University (Japan), and extended his researches in several places including Universiti Sains Malaysia, Max-Born-Insitut für Kurzzeitspektroskopie im Forschungsverbund Berlin, Osaka University, and École Normale Supérieure de Chimie Paris. He is now a research fellow working with the Masuhara group in the Laser Bio/Nano Science Laboratory of National Chiao Tung University, which is supported by a project on laser trapping accompanying photochemical and photophysical processes financed by National Science Council of Taiwan. E-mail: usman@faculty.nctu.edu.tw



Wei-Yi Chiang is a PhD student in the Department of Applied Chemistry, National Chiao Tung University. His research is supported by a project operated in the Masuhara group. He is carrying out research on laser trapping with femtosecond laser pulses on target particles ranging from dielectric nanoparticles, nanocrystals, and quantum dots.
E-mail: dominik.ac99g@nctu.edu.tw

Dr Hiroshi Masuhara graduated from Tohoku University (1966) and obtained his PhD degree from Osaka University (1971). After his retirement from Osaka University, he joined the Department of Applied Chemistry and Institute of Molecular Science of the National Chiao Tung University in Taiwan as a Chair Professor. He is foreign fellow of the National Academy of Sciences India and of the Royal Flemish Academy of Belgium and received the Asian Photochemistry Association Award (2012), the Medal with Purple Ribbon of the Japanese Government (2008), the Porter Medal (2006), Chemical Society of Japan Award (2006), Osaka Science Prize (1994), and Moet-Hennessy-Louis-Vuitton International Prize "Science for Art" Da Vinci of Excellence (1993). He has published more than 500 papers and 19 books and is now extending his seminal researches on (1) laser-induced crystallisation of molecules and proteins and (2) exploration of new laser-induced molecular phenomena by time-resolved spectroscopy and imaging. He may be contacted at Department of Applied Chemistry, National Chiao Tung University, 1001 Ta Hsueh Road, Hsinchu 30010, Taiwan. E-mail: masuhara@masuhara.jp

ABSTRACT

Optical trapping with continuous-wave lasers has been a fascinating field in the optical manipulation. It has become a powerful tool for manipulating micrometer-sized objects, and has been widely applied in physics, chemistry, biology, material, and colloidal science. Replacing the continuous-wave- with pulsed-mode laser in optical trapping has already revealed some novel

phenomena, including the stable trap, modifiable trapping positions, and controllable directional ejections of particles in nanometer scales. Due to two distinctive features; impulsive peak powers and relaxation time between consecutive pulses, the optical trapping with the laser pulses has been demonstrated to have some advantages over conventional continuous-wave lasers, particularly when the particles are within Rayleigh approximation. This would open unprecedented opportunities in both fundamental science and application. This Review summarizes recent advances in the optical trapping with laser pulses and discusses the electromagnetic formulations and physical interpretations of the new phenomena. Its aim is rather to show how beautiful and promising this field will be, and to encourage the in-depth study of this field.

Keywords: *optical trapping, optical manipulation, continuous-wave lasers, laser pulses, micro- and nano-sized particles, geometrical-optics and Mie regimes, Rayleigh approximation, optical Lorentz force, attractive and repulsive optical forces.*

1. Introduction

It has been more than four decades since the first experimental demonstration of a stable trap in micrometre-sized particles by a single continuous-wave (cw) laser beam.[1] The basic concept of optical trapping is the employment of a tightly focused beam into a diffraction-limited size to produce a steep gradient light intensity, which is responsible to generate optical gradient forces or trapping potential wells.[1-4] This non-invasive technique (termed as optical trapping or optical tweezers)[5] is not only useful to confine but also to move micro-scale objects to desired positions in three-dimensional space; hence, it has become an indispensable tool to immobilise and manipulate single particles or cellular organelles.[6-10] Therefore, since its invention, optical trapping has been showing tremendous, consistent, and increasing impacts on many research areas in physics, chemistry, biology, and materials science.[4,10-14] Potential applications of laser trapping have received much attention particularly in particle deposition,[15-19] particle aggregation,[3,4,20-22] polymerisation,[23] and crystallisation of organic compounds.[14,24-29] For the latter, in particular, this topic is reviewed in detail by Sugiyama *et al*.[14] On the other hand, optical trapping of biological particles extends from living cells,[30,31] bacteria,[32,33] viruses,[30] DNA strains,[34,35] to proteins.[36] These have been reviewed by Moffitt *et al*.[37]

With the idea that the momentum change of light scattering can generate forces on small objects, laser trapping has also been applied to trap target particles with diameters down to the few tens of nanometres scale, such as fluorescent macromolecules,[38] dielectric nanospheres,[5,13] carbon nanotubes,[39] semiconductor nanowires,[40] and metallic nanoparticles.[7,41-49] Reducing the size of the target particle results in an abrupt decrease in the optical gradient force, a shallower trapping potential well, and a higher intrinsic thermal diffusion coefficient. All these effects lead the particle to delocalise and escape from the optical trap; hence, conventional optical trapping is limited to particle sizes for stable traps.[4,5,10,38] The minimum potential depth of ~10 k_BT (where k_B is the Boltzmann constant and T is the absolute temperature in the trap) is usually required to overcome thermal diffusion.[5,50] Both a stronger optical gradient force and a deeper trapping potential well can be achieved by increasing either the intensity of the incident cw beam or the steepness of its gradient. These two approaches, however, are extremely limited by the laser and optical systems. Although, plasmonic effects of metallic nanostructures have been introduced to increase the gradient of the laser intensity, and with these effects a few tens of nanometre-sized polystyrene beads, quantum dots, or even proteins can be

optically trapped by incident cw lasers with the power density as low as 0.1 W cm^{-1},[2,51-53] temperature elevation effects remain a key issue in the nanostructures.[54]

An important step in the development of the optical trap is the utilisation of ultrashort laser pulses instead of cw lasers. Such laser pulses have been demonstrated to be able to control the crystal polymorph of glycine,[55,56] to trap a few nanometre-sized quantum dots,[57] and to manipulate the dimensions and crystalline properties of nanodeposits.[58] Furthermore, optical trapping with laser pulses revealed several new phenomena, which cannot be induced when the trapping beam is a cw laser, particularly when the dimensions of the target particles are much smaller than the incident wavelength.[57,59,60] This article may not cover the full area of laser trapping, but it will give readers an overview of the growing and future challenges in this topic, particularly optical trapping with ultrashort laser pulses. It is organised as follows; in the next section we explain in brief the basic principle, experimental, and theoretical concept of optical trapping with cw lasers. We follow this by a discussion of the optical trapping of single particles or biological molecules that has been achieved by employing nanostructures. We then discuss the novel phenomena attributed to optical trapping experiments with ultrashort laser pulses. By describing nonlinear optical effects and three-dimensional optical forces exerted on dielectric particles in the trapping site that have been performed,[59,60] we give particular emphasis to the electromagnetic formulations of the optical forces and physical interpretations of the new phenomena. With these interpretations, we propose a new concept of the optical trap for ultrashort laser pulses. Finally, we describe their possible future applications to challenging themes in the field of optical trapping, such as optical manipulation of biological molecules, single particle trapping, and dynamics and sorting of Rayleigh particles driven by laser pulses.

2. Optical trapping

2.1. The principles of optical trapping

The key point of the laser trapping phenomenon is the light–matter interaction accompanied with a change in photon momentum that generates attractive and repulsive optical forces. For particles with dimensions in the order of the laser trapping wavelength or larger, namely they are in the geometrical-optics or Mie regimes, the refraction of the light field at the surface of a dielectric sphere results in gradient forces.[5] As long as the refractive index of the particle is higher than its surrounding fluidic medium where it is suspended, the gradient force attracts the particle towards the highest light intensity. In addition, reflection of the light field generates a scattering force that pushes the particle in the direction of light propagation. The spatial gradient of the light intensity is one of the key factors to determine the magnitudes of the gradient and scattering forces as well as the equilibrium position of the particle in the trapping site.

