

Activation Barriers for the Complete Dissolution of Condensation Nucleus and Its Reverse Crystallization in Droplets in the Undersaturated Solvent Vapor

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Received June 10, 2009

Abstract—The behavior of minima and the saddle point of the work of the droplet formation on soluble condensation nucleus as a function of the chemical potential of undersaturated (over the plane surface of pure solvent) solvent vapor is studied. Activation barriers for the direct transition of droplet from the state with partially dissolved nucleus to the state with completely dissolved nucleus and for the reverse transition of the crystallization of nucleus in the droplet are numerically determined within the wide range of the chemical potentials of undersaturated vapor. It is shown that the activation barrier for the direct transition increases rapidly, whereas the activation barrier for reverse transition lowers (although remaining finite) with a decrease in the chemical potential of vapor below its threshold value for the barrierless transition to the state with completely dissolved nucleus. As a result, droplets with completely or partially dissolved nucleus actually do not coexist in the atmosphere of undersaturated vapor. It is demonstrated that, upon variations in the relative humidity of undersaturated vapor, the change in thermodynamically stable and unstable description variables of the states of near-critical droplet takes place and physical meaning of these variables is explained.

DOI: 10.1134/S1061933X1003018X

INTRODUCTION

This work continues the thermodynamic study of the regularities of heterogeneous nucleation on soluble condensation nuclei in solvent vapor started in [1–5]. The interest to the heterogeneous nucleation on soluble nuclei is caused by the fact that aerosols formed precisely on such nuclei are long-lived species in Earth's atmosphere and significantly affect its state [6, 7]. In addition, at present, there is a great body of experimental data that illustrate the dependence of growth factor (the ratio of the radius of condensing droplet to the initial radius of nucleus) on the relative humidity of the vapor–gas medium upon the nucleation on soluble nuclei in undersaturated (over the plane surface of pure solvent) vapor [8–12]. These data can be used to analyze equilibrium states in the condensation nuclei–droplets–vapor system and verify thermodynamic theory of heterogeneous nucleation.

When soluble condensation nuclei are placed into undersaturated (over the plane surface of pure solvent) but supersaturated (over the solution surface) vapor, the equilibrium distribution of emerging droplets is established with the maximum corresponding to the size of droplet which is at stable equilibrium with vapor. Depending on the relative humidity of vapor, these droplets can exist either in the form of liquid film around solid nucleus or the homogeneous droplet of solution of substance comprising completely dissolved

nucleus. Nuclei are completely dissolved in droplets at the values of the chemical potential of vapor near the threshold of nucleus dissolution, which was studied in [1, 3, 12–18]. This process is usually called deliquescence transition. Now, if we noticeably lower chemical potential, a reverse (efflorescence) transition can occur at which solid nuclei will be crystallized and enlarged in solution droplets; then, the final state will be the state of droplets in the form of films of saturated solution around formed nuclei.

To understand the specificity of heterogeneous nucleation on soluble condensation nuclei in undersaturated solvent vapor and specific features of the experimental examination of the equilibrium of droplets with completely or partially dissolved nuclei [6–10], it is noteworthy to study the behavior of the extremes of the work of droplet formation and relevant activation barriers of nucleation as functions of the chemical potential of vapor. These studies in the thermodynamics and kinetics of heterogeneous nucleation upon the partial or complete dissolution of condensation nuclei have not been conducted previously in [1–3, 12–18]. In this paper, we will study this problem.

1. MINIMA AND SADDLE POINT OF THE WORK OF DROPLET FORMATION

Let us consider the closed system inside fixed volume V at absolute temperature T . The system in the initial state is a solid nucleus and vapor of substance

that dissolves solid nucleus upon condensation. Being condensed on the surface of nucleus, the vapor forms liquid spherical film of saturated solution of condensate and substance comprising nucleus. The substance that makes up the nucleus cannot be transferred into the gaseous phase. In the final state, at the same volume and temperature, the system includes the droplet with partially or completely dissolved nucleus and vapor. According to [3, formula (30)], the work of droplet formation in this system has the following form:

$$W = -v(\mu^\beta - \mu_\infty) + k_B T (v_n - v'_n) \left(\ln \frac{x}{x_\infty} - 1 \right) + 4\pi R_n^2 \sigma^{\gamma\alpha} + 4\pi R^2 \sigma^{\alpha\beta} - 4\pi R_n^2 \sigma^{\gamma\beta} + 4\pi R_n^2 l K \exp\left(-\frac{R - R'_n}{l}\right), \quad (1.1)$$

