International Journal of Heat and Mass Transfer 52 (2009) 548–556

Contents lists available at ScienceDirect

International Journal of Heat and Mass Transfer

journal homepage: www.elsevier.com/locate/ijhmt

About use of a method of direct numerical solution for simulation of bulk condensation of supersaturated vapor

N.M. Kortsensteyn [a], E.V. Samuilov [a], A.K. Yastrebov [b,*]

[a] Krzhizhanovsky Power Engineering Institute, Leninskii pr. 19, 119991 Moscow, Russian Federation
[b] Department of Low Temperatures, Moscow Power Engineering Institute (Technical University), Krasnokazarmennaya ul. 14, 111250 Moscow, Russian Federation

ARTICLE INFO

Article history:
Available online 2 September 2008

Keywords:
Nucleation
Bulk condensation
Distribution function
Kinetic equation
Numerical solution

ABSTRACT

The results of direct numerical solution of the kinetic equation for the droplet size distribution function are presented. This method which is not restricted by the Knudsen number was developed using the analogy with a similar method of solution of the Boltzmann kinetic equation. The simulation of vapor behavior at fast creation of supersaturation state in vapor–gas mixture by means of adiabatic expansion was carried out for the verification of the method. The results obtained by this method were compared with those which were obtained by using the method of moments over a broad range of Knudsen number. The relevance of taking into account the dependence between saturation pressure and droplet size on the dynamics of condensational relaxation was studied.

1. Introduction

Description of bulk condensation kinetics in various devices includes numerical solution of system of equations for condensation kinetics and gas dynamics in formulation which corresponds to solved problem. Apparently, this approach was proposed in [1]. Results of such solution have concrete character, and in general they can be applied only to a considered case. Alternative idea, which was proposed and implemented in [2–4], is choose of such method of treatment for obtained calculation data in order for results for simple problem to have general character. In the mentioned papers a simulation of vapor behavior in a mixture with non-condensing gas at adiabatic expansion was such simple problem (statement of a problem is submitted below).

Simulation of bulk condensation of supersaturated vapor was carried out on the basis of the numerical solution of the kinetic equation for droplet size distribution function by method of the moments (see, e.g. [5,6]). The physical kinetics methodology was used for the analysis of simulation results. Bulk condensation was considered as a relaxation process (condensation relaxation) with characteristic time τ_c, which was determined as a time interval during which initial value of supersaturation ratio decreases by a factor of *e*. Use of such approach by analogy with second-order phase transitions made possible to obtain scaling correlations for the important characteristics of first-order phase transition, in particular numerical density of formed droplets n_d and time of condensational relaxation τ_c. Also it turned out to be possible to take into account disturbances of thermodynamic parameters of process (temperature and pressure) relative to average values. It was noted that some time interval existed in beginning of condensation relaxation, during which new droplets formed with constant nucleation rate at nearly constant values of temperature and supersaturation ratio. This time interval was called the induction period τ_i by analogy to combustion theory. Relation between the induction period and the nucleation rate was established at initial values of temperature and supersaturation ratio. In opinion of authors of [3], obtained relations give a principal possibility for experimental determination of nucleation rate one more method. As against many existing methods [7], it can allow to determine the nucleation rate at that stage when nucleating droplets cannot be detected by optical methods.

This paper has the following structure. The problem formulation for condensation relaxation of supersaturated vapor in a mixture with non-condensing gas is presented in Section 2. Also the appropriate system of the equations is presented in Section 2. In Section 3, the new method offered by authors for solving the kinetic equation for droplet size distribution function is described. In Section 4, the results of application of the method offered by authors are submitted, and the comparative analysis is given for obtained results and the solution of the same problem with use of a method of the moments. The basic deductions on work are given in Section 5.

---

* Corresponding author. Tel.: +7 495 362 7841; fax: +7 495 362 7377.
E-mail addresses: naumkor@yandex.ru (N.M. Kortsensteyn), evsam@eninnet.ru (E.V. Samuilov), ars48@yandex.ru, YastrebovAK@mpei.ru (A.K. Yastrebov).

0017-9310/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ijheatmasstransfer.2008.06.033

Nomenclature

C_p	specific heat
D	diffusion coefficient
f	droplet size distribution function
F	velocity distribution function of molecules
g	mass fraction
I	nucleation rate
J	the collision integral
Kn	Knudsen number
L	evaporation heat
n	number density
N_A	Avogadro number
p	pressure
r	droplet radius
$\dot{r}$	droplet growth rate
R	the universal gas constant
s	supersaturation ratio
t	time
T	temperature
v_T	thermal velocity of molecules
V	volume

Greek symbols

α	condensation coefficient
γ	adiabatic index
λ	mean free path of molecules
μ	molar mass
ξ	molecular velocity
ρ	density
Ω	moment of distribution function

Subscripts and superscripts

cr	critical radius
d	parameter of droplets
i	node number in the droplet radius grid
j	time step number
l	parameter of liquid
n	order of moment
s	parameter in state of saturation
v	parameter of vapor
Σ	parameter of vapor–gas–droplets mixture

2. Formulation of the relaxation problem

We considered a mixture of vapor and incondensable gas in an adiabatically isolated cylinder with a moving plunger. At the initial time moment, the vapor is in a steady state at the saturation. Then plunger begins to move, and the velocity of plunger governs the rate of the vapor–gas mixture expansion and the rate of the vapor supersaturation development. The motion of plunger in turn determines the degree of the expansion (the ratio of current volume V to initial volume V_0) and the vapor supersaturation ratio $s = p_\mathrm{v}/p_\infty^\mathrm{s}(T)$, where $p_\infty^\mathrm{s}(T)$ is the saturation pressure over a flat vapor–liquid interface. It was shown in [4] that the supersaturation ratio can be found from following equation:

$$\frac{\mathrm{d}\ln s}{\mathrm{d}t} = A_1\frac{\mathrm{d}\ln V}{\mathrm{d}t} - \alpha\pi r_\mathrm{d}^2 n_\mathrm{d} v_\mathrm{T} A_2. \tag{1}$$

Here

$$A_1 = (\gamma - 1)\left(\frac{L\mu_\mathrm{v}}{RT} - \frac{\gamma}{\gamma - 1}\right), \quad A_2 = 1 + g_\mathrm{v}\frac{L}{C_p T}\left(\frac{L\mu_\mathrm{v}}{RT} - 1\right), \tag{2}$$

where γ is the adiabatic index, L is the heat of evaporation, C_p is the specific heat of the vapor–gas–droplet mixture, v_T is the thermal velocity of vapor molecules, g_v is the vapor mass fraction in the mixture, n_d is the droplet-number density, and r_d is the average droplet size.

