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RADIATIVE EMISSION OF HOT METALLIC CLUSTERS

B.M.Smirnov, Weidele H.[+]

Institute of High Temperatures, 127412 Moscow, Russia

[+]*Laboratorium voor Vaste-Stoffysica en Magnetisme*
B-3001 Leuven, Belgium

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The analysis of experimental data for the relaxation of freely moving hot niobium and tungsten clusters shows that they are cooled as a result of radiative emission. The absorption cross sections per atom of niobium and tungsten clusters in the temperature range of 3100 – 3700 K are $(4-7)\cdot 10^{-18}\,\mathrm{cm}^2$, and the absorption process loses the resonant character at these temperatures.

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Radiative emission of hot metallic clusters determines the heat balance in clusters beams and plasmas. The radiation power can be expressed through the absorption cross section of clusters, which may be a convenient parameter to characterize this process. A reliable method to measure the absorption cross section of clusters is photoinduced dissociation [1]. According to this concept, the absorption of photons leads to the decay of a cluster and, hence, to variation of its mass. The absorption cross section follows from the measurement of the cluster mass abundance spectrum as a function of the laser intensity. By using this method the absorption cross sections for some cold metallic clusters were measured (for example, [2–5]).

However, the radiative parameters of clusters in hot gases are expressed through the absorption cross section of hot clusters which may differ from those of cold clusters. These data may be derived from the measured relaxation parameters of hot clusters [6–8], from which the cooling by radiation has been determined under experimental conditions. The goal of this paper is to find the absorption cross sections of hot clusters on the basis of their relaxation parameters.

The general principle of the experiments under consideration works as follows. Metallic clusters of known size range in a free cluster beam are heated by a laser pulse. Then a certain time after laser irradiation the radiative spectrum of the clusters is measured and the signals are accumulated and summarized from many experimental cycles. As a result, we receive the radiative spectrum of hot clusters as a function of the time delay after the excitation. Assuming a thermodynamic equilibrium within the radiating cluster, one can analyze from these data the character of cluster relaxation and radiation.

Heat balance of hot metallic clusters. We use the Kirchhoff law which establishes the connection between the absorption and emission rates of radiation for a cluster. This corresponds to the principle of detailed balance between the rates of a direct absorption and the reverse process, and we receive for the spectral power of cluster radiation [9]

$$p(\omega) = \hbar\omega i(\omega)\sigma_{abs}(\omega), \qquad (1)$$

where $\sigma_{abs}(\omega)$ is the cluster absorption cross section and

$$i(\omega) = \frac{\omega^2}{\pi^2 c^3} \left[\exp\left(\frac{\hbar\omega}{T}\right) - 1\right]^{-1}. \tag{2}$$

Here $i(\omega)$ is the random photon flux of black body radiation inside a space where this radiation propagates (the temperature is expressed in energetic units). From this we get for the spectral radiation power of a cluster

$$p(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3}\sigma_{abs}(\omega) \left[\exp\left(\frac{\hbar\omega}{T}\right) - 1\right]^{-1}. \tag{3}$$

Let us consider now the heat balance of a cluster which is heated by a laser pulse and is moving freely in vacuum. We assume the cluster to be in a thermodynamic equilibrium which is supported by the kind of the observed cooling processes. Then the state of the cluster is characterized by its temperature, and the heat balance equation during cooling has the form

$$C\frac{dT}{dt} = -\int \hbar\omega i(\omega)\sigma_{abs}(\omega)d\omega - P_{el} - P_{ev}, \tag{4}$$

where C is the cluster heat capacity; the first term on the right-hand side of this equation describes the cluster radiation, the second term takes thermoemission of electrons into account and the third term fragmentation. Considering the bulk model for the cluster, then the heat capacity is expressed by the Dulong – Petit law $C = 3n$, where n is the number of cluster atoms. This formula is valid at high cluster temperatures for $n >> 1$ taking three classical vibrations per cluster atom into account.

When analyzing the thermoemission of electrons from the surface of a metallic cluster [10], it is observed that the spectrum of the released electrons consists of two parts. The first part appeals to thermoemission, and the second one has resonance character and is connected to the formation of autoionization states. If the electron release proceeds under equilibrium conditions, the second mechanism gives only a small contribution to the total thermoemission current which is determined then by the Richardson formula

$$i_{el} = A_R T^2 W \exp\left(-W/T\right). \tag{5}$$

A_R is the Richardson – Dushman constant which corresponds for niobium and tungsten to 57 and 75 $\mathrm{A/cm^2K^2}$ [11], W is the work function which is equal to 4.0 and 4.5 eV respectively [12]. We assume that the thermal energy of the released electrons $\sim T$ is small compared to the work function, thus cooling of the cluster as a result of the liberation of one electron equals to the metal work function. Hence, the power of cluster cooling resulting from thermoemission of electrons for a large metallic cluster is

$$P_{el} = 4\pi r_W^2 \cdot n^{2/3} i_{el} W = 4\pi r_W^2 \cdot n^{2/3} A_R T^2 W \exp\left(-W/T\right), \tag{6}$$

where r_W is the Wigner – Seitz radius which is 1.68 Å and 1.60 Å for niobium and tungsten respectively, n is the number of cluster atoms. We assume the cluster to be large and spherical, so that the cluster radius can be estimated by $r = r_W n^{1/3}$. Thus, formula (6) allows us to estimate the contribution of the thermoemission for the cluster cooling process.