where α , β , and γ superscripts refer to the phases of liquid solution, vapor, and nucleus, respectively, and $\gamma\beta$, $\gamma\alpha$, and $\alpha\beta$ refer to relevant interfaces. The $\sigma^{\gamma\beta}$, $\sigma^{\gamma\alpha}$, and $\sigma^{\alpha\beta}$ values denote surface tensions of relevant surfaces; $4\pi R_n^2$, $4\pi R'^2$, and $4\pi R^2$ are the areas of corresponding spherical surfaces with radii $R_n = R^{\beta\gamma}$, $R'_n = R^{\alpha\gamma}$, and $R = R^{\alpha\beta}$; $v = \left[(4\pi/3)(R^3 - R_n^3) - v_n^\alpha (v_n - v'_n) \right] / v^\alpha$ is the number of solvent molecules in the droplet, where $v_n = 4\pi R_n^3/3v_n$ is the total number of molecules of substance comprising nucleus, $v'_n = 4\pi R_n'^3/3v_n$ is the number of molecules of substance comprising nucleus inside its remaining part with radius R'_n in the droplet, $v_n - v'_n$ is the number of molecules of substance comprising nucleus inside the spherical liquid film of solution with thickness $h = R - R'_n$, μ^β is the chemical potential of vapor molecules; μ_∞ is the chemical potential of condensate molecule at equilibrium with the plane interface between the liquid phase of pure condensate and its vapor; k_B is Boltzmann's constant; $x = (v_n - v'_n)/v$ is the relative concentration that would be in the bulk phase of solution at the same values of the chemical potentials of solvent and solute molecules as in the film around the remaining part of nucleus; and x_∞ is the concentration (solubility) of substance comprising condensation nucleus at equilibrium with the plane interface between the solid phase of substance comprising nucleus and the solution. The latter term in expression (1.1) takes into account the contribution from the overlap of surface layers [19–22] to the work of droplet formation. This term is obtained by the integration of the disjoining pressure in the liquid film. With this approach, the exponential approximation $\Pi = K \exp[-(R - R'_n)/l]$ [19–22] is used for the disjoining pressure, where l is

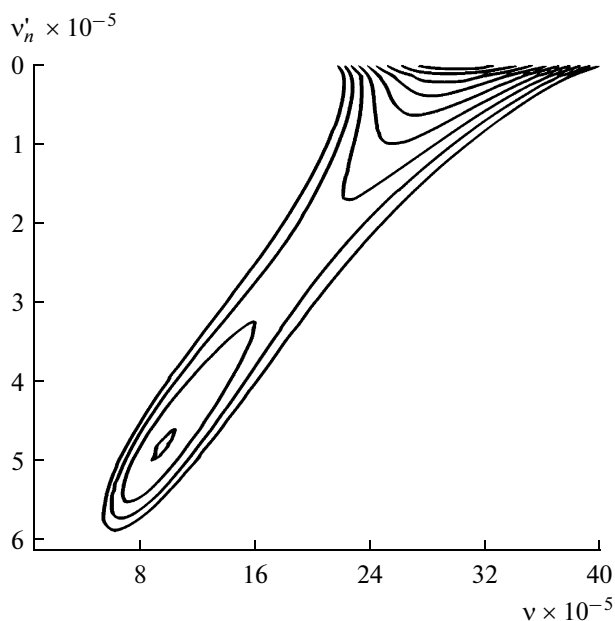


Fig. 1. Lines of level of work F of droplet formation as a function of number of condensate molecules v and number of molecules in remaining part of nucleus v'_n at vapor chemical potential $b = -0.2$.

the parameter called the correlation length in the solution film around the remaining part of condensation nucleus; preexponential factor K is related to $\sigma^{\gamma\beta}$, $\sigma^{\alpha\gamma}$, $\sigma^{\alpha\beta}$ surface tensions and correlation length l by the relation $K = (\sigma^{\gamma\beta} - \sigma^{\alpha\gamma} - \sigma^{\alpha\beta})/l$ [23].

Let us introduce the dimensionless work of droplet formation

$$F \equiv W/k_B T, \quad (1.2)$$

and dimensionless chemical potentials of condensate molecules in the vapor

$$b \equiv (\mu^\beta - \mu_\infty)/k_B T, \quad (1.3)$$

and in the solution inside the droplet

$$b_v \equiv (\mu_v - \mu_\infty)/k_B T. \quad (1.4)$$

For calculations, let us determine the numerical values of parameters in expression (1.1) as follows:

$$\begin{aligned} R_n &= 15 \times 10^{-7} \text{ cm}, \quad v_n = 2 \times 10^{-23} \text{ cm}^3, \\ v^\alpha &= 3 \times 10^{-23} \text{ cm}^3, \quad v_n^\alpha = 2.2 \times 10^{-23} \text{ cm}^3, \\ T &= 298 \text{ K}, \quad \sigma^{\alpha\gamma} = 200 \text{ dyne cm}^{-1}, \\ \sigma^{\alpha\beta} &= 72 \text{ dyne cm}^{-1}, \quad x = 0.2, \quad l = 2 \times 10^{-7} \text{ cm}, \\ K &= 3 \times 10^9 \text{ dyne cm}^{-2}. \end{aligned} \quad (1.5)$$

These parameters are taken for the realistic condensation nucleus and water as condensate.