The first term in right part of (1) describes increase of the supersaturation ratio due to the adiabatic expansion, while the second one describes decrease of the supersaturation ratio due to vapor phase depletion (the first term in A_2) and to an increase in the temperature caused by the heat of the phase transition (the second term in A_2). Eq. (1) was obtained with use of definition of the supersaturation ratio, the temperature dependence of the saturation pressure according to the Clausius–Clapeyron equation, the Poisson adiabatic equation, and the vapor state equation, as well as the balance equations for energy and number of vapor molecules:

$$\rho_\Sigma C_p\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{L\mu_\mathrm{v}}{N_\mathrm{A}}\frac{\mathrm{d}n_\mathrm{c}}{\mathrm{d}t}, \tag{3}$$

$$\frac{\mathrm{d}n_\mathrm{c}}{\mathrm{d}t} = -\frac{\mathrm{d}n_\mathrm{v}}{\mathrm{d}t}. \tag{4}$$

Also it was taken into account that number of vapor molecules decreased due to their collision with droplets with probability α:

$$\frac{\mathrm{d}n_\mathrm{v}}{\mathrm{d}t} = -\alpha\pi r_\mathrm{d}^2 V_\mathrm{T} n_\mathrm{d} n_\mathrm{v}. \tag{5}$$

Here n_v and n_c are the number densities of vapor and condensate molecules, respectively, and N_A is Avogadro number. It should be noted that use of united energy balance equation for both phases in the form (3) is possible if temperature of droplets is equal to one of vapor–gas mixture. We call this case further as one-temperature model [2]. This model was used in this paper as well as in [2–4], and this allowed comparing obtained results.

At such an approach, it is quite possible to account for that fact that the heat release during condensation occurs on the surface of growing droplets followed by the heat transfer to the gaseous phase at a finite rate. In this case, droplets turned out to be superheated compared with the vapor, thus retarding the processes of droplet nucleation and growth. The limits of the variations in droplet temperature are known. At the lower limit, this is the temperature that is identical for both phases. At the upper limit this is the saturation temperature corresponding to the vapor pressure above droplet (the "Oswatitsch assumption"). The one-temperature model is closer to the real situation the higher the vapor dilution with non-condensing gas and the lower the coefficient of condensation. Otherwise, the "Oswatitsch assumption" is close to reality.

The value of $n_\mathrm{d} r_\mathrm{d}^2$ in Eq. (1) is virtually the second moment of droplet size distribution function. For this reason system of equations, which describes process of condensational relaxation, should include corresponding equation for distribution function. This equation has the following form (see, e.g. [5,6]) for homogeneous condensation in an immovable medium without coagulation of droplets:

$$\frac{\partial f}{\partial t} + \frac{\partial(\dot{r}f)}{\partial r} = \frac{I}{\rho_\Sigma}\delta(r - r_\mathrm{cr}). \tag{6}$$

Here f is the mass distribution function of droplet sizes, r is the droplet radius, $\dot{r}$ is the droplet growth rate, I is the nucleation rate, ρ_Σ is the density of the vapor–gas–droplets mixture, δ is the delta function, and r_cr is the critical droplet radius.

If volume condensation is studied, and then overall characteristics of process are of interest usually. Numerical density of droplets, their average size, mass or volume fraction of liquid can be mentioned among these parameters. These values can be found as moments of distribution function:

$$\Omega_n = \int_{r_{\rm cr}}^{\infty} r^n f \, \mathrm{d}r. \tag{7}$$

The zero moment is number of droplets per unit of mixture mass, the third one is their total volume per unit of mixture mass, etc.

As in the kinetic theory of gases, the method of moments [5] can be used to solve the kinetic equation (6). This method allows obtaining system of equations for first four moments of distribution function. This system is equivalent of the kinetic equation (6). In order to do this the kinetic equation (6) should be multiplied by r^n ($n = 0,\ldots,3$) and then integrated over the droplet radius:

$$\frac{\mathrm{d}\Omega_n}{\mathrm{d}t} = n\int_{r_{\rm cr}}^{\infty} \dot{r} r^{n-1} f(r,t)\,\mathrm{d}r + \frac{I}{\rho_\Sigma} r_{\rm cr}^n. \tag{8}$$

Similar approach based on the kinetic equation and moment equations deduced from it was proposed in [5] to study processes of crystallization.

If droplet growth rate does not depend on droplet radius, then the system (8) can be simplified and written as system of differential equations for moments of distribution function:

$$\frac{\mathrm{d}\Omega_n}{\mathrm{d}t} = n\dot{r}\Omega_{n-1} + \frac{I}{\rho_\Sigma} r_{\rm cr}^n. \tag{9}$$

It should be noted that the moment equation (9) are identical to the "Hill chain" [8]. These equations were widely used in works of different authors (see, e.g. [6]). If method of moments is used to solve the kinetic equation (6), then moments Ω_n are obtained as solution, and the distribution function can be calculated from these moments if this is necessary.

The kinetic equation for droplet size distribution function (6) and the set of Eqs. (1)–(5) describe the process of condensation relaxation under adiabatic conditions with allowance for heat liberation when vapor volume varies with time according to an arbitrary law. In the described higher particular case the kinetic equation (6) is replaced by the set of moment equation (8). Such approach was used in [2–4]; in this paper, we obtained solutions directly from the initial kinetic equation (6). As well as in [2,3,11] in this work we considered the case in which supersaturation instantly reaches a preset value. From the physical viewpoint, it means that the time of vapor expansion is much less than the time of vapor condensation. So we could ignore the condensation at the expansion stage and to employ only the second term in the right side of Eq. (1). Later the supersaturation ratio decreases in according to (1) due to both decrease of the vapor partial pressure and rise in the saturation pressure, which grows because of an increase in the system temperature upon vapor condensation.

