Photo-induced force for spectroscopic imaging at the nanoscale

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ABSTRACT

Photo-induced force microscopy (PiFM) is a new scan probe method that enables imaging with spectroscopic contrast at the nanoscale. The operating principle of PiFM is based on the coupling between a sharp atomic tip and a polarizable object, as mediated by the electromagnetic field in the vicinity of the tip-sample junction. In this contribution, we develop a description of the photo-induced force in the limit where the tip and object can be approximated as dipoles. This description provides an insightful picture of the forces at play in the tip-sample junction in terms of the gradient and scattering forces. We consider various approximations that are relevant to experimental conditions. The theoretical approach described here successfully explains the previous spectroscopic PiFM measurements in the visible and in the near-IR range, and the anticipated spectral information that can be retrieved under mid infrared illumination.

Keywords: optical binding force, photo-induced force microscopy and spectroscopy, chemical imaging

1. INTRODUCTION

Photo-induced force microscopy (PiFM) is an imaging technique that combines the high resolution offered by atomic force microscopy (AFM) with the spectroscopic sensitivity provided by optical excitation of the sample. Scan probe methods can be used in a variety of ways to detect optically excited molecules and structures. For instance, some near-field methods detect the optical field by providing a means to transfer near-field information to a far-field photo-detector. Another approach makes use of the expansion of the sample due to thermal heating after optical excitation. The latter method employs a cantilevered tip that is sensitive to minute changes introduced by thermal expansion. PiFM also utilizes a cantilevered tip, but instead of sensing sample heating, this emerging technique is optimized to detect the electromagnetically induced force on the tip.[1] Whenever the tip approaches the sample, the fields in the junction may alter because of the sample's polarizability, which thus leads to net changes in the force experienced by the tip. This form of the photo-induced force is sensitive to the spectroscopic properties of the sample, and can, in principle, be conducted in non-contact mode.

A compelling demonstration of PiFM was given by Rajapaksa *et al* in 2010, who visualized chromophores on a glass coverslip with nanoscale resolution.[2] The image contrast could be related to the absorptive properties of the chromophore, thus showing the promising capabilities of PiFM as a spectroscopic tool. This principle was later extended to Raman excitations,[3] and nonlinear transitions in the molecule induced by a pump-probe scheme.[4] The PiFM method can also be used in a more direct form, where the tip becomes a sensor of the near field. Examples of this capability include the detailed mapping of electric field components in the focus of a high numeral objective[5] and the visualization of propagating surface plasmon polaritons.[6]

The description of the process that gives rise to the observed photo-induced force is not trivial. There are several challenges. First, the cantilevered tip is not a probe that yields a linear response to the photo-induced force. Instead, the dynamics of the cantilever is complex, and detailed modeling is needed to extract the forces in the near field. Some of these approaches have been discussed in the literature.[7] Second, the photo-induced force itself results from complex interaction between the tip, sample and substrate in the presence of a confined optical

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Complex Light and Optical Forces X, edited by Jesper Glückstad, David L. Andrews, Enrique J. Galvez, Proc. of SPIE Vol. 9764, 97641J · © 2016 SPIE
CCC code: 0277-786X/16/$18 · doi: 10.1117/12.2208199

field. A complete description of these interactions takes into account the multiple scattering effects between the tip/sample/substrate, which can grow rather complicated depending on the geometry of the tip and sample. Although full field simulations can be very useful, analytical models are preferred, as they provide more physical insight into the nature of the forces at play.

In this contribution, we focus on an analytical description of the photo-induced force. To simplify the description, several approximations are made, among which the assumption that both the tip and the sample can be described as point dipoles. Under the conditions considered here, relatively simple expressions for the photo-induced force are obtained. We discriminate between the force resulting from the field acting on the tip far away from a substrate (optical tweezer force), the force between the tip and its image dipole in a nearby substrate (image dipole force), and the force between the tip and a small polarizable object (optical binding force). We will show the differences and similarities between these photo-induced forces, and point out the spectroscopic sensitivity that can be achieved in these different scenarios.

