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Vapor condensation on nanoparticles in the mixer of a particle size magnifier

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Abstract

The vapor condensation on nanoparticles in a supersaturated gaseous mixture is considered. Supersaturation was created by mixing two flows with different temperatures in a cylindrical mixer at atmospheric pressure. The conditions for mixing were chosen such that the homogeneous nucleation of vapor did not mask the growth of heterogeneous droplets with nanoparticles inside. A mathematical model of the growth of heterogeneous droplets was developed at one-dimensional description of the mixer. Five parameters that affect the performance of the particles size magnifier were identified: temperature of the saturator and the flow with nanoparticles, the number density and initial radius of the nanoparticles, and ratio of flow rates. The results of the simulation are compared with our experimental data.

Keywords: Supersaturation; Kelvin's effect; Heterogeneous droplet; Depletion; Mixing of flows; Droplets growth

0. Introduction

The development of nanotechnology has led to an important problem of capturing nanoparticles from a gas flow. Different variants of the laminar flow diffusion chamber can be used for this purpose [1–3], but there is a simpler, cheaper and faster devise in the form of a particle size magnifier (PSM) [4–6]. To create a supersaturated medium, the hydrodynamic mixing of flows at different temperatures is used at this devise. The flow, which has relatively low temperature, keeps nanoparticles.

This paper describes some simulations for ethylene glycol as the vapor, and nitrogen as the carrier gas because numerous experimental data have been reported for this vapor [5], some of these findings have been repeated during our previous research on the subject. It is important to create a not very high supersaturation in the mixer of the PSM so that the homogeneous nucleation of ethylene glycol does not contribute. The physical properties of ethylene glycol are taken from reference [7]. The term counting efficiency, introduced in [5], is the ratio of the number density of heterogeneous droplets, measured by an optical counter to the number density, measured by another device, using a different physical principle [5].

The aim of this paper is to provide further insights into PSM performance using simulation methods. The paper is organized as follows: Section 1 gives models for describing PSM parameters after mixing. A mathematical model for the growth of heterogeneous droplets with nanoparticles inside is considered in Section 2. A one-dimensional model was developed for the parameters of the gaseous mixture. The results of the simulation and comparisons with our experimental data are presented in Section 3. Our results and comparison with experimental data are summarized in the final section.

1. Parameters of mixing in PSM

A schematic diagram of the PSM mixer is presented in Fig. 1; details of the design can be found elsewhere [4–6]. The length of the mixer is about 2 cm with much smaller

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Nomenclature

c_d	specific heat capacity of heterogeneous droplet ($\mathrm{J\,kg^{-1}\,K^{-1}}$)
c_m	heat capacity of gaseous mixture ($\mathrm{J\,kg^{-1}}$)
D	diffusion coefficient of vapor ($\mathrm{m^2\,s^{-1}}$)
k	Boltzmann's constant ($\mathrm{J\,K^{-1}}$)
Kn	the Knudsen number (–)
l	the mixer length (m)
m	mass of an ethylene glycol molecule (kg)
n	the number density of vapor molecules ($\mathrm{m^{-3}}$)
n_e	the number density of saturated vapor ($\mathrm{m^{-3}}$)
N_d	the number density of nanoparticles ($\mathrm{m^{-3}}$)
P_e	equilibrium pressure of saturator vapor (Pa)
q	the ratio of flows, Q_s/Q_n (–)
Q_n	volumetric flow rate of nanoparticles ($\mathrm{m^3\,s^{-1}}$)
Q_s	volumetric flow rate of saturator ($\mathrm{m^3\,s^{-1}}$)
R	radius of a spherical nanoparticle (m)
R_d	radius of the liquid cover above nanoparticles (m)
R_f	final radius of heterogeneous droplet at the exit of a mixer (m)
S	supersaturation of vapor (–)
T_m	average temperature in the mixer (K)
T_n	inlet temperature of flow with nanoparticles (K)
T_s	temperature of the saturator (K)
u	average velocity of the mixture in the mixer ($\mathrm{m\,s^{-1}}$)
U	latent heat of condensation per one molecule (J)
v_a	volume per molecule for ethylene glycol in liquid phase ($\mathrm{m^3}$)

