

# TRANSIENT KINETICS OF HOMOGENEOUS NUCLEATION

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The transient stage of nucleation is studied on the basis of the Fokker-Planck equation. The approximate self-similar solutions for the nucleus size distribution function and the nucleation rate are obtained. The non-diffusion phase transition is considered as an illustration of the method developed.

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## 1. INTRODUCTION

As is known, determination of nucleation rate during the first-order phase transition is usually reduced to the solution of the Fokker-Planck (FP) equation for the cluster distribution function in the size space [1-3]. As a rule, theoretical treatments of isothermal phase transitions are limited to consideration of a steady-state nucleation, ignoring a non-stationary stage of the process. Actually, in most cases, nucleation occurs in a pulsed mode, when the saturation ratio is suddenly increased to a value at which homogeneous nucleation exists. Nevertheless, nucleation experiments have always been analyzed within the framework of the steady-state theory. If the incubation period of the nucleation  $t_n$  is much less than the time period of the phase transformation detailed study of a non-steady state of nucleation is of no interest. Frequently, the nucleation kinetics includes a transient stage during which the cluster size distribution changes drastically with time. Examples include (i) vapor condensation in nozzles, (ii) formation of clusters in molecular beams (iii) retarded nucleation when kinetic coefficients are small.

By various methods in [1-4] the characteristic time lag needed for establishment of a steady state nucleation flux in the critical region has been estimated (with accuracy to a numerical factor) as

$$t_n = \Delta^2 / D_c, \quad \Delta^{-2} = \frac{1}{2T} \left( \frac{\partial^2 \Phi}{\partial n^2} \right)_{n=n_c}.$$

Here  $\Phi(n, T)$  is the minimal work required to form the  $n$ -atomic cluster,  $D_c$  is the diffusion coefficient in the size space near the critical point,  $T$  is the temperature in energy units. This expression was obtained taking into account only diffusion in the sizes space, the drift term in FP equation was neglected. It is obvious that the time lag obtained in the "diffusion approximation" does not include the time needed for subcritical clusters to reach steady state, i.e. this time lag is only the time it takes for a cluster to diffuse across the free energy barrier. In last years numerous attempts have been made to describe the transient nucleation kinetics [4-11]. The big variety of results have been obtained, which is explained by diversity approximations used since in general case FP equation with variable coefficients admits no analytical solution. Solutions of the classic equation of nucleation kinetics by Kashchiev [5] are generally

considered to be the most accurate and have been widely used [12,13]; although his choice of the eigenfunction cutoff leads to incorrect results [4]. Similar approach has been developed in [6,7], where the solution of FP equation is expanded in series in eigenfunctions of the corresponding Schrödinger equation. Disadvantage of this approach is poor convergence of solution and difficulty of its comparison with real and numerical experiments. In [8,9] the quadratic approximation for the free energy barrier and constant growth rate of clusters is used. For this particular model a closed analytical solution of FP equation has been found using the Green function approach. The disadvantage of this method is that the solution does not satisfy physical boundary conditions [8]. Evidently, the most reasonable approach to study the non-stationary stage of nucleation is the approach based on the assumption of high nucleation barrier  $\Phi(n_c)/T \gg 1$ . This condition is closely related to applicability of FP equation to the nucleation problem; it is well fulfilled in real experiments. In [10, 11] the asymptotic solutions for the time-dependent distribution function and nucleation rate have been derived by a singular perturbation method. The general solution has been obtained by matching inner solution valid near the critical size with the outer solution satisfying boundary conditions. In fact such a solution well describes the transient nucleation kinetics only for large relaxation times.

The aim of the present work is to describe the transient kinetics of nucleation using the FP approach. The time-dependent self-similar solution is presented for the cluster distribution function and the nucleation rate.

