17. T. Shoop, Solution of Engineering Problems on a Computer [Russian translation], Mir, Moscow (1982).
18. V. S. Uspenskii, "Propagation of an ionization wave in front of a shock wave in a magnetic field," in: Mechanics of Deformable Media [in Russian], Izd. MGU, Moscow (1985).

KINETICS OF THERMAL EMISSION FROM AN AEROSOL PARTICLE

N. N. Belov

UDC 537.36:541.182.2/3

One method of supplying seeding electrons during the development of an optical discharge plasma is thermal electron emission from a target surface [1]. The case of a massive target was studied in [1]. The present paper investigates the special features of thermal electron emission from aerosol particles which can be considered as isolated targets. For these there is typically an increase of the retarding electric field as the emitted charge increases [2].

1. Statement of the Problem. With thermal electron emission a steady state is reached in an aerosol as a result of exchange by electrons between particles [2]. The characteristic time to reach thermal emission equilibrium in the aerosol is $>10^{-6}$ sec [2]. Thus, for $t \leq 10^{-6}$ sec, the problem of thermal electron emission in an aerosol reduces to thermal electron emission from an individual particle. In air under normal conditions for a finely dispersed fraction of aerosol the electron mean free path in the gas surrounding the particle considerably exceeds the particle size. And although this relationship breaks down with increase of the particle radius, the process of thermal electron emission from an individual particle under vacuum can be considered as a first approximation for many actual situations. Suppose that the surface temperature of a spherical particle varies according to the formula

$$T = T_0 + (T_k - T_0)\{1 - \exp(-kt/\tau)\}, \tag{1.1}$$

which is appropriate for describing the influence of the processes of heat outflow from a particle with internal heat sources. If we neglect the influence of heat outflow from the particle, then the variation with time of the particle surface temperature can be approximated by a model dependence of the type

$$T = T_0 + (T_k - T_0)(t/\tau)^s. \tag{1.2}$$

Equations (1.1) and (1.2) model the kinetics of the particle temperature for the most important types of particle heating, for example, due to absorption of electromagnetic radiation. Relation (1.2) with s = 1 corresponds to heating of a particle in the case when the particle heat capacity C and the power supplied to the particle W do not depend on the time. With s = 2, Eq. (1.2) describes a linear increase of W with time, with C = const. We can point to real-life analogies for other values of the constants of Eqs. (1.1) and (1.2). As an upper limit of the temperature T_k of the heated particle it is appropriate to take the boiling temperature T_v of the particle material. This is because most of the processes of nonlinear optics postulate high-temperature heating of the particles to T_v. On the other hand, bipolar ionization of the products of evaporation reduce the role of thermal electron emission in the charging of a particle at temperatures greater than T_v.

2. Methods of Numerical Investigation of Particle Charge. The kinetics of the variation of the charge z of the particle is described by the system of equations

$$J \equiv dz/dt = 4\pi a^2 e^{-1} j; \tag{2.1}$$

$$T = T(t), \tag{2.2}$$

where J is the flux of thermal emission electrons from the particle surface; j is the current density from unit particle surface area, determined by the Richardson–Dushman formula

Moscow. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 6, pp. 27-31, May-June, 1989. Original article submitted November 12, 1987; revision submitted February 2, 1988.

 0021-8944/89/3003-0362$12.50

$$j = 4\pi me(k_b T)^2 h^{-3} \exp(-A/k_b T); \quad (2.3)$$

a is the particle radius; m and e, electron mass and charge; h and k_b, the Planck and Boltzmann constants; A, work done in removing the electron from the particle. Below, as Eq. (2.2) we use one of the equations (1.1) and (1.2). The value of z indicates the number and sign of the uncompensated elementary charges of the particle ($z > 0$ for a positively charged particle). The particle surface loses any electron whose kinetic energy at the particle boundary exceeds the escape work function A_0 from the particle material. An electron leaving a charged particle is acted on by the retarding Coulomb field. The flux of thermal electron emission from the particle forms electrons whose energy exceeds the effective value of A [2]:

$$A = A_0 + e^2 z a^{-1}. \quad (2.4)$$

The stated problem reduces to a Cauchy problem, that of solving the linear ordinary differential equation $dz/dt = f(z, t)$ in the time interval $t \in [0, \tau]$ with the initial condition $z(0) = z_0$. We have solved the problem numerically. To the solution we applied the Euler method, the corrected Euler method, the fourth-order Runge–Kutta method, the first-order Adams extrapolation method, the Adams interpolation method, and a difference approximation of the Picard method [3-6], using a representation of Eq. (2.1) in finite differences:

$$z_{n+1} = z_n + \Delta\tau \left[\sum_{i=1}^{k} \varphi_i(\tau_m, z_m) \right]$$