For this process it is of importance that the liberation of electrons leads to the charging of a cluster which influences the subsequent release of electrons due to the attractive

potential of the positively charged cluster. Indeed, the ionization potential of a large spherical cluster of radius r and charge Z is equal to

$$I_Z = W + Ze^2/r, \tag{7}$$

where the first term corresponds to the bulk metal work function W and the second term accounts for the electric Coulomb potential which the released electron must overcome to be removed from the cluster into infinity. Since the cluster is very large, we can neglect the Coulomb potential which results in a slightly increased estimate for the cooling power due to thermoemission. If we solve equation (4), neglect radiation and fragmentation and use the Dulong – Petit formula for the cluster heat capacity, we get for the relaxation time

$$\tau_{el} = \tau_o \exp\left(I_Z/T\right), \tau_o = \frac{3n^{1/3}e}{4\pi r_W^2 A_R I_Z^2}, \tag{8}$$

where e is the electron charge. We assume the cluster charge Z to be constant during this relaxation process.

Analyzing the character of the process under experimental conditions [6 – 8], we receive $\tau_{el} \gg \tau_o$ by several orders of magnitude. For example, for niobium clusters in the size range of $n = 13400$, whose parameters are given in Table 1, $\tau_o = 2.6 \cdot 10^{-14}$ s, while typical relaxation times range from $10^{-6} - 10^{-5}$ s. From this follows that in the first stage of the relaxation process thermoemission is of importance. Simultaneously to the cooling this leads to cluster charging. As a result, the cluster gets a positive charge and after a certain time the thermoemission process ceases. Note that the temperature decrease resulting from one thermoemission event is relatively small. For example, in the above case the liberation of one electron from the niobium cluster decreases the cluster temperature by $\Delta T = 1.2$ K. Hence, in this cluster size range many electrons may be removed by thermoemission to reach remarkable cooling.

Let us determine the final cluster charge if the process proceeds at the temperature T. Then according to formula (8) the final cluster charge is $I_Z/T \approx 20$. We assumed here a weak dependence of τ_{el} on the type and parameters of the cluster. This gives for the final charge of a large metallic cluster

$$Z \approx \frac{r_W e^2 n^{1/3}}{e^2}(20T - W). \tag{9}$$

For example, in the above case for the niobium clusters of the size $n = 13400$ with an initial temperature of $T = 4000$ K this formula gives $Z = 8$. This corresponds to temperature difference of $\Delta T = 12$ K as a result of cooling by thermoemission. Thus fast thermoemission of the relaxing cluster leads at first stage to cluster charging. On a longer time scale the cluster ceases to cool by thermoemission, and the charged cluster cools by radiative emission.

In the next step, instead of thermoemission let us evaluate the contribution of cooling by the evaporation of atoms from the cluster surface. For a large cluster the power consumed by atom evaporation is equal to $P_{ev} = \varepsilon \nu_n$, where ε is the cluster binding energy per atom which is near the melting point $\varepsilon = 7.35$ eV for bulk niobium and $\varepsilon = 8.6$ eV for bulk tungsten [12], ν_n is the evaporation rate of a large cluster with n atoms. Assuming that the cluster surface is comparable to the bulk surface, and furthermore is considered

as a liquid droplet, we receive for the evaporation rate [13]

$$\nu_n = k_o n^{2/3} N_{sat}(T) \exp\left(-\frac{\varepsilon_n - \varepsilon_o}{T}\right), \quad k_o = \pi r_W^2 \sqrt{\frac{8T}{\pi m}}. \tag{10}$$

Here, m is the atomic mass, $N_{sat}(T) \propto \exp(-\varepsilon_o/T)$ is the number density of atoms at the saturated vapor pressure, ε_n and ε_o are the atom binding energies for the cluster and bulk system. Within the framework of the liquid drop model for the cluster we have $\varepsilon_n - \varepsilon_o = \Delta\varepsilon/n^{1/3}$ and receive for large niobium and tungsten clusters $\Delta\varepsilon = 3.0\,\text{eV}$, which can be derived from the surface tension of bulk metals [12]. The ratios of the evaporation power P_{ev} and the radiation power $P_{rad} = \int p(\omega)d\omega$ of tungsten clusters of the size $n = 200$ are $P_{ev}/P_{rad} = 0.09$ at $T = 3500\,\text{K}$ and $P_{ev}/P_{rad} = 0.003$ at $T = 3000\,\text{K}$. Thus, the contribution of evaporation processes in the heat balance of relaxing clusters is small, but must be taken into account at high temperatures.