2. TIME-AVERAGED PHOTO-INDUCED FORCE

2.1 Dipole approximation

We consider a monochromatic electromagnetic wave with angular frequency ω, which is incident on a polarizable tip and a particle in Fig. 1. The time harmonic electric and magnetic field components at location $\mathbf{r}$ can be written as:

$$\mathbf{E}(\mathbf{r},t) = \mathrm{Re}\left\{\mathbf{E}(\mathbf{r})e^{-j\omega t}\right\} \tag{1}$$

$$\mathbf{B}(\mathbf{r},t) = \mathrm{Re}\left\{\mathbf{B}(\mathbf{r})e^{-j\omega t}\right\} \tag{2}$$

To the first order in the fields, the induced dipole moment of the particle assumes the same time dependence and is given as:

$$\vec{\mu}(\mathbf{r},t) = \mathrm{Re}\left\{\vec{\mu}(\mathbf{r})e^{-j\omega t}\right\}$$

We assume that the particle has no static dipole moment. In this case, to the first order, the induced dipole moment is proportional to the electric field at the particle's position $\mathbf{r}$

$$\vec{\mu}(\mathbf{r}) = \alpha(\omega)\mathbf{E}(\mathbf{r}) \tag{3}$$

where α denotes the polarizability of a particle. Using the discrete dipole approximation for calculating the force on the tip, the force $\mathbf{F}$ due to the electromagnetic field is computed as

$$< \mathbf{F} > = < \frac{1}{2}\,\mathrm{Re}\{(\vec{\mu}^* \cdot \nabla)\mathbf{E} + (\dot{\vec{\mu}}^* \times \mathbf{B})\} > \tag{4}$$

Eq. (4) is a general description of the force for the spatial variation of the field between the particle and the tip dipoles.[8] The first term originates from the inhomogeneous electric field, the second is the familiar Lorentz force. The first term and the second term are not yet defined as a gradient force and scattering force because both of them have a complex polarizability and the curl of each of the terms is non-zero.

2.2 Gradient and Scattering forces

The time averaged dipole force in Eq. (4) can be rewritten as:

$$< \mathbf{F} >= < \frac{1}{2}\,\mathrm{Re}\{(\vec{\mu}^* \cdot \nabla)\mathbf{E} - \vec{\mu}^* \times (\frac{\partial}{\partial t}\mathbf{B}) + \frac{\partial}{\partial t}(\vec{\mu}^* \times \mathbf{B})\} > \tag{5}$$

In the time average, the last term vanishes. By using the Faraday equation, $\partial\mathbf{B}(\mathbf{r},\omega)/\partial t = -\nabla \times \mathbf{E}(\mathbf{r},\omega)$, it is recast as:

$$< \mathbf{F} > = < \frac{1}{2}\,\mathrm{Re}\{(\vec{\mu}^* \cdot \nabla)\mathbf{E} + \vec{\mu}^* \times (\nabla \times \mathbf{E})\} > \tag{6}$$

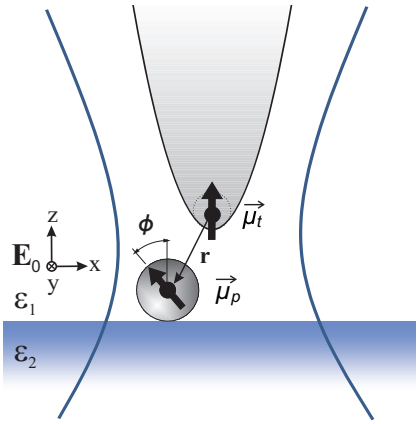

Figure 1. Graphical representation of the symbols used to derive the photo-induced force in the dipole approximation. $\mathbf{r}$ denotes the center of mass coordinate.

