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## DISCONTINUOUS KINETICS OF QUASI-EQUILIBRIUM CONDENSATION

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*Phase portraits of the quasi-equilibrium condensation process are studied at different relations of the relaxation times of sprayed material concentration, desorption current, and surface temperature. It is shown that a single steady state of the quasi-equilibrium condensation is realized at small values of the equilibrium concentration and positive values of the accumulated current. Either the slowing-down evolution or the non-monotonic regime occurs near this state to strengthen the latter with increase in the relaxation time of desorption current.*

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### 1. INTRODUCTION

Method of steady-state condensation, which is closed to the equilibrium one [1, 2], stands out against modern nanotechnologies. From the practical point of view, this is conditioned by the fact that the use of this method allows to obtain structures like stepped nickel surface [3], various aluminum structures [5], scroll copper structures [4], fractal surfaces of carbon and titanium [6, 7], etc. From the physical point of view, quasi-equilibrium condensation method is conditioned by self-organization of multiphase plasma-condensate system. It is shown in the fact that the increase in the energy of adatoms under plasma action promotes the increase in the growth surface temperature, which is compensated by the desorption current of adatoms responsible for supersaturation.

The authors of [2] achieved understanding of the main features of self-organization in adiabatic approximation, which assumes that the growth surface temperature and desorption current of adatoms follow the concentration change. The work is devoted to the investigation of discontinuous kinetics of quasi-equilibrium condensation for different ratios of characteristic times of changing of the pointed values. Within the synergetic ideology, our consideration is based on the three-parameter Lorentz system [9], whose equations with regard to the plasma-condensate system are given in Section 2. In Sections 3-5 we perform the phase analysis of condensation kinetics under the conditions that one of three degrees of freedom has negligibly small relaxation time. Section 6 contains conclusions.

## 2. MAIN EQUATIONS

According to [3, 4], quasi-equilibrium condensation is provided by the self-consistent change in the surface concentration of adatoms  $n$  counted from the equilibrium value  $n_e$ , desorption current  $J$  whose value is given by the accumulated current  $J_{ac}$ , and growth surface temperature  $T$  counted from the ambient temperature. Within the synergetic model [8], the quasi-equilibrium condensation process is conditioned by the fact that with the increase in the supersaturation, condensed atoms transfer the excess energy to the growth surface increasing its temperature  $T$ . This intensifies atom evaporation of condensed matter due to the growth in the absolute value of the desorption current  $J < 0$ , which compensates the initial supersaturation. As a result, the quasi-equilibrium condensation process requires self-consistent description of the time dependences of adatom concentration  $n(t)$ , growth surface temperature  $T(t)$ , and desorption current  $J(t)$ . Evolution equations of the mentioned values contain dissipative contributes and terms, which represent positive and negative feedbacks, whose balance provides the self-organization process. In dimensionless form these equations can be written as [9]

$$\begin{aligned}\tau_n \dot{n} &= -(n - n_e) - J, \\ \tau_T \dot{T} &= -T - nJ, \\ \tau_J \dot{J} &= -(J_{ac} + J) + nT.\end{aligned}\tag{1}$$

Here the dot denotes time differentiation;  $\tau_T$ ,  $\tau_J$ ,  $\tau_n$  are the typical scales of the corresponding variation of the quantities. Adiabatic conditions  $\tau_T$ ,  $\tau_J \ll \tau_n$ , in accordance to which temperature  $T(t)$  and current  $J(t)$  follow the change in concentration  $n(t)$ , hold for the simplest condensation mechanism. Due to this fact we can neglect the left sides of two last equations (1) and they lead to the dependences

$$T = J_{ac} \frac{n}{1 + n^2}, \quad J = -\frac{J_{ac}}{1 + n^2}.\tag{2}$$

As a result, system (1) is reduced to the Landau-Khalatnikov equation

$$\frac{\partial n}{\partial t} = -\frac{\partial F}{\partial n}\tag{3}$$

with the free energy

$$F = (n - 2n_e)n / 2 - J_{ac} \arctg(n).\tag{4}$$

As seen, behavior of the dependence  $F(n)$  is determined by the equilibrium concentration  $n_e$  and accumulated current  $J_{ac}$ .

