Why not use the thermal radiation for nanothermometry?

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The measurement of temperature with nanoscale spatial resolution is an emerging new technology and it has important impacts in various fields of science and technology. An ideal nanothermometer should be not only accurate but also applicable over a wide temperature range and under diverse environmental conditions, and the measurement time should be short enough to follow the evolution of the system. However, many of the existing and competing techniques are limited by drawbacks such as low sensitivity and systematic errors due to fluctuations of fluorescence, local environment, and optical properties of the surrounding medium. Planck’s law offers an relation between the absolute temperature of the system under interrogation and the thermal spectrum. So why not use thermal radiation for nanothermometry?

In 2015, stable aerosol trapping of individual metallic nanoparticles (80-200 nm) under atmospheric pressure was reported. As the thermal conductance of air is much lower than of water, the heating associated with laser irradiation of airborne metallic nanoparticles is expected to be tunable in the range from room temperature to the melting point of gold (1,337 K). Currently, there exists no method to experimentally access the temperature of aerosols of gold NPs. Therefore, I looked into the possibility of accessing the temperature through a spectral analysis of thermal radiation.

Thermal (black-body) radiation has a spectrum that depends entirely on the temperature of the particle. The emission intensity for a specific wavelength can be calculated from Planck’s law and by balancing the absorbed power with the emission power and the heat dissipation, the particle temperature can be extracted.

To my knowledge the first attempts to probe a temperature field at small scales were based on the use of local nanotips used as a nanoscale thermocoupler. This is the so called SThM (scanning thermal microscopy) technique and it was introduced in 2014 by the group of Levy. The authors showed that they, with the nanotip, were able to measure temperature rises of 15 K. In 2016, the group of Süzer reported on another near-field technique to map the temperature of plasmonic nanoantennas. The experiments were conducted in the context of heat-assisted magnetic recording and the technique was termed Polymer Imprint Thermal Mapping (PITM). The technique explores thermosensitive polymers that permanently cross-links upon heating, which causes a thickening that can be subsequently mapped with AFM. However, these near-field techniques are very invasive and thus has limited application, particularly, for nanoparticle aerosols. In the following I will evaluate the possibility of measuring thermal radiation of gold nanoparticles in the far-field, instead of the near-field.

\[ P_{\text{abs}}(I_L) = P_{\text{em}}(T) + c_p \frac{dT}{dt} \]

where \( I_L \) is the laser intensity, \( P_{\text{abs}} \) and \( P_{\text{em}} \) are the power absorbed from the laser and dissipated by the particles, respec-
tively. $T$ is the temperature of the particles and $c_p$ the heat capacity. The absorbed power will be proportional to the laser intensity, according to

$$P_{\text{abs}} = AI_L,$$

(2)

where $A$ depends on geometrical factors like the shape and size of the particles and on optical parameters like the absorption and scattering cross sections given in Fig. 1. As the particles are in low numbers, the heat conduction from particle to particle is neglected. Therefore, in vacuum the only mechanism able to dissipate heat from the particles is blackbody thermal radiation and the emitted power will follow the Stefan-Boltzmann law:

$$P_{\text{em}} = B\sigma_B(T^4 - T_R^4),$$

(3)

where $\sigma_B$ is the Stefan-Boltzmann constant, $T_R$ the room temperature and $B$ a constant that depends on the emissivity and geometry of particles. This blackbody emission can be detected by integrating over all emitted wavelength. Alternatively, the emission in a narrow spectral range around a given wavelength $\lambda$ can be collected through a monochromator. In this case the measured intensity will follow Planck’s spectral radiance:

$$I_{\text{em}}(\lambda) = \varepsilon \frac{2\pihc^2}{\lambda^5(e^{\frac{hc}{\lambda k_B T}} - 1)},$$

(4)

where $\varepsilon$ is the emissivity, $h$ is Planck’s constant, $c$, the speed of light and $k_B$, the Boltzmann constant. For nanoparticles irradiated and heated to a few hundred degrees (Fig. 2), the peak emission is in the NIR spectrum with a tail into the visible regime.

Fig. 2 Spectral radiance over the NIR spectrum for 50° C, 100° C, and 200° C.

