

Size-corrected theory of homogeneous nucleation

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Size-corrected thermodynamic model for clusters is proposed which implies that the cluster chemical potential is a linear function of the number of molecules on its surface and the total number of molecules. The model is free of introduction of the surface tension for small clusters and therefore has no limitation in this size range. The expressions for homogeneous nucleation rates have been obtained in the approximations of small and large critical sizes. Calculated nucleation rates are slightly lower than those predicted by the classical theory for water vapor and much higher for mercury vapor, in agreement with experiments.

I. INTRODUCTION

Studying the nucleation kinetics is of steady interest for more than fifty years. Although the classical nucleation theory¹⁻³ has proved to be the most effective in describing the nucleation rate, numerous deviations have been observed experimentally. Thus, for water the classical theory predicts the nucleation rate by 1-2 orders of magnitude higher than measured in^{4,5}, whereas for mercury it is by 30-35 lower⁶. The ratio of measured nucleation rate to the classical one for n -alcohol vapors varies steadily with n from 10^{-10} for n -methanol to 10^7 for n -hexane revealing the crossover⁷. A number of improvements (or reconsiderations) of the classical theory were undertaken that either proved to be effective in some cases⁸⁻¹⁰, or do not match the experiments¹¹.

The classical theory is based on the liquid drop model. Since clusters containing tens of molecules are to be encountered upon nucleation, the validity of the drop model for such small droplets is problematic. Therefore, the basic problem is a correct description of cluster thermodynamic properties (partition functions). This could be done by quantum chemistry methods, but the complexity of calculation routine prevents its usage for the whole range of the desired cluster sizes.

Thus, a semi-phenomenological approach with size effects correctly taken into account would be the most effective in practice. The accuracy of the classical model in the region of small cluster sizes can be considerably increased if one append another two parameters—the dimer equilibrium constant and the coordination number in a liquid—to those used in the

classical drop model. It is assumed in the model proposed below that cluster surface energy is proportional to the number of molecules on the cluster surface, rather than the cluster surface area (in contrast to the classical theory). Proportionality coefficients can be expressed in terms of micro- and macroscopic parameters using the thermodynamic relationships. In such a way, the surface tension which apparently has no sense for small clusters appear only in the limit of large clusters. Thus the validity range of the model can be extended from dimers to macroscopic droplets which makes it possible to calculate the nucleation rates for different substances in the wide range of state parameters.

In Chap. II the vapor at equilibrium is first considered. Thermodynamic cluster model is formulated and the general form of cluster distribution over sizes is found. In Chap. III some consequences are deduced, namely, the relationship between dimer equilibrium constant and the surface tension coefficient; the size correction for the surface tension is calculated. In Chap. IV non-equilibrium system is treated and the cases of low and high supersaturations are considered to calculate steady-state nucleation rates. In Chap. V the nucleation rates for water and mercury are calculated and juxtaposed with the experiments.

II. CLUSTER DISTRIBUTION OVER SIZES

Consider the equilibrium vapor as an ideal gas mixture of different clusters. The temperature is supposed to be above the melting temperature of the substance and well below the critical one. The state of the molecule in the cluster is determined by its coordination number. Molecules inside the cluster (the inner molecules) must have approximately the same coordination number N as in the bulk liquid. For the others (the surface molecules) the coordination number is less than N . If $g \leq N$ where g is the number of molecules in the cluster, the latter consists only of the surface molecules; if $g > N$ it can be represented as a nucleus surrounded by the layer of the surface molecules. Suppose that cluster chemical potential is a linear function of g and the number of the surface molecules, that is, unlike², the surface energy is proportional to the number of the surface molecules rather than the surface area:

$$\mu_g = T \ln p_g + \chi_g(T), \quad \chi_g(T) = A(T)g_0 + B(T)g + C(T), \quad (1)$$

where μ_g is cluster chemical potential, p_g is partial pressure of these clusters at temperature T , g_0 is the number of the surface molecules, A , B and C are temperature functions to be determined. Eq. (1) is the basic assumption of this model.