3. Method of direct numerical solution

The important applicability condition of the method of moments is absence of radius dependence for droplet growth rate. This condition holds only if droplet radius is much smaller than mean free path of vapor molecules, that is, at large Knudsen numbers $Kn = \lambda/r$. At small or moderate Knudsen numbers droplet growth rate depends on droplet size. In this case transition from the set (8) to set (9) cannot be done, and moment equations remain integer-differential and difficult to solve. Due to this a choice between two approaches is required. First approach is solution of moment equation (8); second one is solution of the kinetic equation (6). In the latter case moments of distribution function, which determine basic parameters of condensation aerosol, can be found from distribution function, which is obtained as result of solution. In principle, it is possible to simplify the system (8) for elimination of droplet radius (for example, in [9,10]). However, some assumptions should be adopted for use of such approach. Validity of these assumptions can be proved by use of more accurate methods. Such estimations are one of our results and are presented later.

This paper is development of our previous work [12], in which we proposed new method for simulation of supersaturated vapor bulk condensation. In our method the kinetic equation (6) is solved instead of the integer-differential moment equation (8). We used the experience of the direct numerical solution of the Boltzmann kinetic equation, which is widely used for study of evaporation and condensation on surfaces. For one-dimensional non-stationary problem it has following form [13]:

$$\frac{\partial F}{\partial t} + \xi_x \frac{\partial F}{\partial x} = J(F). \tag{10}$$

Here F is the velocity distribution function of molecules, ξ_x is the projection of the molecule velocity onto the x-axis, and J is the collision integral:

$$J(F) = \int_0^{\infty}\int_0^{2\pi}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} (F'F_1' - FF_1)|g|b\,\mathrm{d}b\,\mathrm{d}\varepsilon\,\mathrm{d}\xi_{1x}\,\mathrm{d}\xi_{1y}\,\mathrm{d}\xi_{1z}, \tag{11}$$

where $F = F(\xi)$, $F_1 = F(\xi_1)$, $F' = F(\xi')$, $F_1' = F(\xi_1')$, ξ_1 and ξ are velocities before collision, ξ_1' and ξ' are ones after collision, $g = \xi_1 - \xi$ is the relative velocity, b is the impact parameter, ε is the angular parameter of interaction. Values of ξ_1' and ξ' depend on the values of ξ_1, ξ, b and ε, as well as on the potential of molecular interaction.

To date different methods were proposed for solution of the Boltzmann kinetic equation. Among them are method of moments and method of direct numerical solution. The method of moments for the Boltzmann equation solution was once employed to develop a similar method for the solution of the basic kinetic equation of bulk condensation. Problem of intensive evaporation and condensation on phase boundary can be noted as an example of the Boltzmann equation solution by method of moments [14]. It should be noted that method of moments allows obtaining solution only for one-dimensional stationary problems that is its main disadvantage.

The method of direct numerical solution of the Boltzmann kinetic equation was developed in the Computing Center of the Russian Academy of Sciences. There are several variants of this method [15,16], in which different approaches to the calculation of the collision integral are used. In this method the physical process is divided into separate stages on each step of time. The first stage is the free molecular flow

$$\frac{\partial F}{\partial t} + \xi_x \frac{\partial F}{\partial x} = 0, \tag{12}$$

the second stage is the spatially uniform relaxation

$$\frac{\partial F}{\partial t} = J(F). \tag{13}$$

Eqs. (12) and (13) decide one by one. The solution of Eq. (12) is the initial condition for Eq. (13), and the solution of Eq. (13) is the initial condition for Eq. (12) on the next step of time. Both equations should be replaced by finite-difference schemes if the Boltzmann equation is solved numerically.

The method of the direct numerical solution of the Boltzmann equation was used to analyze different problems. Among them, the problem of an unsteady state heat and mass transfer in a vapor film during film boiling [17,18] is the most similar to the subject of this paper. The method of direct numerical solution enabled to solve this problem using non-stationary approach and to clarify the behavioral peculiarities of a vapor film at different stages of the process. In particular, it was established that vapor may be condensed in a vapor film during the unsteady state heating of a cold liquid by a hot body.

Taking the method of the direct numerical solution of the Boltzmann equation as the basis, we developed similar method for the numerical solution of the kinetic equation for droplet size distribution function. While developing this method, we took into account the following differences between Eqs. (10) and (6):

(a) In Eq. (6), the distribution function is differentiated with respect to main variable r, whereas the Boltzmann equation (10) does not imply differentiation with respect to velocity component ξ_x.
(b) The Boltzmann equation is an integer-differential one, while the kinetic equation for droplet size distribution function is a differential one, with the solution of the Boltzmann equation comprising a complex calculation of the collision integral, which requires a long computing time.
(c) The right-hand side of the Boltzmann equation is conservative, while the right-hand side of the condensation kinetics equation is non-conservative; i.e., the existence of the right-hand side in the Boltzmann equation has no effect on the preservation of the total mass, pulse, and energy of vapor molecules, whereas, in the condensation equation, the right-hand side influences the number of droplets, their total volume, etc.

In the vapor homogeneous condensation problem, the following equations describing droplet nucleation and growth may be used as analogs of equations of free molecular flow (12) and spatially uniform relaxation (13):

$$\frac{\partial f}{\partial t}+\frac{\partial(\dot{r}f)}{\partial r}=0, \tag{14}$$

$$\frac{\partial f}{\partial t}=\frac{I}{\rho_\Sigma}\delta(r-r_{\mathrm{cr}}). \tag{15}$$

From physical point of view the formation of droplets (15) should be first stage, and growth of droplets (14) should be second one. The solution of (15) is the initial condition for (14), and the solution of (14) is the initial condition for (15) on the next step of time.

For numerical solution of Eqs. (14) and (15) the droplet radius calculation region should be limited. The natural lower limit is the critical radius, and some sufficiently large radius $r_{\max}$ can be taken as the upper limit. The distribution function at $r = r_{\max}$ should always be equal to zero. In the calculation region, computational grid should be introduced with the critical radius as the first node of the grid.