The resulting expression within the time average can be summarized as:

$$(\vec{\mu}^* \cdot \nabla)\mathbf{E} + \vec{\mu}^* \times (\nabla \times \mathbf{E}) = \alpha^*(E_x\partial_x E_x + E_y\partial_x E_y + E_z\partial_x E_z)\hat{x} + \alpha^*(E_x\partial_y E_x + E_y\partial_y E_y + E_z\partial_y E_z)\hat{y} + \alpha^*(E_x\partial_z E_x + E_y\partial_z E_y + E_z\partial_z E_z)\hat{z} = \sum_i \alpha^* E_i^* \nabla E_i \quad (7)$$

with $\partial_i = \frac{\partial}{\partial i}$ where $i = x, y, z$. Therefore the expression for the force can be simplified as:

$$\langle \mathbf{F} \rangle = < \sum_i \frac{1}{2} \mathrm{Re}\{\mu_i^* \nabla E_i\} > \quad (8)$$

By implementing $\alpha = \alpha' + j\alpha''$, the time-averaged force is recast as:[8]

$$\langle \mathbf{F} \rangle = < \frac{\alpha'}{2} \sum_i \mathrm{Re}\{E_i^* \nabla E_i\} > \; + \; < \frac{\alpha''}{2} \sum_i \mathrm{Im}\{E_i^* \nabla E_i\} > \quad (9)$$

The first term of Eq. (9) is recognized as the *gradient force*, $\mathbf{F}_g$, and the second term is denoted as the *scattering and absorption force*, $\mathbf{F}_{sc}$. The gradient force originates from the field inhomogeneities, and is proportional to the dispersive part (real part) of the complex polarizability, and is a conservative force, i.e. $\nabla \times \langle \mathbf{F}_g \rangle = 0$. On the other hand, the scattering and absorption force is proportional to the dissipative part (imaginary part) of the complex polarizability, and is a non-conservative force, i.e. $\nabla \times \langle \mathbf{F}_{sc} \rangle \neq 0$.

3. PHOTO-INDUCED FORCE FOR VARIOUS GEOMETRIES

Eq. (8) is a general force description of a dipole in an external field. In the following, we will discuss three different geometries, all of which are relevant to actual experimental scenarios. The first geometry is that of a tip exposed to an external field in the absence of a substrate. This force resembles the situation encountered in optical tweezers, where a polarizable object is subject to a strongly focused field. This force is referred to as the optical tweezer force. The second geometry is the force experienced by the tip in the presence of a nearby semi-infinite substrate. This situation is well described by considering the image dipole of the tip in the substrate, and, therefore, we refer to this case as the image dipole force. The last case considered here is that of the tip in presence of a small polarizable object. The force that results from the coupling mediated by the optical field is sometimes referred to as the optical binding force, which we discuss here in some detail.

3.1 Optical tweezer force

If the light is focused on the tip without any sample and substrate, as in Fig. 2 (a), the force is the so-called optical tweezer force.[8] In this geometry, the assumption can be made that the phase of the electric field components

vary slowly in space. This assumption warrants that the field components can be written as a (real) amplitude E_0 and a phase ϕ:

$$\mathbf{E}(\mathbf{r}) = E_0(\mathbf{r})e^{i\phi(\mathbf{r})}\mathbf{n}_E \tag{10}$$

with $\mathbf{n}_E$ denoting the unit vector in the direction of the polarization. In this limit, the expression for the photo-induced force can be recast as:

$$\langle \mathbf{F} \rangle = \frac{\alpha'}{2}\nabla < |\mathbf{E}|^2 > +\omega\alpha'' < \mathbf{E} \times \mathbf{B} > \tag{11}$$

In Eq. (11), the first term is the gradient force whereas the second term represents the scattering force. It can be clearly seen that the gradient force scales with the real part of the tip's polarizability and that the scattering force is proportional to the imaginary part of the tip's response. Note that if the incident field is a plane wave, the gradient force disappears and only the scattering force remains.