Since $g_0 \sim g^{2/3}$ if g is big, the first term in the right-hand side of (1) is transformed into the surface energy of a macroscopic droplet. If g is small, g_0 is much different from $g^{2/3}$, this being responsible for the size effects. The functions A , B and C can be calculated using

thermodynamic relationships. If $g \rightarrow \infty$ at saturation curve, μ_g must turn into the Gibbs energy of the bulk liquid, i.e., $\mu_g/g \rightarrow \mu_L$, where μ_L is the chemical potential of a molecule in the liquid phase. Therefore $B = \mu_L$. Applying (1) for $g_0 = g = 1$ and 2 and solving these two equations relative to A and C , one can find $A = \chi_2 - \chi_1 - \mu_L$, $C = 2\chi_1 - \chi_2$. Using mass action law $\mu_2 = 2\mu_1$ the value of χ_2 can be expressed in terms of dimer equilibrium constant $K_p = p_1^2/p_2$: $\chi_2 = T \ln K_p + 2\chi_1$. Molecule chemical potentials in the bulk liquid and in the vapor are equal: $\mu_L = \mu_{1S} = T \ln p_{1S} + \chi_1$, where the subscript s denotes the saturation curve. Using these relationships, (1) can be rewritten as follows:

$$\mu_g = T \ln p_g + g\chi_1 + (g_0 - 1)T \ln(K_p/p_{1S}) + (g - 1)T \ln p_{1S}. \quad (2)$$

The partial pressure of g -molecule clusters (or their number density $n_g = p_g/T$) can be found from (2) and the mass action law for cluster formation reaction $\mu_g = g\mu_1$:

$$n_g = n_1 \exp[-\Delta\Phi(g)/T],$$

$$\Delta\Phi(g) = (g_0 - 1)T \ln(K_p/p_{1S}) - (g - 1)T \ln S, \quad (3)$$

where $S = p_1/p_{1S}$ is the supersaturation ratio. Eq. (3) is the cluster distribution over sizes. It contains a macroscopic (p_{1S}) as well as a microscopic characteristic (K_p) of the substance. The distribution in the Frenkel's liquid drop model² contains the surface energy term $4\pi\sigma_0 R^2$, where σ_0 is the surface tension coefficient for the flat surface of the liquid, R is the radius of a liquid droplet, instead of the first term in the right-hand side of (3). The distribution (3), in contrast, does not contain the surface tension which apparently have no sense for small clusters.

For $g \leq N$ the clusters consist only of the surface molecules, $g_0 = g$, and from (3) follows

$$p_g = p_1(p_1/K_p)^{g-1}. \quad (4)$$

Note that (4) contains only microscopic parameters and therefore can be valid not only in subcritical region. Since a $N + 1$ -molecule cluster is the first one that contains an inner molecule, the distribution (3) may not be a smooth function of g at $g = N + 1$.

III. SIZE CORRECTION FOR THE SURFACE TENSION

To proceed further the number g_0 should be expressed as a function of g for $g > N$. For the sake of simplicity the consideration will be confined to average (spherical) cluster configuration. Indeed, thermal excitations in liquid clusters must be high enough to smear out the effect of regular lattice structure. The surface layer of a cluster is characterized by some molecule number density and thickness. These values expressed in the units of number

density in the nucleus n_L and liquid molecular cell radius $r_C = (3/4\pi n_L)^{1/3}$ are denoted below by η and λ , respectively. n_L is assumed to be equal to molecule number density in the bulk liquid. Nucleus radius in these units is then $g_1^{1/3}$, $g_1 = g - g_0$, g_0 is defined by the volume of the layer: $g_0 = \eta[(g_1^{1/3} + \lambda)^3 - g_1]$, or

$$g_0 = 3\omega g_1^{2/3} + 3\omega\lambda g_1^{1/3} + \omega\lambda^2, \quad (5)$$

where $\omega = \eta\lambda$. Eq. (5) defines the implicit function $g_0(g)$. For big g it can be expanded in powers of $g^{-1/3}$: $g_0(g) = 3\omega g[g^{-1/3} + g^{-2/3}(\lambda - 2\omega) + o(g^{-1})]$. Substituting this expansion in (3) we can represent $\Delta\Phi(g)$ in the form

$$\Delta\Phi(g) = 4\pi\sigma_0(1 - 2\delta/R)R^2 - (g - 1)T \ln S, \quad (6)$$

$$\sigma_0 = (3/4\pi)\omega T \ln(K_p/p_{1S})/r_C^2, \quad (7)$$

$$\delta = (\omega - \lambda/2)r_C, \quad (8)$$

where σ_0 has been introduced by its thermodynamic definition, δ is the curvature correction defined in the same way as by Tolman¹², $R = r_C g^{1/3}$. Apparently (6a-c) are meaningful only in case of big R .