## 2. BASIC EQUATION

Let us assume that clusters evolve in size by adding or losing only single atoms at a time. Then the distribution function  $f(n, t)$  satisfies the equation [1-2]

$$\frac{\partial f}{\partial t} = I(n-1, t) - I(n, t), \quad (1)$$

where  $I(n, t)$  is the flux of nuclei in the size space

$$I(n, t) = W^+(n)f(n, t) - W^-(n+1)f(n+1, t). \quad (2)$$

Here  $W^+(n)$  and  $W^-(n)$  are probabilities of adding or losing at a time of one atom by the cluster containing  $n$  atoms. According to the Zeldovich theory [1], for

$n_c \gg 1$ , the discrete Eq. (1) can be transformed to a differential form

$$\frac{\partial f}{\partial t} = \frac{\partial}{\partial n} W^+(n) f_0(n) \frac{\partial}{\partial n} \frac{f(n,t)}{f_0(n)}, \quad (3)$$

where  $f_0(n)$  is the equilibrium distribution function

$$f_0(n) = f_0(1) \exp[-\Phi(n,T)/T].$$

The boundary conditions for Eq. (3) are specified at both ends of the size distribution function. At  $n=1$  the monomer concentration is the same as the value used to define the equilibrium distribution [1,2]

$$f(1,t)/f_0(1) = 1. \quad (4)$$

The boundary condition

$$f(n,t)/f_0(n) = 0, \quad n = n^* \gg n_c, \quad (5)$$

describes removal of overcritical nuclei from the system.

Let us consider the transient nucleation kinetics when at  $t=0$  the saturation ratio is suddenly raised to a specified value. Since the initial concentrations of nuclei of all sizes equal zero it is reasonable to take the initial condition in the form  $f(n,0) = f_0(n) \delta_{n,1}$ . In this case the problem is reduced to finding evolution of the distribution function  $f(n,t)$  from zero to quasi-stationary value. The solution of Eq. (3) with boundary conditions (4), (5) and zero initial condition completely determines the time evolution of the system and contains practically all necessary information for determination of transient nucleation rate.

### 3. ASYMPTOTIC SELF-SIMILAR SOLUTION

The approximate analytical solution of Eq. (3) can be obtained if one neglects the size dependence of the diffusion coefficient  $D$  and expands  $\Phi(n,T)$  near the critical point in a power series of  $\Delta n = n - n_c$  up to the second order. It is useful to introduce the dimensionless time  $\tau$ , the free energy barrier  $V(x)$  and the distribution function  $\psi$ , using scaled size  $x$

$$x = n/n_c - 1, \quad \tau = \exp(-V_c) [W^+(n_c)/n_c^2] \cdot t,$$

$$V(x) = \Phi(n,T)/T, \quad \psi(x,\tau) = f(n,t)/f_0(n).$$

In these notations the equation (3) reduces to

$$\frac{\partial \psi}{\partial \tau} = 2\lambda x \frac{\partial \psi}{\partial x} + \frac{\partial^2 \psi}{\partial x^2}, \quad \lambda = -\frac{1}{2} \left( \frac{\partial^2 V}{\partial x^2} \right)_{x=-1} \quad (6)$$

with the following boundary and initial conditions

$$\psi(x,\tau) = f(n,t)/f_0(n), \quad \psi(-1,\tau) = 1, \quad \psi(\infty,\tau) = 0. \quad (7)$$

In the framework of this approximation the kinetic model depends only on single parameter  $\lambda$ . Approximately  $\lambda \approx \Phi_c/T \gg 1$ , where  $\Phi_c$  is the minimal formation energy of the critical cluster. As Zeldovich [1] and Frenkel [2] have noted, Eq. (6) is formally equivalent to the equation of diffusion of the particle moving in the parabolic force potential  $V(x) = \lambda x^2$ . The sta-

tionary solution of Eq. (6) satisfying conditions (7) is given by

$$\psi_{st}(x) = \int_x^\infty \exp(-\lambda z^2) dz / \int_{-1}^\infty \exp(-\lambda z^2) dz. \quad (8)$$