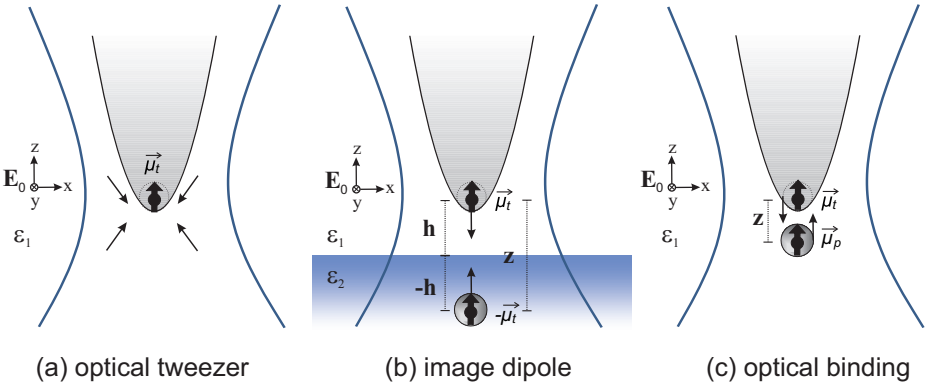

Figure 2. Graphical representation of (a) optical tweezer force (b) image dipole force (c) optical binding force.

3.2 Tip across from an interface: image dipole approximation

If the tip is placed close to a flat, semi-infinite substrate, the mutual coupling between the tip and the substrate material in the presence of the optical field has to be taken into consideration. A convenient way to model this scenario is to consider the image dipole that is induced by the tip in the substrate. Each dipole will interact with the field and, therefore, alter the near-field experienced by the other dipole. This case is sketched in Fig. 2 (b). Because the photo-induced force microscope is very sensitive to the z-directional force due to the tip geometry, for our discussion here, we assume that the forces along the z dimension dominate the cantilever response. We consider $\vec{\mu}_t = \mu_{t_z}\hat{z}$ and $\vec{\mu}_{t'} = \mu_{t'_z}\hat{z}$, the z components of the dipole moment of the tip and the image dipole respectively. In the simple mutual interaction picture, the induced dipole moments in each of the two particles are:

$$\vec{\mu}_t = \alpha_t\mathbf{E} = \alpha_t(\mathbf{E}_0 + \mathbf{E}_{t'}) \tag{12}$$

$$\vec{\mu}_{t'} = \alpha_{t'}\mathbf{E} = \alpha_{t'}(\mathbf{E}_0 + \mathbf{E}_t) \tag{13}$$

where $\mathbf{E}_0$ is the electric field of the incident laser, which is given as $\mathbf{E}_0 = E_{0x}\exp(jkz)\hat{x} + E_{0z}\hat{z}$ and $\vec{\mu}_t$ and $\vec{\mu}_{t'}$ are the effective dipole moments of the tip and the image dipole, respectively. E_{0z} is due to the longitudinal field. $\mathbf{E}_t$ and $\mathbf{E}_{t'}$ are the near-fields of the tip and the image dipole, respectively. Under these conditions, the static electric fields of the induced dipoles are

$$\mathbf{E}_i = \frac{1}{4\pi\varepsilon_0}\frac{(3\vec{\mu}_i \cdot \hat{\mathbf{r}})\hat{\mathbf{r}} - \vec{\mu}_{i_z}}{r^3} \tag{14}$$

where $r = \sqrt{x^2+y^2+z^2}$, $i = t, t'$, and $\hat{\mathbf{r}}$ is the unit vector associated with $\mathbf{r}$. The static dipole field is also defined as $\mathbf{E}_i \equiv E_{ix}\hat{x} + E_{iy}\hat{y} + E_{iz}\hat{z}$ with respect to the tip and molecule. The static fields at $r = \{0, 0, z\}$ are given as:

$$E_{t_z} = \frac{1}{4\pi\varepsilon_0}\frac{2\mu_{t_z}}{z^3} \quad , E_{t'_z} = \frac{1}{4\pi\varepsilon_0}\frac{2\mu_{t'_z}}{z^3}, \tag{15}$$

$$E_{t_x} = E_{t_y} = 0 \quad , E_{t'_x} = E_{t'_y} = 0. \tag{16}$$

Because of the azimuthal symmetry, E_{ix} is same to E_{iy} along to the z-direction. When we apply the incident electric field $\mathbf{E}_0 = E_{0x}\hat{x} + E_{0z}\hat{z}$ to the tip and sample, by substituting Eq. (15) and Eq. (16) into Eq. (12) and Eq. (13), in the near-field limit, the z-component of the tip's dipole moment and its corresponding electric field $\mathbf{E}_t$ can be found as:

$$\mu_{t_z} = \frac{2z^3\pi\alpha_{t_z}\varepsilon_0(\alpha_{t'_z} + 2z^3\pi\varepsilon_0)E_{0z}}{4z^6\pi^2\varepsilon_0^2 - \alpha_{t'_z}\alpha_{t_z}} \tag{17}$$

$$E_{t_z} = \frac{\alpha_{t_z}(\alpha_{t'_z} + 2z^3\pi\varepsilon_0)E_{0z}}{4z^6\pi^2\varepsilon_0^2 - \alpha_{t'_z}\alpha_{t_z}} \tag{18}$$

Eq. (9) is a general description of the gradient and the scattering force for the spatial variation of the *complex field* between the particle and the tip. The gradient and scattering force directed along $\mathbf{z}$ follow from:

$$\langle \mathbf{F}_t \rangle_z = < \frac{\alpha'_{t_z}}{2} \sum_i \mathrm{Re}\{E_i^* \nabla E_i\} >_z \; + \; < \frac{\alpha''_{t_z}}{2} \sum_i \mathrm{Im}\{E_i^* \nabla E_i\} >_z \tag{19}$$

By substituting the Eq. (17) and Eq. (18) into Eq. (19) under the assumption $4z^6\pi^2\varepsilon_0^2 \gg \alpha_{t'_z}\alpha_{t_z}$, or the product of the polarizabilities is very small, the z-component of the gradient force and scattering force take on the following form:

$$\begin{aligned} \langle \mathbf{F}_g \rangle_z &\simeq \frac{\alpha'_{t_z}}{2}\,\mathrm{Re}\{(\frac{Az^3(Az^3)E_{0z}^*}{A^2z^6})(\frac{(3Az^2\alpha_{t'_z})E_{0z}(A^2z^6) - (6A^2z^5)(Az^3\alpha_{t'_z})E_{0z}}{(A^2z^6)^2})\}\hat{z} \\ &= -\frac{3\alpha'_{t_z}\alpha'_{t'_z}}{2\pi\varepsilon_0 z^4}|E_{0z}|^2\hat{z} \end{aligned} \tag{20}$$

$$\begin{aligned} \langle \mathbf{F}_{sc} \rangle_z &\simeq \frac{\alpha'_{t_z}}{2}\,\mathrm{Im}\{(\frac{Az^3(Az^3)E_{0z}^*}{A^2z^6})(\frac{(3Az^2\alpha_{t'_z})E_{0z}(A^2z^6) - (6A^2z^5)(Az^3\alpha_{t'_z})E_{0z}}{(A^2z^6)^2})\}\hat{z} + \frac{k}{2}\alpha''_{t_z}|E_{0x}|^2\hat{z} \\ &\simeq -\frac{3\alpha''_{t_z}\alpha''_{t'_z}}{2\pi\varepsilon_0 z^4}|E_{0z}|^2\hat{z} + \frac{k}{2}\alpha''_{t_z}|E_{0x}|^2\hat{z} \end{aligned} \tag{21}$$

where $A = 2\pi\varepsilon_0$. Eq. (20) shows that the gradient force exhibits a $1/z^4$ distance dependence. It is an attractive and conservative force. The scattering force in Eq. (21) has two terms. The first term shows a $1/z^4$ distance dependence, it is attractive but it is non-conservative. Although this term has the same distance dependence as the gradient force, the physical origin is different.The second term of Eq. (21) is the repulsive constant scattering force related to the momentum of the incident field. By writing $|\alpha_{t'_z}| = \epsilon|\alpha_{t_z}|$ and $\epsilon \equiv |(\varepsilon_2 - \varepsilon_1)/(\varepsilon_2 + \varepsilon_1)|$, the total photo-induced force is rewritten as:

$$\begin{aligned} \langle \mathbf{F}_t \rangle_z &= \langle \mathbf{F}_g \rangle_z + \langle \mathbf{F}_{sc} \rangle_z \\ &\simeq -\frac{3\epsilon^2|\alpha_{t_z}|^2}{2\pi\varepsilon_0 z^4}|E_{0z}|^2\hat{z} + \frac{k}{2}\alpha''_{t_z}|E_{0x}|^2\hat{z} \end{aligned} \tag{22}$$