Figure 1, where the lines of the surface level of work F of droplet formation are plotted as functions on the number v of condensate molecules and the number v'_n of the molecules of the remaining part of nucleus at

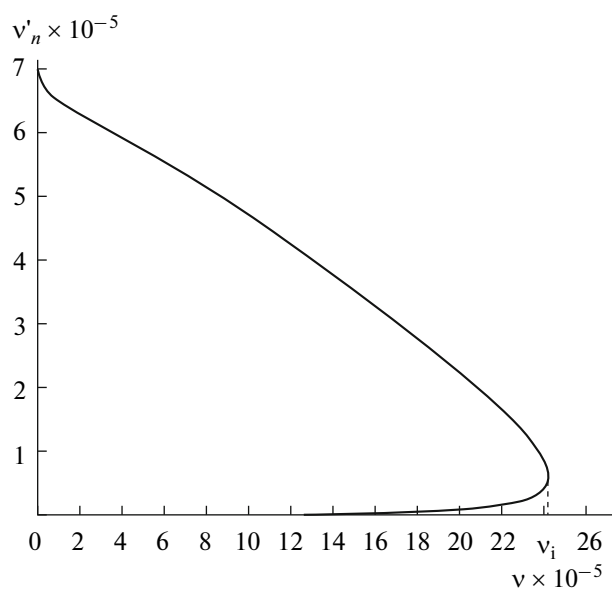


Fig. 2. Dependence of equilibrium v'_n values on v at $R_n = 15$ nm and $v_n = 7.068 \times 10^5$.

the initial size of condensation nucleus $R_n = 15$ nm ($v_n = 7.068 \times 10^5$) and chemical potential $b = -0.2$ clearly demonstrates the first and second minima, as well as the saddle point of the work F of droplet formation. The first minimum of work F is located in the region of small numbers of condensate molecules v and complies with the droplet with a partially dissolved nucleus that is at equilibrium with the solute comprising nucleus and the film of solution at stable equilibrium with the vapor. In the absence of disjoining pressure in the thin film, the presence of which is explained by the overlap of surface layers of thin surface film, the first minimum ceases to exist. The second minimum observed in the upper region of Fig. 1 at

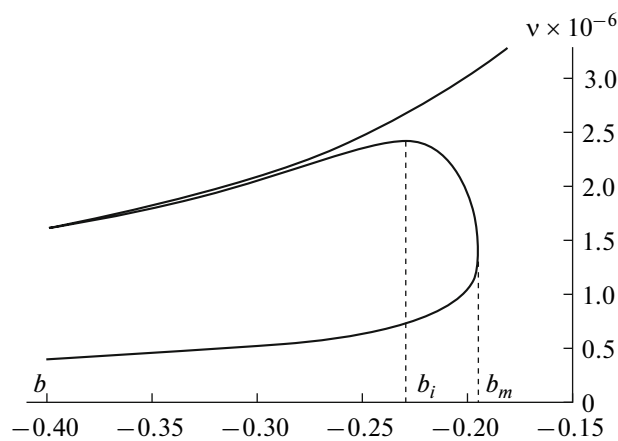


Fig. 3. Dependences of equilibrium v values on b at $R_n = 15$ nm and $v_n = 7.068 \times 10^5$.

$v'_n = 0$ complies with the droplet with completely dissolved nucleus which is at stable equilibrium with the vapor. The saddle point of the work F of droplet formation corresponds to the critical droplet (which is at unstable equilibrium with the vapor) with partially dissolved nucleus, which is at equilibrium with the solute comprising nucleus in the film.

The solution of the generalized Ostwald–Freundlich equation makes it possible to derive the dependence of the solubility of the remainder of nucleus on its size and the size of droplet and, hence, to determine the correlation between the v'_n and v values at equilibrium with the remainder of nucleus and the film of solution. This solution was numerically obtained in [3]. The dependence of equilibrium v'_n values on v obtained in [3] shown in Fig. 2 ([3], Fig. 3) for the initial nucleus size $R_n = 15$ nm ($v_n = 7.068 \times 10^5$) is significant for further analysis. This function is two-valued and is characterized by the turning point $v = v_i$ ($v_i = 2.414 \times 10^6$ and $v'_n(v_i) = 62289$), whereas inverse function $v(v'_n)$ is single-valued function its values lie within the $0 < v(v'_n) < v_i$ range. As the initial nucleus size v_n increases, the number v of condensate molecules in the turning point $v = v_i$ also increases. The existence of turning point and ambiguity of the $v(v'_n)$ function means that the solution film can be in neither stable nor unstable states with the remaining part of nucleus at $v > v_i$.

For further analysis, we also need the dependence of equilibrium number v of condensate molecules on the chemical potential of vapor b , obtained using the combined numerical solution of the generalized Gibbs–Kelvin–Keller and Ostwald–Freundlich equations ([3], Fig. 5). The corresponding dependence is shown in Fig. 3; moreover, it was plotted both in the regions of partial and complete dissolution of nucleus in the droplet. There exists the turning point $b = b_m$ ($b_m = -0.19275$, $v'_n(b_m) = 3.969 \times 10^5$, $v(b_m) = 1.318 \times 10^6$) so that, at $b > b_m$, there are no stable equilibrium v'_n and v values in the region of the partial dissolution of nucleus; however, stable v values appear in the region of nucleus complete dissolution. It is evident that the b_m value is responsible for the threshold value of the chemical potential of undersaturated vapor for the transition from droplets with partially dissolved nuclei to droplets with completely dissolved nuclei so that, at $b \geq b_m$, this transition takes place without overcoming the barrier.