Then the stationary flux is

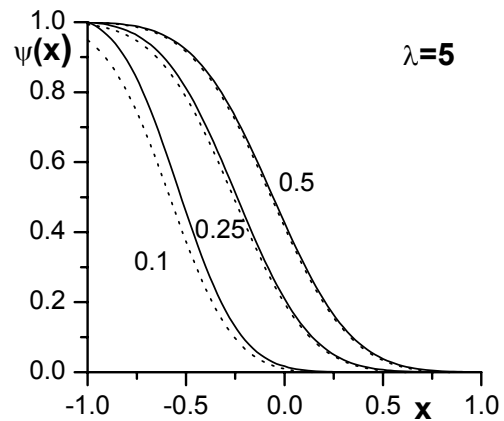
$$I_{st} = f_0(1) \cdot W^+(n_c) \exp(-V_c) / \int_{-1}^\infty n_c \exp(-\lambda z^2) dz. \quad (9)$$

Obviously, when the parameter  $\lambda$  is large enough, the non-stationary solution of the problem (6) and (7) is possible to find as a self-similar solution describing drift-diffusional movement of the "nucleation front" ahead of which there are no clusters of a new phase. The approximate self-similar solution of Eq. (6) and (7) is

$$\psi(x,\tau) = \psi_{st} \left( \frac{x - w(\tau)}{\sqrt{1 - w^2(\tau)}} \right), \quad (10)$$

where the function  $\psi(x,\tau)$  describes position of the nucleation front in the size space. Solution (10) is approximate because at small time it does not satisfy the boundary condition  $\psi(-1,\tau) \neq 1$ . However for a very short interval of time  $\tau_0 \approx 1/\lambda^2 \ll 1$ , this boundary condition is approximately valid and solution (10) is asymptotically exact. Then non-stationary nucleation rate is given by the expression

$$\frac{I(t)}{I_{st}} = \frac{\exp[-\lambda w^2(\tau) / (1 - w^2(\tau))]}{\sqrt{1 - w^2(\tau)}}. \quad (11)$$

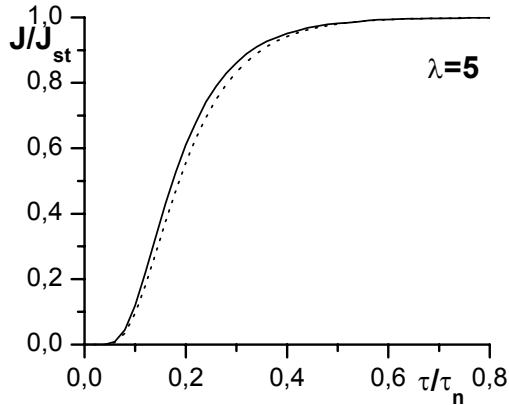


**Fig. 1.** Function  $\psi(x,t)$  in parabolic approximation at  $\lambda=5$  for several values of the relaxation time:  $\tau = 0.1 \cdot \tau_n$ ;  $0.25 \cdot \tau_n$ ;  $0.5 \cdot \tau_n$ . Dotted lines correspond to the analytical solution; solid line is the results of numerical calculation

Fig. 1 compares analytical solution (10) with numerical integration of Eqs. (6) and (7) at  $\lambda=5$ . The normalized transient nucleation rate as a function of dimensionless time is plotted in Fig. 2. Figures show a good agreement of self-similar solutions (10) and (11) with the numerical results almost for all relaxation times at  $\lambda \geq 5$ .

Using (10) it is easy to estimate the time lag  $\tau_n$  after which the function differs from its stationary value by no more than 1%.

$$\tau_n \approx \frac{\ln(10^4 \cdot \lambda)}{4 \cdot \lambda}. \quad (12)$$



**Fig. 2.** Normalized nucleation rate  $I(\tau)/I_{st}$  in parabolic approximation as a function of the normalized time  $\tau/\tau_n$  at  $\lambda = 5$ . The dotted line is the analytical solution; solid line is the numerical calculation