Greek symbols

λ	the mean free path of vapor molecules (m)
ρ_l	density of ethylene glycol ($\mathrm{kg\,m^{-3}}$)
ρ_m	density of capacity of gaseous mixture ($\mathrm{kg\,m^{-3}}$)
σ	surface tension ($\mathrm{N\,m^{-1}}$)

Subscripts

0	initial
d	droplet
e	equilibrium
f	final
l	liquid
m	mixture
n	nanoparticles
s	saturator

internal diameter. For our setup the internal diameter is about 0.2 cm, thus one-dimensional mathematical description of the mixer is well justified. It is well known that the mixing of two flows in any chamber is a complex process [8] and this complexity increases for flows with vapor condensation. For a small chamber (Reynolds number for average flow of about 700) the approximation of instant mixing [8] is a reasonable one. The instant mixing model gives a first approximation of the average parameters of the mixture in the mixer, its results were used as the initial conditions for our one-dimensional mathematical model of heat and mass transfer in the mixer.

The volumetric flow rate and the inlet temperature of flow which contains nanoparticles are defined as Q_n and T_n, respectively. The second flow is a mixture of carrier gas (nitrogen) and vapor (ethylene glycol below). This second flow has the temperature of the saturator, T_s, and the flow rate, Q_s. Using the approximation for instant mixing [4,8] we have the expressions for average parameters of mixture: the averaged number density of vapor molecules, n, and the averaged temperature T_m:

$$n = \frac{P_e(T_s)}{kT_s}\frac{Q_s}{Q_n + Q_s} \tag{1}$$

$$T_m = \frac{Q_nT_n + Q_sT_s}{Q_n + Q_s}, \tag{2}$$

where k is Boltzmann's constant, P_e is the equilibrium pressure of the saturated vapor. For the flux from saturator the vapor number density is equal to $P_e(T_s)/kT_s$. It is useful to transform expressions (1) and (2), introducing a new parameter, q, the ratio of flows,

$$q = Q_s/Q_n.$$

We can rewrite now expressions for the temperature and vapor density after mixing using dimensionless parameter q as following:

$$T_m = \frac{T_n + qT_s}{1+q}, \tag{1'}$$

and

$$n = \frac{P_e(T_s)}{kT_s}\frac{q}{1+q}. \tag{2'}$$

After the mixing of a flow with hot vapor and cold flow with nanoparticles, the vapor in the mixer is cooled. Due to exponential dependence of the saturated vapor density on the temperature the vapor became supersaturated one. The supersaturation S is defined here in the standard manner:

$$S = \frac{n}{\frac{P_e(T_m)}{kT_m}}.$$

For two different temperatures of the saturator, the behavior S versus mixing parameter q is shown in Fig. 2. For large values of q the value of supersaturation S will approach to one. Vapor condensation on micrometer size particles takes place if the supersaturation is larger than

