



Influence of the Fluctuations of the Temperature on the Quasi Equilibrium Condensation

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Based on the three parametric Lorenz system a model, that allows to describe in a self-consistent way the behavior of the plasma-condensate system near phase equilibrium, was developed. Considering the influence of the fluctuations of the growing surface temperature the evolution equation and the corresponding Fokker-Planck equation were obtained. The phase diagram, which determined the system parameters corresponding to the regime of the porous structure formation, was built.

Keywords: Nanoporous structure, Phase equilibrium, Growing surface.

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1. INTRODUCTION

Nanotechnology development in our time is achieved by using a huge number of approaches and methods, one of which is a quasi-equilibrium condensation process [1-5]. For such a method, characterized by arrangement of atoms adsorbed on the active centers of crystallization, whereby it is possible to obtain various structures of the condensate: monocrystals, fractal surface, porous membranes, etc. [1, 2]. Particular attention is attracted to nanoporous materials due to their wide range of applications. Moreover, production of such materials is often associated with a large number of technical problems, and the condensation method in the steady state close to phase equilibrium is one of the most promising.

Quasi-equilibrium condensation is achieved by plasma, which increases the effective temperature of the growth surface, and the natural course of the process provides a self-organization [6-8]. As a result of such a processes (at small values of the deposited flux and the equilibrium concentration n_e) in systems with weak feedback only a stationary condensation mode is realized. Otherwise for deposited flux inversion and increased feedback the already precipitated condensate is disassembled, when the regime of nanoporous structures formation is realized.

2. BASIC EQUATIONS

Considering that on the growing surface a quasi-equilibrium condensation is provided by a self-consistent evolution of the processes in the plasma volume, we will use a two-dimensional (surface) concentration $n=N/a$ (a is a scale factor or lattice parameter).

For a given value of the equilibrium concentration n_e the increasing supersaturation $n-n_e$ is provided by the diffusion component, defined by the Onsager equation [9, 10] for the adsorption flow

$$J_{ad} \equiv D|\nabla N| \simeq \frac{D}{\lambda} N_{ac} - N \quad (2.1)$$

The main drop of the concentration value occurs near the cathode layer, whose thickness is characterized by the screening length λ and the diffusion coefficient D .

Decrease of the supersaturation $n-n_e$ is ensured by the desorption flow J , which is directed up from the growing surface, so that $J < 0$, while the value of the adsorption flow $J_{ad} > 0$. In case of absence of the condensate the condition $J = -J_{ad}$ is performed for the desorption component. Here the accumulated flow J_{ad} is defined by the equation (2.1), where $N = N_e$. The diffusion changes of the deposited atoms concentration N is given by the continuity equation $\dot{n}/a + \nabla J_{ad} = 0$. Here the point denotes the differentiation with respect to time and the source influence is given by the estimate

$$|\nabla J_{ad}| \simeq J_{ad} / \lambda \simeq D / \lambda^2 n - n_e / a. \quad (2.2)$$

Thus, the diffusion dissipation of the concentration is expressed by the equation $\dot{n} \simeq D / \lambda^2 n - n_e / a$.

On the other hand, the velocity of atoms desorption $\int_v \dot{N} dv$ in volume v , based on the growing surface s , is

$$\int_v \dot{N} dv = - \int_v \nabla J dv = - \int_s J ds, \quad (2.3)$$

where the first equation takes into account the continuity condition, and the second – the Gauss theorem. As a result, near the growing surface the total change of the concentration is described by the equation

$$\dot{n} = \frac{n_e - n}{\tau_n} - J. \quad (2.4)$$

τ_n is a characteristic relaxation time of the supersaturation.

Within the synergetic picture [8] the quasi-equilibrium condensation process is determined by the supersaturation $n-n_e$, the growing surface temperature T , and the desorption flow J .

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For the evolution equation of the temperature we have

$$\tau_T \dot{T} = -T - a_T n J + \zeta \quad (2.5)$$

where τ_T is a relaxation time, $a_T > 0$ is a the coupling constant.