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Following the train of thought of Ref. 6 I used this set of equations to calculate the radiation emitted by spherical gold nanoparticles (100 nm). In order to simplify the problem, I considered every particle to absorbs and emits radiation independently, i.e., neglecting shadowing effects. Under these ideal conditions, the constants $A$ and $B$ are simply:

$$A = \pi R^2(1 - e^{-\alpha R})$$

(5)

and

$$B = 4\pi R^2(1 - e^{-\alpha R}),$$

(6)

where $R$ is the radius of the particles, $\alpha$ the mean optical absorption and the quantity in parentheses corresponds to the emissivity of an infinite layer of thickness $R$. The heating of the particles under irradiation with a laser intensity of 456 mW/mm$^2$ was calculated, with parameters detailed in table 1. The temperature evolution has been plotted in Fig. 3 (dashed red curve). Initially, when the laser is turned on, the temperature increases at constant rate as the emitted power is small, hence, the heating rate is proportional to the intensity of the laser. This behavior continues up to $\sim 500^\circ$ C as thermal emission is only important at high temperatures. When the laser is turned off, the aerosol cools proportional to the emitted power, i.e., $T^4 - T_R^4$. Once the temperature evolution as a function of time is known, it is possible to calculate the intensity of radiation emitted at any wavelength by simply introducing $T$ in Planck’s distribution Eq. (4). The emitted intensity at a wavelength of 470 nm (blue) has been calculated and the result is shown in Fig. 3 (solid blue curve). Interestingly, the emitted intensity only raises when temperatures has reached $\sim 500^\circ$, because of the non-linear dependence on $T$ given by the Planck distribution. In contrast, the emission decays rapidly when the laser is turned off.
According to this analysis, the laser beam is able to heat the particles because of the lack of dissipation mechanisms. This is why in vacuum, only radiative thermal emission is significant. However, at atmospheric pressure, heat conduction through the surroundings would be so efficient that no emitted radiation at all would be detected. This means that at intermediate pressures one would detect a progressive diminution of the emitted radiation. This can be easily calculated. At steady state, the energy balance equation will be:

\[ P_{\text{abs}}(I_L) = P_{\text{em}}(T) + P_{\text{gas}}(T), \]

where \( P_{\text{gas}}(T) \) is the power dissipated through the gas. At a low enough pressure, it can be approximately given by the product of the number of gas collisions on the particle surface times the mean energy exchanged in one collision:

\[ P_{\text{gas}} \approx 4\pi R^2 \frac{p}{4\pi mk_B T_R} k_B(T - T_R) \frac{3}{2}, \]

where \( p \) and \( T_R \) are the gas pressure and temperature, respectively, \( m \) is the atomic mass and the factor \( 3/2 \) arises from the assumption of a monoatomic gas. Eq. (7) and Eq. (8) allow us to calculate the dependence of the steady state emission intensity versus gas pressure. The result is an exponential dependence:

\[ I_{\text{em}} = I_0 e^{-p/p_0}, \]

with \( p_0 \) of the order of few Pascals. With the parameters listed in table 1, the emission intensity for atmospheric pressure (~100 kPa) is less than \( 10^{-300} \) of the emitted intensity in vacuum (Fig. 4).

Concluding remarks

Thermal (black-body) radiation has a spectrum that depends entirely on the temperature of the particle and the emission intensity for a specific wavelength can be calculated from Planck’s law. Therefore, by balancing the absorbed power with the emission power and the heat dissipation, the particle temperature can be extracted. However, standard thermal imaging, which is often used to measure heating of nanoparticles in suspension, does not apply for nanothermometry. The reason is that the wavelength of several microns of the peak intensity, given by Planck’s law, would lead to a very poor spatial resolution. Furthermore, as the emission only becomes pronounced for temperatures of several hundreds of degrees, the measurable temperature range is limited to temperatures \( \sim 10^5 \) C. Thus, this method is not appropriate to measure ambient temperature changes of single nanoparticles.

Moreover, most optical components are not transparent in this wavelength range and, in contrast to light that is propagating, heat just diffuses. This makes any temperature distribution arising from a single nanoparticle confined to its vicinity, and not propagating to the far field. For these reasons, thermal imaging for nanothermometry should not be the first option if the goal is to measure the temperature of gold nanoparticle aerosols that are both optically trapped and heated by a single laser.

| Table 1 Parameters |
|--------------------|
| Laser intensity    | \( I_L = 146 \text{ mW/mm}^2 \) |
| Room temperature   | \( T_R = 293 \text{ K} \) |
| Particle radius    | \( R = 100 \text{ nm} \) |
| Heat capacity per particle | \( c_p = 1 \cdot 10^{-14} \text{ J/K} \) |
| Emissivity        | \( \varepsilon = (1 - \exp(-\alpha R)) \) |
| Absorption coefficient | \( \alpha = 1.9386 \cdot 10^{19} \text{ m}^{-1} \) |
| Reflectivity      | \( r = 0 \) |

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