The foregoing assumes that during the transformation of plasma-condensate system, the typical time of change of the concentration  $\tau_n$  holds constant value. In fact [7], the system reaction to the increase in the adatom concentration  $n$  can change this time. Based on the simplest dependence

$$\tau_n = \tau_0 \left( 1 + \frac{\kappa}{1 + n^2 / n_\tau^2} \right)^{-1} \quad (5)$$

characterized by the constants  $\tau_0$ ,  $\kappa$ ,  $n_\tau$ , we show that such behavior transforms the continuous transition into the discontinuous one. Really, substitution of the expression (5) into the first equality (1) leads to the equation (3) with the effective potential

$$F = (n - 2n_e)n/2 - J_{ac} \operatorname{arctg}(n) - \kappa n_e n_\tau \operatorname{arctg}\left(\frac{n}{n_\tau}\right) + \frac{\kappa n_\tau^2}{2} \ln \left[ 1 + \left( n / n_\tau \right)^2 \right], \quad (6)$$

which in comparison with (4) gains two last terms. This potential has two minimums, each of which corresponds to different steady states of the system. At positive values of the accumulated current  $J_{ac}$ , the deepest minimum satisfies supersaturations  $n - n_e > 0$ , and therefore the self-organized condensation process is more profitable. With the decrease in the current  $J_{ac}$  to negative values, the state corresponding to negative supersaturations becomes the most profitable. In this case the steady-state process is realized, which is inverse to the condensation, i.e., the self-organized sputtering of predeposited coating represented by the removal of the condensate. In contrast to the usual sputtering, removal courses in the following way: at first atoms, which are weakly connected with the condensate, are desorbed, then – more connected atoms, and etc.

Positions of the extremums of potential (6) are defined by equation

$$(n_0 - n_e)(1 + n_0^2) \left[ (1 + \kappa) + (n_0 / n_\tau)^2 \right] - J_{ac} \left[ 1 + (n_0 / n_\tau)^2 \right] = 0. \quad (7)$$

Analyzing the equation (7), it is convenient to use the condition of vicinity to the phase equilibrium  $|n_0 - n_e| \ll n_e$ . This allows to replace the steady-state concentration  $n_0$  in factor  $(1 + n_0^2)$  by the equilibrium value  $n_e$ . As a result, equation (7) is reduced to the cubic equation

$$n_0^3 - An_0^2 + Bn_0 - C = 0, \quad (8)$$

$$A = n_e + \frac{J_{ac}}{1 + n_e^2}, \quad B = n_\tau^2 (1 + \kappa), \quad C = n_\tau^2 \left[ n_e (1 + \kappa) + \frac{J_{ac}}{1 + n_e^2} \right], \quad (9)$$

and behavior of its roots is determined by the discriminant

$$d = \left( \frac{3B - A^2}{9} \right)^3 + \left( \frac{A^3}{27} - \frac{AB}{6} + \frac{C}{2} \right)^2. \quad (10)$$

At  $d > 0$  equation (8) has unique solution, otherwise, at  $d < 0$ , three roots are realized, which correspond to two minimums and separating maximum. Such situation is responsible for the discontinuous phase transition. It follows from the explicit dependence of the steady-state concentration  $n_0$  on the accumulated current  $J_{ac}$  that at large positive values of the accumulated current, when equation (8) has unique solution, the system is under condensation con-

ditions. With the decrease in  $J_{ac}$  to the critical value  $J_{c2}$ , which is defined by the condition  $d = 0$ , bifurcation occurs. It corresponds to the transition into bistable state, in which both condensation and removal of deposited surface are possible. And, finally, at negative values of the accumulated current  $J_{ac} < J_{c1}$ , where lower critical value  $J_{c1}$  is also determined by the condition  $d = 0$ , the system is found to be in the state of self-organized surface removal. In this case bistable states are realized only at large absolute values of the parameter  $\kappa$ , which defines the dispersion of the relaxation time (5).

A further problem consists in the investigation of kinetics of quasi-equilibrium condensation. At arbitrary proportion of the time scales  $\tau_T$ ,  $\tau_J$ ,  $\tau_0$ , its consideration is sufficiently complex. Therefore, it is convenient to pass to the study of the limiting cases, when one of the mentioned times becomes negligibly small, and it is possible to use the phase-plane method [8-10].

