Comment on “Optimal detection angle in sub-diffraction resolution photothermal microscopy: application for high sensitivity imaging of biological tissues”

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Abstract: A recent publication [Opt. Express, 22(16), 18833–18842 (2014)] discusses the optimal detection aperture in photothermal single particle microscopy. This new theory is in contradiction with rigorous ab-initio electrodynamic calculations. Nonetheless, the experimentally verified conclusion that a maximum signal occurs at a finite numerical detection aperture remains valid and is in accord with existing models.

OCIS codes: (190.4870) Photothermal effects; (110.6820) Thermal imaging; (260.1960) Diffraction theory; (050.1965) Diffractive lenses; (050.5080) Phase shift; (180.5810) Scanning microscopy.

References and links

1. J. Miyazaki, H. Tsurui, K. Kawasumi, and T. Kobayashi, “Optimal detection angle in sub-diffraction resolution photothermal microscopy: application for high sensitivity imaging of biological tissues,” Opt. Express **22**(16), 18833–18842 (2014).
2. M. Selmke, A. Heber, M. Braun, and F. Cichos “Photothermal single particle microscopy using a single laser beam,” Appl. Phys. Lett. **105**, 0135011 (2014).
3. M. Selmke and F. Cichos, “Energy-Redistribution signatures in transmission microscopy of Rayleigh and Mie particles,” J. Opt. Soc. Am. A **31**(11), 2370–2384 (2014).
4. M. Selmke, “Photothermal single particle detection in theory & experiments,” Dissertation, Universität Leipzig, Institute for experimental physics I, (2013).
5. M. Selmke, M. Braun, and F. Cichos, “Photothermal single particle microscopy: detection of a nanolens,” ACS Nano **6**(3), 2741–2749 (2012).
6. M. Selmke, M. Braun, and F. Cichos, “Nano-lens diffraction around a single heated nano particle,” Opt. Express **20**(7), 8055–8070 (2012).
7. M. Selmke, M. Braun, and F. Cichos, “Nano-lens diffraction around a single heated nano particle: errata,” Opt. Express **21**(21), 25344–25345 (2013).
8. M. Selmke, M. Braun, and F. Cichos, “Gaussian beam photothermal single particle microscopy,” J. Opt. Soc. Am. A **29**(10), 2237–2241 (2012).
9. M. Selmke and F. Cichos “Photothermal single particle Rutherford scattering microscopy,” Phys. Rev. Lett. **110**, 103901 (2013).
10. M. Tokeshi, M. Uchida, A. Hibara, T. Sawada, and T. Kitamori, “Determination of subyoctomole amounts of nonfluorescent molecules using a thermal lens microscope: subsingle-molecule determination,” Anal. Chem **73**, 2112–2116 (2001).
11. D. Boyer, P. Tamarat, A. Maali, B. Lounis, and M. Orrit, “Photothermal imaging of nanometer-sized metal particles among scatterers,” Science **297**, 1160 (2002).
12. A. Gaiduk, P. V. Ruijgrok, M. Yorulmaz, and M. Orrit, “Making gold nanoparticles fluorescent for simultaneous absorption and fluorescence detection on the single particle level,” Phys. Chem. Chem. Phys. **13**, 149–153 (2011).

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13. J. Hwang and W. E. Moerner, “Interferometry of a single nanoparticle using the Gouy phase of a focused laser beam,” Optics Commun. **280**, 487–491 (2007).
14. M. Selmke and F. Cichos “Photonic Rutherford scattering: a classical and quantum mechanical analogy in ray- and wave-optics,” Am. J. Phys. **81**(6), 405-413 (2013).
15. V. G. Baryshevskii, I. D. Feranchuk, and P. B. Kats, “Regularisation of the Coulomb scattering problem,” Phys. Rev. A, **70**(5), (2004).
16. S. Berciaud, D. Lasne, G. A. Blab, L. Cognet, and B. Lounis, “Photothermal heterodyne imaging of individual metallic nanoparticles: theory versus experiment,” Phys. Rev. B 73(4), 045424 (2006).
17. L. Novotny and B. Hecht, *Principles of nano-optics* (Cambridge University, 2006).
18. W. Zakowicz, “Classical properties of quantum scattering,” J. Phys. A: Math. Gen. **36**(15), 4445–4464 (2003).
19. W. Zakowicz, “Scattering of narrow stationary beams and short pulses on spheres,” Europhys. Lett. **85**(4): 40001 (2009).
20. D. Drosdoff and A. Widom, “Snells law from an elementary particle viewpoint,” Am. J. Phys. **73**(10), 973–975 (2005).
21. G. Gouesbet and G. Gréhan, “Generalized LorenzMie theory for assemblies of spheres and aggregates,” J. Opt. A: Pure Appl. Opt. **1**, 706–712 (1999).

