



# Multivariable theory of droplet nucleation in a single-component vapor

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## HIGHLIGHTS

- The multivariable (volume, temperature, volume change rate)-theory of droplet nucleation is constructed.
- The limiting effect of heat exchange between the droplet and vapor on nucleation is shown.
- The calculated steady state distribution function of droplets shows their overheating in average.
- An inert carrier gas is shown to diminish the nonisothermal effect.

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## ABSTRACT

The multivariable theory of nucleation (Alekseechkin, 2006) is applied to the droplet nucleation in a supersaturated single-component vapor; the droplet volume  $V$ , temperature  $T$ , and volume change rate  $U = \dot{V}$  are the variables of the theory. A new approach based on macroscopic kinetics is developed for the droplet evolution and results in the derived equations for  $\dot{U}$ ,  $\dot{V}$ , and  $\dot{T}$ . It is shown that there is no viscosity effect in the employed ideal gas approximation, therefore the variable  $U$  can be omitted. The nonisothermal effect (the discrepancy between the actual and isothermal nucleation rates) earlier studied numerically is analytically examined here. This effect is shown to be strongly pronounced for pure vapor in the case of the condensation coefficient  $\beta$  close to unity. The theory predicts no nucleation for  $\beta = 1$  due to the suppression of the process of heat exchange between the droplet and vapor (the absence of reflected molecules carried this exchange). This result shows the limiting effect of kinetic processes on nucleation which cannot be revealed within the one-dimensional (isothermal) classical nucleation theory. The calculated steady state distribution function of droplets shows their average overheating relatively the vapor temperature. An inert background gas is shown to diminish the nonisothermal effect in comparison with a pure vapor case.

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## 1. Introduction

Calculation of the nucleation rate of liquid droplets in the process of condensation of a supersaturated vapor [1–18] is the classical problem of the nucleation theory which starts from the thirties of last century [1–4] and still topical. In the case of a single-component vapor, the employed theory, as a rule, is (i) one-dimensional and (ii) based on the standard (*microscopic*) pattern of evolution of the new phase embryo: the change of its size occurs due to the attachment (with the probability

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$w_+$  per unit time per unit area) and detachment (with the probability  $w_-$ ) of monomers. The probabilities  $w_+$  and  $w_-$  are related by the detailed balance

$$f_{eq}(N)A(N)w_-(N) = f_{eq}(N-1)A(N-1)w_+ \quad (1)$$

from where  $w_-(N)$  is found via the known probability  $w_+$ . Here  $A(N)$  is the surface area of a cluster consisting of  $N$  monomers,  $f_{eq}(N)$  is the equilibrium distribution function of clusters. Such model leads to the equation for the distribution function  $f(N)$  similar to the Einstein–Smoluchowski equation in the diffusion theory [4]. In turn, the latter relates to the case of “high viscosity” [19]. In this connection, an interesting question of the cases of arbitrary and low viscosity arises which cannot be studied in the framework of the standard classical theory. This issue, as well as other, can be considered within a multivariable theory coupled with *macroscopic* kinetics.

The multivariable nucleation theory starting with the classical work of Reiss [20] has been developed in subsequent works [21–24]. It is important that not only the composition of a cluster can be the variable  $x_i$  of its description (so that a multivariable theory is identified sometimes with a multicomponent one), but also another state variables (volume, density, temperature, etc. [25]); the complete set of variables  $\{x_i\}$  describing the state of an embryo is determined in a specific problem. In other words, the nucleation theory is multivariable even in a single-component case. In particular, the inclusion of temperature in the theory allows investigating and evaluating the nonisothermal effect in nucleation [5,6,11–16].