In contrast to the Eq.(2.4) we assume that the dissipation leads to the relaxation of the growing surface temperature to the value $T=0$. The second term represents the nonlinear feedback of \dot{T} with concentration and flow. Since the porous structures were obtained at unstable temperature regime [1-3] we have to include a stochastic source, representing the Ornstein-Uhlenbeck process:

$$\langle \zeta \rangle = 0, \quad \langle \zeta(t) \zeta(t') \rangle = \frac{I}{\tau_\zeta} \exp\left\{-\frac{|t-t'|}{\tau_\zeta}\right\}. \quad (2.6)$$

Here I is the intensity of the temperature fluctuations and τ_ζ is the time of their correlation.

For the flow we postulate the equation

$$\tau_J \dot{J} = -(J_{ac} + J) + a_J n T. \quad (2.7)$$

where τ_J is a corresponding relaxation time, J_{ac} – the accumulation flow, $a_J > 0$ is a constant of a positive feedback, allowing the growth of the J .

So our task is to study the regime of the porous structures formation in the stochastic plasma-condensate system.

For the most simple investigation of the system (2.4), (2.5), (2.7) we must use a dimensionless variables for the time t , the concentration n , the temperature of the growing surface T , the flow J , and for the intensity of the temperature fluctuations I . Thus, the dimensionless system of equations takes the form

$$\begin{aligned} \dot{n} &= -n - n_e - J, \\ \varepsilon \dot{T} &= -T - nJ + \zeta, \\ \sigma \dot{J} &= J_{ac} + J + nT, \end{aligned} \quad (2.8)$$

where $\varepsilon = \tau_T / \tau_n$, $\sigma = \tau_J / \tau_n$.

3. RESULTS AND DISCUSSION

To analyze Eqs.(2.8) we will use the approximation $\tau_n \approx \tau_J \gg \tau_T$, which corresponds to the rapidly varied temperature (unstable cooling).

After certain mathematical approach [9] the system (2.8) reduces to the evolution equation

$$\sigma \ddot{n} + \gamma n \dot{n} = f n + g n \zeta. \quad (3.1)$$

Here, the friction coefficient γn , the force $f n$ and the noise amplitude $g n$ are given by the relations

$$\begin{aligned} \gamma n &= 1 + \sigma + n^2, \\ f n &= J_{ac} - n - n_e - 1 + n^2, \\ g n &= n. \end{aligned} \quad (3.2)$$

Then we must find a distribution function of the system in the phase space constructed by the concentration n and time t .

The Fokker-Planck equation [10] corresponding to Eq.(3.1) is given by

$$\frac{\partial P(n,t)}{\partial t} = \frac{\partial}{\partial n} [D_1 n P(n,t)] + \frac{\partial^2}{\partial n^2} [D_2 n P(n,t)], \quad (3.3)$$

where the drift coefficient

$$D_1 n = \frac{1}{\gamma n} \times \left[f n - M_0 t \frac{g^2 n}{\gamma^2 n} \frac{\partial \gamma n}{\partial n} + M_1 t g n \frac{\partial g n}{\partial n} \right] \quad (3.4)$$

and the diffusion coefficient

$$D_2 n = M_0 t \frac{g^2 n}{\gamma^2 n}. \quad (3.5)$$

The moments of the correlation function

$$M_1 t = \frac{1}{i!} \int_0^\infty \langle \zeta(t) \zeta(0) \rangle dt, \quad (3.6)$$

for the zeroth and first moments give

$$M_0 t = I, \quad M_1 t = I \tau_\zeta. \quad (3.7)$$

A stationary solution of the Fokker-Planck equation [10] gives a stationary distribution

$$P(n) = \frac{Z^{-1}}{D_2 n} \exp \int_0^n \frac{D_1 n'}{D_2 n'} dn', \quad (3.8)$$

where Z is a partition function

$$Z = \int_0^\infty \frac{dn}{D_2 n} \exp \int_0^n \frac{D_1 n'}{D_2 n'} dn'. \quad (3.9)$$

The extremum condition for the distribution (3.8)

$$D_1 n - \frac{\partial}{\partial n} D_2 n = 0 \quad (3.10)$$

defines the stationary states of the plasma-condensate system. Substituting obtained expressions we arrive to the stationary concentration dependence

$$J_{ac} = \frac{2I(1+\sigma n)}{[1+\sigma+n^2]^2} + n - n_e - 1 + n^2 - I \tau_\zeta n. \quad (3.11)$$

