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Modelling of water clusters nucleations with the Monte-Carlo methods

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ABSTRACT

Modeling and research of clusters structure will give mankind an alternative energy source, creation of chips in the size in some nanometer, devices of memory with superdense record of the information, integrated quantum schemes, will allow to find out their influence on an environment. The most difficult case is to simulate the collision between clusters. The purpose of this paper is to present the idea of method to simulate the collision between clusters.

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KEYWORDS

Clusters;
Monte-Carlo method;
Thermodynamics of natural gas;
Quantum views;
Molecular collisions.

INTRODUCTION

Formation process of condensation's initial nucleuses is one of the most difficult and incompletely determinate problems in new phase formation theory. These nucleuses are able to have a small size and consist only of some molecules (Figure 1), called "clusters" or microcluster. Microcluster is the smallest units included from two to hundred and more atoms. Modern quantum-chemical methods let to find an inertia moment, frequencies of intermolecular and intermolecular oscillations in the clusters and their dissociation energy. On the basis of these calculations it's possible to calculate all the thermodynamic and also kinetic characteristics of the clusters. The clustered method underlies in thermodynamic of natural gas components.

Modeling and research of clusters structure will give mankind an alternative energy source, creation of chips in the size in some nanometer, devices of memory with superdense record of the information, integrated quantum schemes, will allow to find out their influence on an

environment (destruction of an ozone cloud, change of a climate of Earth).

Clathrates - the structures similar to an ice in which various gases "visitors" contain in the crystal cells generated by molecules of water "owner", which actually also are clusters. Clathrates structures are formed on the basis of various substances like football coordination of atoms: gas hydrates – "Clathrates ice". More important is hydrate of methane. Stocks of power resources on the Earth (coal, gas, oil) will suffice, at modern rates of their use, on different sources, on 50 - 100 years. There is a problem of use of alternative sources of fuel. To such concern clathrates of methane which stocks in ground adjournment of the World Ocean and in permafrost are practically inexhaustible and make not less than 250 billion cubic meters. In recalculation on traditional kinds of fuel it more than twice exceeds quantity available on a planet. Special danger is represented with warming a climate which can start the mechanism of allocation of methane from crystal-hydrate ocean with pernicious consequences for all alive on the Earth.