On the other hand, for particles with sizes being sufficiently smaller than the wavelength of the laser trapping beam, the Rayleigh approximation is applied.[3,5,7,50,61] With this approximation, the optical forces exerted on the small dielectric sphere can be calculated by treating the particle as a point dipole that minimises its energy in the light field gradient. The attractive force is associated with the Lorentz force acting on the dipole, whereas the repulsive forces are associated with momentum transfer or absorption of the electromagnetic wave due to the scattering or absorption by the particle, respectively.[3,5,7,50,61,62]

Irrespective of the dimensions of the target particles, optical traps involve the balance of the attractive and repulsive forces.[5] The magnitudes of the attractive and repulsive forces are basically determined by the laser power, as they are proportional to the light intensity, and optical properties of the trapped particles. More detailed information on the basic principles of optical trapping is given in the excellent reviews by Molloy *et al*.[12] or Dholakia *et al*.[13]

2.2. Experimental setup

The optical trapping setup which is based on a microscope system has been addressed in many reported works.[1,4,5] Briefly, a monochromatic laser beam is tightly focused at normal incident to a sample cell mounted on the microscope stage. Since the steepness of the gradient light intensity determines the strength of the gradient force and ensures a three-dimensional confinement, a spatially collimated and a tightly focused light beam are required. To achieve such a condition, a high-magnification microscope objective lens with a high numerical aperture (NA) is necessary. A sensitive detection of the position of the particle in its trapping site is also a key feature of the optical trapping experiments. The detection system varies from micro-imaging to micro-spectroscopic techniques, and the information at the trapping site is collected and detected either through a condenser lens or via the same objective lens.[3,4,12,13,49]

We should note that the utilisation of a high NA objective leads to several consequences. Firstly, in the focal spot, the electric field of a linearly polarised incident beam is distributed into the transverse and longitudinal components, and the distribution of their intensities are determined by the NA.[63,64] In Section 3.3, we will discuss that, with the transverse and longitudinal fields, the objective lens can be used as a handle to control the trapping behaviour of the Rayleigh particles. Secondly, a higher NA corresponds to a higher divergence angle and a shorter working distance of the focused beam. Since the working distance is typically within a few hundreds of micrometres, and since the sample cell itself consists of 130-μm-thickness coverslips, the trapping position is restricted to 100–200 μm inside the sample cell.

2.3. The basic theory

As mentioned above, optical trapping should be based upon the interaction between the focused light with the particle. Electromagnetic theory is therefore obviously the preferred approach to obtain quantitative descriptions of the optical forces exerted on the particles. By considering the relative particle size with respect to the incident wavelength, in principle, we can adopt two distinct approaches, namely the ray optics treatment for particles in the geometrical-optics or Mie regimes and the perturbative formulation for particles in the Rayleigh regime.[5] Here we will take a brief look at a description of optical trapping based on both approximations.

With the ray-optics treatment, the attractive force acting on a transparent object is related to the change in photon momentum of the trapping beam due to refraction by the particle.[61] The force F is given by[61,65]

$$F = Q\frac{n_m P}{c} \tag{1}$$

where n_m is the refractive index of the surrounding medium, P is the laser power, c is the speed of light, and Q is a dimensionless quantity which is related to the configuration of the trapped object.[61] In other words, the Q value, which has been accurately estimated to be around 0.03–0.2,[12,65] is a measure of the coupling between the optical momentum of the trapping light field and the trapping force exerted on the object. Thus, the Q value is also related to the trapping efficiency of the particles in the geometrical-optics or Mie regimes. For the case of a tightly focused light impinging on the particles in the Rayleigh regime, the attractive force is associated with the Lorentz force of the dipole in the electric field, while the scattering and absorption forces are related to the scattering and absorption process of the electromagnetic wave by the dipole.[2,50,62] The optical forces are given by[2,50,62]

$$\vec{F}_{Lorentz} = \left[\vec{P}.\vec{\nabla}\right]\vec{E} + \alpha\mu_0\partial_t\left\langle\vec{E}\times\vec{H}\right\rangle \tag{1a}$$

$$\vec{F}_{scattering} = (n_m\sigma_p / c)\left\langle\vec{E}\times\vec{H}\right\rangle \tag{1b}$$

$$\vec{F}_{absorption} = (n_m\sigma_a / c)\left\langle\vec{E}\times\vec{H}\right\rangle \tag{1c}$$

Here, $P = \chi^{(1)}E + \chi^{(2)}EE + \chi^{(3)}\ EEE + ...$ is the light-induced polarisation; $\chi^{(1)}$, $\chi^{(2)}$, $\chi^{(3)}$ are the linear and nonlinear susceptibilities. The linear susceptibility is expressed as $\chi^{(1)} = n^2{}_m\varepsilon_0\alpha$, where $\alpha = 4\pi\alpha^3[((n_p / n_m)^2 - 1)/((n_p / n_m)^2 + 2)]$ is the real part of the polarisability, α is the radius, n_p is the refractive index, and $\sigma_p = k^4|\alpha|^2 / 6\pi$ and $\sigma_a = k\alpha$" are the scattering and absorption cross-sections of the individual particles, respectively. In these expressions, $k = 2\pi n_m / \lambda$ is the wavenumber in the medium, λ is the wavelength, α" is the imaginary part of the polarisability, E and H are the electric and magnetic fields of the laser light, and ε_0 and μ_0 are the vacuum permittivity and permeability, respectively. It is apparent that the directions of the optical forces are governed by the vectors of the electric field and the wavefront of the incident light. As the linearly-polarised light, tightly focused by a high NA objective lens posseses orthogonal field components in the focal spot,[64] the distribution of the transverse and longitudinal component fields, and not just the intensity of the incident light field, should be taken into account.

Notably, since conventional optical trapping experiments employ monochromatic cw laser sources, temporal dependence does not become an issue and the second term in Eqn (1a) is naturally neglected. For isotropic particles with negligibly low nonlinear susceptibilities, the gradient force is equivalent to the spatial Lorentz force and it can therefore be written as,[2,50,66]

$$\vec{F}_{gradient} = \frac{1}{2}n_m^2\varepsilon_0\alpha\vec{\nabla}\left|E\right|^2 \tag{2}$$

As $|E|^2$ is proportional to the light intensity, the force depends on the polarisability and gradient of the light intensity. For an incident beam linearly polarised along the x-axis, the electric field of the beam is expressed as

$$E_x = E_0\frac{i}{i+2\zeta}\exp\left[i(\omega_0 t - kz - \frac{2\zeta\rho^2}{1+4\zeta^2})\right]\exp\left[-\frac{\rho^2}{1+4\zeta^2}\right] \tag{3}$$

where E_0 is the electric field at the central intensity peak, $\rho^2 = \xi + \eta^2$, $\xi = x / w_0$, $\eta = y / w_0$, and $\zeta = z / kw_0^2$ are the normalised spatial coordinates in the focal spot, w_0 is the beam

waist, and ω_0 is the carrier frequency of the beam. By substituting Eqn (3) into Eqn (2), the gradient force can be written as:

$$\vec{F}_{gradient} = -\hat{x}\frac{\xi}{(1+4\zeta^2)^2}\frac{n_m^2\varepsilon_0\alpha E_0^2}{w_0}\times e^{-\frac{2(\xi^2+\eta^2)}{(1+4\zeta^2)}} \quad (4)$$

In Figure 1, panel (a) shows $F_{gradient}$ as a function of ξ, indicating that it acts as a restoring force to attract the particles from the radial distances up to a few times of the beam waist to the focal point. Thus, it is likely to create a trapping potential well within which the particle is trapped. Such a potential trapping well in the area around the focal spot is related to the potential energy of the polarisation in the electric field;

$$U_{trap} = -\left\langle \vec{P}.\vec{E} \right\rangle = -n_m^2\varepsilon_0\alpha E_x^2 \quad (5)$$

The plot of U_{trap} as a function of ξ is also shown in Figure 1 (panel (b)).

