Pyrometric investigation of nanoparticles condensation process in gaseous and superfluid helium

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Abstract. The work is devoted to the study of thermal radiation accompanying the condensation of products of pulsed laser ablation of a tungsten target in vacuum, superfluid and gaseous helium. Pyrometric measurements have shown that the radiation characteristics depend on the medium. The obtained data imply that the sources of radiation in vacuum and gas are predominantly submicron particles, while in superfluid helium (He II) they are nanometer particles. These conclusions have been confirmed by electron microscopy data.

1. Introduction
Pulsed laser ablation (PLA) is a common way to produce nanoparticles due to its versatility and ease of use. PLA normally yields spherical clusters with a broad size distribution (from units to hundreds of nanometers) that depends on the target material, laser beam parameters and the medium in which ablation is carried out [1]. Meanwhile, the ablation of metals in superfluid helium (He II), which is a quantum liquid, yields quite different products — networks of thin (d ~ 2–8 nm) nanowires [2]. Such a difference should be associated with the features of He II — the presence of quantized vortices and record high thermal conductivity, which only enhances an interest in studying the condensation processes involved.

The mechanism of nanowires growth was proposed in [2]. It includes the concentration of metal nanoparticles in quantized vortices and their melting during mutual collision inside of the vortex core due to the heat released when the surface energy decreases. The study of the features of thermal radiation of clusters accompanying the process of nanostructures synthesis allows us to obtain information on the dynamics of processes occurring in the medium. Thus, the objective of this work was to explore the thermal radiation accompanying the condensation of clusters in vacuum, gaseous and superfluid helium, and with its help to establish some features of the particle growth mechanisms inherent to each of these media.

2. Experimental
Experimental technique and apparatus employed in this study (see figure 1) were described in detail elsewhere [3]. Its basis was a pumped-out helium cryostat equipped with optical windows (d = 40 mm).
Ablation of a target located inside the cryostat was carried out by using a solid-state Nd:LSB pulsed laser with the following beam characteristics: \(\lambda = 1.064 \, \mu\text{m}\), pulse energy \(E = 0.1 \, \text{mJ}\), pulse duration \(\tau = 0.4 \, \text{ns}\), and pulse repetition frequency \(f = 50 \, \text{Hz}\). Ablation was carried out at room temperature and a pressure of \(10^{-1} \, \text{torr}\) in vacuum, and at room temperature and atmospheric pressure in gaseous helium. Ablation in He II was carried out at pressure 1 torr, which corresponds to \(T \approx 1.2 \, \text{K}\). The geometry of the entire system remained unchanged during ablation in all media.

Visible radiation accompanying the condensation of ablation products was monitored by a photomultiplier (PMT) with a gate function (Hamamatsu H11526-01-NN), which allows protecting the PMT from "exposure" by scattered laser radiation by means of organization of a small turn-on delay time (~ 100 ns) relative to the moment of laser pulse.

![Experimental setup](image)

**Figure 1.** Experimental setup

Other details of our pyrometric measurements can be found in [3]. Emission spectra were taken using a set of narrow-band (~10 nm) interference filters (Thorlabs) within the range 400–700 nm (with intervals of 50 nm) and a reference source (incandescent lamp SLS201L, Thorlabs) with a known brightness temperature (2796 K). Tungsten nanoparticles were selected as an object of study because of high melting point of tungsten (3695 K) which leads to high intensity of black-body emission arising during condensation of its ablation products.

3. **Thermal radiation from nanoparticles**

As is known [4–6], the emissivity \(\varepsilon\) of spherical nanoparticles increases with a decrease in their radius \(r\) given that \(r \ll \lambda\), where \(\lambda\) is the emission wavelength. In literature on the pyrometry of nanoparticles the Planck formula is often used with the emissivity \(\varepsilon \sim 1/\lambda\) or, equivalently, the inversely proportional to the wavelength effective cross section \(\sigma = \sigma(\lambda)\) of the radiation process is introduced. In this case, it is believed that the bulk of the particles is optically transparent relative to their thermal emission in contrast to the case of large particles, when the surface radiates. In this work, for processing of experimental data a following fitting dependence was applied:

\[
P_{\lambda} = \sigma(\lambda) \cdot \frac{2\pi hc^2}{\lambda^5} \cdot \frac{1}{e^{\frac{hc}{kT}} - 1},
\]

where \(P_{\lambda}\) is the radiation power per unit spectral range, \(\pi\), \(h\), \(c\), \(k\) are fundamental constants, \(\sigma = \sum \pi r^2 \frac{1}{2} f(\lambda)\) is the total radiation cross section of the ensemble of particles, \(f(\lambda)\) is the fractional rational function of the complex dielectric constant, which is slightly different from unity for tungsten (the value \(f(\lambda) \equiv 1\) was used in the calculations to estimate). Thus, the additional factor \(1/\lambda\) in the Planck formula applied to the ensemble of nanoparticles arises due to the specific features of the emissivity of small nanoparticles.
Integration over all wavelengths leads to the following expression for the total radiation power of the ensemble depending on temperature:

\[ P = \int_0^\infty P_\lambda(\lambda) d\lambda = \frac{36\pi \zeta(5)}{\hbar^4 c^3} \cdot V \cdot (kT)^5, \]

where \( \zeta(n) \) is the Riemann zeta function, which can be estimated numerically for an odd argument. It can be seen from the obtained formula that for small particles the radiated power is \( P \sim V \cdot T^5 \), while for large particles, in accordance with the Stefan-Boltzmann law \( P \sim S \cdot T^4 \). Thus, small particles emit much more efficiently.

4. Results and discussion

Figure 2 represents time dependence of measured color temperature \( T_c \) during laser ablation of W in vacuum, superfluid He, and gaseous He.

For ablation in vacuum (curve 1), the initial stage \( t < 10 \mu s \) corresponds to plasma expansion [7], where the adopted formalism is improper. Later (up to \( t = 175 \mu s \)), \( T_c \) is sustained on a level around the W melting point \( 4000 \) K which is almost \( 1000 \) K higher than in He II. In a gas, temperature \( T_c \) decreases faster due to direct heat transfer from spreading tungsten nanoparticles to gas molecules.

Figure 3 shows the decay curves for the emission intensity at \( \lambda = 700 \) nm during laser ablation of W in vacuum, superfluid He, and gaseous He. All curves are becoming linear in semi-logarithmic coordinates. The initial intensities and cooling rates are higher in the case of He II, despite the fact that the temperature of the emitting particles is higher in vacuum (see figure 2). Apparently, in superfluid helium, both initially and throughout the process, particles emit brighter and thereby cool down more efficiently. At the initial moments, the radiation intensity in vacuum and in gas coincides. These data indicate that in the case of helium gas and vacuum we are dealing with a small number of large particles, while in He II, on the contrary, we have a large number of small particles.

Figure 2. The radiation temperature of tungsten clusters during its condensation in vacuum (1), in He II (2) and in a helium gas under normal conditions (3). \( T_m \) is melting point of W (3695 K).

Figure 3. The radiation intensity versus time for a wavelength of 700 nm in vacuum (1), in superfluid helium (2) and in gaseous helium under normal conditions (3).

The same conclusion can be made if we analyze the time dependence of the effective particle emission cross sections \( \sigma(t, \lambda = \text{const}) \), calculated on the basis of intensity and temperature data and shown in figure 4 for cases of vacuum, gas and superfluid helium. Figure 4 clearly demonstrates that the cross sections in the case of He II are an order of magnitude greater in absolute value and retain higher values for much longer time than in case of vacuum or gas.
Figure 4. Dependence of the particle emission cross section $\sigma$ on time for a wavelength of 700 nm in vacuum (1), in superfluid helium (2), and in gas at 1 atm (3).

It is important to note that, although the figure shows only the cross section for a certain wavelength of 700 nm, the particle emission cross sections for all measured wavelengths (400 - 700 nm) show very similar temporal behavior (in vacuum at times greater than 10 $\mu$s), which confirms accepted model of blackbody radiation.

Assuming that the mass of tungsten evaporated by a single laser pulse does not depend on the medium, which is confirmed by microscopy of targets performed after ablation, the differences in effective cross sections should be interpreted as differences in how the mass of the substance is distributed over the ensemble of nanoparticles. Indeed, in the case of vacuum, for which the cross section is an order of magnitude lower, a significant part of the mass is most likely concentrated in large optically opaque particles, radiation in this case occurs from the surface of the particles. In He II, the mass is distributed between a large number of small particles that efficiently emit from their entire volume due to the optical transparency of the ensemble for the visible range, which provides both a large effective cross section and a higher energy loss rate (see figure 3).

Figure 5. Electron microscopy of tungsten nanoparticles obtained in vacuum (a) and in superfluid helium (b).

The TEM results in figure 5 suggest that the emitting species in vacuum are large balls while in He II they are nano-sized wires. In this case, long $\sigma$ decay times in He II can be rationalized in terms of the mechanism suggested [2] for formation of nanowires in quantum vortexes. Concomitant process of local heating at contact points can be a cause for rapid decay of radiation intensities in He II.
5. Conclusion
The thermal radiation of as-released by means of PLA nanoparticles has demonstrated its features, which are reflecting the specifics of both the composition of the generated ensembles of nanoparticles and their interaction with the medium (He II, vacuum and atmospheric pressure He gas). These features allow us to say that in He II right after the laser pulse evaporated metal is represented as a large number of small optically transparent particles, whereas in vacuum and gas the main products of condensation just after the laser pulse are large opaque particles. Electron microscopy of ablation products supports that conclusion.

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