Eqs. (14) and (15) should be replaced by finite-difference schemes. In Eq. (15) the delta-function should be removed or approximated. It can be done as follows. Eq. (15) is integrated over all particle radii:

$$\int_{r_{\mathrm{cr}}}^{\infty}\frac{\partial f}{\partial t}\,\mathrm{d}r=\frac{I}{\rho_\Sigma}. \tag{16}$$

Then the integral in (16) is replaced by the sum over all the grid nodes:

$$\sum_i\frac{\partial f_i}{\partial t}\Delta r_i=\frac{I}{\rho_\Sigma}. \tag{17}$$

Here i is a node number in the droplet radius grid. According to (15), only the distribution function at the critical radius can be variable, because at $r \neq r_{\mathrm{cr}}$ the right side of (15) is equal to zero. Therefore, all the terms in the left side of (17), except for the first one, are equal to zero. So the final form of the difference scheme for the nucleation equation is as follows:

$$\frac{f_1^{j+1}-f_1^j}{\Delta t}\Delta r_1=\frac{I}{\rho_\Sigma}. \tag{18}$$

Here the value of distribution function f_1 corresponds to the critical radius, $\Delta r_1 = r_2 - r_1$, and j is a time step number.

At the growth stage new droplets do not form; therefore, the finite-difference scheme for Eq. (14) should imply that the zero moment of the distribution function (i.e., the number of droplets) remains constant as follows:

$$\frac{\partial}{\partial t}\int_{r_{\mathrm{cr}}}^{\infty}f\,\mathrm{d}r=0. \tag{19}$$

In the numerical solution, the integral in (19) is replaced by the sum over all grid nodes. Time and droplet radius are independent variables; hence, the order of differentiation and integration can be changed. Thus, following condition can be obtained from (19):

$$\sum_{i=1}^{N}f_i^{j+1}(r_i-r_{i-1})=\sum_{i=1}^{N}f_i^{j}(r_i-r_{i-1}). \tag{20}$$

The droplet growth equation is solved using the explicit difference scheme having first-order accuracy with respect to time and coordinate as follows:

$$\frac{f_i^{j+1}-f_i^j}{\Delta t}+\frac{\dot{r}_i^jf_i^j-\dot{r}_{i-1}^jf_{i-1}^j}{r_i-r_{i-1}}=0. \tag{21}$$

Similar difference scheme was used for the free molecular flow equation (12) in [16]. Difference scheme (21) satisfies the condition of a constant zero moment (20), if the distribution function at $r = r_{\max}$ always remains equal to zero.

If the scheme (21) is used, then following condition of stability should be fulfilled:

$$\Delta t\leqslant\Delta r/\max(\dot{r}). \tag{22}$$

This condition means that each droplet can move only to an adjacent mesh of the droplet radius grid during their growth.

The general order of the calculations at each time step is as follows:

(1) The growth rate of at all of the grid nodes and the nucleation rate are calculated.
(2) The nucleation equation (18) is solved.
(3) The droplet growth equation (21) is solved.
(4) The distribution function moments, new values of the vapor–gas mixture temperature, the supersaturation ratio and mass fraction of vapor are calculated.

To solve the equations, it is necessary to represent the rates of nucleation and droplet growth as explicit functions of the current values of the temperature, the supersaturation ratio, and the vapor concentration in the mixture. The critical radius also depends on the supersaturation ratio, so the droplet radius grid should vary. However, variations in the supersaturation ratio cause the critical radius to vary quite slowly (in an inverse proportion to its logarithm); therefore, at each time step, a new grid is formulated with its first node being equal to the current value of r_{cr}.

4. Calculation results and discussion

Process of condensational relaxation was studied for two mixtures. In both cases incondensable gas was argon, vapor was cesium in the first case and ethane in the second one. Droplet growth regime was free molecular for cesium–argon mixture and transitional for ethane–argon mixture. Solution for mixture of cesium and argon allowed testing of the developed method, because the kinetic equation (6) had been solved previously by method of moments. Fig. 1 presents the Knudsen number dependence on time during condensation in both the mixtures. The average droplet radius was taken as the characteristic size in the Knudsen number.

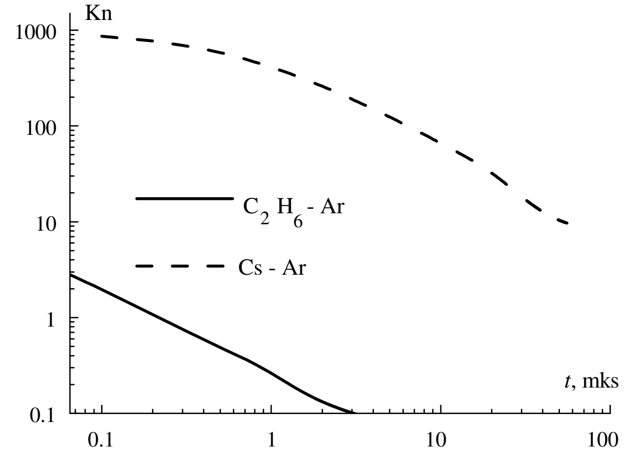

Fig. 1. The time dependence of the Knudsen number in the course of bulk condensation.

We used the Frenkel–Zeldovich formula [19] to calculate the nucleation rate and the Fuchs interpolation formula to calculate the droplet growth rate. This formula can be used at arbitrary Knudsen number, and it is written as follows [20]:

$$\dot{r} = \frac{\alpha(p_{\mathrm{v}} - p^{\mathrm{s}})}{\rho_{\mathrm{l}}\sqrt{2\pi RT/\mu_{\mathrm{v}}}}\left(1 + \frac{\alpha}{D}\sqrt{\frac{RT}{2\pi\mu_{\mathrm{v}}}}\frac{r^2}{r+\lambda}\right)^{-1}. \tag{23}$$

Here ρ_{l} is density of liquid, and D is diffusion coefficient.

4.1. Free molecular regime of droplet growth

Initial parameters for mixture of cesium and argon were given as follows. Pressure of vapor–gas mixture was 0.017 MPa, temperature was 560 K, and ratio between partial pressures of vapor and gas was 0.138. At these parameters initial supersaturation ratio was equal to 9.956.