Although the optical trapping process can be considered as acting as a transducer of light forces to micro- and nano-sized particles to attract them to the focal point, it is always confronted with the issue of Brownian motions that can expel the particle out of the trapping site. A trap is considered to be stable when the potential trapping well is deep enough to overcome the kinetic energy of the particles due to Brownian motion. Practically, the optical forces exerted on the particle can be treated as if it works as a microscopic spring, and the potential trapping well can be approximated as harmonic. With this approximation, the optical gradient force is proportional to the displacement of the particle from the beam centre, and the stiffness of optical trap (κ) is used as the parameter related to the equilibrium between the optical, viscous, and Brownian forces.[12,13] For particles in geometrical-optics or Mie regimes, typically, the κ value is inversely proportional either to the particle size[67] or to the NA of the objective lens.[68] The κ is of the order of 1.6×10^{-4} N m^{-1} W^{-1} for polystyrene microparticles,[67] 2.4×10^{-3} N m^{-1} W^{-1} for quantum dots,[69] and 4.1×10^{-3} N m^{-1} W^{-1} for gold or silver particles.[43]

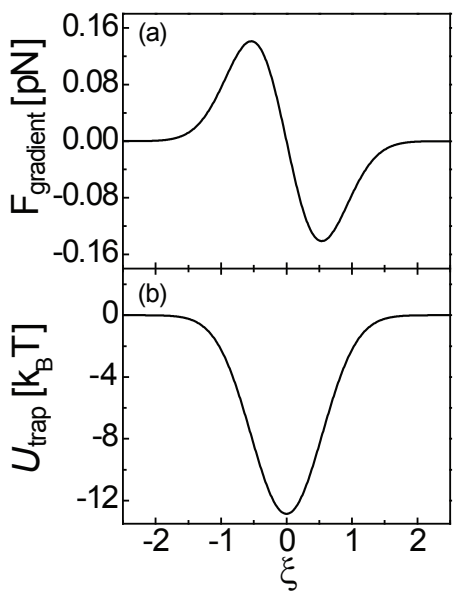


Figure 1 *Plots of (a)* $F_{gradient}$ *[Eqn (4)], and (b)* U_{trap} *[Eqn (5)] as a function of* ξ *for isotropic spherical dielectric nanoparticles under focused cw lasers.*

In the work by Ashkin *et al.*,[5] the necessary potential depth to compensate the stochastic kicks of the particle out of the trapping site due to thermal Brownian motion has been established to be ~10 k_BT. With such a criterion, one can estimate the smallest limit of the particle size in optical trapping experiments. For example, by using a power of sub-W level of the focused beam close to the limiting spot diameter of 1 μm, the minimum sizes of metallic or dielectric polystyrene particles that can be trapped are about 10–20 nm.[5,48,50] However, such a criterion for a stable trap is not applicable for optical trapping experiments with ultrashort pulsed lasers, as will be addressed in detail in Section 3.4.

2.4. Optical trapping of single particles

Optical trapping that can precisely manipulate the target particles on the micrometre or nanometre scales has opened up a new area of researches in so-called micromanipulation. Though 10–20 nm-sized metallic or dielectric polystyrene particles can be trapped by conventional optical trapping with cw lasers,[5,48,50] to achieve stable traps the minimum particle size of biological objects is about the size of living cells,[31] bacteria,[32] or viruses.[32] For smaller sizes, such as DNA, tethering the biomolecules to microparticles is required.[34,70] Since conventional optical trapping of single particles, molecules, or biomaterials without tethering to a bead is restricted by the minimum size of the objects,[4,5,10] several approaches have been developed to overcome this size limit as well as to increase the trapping efficiency. Among the different approaches, the utilisation of surface plasmonic effects based on gap-mode-excitation of adjacent metallic nanoparticles and the use of a double-nanohole on a gold-thin-film substrate have been of interest for applications.[51,54,71,72] The bottom line of these approaches is to increase the steepness of the gradient of the electromagnetic field at the focal spot. By exploiting the surface plasmonic field at the nanogap between adjacent metallic nanoparticles of a patterned substrate that localises the incident field beyond the diffraction limit known as hot spots,[73-75] small target particles can be trapped.[71,72,76-78] The size limit then has been reduced down to the nanometre-scales, such as single fluorescent molecules,[76] *Escherichia coli* bacteria,[78] or 10-nm-sized quantum dots.[72] With a tip separation of 15–30 nm, optical trapping of a 12 nm silica sphere or a single protein molecule has been demonstrated.[52,53] By simultaneously reducing the limit size and strengthening the local optical fields, the surface plasmonic effects in the optical trapping with cw lasers become powerful for nanobioimaging,[79] stacking,[80] and nonlinear optical imaging.[81]

Since the laser power necessary to trap a particle is inversely proportional to the fourth power of the particle size, there remains the difficulty of trapping single nanometre-sized dielectric particles, although the particle itself has been shown to have a positive role in the trapping.[51,82,83] In addition, metallic nanostructures themselves strongly absorb the photon energy. This causes the temperature around the focal spot to increase,[84] and such photothermal effects should increase the diffusion of the nanoparticles and destabilise the optical trap.[44]

3. Optical trapping with ultrashort laser pulses

3.1. Substituting cw- with pulsed-mode lasers

As laser trapping has become a key tool in the field of micromanipulation, an aim should be to manipulate single nano-sized particles. The obvious requirement is to utilise a steep and intense light field at the focal spot. Thus, one may ask the question: can we use laser pulses to replace cw lasers? Such a question reflects the fact that the peak powers of laser pulses can generate a very intense light field;[85] hence, a steep gradient at the focal spot can be achieved.

The first uses of nano- or femto-second (ns or fs) laser pulse irradiations were reported in 1996 in the laser-induced crystallisation of urea.[86] This was followed by laser-induced crystallisation of glycine[55] and laser-induced crystal growth of 4-dimethylamino-N-methyl-4-stilbazolium tosylate in 2002.[87] Then, this method was applied in the fs laser pulse-

induced crystallisation of lysozyme, where protein crystals were obtained by the focused light irradiation from normally unfavourable conditions for spontaneous crystallisation.[88] These results indicate that focused laser irradiation with intense ultrashort laser pulses opens a new approach to generate nuclei of organic compounds or protein crystals and to grow them into sizeable crystals. On the other hand, the optical forces of microsecond laser pulses have been applied in the optical levitation and manipulation of microscopic particles that are stuck on a glass surface.[89]

The optical trapping of dielectric particles by fs laser pulses was started with the trapping of a 1.28-μm silica sphere.[90] In this study, the highly repetitive laser pulses were demonstrated to have an ability to trap the microscopic particle equal to that of cw lasers. This finding offered the conclusion that the average power, rather than peak power, is the key parameter for laser trapping.[90] The advantage of laser pulses over cw lasers, however, was realised for the first time when picosecond (ps) laser pulses at a laser power as low as 100 mW could stably trap 3.3-nm-sized quantum dots, which cannot be achieved by cw lasers as this would require a laser power of more than 20 W to induce similar optical trapping.[57] This provided a hint that optical trapping with laser pulses would be fruitful and give some advantages when the target particles are in the Rayleigh regime.[57] This idea has been supported by our recent work in which we have shown that larger numbers of the 50-nm-sized polystyrene or silica spheres are optically trapped upon replacing a cw- with an fs pulse-mode laser as the trapping beam.[60,91]

3.2. Nonlinear optical effects

A distinctive advantage offered by ultrashort laser pulses is that high impulsive peak powers can induce nonlinear optical (NLO) processes in the trapped particles. The first experimental observation was the fs laser trapping-induced two-photon fluorescence of optically trapped dye-doped microscopic polystyrene beads; and such two-photon fluorescence was absent when using a cw laser.[90] The most astonishing behaviour of the NLO effects, however, is the splitting of the trapping site of gold nanoparticles into two off-axis positions parallel to the laser polarisation.[59]

Electromagnetic formulations of the optical forces have been the key to detailed understanding of laser trapping with ultrashort laser pulses. To avoid complexity, the formulations of the NLO effects have been limited to the impulsive peak powers of the laser pulses and the NLO properties of the trapped particles. In this case, considering a nonzero third-order susceptibility of light-induced polarisation, one can rewrite the gradient force related to the spatial Lorentz force in Eqn (1b) as,[59]

$$\vec{F}_{grad} = \frac{1}{2}\alpha\vec{\nabla}\left\{1-(4/3)\tilde{a}\left|E\right|^2\right\}E^2 \tag{6}$$

where $\tilde{a} = -(3/4)\,\chi^{(3)} / \chi^{(1)}$. Here, the time-dependent electric field along the x-axis is given by,[50,92]

$$E_x = E_0\frac{i}{i+2\zeta}\exp\left[i(\omega_0 t - kz - \frac{2\zeta\rho^2}{1+4\zeta^2})\right]\exp\left[-\frac{\rho^2}{1+4\zeta^2}\right]\exp\left(-\frac{t^2}{\tau^2}\right) \tag{7}$$

where τ is the pulse duration. By substituting $E_x$of Eqn (7) into Eqn (6), we obtain the gradient force as given by

$$\vec{F}_{gradient} = -\hat{\mathbf{x}}2\alpha n_m \varepsilon_0 c|E_x|^2 \left\{\left[2\xi/\omega_0 - K^2\xi/\omega_0 + 2K^2\xi^3/\omega_0\right] + \right.$$
$$\left. + 4\tilde{a}\,\alpha n_m \varepsilon_0 c|E_x|^2 \left[2\xi/\omega_0 - K^2\xi/\omega_0 + 4K^2\xi^3/\omega_0 - 2K^4\xi^3/\omega_0 + K^4\xi^5/\omega_0\right]\right\} \quad (8)$$

The trapping potential well is expressed as

$$U_{trap} = -\frac{1}{2}\alpha\left\{\left(1+K^2\xi^2\right)|E_x|^2 - \tilde{a}\left(\left[1+K^2\xi^2\right]|E_x|^2\right)^2\right\} \quad (9)$$

In Figure 2 panels (a) and (b), the $F_{gradient}$ and U_{trap} of Eqns (8) and (9) are plotted against ξ for different values of $\tilde{a}|E_x|^2$. The curvature of $F_{gradient}$ and U_{trap} are modified as $\tilde{a}|E_x|^2$ increases. For $\tilde{a}|E_x|^2 > 0.5$, the trapping site is no longer a single spot at the focal centre, but it splits into two off-axis positions as there are two minima parallel to the incident polarisation direction (x-axis).[59] Since this finding, such utilisation of laser pulses has opened new horizons in both the fundamental science and application of optical trapping.