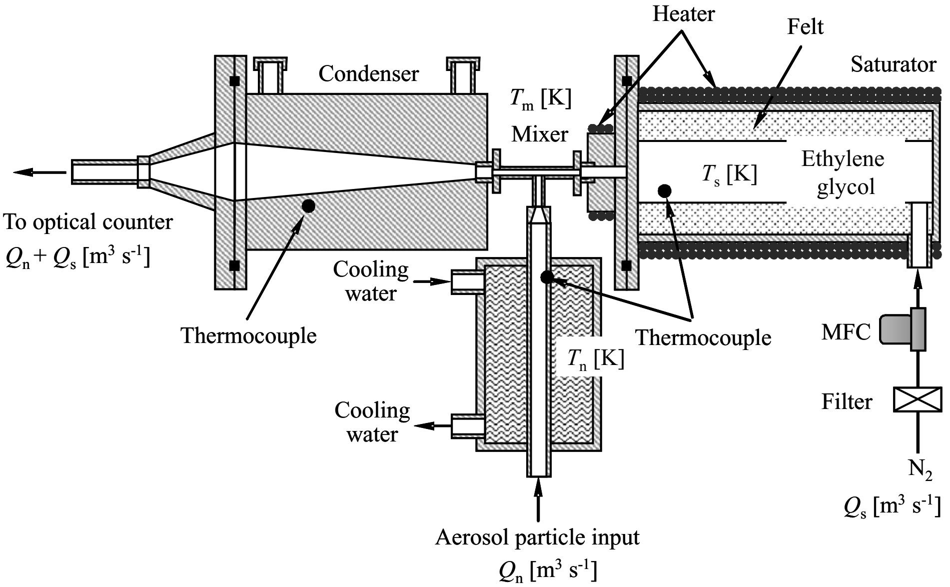

Fig. 1. Schematic diagram of a typical particle size magnifier (PSM).

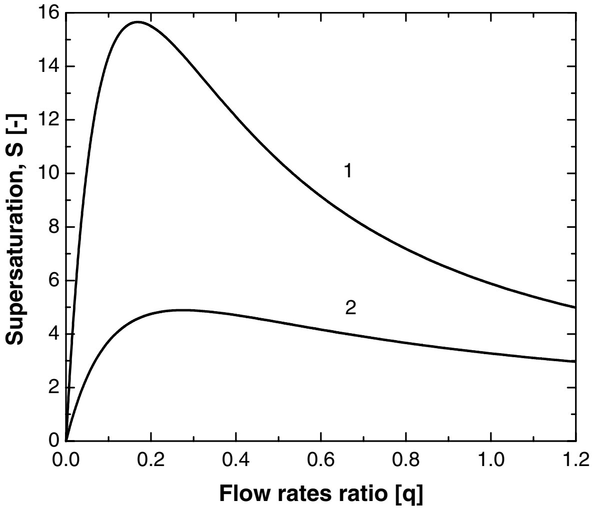

Fig. 2. Supersaturation of ethylene glycol versus q. Curve 1: $T_s = 373$ K, curve 2 $T_s = 343$ K at $T_n = 283$ K.

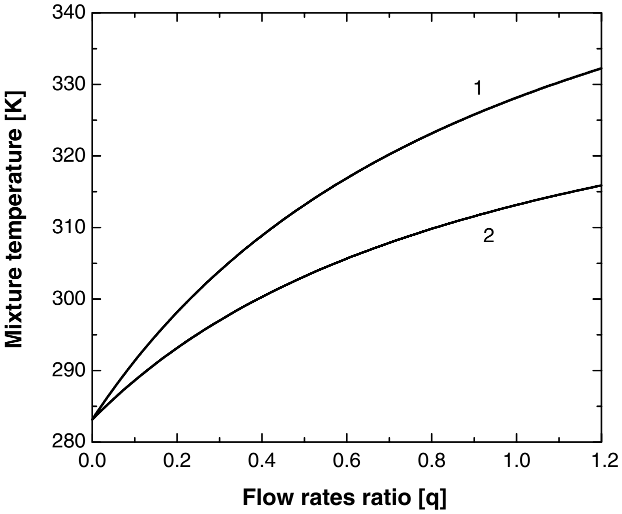

Fig. 3. Mixing temperature versus q. Curve 1 $T_s = 373$ K, curve 2 $T_s = 343$ K at $T_n = 283$ K.

one. For effective condensation on nanoparticles supersaturation has to be higher due to the Kelvin effect, which connects the equilibrium pressure of saturated vapor with the radius of interfacial surface. The plot of the mixing temperature, T_m, versus the parameter q is shown in Fig. 3. The mixing temperature, which substantially determines the value of diffusion coefficient of vapor D and the value the saturated number density of the vapor n_e, is the important parameter for the vapor condensation on nanoparticles.

Vapor condensation on the thermally isolated walls of the mixer is neglected below, because, after a short transition time the wall is covered by a thin liquid film. We assume that this film is in equilibrium with the vapor.