Fig. 2 illustrates the time dependences for the temperature of the vapor–gas mixture, the supersaturation ratio, and the number density of droplets during the condensation relaxation process. It is known that the heat release due to condensation is proportional to the rate of droplet volume growth. This value is proportional to the squared droplet radius if droplet growth rate does not depend on radius. Therefore, at the initial stage (during the induction period [2]) the formation and growth of droplets does not lead to variations in the temperature and the supersaturation ratio. As a result, the rate of nucleation is virtually constant and an increase in the number of droplets obeys a linear law. When droplets become relatively large, the temperature begins to rise and the supersaturation ratio declines. Because the rate of nucleation strongly depends on the supersaturation ratio, the formation of new droplets soon ceases.

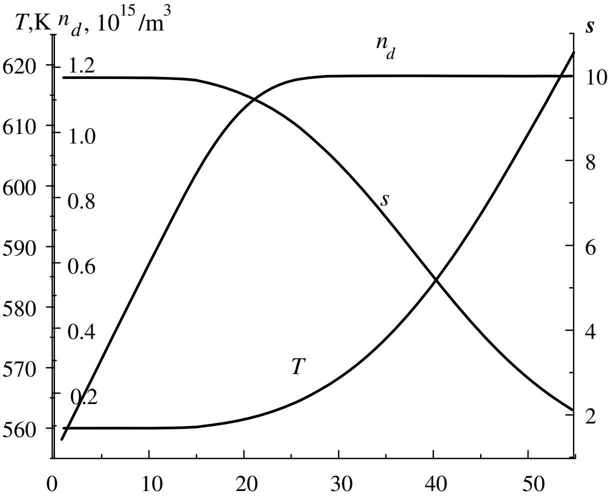

Fig. 2. Temperature, supersaturation ratio and number density of droplets for mixture of cesium and argon.

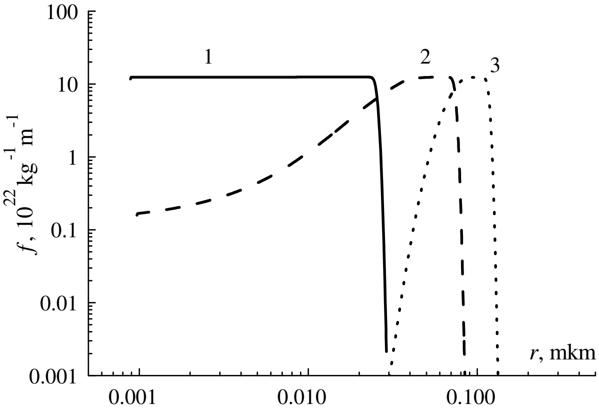

Fig. 3. Distribution functions for mixture of cesium and argon.

The evolution of the droplet size distribution function is illustrated in Fig. 3. It can be seen that the pattern of the distribution function corresponds to a constant formation rate of droplets during the induction period (curve 1). Soon after end of the induction period (curve 2) the distribution function changes according to reduction in the nucleation rate. By a time moment corresponding to approximately four induction periods (curve 3), the distribution function acquires its final form without formation of new droplets. Note that the right-hand branch of the distribution function shifts along the droplet size axis without distortions (curves 1–3), thus indicating that formed droplets grow at a constant rate. The results obtained by the proposed method both qualitatively and quantitatively coincide with ones obtained earlier by the method of moments [2–4].

4.2. Transitional regime of droplet growth

Successful testing of the proposed new method allowed us to apply this method to the case of intermediate Knudsen numbers. The results presented in this section were obtained for an ethane (vapor) and argon (gas) mixture with initial pressure of 0.2 MPa, temperature of 160 K, and ratio between partial pressures of the vapor and gas of 0.25. Under these conditions the droplet growth regime changes from free molecular to continual. At the onset of the process, only droplets with an almost critical radius are present in the system, Knudsen number is much larger than unity, and their growth regime is near to free molecular one. With time, the droplets grow, their radii become comparable with the free path, and the growth regime changes.

In this case the method of moments is difficult to use because differential equations for moments (9) cannot be written. So integer-differential equation (8) should be used, but they are very difficult to solve. However, the method of moments can be modified as follows. The rate of droplet growth is calculated with use of the Fuchs formula, in which the droplet radius r was replaced by the average radius of droplets r_{d}. Such approach was used in [10] to study turbulent vapor flow with condensation in Laval nozzle. If this calculation procedure for the growth rate is used, then moment equations remain differential because droplet growth rate becomes the same for all droplets. When the moment equations are solved numerically, the average radius, which is required for calculating the growth rate, is determined from the moments calculated on a previous time step.

In order to verify the validity of this approach, we compared the results obtained by our numerical method with and without this approximation. We obtained two solutions for the mixture of ethane and argon in which the rate of the droplet growth was calculated from the current and average radii.

The time dependences of the vapor–gas mixture temperature, the supersaturation ratio, and the number density of droplets are shown in Fig. 4. Results for different procedures of droplet growth rate calculation do not differ significantly. Comparison of Fig. 4 with Fig. 2 indicates that decrease in the Knudsen number does not qualitatively change the character of the time dependences of the temperature, the supersaturation ratio, and the number density of droplets. Similar to the free molecular droplet growth regime, an induction period is observed. Note that the induction period of the ethane–argon mixture is shorter than one of the cesium–argon mixture. This fact is associated with a corresponding increase in the density of the vapor–gas mixture due to a lower temperature and higher pressure.

Evolution of the droplet size distribution function is shown in Fig. 5 for both average and current radius in the Fuchs formula. It is easy to see that the distribution functions are qualitatively different. The droplet growth rate does not depend on droplet radius for r_d in the Fuchs formula as well as for free molecular regime; and it decreases with increase of droplet radius for r. So in the first case profile of distribution function moves without deformation, and in the second case it becomes narrower.