(τ_m is a time mesh with step size $\Delta\tau$, and z_m is the mesh function of the charge). The type and number of functions applied in the finite-difference equation have been described in [3-6] for each of the methods of solving the differential equation (2.1). The charging kinetics was calculated with a step size of 10^{-8} sec in the time interval [0, 1 μsec], at the end of which the particle was heated from 300 K to the boiling temperature of the particle material. The calculations were performed for particles made of aluminum, copper, iron, silver, gold, tungsten, and molybdenum of radii from 10^{-6} to 0.1 cm (see Table 1). The results computed by the Picard method for the first stage of the process agree up to the second or third place with those obtained by the other methods. However, beginning at t = 0.3-0.5 μsec, the computing error in the Picard method grows quickly, increasing to hundreds and thousands of percent at $t = 10^{-6}$ sec. Evidently, this is because the initial approximation of the first iteration ($i = 0$, $z_n = z_0$) is intrinsically far from the final solution. However, the results of computing with the methods of Euler, Runge–Kutta, and Adams show good agreement. For example, with k = 1 in Eq. (1.1) for aluminum particles of radius 0.1 cm, they coincide to better than the third place. A certain difference of the values of z_n in the region of greatest temperature increase (with equality of dz/dt to better than the third place) is due to the difference of the difference schemes of these methods, as indicated by the rapid improvement of the agreement between them as the time mesh step size is reduced. The high reliability of the program developed is confirmed also by the agreement of the results of numerical dif-

TABLE 1

Curve number in Fig. 1	Metals	T_v, K [9]	A_0, eV [10]
6	Molybdenum	5073	4,3
7	Tungsten	6173	4,54
8	Gold	3120	4,3
9	Silver	2436	4,3
10	Iron	3443	4,31
11	Copper	3150	4,4
12	Aluminum	2621	4,25

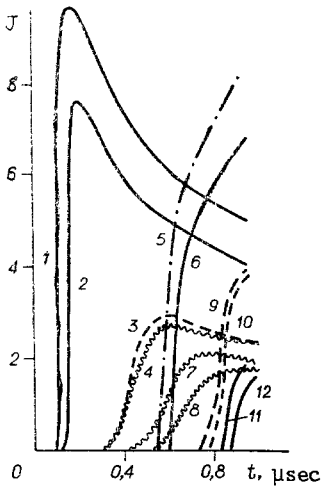

Fig. 1

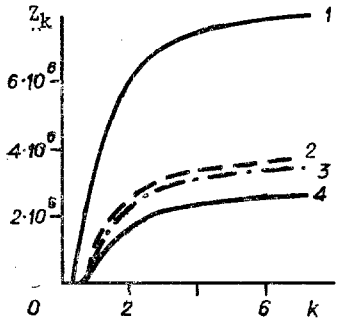

Fig. 2

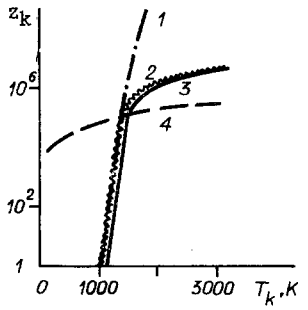

Fig. 3

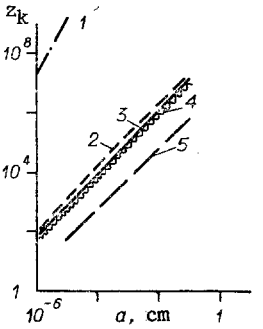

Fig. 4

ferentiation of the problem with results found analytically by methods [see Eq. (3.1)] with T = const. Calculations have shown that the distribution with time of the flux of thermal electron emission from particles of different metals with identical T(t) dependences are very similar (Fig. 1).

Figure 1 shows the calculated variation with time of the flux of electrons from particles ($a = 10^{-5}$ cm) of aluminum – curves 7 and 11, of iron – curves 4 and 10, of copper – curve 3, of silver – curves 8 and 12, of gold – curve 9, of tungsten – curves 1 and 5, and of molybdenum – curves 2 and 6. The variation with time of the particle temperature was computed using Eq. (1.2) with s = 0.5 (curves 1-4, 7, and 8) and for s = 2 (curves 9-12, 5, and 6). Single units on the ordinate axes for curves 1-4, 7, and 8 correspond to 10^8 sec^{-1}, and for curves 9, 12, 5, and 6, $2 \cdot 10^8$ sec^{-1}. It can be seen that particles of the different metals give closely adjacent thermal emission curves. However, the change of the form of the kinetics of heating substantially changes the form of the dependence J(t) for any particle considered. The maximum electron flux arrives at the beginning of the high-temperature part of the heating pulse. In most cases at the concluding stage of the pulse the rapidly increasing Coulomb field basically blocks the emission. The charge z_k which is reached on the particle at the end of the pulse is determined primarily by the particle temperature at the end of the pulse, and depends slightly on T(t). This position is illustrated in Fig. 2, which shows the variation of z_k with increase of the time t_m for the particle temperature to relax to the final value T_v [t_m decreases with increase of k in Eq. (1.1)]. The data of Fig. 2 were obtained for particles of molybdenum, copper, iron, and aluminum (lines 1-4) of radius 0.1 cm, heated to the boiling temperature of the corresponding material in 10^{-6} sec. It can be seen that for $k \geq 3$ the value of z_k is practically independent of the particle heating rate.