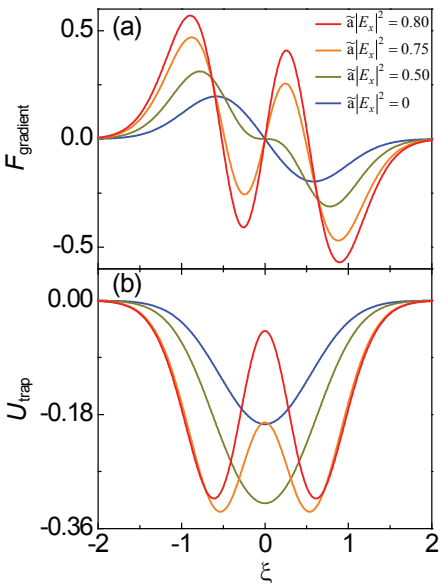


Figure 2 *NLO effects in optical trapping; (a)* $F_{gradient}$ *[Eqn (8)], and (b)* U_{trap} *[Eqn (9)] plotted against the distance* ξ *for different values of* $a|E_x|^2$ *, when spherical gold nanoparticles are trapped by the laser pulses.*

3.3. Three-dimensional attractive and repulsive optical forces

One of the very recent findings in the field of optical trapping based on ultrashort laser pulses is our report on the optical trapping and directional ejections of nanoparticles.[60] In our experiment with tightly focused 800 nm laser pulses, 50-nm sized polystyrene beads were optically trapped and ejected in the directions perpendicular to the laser polarisation. This experimental observation of a unique feature driven by laser pulses has been beyond theoretical elucidation of optical trapping hitherto. As this is a fundamentally different phenomenon from that generally regarded as a stable trap by a focused cw laser beam, we have to consider that, as compared with the cw laser the utilisation of impulsive peak powers

in optical trapping actually induces much more complicated three-dimensional optical controls. Although the one-dimensional field along the laser polarisation is sufficient to explain the trapping behaviour of gold nanoparticles, in the case of the directional ejections of nanoparticles, it is important to take the transverse and longitudinal fields that coexist at the trapping site into account. In addition to the optical gradient, the second term of the Lorentz force [see Eqn (1)] is related to the instantaneous momentum transfer that induces temporal pulse radiation forces (also called temporal forces) which acts as a repulsive force.[62,92,93] As the NLO susceptibilities of the trapped dielectric particles are negligibly low, in this case we have introduced the presence of temporal forces and the transverse and longitudinal components of electric fields produced by the high NA objective lens in the electromagnetic formulations of the optical forces.[60] The transverse and longitudinal components have been derived using the paraxial approximation,[63,64] namely using the relations of $E_z = (-i / k)\partial_x E_x$ and $E_y = (1 / k^2)\partial_y \partial_x E_x$, giving

$$E_z = -KE_0 \frac{\xi(1+i2\zeta)}{(i+2\zeta)(1+4\zeta^2)} \exp\left[i(\omega_0 t - kz - \frac{2\zeta\rho^2}{1+4\zeta^2})\right] \exp\left[-\frac{\rho^2}{1+4\zeta^2}\right] \exp\left(-\frac{t^2}{\tau^2}\right) \quad (10a)$$

$$E_y = K^2 E_0 \frac{i\xi\eta(1+i2\zeta)^2}{(i+2\zeta)(1+4\zeta^2)^2} \exp\left[i(\omega_0 t - kz - \frac{2\zeta\rho^2}{1+4\zeta^2})\right] \exp\left[-\frac{\rho^2}{1+4\zeta^2}\right] \exp\left(-\frac{t^2}{\tau^2}\right) \quad (10b)$$

where $K = 2 / kw_0$.[59,64]

By combining Eqns (1), (7), and (10), we obtained expressions for the optical forces as a function of the parameters of the laser beam, spatial positions of single NPs in the focal spot, and optical properties of the NPs, as given by

$$\vec{F}_{gradient} = -\left\{\left[\hat{x}\frac{\xi}{(1+4\zeta^2)^2} + \hat{y}\left(\frac{K^4\xi^2\eta^3}{(1+4\zeta^2)^7} - \frac{K^4\xi^2\eta}{2(1+4\zeta^2)^6}\right) \times \left((1-12\zeta^2)^2 + \zeta^2(6-8\zeta^2)^2\right) + \right.\right.$$
$$\left.\left. + \hat{z}\left(\frac{4K^2\xi^2\zeta}{(1+4\zeta^2)^3} - \frac{4K^2\xi^2\zeta(\xi^2+\eta^2)}{(1+4\zeta^2)^4}\right)\right]\right\} \times \frac{n_m^2\varepsilon_0\alpha E_0^2}{w_0} \times e^{-\frac{2(\xi^2+\eta^2)}{(1+4\zeta^2)}} \times e^{-\frac{2t^2}{\tau^2}} \quad (11a)$$

$$\vec{F}_{scattering} = \left\{\hat{x}\frac{K^2\xi^2}{(1+4\zeta^2)^2} + \hat{y}\frac{K^4\xi^2\eta^2\left((1-12\zeta^2)^2 + \zeta^2(6-8\zeta^2)^2\right)}{(1+4\zeta^2)^6} + \hat{z}\frac{1}{1+4\zeta^2}\right\} \times$$
$$\times \frac{n_m^2\varepsilon_0\sigma_p E_0^2}{2} \times e^{-\frac{2(\xi^2+\eta^2)}{(1+4\zeta^2)}} \times e^{-\frac{2t^2}{\tau^2}} \quad (11b)$$

$$\vec{F}_{temporal} = \left\{\hat{x}\frac{K^2\xi^2}{(1+4\zeta^2)^2} + \hat{y}\frac{K^4\xi^2\eta^2\left((1-12\zeta^2)^2 + \zeta^2(6-8\zeta^2)^2\right)}{(1+4\zeta^2)^6} + \hat{z}\frac{1}{1+4\zeta^2}\right\} \times$$
$$\times \frac{-2n_m^3\varepsilon_0\alpha E_0^2 t}{c\tau^2} \times e^{-\frac{2(\xi^2+\eta^2)}{(1+4\zeta^2)}} \times e^{-\frac{2t^2}{\tau^2}} \quad (11c)$$

We found that the optical forces are three-dimensional. As a practical form, we have summarised the forces into three components as follows;

$$\vec{F}_x = \hat{x}F_{gradient} + \hat{x}F_{scattering} + \hat{x}F_{temporal} \quad (12a)$$

$$\vec{F}_y = \hat{y}F_{gradient} + \hat{y}F_{scattering} + \hat{y}F_{temporal} \quad (12b)$$

$$\vec{F}_z = \hat{z}F_{gradient} + \hat{z}F_{scattering} + \hat{z}F_{temporal} \quad (12c)$$

Figure 3 shows the spatio-temporal maps of the $\vec{F}_x$, $\vec{F}_y$, and $\vec{F}_z$ components exerted on a 50-nm-sized polystyrene bead optically trapped with laser pulses (800 nm, τ = 90 fs, 80 MHz) tightly focused by an objective lens (NA 0.90).[60] As shown in panels (a)–(e), the $\vec{F}_x$ acts as an attractive force directing the nanoparticles towards the focal point. This indicates that the gradient force overcomes completely the repulsive forces in the direction parallel to the incident laser polarisation. This is commonly observed in optical trapping experiments.[5,94] The $\vec{F}_x$ increases rapidly in the first half of the pulse envelope, reaches a maximum magnitude on the scale of nN, and then decreases in the second half of the pulse envelope. Such a transient attractive force by the fs pulsed laser is much higher than the constant pN attractive forces of cw laser beams.[1-3,49] Panels (f)–(j) show that $\vec{F}_z$ is along the positive z-axis during the first half of the pulse envelope and turns into the opposite direction in the second half. Thus, the attractive force is depleted along the