Note that the maximum on the equilibrium curve $v(b)$ in the region of the partial dissolution of nucleus corresponds to $b = b_i$ ($b_i = -0.22892$, $v(b_i) = 2.414 \times 10^6$, and $v'_n(b_i, v(b_i) = 62289$) indicated in Fig. 3, while equilibrium values $v(b_i)$ и $v'_n(b_i, v(b_i)$ coincide with the coordinates of the turning point in Fig. 2. Figure 3 gives rise

to deceptive impression that branches of curve $v(b)$ in the regions of partial and complete dissolution of nuclei are merged at $b \leq -0.32$, that correspond to large undersaturation of the vapor. However, this is not the case. Branches are getting closer to one another at $b \rightarrow -\infty$, but they are not merged.

At the fixed temperature of a system and fixed chemical potential of the vapor, the work F of droplet formation is a function of two independent variables, i.e., the number of condensate molecules v and the number of molecules in the remaining part of nucleus v'_n . For this reason, the criterion of the existence of the minimum of the $F(v, v'_n)$ function is written in the following form:

$$\left. \frac{\partial^2 F}{\partial v^2} \right|_{v_e, v'_e} > 0, \left[\frac{\partial^2 F}{\partial v^2} \frac{\partial^2 F}{\partial v_n'^2} - \left(\frac{\partial^2 F}{\partial v \partial v'_n} \right)^2 \right]_{v_e, v'_e} > 0, \quad (1.6)$$

the criterion of the saddle point is written as

$$\left[\frac{\partial^2 F}{\partial v^2} \frac{\partial^2 F}{\partial v_n'^2} - \left(\frac{\partial^2 F}{\partial v \partial v'_n} \right)^2 \right]_{v_c, v'_c} < 0, \quad (1.7)$$

where additional subscripts e and c denote the values taken in the points of minima and the saddle point, respectively.

Values $D \equiv (\partial^2 F / \partial v^2)(\partial^2 F / \partial v_n'^2) - (\partial^2 F / \partial v \partial v'_n)^2$ and $\partial^2 F / \partial v^2$ as functions of the chemical potential of the vapor, b , at partially dissolved condensation nucleus in the droplet taken in points $v = v(b)$ and $v'_n = v'_n(b, v(b))$, that corresponds to curves in Figs. 2 and 3 at consecutive transition from small to large v'_n values are shown in Figs. 4 and 5 (upper curves). The lower curve in Fig. 5 confirms to the region of the complete dissolution of nucleus in the droplet. The apparent merging of lower and upper curves in Fig. 5 at b , values corresponding to the strong undersaturation of the vapor is deceptive; the curves get closer to one another but do not merge. With allowance for conditions (1.6) and (1.7), the dependences presented in Figs. 2–5 lead us to conclude that, at $b_m < b < 0$, the work of droplet formation is only characterized by the minima at the complete dissolution of nucleus in the droplet. The upper curve in Fig. 3 complies with these minima at $b_m < b < 0$. Moreover, at every value of the chemical potential of the vapor taken from the $-\infty < b < b_m$ interval, two minima exist simultaneously at the complete and partial dissolution of nucleus in the droplet and the saddle point of the work of droplet formation at the partial dissolution of nucleus. The upper curve in Fig. 3 corresponds to minima at the complete dissolution of nucleus; the lowest curve in Fig. 3 at $-\infty < b < b_m$ refers to minima with the partial

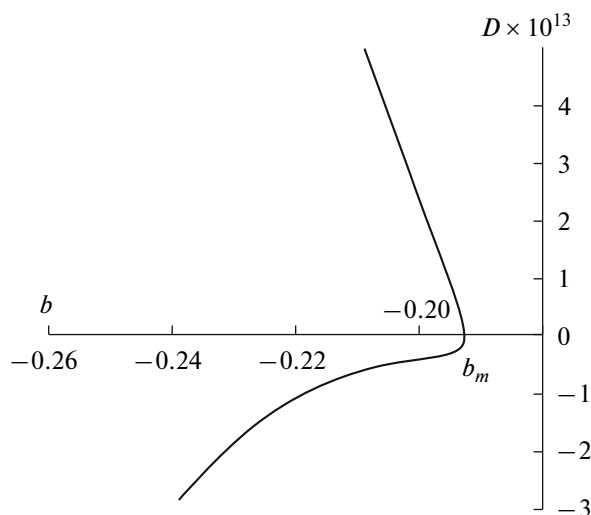


Fig. 4. Dependence of D on vapor chemical potential b at $R_n = 15$ nm and $v_n = 7.068 \times 10^5$.

dissolution of nucleus. The middle branch of the curve in Fig. 3 at $-\infty < b < b_m$ complies with the saddle point.