Let us study now the transient to steady state of nucleation in a general case without expansion of the free energy near the critical point, and taking into account size dependence of the “diffusion coefficient”  $D$ . Then the equation for the distribution function becomes

$$\frac{\partial \psi}{\partial \tau} = -D(x) \frac{\partial V}{\partial x} \frac{\partial \psi}{\partial x} + \frac{\partial D(x)}{\partial x} \frac{\partial \psi}{\partial x} + D(x) \frac{\partial^2 \psi}{\partial x^2}, \quad (13)$$

where  $D(x) = W^+(x)/W_c^+$ ,  $\tau = tW_c^+/n_c^2$ . Steady state distribution function in this case equals [4]

$$\psi_{st}(x) = \int_x^\infty \frac{1}{D(z)} \exp(V(z)) dz / \int_{-1}^\infty \frac{1}{D(z)} \exp(V(z)) dz. \quad (14)$$

For sufficiently large  $\lambda$  that in this case equals  $n_c^2 \Phi^+(n_c)/2T$ , the second term in the right hand side of Eq. (13) can be neglected. Then asymptotic solution at  $\tau \rightarrow \infty$  is again similar to Eq. (10), but now the coordinate of the “nucleation front” is found from the equation

$$\frac{dw}{d\tau} = -D(w) \frac{dV(w)}{dw}, \quad (15)$$

with  $w(0) = -1$ . Hence, time needed to reach steady state becomes

$$\tau_n = \int_{-1}^{-\varepsilon} \frac{dx}{|dV/dx| D(x)}. \quad (16)$$

Here  $\varepsilon$  is the cutoff parameter determining the required accuracy of stationary value of distribution function. Taking into account (15) the transient nucleation rate is

$$\frac{I(t)}{I_{st}} = \frac{\exp\left(V(-w(\tau)/\sqrt{1-w^2(\tau)}) - V(0)\right)}{\sqrt{1-w^2(\tau)} D\left(-w(\tau)/\sqrt{1-w^2(\tau)}\right)}, \quad (17)$$

$$I_{st} = f_0(1) \cdot W_c^+ / \int_{-1}^\infty \frac{n_c \exp(V(z)) dz}{D(z)}. \quad (18)$$

To illustrate the obtained results, consider the “drop model” of non diffusion transformation (no stoichiometric difference between two phases). In this model the minimal work sufficient to form the spherical nucleus [2, 14] in dimensionless variable is written as

$$V(x) = 3\lambda \cdot [3(x+1)^{2/3} - 2(x+1)], \quad (19)$$

where  $\lambda = \Phi_c/3T$  is the barrier for nucleation; and size dependence of the diffusion coefficient is [2]

$$D(x) = W^+(x)/W_c^+ = (x+1)^{2/3}. \quad (20)$$

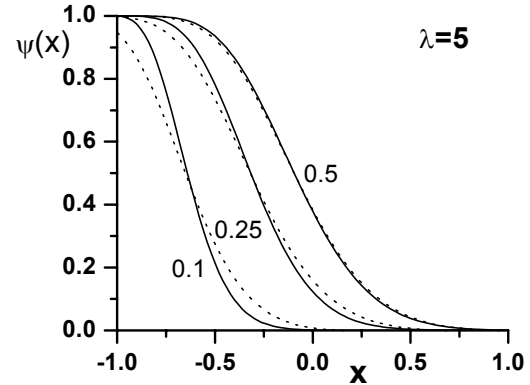
According to Eq. (16) the equation determining position of the “nucleation front” is given by

$$\exp(-2\lambda\tau) = \left(1 - \sqrt[3]{1+w(\tau)}\right) \exp(\sqrt[3]{1+w(\tau)}). \quad (21)$$