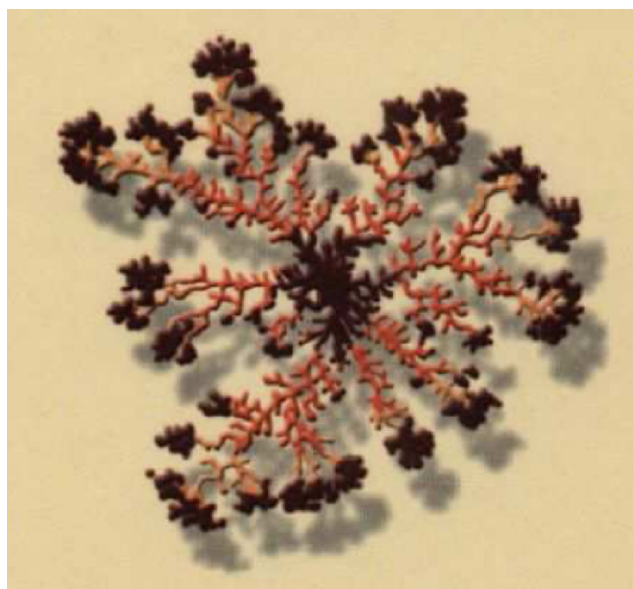


Figure 1

MONTE-CARLO SIMULATION

The idea of method of clusters dynamics at nucleation is follow. We can see that the volume gas consists of monomers and n-mers clusters. This system is in equilibrium. The most difficult case is to simulate the collision between clusters. Let us consider the problem of nucleation of new phase. In the initial moment of time system consists only from monomers then we choose a little time $\Delta t \rightarrow 0$. During this time molecules-monomers collide each other. The law of collision depends on the sort of molecules. It may be solid sphere – the most simple case, the pseudo maxwell molecules, Lennard-Jones law and other. If molecules have complex structure it is necessary to consider internal free degrees change: rotational and vibration energy As we will see later at the processes of nucleation there is very important the quantum properties of molecules, besides we must know the criteria of conglutination. At usually it is some threshold energy E_p On next time step Δt we have already a mixture from monomers and dimmers. Now we must know law of the interaction between monomers and dimmers. Besides we must know the threshold energy of conglutination monomer-dimmer and dimmer-dimer. Moreover we must know the criteria of jarring. On the n-th time step we will have a mixture from n kind of clusters from monomer, dimmer to n-mers. And we must have models of interaction of different clusters with each other and criteria of conglutination and jarring of molecules. Below the calcu-

lation of model problem of nucleation of vapour from monomers to dimmers ... n-mers etc. until creation of new phase (Figure 2 a,b).

For establishment of low of interaction of different substances it is necessary to consider physics-chemical properties of the substance. As the most important problem we consider property of water clusters.

Calculation of the speed of liquid clusters nucleation according to a classical theory

Nucleation classical theory is originated as far back

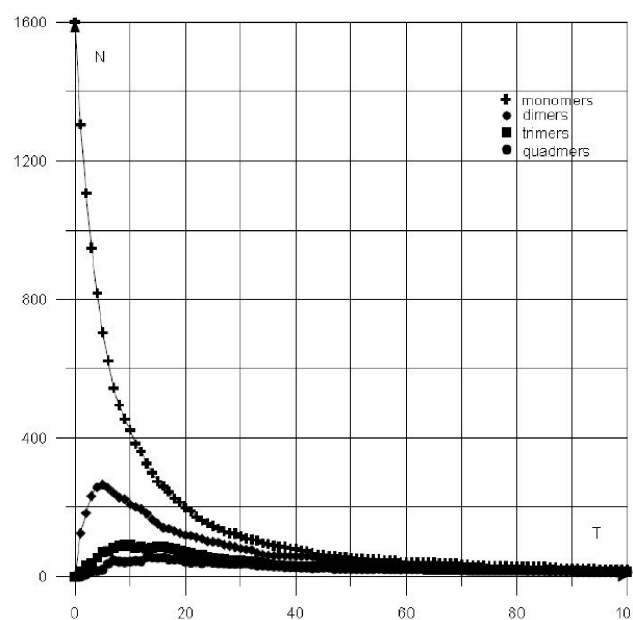


Figure 2a

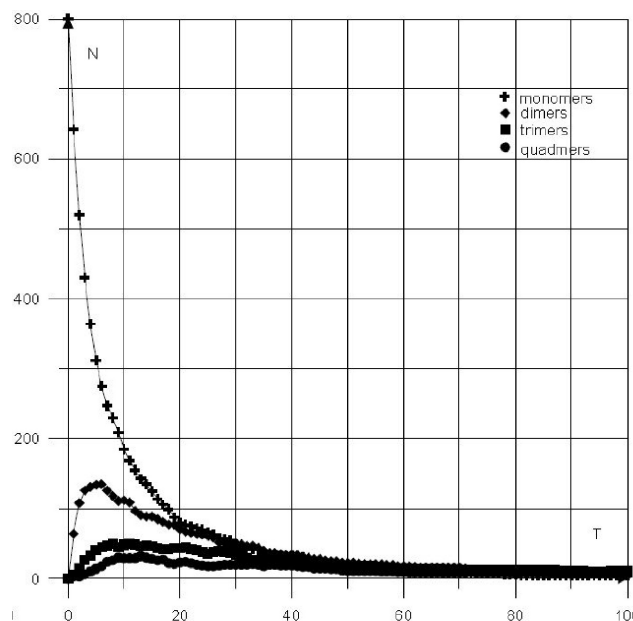


Figure 2b

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as 30th and it's based on two main approximations: Szilard's model and liquid-drop model. It's supposed that oversaturated steam consists of the mixture of a steam of monomers and clusters, contained different number of molecules, in Szilard's model. Clusters can grow and evaporate, adding or losing only one molecule at the same time. In the context of this model it's possible to calculate the compact expression for the permanent isometric nucleation's speed.