To understand the specificity of the stage of moistening and peculiarities of its experimental examination, it is necessary to know only the behavior of minima and the saddle points of the work F of droplet formation as functions of chemical potential. Such dependences for F_{e1} and F_{e2} values of the work of droplet formation in the points of its minima at the partial and complete dissolution of nucleus, respectively, and

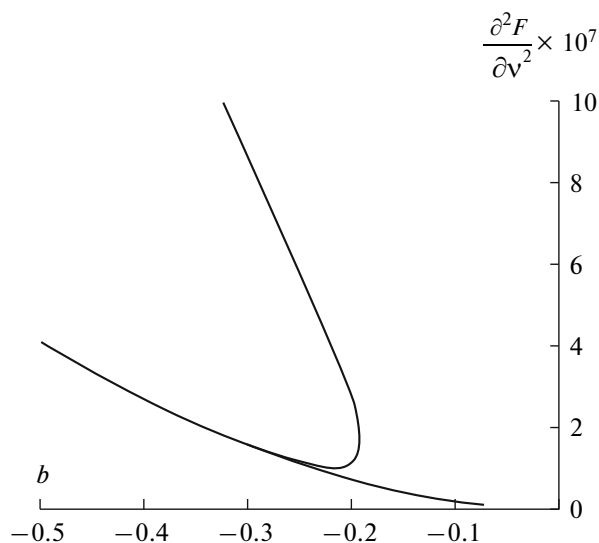


Fig. 5. Dependences of $\partial^2 F / \partial v^2$ on vapor chemical potential b at $v'_n = v'_n(b)$ and $v = v(b)$; $R_n = 15$ nm and $v_n = 7.068 \times 10^5$. See text for explanation.

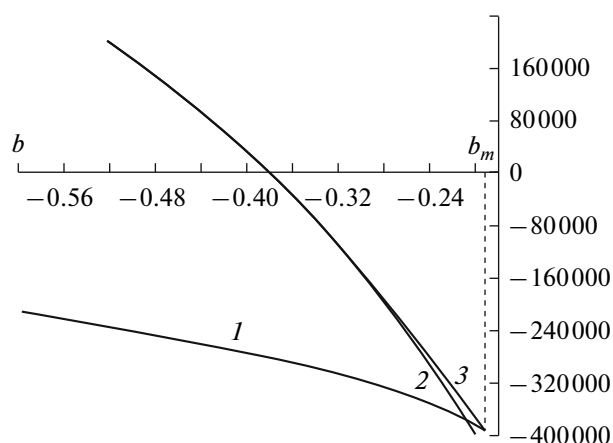


Fig. 6. Dependences of minima (1) F_{e1} and (2) F_{e2} and (3) saddle point F_c of work F on vapor chemical potential b at $R_n = 15$ nm and $v_n = 7.068 \times 10^5$.

the values of work F_c in the saddle point are shown in Fig. 6. These functions are plotted, using Eqs. (1.1)–(1.5), in points $v = v(b)$ and $v'_n = v'_n(b, v(b))$, corresponding to curves in Figs. 2 and 3 with allowance for the classification of these points performed by Figs. 4 and 5. Note that Fig. 6 can lead to deceptive impression that curves for F_c and F_{e2} are merged at b values that correspond to strong undersaturation of the vapor. In fact, F_c and F_{e2} curves are getting closer to one another at $b \rightarrow -\infty$, but they do not merge.

2. BARRIERS FOR DIRECT AND REVERSE TRANSITIONS UPON DISSOLUTION AND EMERGENCE OF SOLID NUCELUS IN THE DROPLET

It was shown in the previous section which points on $v(b)$ curve (Fig. 3) correspond to the minima of the work of droplet formation and which points match saddle points. The activation energies of transitions from the stable droplet with partially dissolved nucleus to the critical droplet containing smaller nucleus and is at unstable equilibrium with the vapor and the transition from the stable homogeneous droplet of solution to the critical droplet containing emerged solid nucleus play an important role for the kinetic analysis of heterogeneous nucleation of vapor on nuclei and the crystallization of nuclei in droplets. The heights of activation barriers at direct and reverse transitions between states of droplet with partially and completely dissolved nucleus are determined using the following expressions:

$$\Delta F_1 \equiv F_c - F_{e1}, \quad (2.1)$$

$$\Delta F_2 \equiv F_c - F_{e2}. \quad (2.2)$$

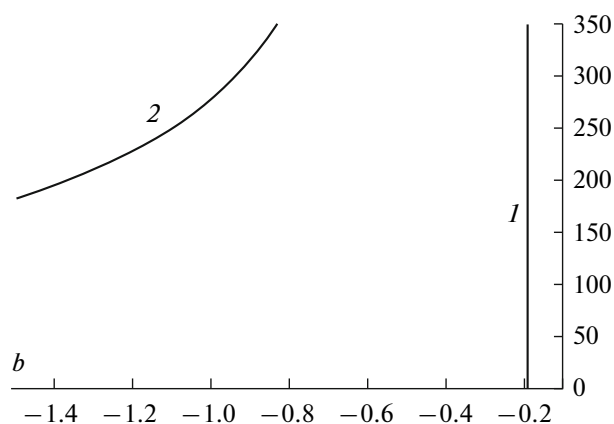


Fig. 7. Dependence of height of activation barrier for (1) direct $\Delta F_1 = F_c - F_{e1}$ and (2) reverse $\Delta F_2 = F_c - F_{e2}$ transitions on vapor chemical potential b at $R_n = 15$ nm and $v_n = 7.068 \times 10^5$.

