Numerical modeling of the initial fluctuation condensation stage with charge drops

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Abstract. This paper deals with a mathematical model of the phase transition of the first kind at the initial stage of forming drops in a liquid or in melted state in a volume of steam with a fixed charge on drops. The model of the process is represented by superposition of random diffusion and jump stochastic processes. The algorithms for solving stochastic differential equations (SDEs) of the model of processes, which form the cluster size, allow one to calculate a distribution function of drops according to their size. The kinetic approach makes possible evaluate the role of the Rayleigh capillary instability at the initial condensation stage and to employ the analysis of electrodispersion mechanisms in the production of metal and semiconductor powders.

1. Introduction

Numerical investigation of phase transitions as processes of particle association in clusters is connected with many applications, such as the formation of aerosols in the atmosphere (gas and dust interplanetary clouds, comet tails, etc.), condensation in high-velocity gas streams issuing from a nozzle, polymerization and crystallization, metals vapor deposition and some others.

Vapor condensation phenomena at the nucleation step in terms of non-equilibrium kinetics of physical and chemical processes can be viewed as a continuous process of forming the germs clusters [1]. The numerical model of the initial fluctuation stage of condensation has been developed on the assumption that clustering germs of liquid drops in the vapor are represented by the diffusion in the phase space of the clusters size, the density of the transition probability of the process being described by the Fokker-Planck-Kolmogorov equation (FPK) [2, 3]. Statistical algorithms for solving the SDE, which are equivalent to the FPK were built based on of numerical methods for solving SDE [4, 5]. Also, efficient algorithms for modeling an inhomogeneous Poisson flow have been developed to simulate random jump processes [6].

Earlier the stochastic models and the kinetic approach to the simulation of non-equilibrium collisional processes in gases and plasmas [7] and, also, the formation of new-phase islands [8] and *3C–SiC* powders [9] at the initial stage of vapor condensation were generalized to the formation of porosity in solids. This problem was considered as specific features of the development of pores (as

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new-phase germs) in metal [10] and 3C–SiC silicon carbide [11]. In this case, at small times instants ranging from 10^{-10} to 10^{-4} s, the phase transition of the first kind occurs, which accompanies Xe^{++} implantation of ions. The above phenomena are caused by fluctuations of the thermodynamic parameters of the “gases or vacancies in a crystal lattice” [2] or "vapor and liquid (melt)" [9].

How does the fluctuation of the phase transition stage of the vapor condensation occur if the drops acquire a charge in the discharge plasma, or as a result of thermionic emission, or otherwise? According to the criterion of the Rayleigh capillary instability, beginning with a certain cluster size the drops start crushing. In the "open" physical system, the non-equilibrium distribution of the germs size becomes bimodal. We use the generalized asymptotically unbiased method of the Rosenbrock type for solving the SDE (for the evolution of the cluster size) at irregular time discretization comprising the moments of drops division. Numerical simulation can be claimed in the problems of dispersing a charge during the preparation of powders. For the composite of particles, it is necessary to include particles of increased strength and resistance to various kinds of damage such as crystal defects, so it is necessary to obtain amorphous powders. Models of the non-equilibrium phase transition are based on the methods developed in the plasma physics [12] as well as computational experiments, object-oriented plasma kinetics codes [13] and calculations of dusty plasma charging [11].

2. A clustering model and approximation used

The simulation of the fluctuation stage of phase transition (PT) of the first kind for the cluster formation process is carried out under conditions of an "open" physical system. Non-equilibrium processes, forming clusters, cause the PT fluctuation instability.

The process of forming clusters (aggregates of molecules formed in the course of the volume condensation or on the surface of a solid) is considered as consecutive reactions:

$$a_1 + a_1 \leftrightarrow a_2,$$
$$\cdot \quad \cdot \quad \cdot$$
$$a_{n-1} + a_1 \leftrightarrow a_n,$$

leading to diffusion in the clusters sizes space.