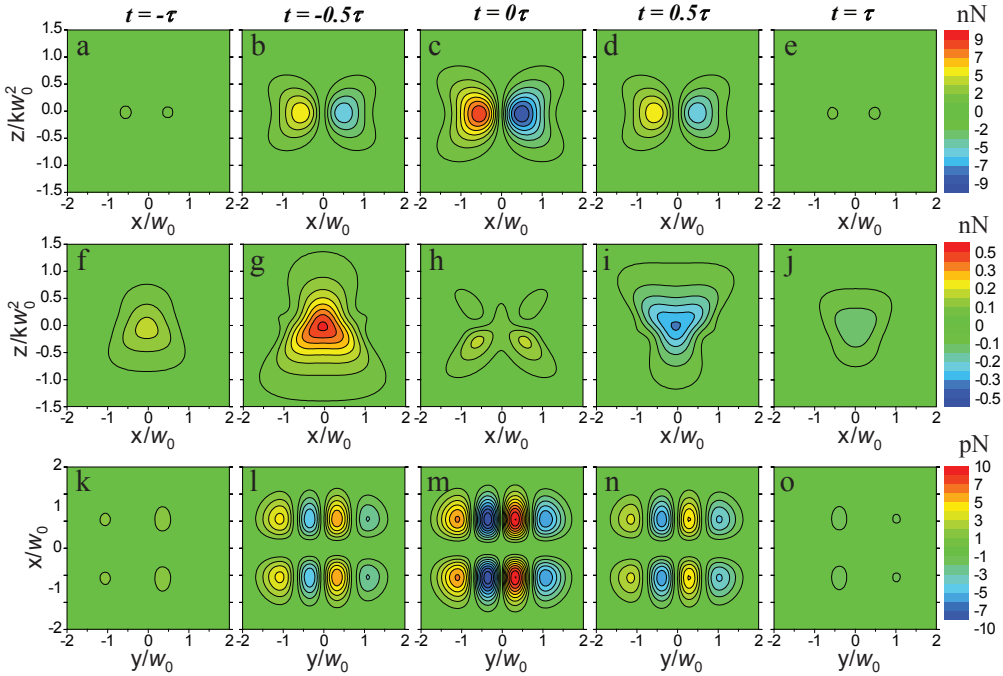


Figure 3 *Representative calculated spatio-temporal maps of optical forces exerted on polystyrene nanoparticles at the focal spot [Eqns (11)] for polarisation of the incident laser beam along the x-axis. The $\vec{F}_x$, $\vec{F}_z$, and $\vec{F}_y$ components are shown in panels (a)–(e), (f)–(j), and (k)–(o), respectively, with the scales of the forces being given at the end of each row. Each column represents the times with respect to the existence of a single pulse in the focal spot. The positive or negative values of the forces mean their directions along the positive or negative x-, y-, and z-axis, respectively.*

z-axis, and $\vec{F}_z$ acts as a repulsive force. We note that $\vec{F}_z$ is asymmetric with respect to the pulse propagation, as $\vec{F}_z$ reaches a maximum magnitude of +0.46 nN at $t = -0.5\tau$ in the first half and –0.34 nN at $t = 0.5\tau$ in the second half of the pulse envelope. Consequently, $\vec{F}_z$ is intrinsically favourable for ejection of NPs along the beam propagation. This force is therefore reasonably related to the ejection force to overcome the adhesive interaction between a polystyrene microparticle and a glass surface in optical levitation experiments.[89] As shown in panels (k)–(o), $\vec{F}_y$ is positive along the positive y-axis and negative along the negative y-axis, irrespective of its spatial position along the z-axis, indicating that $\vec{F}_y$ also acts as a repulsive force. Since the $\vec{F}_y$ is almost symmetric along the y-axis, this force should eject the nanoparticles equally along the positive and negative y-axis. Thus, the theoretically calculated forces, overall, suggest that optical trapping of dielectric nanoparticles with the ultrashort laser pulses relies solely on the attractive force along the x-axis, whereas the nanoparticles are ejected by the resultant of repulsive forces along the $\pm y$- and $\pm z$-directions, as illustrated in Figure 4. This interesting feature implies that the nanoparticles are ejected from the trapping site by two repulsive forces perpendicular to the laser polarisation. The theoretical finding of the three-dimensional optical forces at the focal spot explains fairly well the directional ejections of the nanoparticles out of the trapping site.[60]

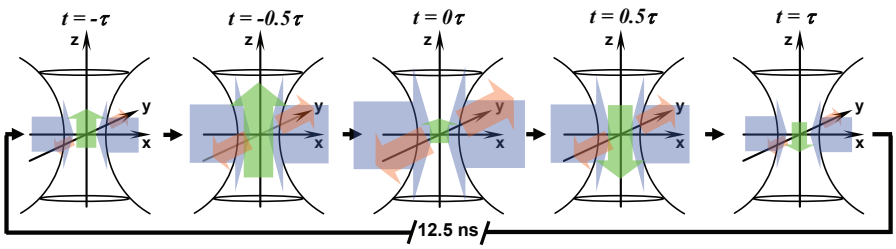


Figure 4 *Schematic illustrations of the optical forces in the focal spot during the single pulse envelope. Blue, green, and red arrows denote $\bar{F}_x$, $\bar{F}_z$, and $\bar{F}_y$ components, respectively.*

3.4. Trap stability

We recall that the optical trapping of nanoparticles relies solely on the periodical attractive force parallel to the incident laser polarisation, but they might be accelerated and pushed out of the trapping site in the directions orthogonal to the laser polarisation. Consequently, Brownian motion of the nanoparticles in the trapping site could be completely overcome by the optical forces during laser pulse irradiation, and we can neglect the criterion for a stable trap with a necessary energy of 10 k_BT.[5,50] The stiffness of the optical trap with regard to laser pulses should be therefore distinct from that with a cw laser, although further evaluation this issue is desirable and this is in progress in our laboratory.

With the concept of three-dimensional dynamics of Rayleigh particles driven by tightly focused laser pulses,[60] we note that competition between the transient attractive and repulsive forces in all directions are crucial to determine the stability and efficiency of optical traps. A stable trap can be achieved only when the repulsive forces are overcome by the attractive force or they are naturally suppressed. To achieve such conditions one could consider three consequences. Firstly, one can decrease the particle size to reduce the scattering force, as σ_p is proportional to the sixth power of the particle radius. Secondly,

expanding the pulse width will reduce the temporal pulse radiation force, which is inversely proportional to the pulse duration. Thirdly, the objective lens can act as a handle for controlling the trapping behaviour of the Rayleigh particles through the K^2 and K^4 terms [see Eqn (11)]. With the two former conditions, essentially tight and stable optical trapping of 3.3-nm-sized quantum dots by a 3.5-ps-pulsed laser has been experimentally demonstrated and evaluated in detail by Tamai's group.[57]

4. Possible future applications of optical trapping with ultrashort laser pulses

The field of optical trapping is basically multidisciplinary, involving physics, optics, and lasers.[11] The advent of optical trapping opened a new area of research on nanometre-sized objects. It has enabled us to manipulate particles with sizes from the nanoscale upwards and to provide insights into biological molecular machines.[36,95] The long journey of this field leads to its widespread applications in a large variety of fields in physics, chemistry, biology, materials, and colloidal science. Although still in its infancy, replacing cw lasers with ultrashort laser pulses as the trapping beam has already shown some fascinating behaviour in optical trapping, and it will develop optical trapping further to a new level in both fundamental science and applications.[57,59,60,91] Laser trapping with ultrashort laser pulses is characterised by two distinctive features; periodical impulsive peak powers and the relaxation time between consecutive pulses.