4.3. Dependence of the saturation pressure on droplet radius

In general, saturation pressure over curved surface depends not only on temperature but on curvature of this surface. For spherical droplets this dependence has the following form:

$$p^s = p^s(T, r) = p^s_\infty(T)\exp\left(\frac{r_{cr}\ln s}{r}\right). \tag{24}$$

Method of moments is difficult to use even for free molecular regime of droplets growth, if this dependence is taken into account. In this case it follows from the Fuchs formula (23) for large Knudsen numbers that droplet growth rate depends on droplet radius, and equation for moments remain integer-differential and difficult to solve. However, it is not obvious that a problem should be solved taking account of dependence (24). Conversely, it is usually assumed that saturation pressure depends on droplet radius only for droplets of very small size, so this dependence can be neglected.

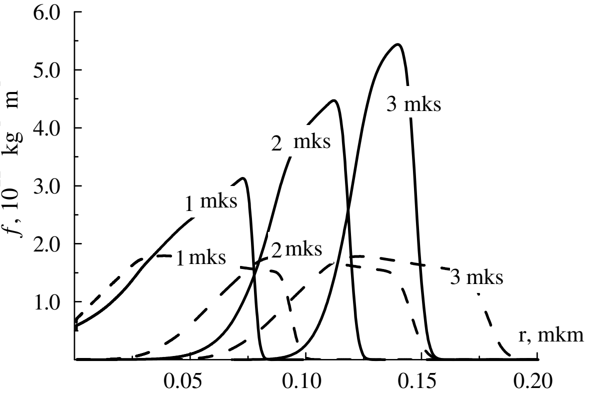

Fig. 5. Distribution function for mixture of ethane and argon (solid and dashed lines are for r and r_d in the Fuchs formula, respectively).

Method of direct numerical solution allowed solving the kinetic equation for droplet size distribution function with taking account of (24) and to clarify how saturation pressure dependence on droplet size affects characteristics of volume condensation process. For both mixtures we considered two variants of saturation pressure calculation:

(i) Saturation pressure depends only on temperature, i.e., $p^s = p^s_\infty(T)$.
(ii) Saturation pressure depends on temperature and droplet radius, i.e., $p^s = p^s(T, r)$.

Fig. 6 illustrates the time dependences for the temperature of the vapor–gas mixture, the supersaturation ratio, and the number density of droplets for mixture of argon and cesium. For variant (ii), in the case of the allowance for the saturation pressure dependence on the droplet radius, the induction period is longer, by approximately a factor of 1.5, than in the case of variant (i), where this

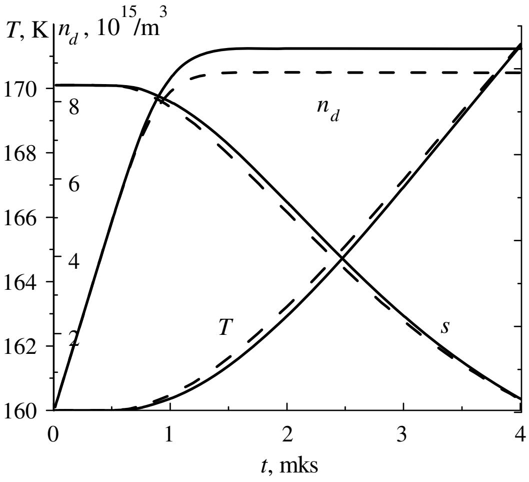

Fig. 4. Temperature, supersaturation ratio and number density for mixture of ethane and argon (solid and dashed lines are for r and r_d in the Fuchs formula, respectively).

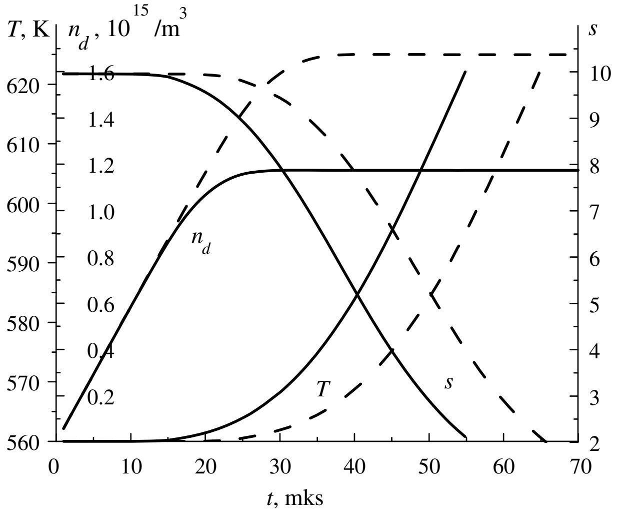

Fig. 6. Time dependence of temperature, supersaturation ratio and number density of droplets for cesium and argon mixture (solid lines are for $p_s(T)$, dashed ones are for $p_s(T, r)$).

dependence is ignored. In the former case, the stationary value of the droplet-number density increases proportionally. Comparing the time dependences for temperature and the supersaturation within the condensation regions, we can conclude that, for both variants, the indicated quantities attain values close to each other. However, there exists a certain time shift; i.e., the duration of the relaxation period increases if we take into account the dependence of the saturated-vapor pressure on the current droplet radius. Apparently, this is associated with the fact that the growth rate for droplets of the size slightly exceeding the critical size is considerably lower for variant (ii) than for variant (i).

Dynamics for the formation of the droplet size distribution function is presented in Fig. 8 for mixture of argon and cesium. The droplet size distribution functions for the variants under discussion are considerably different in the region of near-critical droplet size. There exists the tendency to a decrease in their difference with time. On the right side corresponding to the supercritical droplet size, the situation is noticeably distinguished. As is seen, the tendencies to the transformation of the droplet-size distribution functions have a common character with the above-noted time retardation of the condensation–relaxation processes for variants (i) and (ii). Similar form of distribution function was obtained in [21]. Authors of that paper held that large values of distribution function for small droplets cannot be obtained with help of classic nucleation theory. It can be seen from Fig. 7 that this conclusion is correct only if saturation pressure is not considered to be dependent on droplet radius.