It is worth noting that for explanation of our experimental results we have to use the simple generalization of the model of the instant mixing, which takes into account the two largest vortex structures, existing in the mixer of PSM [9]. In the case of $Q_n > Q_s$ the structures are schematically shown in Fig. 4. We apply the approximation of the instant mixing to first part of the mixer, where the vapor flow from the saturator is mixing with the half of cold flow. Expressions (1′) and (2′) can be applied directly to this process, keeping in mind that the flow rate of the carrier gas is twice smaller. Thus, the mixing temperature and the number density of vapor are higher in the zone of the first vortex. We consider that this generalized model of the instant mixing produces a more accurate description of temperature and vapor density in the mixer. Some details are given at Section 3.

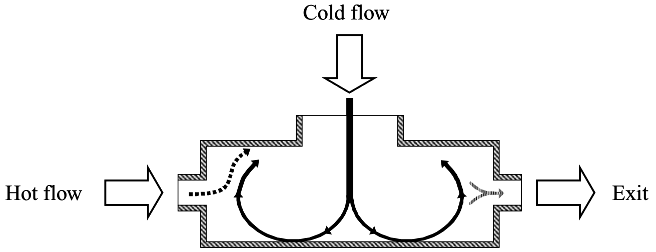

Fig. 4. Schematic diagram of vortex structures in the PSM mixer.

2. Mathematical model of nanoparticles growth

The mathematical model of the growth of heterogeneous droplets, which have nanoparticles inside in the mixer of the PSM, has three equations. For all these equations we use the following transition from the temporal variable t to spatial one z: $\mathrm{d}z = u\mathrm{d}t$, where u the average velocity of flow through the mixer.

The first equation, which is the conservation law for droplet mass, describes the change in radius of heterogeneous droplets due to the competition between vapor condensation and evaporation [10]:

$$\frac{\mathrm{d}R_\mathrm{d}}{\mathrm{d}z} = L(R_\mathrm{d})(n(z) - n_\mathrm{e}(T_\mathrm{m})\exp[2\sigma v_\mathrm{a}/R_\mathrm{d}kT_\mathrm{m}]), \tag{3}$$

where R_d is the radius of the heterogeneous droplet, v_a is the volume per molecule of liquid (ethylene glycol), σ is the surface tension of liquid. Eq. (3) takes account the Kelvin effect [11]. The right-hand side of Eq. (3) gives the exact expression for isothermal growth at the free molecular regime and at the continuous medium regime [12]. It also provides a good reasonable description of the growth rate for intermediate the Knudsen numbers, $Kn = \lambda/R_\mathrm{d}$. The expression for L is taken from [12]:

$$L(R_\mathrm{d}) = \frac{Dm}{u\rho_\mathrm{l}R_\mathrm{d}}\left(\frac{1}{1 + (D/R_\mathrm{d})\sqrt{2\pi m/kT}}\right), \tag{4}$$

where D is the diffusion coefficient of ethylene glycol in air, ρ_l is the density of liquid ethylene glycol, m is the mass of an ethylene glycol molecule, λ is the mean free pass of vapor molecules.

The second equation describes the change of the number density of vapor in the mixer due to growth of heterogeneous droplet. This equation is the continuity equation for vapor with the sink:

$$u\frac{\mathrm{d}n}{\mathrm{d}z} = -I_\mathrm{n}(n - n_\mathrm{e}(T_\mathrm{m})), \tag{5}$$

where coefficient I_n, which is proportional to the total interfacial surface of all droplets $4\pi R_\mathrm{d}^2 N_\mathrm{d}$:

$$I_\mathrm{n} = \frac{4\pi R_\mathrm{d}^2\rho_\mathrm{l}}{m}N_\mathrm{d}L(R_\mathrm{d}). \tag{6}$$

N_d is the number density of heterogeneous droplets (nanoparticles) [3].

