An estimate of size of copper nanoparticles levitating over the melt surface using the measurements of spectral reflectance

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Abstract. A strong decrease in normal reflectance of a probe laser beam of 660 nm wavelength reflected from the surface of copper sample just after the beginning of the sample melting in a rarefied argon atmosphere has been observed recently by the authors. A similar time dependence of the reflectance is obtained in the laboratory experiments of the present paper at the wavelengths of 532 nm. The additional spectral measurements enable the authors to estimate the size of condensed nanoparticles levitating over the copper melt.

1. Introduction
The condensation of vapor of molten substances is extensively used to produce nanoparticles during the last two decades. The state-of-the-art including the production of metal nanoparticles has been reported in the literature [1–6]. Laboratory experiments of [7, 8] in a vacuum chamber at a very low pressure of argon showed that the specular reflection of the probe laser radiation with the wavelength of $\lambda = 660$ nm from the copper sample strongly decreases, almost immediately after the beginning of copper melting. This is explained by formation of a cloud of condensed nanoparticles over the copper melt similar to that for the levitating droplet cluster [9]. The theoretical model for interaction of the laser radiation with the cloud has been suggested in [8]. It was shown for the first time that the abnormal decrease in the sample reflectance is explained by the dependent scattering of laser radiation by closely spaced copper nanoparticles formed over the sample surface. The particular objective of the present paper is to measure the reflectance at $\lambda = 532$ nm and to analyze the experimental results for possible estimation of the particle size.

2. Laboratory set-up and experimental procedure
The modified laboratory set-up is presented in figure 1. The bead of thermocouple was separated from the lower surface of the sample by 100 µm nickel layer. Two probe lasers with wavelength of $\lambda = 660$ nm and 532 nm, power of 42 and 25 mW, and beam diameter of 8 and 2.5 mm, respectively, were used. The incidence angle was about 5°. The fluctuations of laser power were measured by sensors 13, whereas the sensors 14, 15 were used to measure the radiation intensity reflected from the sample in the specular direction. The corresponding normalized value is hereafter called as the normal reflectance. Both the screen and camcorder were used to observe the patterns of the light scattered by the sample. The thermo-emf of thermocouple, the data of sensors and the scattering patterns were registered by a computer.
3. Copper sample and experimental results

The sample of 99.9% Cu was placed in a vacuum chamber filled by argon at pressure of 10 or 30 kPa. The upper surface of a cylindrical sample of diameter 10 mm and height of 2.2 mm was ground in one direction. The grooves of roughness about 70 nm on the original surface make evident the melting of a surface layer with the use of scattering patterns. At low temperatures, the pattern looks as a bright central spot and the narrow strip in the direction perpendicular to the grooves. Obviously, the melt surface is smooth, and the melting can be well identified by a disappearing the strip. This technique proposed in [10] was successfully used in [7, 8].

Some results of measurements during the experiment are presented in figure 2. The time dependence of thermo-emf, $U$, follows the sample temperature. The almost constant temperature corresponds approximately to the final stage of copper melting. The “plateau” in the dependence of $U(t)$ is explained by the latent heat of copper melting. The maximum normal reflectance, $R_n^{\text{max}}$, at the complete melting of the sample surface was used to normalize the reflectance value: $\bar{R}_n = R_n / R_n^{\text{max}}$. The abnormally strong decrease in the normal reflectance is more pronounced at larger pressure of argon. The effect of argon pressure agree with the data of [11] on the role of argon in the formation of condensation nuclei.

Figure 2. Time variation of thermo-emf and normalized reflectance: a – measurements at two wavelengths, b – effect of argon pressure.
4. Theoretical model for interaction of laser radiation with a cloud of copper nanoparticles

Let us compare the optical properties of single spherical particles calculated using the rigorous Mie theory and the Rayleigh approximation [12, 13]. The following values of complex index of refraction of copper, \( m = n - i\kappa \), where \( n \) is the index of refraction and \( \kappa \) is the index of absorption, were used in the calculations (see [8] for more details) [14]:

\[
m = 0.776 - 2.42i \text{ at } \lambda = 532 \text{ nm}, \quad m = 0.128 - 3.754i \text{ at } \lambda = 660 \text{ nm}
\] (1)

One can see in figure 3 that the Rayleigh approximation can be used only for very small copper particles with radius of \( a < 30 \) nm at \( \lambda = 532 \) nm, whereas this approximation is acceptable for particles with radius \( a < 100 \) nm at \( \lambda = 660 \) nm. The data for \( \lambda = 660 \) nm made it possible to suggest the theoretical model for the normal reflectance of the particle cloud in paper [8].

\[\text{Figure 3.}\] The efficiency factor of absorption, \( Q_a \), and transport efficiency factor of scattering, \( Q_s^{tr} \), for copper particles at \( \lambda = 532 \) nm (a) and 660 nm (b). Solid lines—the Mie theory, dashed lines—the Rayleigh theory.

When the optical properties of individual spherical nanoparticles are well described by the Rayleigh theory, one can use the Maxwell-Garnett theory [15, 16] for the effective optical constants of the particle cloud. This approach is widely used in quite different applications like microwave radar scattering by cumulus clouds [17] or absorption of solar radiation by soot-containing ice grains in the polluted snow [18]. The complex permittivity of a cloud medium is calculated in terms of particle polarizability by applying the Lorentz–Lorenz formula. In our case, the effective complex index of refraction, \( m_{\text{eff}} = n_{\text{eff}} - i\kappa_{\text{eff}} \), is expressed as follows:

\[
m_{\text{eff}}^2 = \frac{1 + 2f_v\psi}{1 - f_v\psi}, \quad \psi = \frac{m^2 - 1}{m^2 + 2},
\] (2)

where \( f_v \) is the volume fraction of particles in the cloud. A combination of Eq. (2) with the known equation for the normal reflectance of the optically thick cloud

\[
R_n^{\text{min}} = \left( \frac{n_{\text{eff}} - 1}{n_{\text{eff}} + 1} \right)^2, \quad \text{when } \kappa_{\text{eff}} \ll n_{\text{eff}},
\] (3)

where \( R_n^{\text{min}} = R_n^{\text{min}} \times R_n^{\text{max}} \approx 0.04 \times 0.84 = 0.036 \) at \( \lambda = 660 \) nm, yields \( f_v \approx 0.22 \).

Using this value of \( f_v \) one can easily show that the above theoretical model is inapplicable at the wavelength of \( \lambda = 532 \) nm because a theoretical prediction does not agree with the experimental value of \( R_n^{\text{min}} \approx 0.03 \). This means that the Rayleigh approximation (as one can expect, see figure 3a) cannot be used for copper nanoparticles at \( \lambda = 532 \) nm. Fortunately, this result enables us to estimate the range of particle radius: \( a < 30 \) nm. Note that the latter estimate was obtained for the first time.

5. Conclusions

The recently developed theoretical model of reflection of laser radiation from the optically thick cloud of condensed nanoparticles levitating over the copper melt is true only in the Rayleigh regime of scattering by single particles. At the wavelength of 660 nm, the Rayleigh theory is correct for copper nanoparticles with radius up to 100 nm. The Mie theory calculations showed that the new measurements at the wavelength of 532 nm cannot be analyzed using the same model because the Rayleigh
approximation is correct only for very small particles. This enables us to estimate for the first time the radius of copper nanoparticles in the cloud: it is less than 30 nm.

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