According to the ideas discussed in [1], the clusters are formed as a result of the fact that to the new phase germs a greater number of particles is sticked than vaporized per time unit. Fluctuations of thermodynamic parameters (such as temperature, supersaturation and vapor pressure) cause clustering the germs at a new thermodynamic phase. The growth of the cluster size g is described by a random diffusion process in the phase space of the cluster sizes G. The kinetic Kolmogorov-Feller equation for the distribution density of germs according to their size has the following form

$$\frac{\partial f(g,t)}{\partial t} = \frac{1}{kT}\frac{\partial}{\partial g}\left[D(g,t)f(g,t)\frac{\partial \Delta\Phi(g,t)}{\partial g}\right] + \frac{\partial}{\partial g}\left[D(g,t)\frac{\partial f(g,t)}{\partial g}\right] + S - Q, \tag{1}$$

$$f(g,0) = f_0, \quad \frac{df(g,t)}{dg}\Big|_{g=2} = 0, \quad f(g,t)\big|_{g<2} = 0,$$

where g is the number of atoms in the cluster, D is the diffusion coefficient; $\Delta\Phi(g,t)$ is free energy of nucleus formation (or Gibbs energy); S is the source of particles forming a nucleus (the source of “monomers”); Q is the “monomers” particles run-off. The diffusion coefficient is defined as follows:

$$D(g) = g^{2/3} \cdot n_1^2 \beta_k (4\pi)^{1/3} (3V_l)^{2/3} (kT)^{1/2} (2\pi m)^{-1/2},$$

where V_l is the volume per one particle of the liquid phase, $\beta_k = \beta_k(T)$ is the accommodation coefficient of particles on the cluster surface, n_1 is the density of the gaseous phase, m is the mass of

vapor molecules. The value $f(g,t)dg$ determines the number of clusters in the size range (per volume unit of the medium). The range of variables: $g \in [2, g_{\max}]$, $t \in [0,\infty]$.

The function $f(g,t)$ is normalized so that the volume unit is, at least, one cluster comprising no less than two particles. Macroscopic characteristics of the gas-vapor mixture (such as the number of clusters per volume unit, etc.) can be calculated with allowance for the function $f(g,t)$. The computer implementation of mathematical models of clustering (1) requires the solution of quasilinear partial integro-differential equations of the second order. In this paper, this equation is solved with the help of the stochastic analog method [2], which is based on the theorems according to which the kinetic equations are uniquely associated with stochastic differential equations [3].

Let us write down the SDE for Markov random process (MP) g (t), whose density function is a solution of the corresponding kinetic equation (1).

Let us consider the case $S = Q = 0$. If from physical considerations the following expression holds:

$$\frac{\partial}{\partial g}\left[\frac{\partial D(g,t)}{\partial g} f(g,t)\right] = 0, \tag{2}$$

then equation (1) corresponds to the SDE in the Stratonovich sense:

$$dg(t) = -\frac{D(g,t)}{kT}\frac{\partial \Delta\Phi(g,t)}{\partial g}dt - \frac{1}{2}\frac{\partial D(g,t)}{\partial g} + \sqrt{2D(g,t)} \circ dw(t), \quad g(t_0) = g_0. \tag{3}$$

If (*) is not satisfied, then equation (1) will correspond to the SDE in the Stratonovich sense

$$dg(t) = -\frac{D(g,t)}{kT}\frac{\partial \Delta\Phi(g,t)}{\partial g}dt + \frac{1}{2}\frac{\partial D(g,t)}{\partial g} + \sqrt{2D(g,t)} \circ dw(t), \quad g(t_0) = g_0. \tag{4}$$

An additional factor of non-disequilibrium of the condensation process is the instability of large drops, which is associated either with the fact that the vapor moves with a certain velocity (the Weber criterion), or condensation drops are in conditions where there is charge on the drop surface [14]. There is implemented a reaction $a_i \to a_k + a_l$, where indices mark the drops, whose specific choice occurs when the law of conservation of mass of clusters holds. In the Kolmogorov-Feller equation (1) one should take into account the type of a collision model (drops decay)

$$\int_G \int_\Gamma f(\xi,t)[\delta(g-\xi-c(\xi,t,\theta)) - \delta(g-\xi)]\pi(\theta,\xi,t)d\theta d\xi, \tag{5}$$

where δ is the Dirac delta-function, and the functions c, π and a set $\Gamma \in R$ are determined by properties of the medium. The function π is a scalar non-negative function, which specifies probabilities of crushing the drops and also determines the decay intensity. Then equations (1), (5) under condition (2) correspond to the SDE, combining diffusive and the Poisson components:

$$dg(t) = -\frac{D(g,t)}{kT}\frac{\partial \Delta\Phi(g,t)}{\partial g}dt - \frac{1}{2}\frac{\partial Dg,t)}{\partial g} + \sqrt{2D(g,t)} \circ dw(t) + \int_\Gamma z(g(t^-),t^-,\theta)\nu(d\theta \times dt), \tag{6}$$

where the function z is determined by the type of drop decay, ν is the Poisson random measure on the set $\Gamma \times [0, T_{finish}]$ with the characteristic measure

$$\Pi(A) = \int_A \pi(\theta)d\theta, \quad A \in \Gamma, \quad \Pi(\Gamma) < \infty, \tag{7}$$

$z(t^-)$ is the value of the function at the point $(t-0)$. As is noted in [15], the introduction of the dependence of the function $\pi(\theta,g,t)$ on g and t makes the Poisson measure inhomogeneous, but it allows one to form a broader class of Markov processes than in the case when $\pi(\theta)$ is independent of g and t.

The next section describes the numerical method for solving stochastic differential equations used. Note that the numerical simulation of the SDE (6) requires not only the modeling of the Wiener component, but also an inhomogeneous Poisson measure, which is a special case of Poisson ensemble [6].

3. Numerical Methods for solving Stochastic Differential Equations

In general, the Cauchy problem for stochastic differential equations in the sense of Ito is written as

$$dY(t) = H_1(Y,t)dt + \tilde{\sigma}(Y,t)dW(t), \quad Y(t_0) = Y_0,\ t \in [0, T_{finish}], \tag{8}$$

where $Y(t)$ is a continuous random process of dimension n; $W(t)$ is m-dimensional standard Wiener process; $H_1(Y,t)$ is n-dimensional vector function; $\tilde{\sigma}(Y,t)$ is the matrix function of the size $n \times m$. The initial state of the system is set by a random vector Y_0. If the matrix $\tilde{\sigma}(Y,t)$ is differentiable, then the Cauchy problem for the SDE (8) in the Ito sense corresponds to the Cauchy problem for the SDE in the Stratonovich sense

$$dY(t) = H(Y,t)dt + \tilde{\sigma}(Y,t) \circ dW(t), \quad Y(t_0) = Y_0, \tag{9}$$

where

$$H(Y,t) = H_1(Y,t) - \frac{1}{2}\frac{\partial \tilde{\sigma}(Y,t)}{\partial Y}\tilde{\sigma}(Y,t), \quad \left(\frac{\partial \tilde{\sigma}(Y,t)}{\partial Y}\tilde{\sigma}(Y,t)\right)_i = \sum_{k=1}^{n}\sum_{j=1}^{n}\frac{\partial \tilde{\sigma}_{ij}(Y,t)}{\partial y_k}\tilde{\sigma}_{kj}(Y,t).$$

Equations (8) and (9) are equivalent. The one-dimensional probability density function of the SDE solutions satisfies the direct Kolmogorov equation

$$\frac{\partial p(Y,t)}{\partial t} = -\sum_{i=1}^{n}\frac{\partial}{\partial y_i}\left[(H_1)_i(Y,t)p(Y,t)\right] + \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\frac{\partial^2}{\partial y_i \partial y_j}\left[b_{ij}\,p(Y,t)\right], \quad p(Y,t_0) = \psi_0(Y_0), \tag{10}$$

where ψ_0 is the probability density function of the distribution of the phase coordinates at the initial time t_0, $B = \tilde{\sigma}\tilde{\sigma}^T$, $b_{ij} = \sum_{k=1}^{m}\tilde{\sigma}_{ik}\tilde{\sigma}_{jk}$ is the diffusion matrix.

For the numerical solution of the SDE in the Stratonovich sense (9) we use the generalized method of the Rosenbrock type

$$Y_{k+1} = Y_k + [I - \frac{h_k}{2}\frac{\partial H}{\partial Y}(Y_k)]^{-1}[h_k H(Y_k) + h_k H(Y_{k+1}^p)] + \sqrt{h_k}\sum_{j=1}^{n}(\tilde{\sigma}_{\bullet j_2}(Y_k) + \tilde{\sigma}_{\bullet j_2}(Y_{k+1}^p))\xi_{jk}], \tag{11}$$

$$Y_{k+1}^p = Y_k + \tilde{\sigma}(Y_k)\sqrt{h_k}\,\xi_k.$$

This method converges with second order for the SDE systems with single noise and is asymptotically unbiased. These properties of the method allow one to use it for solving unstable SDE systems with high accuracy.