There is the release of latent heat of the phase transition during condensation in the mixer of PSM. This effect is described by the third equation of our mathematical model, which is the continuity equation for total thermal energy of the flow in the mixer of the PSM:

$$u\frac{\mathrm{d}T}{\mathrm{d}z} = I_\mathrm{t}(n - n_\mathrm{e}(T(z))), \tag{7}$$

where the heat source I_t is described by the formula:

$$I_\mathrm{t} = UI_\mathrm{n}/(\rho_\mathrm{m}c_\mathrm{m} + N_\mathrm{d}4\pi R_\mathrm{d}^3\rho_\mathrm{l}c_\mathrm{d}/3), \tag{8}$$

where U is the latent heat of condensation per vapor molecule, ρ_m and c_m are the density and specific heat capacity of a gaseous mixture, respectively, c_d is the specific heat capacity of a heterogeneous droplet. The denominator at expression (8) is the total heat capacity per unit of volume. Thus, expression (8) takes into account the heat capacity of droplets in order to calculate the change of the mixture temperature [3].

For our mathematical model (3)–(8) the initial conditions are:

$$\begin{aligned} &\text{At } z = 0\\ &R_\mathrm{d}(0) = R_0\\ &n(0) = n\\ &T(0) = T_\mathrm{m}. \end{aligned} \tag{9}$$

We use the steady-state approximation of the performance of the mixer of PSM. It should be noted that the results, reported in [9], shown that the transition time to the steady-state regime is about (3–5) l/u, where l is the length of the mixer.

It is useful to obtain the analytical estimate of the growth of heterogeneous droplet in the mixer of PSM. For the diffusion regime of growth the function $L(R_\mathrm{d})$ is equal to:

$$L(R_\mathrm{d}) = D\frac{m}{uR_\mathrm{d}\rho_\mathrm{l}},$$

and for $S > 1$, using expression (2), we transform the difference $(n - n_\mathrm{e}(T(z)))$:

$$n - n_\mathrm{e}(T(z)) \approx \frac{n_\mathrm{e}(T_\mathrm{s})q}{1 + q}.$$

Using these transformations, the analytic solution of Eq. (3) gives the approximate expression for the final droplet size, R_f, in the mixer:

$$R_\mathrm{f} \sim \sqrt{D\frac{mlq}{u\rho_\mathrm{l}(1 + q)}n_\mathrm{e}(T_\mathrm{s})}. \tag{10}$$

It follows from expression (10) that the final droplet radius is exponentially depends on the saturator temperature T_s; the influence of the mixing parameter q is quite strong also, because by increasing q (within reasonable limits), we additionally increase the temperature of the gaseous mixture and value of the diffusion coefficient.

3. Simulation results

For different values of the mixing parameter q the final radius of heterogeneous droplet in the mixer are shown

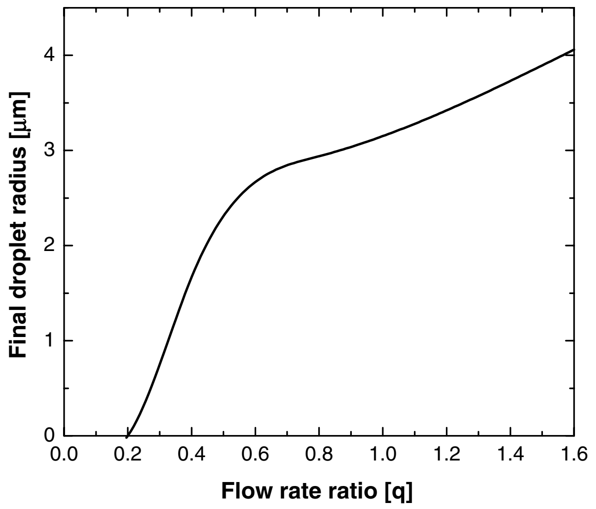

Fig. 5. Final droplet radius versus q at $T_s = 343$ K.

in Fig. 5. These droplets grow during traveling on the way one centimeter. For this simulation the initial radius of the nanoparticle is 2 nm. It should be noted that for $T_s = 343$ K the Kelvin effect prevents a droplet growth for the mixing parameter $q \leqslant 0.2$. For $T_s = 373$ K as our simulation shows there is no influence of the Kelvin effect on the final radius of heterogeneous droplets. The reason for this is that a major change takes place in the diffusion regime of the growth and the Kelvin radius [12] is smaller than 2 nm. The changes of vapor density due to the condensation on nanoparticles are shown in Fig. 6. The number density of the vapor in the saturator is used as the scale for the transition to a dimensionless variable. This plot also shows the limits of approximation for instant mixing. Data in Fig. 6 show that the applicability of the instant mixing model is strongly dependent on mixing parameter q and the number density of the nanoparticles. The changes in the temperature of the mixture are quite small and are not shown.