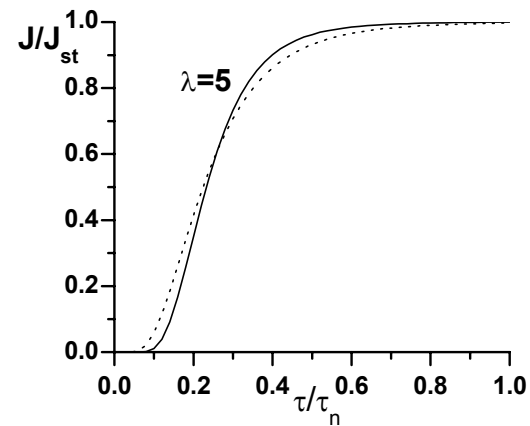
In the limit  $t \rightarrow \infty$  we obtain

$$w(\tau) = 3 \exp(-2\lambda\tau - 1), \quad (22)$$

and time lag required to reach the steady-state nucleation practically coincides with Eq. (12). In Fig. 3, the distribution function  $\psi(x, \tau)$  is shown for  $\lambda = 5$ , that was obtained using the self-similar solution (10). The transient nucleation rate as a function of  $\tau/\tau_n$  for the same values of  $\lambda$  is plotted in Fig. 4.



**Fig. 3.** Function  $\psi(x, \tau)$  for “drop model” at  $\lambda = 5$ , for several values of normalized time  $\tau/\tau_n = 0.1, 0.25$  and  $0.5$ . Dotted lines correspond to the analytical solution; solid lines is the results of the numerical calculation



**Fig. 4.** Normalized nucleation rate  $I(\tau)/I_{st}$  for “drop model” in the parabolic approximation as a function of the normalized time  $\tau/\tau_n$  at  $\lambda = 5$ . The dotted line is the analytical solution; solid line is obtained from the numerical solution

It is necessary to note one important feature of the obtained self-similar solution. In contrast the “diffusion” approximation used usually for the transient nucleation rate  $I = I_{st}(1 - \exp(-t/t_n))$  [3], Eq. (17) obtained in the present work contains some time lag needed for subcritical nuclei to reach the critical size. As it follows from Eqs. (17) and (21), this time is about

$$t_w \approx \frac{\ln \lambda}{4\lambda W_c^+} n_c^2,$$

and can vary from 10% to 50% of the total time needed to reach the steady state. In the “diffusion” approximation the relaxation time is only the time required for a nucleus to “diffuse” across the energy barrier; hence this approach underestimate the incubation period of nucleation.

Note cases when the self-similar solution becomes incorrect. The presence of self-similar universality behaviour means satisfaction of the following condition  $\Phi_c/T \gg 1$ . In the high supersaturation regime the universality can be violated, but then the conditions of applicability of the FP equation are violated too. Namely the presence of the large parameter makes behaviour of nucleation process universal, independent on a type of kinetic coefficients.

#### 4. CONCLUSIONS

The incubation stage of nucleation has been investigated using the time dependent FP equation for the nucleus size distribution for realistic boundary and initial conditions. The asymptotic exact expressions for the distribution function and the nucleation rate have been obtained. This allowed us to describe completely the nucleation kinetics both for quadratic approximation and for general case of arbitrary size dependence of nucleus free energy. By numerical integration of FP equation it is shown that obtained analytical solution well describes the transient kinetics of nucleation practically for all relaxation times.

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#### КИНЕТИКА НЕСТАЦИОНАРНОЙ СТАДИИ ГОМОГЕННОГО ЗАРОЖДЕНИЯ

М.П. Фатеев

На основе уравнения Фоккера-Планка исследована нестационарная стадия гомогенного зарождения. Получено приближенное автомодельное решение для функции распределения зародышей по размерам и скорость зарождения как в квадратичном приближении, так и в случае произвольной зависимости свободной энергии образования зародышей от размеров. Метод иллюстрирован случаем бездиффузионного фазового превращения.

#### КИНЕТИКА НЕСТАЦИОНАРНОЇ СТАДІЇ ГОМОГЕННОГО ЗАРОДЖЕННЯ

М.П. Фатеев

На основі рівняння Фоккера-Планка досліджено нестационарну стадію гомогенного зародження. Одержано наближене автомодельне рішення для функції розподілу зародків за розміром та швидкість зародження як у квадратичному наближенні, так і у випадку довільної залежності вільної енергії утворення зародків за розміром. Метод ілюстровано у випадку бездифузійного фазового перетворення.