Dynamics for the droplet fractional composition of the condensation aerosol is presented in Fig. 8 for the same mixture. Only one fraction of droplets having the near-critical size is present during the induction period for both variants. Further, due to the growth of the droplets formed and the slowing down of the nucleation process, the formation of the additional fraction of supercritical droplets occurs. Upon completing the induction period, the rapid depletion of the near-critical droplet fraction takes place, which is accompanied by the appearance of new fractions

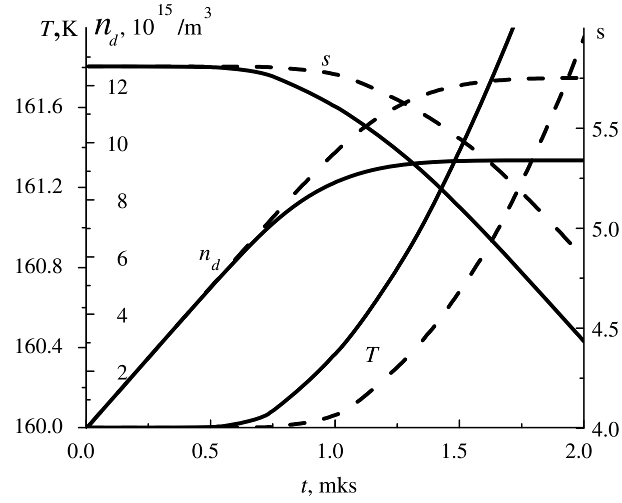

Fig. 9. Time dependence of temperature, supersaturation ratio and number density of droplets for ethane and argon mixture (solid lines are for $p_s(T)$, dashed ones are for $p_s(T,r)$).

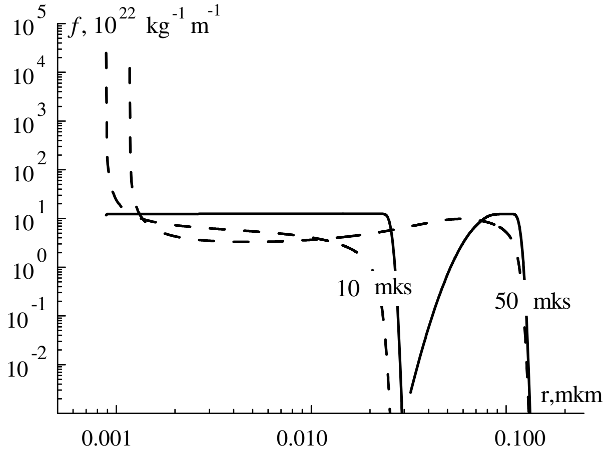

Fig. 7. Distribution function for cesium and argon mixture (solid lines are for $p_s(T)$, dashed ones are for $p_s(T,r)$).

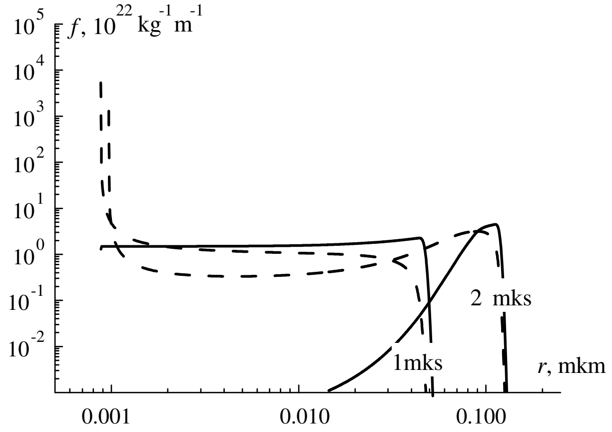

Fig. 10. Distribution function for ethane and argon mixture (solid lines are for $p_s(T)$, dashed ones are for $p_s(T,r)$).

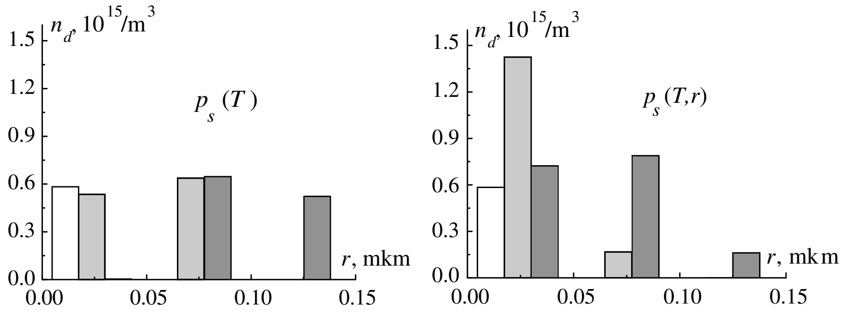

Fig. 8. Dynamics of fractional composition of aerosol for cesium and argon mixture (white for 10^{-5} s, light grey for 3×10^{-5} s, and dark grey for 5×10^{-5} s).

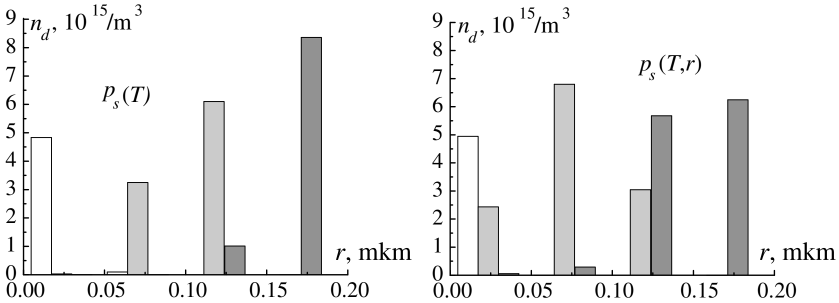

Fig. 11. Dynamics of fractional composition of aerosol for ethane and argon mixture (white for 10^{-6} s, light grey for 2×10^{-6} s, and dark grey for 3×10^{-6} s).

of super-critical droplets. It should be noted that significant difference of distribution functions led to considerably smaller difference of fractional compositions. The reason for this is that range of droplet radius is very narrow for high values of distribution function for variant (ii).

The same calculations were carried out for mixture of argon and ethane. Time dependences for temperature of vapor–gas mixture, supersaturation ratio and numerical density of droplets (Fig. 9) are similar to results presented above for mixture of argon and cesium. In both cases duration of induction period and stationary density of droplets is for variant (ii) larger than for variant (i). Evolution of distribution function (Fig. 10) and fractional composition of aerosol (Fig. 11) are similar also. Essential feature of moderate Knudsen numbers is decrease of time lag during process of condensation for variant (ii) in comparison with variant (i).