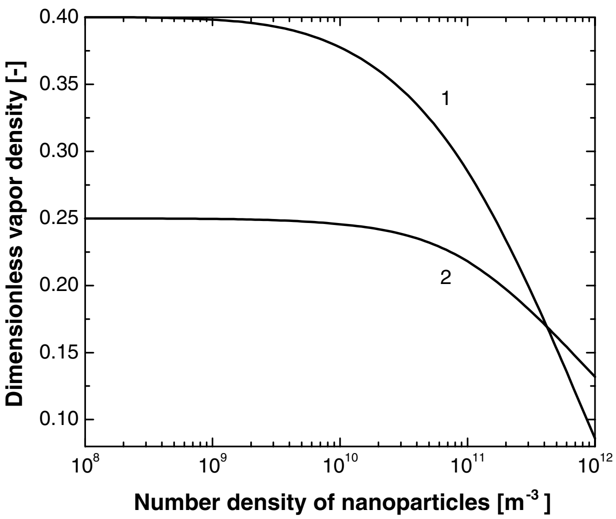

Fig. 6. The dimensionless vapor density versus the number density of nanoparticles. Curve 1 is for $q = 0.67$, curve 2 is for $q = 0.33$; $T_s = 373$ K.

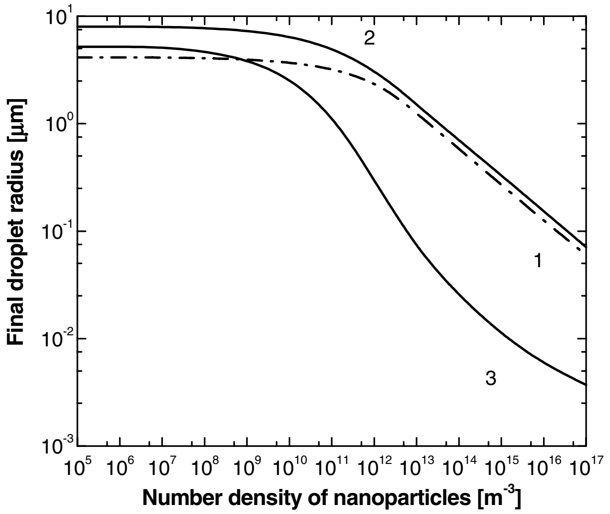

Fig. 7. Final droplet radius versus the number density of nanoparticles at $T_s = 373$ K and $q = 0.2$.

For our generalized model of mixing in the mixer, simulation results for final droplet radius are shown in Fig. 7. Algorithm for the calculations is described in the following. We take into account the existence of two largest vortexes in the mixer. To obtain initial values to our mathematical model we apply the model of instant mixing to the full flow rate of the vapor and half the flow rate of the carrier gas with nanoparticles. Subsequently we apply our one-dimensional model for calculating of the growth of heterogeneous droplets and the temperature and the number density of vapor. After calculation we again apply the model of instant mixing of the two flows. One flow is with grown heterogeneous droplets; another flow has initial nanoparticles. Thus we have one group of nanoparticles and one group of heterogeneous droplets of the same radius. So our mathematical model has to include the additional equation for smaller nanoparticles. This equation has the same mathematical form as Eq. (3). For two groups of independently growing droplets we use the approach, developed at [3]. In Fig. 7 curve 1 is the result of the standard application of instant mixing model, curve 2 corresponds to the first half of the nanoparticles, curve 3 corresponds to the second half of nanoparticles, which grow at a smaller rate. It is important to note that if N_d is about 10^{11} particles/m^3, the radius of the heterogeneous droplets of the second group (curve 3) is only about one micron. We predict that it will not be possible to count such droplets by optical methods. If N_d is about 3×10^{13} particles/m^3, an optical counter will show that there are no particles at all.