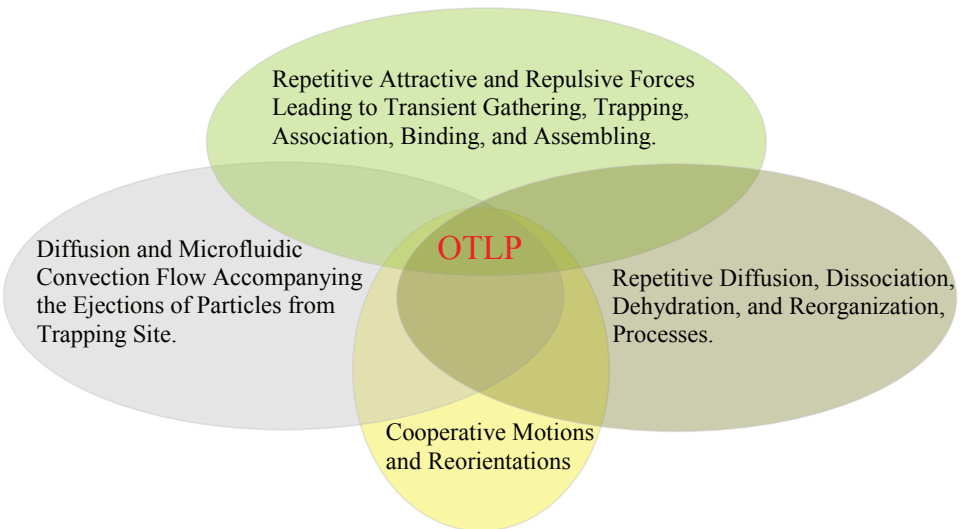


Figure 5 *Several aspects that govern the kinetic behaviour of nanoparticles around the focal spot under optical trapping with laser pulses. OTLP stands for optical trapping with laser pulses.*

In general, the optical, medium, and material effects, and their cooperation, that govern optical trapping with laser pulses are summarised in Figure 5. The periodical attractive and repulsive forces by the laser pulses dramatically influence the stability and efficiency of the optical trap. On the material side, as a large number of nanoparticles are packed in the trapping site, they may associate optically into a kind of transient assembly, as such an assembly was observed for polystyrene beads optically trapped with a cw laser.[21,22] We also have to consider that the particles ejected out of the trapping site may be accompanied by convection or microfluidic flow in the medium. One advantage offered by the laser pulses

is that the repetitive relaxation between pulses will allow the trapped particles or biological substances to relax, diffuse, dissociate, re-associate or reorganise. Since such optically-mediated particle–particle interactions (as so-called optical binding)[96] would govern their trapping behaviour and play an important role in the laser-induced organisation of the colloids, clusters, or molecules into solid-state materials, they are of interest to be explored using laser trapping with laser pulses. The other important viewpoint is that the temperature elevation or heating effect of the laser light[97,98] could be suppressed due to the dissipation of heat from the trapped particles to the surrounding fluid during the interval times, although further detailed experimental data are still desired. Optical trapping without a heating effect is an ideal condition which occurs in many experiments with biological substances with the risk of, for instance, thermally-induced cell death or protein denaturation.

Regarding the development of optical trapping with ultrashort laser pulses, it seems that the ongoing research in this subject will reveal more novel phenomena and have significant impacts in the evolving area of optical micromanipulation. The most potential advantage offered by ultrashort laser pulses is their high impulsive peak powers that will not only confine and manipulate single nano-sized particles or molecules with higher trapping ability but also induce NLO processes in the trapped particles. With the NLO processes, one can explore the effects of two- or three-photon processes in optical trapping or even optimise them to enhance the trapping abilities. The other key features to be considered is that the distribution of the transverse and longitudinal components of electric fields produced by high NA objective raises a kind of competition between the attractive and repulsive optical forces. However, the repulsive forces associated with the controllable directional ejections of the nanoparticles will be a useful tool for controlling the kinetic motions of the particles and light-driven microfluidic circulation and micromachines.[60] As the repulsive force is determined by the polarisability of the particles, one of the most promising applications of the repulsive forces is the sorting of nanoparticles driven by laser pulses, as illustrated in Figure 6(a). The sorting of the dielectric nanoparticles from their mixtures in polydisperse colloids can be based on their size and refractive index. Laser trapping can also induce phase transitions, such as if the trapped particles form aggregates with different solubility from their monomers, as illustrated in Figure 6(b).

In biology and biomedicines, similarly to conventional optical trapping with cw lasers that was quickly applied as a tool in the optical manipulation of biological substances, such as viruses, bacteria, and cells, cell organelles, proteins, and DNA,[6,8,30-36] ultrashort laser pulses have been utilised as tools for imaging based on linear and NLO processes,[99] as tweezers for single protein molecules,[53] or as optical scissors in subcellular nanosurgery.[100,101] We consider that replacing cw lasers with ultrashort laser pulses in biological applications would lead optical trapping to be more efficient in optical trapping and manipulation. Thus, one might be able to inject a single tagged molecule into a desired position inside a cell. As a tool for optical sorting in biology, laser pulses may be expected to sort different biological substances, such as red and white blood cells from a culture medium or different proteins in purification steps.

The other fascinating application in biology is the crystallisation of proteins.[55,88] Since many proteins are difficult to crystallise or the processes are time-consuming, ultrashort laser pulses would be applicable in the crystallisation of such proteins. In this case, repetitive optical pulses, which induce gathering, trapping, binding, and assembling molecular clusters coupled with diffusion, dissociation, dehydration, reorganisation, and cooperative reorientation processes[14] would be beneficial for the soluble protein molecules

in the culture medium to be sorted or crystallised *in situ*, as illustrated in Figure 6(c). Moreover, as laser trapping can precisely control the crystal polymorph, allowing one to fabricate a bulk solid organic crystal containing various crystal structures by switching different trapping beams. Such a solid crystal might be used, for instance, to optimise its phase matching conditions for NLO applications or photonic crystals.

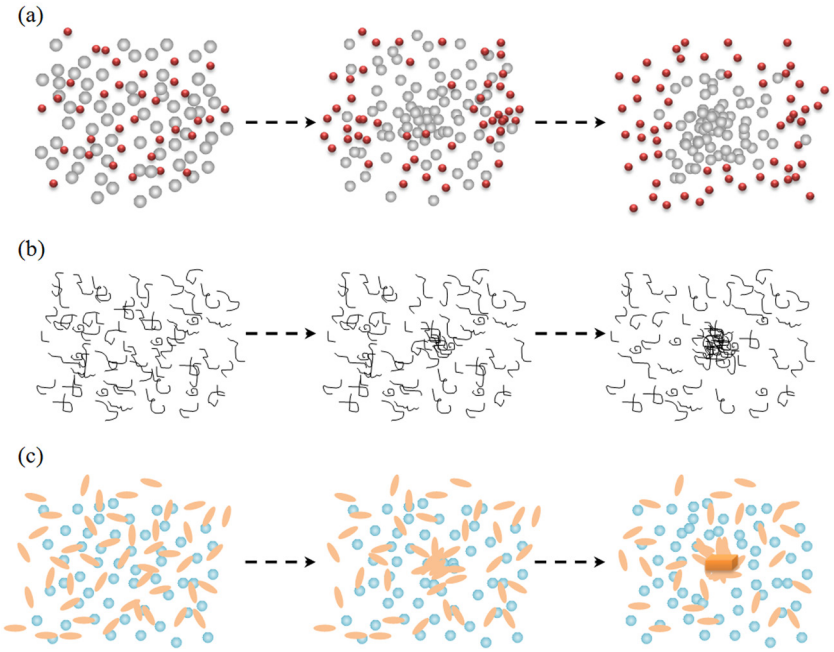


Figure 6 *Illustrations for laser trapping-induced (a) particle sorting, (b) phase transition from soluble monomer to dissoluble aggregates, and (c) gathering, trapping, binding, and assembling molecular clusters leading to crystallisation. The dashed arrows denote a large number of repetitive pulses.*

In addition to biological substances, optical trapping applications have been intensively explored for metallic particles.[7,41-43,45-49,102,103] For the latter case, scattering and absorption cross-sections operate much more strongly than for dielectric and biological particles, thus they can easily induce non-negligible scattering and absorption forces in the front of the gradient forces. Metallic nanoparticles usually have high refractive indices and NLO optical susceptibilities,[104] and their interparticle interactions can produce plasmonic field effects.[105,106] With these excellent optical properties, intensive research on the optical trapping of metallic nanoparticles with laser pulses might lead to new discoveries in optical trapping and manipulating nanometre-sized metallic particles, not just distinct optical trapping behaviours from those of dielectric particles.