Figure 7 shows the dependences of the heights of activation barriers for direct ΔF_1 and reverse ΔF_2 transitions defined by Eqs. (2.1) and (2.2). As can be seen from Fig. 6, the F_{e1} and F_c curves are merged at threshold value $b = b_m$ of the chemical potential of the vapor. Correspondingly, ΔF_1 curve in Fig. 7 achieves zero at $b = b_m$. It follows also from this figure that, at certain $b = b_e$ value, F_{e1} and F_{e2} branches can be intersected. Then, at $b = b_e$, heights ΔF_1 and ΔF_2 of activation barriers for direct and reverse transitions become identical. At the values of the parameters of a problem indicated in (1.5), we have $b_e = -0.21$ and $\Delta F_1(b_e) = \Delta F_2(b_e) = 16795$. However, it should be noted that, in the real situation, transitions between the states of droplet with partially and completely dissolved nuclei are only possible at $\Delta F_1 \leq 100$ or $\Delta F_2 \leq 100$. Hence, the value of vapor chemical potential $b_e = -0.21$ cannot play any role in the consideration of the kinetics of a process. As can also be seen from Fig. 7, at the chosen values of the parameters of a problem and the same values of the chemical potential of undersaturated vapor at which activation barrier ΔF_1 is low, activation barrier ΔF_2 is always very high and, vice versa, at vapor chemical potentials at which activation barrier ΔF_2 is low, activation barrier ΔF_1 turned out to be high. Thus, we can conclude that a direct transition occurs at the values of vapor chemical potential in the vicinity of threshold value $b = b_m = -0.193$. No analogous threshold value is observed for the reverse transition. However, at fairly low values of vapor chemical potential (at low relative humidity), when activation barrier ΔF_2 decreases to values on the order of 10^2 and homogeneous crystallization becomes possible at which the growth of small

nucleus in the droplet corresponding to the transition over the saddle point occurs at nearly unchanged droplet size. As we will see in the next section, this change in the mechanism of nucleation laid in the structure of expression (1.1) for the work of droplet formation.

3. STABLE AND UNSTABLE DESCRIPTION VARIABLES OF STATES OF DROPLET IN VICINITY OF SADDLE POINT

To construct the kinetics of direct and reverse transitions between states of droplets with partially and completely dissolved nuclei, it is necessary to examine the behavior of the formation work of droplet in the vicinity of its saddle point and minima. The kinetics of direct transitions were considered for the first time in [15] using previously obtained results [24–26] for the nucleation in vapor binary mixtures. We will also use these results; moreover, we are first interested in understanding how changes in the chemical potential of undersaturated vapor of solvent will affect the vicinity of the saddle point and minima of the work of droplet formation.

The work of droplet formation $F(v, v'_n)$ in the vicinity of minima and saddle point at partially dissolved condensation nucleus can be approximated by the quadratic form [15]

$$F = F_{e,c} + \frac{1}{2} \left[\frac{\partial^2 F}{\partial v^2} \right]_{e,c} (v - v_{e,c})^2 + \left[\frac{\partial^2 F}{\partial v \partial v'_n} \right]_{e,c} (v - v_{e,c}) (v'_n - v'_{n_{e,c}}) + \frac{1}{2} \left[\frac{\partial^2 F}{\partial v_n'^2} \right]_{e,c} (v'_n - v'_{n_{e,c}})^2, \quad (3.1)$$

where subscripts e and c denote the points of the minima and saddle points of the work of droplet formation, respectively. Quadratic form (3.1) can be reduced to the diagonal type

$$F = F_{e,c} + Q_{e,c} (y^{(e,c)})^2 + P_{e,c} (z^{(e,c)})^2, \quad (3.2)$$

In variables $y^{(e,c)}$ and $z^{(e,c)}$, this operation can be carried out using the transformation of the rotation of $v - v_{e,c}$ and $v'_n - v'_{n_{e,c}}$ variables as follows:

$$y^{(e,c)} = (v - v_{e,c}) \cos \varphi_{e,c} + (v'_n - v'_{n_{e,c}}) \sin \varphi_{e,c}, \quad (3.3)$$

$$z^{(e,c)} = -(v - v_{e,c}) \sin \varphi_{e,c} + (v'_n - v'_{n_{e,c}}) \cos \varphi_{e,c}. \quad (3.4)$$