The theoretical model for the frequency dependent photothermal (PT) signal as introduced in [1], Miyazaki et al., is based on a series of erroneous assumptions. In consequence, it is in contradiction to quantitative ab-initio calculations in a rigorous and experimentally verified electrodynamic formalism [2–4]. In contrast to the model put forward in [1], the PT signal is exactly zero for the assumptions made in that reference, i.e. for zero probe beam to particle offset, analog to the quasi-static limit [4–9].

Applicability of previous models to finite modulation frequencies

In section 2. of [1] the model is motivated with the following introductory statement:

> “…Selmke and Cichos et al. calculated the difference in transmissivity of the focusing probe beam between two steady states, in the presence and absence of the pump beam, using generalized Lorenz-Mie theory [18-20]. (…) However, their model is based on a steady-state calculation and not applicable to the case when thermal diffusion length during one period of the modulating pump beam is comparable to or smaller than the focusing spot size of the probe beam.”

This is incorrect. *The model which uses the generalized Lorenz-Mie theory [5, 6] is well capable of analyzing the full time-dependent thermal wave field*. This is intrinsic to the use of an arbitrary multilayered scatterer which permits any refractive index profile to be considered. In fact, [5], Selmke et al., already considered an exponential refractive index profile for comparison. In a work [2] submitted on the very same day as [1] we have followed this route and described the frequency dependence of the PT signal using the rigorous GLMT approach. This was suggested already in the 2012 article [5]. The results of this approach are in contradiction to the results of [1], Miyazaki et al.

A signal where there should be none

The authors of [1], Miyazaki et al., begin their discussion under the assumption that $\mathbf{r_0} = \mathbf{0}$, as stated following between Eq. (15) and (16). *However, not only does a zero offset lead to a zero PT signal, but also the angular distribution of the PT signal changes with changing offset.* This has been shown using a (paraxial) diffraction formalism (cf. Fig. 2(b) of [6]) and a rigorous vectorial scattering treatment in the generalized Lorenz-Mie theory of a finely layered scatterer (cf. Fig. 5(a) of [6]). *This shifts the optimal detection aperture depending on the offset.*

> “…However, in the present study, the amplitude of the lock-in signal exhibited

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> only a single peak and the phase was nearly flat and did not exhibit the π shift at the origin. . . . ”

This experimental observation is in accord with an axial offset of the pump and the probe beam which maximizes the photothermal signal. It is however inconsistent with the claim that (or alternatively indicates grave aberrations of the beams)

> “The pump and probe beams were collimated so that they focused at the same position.”

Indeed, an adjusted laser-offset is a reasonable and often-used calibration of a single particle photothermal setup [5, 10–12]. Typically, this offset between both lasers is about one confocal distance of the probe laser [4–6, 8]. For any configuration and any forward collection angle the zero crossing of the PT signal for vanishing pump-beam offset ($\mathbf{r_0} = \mathbf{0}$) remains.

For the quasi-static thermal lens, various approximation schemes explicitly give the axial dependence of the PT signal [6, 9], again in perfect accord with GLMT calculations [4, 7].

This behaviour does not change when the time-modulated thermal lens is considered [2, 4]. *Both in-phase and out-of-phase components of the PT signal are zero for zero offset* $\mathbf{r_0} = \mathbf{0}$.

This is in accord with analytical models for the transmission signal of non absorbing Rayleigh scatterers [3, 13]. Only at the highest of frequencies, as correctly presumed by the authors of [1], the modulated scattering signal of the central nanoparticle will play a role and lead to a finite signal at zero particle offset due to modulated absorption [2, 4].

The only other reason for a non-zero signal at zero probe-beam offset are aberrations of the probe-beam’s point-spread-function [4, 5]. Both are not part of the model described in [1], Miyazaki et al.

Statements regarding the sign and amplitude of the in-phase and out-of-phase components of the PT signal made in [1], Miyazaki et al., therefore lose their obvious meaning.

The focused beam plane-wave spectrum Eq. (12)

The authors of [1], Miyazaki et al., apply the wave packet formalism which was put forward in the context of the quasi static thermal lens $n(r)$ [4, 9, 14] (based on [15], Baryshevskii et al.) to the time-modulated thermal lens $n(r,t)$. To this end, the solution to the plane wave scattering problem [4, 16] was used to construct the scattered probe-beam, whereafter the interference is computed. *However, the particular plane-wave spectrum chosen is ill-defined.*

Firstly, the spectrum given is divergence around the beam focus $\mathbf{r} \to \mathbf{r_0}$. This adds to the already present divergence of the idealized scattering potential.