Figure 3 shows a representation of the dependence of z_k on the final material temperature of a particle of radius 0.1 cm, and on this scale we do not see differences of z_k for particles of the same radius but different metals (aluminum, copper, iron, silver, and gold). Therefore, the curves can be used to estimate the charge of any of these metals. Curve 3 was obtained by numerically solving the system (1.1), (2.1)-(2.4) for particles of these metals, heated in 10^{-6} sec from 300 K to a final temperature T (the abscissa axis of Fig. 3) for k =

5.7 and 10. It can be seen that in the high-temperature region the dependence $z(T_k)$ becomes almost linear, while at low temperatures it has an exponential character.

3. The particle radius has a strong influence on z_k. Curve 4 of Fig. 4 shows the dependence $z_k(a)$ obtained by solving the system of equations (1.1), (2.1)-(2.4) for molybdenum particles heated from T_0 = 300 K to T_v in a time of 10^{-6} sec (k = 1). It can be seen that for the function $z_k(a)$ a linear approximation is appropriate, i.e., the charge is proportional to the particle radius. The flux of thermal electron emission from the particle is also proportional to its radius (other conditions being equal). We note that for T(t) = const, the system (2.1)-(2.4) has an analytical solution which with the initial condition $z_0 = 0$ has the form

$$z(t) = ak_bTe^{-2} \ln [BatT \exp(-A_0/k_bT) + 1] \quad (3.1)$$

[$B = mk_b(4\pi e)^2h^{-3}$]. In cgs units $B = 1.575004 \cdot 10^{19}$. If the expression under the logarithm sign is very little different from 1, the charge is proportional to the particle area:

$$z_1(t) = Btk_b(aT)^2e^{-2} \exp(-A_0/k_bT). \quad (3.2)$$

But if the expression under the logarithm sign is appreciably greater than 1, then the dependence of the particle charge on its radius differs from linearity by the logarithmically small correction:

$$z_2(t) = ak_bTe^{-2}[-A_0/k_bT + \ln(BatT)]. \quad (3.3)$$

The numerically computed values of z_k agree very satisfactorily with values of z_k calculated from Eq. (3.1) with $T = T_k$ and $t = \tau$. Curves 1 and 2 in Fig. 3 show values of z_k computed from Eqs. (3.1) and (3.2), and curve 2 for $T \geq 1500$ K shows values computed from Eq. (3.3). It can be seen that Eq. (3.1) gives a satisfactory value of the particle charge in all temperature regions, that Eq. (3.2) is satisfactory at low temperatures, and that Eq. (3.3) is satisfactory at high temperatures. Figure 3 (curve 4) also shows the particle charge dependence evaluated from the formula

$$z = ak_bTe^{-2}. \quad (3.4)$$

It can be seen that this evaluation gives too great an error, as a rule. In Fig. 4, the numerically computed values of $z_k(a)$ (curve 4) are compared with results from Eqs. (3.1)-(3.4), on lines 2, 1, 3, and 5. Curve 1 is at a considerable distance from the exact solution because the low-temperature approximation of Eq. (3.2) is inappropriate at the temperature considered. It follows from Eq. (3.1) that if the particle temperature is unchanged, then: a) z depends logarithmically weakly on time, and b) z is proportional to the particle radius and temperature (to within a logarithmically weak correction). The data presented above show that these special features are inherent in the solution z(t) of the system (2.1)-(2.4) for $T(t) \neq$ const if, beginning at some time, the increase of T becomes negligibly small. Thus, Eq. (3.1) can be used to evaluate the particle charge, by substituting there the maximum value of particle temperature. The value from Eq. (3.1) can be used in the case where the time t of particle exposure at high T exceeds the time to attain the quasiequilibrium charge

$$t_{ch} = e^{-2}h^3(4\pi)^{-2}(ak_bmT)^{-1} \exp(A_0/k_bT).$$

4. Absorption of Electromagnetic Radiation by Jumping Electrons. The particle boundaries continuously intersect electrons flying out from the particle. This electron flux can be divided into two groups. In the first group we put electrons whose energy ε is sufficient to overcome the effective exit work function, $\varepsilon > A$. This electron flux J also contains the self-thermal electron emission from the particles, considered above. The current density of the thermal electron emission is found from the Richardson–Dushman formula (2.3), in which the exit work function A is determined by Eq. (1.1).