Coefficients $Q_{e,c}$, and $P_{e,c}$ in expression (3.2) and angles $\varphi_{e,c}$ in transformations (3.3) and (3.4) are determined in a standard way using second derivatives of

work $F(v, v'_n)$ of droplet formation by the following relations:

$$Q_{e,c} = \frac{1}{2} \left[\left(\frac{\partial^2 F}{\partial v^2} \right)_{e,c} \cos^2 \varphi_{e,c} + \left(\frac{\partial^2 F}{\partial v \partial v'_n} \right)_{e,c} \sin 2\varphi_{e,c} + \left(\frac{\partial^2 F}{\partial v_n'^2} \right)_{e,c} \sin^2 \varphi_{e,c} \right], \quad (3.5)$$

$$P_{e,c} = \frac{1}{2} \left[\left(\frac{\partial^2 F}{\partial v^2} \right)_{e,c} \sin^2 \varphi_{e,c} - \left(\frac{\partial^2 F}{\partial v \partial v'_n} \right)_{e,c} \sin 2\varphi_{e,c} + \left(\frac{\partial^2 F}{\partial v_n'^2} \right)_{e,c} \cos^2 \varphi_{e,c} \right], \quad (3.6)$$

$$\operatorname{tg} 2\varphi_{e,c} = \frac{2 \left(\frac{\partial^2 F}{\partial v \partial v'_n} \right)_{e,c}}{\left(\frac{\partial^2 F}{\partial v^2} \right)_{e,c} - \left(\frac{\partial^2 F}{\partial v_n'^2} \right)_{e,c}}. \quad (3.7)$$

Let us study the dependence of coefficients $Q_{e,c}$ and $P_{e,c}$ on dimensionless chemical potential of vapor b . Dependences of coefficients $Q_{e,c}$ and $P_{e,c}$ on the chemical potential of vapor b in the vicinity of threshold value $b = b_m$ is presented in Fig. 8. When plotting curves in Fig. 8, we used expressions (3.5)–(3.7) and relations (1.1)–(1.5) the values of parameters of which were taken for points $v = v(b)$ and $v'_n = v'_n(b, v(b))$, corresponding to curves in Figs. 2 and 3 upon consecutive transition from large to small v'_n values. Note that Q_e and Q_c curves, as well as P_e and P_c curves, are joined at the threshold value $b = b_m$ of the chemical potential of vapor.

It was shown [24–26] that squared variables with positive coefficients in diagonal expression (3.2) describing the state of near-critical droplet in the vicinity of saddle point remain stable upon changes in the state of droplet. This means that the droplet tends to return to the equilibrium state after the deviation of this variable from equilibrium value (equals zero in this case). The negative sign of coefficient before the square of description variable implies that this variable is unstable in the process of transition; i.e., the transition proceeds in the direction of this variable change. It is evident that, in the vicinity of the minimum of work of droplet formation upon the incomplete dissolution of nucleus in the droplet, both description variables of droplet state are stable.

It can be seen from Fig. 8 that, in the range of b_m to b_u , coefficient $Q_c < 0$, whereas $P_c > 0$. With allowance for expression (3.2), we can conclude that, in this range of chemical potential, $y^{(c)}$ is a thermodynamically

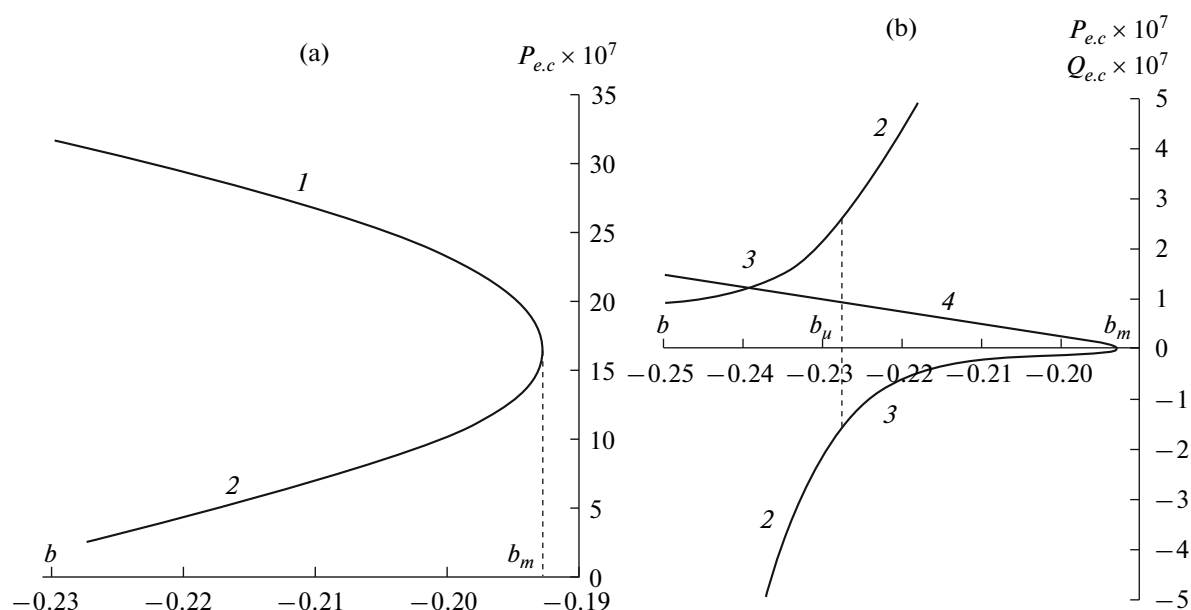


Fig. 8. Dependences of (1) P_e , (2) P_c , (3) Q_c , and (4) Q_e coefficients on vapor chemical potential b at $R_n = 15$ nm and $v_n = 7.068 \times 10^5$.

cally unstable description variable of the state of near-critical droplet in the course of direct and reverse transitions of droplet over the activation barrier, while $z^{(c)}$ remains thermodynamically stable description variable during these transitions.