The small contributions of the thermoemission and evaporation process to the cluster cooling can be explained as follows. The relaxation process proceeds at relatively small cluster temperatures when the energy of one relaxation event ε is large compared to the thermal energy, thus the energy per act of the thermoemission and evaporation process is larger than that of the radiative process. Since the rate of the relaxation processes, fragmentation and thermoemission, is exponentially declining $\nu \sim \exp(-\varepsilon/T)$, the cooling of a freely moving cluster mainly has radiative character.

Finally, let us analyze the experimental data using the radiative character of cluster cooling. Note that the effective cluster temperature which is found from the measured radiative spectrum of the cluster coincides with the real cluster temperature only if the absorption cross section $\sigma_{abs}(\omega)$ does not depend on the wavelength. Below we assume a weak wavelength dependence for the absorption cross section, i.e. we take near a frequency ω_o

$$\sigma_{abs}(\omega) = \sigma_{abs}(\omega_o) + \frac{d\sigma_{abs}}{d\omega}(\omega - \omega_o). \tag{11}$$

The cluster heat balance in the course of relaxation is described by equation (4) accounting the radiative processes by

$$C\frac{dT}{dt} = -\int \hbar\omega i(\omega)\sigma_{abs}(\omega)d\omega. \tag{12}$$

Using formula (11) for the absorption cross section, we can rewrite this equation in the form

$$C\frac{dT}{dt} = -\frac{\sigma_{abs}(\omega_o)}{4}\kappa T^4, \tag{13}$$

where κ is the Stefan – Boltzmann constant. The optimal photon energy $\hbar\omega_o$ follows from the relation

$$\int_0^\infty (\omega - \omega_o)p(\omega)d\omega = 0.$$

Restricting the exponential dependence in formula (2) by $i(\omega) \sim \omega^2 \exp(-\hbar\omega/T)$ and accounting for $\sigma_{abs}(\omega) \sim \omega$, we obtain for the optimal photon energy $\hbar\omega_o \approx 5\,\text{T}$. This relation is used in the subsequent Tables.

The solution of the heat balance equation (13) gives

$$\frac{\sigma_{abs}(\omega_o)}{n} = \frac{4}{\Delta t}\left(\frac{1}{T_2^3} - \frac{1}{T_1^3}\right). \tag{14}$$

Within the time interval Δt the cluster temperature changes from T_1 to T_2. Note that from general considerations (for example [14]) one can derive that the absorption cross section of a particle, which is small compared to the radiation wavelength, is proportional to the particle volume or to the number of atoms which constitute the particle. Therefore, the relaxation time Δt from temperature T_1 up to T_2 does not depend on the particle size.

Table 1

Absorption parameters of niobium clusters derived from experiments [7, 8] on the basis of formula (14)

ΔT, K	3479–3408	3408–3345	3345–3193	3550–3170
Δt, μs	3.7–5.9	5.9–8.0	8.0–18.7	6.4–31.1
$\sigma_{abs}(\omega_o)/n$, 0.01 Å^2	6.7	6.7	3.6	3.6
λ_o, μ	0.84	0.85	0.88	0.86

Table 2

Absorption parameters of tungsten clusters derived from experiments [7] on the basis of formula (14)

ΔT, K	3605–3301	3301–3138	3500–3200	3500–3100	3700–3200
Δt, μs	8.3	9.5	16	17	18
$\sigma_{abs}(\omega_o)/n$, 0.01 Å^2	7.5	4.7	5.8	5.8	5.7
λ_o, μ	0.83	0.89	0.86	0.86	0.83

Table 1 contains experimental data [7, 8] for niobium clusters which are treated on the basis of formula (14). The same data for tungsten clusters with $n \approx 200$ [6] are given in Table 2. The average photoabsorption cross section per atom according to these data is $\sigma_{abs}(\omega_o)/n = (0.06 \pm 0.01)$ Å^2. However, there is a large error in the treatment of the individual experimental curves which exceeds the statistical error of all data and the difference between niobium and tungsten clusters. The resulting photoabsorption cross sections of hot niobium and tungsten clusters are by more than one order of magnitude smaller compared to cold lithium, potassium, and silver clusters [2–5]. This difference requires an additional analysis.

Considering the mechanism of the absorption process within the framework of two mechanisms [15], one can understand the difference of the absorption cross sections for cold and hot clusters. In the first case absorption of cold clusters results from excitation of plasma oscillations, and the resonance width is due to electron scattering on nuclei. In the second case the absorption process is determined by atom resonant lines which spectrum is split and broaden owing to interaction with surrounding atoms, and the resonance width is created also by scattering of individual electrons. Increase of the temperature leads to decrease of a typical time of electron scattering that corresponds to broadening of the absorption spectrum and decrease of the maximum absorption cross section. One can conclude on the basis of the experimental data for tungsten and niobium clusters that at temperatures above 3000 K the absorption process loses the resonance character and becomes like to that of black body.

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