Here Y_k is the numerical solution of (9) at a grid node t_k; $h_k = t_{k+1} - t_k$ is the integration step; $\xi_k = (\xi_{1k}, \ldots, \xi_{nk})^T$ is the vector of mutually independent normal random variables with zero mean and unit variance; $\tilde{\sigma}_{\bullet j}^{(l)}$ denotes the j-th column of the matrix $\tilde{\sigma}^{(l)}$; I is the identity matrix; $\partial a^{(l)} / \partial Y$ is the

Jacobi matrix. We supplement the stochastic differential equation (9) with a stochastic integral with respect to the Poisson measure

$$dY(t) = H(Y,t)dt + \tilde{\sigma}(Y,t) \circ dW(t) + \int_{\Gamma} z(Y(t^-),t^-,\theta)\nu(d\theta \times dt),\ Y(t_0) = Y_0\,, \tag{12}$$

$z(Y,t,\theta)$ is *n*-dimensional vector-function; π is the non-negative scalar function defining characteristic measure (7); the set $\Gamma \in R^n$.

Let us write down the *algorithm of the simulation of the SDE solution with a Poisson component (12) when the Poisson measure is homogeneous*:
previously, for each trajectory we simulate the time instants of the trajectory discontinuity points (for model (1) these are the time instants of decay) $\tau_1,\ldots,\tau_l < T_{fihish}$ by the formula $\tau_s = \tau_{s-1} + \zeta_s$, $\tau_0 = 0$, where ζ_s are independent random variables with the probability density $p(x) = \Pi(\Gamma)\exp(-\Pi(\Gamma)x)$ (according to the formula $\zeta_s = -\ln\alpha_s / \Pi(\Gamma)$, α_s are independent uniformly distributed random variables on the interval (0,1));

0) *k*:=0; simulate according to the specified initial values;
1) solve equation (9) on the interval $[\tau_k, \tau_{k+1}]$ by numerical method (11) with the step *h* and find Y_{k+1} at the time instant τ_{k+1}; the step *h* should be coordinated with the transition intensity, for example, $h \le 0.1/\Pi(\Gamma)$;
2) $k := k + 1$;
3) simulate a random variable θ according to the density $p(x) = \pi(x)/\Pi(\Gamma)$, then $Y_k := Y_k + z(Y_k, \tau_k, \theta)$;
4) if $\tau_k < T$, then go to step 1, otherwise the trajectory simulation is completed.

Using the method of maximum cross-section, the algorithm can be generalized to the case of inhomogeneous Poisson measure [6].

4. Numerical Experiments

With the algorithm proposed let us carry out the numerical simulation, illustrating the formation of the condensation nuclei with a fixed charge on the drops with the diffusion coefficient and the Gibbs energy of the form

$$D = D_0 g^{2/3}, \tag{13}$$

$$\Delta\Phi = \Delta\Phi_{chem} + \Delta\Phi_{st} + \Delta\Phi_{ch} = -ag + bg^{2/3} + cg^{-1/3}, \tag{14}$$

where $\Delta\Phi_{chem} = -ag$, $a = \eta(\chi_\beta - \chi_\alpha)$, and $(\chi_\beta - \chi_\alpha)$ is the difference between the chemical potentials of phases, and $\eta = 2\pi/3V$ and V is the volume of a water molecule. The second term in (14) is $\Delta\Phi_{st} = bg^{2/3}$, where $b = (36\pi)^{1/3}V^{2/3}\sigma$ and σ being the surface tension at the boundary of a drop. The third term in (14), related to the drop charge, is $\Delta\Phi_{ch} = cg^{-1/3}$, where $c \sim eZ$ with Z being the drop charge measured in thousands of elementary charges. We assume that the drop charge is matched in accordance with [9, 11, 12]. For coefficients (13) - (14), the equation model (6) takes the form

$$dg(t) = H(g)dt + \tilde{\sigma}(g) \circ dw(t) \quad + \int_{\Gamma} z(g(t^-),t^-,\theta)\nu(d\theta \times dt), \quad g(t_0) = g_0, \tag{15}$$

where

$$H = -\frac{D_0}{kT}\left(-ag^{2/3} + \frac{2}{3}bg^{1/3} - \frac{c}{3}cg^{-2/3}\right) - \frac{D_0}{3}g^{-1/3}, \quad \tilde{\sigma} = \sqrt{2D(g,t)}, \quad z = z_0 g. \qquad (16)$$