### 3. FAST RELAXATION OF THE CURRENT ( $\tau_J \ll \tau_0, \tau_T$ )

In this case the last equality of system (1) gives  $J = -J_{ac} + nT$ , and other equations take the form

$$\begin{aligned} \dot{n} &= (n_e - n) \left( 1 + \frac{\kappa}{1 + n^2/n_\tau^2} \right) + J_{ac} - nT, \\ \delta \dot{T} &= nJ_{ac} - T(1 + n^2), \end{aligned} \quad (11)$$

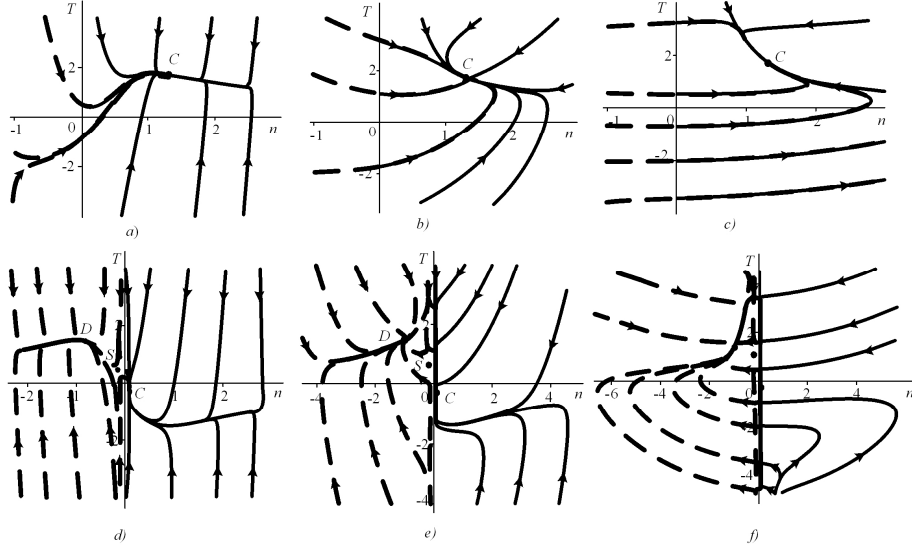
where time is measured in units of  $\tau_0$ ; parameter  $\delta \equiv \tau_T/\tau_0$  is introduced; and equality (5) is taken into account. Coordinates of singularities of equations (11) are defined by the expression

$$\frac{(n_e - n_0)(1 + \kappa + n_0^2/n_\tau^2)}{1 + n_0^2/n_\tau^2} + \frac{J_{ac}}{1 + n_0^2} = 0 \quad (12)$$

and temperature dependence on the concentration

$$T_0 = \frac{n_0 J_{ac}}{1 + n_0^2}. \quad (13)$$

Solutions of differential equations (11) are described by the phase portraits shown in Fig. 1. As seen from this figure, at small values of the equilibrium concentration  $n_e$  only the condensation process is realized. With the growth of  $n_e$  and inversion of the accumulated current  $J_{ac}$  one more steady state in the point  $D$  appears. However, this does not mean the appearance of the removal process, since point  $D$  corresponds to the negative values of the steady-state concentration  $n_0$ . Comparing different fields (Fig. 1), the acceleration behavior of the system evolution along the temperature axis with the decrease in the parameter  $\delta \equiv \tau_T/\tau_0$  is explicitly noticeable. At the same time, in the vicinity of the stationary point  $C$  it is possible to separate either the region of slow evolution (the large river bed) or the spiral region where the nonmonotonic condensation mode is realized.