In the second group we put electrons with energy $\varepsilon \in [A_0, A]$, and a characteristic special feature of their motion is the return of each to the particle surface at some time after their release from a particle. Thus, electrons of this group can be called jumping electrons. During their motion above the particle surface the jumping electrons absorb part of the incident radiation, which is then given to the particle when the electron falls back down.

We can evaluate the number of these electrons leaving the particle per unit time from the formula

$$J_p = [1 - \exp(-e^2z/ak_bT)](4\pi ak_b)^2mh^{-3}\exp(-A_0/k_bT)T^2t.$$

Each jumping electron absorbs a certain energy $\Delta\varepsilon$ from the electromagnetic field and transmits it to the particle. From analogy with the inverse decelerating radiation [7, p. 21] it can be shown that one jump of an electron in the charged particle field increases its energy by

$$\Delta\varepsilon = 2\varepsilon_c\omega^2\left(\omega^2 + t_p^{-2}\right)^{-1},$$

where $\varepsilon_c = e^2E_0{}^2/(2m\omega^2)$ is the kinetic energy of oscillations of the electron in an electromagnetic field of intensity E_0; ω is the circular frequency of the electromagnetic wave; and t_p is the time of motion of the electron in the Coulomb field of the particle. The energy absorbed by the jump electrons in the electromagnetic field is expended in heating of the particle upon capture of the electron at the end of its trajectory, or in ionizing the gas molecules surrounding the particle. Both of these channels for conversion of the incident radiation energy lead to the development of an optical discharge (the first by a mechanism of thermal breakdown of the particle, and the second by the traditional mechanism of avalanche ionization in which the charged particle plays the role of the basic scatterer [8]). Simple estimates in conditions characteristic for the development of an optical discharge under the action of brief infrared pulses show that some finite number of electrons that are resonant with respect to the frequency of the laser radiation communicate enough energy to a submicron particle to cause thermal breakdown. The number N of such electrons necessary for thermal breakdown of a particle can be estimated as follows:

$$N = (4/3)\pi a^3C\gamma T_v t_p(\Delta\varepsilon\tau)^{-1} \qquad (4.1)$$

(Here C, γ, and T_V are the specific heat, density, and boiling temperature of the material of a particle of radius a). According to Eq. (4.1), a particle of radius 10^{-8} m (C = 1 J/deg, γ = 1 g/cm^3, and $T_V = 3\cdot10^3$ K) located in a radiative field with λ = 10.6 μm ($\tau = 10^{-6}$ sec, $I = 10^8$ W/cm^2), is heated to $T_V \sim 3\cdot10^3$ by three jumping electrons, if their jump time is $t_p \approx (5\text{-}6)\cdot10^{-15}$ sec. Since at the initial particle temperature (~300 K) the thermal emission from the particle is negligibly small, the development of a thermal emission instability precedes particle heating due to self-absorption of radiation by the particle material or auto-electronic or multiphoton emission of electrons at the beginning of the action of the electromagnetic radiation on the particle.

LITERATURE CITED

1. N. V. Bochkov and B. N. Chetverushkin, "An algorithm for numerical solution of the equations of breakdown kinetics," Preprint, Institute of Applied Mathematics, Academy of Sciences of the USSR, No. 123, Moscow (1985).
2. A. A. Arshinov and A. K. Musin,"Equilibrium ionization in disperse systems," Radiotekh. Elektron., 7, No. 5 (1962).
3. A. A. Samarskii, Theory of Difference Schemes [in Russian], Nauka, Moscow (1977).
4. R. D. Richtmeyer, Difference Methods of Solving Boundary Problems [Russian translation], Inostr. Lit., Moscow (1969).
5. E. A. Volkov, Numerical Methods [in Russian], Nauka, Moscow (1982).
6. A. Yu. Potyagailo, Introduction to Numerical Methods of Solving Problems in Heat Conduction and Diffusion [in Russian], LITMO, Leningrad (1982).
7. Yu. P. Raizer, The Laser Spark and Propagation of Discharges [in Russian], Nauka, Moscow (1974).
8. N. N. Belov, "Thermal electron emission from particles of metals," in: Papers of the 14th All-Union Conference on Current Topics in Physics of Aero-Disperse Systems, I. I. Mechnikov Odessa Gos. Univ., Odessa (1986), Vol. 2.
9. Chemistry Handbook [in Russian], GNTI, Leningrad–Moscow, Vol. 1 (1962).
10. V. S. Fomenko and I. P. Podcheriyaeva, Emission and Absorption Properties of Substances and Materials [in Russian], Atomizdat, Moscow (1975).