Eq. (6b) can be treated as the relationship between the surface tension, dimer equilibrium constant and the saturation pressure. It contains a specific parameter ω . Its value can be crudely estimated as follows. Consider $N + 1$ -molecule cluster ($g_0 = N$, $g_1 = 1$). From (5) follows $\omega = N/(3 + 3\lambda + \lambda^2)$. Assuming that the surface atoms form a monolayer with the thickness $n_L^{-1/3}$ ($\lambda = (4\pi/3)^{1/3}$) and adopting the value $N = 8.5$ which is typical for most liquids¹³, we get $\omega \cong 0.81$.

The whole set of parameters in (6b) (σ_0 , K_p , p_{1S} and r_C) is known for many substances. The data in¹⁴⁻¹⁷ allow to calculate some specific values of ω (Table 1). They are practically independent on temperature and not much different for various substances (mean value $\bar{\omega} \cong 0.80$). Standard deviation from $\bar{\omega}$ is about 10% which is of the order of the experimental error in σ_0 measuring. Eq. (6b) with $\omega = \bar{\omega}$ can therefore be treated as an approximate universal relationship. It is similar to that proposed by Frenkel and Langmuir^{2,18} ($\kappa = 4\pi\sigma_0 r_C^2/q \cong 0.64$, q is molecule evaporation heat), but valid not only at melting temperature. Eq. (6b) can as well be considered as the surface tension temperature dependence. The temperature coefficients calculated in such a way are in reasonable agreement with the experiments (see Table 1).

Table 1: The values of ω and surface tension temperature coefficients for different substances at melting temperatures in dyne/(cm K). $(d\sigma_0/dT)_{th}$ is the calculation, $(d\sigma_0/dT)_{ex}$ is the experimental value.

Element	Li	Na	K	Cs	Rb
ω	0.823	0.920	0.771	0.698	0.801
$-(d\sigma_0/dT)_{th}$	0.226	0.117	0.095	0.060	0.056
$-(d\sigma_0/dT)_{ex}$	0.147	0.101	0.069	0.049	0.060
Element	Al	Cu	Hg	Ar	Ne
ω	0.823	0.782	0.783	0.565	0.664
$-(d\sigma_0/dT)_{th}$	0.333	0.397	0.360	0.197	0.180
$-(d\sigma_0/dT)_{ex}$	0.416	0.397	0.231	0.222	0.321

The relationship between ω , λ and N can be rewritten as

$$\lambda = (N/\omega - 3/4)^{1/2} - 3/2. \quad (9)$$

Adding N to the set of parameters used above one can estimate the curvature correction to the surface tension by using (6c). It is assumed that the coordination number is not strongly dependent on the liquid density and the way it was defined. Since the coordination number is the least sensitive parameter in the theory, its any definition can be applied without substantial numerical change in the result. Nevertheless, (6c) may not work for substances like argon, for which N is strongly dependent both on the density and the definition.

For different substances δ can be positive as well as negative. It is especially important for small clusters defining qualitatively their distribution over sizes. To demonstrate the effect of the size correction one can introduce formally the size-dependent surface tension coefficient $\sigma(R)$. Substituting the first (surface) term in the right-hand side of (3) by $4\pi\sigma(R)R^2$ and using (6b) one obtains