$$J_0 = \frac{n_1 \beta_1}{\left(1 + \sum_{g=2}^{g^*-1} \prod_{i=2}^g \frac{\alpha_i}{\beta_i}\right)} \quad (1.1)$$

in which n_1 - monomers' concentration (it's supposed that monomers' steam doesn't become weak in the condensation process), β_i - speed of molecule joining to cluster, g_i - evaporation speed, g^* - nucleus's critical size. Using then liquid drop model, i.e. supposing that clusters are spherical and similar, one can get the expression for nucleation speed:

$$J_0 = an_1^2 v \sqrt{\frac{2\gamma}{\pi m}} B \exp \left[-\frac{16\pi v^2}{3(\ln S)^2} \left(\frac{\gamma}{kT} \right)^3 \right] \quad (1.2)$$

in which a - adhesion factor, v - one liquid molecule volume, γ - surface tension, $S = P/P_\infty$ - supersaturation, B - Varnard's correction.

$$B = \exp \left(-\ln S + \frac{4\pi \left(\frac{3v}{4\pi} \right)^{2/3} \gamma}{kT} \right) \quad (1.3)$$

that arises at the consecutive kinetic method and is absent on the calculation from classical thermodynamically method, e.g. on calculation of work that is necessary for nucleus (size g) creation. In the latter case we get Zeldovitch-Frenkel's formula:

$$J_0 = an_1^2 v \sqrt{\frac{2\gamma}{\pi m}} \exp \left[-\frac{16\pi v^2}{3(\ln S)^2} \left(\frac{\gamma}{kT} \right)^3 \right] \quad (1.4)$$

In classical theory pressure and critical nucleus' size are joined by Calvin-Gibbs' formula:

$$\ln \frac{P}{P_\infty} = \frac{2\gamma v}{r_{g^*} kT} \quad (1.5)$$

Or

$$\ln S_{Cr} = \frac{2\gamma v}{r_{g^*} kT} \quad (1.6)$$

in which r_{g^*} - critical nucleus' size

$$r_{g^*} = \left(\frac{3g^* v}{4\pi} \right)^{1/3} \quad (1.7)$$

From this

$$g^* = \frac{4\pi 8}{3} \left(\left(\frac{m}{\rho} \right)^{2/3} \frac{\gamma}{kT \ln S_{Cr}} \right)^3 \quad (1.8)$$

For water –

$$\lg S_{Cr} = \frac{1.2}{\sqrt{\lg k}} \frac{\mu}{\rho} \left(\frac{\gamma}{T} \right)^{3/2} \cong 0.242 \frac{\mu}{\rho} \left(\frac{\gamma}{T} \right)^{3/2} \quad (1.9)$$

Surface tension for small-sized water clusters was calculated to high accuracy in the experiment^[1] (Figure