**Fig. 1** – Phase portraits at  $\tau_J \ll \tau_0, \tau_T, n_\tau = 0, 1$  and:  $n_e = 0, 1, J_{ac} = 3, 5, \kappa = 1$  (fields a, b, c correspond to  $\delta = 0, 1, 1, 10$ , respectively);  $n_e = 0, 5, J_{ac} = -3, \kappa = 10$  (fields d, e, f correspond to  $\delta = 0, 1, 1, 10$ , respectively)

To ascertain the realization conditions of this mode we consider the Lyapunov exponents

$$\lambda_{1,2} = -\frac{1}{2\delta} \left\{ (1+n_0^2) + \delta(1-\alpha+T_0) \pm \sqrt{[(1+n_0^2) - \delta(1-\alpha+T_0)]^2 + 4\delta n_0(2n_0T_0 - J_{ac})} \right\}, \quad (14)$$

where we have denoted  $\alpha = \{2n_0[n_e + J_{ac} - n_0(1+T_0)] - \kappa n_\tau^2\} / (n_0^2 + n_\tau^2)$ . Analysis of the expression (14) shows that nonmonotonic condensation mode, when  $\lambda$  takes imaginary values, is realized in the interval  $\delta_- < \delta < \delta_+$ , whose boundaries are determined by the equality

$$\delta_\pm = \frac{1}{\delta^2(\alpha)} \left[ (1+n_0^2)\delta(\alpha) - 2\delta(J_{ac}) \pm 2\sqrt{\delta^2(J_{ac}) - (1+n_0^2)\delta(\alpha)\delta(J_{ac})} \right], \quad (15)$$

where  $\delta(\alpha) = 1 - \alpha + T_0$ ;  $\delta(J_{ac}) = n_0(2n_0T_0 - J_{ac})$ .

#### 4. FAST RELAXATION OF THE TEMPERATURE ( $\tau_T \ll \tau_J, \tau_0$ )

The given case is of minimal experimental interest, since it is difficult to expect that the temperature, which is the thermodynamic parameter, changes much faster than the desorption current and concentration, which are the dynamic variables of the condensation process. However, following the conventional line of consideration, we assume that the growth surface temperature follows the changes in the concentration and current according to the equality  $T = -nJ$ , which results from the second equation of system (1). As a result, this system takes the form

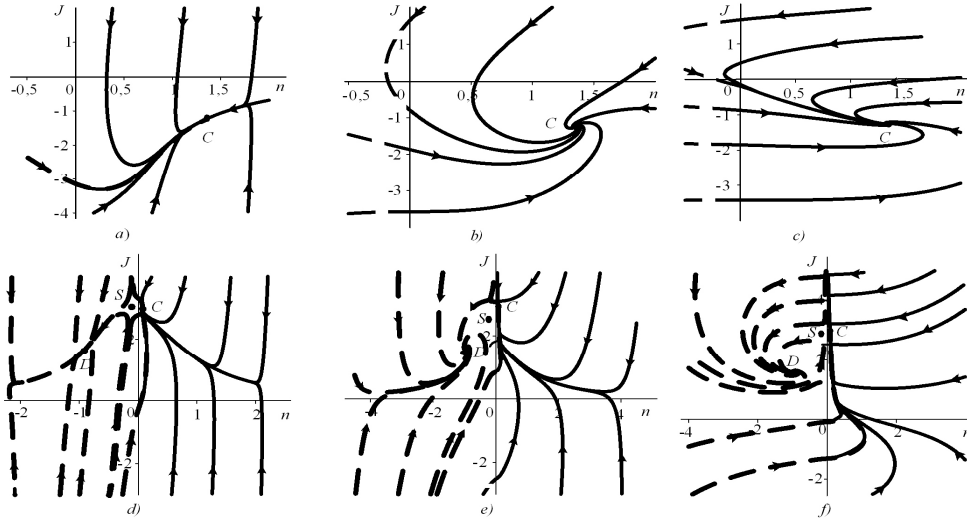
$$\begin{aligned}\dot{n} &= (n_e - n) \left( 1 + \frac{\kappa}{1 + n^2/n_\tau^2} \right) - J, \\ \sigma \dot{J} &= -[J_{ac} + J(1 + n^2)],\end{aligned}\quad (16)$$

where we have introduced the parameter  $\sigma \equiv \tau_J/\tau_0$ ; and time is measured in units of  $\tau_0$ .