$$\sigma(R)/\sigma_0 = (r_C/R)^2[g_0(R^3/r_C^3) - 1]/3\omega. \quad (10)$$

The size dependences (8) are shown in Fig. 1 for water and mercury. It is interesting to note that for water $\delta < 0$, which is not typical for most liquids (see Chap. V). Comparison with the calculations by the Tolman formula¹² $\sigma(R)/\sigma_0 = (1 + 2\delta/R)^{-1}$ with the same values of δ reveals a qualitative disagreement in the range of small sizes for $\delta < 0$ and a quantitative one for $\delta > 0$. Although asymptotes coincide, there still exists a quantitative disagreement even for the large clusters. It means that the high-order terms in $g^{-1/3}$ -power (or r_C/R -power) expansion of $\sigma(R)$ which are usually neglected are not so small even at $g \cong 1000$ ($R/r_C \cong 10$). For positive δ the size correction always reduces the surface tension and is a sharp function of size for $g < 50$. In contrast, for negative δ $\sigma(R)$ reaches the maximum and then decreases very slowly down to σ_0 , the surface energy being not much different from that of a macroscopic droplet already at $g \cong 30$. In general, if $\delta \leq 0$ for some substance, the surface tension is practically size-independent even for the clusters containing several tens of atoms.

IV. HOMOGENEOUS NUCLEATION RATE

If equilibrium cluster distribution is known, a set of kinetic equations for the case of steady-state isothermal homogeneous nucleation can be solved exactly¹⁹:

$$J = r_C^2 n_1 (8\pi T/M)^{1/2} / \sum_{g=1}^{\infty} g^{-2/3} n_g^{-1}, \quad (11)$$

where J is the number of embryos appearing in unit volume per unit time (homogeneous nucleation rate), n_1 is monomer number density, n_g is the equilibrium cluster distribution over sizes corresponding to n_1 , M is atom mass. Only one-molecule evaporation and condensation were assumed to be the elementary processes, condensation coefficient was set to unity. The product under summation in (9) has a sharp maximum corresponding to the maximum of $\Delta\Phi(g)$ at some $g = g_*$ called the critical size. Therefore the main contribution to the sum is that from the clusters which sizes are about g_* .

For the case of big g_* the same routine as in³ is applicable: neglecting the curvature correction in (6a), substituting it into (9) and expanding $\Delta\Phi(g)$ about maximum we have

$$J = (1/S)J_{cl}, \quad J_{cl} = (n_1^2/n_L)(2\sigma_0/\pi M)^{1/2} \exp(-4\pi\sigma_0 R_*^2/3T), \quad (12)$$

$$R_* = r_C g_*^{1/3} = 2\sigma_0/n_L T \ln S, \quad (13)$$

where J_{cl} is homogeneous nucleation rate in the classical theory¹⁹, R_* is the critical radius. Formula (10a) is known as a Zeldovich formula with the Courtney correction factor⁸ $1/S$. The critical radius (10b) is big if supersaturation is low, so it is also the case of low S . J is extremely sharp function of σ_0 and therefore quite sensitive to the size correction.

Consider the opposite case of small g_* (high S). Upon increasing S the critical size g_* first follows the dependency (10b) and decreases. In the classical theory $g_* = 0$ at $S = \infty$; in this limit the maximum of $\Delta\Phi(g)$ disappears. However, it follows from (3) that the maximum disappears at some finite supersaturation $S = K_p/p_{1S}$. At this point $\Delta\Phi(g) \equiv 0$ for $1 \leq g \leq N$ and $\Delta\Phi(g) < 0$ for $g > N$. Consequently, the minimum value of g_* is N . In the vicinity of this point, i.e., if $\ln S \gg \Phi_m/T(N-1)$, where Φ_m is the maximum value of $\Delta\Phi(g)$, but $S < K_p/p_{1S}$, one can approximately set $g_* = N$. Then using (6b) we have

$$\Phi_m = (N-1)T[\ln(K_p/p_{1S}) - \ln S] = (N-1)T[(4\pi/3)(\sigma_0 r_C^2/T\omega) - \ln S]. \quad (14)$$

In this case it is not necessary to calculate the pre-exponential factor exactly, so one can assume that only the critical clusters ($g = N$) contribute to the sum in (9) and find

$$J = n_1^2 r_C^2 N^{2/3} (8\pi T/M)^{1/2} \exp(-\Phi_m/T). \quad (15)$$

Eqs. (11a,b) are valid for extremely high values of S . For intermediate values the summation in (9) should be carried out numerically. In addition, if nucleation occurs at temperatures close to melting one, the difference between the total and monomer partial pressures is in most cases negligibly small, so that $S = p/p_S$, where p is the total pressure (see also Chap. V).