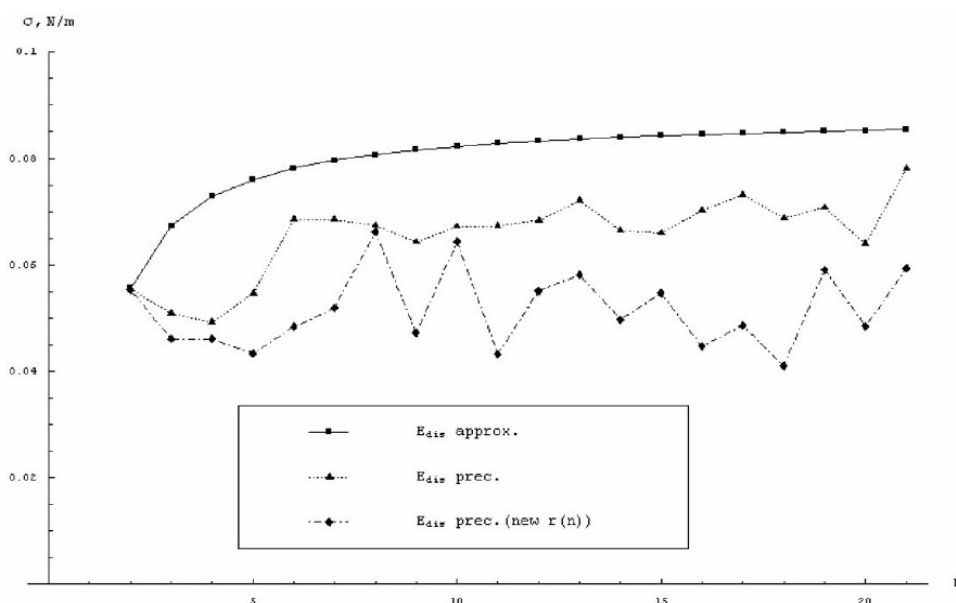


Figure 3 : Surface tensions dependence on cluster's size

3). The results were made according to calculation of cluster's size with exact coordinates of atoms in cluster. From this it follows that real surface tension of small-sized clusters is 30-50% less than for liquid usual drops.

g_* - In this case equals order 3 for $T = 230$ -250 K (considered temperature), while $g_* \sim 5$ for abovementioned temperatures on the classical theory

Then we can rewrite the formula (1.1) as:

$$J = \frac{n_1 \beta_1}{\left(1 + \sum_{g=2}^{g_*-1} \sigma_g\right)} \quad (1.10)$$

In which

$$\sigma_g \equiv \prod_{j=2}^g \frac{\alpha_j}{\beta_j} = \exp \left(- \frac{(g-1)f(g_*) - \sum_{j=2}^g f(j)}{kT} \right) \quad (1.11)$$

Function $f(g)$ is determinate as:

$$f(g) = kT \ln \frac{v_g}{v_\infty} \quad (1.12)$$

For $f(g)$ function was used a dependence calculated with molecular dynamic method in experiment^[2].

According to nucleation classical theory the evaporation speed of clusters with g molecules is written down as:

$$\alpha_g = S_g v_\infty \exp \left(- \frac{\Delta S_g \gamma}{kT} \right) \quad (1.13)$$

In which

$$S_g = 4\pi \left(\frac{3v}{4\pi} \right)^{2/3} g^{2/3} - \text{surface square of cluster that}$$

consists of g - molecules, v - one molecule's (monomer) volume, and then

$$\Delta S_g = S_g - S_{g-1} \approx \frac{2}{3} 4\pi \left(\frac{3v}{4\pi} \right)^{2/3} g^{-1/3} - \text{surface change due}$$

to evaporation of one molecule

$$v_\infty = A \exp \left(- \frac{E_\infty}{kT} \right) - \text{evaporation speed from unit of}$$

area of flat limit of division/section, E_∞ - evaporation heat from plane.

In nucleation classical theory nucleuses speed growth β_g is expressed through number of collision with monomers in time unit:

$$\beta_g = a S_g n_1 \sqrt{\frac{kT}{2\pi m}} \quad (1.14)$$

Comparison of Measured and Calculated Nucleation Rates for Water

(Temperatures in K – Strey et al. high temperatures are 259, 254, 249, 244) [11]

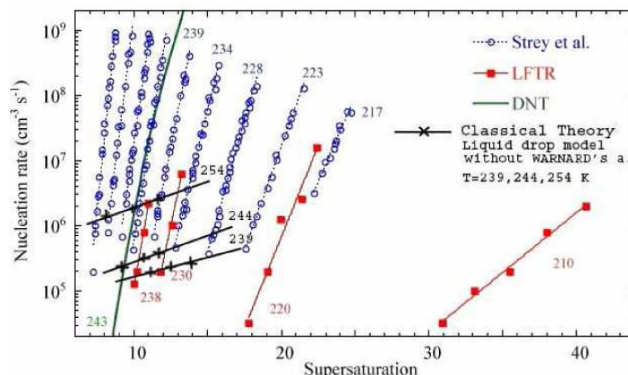


Figure 4 : Nucleation speed according to classical theory (liquid-drop model without Varnard's amendment)