The first term is the attractive *local* image dipole force. This local force is proportional to to the magnitude of the polarizability of the tip, i.e. $|\alpha_{t_z}|^2 = \alpha_t'^2 + \alpha_t''^2$. The second term in Eq. (22) is the repulsive *non-local* scattering force that is related to the momentum of the incident field, and acts as a constant pressure on the tip.

3.3 Forces between tip and small object: optical binding force

In this section we consider the tip placed in the vicinity of a small and polarizable object. Similar to the situation of the image dipole, the resulting force is sensitive to the mutual interaction between the tip and sample dipole. To describe this geometry, shown in Fig.2 (c), we consider both the induced dipole moment of the tip $\mu_t(\mathbf{r}_1)$ placed at $\mathbf{r}_1$, and the induced dipole moment of the particle $\mu_p(\mathbf{r}_2)$, which is placed at $(\mathbf{r}_2)$. The dipole components can be expressed as:

$$\mu_i^t(\mathbf{r}_1) = \alpha_i^t \mathbf{E}_i(\mathbf{r}_1), \quad \mu_i^p(\mathbf{r}_2) = \alpha_i^p \mathbf{E}_i(\mathbf{r}_2) \tag{23}$$

where α^t and α^p are the scalar polarizabilities of the tip and particle, respectively, and i denotes x, y, z. The total electric field at the position of the dipole is given by the sum of the incident field $\mathbf{E}_0(\mathbf{r})$and the field emitted by the other dipole,

$$\begin{aligned} \mathbf{E}_i(\mathbf{r}_1) &= \mathbf{E}_{0i}(\mathbf{r}_1) + G_{ii}(\mathbf{r}_1, \mathbf{r}_2)\alpha_i^p \mathbf{E}_i(\mathbf{r}_2), \\ \mathbf{E}_i(\mathbf{r}_2) &= \mathbf{E}_{0i}(\mathbf{r}_2) + G_{ii}(\mathbf{r}_2, \mathbf{r}_1)\alpha_i^t \mathbf{E}_i(\mathbf{r}_1), \end{aligned} \tag{24}$$

where we used the field propagator between the two dipoles $\bar{\mathbf{G}}$ (also called the dyadic Green′s function) in the form

$$G_{lm} = \frac{\exp(jkR)}{r\pi\varepsilon_0\varepsilon_m R^3}[(3 - 3ikR - k^2R^2)\frac{R_l R_m}{R^2} + (k^2R^2 + jkR - 1)\delta_{lm}]. \tag{25}$$

Here R is the length given by $\mathbf{R} = \mathbf{r}_1 - \mathbf{r}_2$, $k = 2\pi/\lambda$ is the wave number of the light in the medium, ε_0 is the permittivity of vacuum, ε_m is the relative permittivity of the medium, and δ_{jk} denotes the Kronecker delta. The solution of Eq. (24) at the tip is given as:

$$\mathbf{E}_i(\mathbf{r}_1) = [\bar{\mathbf{I}} - \bar{\mathbf{G}}(\mathbf{r}_1, \mathbf{r}_2)\alpha_p \bar{\mathbf{G}}(\mathbf{r}_2, \mathbf{r}_1)\alpha_t]_{ii}^{-1}(E_{0i}(\mathbf{r}_1) + G_{ii}\alpha_i^p E_{0i}(\mathbf{r}_1)) \tag{26}$$

Once the total electric component of the optical field is known, by substituting Eq. (26) into Eq. (8) the time-averaged component F_z of the optical force acting on the tip can be expressed as

$$F_z^t = \frac{1}{2}\,\mathrm{Re}\{\alpha_i^{t*}[E_{0j}(\mathbf{r}_1) + G_{ii}\alpha_i^p E_{0i}(\mathbf{r}_2)]^* \times [\partial_{z_1} E_{0i}(\mathbf{r}_1) + \partial_{z_1}(G_{ii})\alpha_i^p E_{0i}(\mathbf{r}_2)]\} \tag{27}$$