V. RESULTS AND DISCUSSION

As it has been shown above, the size correction to cluster equilibrium distribution over sizes and therefore to homogeneous nucleation rate is completely determined by the values of K_p and N . K_p , when unknown from independent sources, can be estimated using the equilibrium PVT-data. Compressibility factor of the vapor is $Z = pM/\rho T = \sum_{g=1}^{\infty} n_g / \sum_{g=1}^{\infty} g n_g$, where ρ is the density of the vapor. Assuming that only the clusters with $g \leq N$ contribute substantially to the equation of state, substituting their distribution (4) into above expression and performing the summation one can find

$$Z(p, T) = [1 + p/K_p(T)]^{-1}. \quad (16)$$

Eq. (12) is valid for moderate density vapors and can be used to estimate p_1 ; if $p/K_p \ll 1$ then $p \cong p_1$. Equilibrium constant $K_p(T) = C_0 T^{1/2} \exp(-D/T)$ in (12) can be found by varying the constants C_0 and D in this temperature dependence to curve fit the PVT-data. A satisfactory accuracy can be attained if $Z(p, T)$ is noticeably different from unity at temperatures less than dimer dissociation energy D and moderate densities. It is the case for water. Having used experimental values of isothermal compressibility factor for steam²⁰ at temperatures $T = 523, 623, 723$ and 823 K and densities $\rho < 0.02$ g/cm³ the following values were found: $C_0 = 1110$ bar/K^{1/2}, $D = 2500$ K. The value of D for water dimer is in agreement with both quantum chemistry calculations²¹ ($D = 2501 \pm 186$ K) and the experimental measurement of its enthalpy of formation²² (3.7 kcal/mol).

Adopting the value $N = 5.5$ which is the limiting number of the nearest neighbors in the large clusters obtained in the molecular dynamics calculations^{23,24} one can find for water $\omega = 0.546$, $\lambda = 1.554$ and $\delta = -0.232r_C$. For mercury $K_p(T)$ can be calculated directly with the help of spectroscopic data on Hg₂¹⁷; $N = 6$ ¹³. Consequently, $\omega = 0.783$, $\lambda = 1.129$ and $\delta = 0.218r_C$. Thus, δ has approximately the same absolute values for water and mercury but differs in sign.

Homogeneous nucleation rates were calculated for both substances. The summation in (9) was performed numerically; the expressions (3) and (5) were used for equilibrium cluster distribution over sizes. The ratios of calculated nucleation rates to J_{cl} (10a) are shown in Fig. 2 as the functions of the maximum values of $\Delta\Phi(g)$, $\Phi_m(S, T)$, which were also determined numerically. The calculations were carried out for $T = 293$ K (water) and $T = 312$ K (mercury). The result for water is practically independent on temperature for $T = 290$ – 340 K. It is worth mentioning that although the embryos may have the sizes of the same order ($g_* = 33$ at $\Phi_m/T = 26$ for water and $g_* = 23$ at $\Phi_m/T = 65$ for mercury), the ratio J/J_{cl} is not much different from unity for water and more than by 30 orders of magnitude higher for mercury. It can be clearly seen in Fig. 1 that for such sizes the size

correction for mercury is considerable (curve 4) and the decrease in $\sigma(R)$ results in the sharp increase of J . For water $\sigma(R)/\sigma_0 = 1$ at $g = 36$; for $g \geq 36$ the size correction is small (curve 3) and this effect is not so pronounced. Apparently, in this size range the Tolman formula is not useful for both substances. The calculations are in agreement with the experiments performed in the diffusion cloud chamber^{4,6} and in the Wilson chamber⁵. Thus, the sign change of δ is responsible for the drastic change in nucleation rate. It might be responsible for a steady growth of J/J_{cl} in homologous row of n -alcohol vapors (“nucleation crossover”) observed in⁷.