Comparison of Measured and Calculated Nucleation Rates for Water

(Temperatures in K – Strey et al. high temperatures are 259, 254, 249, 244)

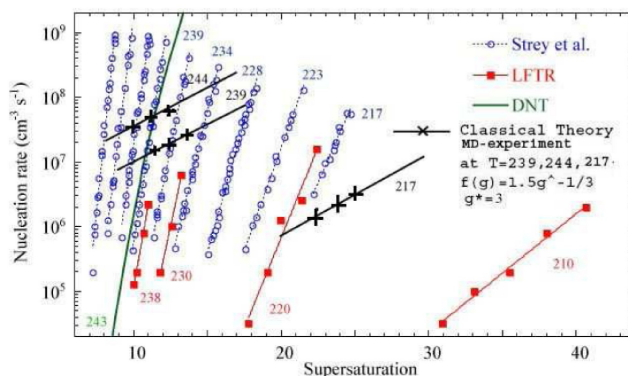


Figure 5 : Nucleation speed according to classical theory (experiment of molecular dynamic, for $g_* = 3$)

where a – adhesion factor, that is indeterminate value and can be from 0.01 to 1.

On the basis of abovementioned data nucleation speed for liquid-drop model with Varnard's amendment (1.2), (Figure 4), without Varnard's amendment (1.4), (Figure 5), nucleation speed received on the basis of experiment of molecular dynamic at different temperatures and g_* , (1.10) (Figure 4, 5). Findings were compared with last experimental data^[3].

Evidently, classical method for nucleation theory doesn't make satisfactory results. Further, quantum-mechanical method will be used and demonstrated for calculation of nucleation speed.

Calculation of water clusters nucleation speed according to quantum-mechanical theory

Let's examine a system included gas-phase mol-

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ecules A_1 of condensed matter (monomers) and molecular units A_n (clusters) included two or more molecules: $n \geq 2$. Cluster A_n with dimension n has energy of dissociation (rupture of connection) E_n , three moments of inertia $I_A(n)$, $I_B(n)$, $I_C(n)$, and also $3nl-6$ oscillation degrees of freedom, from which $(3l-6)n$ belong to intramolecular oscillations, and a $(6n-6)$ – to intermolecular oscillations (l – number of atoms in monomer).

First, let's examine a pared-down model of clusterization and suppose that a clusters growth is a result of joining a single monomer of a molecule-association to them. And the clusters' destruction is a result of intermediate stage – activated complex formation and decay^[4].

Omitting a stage of activated complex and taking into account only a reaction final product, succession of elementary processes of formation and destruction of clusters A_n can be written down in the summary form:



$$K_d(n+1)$$

Here M – any molecule or gas-phase cluster; $K_a(n)$ и $K_d(n+1)$ – constants of direct and inverse reactions' speeds, $K_a(n)$ – a constant of speed of a monomer joining to a cluster A_n , and $K_d(n+1)$ – a constant of speed of a cluster dissociation A_{n+1} to a cluster A_n and a monomer.

For concentration N_n clusters with A_n form on the basis of (2.1) one can write down an equation of their change with time in the form of^[4]:

$$\frac{dN_n}{dt} = J_{n-1} - J_n \quad (2.2)$$

$$J_n = N_n N_1 M K_a(n) - N_{n+1} M K_d(n+1) \quad (2.3)$$

Here J_n – clusters flow in a space of number of monomers in them, e.g. number of clusters passing on in a unit time from n point to $n+1$ point.

In the terms of thermodynamic balance the speeds of direct and inverse reactions $K_a(n)$, $K_d(n+1)$ are connected through a balance constant:

$$K_n = \frac{K_a(n)}{K_d(n+1)} = \frac{N_{n+1}}{N_n N_1} = \frac{P_{n+1}}{P_n P_1} kT = K_p kT \quad (2.4)$$

Here $P_i = \alpha_i P$, $\alpha_i = N_i/N$ – a partial pressure and molar part of component i ;

$$K_p = \frac{P_{n+1}}{P_n P_1} - \text{Balance constant of reaction (2.1), ex-}$$

pressed in partial pressure terms of components ($[K_p] = 1 \text{ atm}^{-1}$).