According to the Rayleigh criterion for the charged drops of radius r_d with a constant charge Z the instability condition in dimensionless form looks like the following [14]:

$$W = \frac{Z^2}{16\pi\sigma r_d^3} \geq 1.$$

We have studied the fluctuation stage of the phase transition of the water vapor condensation with allowance for the Rayleigh instability criterion of the charged drop [14]. In this case the temperature $T = 350K$, the pressure vapor $p = 0.5M\Pi a$, the saturation $s = 2$, the value of a charge is measured in $1.6 \cdot 10^{-16}$ coulomb, the clusters concentration of the condensation vapor is $3 \cdot 10^5\, cm^{-3}$. The parameters were taken from [16]. The parameters (figures 1-5) provide the value of the dimensionless time step $h = 5.43 \cdot 10^{-11}$ s. We have considered the following dimensionless parameters of the model:

$$a = 0.24318,\ b = 2.366613,\ c = 25,\ D_0 = 0.25,\ kT = 1,\ \Gamma = (0,1),\ \pi(\theta) \equiv 1,\ \Pi(\Gamma) = \int_\Gamma \pi(\theta)d\theta = 1. \qquad (17)$$

The Gibbs energy (14) for the model parameters (17) is shown in figure 1.

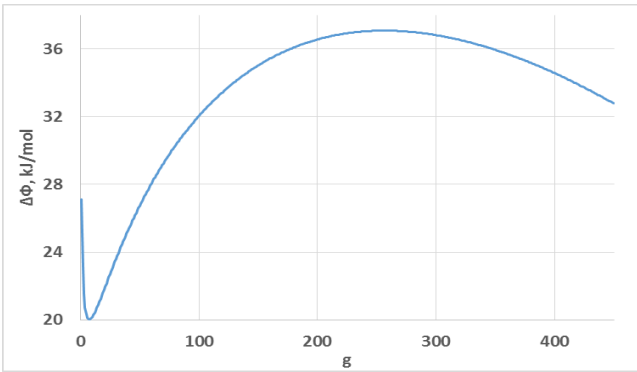

Figure 1. The Gibbs energy (14), (17) of forming drops (with the drop charge) as a function of the cluster size g.

For the numerical solution of SDE (15) with parameters (16)-(17) we used the algorithm developed. The grid on the interval [0, 30] is constructed for each trajectory of the numerical solution and includes a uniform grid with the step $h = 0.5$ and all the time instants of the drop decay. The simulation of the drop decay time instants was carried out by the formula $s_0 = 0,\ \ s_k = s_{k-1} - \ln\alpha / \Pi(\Gamma),\ \ k = 1,\ldots,k_T,\ \ s_{k_T} < T_{finish} = 30$. The RAND pseudorandom generator was used for the simulation of uniform random variables α on the interval [0, 1]. In the numerical experiment, 10^6 trajectories of the solution were used.

The initial conditions were chosen from the "critical" area of energy values $\Delta\Phi - kT \sim 3kJ/mol$. The critical value g_{crit} is found from the condition $\partial\Delta\Phi/\partial g = 0$. The initial cluster size was set larger than the critical size ($g_0 = 400,\ \ g_{\max} = 420,\ \ g_{crit} = 274$). Since the initial value was not random but the same for all simulated trajectories, then the distribution density of nuclei clusters at the initial time is the delta-function. The figures show the evolution of the distribution of clusters size of the water (figures 2, 4 without taking into account the drops charge; figures 3, 5 with the drops charge).

The drops decay as a result of capillary instability leads to a non-equilibrium distribution of the clusters size (figures 3, 5).