Finally, we should note that theoretical modelling and numerical approaches based on a light field continuously irradiated on the target particles, play a role in understanding the basic concept of optical trapping, approximations, and the specific properties of the target nanoparticles.[2,50,66,107] Since many novel optical trapping phenomena are reported and the field of optical trapping is expanding rapidly, theoretical modelling should be developed following the experimental observations. For instance, theoretical modelling has recently been extended to involve resonance effects when the trapped nanoparticles are simultaneously excited by a one-photon process.[108-110] Such theoretical understanding

not only explained and showed some good agreement with the experimental findings,[111] but they provided detailed predictions of the resonance effects in optical trapping as well as some clues in designing experiments to optimise the effects. Despite recent progress on the optical forces and trapping potential well of laser pulses,[59,60,92,93] much theoretical and numerical work still needs to be done to take into account the periodical attractive and repulsive forces as well as the diffusion, kinetic, optical binding, association, and dissociation of the nanoparticles at and around the focal spot. The other interesting viewpoints that we also need to take into account would be the NLO effects; *e.g.* how the two- or three-photon excitation and intermolecular interactions in the excited state exert an effect on the laser trapping or even on the laser-induced organisation of the molecules into solid-state materials. All these remain a task to be done and much work needs to be accomplished in the future, but the basic ideas have already been started.

Acknowledgement

Professor H. Masuhara is grateful to the Ministry of Education of Taiwan (MOE-ATU Project; National Chiao Tung University), the National Science Council of Taiwan (Grant No. NSC 100-2113-M-009-001), and the Foundation of the Advancement for Outstanding Scholarship of Taiwan.

References

1. Ashkin, A. (1970) *Phys. Rev. Lett*., **24**, 156.
2. Tlusty, T., Meller, A., and Bar-Ziv, R. (1998) *Phys. Rev. Lett*., **81**, 1738.
3. Bartlett, P. and Henderson, S. (2002) *J. Phys.: Condens. Matter*, **14**, 7757.
4. Neuman, K.C. and Block, S.M. (2004) *Rev. Sci. Instrum*., **75**, 2787.
5. Ashkin, A., Dziedzic, J.M., Bjorkholm, J.E., and Chu, S. (1986) *Opt. Lett*., **11**, 288.
6. Ashkin, A., Schütze, K., Dziedzic, J.M., Euteneuer, U., and Schliwa, M. (1990) **Nature**, **348**, 346.
7. Sasaki, K., Koshiuka, M., Kitamara, N., and Masuhara, H. (1991) *Opt. Lett*., **16**, 1463.
8. Svoboda, K. and Block, S. M. (1994) *Ann. Rev. Biophys. Biomol. Struct*., **23**, 247.
9. Ashkin, A. (1997) *Proc. Natl. Acad. Sci. USA*, **94**, 4853.
10. Grier, D.G. (2003) *Nature*, **424**, 810.
11. Ashkin, A. (2000) *IEEE J. Quantum Electron*., **6**, 841.
12. Molloy, J.E. and Padgett, M.J. (2002) *Contemp. Phys*., **43**, 241.
13. Dholakia, K., Reece, P., and Gu, M. (2008) *Chem. Soc. Rev*., **37**, 42.
14. Sugiyama, T., Yuyama, K., and Masuhara, H. (2012) *Acc. Chem. Res*., **45**, 1946.
15. Hotta, J., Sasaki, K., and Masuhara, H. (1996) *J. Am. Chem. Soc*., **118**, 11968.
16. Hofkens, J., Hotta, J., Sasaki, K., Masuhara, H. and Iwai, K. (1997) *Langmuir*, **13**, 414.
17. Ito, S., Yoshikawa, H., and Masuhara, H. (2001) *Appl. Phys. Lett*., **78**, 2566.
18. Ito, S., Yoshikawa, H., and Masuhara, H. (2002) *Appl. Phys. Lett*., **80**, 482.
19. Urban, A.S., Lutich, A.A., Stefani, F.D., and Feldmann, J. (2010) *Nano Lett*., **10**, 4794.
20. Borowicz, P., Hotta, J., Sasaki, K., and Masuhara, H. (1997) *J. Phys. Chem. B*, **101**, 5900.
21. Hosokawa, C., Yoshikawa, H., and Masuhara, H. (2004) *Phys. Rev. E*, **70**, 061410.
22. Hosokawa, C., Yoshikawa, H., and Masuhara, H. (2005) *Phys. Rev. E*, **72**, 021408.
23. Ito, S., Tanaka, Y., Yoshikawa, H., Ishibashi, Y., Miyasaka, H., and Masuhara, H. (2011) *J. Am. Chem. Soc*., **113**, 14472.
24. Sugiyama, T., Adachi, T., and Masuhara, H. (2007) *Chem. Lett*., **36**, 1480.
25. Sugiyama, T., Adachi, T., and Masuhara, H. (2009) *Chem. Lett*., **38**, 482.
26. Alexander, A.J. and Camp, P.J. (2009) *Cryst. Growth Des*., **9**, 958.
27. Rungsimanon, T., Yuyama, K., Sugiyama, T., Masuhara, H., Tohnai, N., and Miyata, M. (2010) *J. Phys. Chem. Lett*., **1**, 599.
28. Tsuboi, Y., Shoji, T., and Kitamura, N. (2010) *J. Phys. Chem. C*, **114**, 5589.

29. Masuhara, H., Sugiyama, T., Rungsimanon, T., Yuyama, K., Miura, A., and Tu, J.-R. (2011) *Pure Appl. Chem*., **83**, 869.
30. Ashkin, A., Dziedzic, J.M., and Yamane, T. (1987) *Nature*, **330**, 769.
31. Liu, Y., Sonek, G.J., Berns, M.W., and Tromberg, B.J. (1996) *Biophys. J*., **71**, 2158.
32. Ashkin, A. and Dziedzic, J.M. (1987) *Science*, **235**, 1517.
33. Block, S. M., Blair, D.F., and Berg, H.C. (1989) *Nature*, **338**, 514.
34. Wang, M.D., Yin, H., Landick, R., Gelles, J., and Block, S.M. (1997) *Biophys. J*., **72**, 1335.
35. Yang, A.H.J., Moore, S.D., Schmidt, B.S., Klug, M., Lipson, M., and Erickson, D. (2000) *Nature*, **457**, 71.
36. Finer, J.T., Simmons, R.M., and Spudich, J.A. (1994) *Nature*, **368**, 113.
37. Moffitt, J.R., Chemla, Y.R., Smith, S.B., and Bustamante, C. (2008) *Ann. Rev. Chem*., **77**, 205.
38. Osborne, M.A., Balasubramanian, S., Furey, W.S., and Klenerman, D. (1998) *J. Phys. Chem. B*, **102**, 3160.
39. Maragò, N.M., Bonaccorso, F., Saija, R., Privitera, G., Gucciardi, P.G., Iatì, M.A., Calogero, G., Jones, P.H., Borghese, F., Denti, P., Nicolosi, V., and Ferrari, A.C. (2010) *ACS Nano*, **4**, 7515.
40. Reece, P.J., Toe, W.J., Wang, F., Paiman, S., Gao, Q., Tan, H.H., and Jagadish, C. (2011) *Nano Lett*., **11**, 2375.
41. Gu, M. and Morrish, D. (2002) *J. Appl. Phys*., **91**, 1606.
42. Yoshikawa, H., Matsui, T., and Masuhara, H. (2004) *Phys. Rev. E*, **70**, 061406.
43. Hansen, P. M., Bhatia, V. K., Harrit, N., and Oddershede, L.B. (2005) *Nano Lett*., **5**, 1937.
44. Seol, Y., Carpenter, A.E., and Perkins, T.T. (2006) *Opt. Lett*., **31**, 2429.
45. Bosanac, L., Aabo, T., Bendix, P. M., and Oddershede, L.B. (2008) *Nano Lett*., **8**, 1486.
46. Dienerowitz, M., Mazilu, M., and Dholakia, K. (2008) *J. Nanophotonics*, **2**, 1.
47. Guffey, M.J. and Scherer, N.F. (2010) *Nano Lett*., **10**, 4301.
48. Hajizadeh, F. and Reihani, S.N.S. (2010) *Opt. Express*, **18**, 551.
49. Uwada, T., Sugiyama, T., and Masuhara, H. (2011) *J. Photochem. Photobiol. A: Chemistry*, **221**, 187.
50. Harada, Y. and Asakura, T. (1996) *Opt. Commun*., **124**, 529.
51. Juan, M.L., Gordon, R., Pang, Y., Eftekhari, F., and Quidant, R. (2009) *Nature Physics*, **5**, 915.
52. Pang, Y. and Gordon, R. (2011) *Nano Lett*., **11**, 3763.
53. Pang, Y. and Gordon, R. (2012) *Nano Lett*., **12**, 402.
54. Juan, M.L., Righini, M., and Quidant, R. (2011) *Nature Photonics*, **5**, 349.
55. Garetz, B.A., Matic, J., and Myerson, A.S. (2002) *Phys. Rev. Lett*., **89**, 175501.
56. Matic, J., Sun, X., Garetz, B.A., and Myerson, A.S. (2005) *Cryst. Growth Des*., **5**, 1565.
57. Pan, L., Ishikawa, A., and Tamai, N. (2007) *Phys. Rev. B*, **75**, 161305.
58. Sanz, M., de Nalda, R., Marco, J.F., Izquierdo, J.G., Banares, L., and Castillejo, M. (2010) *J. Phys. Chem.C*, **114**, 4864.
59. Jiang, Y., Narushima, T., and Okamoto, H. (2010) *Nature Physics*, **6**, 1005.
60. Usman, A.; Chiang, W.-Y., and Masuhara, H. (2012) *J. Photochem. Photobiol. A: Chemistry*, **234**, 83.
61. Ashkin, A. (1992) *Biophys. J*., **61**, 569.
62. Gordon, J.P. (1973) *Phys. Rev. A*, **8**, 14.
63. Davis, L.W. (1979) *Phys. Rev. A*, **19**, 1177.
64. Novotny, L. and Hecht, B. (2006) *Principle of Nano-Optics*, Cambridge Univ. Press.
65. Felgner, H., Müller, O., and Schliwa, M. (1995) *Appl. Opt*., **34**, 977.
66. Wood, T.A., Gleeson, H.F., Dickinson, M.R., and Wright, A.J. (2004) *Appl. Phys. Lett*., **84**, 4292.
67. Sasaki, K., Tsukima, M., and Masuhara, H. (1997) *Appl. Phys. Lett*., **71**, 37.
68. Chow, T.H., Lee, W.M., Tan, K.M., Ng, B.K., and Sheppard, C.J.R. (2010) *Appl. Phys. Lett*., **97**, 231113.
69. Jauffred, L., Richardson, A.C., and Oddershede, L.B. (2008) *Nano Lett*., **8**, 3376.
70. Abbondanzieri, E.A., Greenleaf, W.J., Shaevitz, J.W., Landick, R., and Block, S. M. (2005) *Nature*, **438**, 460.
71. Quidant, R. and Girard, C. (2008) *Laser Photon. Rev*., **2**, 47.
72. Tsuboi, Y., Shoji, T., Kitamura, N., Takase, M., Murakoshi, K., Misumoto, Y., and Ishihara, H. (2010) *J. Phys. Chem. Lett*., **1**, 2327.
73. Stockman, M. I. (2004) *Phys. Rev. Lett*., **93**, 137404.
74. Muhlschlegel, P., Eisler, H.-J., Martin, O.J.F., Hecht, B., and Pohl, D.W. (2005) *Science*, **308**, 1607.
75. Schuck, P.J., Fromm, D.P., Sundaramurthy, A., Kino, G.S., and Moerner, W.E. (2005) *Phys. Rev. Lett*., **94**, 017402.
76. Xu, H. and Kall, M. (2002) *Phys. Rev. Lett*., **89**, 246802.
77. Quidant, R., Petrov, D., and Badenes, G. (2005) *Opt. Lett*., **30**, 1009.