Calculation of a speed constant of cluster dissociation is based on monomolecular reactions theory RRKM (of Rise-Ramsperger-Kassel-Marcus)^[5], here you can see the final result:

$$K_d = \frac{LQ_1^+ \exp(-E_0/kT)}{hQ_1 Q_2} \int_{E^*=0}^{\infty} \frac{\sum_{E_{vr}^+}^{E^+} P(E_{vr}^+) \exp(-E^+/kT) dE^+}{1 + k_a(E_0 - E^+)/k_2[M]} \quad (2.5)$$

Where,

$$E^* = E^+ + E_0$$

$$k_a(E_0 + E^+) = \frac{LQ_1^+}{hQ_1 N^*(E_0 + E^+)} \sum_{E_{vr}^+=0}^{E^+} P(E_{vr}^+)$$

Here L – number of paths, that are equal in terms of energy (for example, $L=2$ for dissociation of H_2O to H and OH), Q_1 and Q_1^+ – static sums for gyration in molecule and activated complex accordingly (it was used $Q_1^+/Q_1=1$ in calculations), Q_2 – total (oscillation and rotary) static sum for dissociate molecule,

$\left[\sum_{E_{vr}^+}^{E^+} P(E_{vr}^+) \right]$ – number of vibrational and rotary condition of activated complex in interval of energies $[0, E^+)$, N – density of oscillation and rotary reagent levels. Condition number of activated complexes and density of energy of reagent small-sized molecules were calculated by direct converting (for that all the normal oscillations' frequencies were divided into 9 groups). For large clusters Vitten-Rabinovitch's analytic approximation were used^[5]. Cluster $K_a(n)$ formation constant was determinate through dissociation constant $K_d(n+1)$ and balance constant K_n according to (2.4).

In quasi-equilibrium terms $dN_n/dt=0$, so J doesn't depend on n , as according to (2.2) $J_n = J_{n-1}$ for any n . In this case equation (2.3) becomes

$$J_0 = N_n N_1 M K_a(n) - N_{n+1} M K_d(n+1) \quad (2.6)$$

Totality of equations (2.6) represented investigated heterogeneous linear system relatively N_n in balance terms, when speeds of any direct and inverse processes are balanced, system (2.6) comes to similar equations

$$0 = N_n^0 N_1^0 K_a(n) - N_{n+1}^0 K_d(n+1) \quad (2.7)$$

Here N_n^0 – quasi-balanced distribution function in the absence of flow ($J_0=0$).

The solution of (2.7) is:

$$N_n^0 = N_1^n \prod_{j=2}^n \frac{K_a(j)}{K_d(j+1)} \quad (2.8)$$

Let's put a degree of steam S supersaturation in the following way:

$$S = \frac{N_1^0}{N_{1eq}} \quad (2.9)$$

Here N_1^0 - numerical density of monomers, N_1^0 - balanced numerical density of monomers above the clusters with maximum large size.

$$N_{1eq} = \frac{K_d(\infty)}{K_a(\infty)} = \lim_{n \rightarrow \infty} \frac{Q_n Q_{n-1}}{Q_n} \frac{1}{P_1 V} = \lim_{n \rightarrow \infty} [K_p(n) kT]^{-1},$$

$$N_{1eq} = 5.6757 \cdot 10^{17} \frac{T^3 A_1^{3/2}}{\sigma_1} \sqrt{I_a(l) I_b(l) I_c(l)} \left(1 - \exp\left(-\frac{\bar{\theta}}{T}\right)\right)^6 \exp\left(-\frac{E_{dis}(\infty)}{kT}\right), \quad (2.10)$$

in which $E_{dis}(\infty)$ - separation energy of monomer from maximum large-sized cluster, "average statistical" discriminatory oscillation temperature of cluster with n - $\bar{\theta}_n$ size is terminated with following correlation:

$$\left(1 - e^{-\frac{\bar{\theta}_n}{T}}\right)^{6n-6} = \prod_{i=1}^{6n-6} \left(1 - e^{-\frac{\theta_i(n)}{T}}\right), \quad (2.11)$$