Let us now consider the behavior of coefficients Q_c and P_c at the $b \leq b_i$ values of vapor chemical potential; i.e., at much lower values than the threshold $b = b_m$ value. As can be seen from Fig. 8, in the $b = b_u$ point ($b_i \leq b_u$), a jump in the Q_c and P_c coefficients takes place. The values of both coefficients reverse their signs while passing through $b = b_u$ point: coefficient Q_c

becomes positive in the $b < b_u$ region, whereas it was negative in the $b_u < b \leq b_m$ range; on the contrary, coefficient P_c is negative in the $b < b_u$ region, whereas it was positive at $b_u < b \leq b_m$. Thus, we can conclude that the description variables of the state of near-critical droplet, $y^{(c)}$ and $z^{(c)}$, change their roles when the chemical potential of vapor passes $b = b_u$ values. The description variable $y^{(c)}$ of the state of near-critical droplet becomes thermodynamically stable, whereas variable $z^{(c)}$ becomes thermodynamically unstable upon direct and reverse transitions over barrier in the $b < b_u$ region. Previously, this feature of the behavior of the work of droplet formation was not noted.

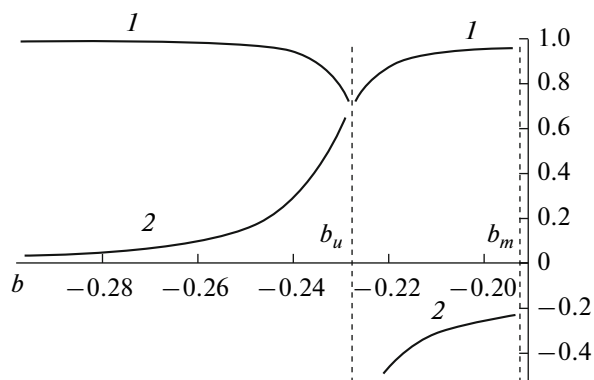


Fig. 9. Dependences of (1) $\cos \varphi_c$ and (2) $\sin \varphi_c$ coefficients of linear transformations (3.3) and (3.4) on vapor chemical potential b at $R_n = 15$ nm and $v_n = 7.068 \times 10^5$.

Let us now consider the physical meaning of variables $y^{(c)}$ and $z^{(c)}$. Figure 9 presents the dependences of coefficients $\cos \varphi_c$ and $\sin \varphi_c$ of linear transformations (3.3) and (3.4) on the chemical potential of vapor, b , plotted with the aid of expression (3.7) and allowance for relations (1.1)–(1.5) and curves shown in Figs. 2 and 3. It can be seen from Fig. 9 that, at the values of chemical potential b close to b_m , variable $y^{(c)}$ nearly coincides with $v - v_c$, while variable $z^{(c)}$ coincides with $v'_n - v'_{nc}$. At significant deviations of b from b_m and $b > b_u$, the situation is different; however, at $b < b_u$, variable $y^{(c)}$ once again gradually approaches $v - v_c$ and $z^{(c)}$ tends to $v'_n - v'_{nc}$. Thus upon the direct transition of near-critical droplet in the vicinity of

$b = b_m$, the approximate number of condensate molecules becomes an unstable variable, whereas the number of molecules in the remaining part of nucleus becomes stable variable. Upon the reverse transition, at $b < b_u$, the opposite situation is observed, i.e., the unstable variable is the approximate number of molecules in the crystalline nucleus and the number of condensate molecules in the droplet becomes a stable variable.

Taking into account the information presented in Section 2 on the behavior of activation barriers for direct and reverse transitions of the droplet, the following conclusion can be formulated. The change in the roles of description variables of the state of the droplet in a physical sense matches the change (with a decrease in the chemical potential of vapor b below its threshold value b_m) from the mechanism of heterogeneous nucleation of droplets on condensation nuclei in the vapor (the direct transition with relatively slow dissolution of nuclei in droplets and fast growth of droplet sizes) to the homogeneous crystallization of nuclei in droplets composed of supersaturated solution (the reverse transition with relatively fast formation of nuclei and slow decrease in droplet sizes).

ACKNOWLEDGMENTS

This work was supported by the Federal Program "Development of Scientific Potential of Higher Education (2009–2010)," project no. RNP.2.1.1.4430. I.V. Shabaev would like to acknowledge the Russian Foundation for Basic Research, project no. 09-03-01005-a and the St. Petersburg Government, project no. 2.4/04-05/092.

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