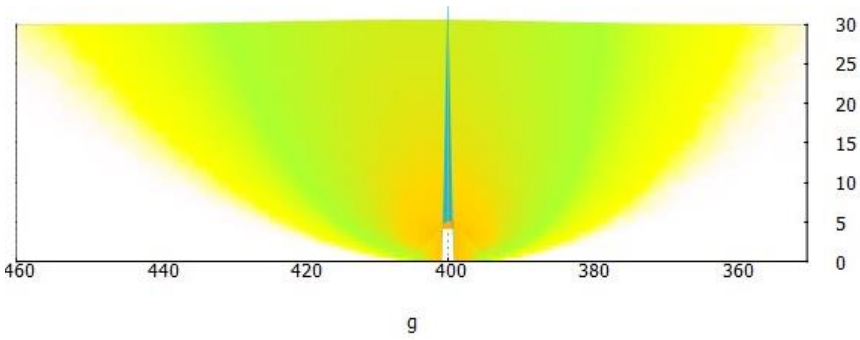

Figure 2. The evolution of the distribution of cluster size. (without drop charge).

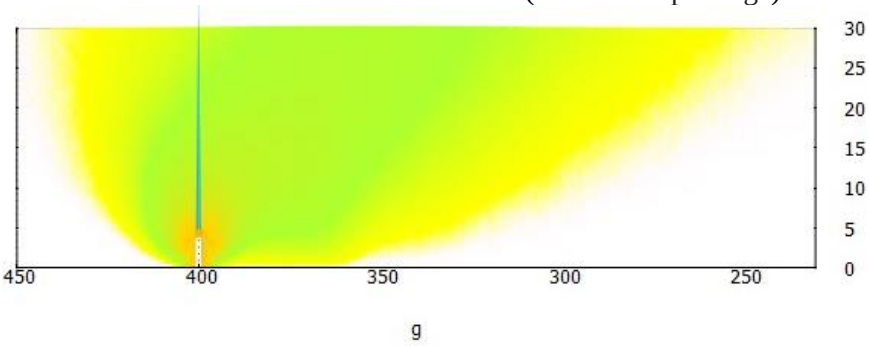

Figure 3. The evolution of the distribution of cluster size. (with the drop charge)

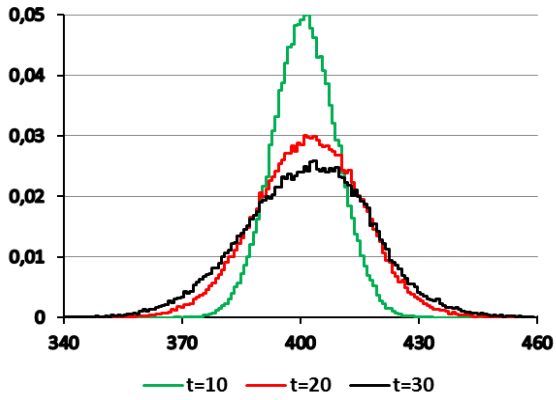

Figure 4. Histograms of the cluster size distribution (without drop charge) at three time instants.

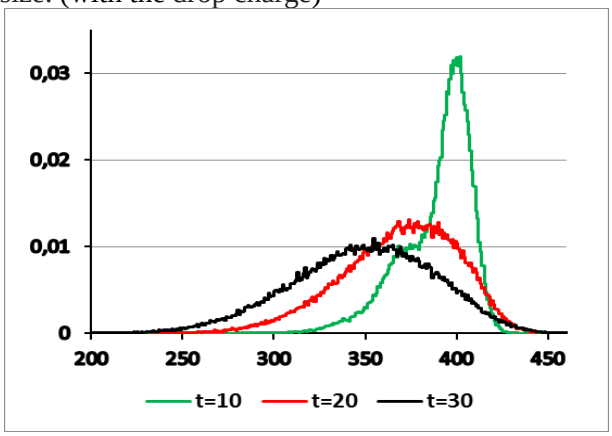

Figure 5. Histograms of the cluster size distribution (with the drop charge) at three time instants.

The algorithm developed allows one to simulate the phase transition of the first kind at the initial stage of the drops formation with a fixed charge on the drops. The numerical experiments show the fluctuation instability resulting in the bimodal distribution of the condensate drop size. The kinetic approach makes possible evaluate the role of the Rayleigh capillary instability at the initial condensation stage and to employ the analysis of electrodispersion mechanisms in the production of metal and semiconductor powders.

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