Quasi-equilibrium distribution (2.8) becomes:

$$N_n^0 = N_1^0 \exp\left\{-\frac{\Delta E}{kT} (n-1)^\alpha + (n-1) \ln S\right\} \cdot n^{3/2} \left(1 - \exp(-\bar{\theta}/T)\right)^{6(n-1)}$$

$$\prod_{j=2}^n \left(\frac{R_j}{R_{j-1}}\right) \cdot \left(\frac{V_{j-1}}{V_j}\right) \cdot \left(\frac{\sigma_{j-1}}{\sigma_j}\right) \quad (2.12)$$

Here - separation energy of monomer from infinitely large-sized cluster, - energy of dissociation of dimer, - parameter^[4].

In experiment^[4] expression for quasi-equilibrium distribution of the clusters with n monomers were got:

$$N_n^0 = N_1^0 \exp\left\{-\frac{\Delta E}{kT} (n-1)^\alpha + (n-1) \ln S\right\}, \quad (2.13)$$

it is fully congruent to equation that was got in approximation of liquid-drop model in classical theory of condensation, if

$$E_{dis}(n+1) = E_{dis}(\infty) - 4\pi\sigma(r_{n+1}^2 - r_n^2)$$

and $\alpha = 2/3$,

Where r_n , σ - radius and surface tension.

Equation (2.12) is differing from classical and from equation (2.13) of the experiment^[4] because of the evident calculation of structure and energy characteristics

of intermolecular quantum motions in n -size cluster.

Statistic sum of ideal gas with internal freedom degrees, consisted of N indistinguishable identical particles - n -sized clusters, is^[6]:

$$Z_n = \frac{1}{N!} Q_n^N$$

So, for one mol of n - sized clusters

$$\ln(Z_n) = N_A \ln \left[1.4949 \cdot 10^{77} \frac{M_1^{3/2} T^{4n^{3/2}} R_n}{\sigma_n P V_n} g_e (2S_1 + 1)^n \exp \left(\frac{-U_n - \frac{k}{2} \sum_{s=1}^{6n-6} \theta_s(n)}{kT} \right) \right] \quad (2.14)$$

where N_A - Avogadro constant, M_1 - monomer's mass, g_e - degeneration of electronic level of cluster, S_1 - monomer's nuclear spin.

Knowledge of Z_n gives a possibility to calculate all the necessary thermodynamic functions for one mol of n - sized clusters^[6]. In quasi-equilibrium approximation increase of Gibbs' free energy can be reduced to the following:

$$\Delta G_{n,n-1}^0 = -RT \ln \left[\frac{P_1^0}{P_1} S \left(\frac{\sigma_{n-1}}{\sigma_n} \right) \left(\frac{n}{n-1} \right)^{3/2} \cdot \frac{R_n}{R_{n-1}} \frac{V_{n-1}}{V_n} \exp\left(\frac{E_{dis}(n)}{kT}\right) \left(1 - \exp\left(-\frac{\bar{\theta}}{T}\right)\right)^6 \right], \quad (2.15)$$

Here, R - universal gas constant.

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(Temperatures in K - Strey et al. high temperatures are 259, 254, 249, 244)

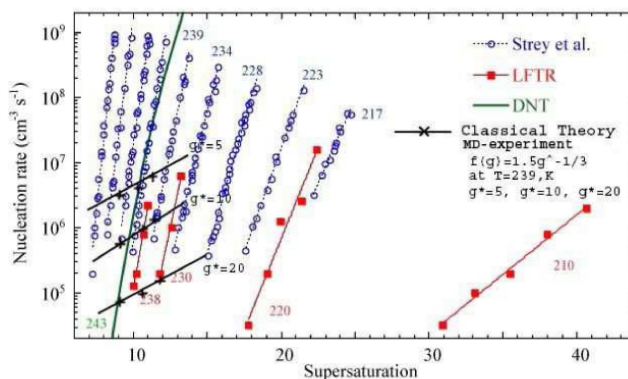


Figure 6 : Nucleation speed according to classical theory (experiment of molecular dynamic, for different g_*)

