

Statistical Way of Calculating the Average Number of Molecules of Critical Nuclei in Homogeneous Nucleation

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Abstract—A way of estimating the average number of molecules in the nuclei of a condensing liquid phase is proposed. The procedure is based on statistical calculations of fluctuations in the density of molecules in a medium. The average number of molecules in the nuclei of water droplets of critical size is calculated in the temperature range of 273 to 373 K using data from molecular dynamics modeling.

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INTRODUCTION

The classical theory of nucleation developed by Gibbs [1], Volmer [2], and Cassel considers phase transitions of the first kind [3, 4], including homogeneous nucleation of the liquid phase during the vapor–liquid transition. Nuclei form due to a series of density fluctuations—rearrangements of atoms in small volumes within the system [5]. As a result of such fluctuations, the energy barrier caused by the formation of a surface (interphase) layer can be overcome, resulting in the formation of critical-sized nuclei capable of stable growth [6]. One of the key thermodynamic parameters is the free surface energy, which is the work spent on creating the interface between the nucleus of the liquid phase and the parent phase of steam [6–8].

Critical-sized nuclei consist of only a few tens of molecules and are nearly spherical in shape. For nuclei with such curved surfaces, it is difficult to estimate the forces of surface tension. To determine the surface free energy and nucleation barrier of a nucleus, we must estimate the average number of molecules in a nucleus of critical size. Computer approaches (molecular dynamics) are now widely used in theoretical studies of the statistical parameters of systems [9, 10]. The average number of molecules in nuclei of critical sizes can be calculated from data of classical molecular dynamics. The author of [11, 12] used computer modeling to examine the change in the chemical potential of molecules that participate in fluctuations. The negative value of the derivative of the chemical potential with respect to the number of these molecules determined the fundamental possibility of the formation of a nucleation barrier, the existence of a critical size of nuclei, and the creation of metastable states of a supersaturated vapor. Analyzing the average time of the emergence of nuclei is the most widely used way of

estimating the average number of molecules in a nucleus from modeling data [13, 14]. The input parameters are the growth trajectories of the nuclei of a new phase, which are extracted from the data of molecular dynamics modeling. The critical size of the nucleus was determined by the authors using the statistical inverted averaging of growth curves [15, 16].

The aim of this work was to develop another theoretical way of estimating the average number of molecules of nuclei of critical size, based on statistical calculations that consider fluctuations in the density of molecules in space. Compared to calculations based on the data from classical molecular dynamics, our approach does not require the creation of complex computer models and calculations; instead, it is based on the classical concepts of the variability of a statistical sample. Theoretical calculations were made and the results were interpreted on the basis of data from modeling droplet nucleation in supersaturated water vapor. Our theoretical calculations are in good agreement with the modeling results presented in [13].

THEORETICAL APPROACH TO CALCULATING THE AVERAGE NUMBER OF MOLECULES IN NUCLEI

Let us consider a system with fixed volume V , which contains N molecules. Let the system be in a state of supercooled (supersaturated) vapor where external forces do not act on this system. Over time, homogeneous droplet nucleation will occur in such a system as a result of stochastic density fluctuations.

We use the basic principles of the theory of fluctuations in statistical systems to determine the number of fluctuating molecules that are potential foci of the liquid phase. The distance between molecules in a gas varies statistically, altering the volume per molecule.

Let us divide the system into small volumes v_i with identical numbers of molecules $n = n_i$ (here $i = 1, 2, \dots, k$, k is the number of small volumes), so that condition $\sum_{i=1}^k n_i = N$ is met. Let us consider a statistical sample of small volumes. The fluctuation of varying small volumes is expressed as [17]

$$\langle (\Delta v)^2 \rangle = -k_B \left(\frac{\partial v}{\partial P} \right)_T \quad (1)$$

or

$$\langle (\Delta v)^2 \rangle = \frac{\sum_{i=1}^k (v_i - v)^2}{k},$$

where v is the arithmetic mean of small sample sizes, k is the sample size, P is pressure, k_B is the Boltzmann constant, and T is temperature.

We divide both sides of equality (1) by n^2 and find the fluctuation of the volume per molecule:

$$\left\langle \left(\frac{\Delta v}{n} \right)^2 \right\rangle = -\frac{k_B T}{n^2} \left(\frac{\partial v}{\partial P} \right)_T. \quad (2)$$

Using (2), we can create an inverse sample from the number of molecules that occupy small fixed volumes. To do so, we differentiate with respect to n in ratio $\Delta \left(\frac{v}{n} \right)$, replacing the sign of differentiation with that of small increments (Δ):

$$\Delta \left(\frac{v}{n} \right) = v \Delta \left(\frac{1}{n} \right) = - \left(\frac{v}{n^2} \right) \Delta n. \quad (3)$$