78. Righini, M., Ghenuche, P., Cherukulappurath, S., Myroshnychenko, V., Garcia de Abajo, F.J., and Quidant, R. (2009) *Nano Lett*., **9**, 3387.
79. Garcia-Parajo, M.F. (2008) *Nature Photonics*, **2**, 201.
80. Roxworthy, B.J., Ko, K.D., Kumar, A., Fung, K.H., Chow, E.K.C., Liu, G.L., Fang, N.X., and Toissaint Jr., K.C. (2012) *Nano Lett*., **12**, 796.
81. Kim, S., Jin, J., Kim, Y.-J., Park, I.-Y., Kim, Y., and Kim, S.-W. (2008) *Nature*, **453**, 757.
82. Rohrbach, A. and Stelzer, E.H.K. (2001) *J. Opt. Soc. Am. A*, **18**, 839.
83. Chaumet, P.C., Rahmani, A., and Nieto-Vesperinas, M. (2002) *Phys. Rev. Lett*., **88**, 123601.
84. Werner, D., Hashimoto, S., and Uwada, T. (2010) *Langmuir*, **26**, 9956.
85. Bahk, S.-W., Rousseau, P., Planchon, T.A., Chvykov, V., Kalintchenko, G., Maksimchuk, A., Mourou, G.A., and Yanovsky, V. (2005) *Appl. Phys. B*, **80**, 823.
86. Garetz, B.A., Aber, J.E., Goddard, N.L., Young, R.G., and Myerson, A.S. (1996) *Phys. Rev. Lett*., **77**, 3475.
87. Tsunesada, F., Iwai, T., Watanabe, T., Adachi, H., Yoshimura, M., Mori, Y., and Sasaki, T. (2002) *J. Cryst. Growth*, **237-239**, 2104.
88. Adachi, H., Takano, K., Hosokawa, Y., Inoue, T., Mori, Y., Matsumura, H., Yoshimura, M., Tsunaka, Y., Morikawa, M., Kanaya, S., Masuhara, H., Kai, Y., and Sasaki, T. (2003) *Jpn. J. Appl. Phys*., **42**, L798.
89. Ambardekar, A.A. and Li, Y.-Q. (2005) *Opt. Lett*., **30**, 1797.
90. Agate, B., Brown, C.T.A., Sibbett, W., and Dholakia, K. (2004) *Opt. Express*, **12**, 3011.
91. Usman, A., Chiang, W.-Y., and Masuhara, H. (2012) *Proc. SPIE*, **8458**, 845833.
92. Wang, L.-G. and Zhao, C.-L. (2007) *Opt. Express*, **15**, 10615.
93. Wang, L.-G. and Chai, H.-S. (2011) *Opt. Express*, **19**, 14389.
94. Zemánek, P., Jonáš, A., Šrámek, L., and Liška, M. (1999) *Opt. Lett*., **24**, 1448.
95. Bustamante, C., Chemla, Y.R., Forde, N.R., and Izhaky, D. (2004) *Ann. Rev. Chem*., **73**, 705.
96. Dholakia, K. and Zemánek, P. (2010) *Rev. Mod. Phys*., **82**, 167.
97. Juodkazis, S., Mukai, N., Wakaki, R., Yamaguchi, A., Matsuo, S., and Misawa, H. (2000) *Nature*, **408**, 178.
98. Ito, S., Sugiyama, T., Toitani, N., Katayama, G., and Miyasaka, H. (2007) *J. Phys. Chem. B*, **111**, 2365.
99. Denk, W., Strickler, J.H., and Webb, W.W. (1990) *Science*, **248**, 73.
100. Liang, H., Wright, W.H., Rieder, C.L., Salmon, E.D., Profeta, G., Andrews, J., Liu, Y., Sonek, G.J., and Berns, M.W. (1994) *Exp. Cell Res*., **213**, 308.
101. König, K., Riemann, I., Fischer, P., and Halbhuber, K.J. (1999) *Cell. Mol. Biol*., **45**, 195.
102. Sato, S., Harada, Y., and Waseda, Y. (1994) *Opt. Lett*., **19**, 1807.
103. Furukawa, H. and Yamaguchi, I. (1998) *Opt. Lett*., **23**, 216.
104. Lippitz, M., van Dijk, M.A., and Orrit, M. (2005) *Nano Lett*., **5**, 799.
105. Ohlinger, A., Nedev, S., Lutich, A.A., and Feldmann, J. (2011) *Nano Lett*., **11**, 1770.
106. Messina, E., Cavallaro, E., Cacciola, A., Iatì, M.A., Gucciardi, P.G., Borghese, F., Denti, P., Saija, R., Compagnini, G., Meneghetti, M., Amendola, V., and Maragò, O.M. (2011) *ACSNano*, **5**, 905.
107. Mansuripur, M. (2004) *Opt. Express*, **12**, 5375.
108. Iida, T. and Ishihara, H. (2008) *Phys. Rev. B*, **77**, 245319.
109. Kudo, T. and Ishihara, H. (2011) *Phys. Status Solidi C*, **8**, 66.
110. Kudo, T. and Ishihara, H. (2012) *Phys. Rev. Lett*., **109**, 087402.
111. Hosokawa, C., Yoshikawa, H., and Masuhara, H. (2006) *Jpn. J. Appl. Phys*., **45**, L453.