The divergence in results obtained for different Knudsen numbers are associated with that droplet growth rate depends on radius differently. For moderate Knudsen numbers droplet growth rate can be calculated by the Fuchs formula (22), for free molecular regime this equation transforms into Hertz–Knudsen formula:

$$\dot{r} = \frac{\alpha(p_{\mathrm{v}} - p^{s})}{\rho_{\mathrm{l}}\sqrt{2\pi RT/\mu_{\mathrm{v}}}}. \qquad (25)$$

In (25) droplet growth rate can depend on droplet size only if the dependence (24) is taken into account. If droplet radius increases then saturation pressure tends to inferior limit and droplet growth rate tends to superior one as provided by (25). For moderate Knudsen numbers this effect is less noticeable because both numerator and denominator in the Fuchs formula (23) are increasing functions of droplet radius.

5. Conclusion

The method of the direct numerical solution of the kinetic equation developed before by authors was used for the study of the bulk condensation at fast creation of supersaturation state in vapor–gas mixtures cesium–argon and ethane–argon. The regime of droplets growth for the first mixture was a free molecular one, for the second one the regime was transient – from the free molecular to continual one.

The use of the method developed has shown that in the first case the direct numerical solution and the method of moments produced the same results. In the second case the results obtained by the developed method and by the method of moments with simplified equation for the droplet growth rate were compared. It follows from the results of the comparison that in the second case the simplified method can be used for finding the integral parameters of condensation aerosol. However, the calculation of droplet size distribution function by means of this method can lead to substantial errors.

It was shown that the solution of the kinetic equation without taking into account the dependence between saturation pressure and droplet size led to understatement of condensational relaxation time and numerical density of droplets. Furthermore, in this case the profile of droplet size distribution function was distorted for the near critical droplet radius. It was shown that these effects were more apparent for large Knudsen numbers.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research, project 07-08-00082. Authors are grateful to S.P. Fisenko for useful remarks.

References

[1] K. Oswatitsch, Kondensationserschenungen in Übershalldüsen, Z. Angew. Math. Mech. 22 (1942) 1–14 (in German).
[2] N.M. Kortsenshtein, Analysis of the results of numerical simulation of the supersaturated vapor condensation relaxation, Colloid J. 64 (2002) 567–576.
[3] N.M. Kortsenshtein, E.V. Samuilov, On the possibility of the experimental determination of the nucleation rate in a supersaturated vapor, Dokl. Phys. Chem. 392 (2003) 243–247.
[4] N.M. Kortsenshtein, E.V. Samuilov, Condensation relaxation of supersaturated vapor under static and dynamic conditions, Dokl. Phys. Chem. 397 (2004) 169–173.
[5] H.M. Hulburt, S.M. Katz, Some problems in particle technology: a statistical mechanical formulation, Chem. Eng. Sci. 19 (1964) 555–574.
[6] M. Frenclach, S.J. Harris, Aerosol dynamics modeling using the method of moments, J. Colloid Interface Sci. 118 (1987) 252–261.
[7] J. Wölk, R. Strey, B.E. Wyslouzil, Homogeneous nucleation rates of water: state of the art, in: Proceedings of 16th International Conference on Nucleation and Atmospheric Aerosols, 2004, pp. 101–114.
[8] P.G. Hill, Condensation of water vapor during supersonic expansion in nozzles, J. Fluid Mech. 25 (1966) 593–620.
[9] V.A. Shneidman, A.L. Shubenko, Formation and evolution of the liquid-phase particle size spectrum in the presence of non-equilibrium homogeneous condensation, Fluid Mech. (Soviet) 1 (1990) 91;
V.A. Shneidman, Violation of adiabatic scaling in distribution of particles nucleated in a rapid quench, Phys. Rev. Lett. 75 (1995) 4634–4637.
[10] A.R. Avetissian, V.M. Alipchenkov, L.I. Zaichik, Simulation of a flow of spontaneously condensing moist steam in Laval nozzles, High Temp. 40 (2002) 872–880.
[11] A.P. Grinin, F.M. Kuni, A.V. Karachentsev, A.M. Sveshnikov, Statistics of the nucleation process under the conditions of instantaneous creation of the initial supersaturation of a vapor, Colloid J. 62 (2000) 32–39.
[12] N.M. Kortsenshtein, E.V. Samuilov, A.K. Yastrebov, On the possibility of modeling the bulk condensation of supersaturated vapor by the method of direct numerical solution of the basic kinetic equation, Dokl. Phys. Chem. 408 (2006) 160–164.
[13] M.N. Kogan, Rarefied Gas Dynamics, Plenum Press, New York, 1969.
[14] D.A. Labuntsov, A.P. Kryukov, Analysis of intensive evaporation and condensation, Int. J. Heat Mass Transfer 22 (1979) 989–1002.
[15] F.G. Tcheremissine, Conservative Discrete Ordinates Method for Solving Boltzmann Kinetic Equation, Computing Center of the Russian Academy of Sciences, Moscow, 1996.
[16] V.V. Aristov, Direct Methods for Solving the Boltzmann Equation and Study of Non-Equilibrium Flows, Kluwer Academic Publishers, Dordrecht, 2001.

[17] A.P. Kryukov, A.K. Yastrebov, Analysis of the transfer processes in a vapor film during the interaction of a highly heated body with a cold liquid, High Temp. 41 (2003) 680–687.

[18] A.P. Kryukov, A.K. Yastrebov, Heat and mass transfer through a vapor film in view of the motion of liquid–vapor interface and the rise of temperature at the interface, High Temp. 44 (2006) 556–564.

[19] D. Kashchiev, Nucleation: Basic Theory with Applications, Butterworths–Heinemann, Oxford, 2000.

[20] N.A. Fuchs, Evaporation and Droplet Growth in Gaseous Media, Pergamon Press, New York, 1959.

[21] A.A. Gorbunov, S.I. Igolkin, Nucleation theory: basic physics, numerical modelling and results of experiments, in: Proceedings of 4th Russian National Conference on Heat and Transfer, vol. 5, 2006, pp. 97–100 (in Russian).