Critical supersaturation S_{cr} for mercury at which $J = 15 \text{ sec}^{-1} \text{ cm}^{-3}$ as the function of temperature is shown in Fig. 3. The curve 1 has been calculated numerically with the help of (9). The theory matches the experiment⁶, and at $T < 300 \text{ K}$ the formulas (11a,b) are the good approximation (curve 2). The classical theory (10a) overestimates S_{cr} by two to four orders of magnitude (dashed curve). However, as the temperature increases, this curve and the curve 1 are brought together.

It follows from (11a) that the supersaturation at spinodal, where $\Phi_m = 0$, is $S_{sp}(T) = K_P(T)/p_{1S}(T)$. It is of interest to juxtapose this equation with spinodal defined by the van der Waals equation $Z = (1 - \tilde{\rho}/3)^{-1} - 9\tilde{\rho}/8\tilde{T}$ under the condition $(\partial p/\partial \rho)_T = 0$, where $\tilde{\rho} = \rho/\rho_c$, $\tilde{T} = T/T_c$, ρ_c and T_c are critical density and temperature, correspondingly. Since $S_{sp} \gg 1$, the result would be qualitatively unchanged if we set $p \cong p_1$. It can be seen in Fig. 4 that the discrepancy between this theory and the van der Waals spinodal is not big. Therefore, (11a,b) must give reasonable results even for extremely high supersaturations. Such values are to be expected upon high vapor cooling rates, e.g., expansion in supersonic nozzles.

Summing up, the size correction can be fully described by two numeric parameters, ω and λ , appeared in the model due to the introduction of the additional parameters, K_p and N . The size correction makes it possible to describe the data on homogeneous nucleation in the wide range of supersaturations and state parameters.

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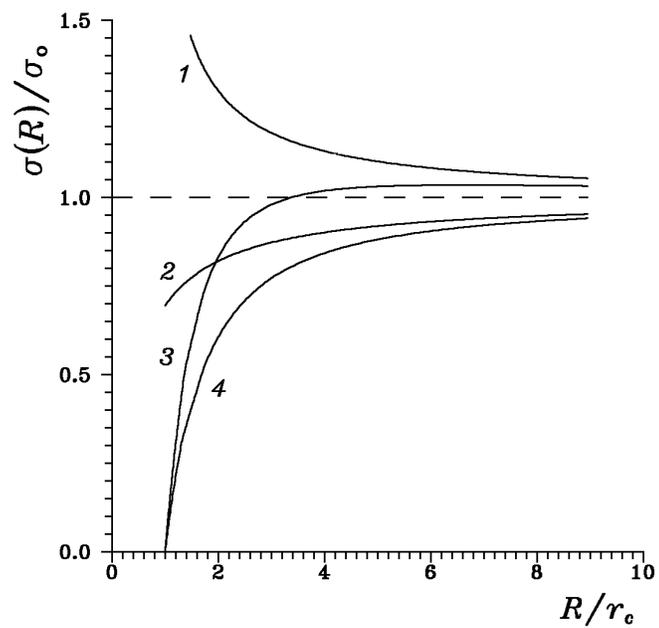


Figure 1: Size-dependent surface tension for water ($\delta = -0.232r_C$, curves 1, 3) and mercury ($\delta = 0.218r_C$, curves 2, 4) calculated by the Tolman formula (1, 2) and the formula (8) (3, 4).