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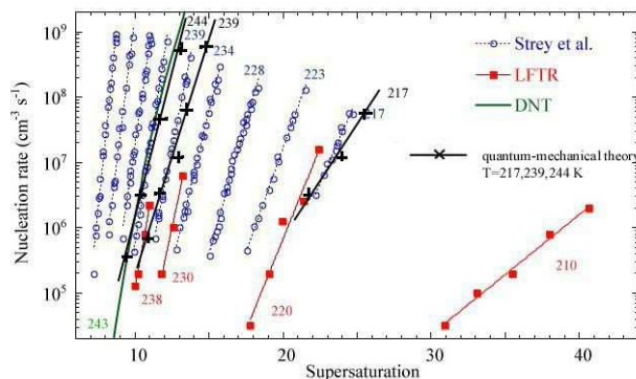


Figure 7 : Nucleation speed accordingly quantum-mechanical theory for different T (217, 239, 244, K)

Solution of dissimilar system (2.6) in quasi-equilibrium approximation is calculated as following^[7]:

$$N_n = C_n N_n^0 \quad (2.16)$$

in which - quasi-equilibrium distribution of clusters in according to the sizes in the absence of flow ($J_0 = 0$).

Solution of dissimilar system (2.6) in quasi-stationary case $J_0 \neq 0$ is converted to:

$$N_n = N_n^0 \left(1 - J_0 \sum_{j=1}^{n-1} \frac{1}{N_1 N_j^0 K_a(j)} \right) \quad (2.17)$$

Where

$$J_0 = \left(\sum_{j=1}^{n-1} \frac{1}{N_1 N_j^0 K_a(j)} \right)^{-1} \quad (2.18)$$

When constants of clusters association and dissociation are known, quasi-equilibrium solution can be calculated and then - using (2.18), number of nucleuses in volume unit, passing from n point (n -sized cluster) to $n+1$ unit ($n+1$ -sized cluster) on in time unit, is calculated for the system with density of monomers – N_1 .

As we see in (2.17), numerical density of clusters in stationary state is less than corresponding numerical density in quasi-equilibrium state. Decrease of numerical density of clusters in stationary state in comparison with quasi-equilibrium state is so much larger than its n size is larger.

For calculation of J_0 a computer program of the experiment^[1] was used. As it's at the Figure 7, when using this quantum-mechanical method, we get a result that is very similar to an experimental result. And it confirms the necessity of using this method.

Further, quantum-mechanical method for thermodynamic functions of water clusters will be demonstrated.

CONCLUSIONS

Comparison of two theories – classical and quantum-mechanical - for calculation of water nucleation speed was carried out. The main problem in nucleation speed determination in classical theory of condensation, as it was discovered in a lot of authors' works, comes to necessity of describing with maximum precision the surface tension γ , which makes its contribution on the speed. Classical liquid-drop model can't give the exact value γ for small particles, and so a divergence with experiment appears. E.g. γ concept is losing meaning for small clusters. Calculations of energies and heat capacities of different clusters were made at different temperatures and pressures and their contribution to the total system's heat capacity were estimated.

As a result we have following: it's necessary to take into account the clusters' contribution into general characteristics of the system for the correct description of thermodynamic functions of a matter, in particular for water and its steams. In particular, heat capacity of water's monomer greatly differs from water's heat capacity taking into account dimers', threemers' and tetramers' contribution.

It's necessary to attract quantum-mechanical performances for investigation of clusters' characteristics and their influence to the environment.

Moreover, development of clusters' theory helps a mastering of the technology of mining - potential generator in future.

Besides progress theory clusters help better master technology gas-hydrate methane production potentials source of energy in the future.

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