Combining micro- and macroscopic approaches in a model of a thermal lens experiment in disperse media

Vyrko EA$^{(1)}$*, Khabibullin VR$^{(1)}$, Volkov DS$^{(1)}$, Proskurnin MA$^{(1)}$

(1) Department of Analytical Chemistry, Chemistry Department, Lomonosov Moscow State University, Moscow, Russia

*Corresponding author's email: evgvyr@disroot.org

An exact mathematical solution for the problem of heat dissipation by a single immobile sphere was combined with ideas of the aberrant approach to thermal-lens signal computation into a simplified computational model of a thermal lens experiment in a solution of noble metal nanoparticles. The model predictions for solutions of 5, 20, and 40 nm gold and silver nanoparticles were compared with the behavior of the homogeneous system with equivalent optical properties to estimate the individual impact of such heterogeneous factors as particle size and concentration on the divergence of the model from the homogeneous system was estimated.

Natural and technological finely dispersed heterogeneous systems are essential chemical and biochemical objects and materials. Identifying and determining the components of such systems in several forms and the composition of different phases *in vivo* or *in situ* are required. Often, solving these tasks requires highly sensitive and non-destructive methods simultaneously. Today, there is no straightforward solution to this problem; various approaches are being developed. Photothermal spectroscopy (PTS) provides simultaneous non-destructive chemical-analysis opportunities in a wide spectral range and non-destructive testing (size and thermophysical parameters estimation) of dispersed systems and nanosystems, which most other methods cannot implement.

However, the multisignal nature of PTS is also a disadvantage since it requires understanding the signal-generation mechanisms for practically significant objects. Despite a relatively large number of models considering individual aspects of liquid heterogeneous systems, there is still no general model that describes all the photothermal features in such systems. This problem complicates the use of PTS in the qualitative and quantitative assessment of dispersed systems.

The aim of this study is the development of a photothermal response model for finely dispersed systems with thermal lens spectrometry (TLS) as the universal method of PTS and determination of analytical parameters for components of such systems in macro- and microscopic versions on several models and natural systems (nanoparticles of noble metals, carbon nanomaterials, and natural nanoparticles).

On the one hand, we started from the models based on the so-called efficient heat capacity, but they have limitations. In particular, it is assumed that the kinetics of the photothermal effect remains unchanged, which is not always valid for natural objects. On the other hand, photothermal confocal microscopy and femtosecond photoabsorption spectroscopy have models of heat propagation from a single particle. Such models can be used in TLS but need to be generalized to a system of many particles. Thus, we developed static models of a photothermal signal for TLS based on thermodynamic models of heat propagation, electromagnetic interaction of nanosized particles (homogeneous and of the core-shell type) with laser radiation, and the aberration model of the thermal lens effect. Static models are the basis for the next stage, dynamic models, considering the influence of local dynamic concentration fluctuations of dispersed particles on developing a photothermal signal.

An exact mathematical solution for the problem of heat dissipation by a single immobile sphere was combined with ideas of the aberrant approach to thermal-lens signal computation into a simplified computational model of a thermal lens experiment in a solution of noble metal nanoparticles. A model of thermal-lens experiment in a solution of noble metal nanoparticle built upon the problem of heat dissipation by an immobile sphere of a perfect conductor in an infinite medium was implemented as a software unit. The spatial frame of nanoparticles in a disperse solution was regarded as a rigid rectangular lattice. This simplified model considers the specificities of heat exchange at the particle-liquid interface and the discrete nature of heat generation in a disperse system.

The model predictions for solutions of 5, 20, and 40 nm gold and silver nanoparticles for a wide range of conditions (particle size and concentrations, excitation power, thermophysical parameters; see Fig. 1, as an example of transient calculations) were compared with the behavior of the homogeneous system with same optical properties. The latter was used to estimate the individual impact of such heterogeneous factors as particle size and concentration on the divergence of the model from the homogeneous system. The details of the used approach and applicability limits of both the classical theory of the thermal lens effect and variants of the heterogeneous model will be discussed in the presentation.

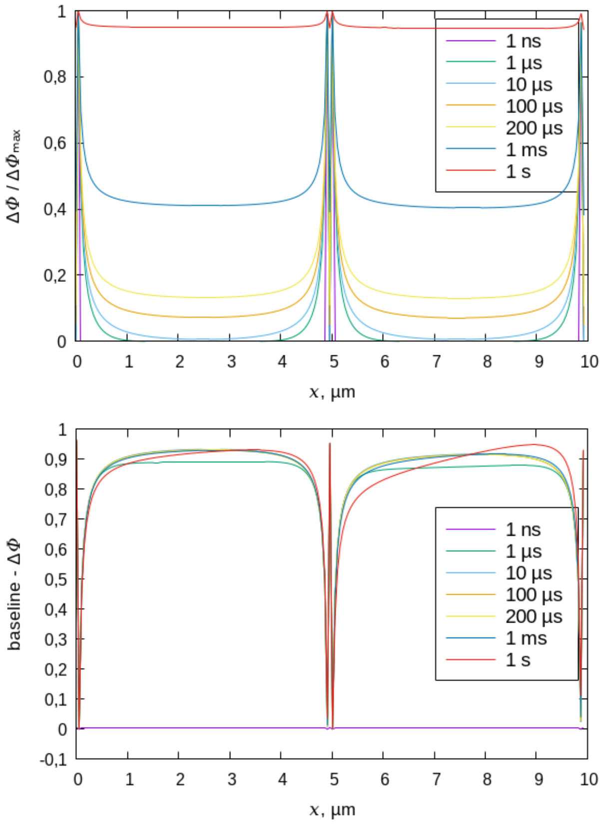

Fig. 1. Initial segment of the temperature curve in a monodisperse 40 nm gold nanoparticle solution. Dashed line demarcates the phase shift curve for a homogeneous solution with the equivalent optical and thermophysical properties; absorption cross-section, 3.38172×10^{-15} m²; nanoparticle volume concentration, $8.2\times\cdot10^{14}$ particles/m³ (0.53 mg/L), excitation power, 1 mW; absorbance, 0.012.

Further tests showed that these two typical heterogeneous features, taken alone, cannot describe the complexity of the transient thermal-lens experiment in a real heterogeneous system. Instead, it suggests the existence of other factors playing a significant role in the time domain of the standard thermal lens technique. A plausible candidate is the thermally induced particles drift.

Acknowledgments – The study was funded by the Russian Foundation for Basic Research, project number 21-33-70143 mol_a_mos. This research was performed according to the Development program of the Interdisciplinary Scientific and Educational School of Lomonosov Moscow State University, “The future of the planet and global environmental change”.