The force acting on the particle can be obtained by interchanging the letters t and p and positions $\mathbf{r_1}$ and $\mathbf{r_2}$. The total optical force (27) can be further simplified by assuming that only particles much smaller than the radiation wavelength are included. Their polarizabilities are generally very small and therefore terms with a product of three or more α_i can be ignored. The resulting expression of the force on the tip is:

$$F_z^t \simeq \frac{1}{2}\,\mathrm{Re}\{\alpha_i^{t*} E_{0i}^*(\mathbf{r}_1)\partial_{z_1} E_{0i}(\mathbf{r}_1) + \alpha_i^{t*} G_{ii}^* \alpha_i^{p*} E_{0i}^*(\mathbf{r}_2)\partial_{z_1} E_{0i}(\mathbf{r}_1) + \alpha_i^{t*} E_{0i}^*(\mathbf{r}_1)\partial_{z_1}(G_{ii})\alpha_i^p E_{0i}(\mathbf{r}_2)\} \tag{28}$$

Writing the incident electric field is $\mathbf{E}_0 = E_{0x}\exp(jkz)\hat{x} + E_{0z}\hat{z}$, the force acting on a tip is found as:

$$F_z^t \simeq \frac{k}{2}\,\mathrm{Im}\{\alpha_t\}|E_{0x}|^2\hat{z} + \frac{\mathrm{Re}\{\alpha_t^*\alpha_p\}|E_{0z}|^2}{8\pi\varepsilon_0\varepsilon_m z^4}[(2k^2z^2 - 6)\cos(kz) - 6kz\sin(kz)]\hat{z} \tag{29}$$

In the near-field limit $kz << 1$,

$$F_{t_z} \approx \frac{k}{2}\,\mathrm{Im}\{\alpha_t\}|E_{0x}|^2\hat{z} - \frac{3\,\mathrm{Re}\{\alpha_t^*\alpha_p\}|E_{0z}|^2}{4\pi\varepsilon_0\varepsilon_m z^4}\hat{z} \tag{30}$$

In Eq. (30) the first term is the constant scattering force due to radiation pressure. The second term of Eq. (30) is the attractive local force due to field inhomogeneities. The localized force is proportional to the real part of complex polarizability product of the tip and the sample, given as $\mathrm{Re}\{\alpha_{t_z}^*\alpha_{p_z}\} = \alpha_t'\alpha_p' + \alpha_t''\alpha_p''$, and carries the spectroscopic information of the particle. Note that this latter term has the same distance dependence $1/z^4$ as found for the local force of the image dipole.

4. DISCUSSION

The photo-induced force sprouts from the intricate interplay between tip, sample and substrate in the presence of the electromagnetic field. A detailed model of the photo-induced force should thus include not only the tip–sample interactions, but also the simultaneous multiple scattering effects between the tip and substrate, and between the sample and substrate. Such interactions require more advanced descriptions than what is presented here. Nonetheless, the expressions discussed in this contribution touch on several relevant cases that yield intuitive results within the dipole approximation. The optical tweezer force, image dipole force and optical binding force all represent interpretable contributions to the photo-induced force in a typical experiment. The separation into gradient and scattering forces highlights the physical underpinning of the forces in terms of dispersive and dissipative contributions to the measured photo-induced force. In the cases of the image dipole force and the optical binding force along the **z** dimension, we find a natural separation into a local and a non-local force. The attractive local force bears a steep distance dependence ($1/z^4$), and is manifest only for nanometer scale tip-sample distances. The repulsive non-local force extends over the dimensions of the incident electromagnetic field, which approaches $\sim \mu$m distances for tightly focused optical fields.