Rationale for the use of macroscopic kinetics in nucleation phenomena is as follows. We assume that the evolution of the distribution function  $f(\{x_i\}, t)$  of clusters subjected by the stochastic action of the thermostat (the surrounding mother phase) is described by the Fokker–Planck equation

$$\frac{\partial f(\{x_i\}, t)}{\partial t} = - \frac{\partial J_i(\{x_i\}, t)}{\partial x_i} \quad (2)$$

$$J_i = -d_{ij} \frac{\partial f}{\partial x_j} + \dot{x}_i f \quad (3)$$

where  $\mathbf{J}(\{x_i\}, t)$  is the vector of the flux density of clusters in the space  $\{x_i\}$ .

The equilibrium distribution function  $f_{eq}(\{x_i\})$  [23],

$$f_{eq}(\{x_i\}) = N_0 \sqrt{\frac{h_{11}^{-1} \det \mathbf{H}}{(2\pi kT)^{p-1}}} e^{-\frac{W(\{x_i\})}{kT}} \quad (4)$$

vanishing the flux (3) gives an equation for  $\dot{x}_i$ :

$$\dot{x}_i = -\frac{d_{ij}}{kT} \frac{\partial W}{\partial x_j} = -\frac{d_{ij}}{kT} h_{jk}(x_k - x_k^*) \equiv -Z_{ik}(x_k - x_k^*), \quad \mathbf{Z} = \mathbf{DH}/kT. \quad (5)$$

Here  $W(\{x_i\})$  is the work of formation of the cluster in the state  $\{x_i\}$ ; it can be represented in the vicinity of the saddle point  $\{x_i^*\}$  as the quadratic form  $W = W_* + (1/2)h_{ik}(x_i - x_i^*)(x_k - x_k^*)$ ;  $p$  is the number of variables  $x_i$ ;  $N_0$  is the normalizing constant of the one-dimensional distribution function  $f_{eq}(x_1)$ .  $\mathbf{D}$  is the matrix of “diffusivities”, its elements  $d_{ij}$  are assumed to be constant and equal to the values at the saddle point. The prefactor  $N_0$  can be calculated in the framework of statistical mechanical approach [26–30] for the distribution function  $f_{eq}(N)$  of clusters of  $N$  molecules; in this way, the following expression was obtained in Ref. [27]:

$$N_0 = \frac{\rho_{liq}}{\rho_{vap}} N_{vap} \equiv \zeta N_{vap} \quad (6)$$

where  $\rho_{vap}$  and  $\rho_{liq}$  are the densities of vapor and liquid, respectively;  $N_{vap}$  is the total number of molecules of vapor. The factor  $\zeta = \rho_{liq}/\rho_{vap}$  is the product of the replacement free energy factor,  $\rho_{liq}/\rho_{vap}^{(e)}$ , and the inverse supersaturation factor,  $\rho_{vap}^{(e)}/\rho_{vap}$ , which are shown in Ref. [27] to have their origins in the inclusion of the mixing entropy in the theory (the subscript (e) refers to the saturated vapor). This analysis was further developed and modified in Refs. [28,29]. However, here Eq. (6) is employed for calculating the distribution functions of droplets as some suitable approximation. The parameter  $\zeta$  also plays an important role in the presented theory as a whole.

The steady state flux of embryos, or the nucleation rate, has been calculated in a general form in Ref. [23]:

$$I = N_0 \sqrt{\frac{kT}{2\pi}} |h_{11}^{-1}| |\kappa_1| e^{-\frac{W_*}{kT}} \quad (7)$$

where subscript 1 relates to the unstable variable  $x_1$  (the volume  $V$  of a cluster here),  $\kappa_1$  is the negative eigenvalue of the matrix  $\mathbf{Z}$ .

As is known [31], the velocities  $\dot{x}_i$  and diffusivities  $d_{ij}$  in the Fokker–Planck equation are defined as follows:

$$\dot{x}_i = \lim_{\Delta t \rightarrow 0} \frac{\langle \Delta x_i \rangle_{\Delta t}}{\Delta t}, \quad d_{ij} = \lim_{\Delta t \rightarrow 0} \frac{\langle \Delta x_i \Delta x_j \rangle_{\Delta t}}{\Delta t} \quad (8)$$

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