We square the result and substitute it in (2) to obtain

$$\langle (\Delta n)^2 \rangle = -k_B T \frac{n^2}{v^2} \left(\frac{\partial v}{\partial P} \right)_T. \quad (4)$$

As in [17], we divide total volume V containing $N = \text{const}$ molecules into volumes $V_i = \text{const}$. There are then N_i molecules in each volume V_i , and expression (4) can easily be extended to these small subsystems:

$$\langle (\Delta N_i)^2 \rangle = -k_B T \frac{N_i^2}{V_i^2} \left(\frac{\partial V_i}{\partial P} \right)_T. \quad (5)$$

In expression (5), mean square $\langle (\Delta N_i)^2 \rangle$ represents standard deviations from the average number of molecules per volume V_i . Since the standard deviations in (5) are represented by sums, they can also be summed as the volumes from expressions (5). We can therefore create a final expression reflecting the spatial fluctuation in the molecular density distribution of in the gaseous phase as a whole over volume V , and for the entire ensemble N :

$$\langle (\Delta N)^2 \rangle = -k_B T \frac{N^2}{V^2} \left(\frac{\partial V}{\partial P} \right)_T. \quad (6)$$

Expression (6) determines the processes of fluctuations in the molecular density distribution in space, which is associated with the formation of nuclei of the condensed phase. Since the formation of a nucleus of a new phase is a consequence of fluctuations [12], the basic statistical parameters (primarily the error of the mean) can be used to describe this process. Let us assume that the error in the average value of the number of molecules in a certain volume will be a quantitative expression of the formation of a nucleus of a new phase. Since the error of the mean determines the deviation up or down, to exclude the sign of the deviation we assume that the number of possible fluctuating molecules in volume V is proportional to the square of the error of the mean:

$$m^2 = \frac{\langle (\Delta N)^2 \rangle}{N} = -k_B T \frac{N}{V^2} \left(\frac{\partial V}{\partial P} \right)_T = \frac{N^2 (k_B T)^2}{V^2 P^2}. \quad (7)$$

The equation of state of an ideal gas, $PV = Nk_B T$, was considered in transforming the derivative, since fluctuations occur in the gaseous phase. The number of potentially possible foci of the liquid phase was proportional to $\sim gm^2$. Multiplier g was determined from the time required to stabilize the averages of the generalized sample and was inversely proportional to the probability of finding a molecule in any part of the phase space.

It should be noted that not all emerging nuclei reach critical size. Let the number of molecules in nuclei of critical size be some part f of the total number of molecules. The number of nuclei of critical size are then the corresponding part of f of the total number of nucleation foci. To calculate the number of molecules in a nucleus, we must divide the total number of molecules that form critical nuclei by the number of nuclei of critical size:

$$n_c = \frac{fN}{fgm^2} = \frac{N}{gm^2}. \quad (8)$$

It should be noted that the remaining foci of nucleation will have fewer molecules of the liquid phase than in the critical nucleus, so molecules of the gaseous phase will remain in the system.

We assume that $g = \frac{t}{\Delta t}$, where t is the time of the formation of a nucleus drop and Δt is the fraction of total time t in which the particles of the system are in a certain part of the phase space. We also assume that quantity $g = \frac{t}{\Delta t}$ does not depend much on temperature in the range of 273–373 K, and limit $\omega = \lim_{t \rightarrow \infty} \frac{\Delta t}{t}$ is assumed [17]. We may assume this if the volume of the phase space grows, depending on temperature more than the velocity of the particle. As a result, time Δt spent by the particle in a given volume of phase space increases. In this case, Δt will grow along

Table 1. Average number of molecules of a critical nucleus in the 273–373 K range of temperatures

T, K	273	283	293	303	313	323	333	343	353	363	373
n_c^{Theory}	76 ± 2	70 ± 2	66 ± 2	61 ± 2	58 ± 2	54 ± 1	51 ± 1	48 ± 1	45 ± 1	43 ± 1	40 ± 1
n_c^{MD}	75 ± 25	71 ± 27	65 ± 27	58 ± 22	55 ± 21	52 ± 18	50 ± 15	45 ± 13	42 ± 12	41 ± 12	40 ± 10

with temperature in proportion to t . We may also assume that Δt can grow from uncertainty relation $\sqrt{\langle(\Delta E)^2\rangle} \frac{\Delta t(t)}{N} \geq \frac{\hbar}{2}$, where $\langle(\Delta E)^2\rangle \frac{3}{2} (k_B T)^2$ [17] is the average square of the fluctuation in the kinetic energy of the molecule. The equal sign will be observed at a temperature of 273 K and $\Delta t \approx 0.092$ ns. The number of fluctuating particles in volume V , which is equal to m^2 , will then appear in a time interval of 0.092 ns. At the time of the formation of a nucleus droplet [13, 14] at 273 K (1.07 ns), coefficient $g \approx 1.07/0.092 \approx 11.65$. Based on the assumptions made about the low variability of g as the temperature rises, the calculated value was also used for other nuclei with fewer particles.