The local component of the optical binding force carries spectroscopic information, which is contained in the term $\mathrm{Re}\{\alpha^*_{t_z}\alpha_{p_z}\} = \alpha'_t\alpha'_p + \alpha''_t\alpha''_p$. Note that the polarizabilities are functions of frequency. It is interesting to consider a few limiting cases. If the plasmonic resonance of the tip is far from the frequency ω of the incident radiation, the α''_t contribution is relatively small, whereas the real part of the tip polarizability may still be substantial. In this case, the dominant term in the photo-induced force is $\alpha'_t\alpha'_p$. For narrow resonances of the particle, the resulting frequency dependence of the force near resonance will follow a dispersive line shape. Such conditions were examined for the ~ 809 nm resonance of Si-naphthalocyanine, which produced a dispersive PiFM line shape. [1] On the other hand, if ω is close to a tip resonance, the term $\alpha''_t\alpha''_p$ can be substantial, resulting in a Lorenztian-shaped PiFM frequency dependence. Therefore, the spectral line shape in PiFM strongly depends on the experimental conditions. Knowledge of the tip resonances can be used to enhance and control the spectroscopic readout in PiFM measurements.

5. CONCLUSION

In this work, we discussed a theoretical description of the photo-induced force between a sharp polarizable tip and a polarizable particle on the substrate. We discussed the limiting cases of the optical tweezer force, image dipole force and optical binding force, and provided compact analytical expressions for each of these cases. In actual PiFM experiments all of these forces may contribute simultaneously, but the spectroscopic information derives from the mutual interaction between the tip and the polarizable particle (optical binding force). The spectral curve of the PiFM response depends on both the tip's and the sample's polarizabilities, and is given as $\alpha'_t\alpha'_p + \alpha''_t\alpha''_p$. This theory successfully explains the PiFM spectra in the visible [2] and in the near-IR .[1] The PiFM approach is compatible with a wide range optical excitation frequencies, from the visible to the mid-infrared, enabling nanoscale imaging contrast based on either electronic or vibrational transitions in the sample. These properties make PiFM an attractive method for the visualization and spectroscopic characterization of a vast variety of nano materials, from semi-conducting nanoparticles to polymer thin films to sensitive measurements of single molecules.

REFERENCES

[1] Jahng, J., Fishman, D. A., Park, S., Nowak, D. B., Morrison, W. A., Wickramasinghe, H. K., and Potma, E. O., "Linear and nonlinear optical spectroscopy at the nanoscale with photo-induced force microscopy," *Acc. Chem. Res.* **48**, 2671–2679 (2015).

[2] Rajapaksa, I., Uenal, K., and Wickramasinghe, H. K., "Image force microscopy of molecular resonance: A microscope principle," *Appl. Phys. Lett.* **97**, 073121 (2010).

[3] Rajapaksa, I., Uenal, K., and Wickramasinghe, H. K., "Raman spectroscopy and microscopy based on mechanical force detection," *Appl. Phys. Lett.* **99**, 161103 (2011).

[4] Jahng, J., Brocious, J., Fishman, D. A., Yampolsky, S., Nowak, D. B., Huang, F., Apkarian, V. A., Wickramasinghe, H. K., and Potma, E. O., "Ultrafast pump-probe force microscopy with nanoscale resolution," *Appl. Phys. Lett.* **106**, 083113 (2015).

[5] Huang, F., Tamma, V. A., Mardy, Z., Burdett, J., and Wickramasinghe, H. K., "Imaging nanoscale electromagnetic near-field distributions using optical forces," *Sci. Rep.* **5**, 10610 (2015).
[6] Jahng, J., Ladani, F. T., Khan, R. M., Li, X., Lee, E. S., and Potma, E. O., "Visualizing surface plasmon polaritons by their gradient force," *Opt. Lett.* **40**, 5058–5061 (2015).
[7] Jahng, J., Brocious, J., Fishman, D. A., Huang, F., Li, X., Tamma, A., V., Wickramasinghe, H. K., and Potma, E. O., "Gradient and scattering forces in photoinduced force microscopy," *Phys. Rev. B* **90**, 155417 (2014).
[8] Novotny, L. and Hecht, B., [*Principles of Nano-Optics (2nd ed.)*], Cambridge University Press, New York (2012).