For any N_d, the supersaturation of the vapor at the exit of the mixer is greater or equal to one. Thus the correct use of the condenser can enhance the performance of the PSM [6].

4. Discussion of results

We developed the mathematical model to describe vapor condensation on nanoparticles in the mixer of a particle size magnifier (PSM), original design of which was reported in [4]. It was shown that if vapor supersaturation and temperature are high enough in the mixer, then the final radius of heterogeneous droplet reaches several microns. Such droplets are optically detectable. It was demonstrated also that the number density of the nanoparticles is an important parameter. In particular for high number densities, above 10^{10} particles/m^3, the efficiency of the PSM is decreased due to depletion effect.

An analysis of experimental data and our calculations show that supersaturation and the temperature for the mixer must be selected in such manner as to avoid the manifestation of Kelvin effect, which is substantial for nanoparticles with radii of about 10 nm and smaller. Homogeneous nucleation also masks the performance of a PSM. Thus, the mixing parameters in the mixer should be selected at such a manner that the supersaturation is not too large. The developed mathematical model helps to make correct choice of parameters.

For example, our experiments with ethylene glycol showed that for $T_s = 343$ K and $T_n = 283$ K no homogeneous nucleation occur for all values of mixing parameter q. Thus this regime is ideal one for correct performance of a PSM. The calculated supersaturation and temperature for $T_n = 283$ K are shown in Figs. 2 and 3 for all values of mixing parameter q and two saturator temperatures. For the final radius of heterogeneous droplets the approximate expression (10) was obtained. This expression qualitatively well describes simulation results. It shows that the main factor for droplet growth is the ratio $Dqn_e(T_s)/u(1+q)$. For a constant saturator temperature, increasing the mixing parameter q, increases the efficiency of PSM performance and helps to avoid homogeneous nucleation. Our measurements of PSM performance with gold nanoparticles with a radius of 15 nm, made at Hiroshima University, showed that, even for the worst regime with $q = 0.2$, the counting efficiency was about 100%. It is also noteworthy that our calculations shown that if the radius of nanoparticles is greater than 10 nm, a charge of the nanoparticles has no effect on vapor condensation.

The generalized model of the instant mixing, which takes into account some elements of the hydrodynamic structure of flows in the mixer of PSM, was developed. In particular, this model divides all nanoparticles on two groups, growing at different parts of mixer. This model shown that, at some conditions, one of two groups of nanoparticles is not detectable by optical methods. As a result, the counting efficiency, experimentally and operationally determined in [5], will be about 0.5. At our experiments with gold nanoparticles with a radius of 5 nm for $q = 0.2$, the counting efficiency is about 0.64 if $T_s < 373$ K. This result means that, for the second part of mixer, supersaturation is not sufficiently high. This conclusion is confirmed by experimental observations reported in [5]. In addition, in our recent experiments, which will be published later, show that for a saturator temperature, T_s, of 373 K and a mixing parameter $q = 0.2$ condensation due to Kelvin effect is not retarded; counting efficiency is about 100% even for gold nanoparticles with a radius of 5 nm. This result is in complete agreement with our calculations.

It was also discovered at our experiments that for high temperatures of the saturator, the counting efficiency is higher than one. This is clearly a manifestation of homogeneous nucleation and subsequent growth of droplets. Interestingly, the larger the size of the nanoparticles, the smaller is the deviation of the counting efficiency from 100%. The reason for this effect is, probably, fast vapor condensation on larger nanoparticles, which prevents homogeneous nucleation.

For nanoparticles with a radius of several nanometers (smaller than 3 nm) the formation of a wetting layer has a stochastic nature, related with the overcoming the thermodynamic barrier by means of thermal fluctuations. This important effect is currently under consideration.

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