Secondly, the plane-wave spectrum should at most depend on the axial coordinate z per definition (i.e. must not dependent on $|\mathbf{r} - \mathbf{r_0}|$), see for instance the book of L. Novotny and B. Hecht [17]. A meaningful description of the probe beam can be found in the literature on electromagnetic beam scattering [18, 19] and has been successfully applied before to the quasi-static PT microscopy scenario [4, 9, 14]. Only towards the end of their discussion, the authors of [1] correctly suggest that such a pw-spectrum is more appropriate.

Regarding the scattering amplitude

The authors of [1], Miyazaki et al., assume that the scattering amplitude is small compared to unity, $f_k(\theta,t) \ll 1$. At low frequencies this becomes a questionable assumption. In the low-frequency limit of $kr_c \to \infty$ the in-phase amplitude (the second term of Eq. (6) in [1]) attains its maximum value of $(\Delta n/n_0)Rk^2r_c^2/2$ of in a forward direction where $1/\sin(\theta/2) = \sqrt{2}kr_c$. While the refractive index perturbation $\Delta n/n_0$ may be small, the amplitude diverges as $k^2r_c^2$ becomes arbitrarily large [4].

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In calculations within the generalized Lorenz-Mie scattering framework we found that it is necessary to include both the scattering and the interference contribution to the forward transmission and therefore the photothermal signal [2,4–6]. In these works we also found that each individual contributions is non-zero while it is only their sum gives the experimentally observed correct zero PT signal for vanishing probe beam offset. It may be speculated that this is the reason for the incorrect non-zero signal found in [1], i.e. the restriction to the interference term only. For the reasons given above, it appears to be at least a non-trivial assumption that should be scrutinized. Only in the limit of high frequencies and small thermal diffusion lengths $r_c \ll \lambda$ the assumption of a purely interferometric signal is appropriate [3].

The scattering amplitude in Eq. (6) of [1], Miyazaki et al., is also missing an overall factor $-2k^2$. As it stands, the amplitude has units of $[\mathrm{m}^3]$ instead of $[\mathrm{m}]$ as required by the. (5) of Ref. [1] which defines the unitless scalar optical far field via $U \to e^{ix} + f_k e^{ikr}/r$. As a consequence, a spurious wavelength dependence is present in the Rutherford cross-section component, i.e. in the first summand of the amplitude. Similar to the quantum mechanical treatment of the Coulomb scattering problem, the scattering cross-section $\mathrm{d}\sigma/\mathrm{d}\Omega = |f_k(\theta)|^2 = R^2 \Delta n^2 \sin^{-4}(\theta/2)/4n_0^2$ is found to be identical to the classical one and should thus be wavelength independent. This is indeed what was found before [4,9,14,20].

Regarding the angle θ

Following Eq. (5) in [1], Miyazaki et al., the angle θ is defined as the angle between $\mathbf{k}$ and the scattering field wave vector $\mathbf{k}_{\mathrm{sc}}$. *However, in view of Fig. 1 and especially in combination with the following Eq. (14) it is confusing as to what* θ *actually refers. The figure seems to suggest that it is an angle relative to the fixed optical axis just the way it is actually used in Eq. (14).* Performing the integration in the angular spectrum and in the scattered probe beam evaluation a reorientation of the solution is necessary for each partial wave contribution [4,9,14], i.e. the evaluation of $U_{\mathrm{sc}}(\vartheta, \varphi)$ via Eq. (11) in [1] requires to set

$$\theta = \arccos\left(\cos(\vartheta)\cos\left(\phi'\right) + \sin(\vartheta)\sin\left(\phi'\right)\cos(\phi - \varphi)\right), \qquad (1)$$

with ϑ and φ being the polar and azimuthal coordinates of $\mathbf{r}$ and (adopting the notion of [1]) ϕ' and θ' being the polar and azimuthal angles of $\mathbf{k}$.

Regarding the optical resolution

The following statement is made in [1], Miyazaki et al.:

> ”In this regard, it is interesting to examine the spatial resolution with changing modulation frequencies, because when r_c is much smaller than the focal spot size, the spatial resolution (the point-spread-function) should be determined by the product of the pump and probe beam intensity at the focal point.”

As discussed before, the PT signal at the focal point is zero. In general, *the spatial dependence of the PT signal is not given by the product of the two beam’s point-spread-functions.* While this has been suggested before [16], the incorrectness of this hypothesis is demonstrated by the fact that the signal possesses a zero-crossing as discussed above.

The spatial extent of the resulting PT signal can be inferred exactly from calculation in the GLMT framework using the full thermal wave field [2–5]. Naturally, the PT signal is still limited by diffraction contrary to the claim constructed already in the title of [1], Miyazaki et al.

The resolution remains a problem to be solved, i.e. the combined PT signal when two absorbing particles are nearby and probed is yet to be explored, both experimentally as well as theoretically. The generalized Lorenz-Mie theory for multiple scattering centers [21] would allow a theoretical assessment of this problem.

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