Coordinates of singularities of equations (16) are defined by the solution of equation (12) and dependence of the current on the concentration

$$J_0 = -\frac{J_{ac}}{1 + n_0^2}. \quad (17)$$

The corresponding phase portraits are represented in Fig. 2. According to this figure, change in the equilibrium concentration  $n_e$  and the accumulated current  $J_{ac}$  influences the system behavior similar to the case considered in the Section 3: at small values of  $n_e$  and positive current  $J_{ac}$ , a unique state  $C$  is realized. This state corresponds to the steady-state condensation process, and the growth of  $n_e$  and inversion of  $J_{ac}$  lead to the appearance of the point  $D$ , which corresponds to the negative values of the steady-state concentration  $n_0$ . Thus, we can conclude that the fast changes in the temperature also cannot lead to the process of condensate removal.



**Fig. 2** – Phase portraits at  $\tau_T \ll \tau_J = \tau_0$ ,  $n_\tau = 0,1$  and:  $n_e = 0,1$ ,  $J_{ac} = 3,5$ ,  $\kappa = 1$  (fields *a, b, c* correspond to  $\sigma = 0,1, 1, 10$ , respectively);  $n_e = 0,5$ ,  $J_{ac} = -3$ ,  $\kappa = 10$  (fields *d, e, f* correspond to  $\sigma = 0,1, 1, 10$ , respectively)

At the same time, Fig. 2 shows that the increase in the relaxation time of the current leads to the torsion of the trajectory nearby the steady state  $C$ . Behavior of nonmonotonic attainment of the steady-state regime is defined by the Lyapunov exponents

$$\lambda = -\frac{1}{2\sigma} \left\{ 1 + n_0^2 + \sigma(1-\gamma) \pm \sqrt{[1 + n_0^2 - \sigma(1-\gamma)]^2 + 8\sigma n_0 J_0} \right\}, \quad (18)$$

where parameter  $\gamma = \{2n_0[(n_e - n_0) - J_0] - \kappa n_\tau^2\} / (n_0^2 + n_\tau^2)$  is introduced. As seen,  $\lambda$  takes imaginary values at the parameters  $\sigma$  from the interval  $\sigma_- < \sigma < \sigma_+$  with the boundaries

$$\sigma_\pm = \frac{1}{(1-\gamma)^2} \left\{ (1-\gamma)(1+n_0^2) - 4n_0 J_0 \pm 2\sqrt{4n_0^2 J_0^2 - 2n_0 J_0 (1-\gamma)(1+n_0^2)} \right\}. \quad (19)$$

### 5. FAST RELAXATION OF THE CONCENTRATION ( $\tau_0 \ll \tau_J, \tau_T$ )

Finally we consider the case when the concentration changes so fast that it has time to follow the changes in the current and the growth surface temperature. Then we can neglect the left side of the first equation (1), and, as a result, we obtain the equation

$$n^3 - (n_e - J)n^2 + (1+\kappa)n_\tau^2 n + n_\tau^2 [J - n_e(1+\kappa)] = 0, \quad (20)$$

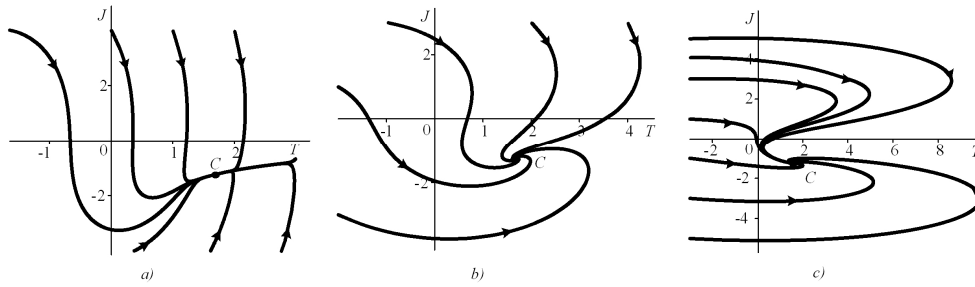
where correlation (5) is taken into account. Solution of this equation can be represented in the form

$$\begin{aligned} 3n &= (n_e - J) + n_+(J) + n_-(J); \\ n_\pm(J) &\equiv \left( J_1 \pm \sqrt{J_1^2 + J_2^3} \right)^{1/3}, \\ J_1 &\equiv 9n_\tau^2 [(1+\kappa)n_e - (1-\kappa/2)J] + (n_e - J)^3, \\ J_2 &\equiv 3(1+\kappa)n_\tau^2 - (n_e - J)^2. \end{aligned} \quad (21)$$