Then the condition, that restricts the domain of the existence of the solution $n = 0$ corresponding to the complete evaporation, has the form

$$J_{ac} = -n_e. \quad (3.12)$$

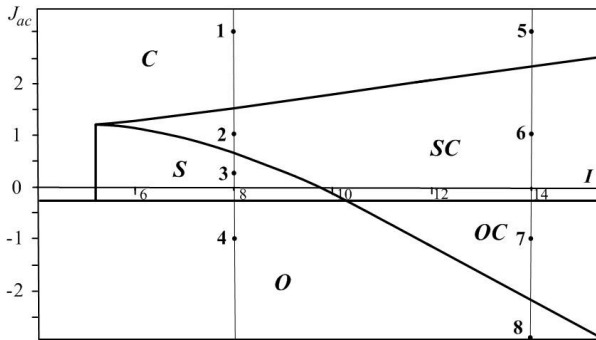


Fig. 1 – Phase diagram of the system for $n_e = 0.25$, $\tau_c = 0.5$. The letters indicate the relevant domains of the phase diagram, and the dots marked by numbers correspond to the parameters at which the stationary concentration dependence (Fig.2) is analyzed.

The corresponding phase diagram of the system is shown in Fig.1.

In Figure 1 the domain C corresponds to the condensation process, domain S is characterized by the formation of porous structures, at the domain O the complete evaporation of condensed matter occurs. Domains, which are indicated by two letters, meet the coexistence of the mentioned above regimes.

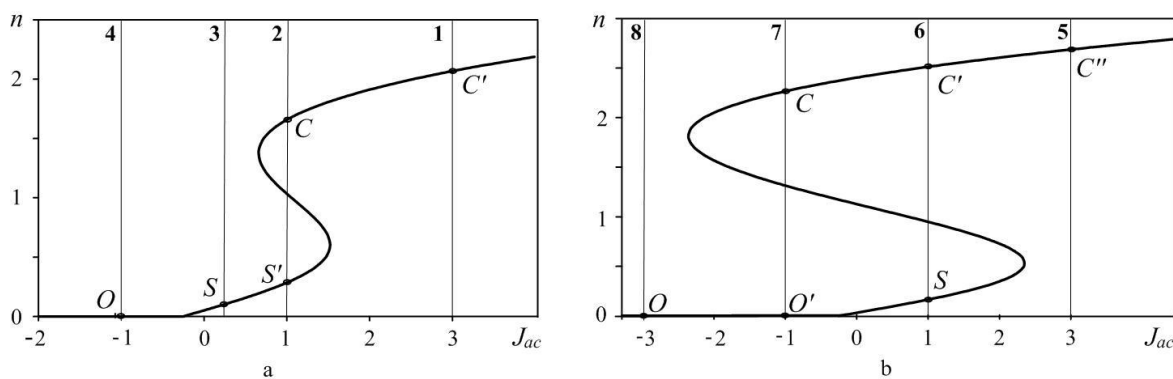


Fig. 2 – The dependence of the stationary concentration n from the accumulated flow J_{ac} at $n_e = 0.25$, $\tau_c = 0.5$, (a) $I=8$, (b) $I=14$.

4. CONCLUSION

Based on our analysis, we can conclude that processes occurring in the plasma-condensate system can be presented within the synergetic system (2.8) describing the self-consistent behavior of the concentration, temperature of the growing surface and desorption flow. Accounting the growing surface temperature fluctuations it is possible to describe the most specific state, when porous nanostructures is formed. In addition, as shown in Fig.1 the system parameters have a significant effect on the domain of such structures formation. With increasing the

correlation time of fluctuations this domain is significantly decreased and shifted towards the lower values of the fluctuation intensity, while the increase in the equilibrium concentration results in a less significant decrease, and in a shift along two axis (fluctuation intensity and accumulated flow). As a real experiment [1, 2] our theoretical approach has been shown that surface disassembly is rarely realized. However, controlling the parameters of the system, we can achieve the regime under which a porous nanostructure will be formed.

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