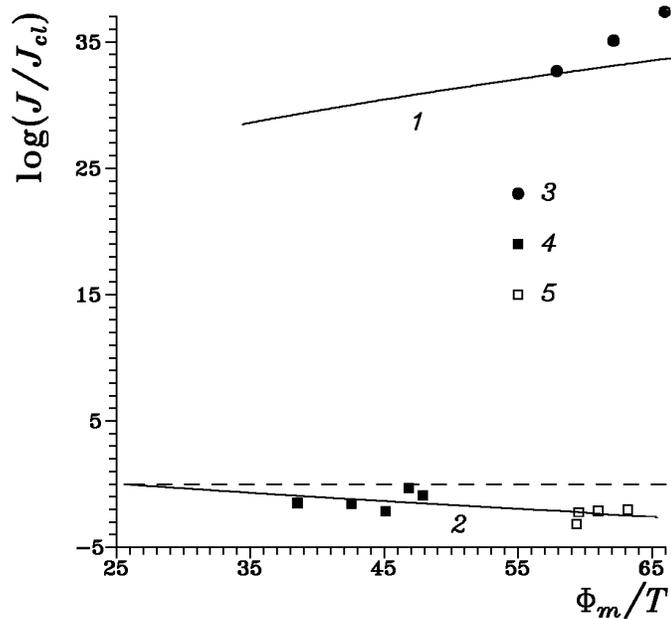


Figure 2: Homogeneous nucleation rates for mercury and water vapors. Calculations: 1 (mercury) and 2 (water). Experiments, mercury: 3 6 ($T = 312$ K) and water: 4 5 ($T = 293 - 338$ K), 5 4 ($T = 290 - 320$ K). Dashed curve is the classical theory.

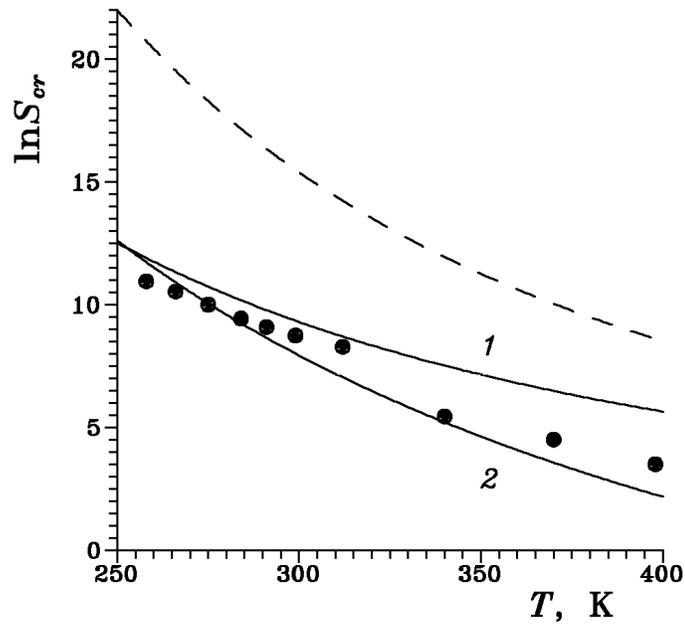


Figure 3: Critical supersaturation for mercury vapor as the function of temperature calculated numerically using (9) (curve 1) and the formulas (11a,b) (curve 2). Dashed curve is the classical theory. Dots are the experiment⁶.

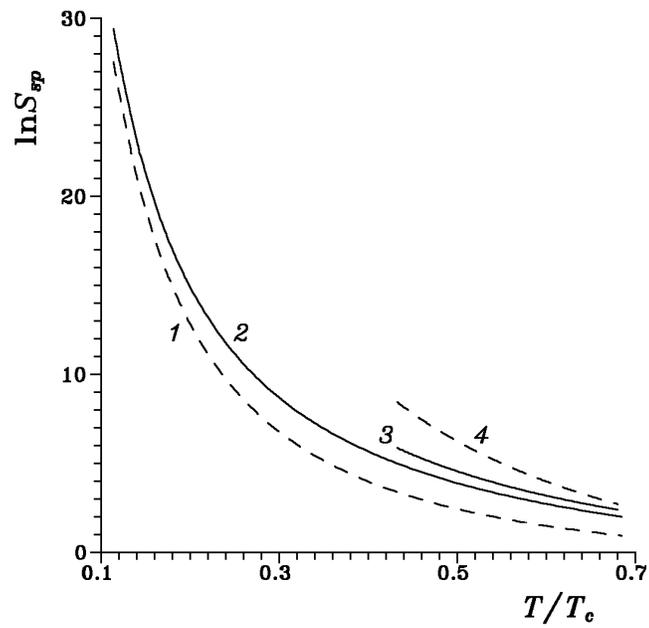


Figure 4: Supersaturations at spinodal as the functions of temperature. The van der Waals equation, dashed curves: *1* (mercury) and *4* (water); the formula (11a), solid curves: *2* (mercury) and *3* (water).