As a result, system (1) is reduced to the equations

$$\begin{aligned} \dot{T} &= -T - \frac{1}{3} [n_e - J + n_+(J) + n_-(J)] J, \\ \beta \dot{J} &= -(J_{ac} + J) + \frac{1}{3} [n_e - J + n_+(J) + n_-(J)] T, \end{aligned} \quad (22)$$

where time is measured in units of  $\tau_T$  and the correlation  $\beta = \tau_J / \tau_T$  is introduced. An enumeration of the possible values of the physical parameters  $n_\tau, \kappa, n_e, J_{ac}$ , and  $\beta$  shows that at fast change in the concentration a unique steady state is realized. It corresponds to the point  $C$  on the phase portraits illustrated in Fig. 3. It is seen from this figure that, as well as in the previous case ( $\tau_T \ll \tau_J, \tau_0$ ), the increase in the relaxation time of the current leads to the torsion of the trajectory nearby the steady state  $C$ . However, from the analytical point of view, investigation of the regime  $\tau_0 \ll \tau_J, \tau_T$  is found to be so complex that determination of the coordinates of the stationary point and the corresponding values of the Lyapunov exponent is not possible.



**Fig. 3** – Phase portraits at  $\tau_0 \ll \tau_T$ ,  $\tau_J$ ,  $n_\tau = 0,1$ ,  $\kappa = 1$ ,  $n_e = 0,1$ ,  $J_{ac} = 3,5$  (fields a, b, c correspond to  $\beta = 0,1, 1, 10$ , respectively)

## 6. CONCLUSIONS

Kinetics of the quasi-equilibrium condensation process is studied at different relations of the relaxation times of the condensed matter supersaturation, desorption current, and growth surface temperature. Phase portraits represented in Figs. 1-3 show that the condensation process corresponds to the singularity, which is realized at small values of the equilibrium concentration  $n_e$  and positive value of the accumulated current  $J_{ac}$ . In conditions of fast changes in the desorption current and surface temperature at large values of  $n_e$  and inverted current  $J_{ac}$ , the formation of one more attractive node is possible, which does not mean the removal process, since this corresponds to the negative values of the steady-state concentration  $n_0$ . Comparison of the phase portraits corresponding to different relations of the relaxation times confirms that the fastest system evolution occurs along the axis corresponding to the lowest of these times. In this case, near the stationary points one can observe either the region of slow evolution or the spiral region where the nonmonotonic condensation mode is realized. Investigation of the conditions of realization of this mode shows that the increase in the relaxation time of the current favors this mode.

## REFERENCES

1. V.I. Perekrestov, Yu.A. Kosminskaya, *JETP Lett.* **78**, 223 (2003).
2. V.I. Perekrestov, A.S. Kornysushenko, Yu.A. Kosminskaya, *Tech. Phys. Lett.* **32**, 868 (2006).
3. V.I. Perekrestov, A.I. Olemskoi, A.S. Kornysushchenko, Y.A. Kosminskaya, *Phys. Solid State* **51**, 1060 (2009).
4. A.I. Olemskoi, V.I. Perekrestov, I.A. Shuda, V.N. Borisyuk, A.A. Mokrenko, *Metallofiz. noveishie tekhnologii* **31** No11, 1505 (2009).
5. A.I. Olemskoi, A.A. Katsnelson, *Sinergetika kondensirovannoi sredy* (M.: Editorial URSS: 2003).
6. A.I. Olemskoi, *Sinergetika slozhnyh sistem: Fenomenologiya i statisticheskaya teoriya* (M.: izd-vo KRASAND: 2009).
7. E.M. Lifshitz, L.P. Pitaevskiy, *Fizicheskaya kinetika* (M.: Nauka: 1979).
8. L.D. Landau, E.M. Lifshitz, *Statisticheskaya fizika*, Chast' 1 (M.: Nauka: 1976).
9. A.A. Andronov, A.A. Witt, S.E. Haikin, *Teoriya kolebaniy* (M.: Nauka: 1981).
10. F.K. Moon, *Khaoticheskie kolebaniya* (M.: Mir: 1990).