CALCULATED RESULTS COMPARED TO MODELING DATA

We calculated the average number of molecules in nuclei using the statistical approach described above. The data on system parameters given in [13, 14] were used in performing theoretical calculations.

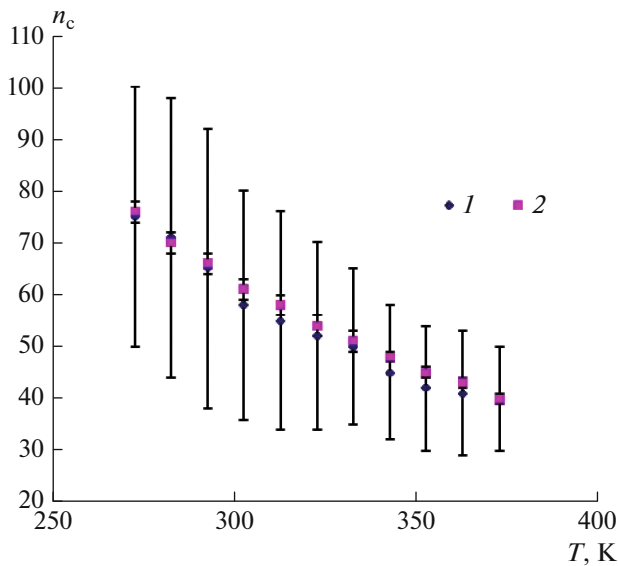


Fig. 1. Critical size n_c as a function of temperature: (1) modeling data n_c^{MD} from [13]; (2) theoretical values n_c^{Theory} , obtained with formula (8).

In [13], the average number of water droplet nuclei molecules of critical size was calculated using data from classical molecular dynamics modeling of the condensation of supercooled water vapor. Details of the modeling were given in [15, 18, 19]. The modeling in [13] was done using an anisotropic coarse-grained Stillinger–Weber potential adapted for water [19, 20]. The system considered in [13] consisted of $N = 8000$ molecules inside a cubic modeling cell with volume $V = 10^{-22} \text{ m}^3$. The supercooled sample of the system was prepared by rapidly cooling water vapor heated to a temperature of 900 K at a pressure of 1 atm. [13, 14]. The rate of cooling was $10^{10} \text{ deg s}^{-1}$. The system was cooled to the required temperature in the range of 273 to 373 K at a constant pressure of 1 atm. Based on the results from modeling, the authors of [13, 14] concluded that the formation of water droplets in supercooled water vapor is qualitatively consistent with classical concepts of condensation through the mechanism of homogeneous nucleation [5, 6]. Under the considered thermodynamic conditions, the vapor–liquid phase transition begins with the formation of a great many nuclei of the liquid phase.

The results from theoretical calculations of the values of critical size n_c^{Theory} of the nuclei obtained with formula (8) using data from molecular dynamic modeling are presented in Table 1 and Fig. 1. For comparison, the values of the critical size of nuclei n_c^{MD} obtained in [13] are given in Table 1 and Fig. 1.

We can see that the theory and modeling are in good agreement for considered temperature interval $273 \leq T \leq 373 \text{ K}$. The proposed theory in this case correctly reproduces the dynamics of changes in the critical size of the nucleus with temperature. The critical size falls from 76 to 40 molecules as the temperature rises. The difference between the values of the critical size, calculated theoretically and obtained by modeling, is negligible. In addition, the theoretical values fit perfectly into the range of errors of the modeling data obtained in [13], which were defined as the width of the range of curvature in the distributions of the average time of the first occurrence [13, 18]. These errors should be considered as probable statistical deviations from critical size n_c . The agreement observed between calculated values n_c^{Theory} and modeling data n_c^{MD} confirms the adequacy and applicability of the proposed theoretical approach to estimating the average

number of water droplet molecules of critical size. At the same time, our theoretical approach can be adapted to estimate the average number of molecules of liquid phase nuclei in systems with different types of intermolecular interaction during a vapor–liquid transition.

CONCLUSIONS

A statistical way of estimating the average number of molecules of nuclei of a liquid phase was proposed. The procedure is based on the concept of the theory of fluctuations in statistical systems. It is considered that the formation of a nucleus of a new phase is a consequence of fluctuations in the molecular density distribution in space, and the quantitative expression of this process is the error in the average number of molecules in a certain volume. The number of potential foci of the liquid phase is thus proportional to the squared error of the mean. The proposed procedure was used to calculate the average numbers of molecules of nuclei–water droplets of critical size in the 273 to 373 K range of temperatures, based on the example of droplet nucleation in supercooled water vapor. These values are in good agreement with results from molecular dynamics calculations, obtained via computer modeling.

CONFLICT OF INTEREST

The author declares that he has no conflicts of interest.

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