

# Thermodynamics of droplet formation around a soluble condensation nucleus in the atmosphere of a solvent vapor

A. K. Shchekin,<sup>a)</sup> I. V. Shabaev, and A. I. Rusanov  
*St. Petersburg State University, St. Petersburg 198504, Russia*

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An expression for the work of formation of a spherical droplet condensing on a soluble condensation nucleus out of a solvent vapor is derived. The dependence of the formation work on the solvent vapor chemical potential and the droplet and the nucleus residue sizes is analyzed. The balance of the solute matter between the liquid film and the nucleus residue and the effect of overlapping the surface layers of the thin film have been taken into account. It is shown that the equations of the chemical equilibrium of a solute and a solvent in the droplet, resulting from the generating properties of the formation work, coincide with the generalized Gibbs–Kelvin–Köhler and Ostwald–Freundlich equations. The numerical solution of these equations at a fixed number of molecules of the nucleus matter (at an initial size of the nucleus specified) has been performed in the case of the solvent vapor undersaturated over the bulk liquid solvent phase. The solution links the equilibrium sizes of the droplet and the soluble nucleus residue with the chemical potential or the pressure of the solvent vapor saturated over the droplet. It also determines the limiting sizes of the droplet with small nucleus residue above which the chemical equilibrium of the residue surface and the solution film does not exist. The existence of the limiting sizes is responsible for the specific behavior of the droplet thermodynamic characteristics and the work of droplet formation at deliquescence transition from the droplet state with a partly dissolved nucleus to the state of complete dissolution of the nucleus. © 2008 American Institute of Physics. [DOI: 10.1063/1.3021078]

## I. INTRODUCTION

The initial stage of nucleation on soluble solid particles in the atmosphere of a solvent vapor with formation of droplets consisting of the liquid solution film around incompletely dissolved particles (the deliquescence stage) attracted recently a considerable attention of experimentalists.<sup>1–4</sup> In the case of the solvent vapor undersaturated over the bulk liquid solvent phase, the experiments<sup>1–4</sup> reported a hysteresis behavior of isotherms for the solvent vapor pressure versus droplet size at a fixed initial radius of the condensation nucleus and existence of the deliquescence (associated with a dissolution) and efflorescence (associated with a crystallization) thresholds for transitions between the droplet states with partially and completely dissolved condensation nucleus.

In the atmosphere of a supersaturated solvent vapor, soluble solid particles serving as condensation nuclei dissolve completely in growing supercritical droplets on subsequent nucleation stages. However, the deliquescence stage is the only stage of nucleation in the atmosphere of the undersaturated solvent vapor. This stage finishes with establishing the aggregative equilibrium between nucleated droplets with partially and completely dissolved condensation nuclei.

The theory of the deliquescence stage has been considered in the literature within the frameworks of one-dimensional<sup>5–7</sup> and two-dimensional<sup>8–13</sup> approaches. The one-dimensional approach assumes that the solute equilib-

rium between the surface of the condensation nucleus residue and the liquid solution film within a droplet establishes faster than the droplet radius changes in the nucleation process through the chain of intermediate equilibria. If the temperature and the initial size of a condensation nucleus are fixed, the intermediate equilibrium state of the droplet and the corresponding nucleus residue can be characterized with the help of a single variable. It may be, for instance, the droplet radius.

The two-dimensional approach is more general because it admits that the solute equilibrium between the surface of the nucleus residue and the surrounding solution film may be not reached for larger (critical or supercritical) droplets for thermodynamic or kinetic reasons. We need two independent variables (for instance, the radii of the droplet itself and of the nucleus residue inside it) to describe thermodynamic peculiarities of the droplet formation in this case.<sup>10</sup> A corresponding nucleation path may also be different from the equilibrium one.

Relying upon the previous deliquescence theory<sup>5–10</sup> and the results<sup>14–16</sup> on the chemical potential at the surface of a solid nanoparticle, we will reconsider in this paper the thermodynamics of formation of a droplet with a spherical solution film on a soluble solid nucleus in the atmosphere of a solvent vapor. The paper continues the investigation started in Ref. 17. We will present a new analysis of a two-dimensional expression for the minimal work of formation of a solution film around a nucleus residue with focusing on the case of a droplet with a thin film (when the properties of the bulk liquid phase are not reached within the film) and a large

<sup>a)</sup>Electronic mail: akshch@list.ru.

nucleus residue and the case of a droplet with a thick film and a small nucleus residue. We will show that the equations of the equilibrium with respect to a solute and a solvent in the droplet, resulting from the generating properties of the nucleation work, coincide with the generalized Gibbs–Kelvin–Köhler and Ostwald–Freundlich equations derived in Ref. 17 for an equilibrium spherical liquid film of solution on a soluble nanoparticle with account of the disjoining pressure of the film. A numerical solution of these equations at a fixed number of molecules of the nucleus matter (at an initial size of the nucleus specified) will be performed to describe explicitly the dependence of thermodynamic nucleation characteristics on the film thickness and the nucleus residue size. The list of such characteristics includes the chemical potentials of a solvent and a solute in the solution film, the solvent saturated vapor chemical potential, and the solvent saturated vapor pressure. The numerical solution will allow us to determine the limiting sizes of the droplet above which the chemical equilibrium of the nucleus residue surface and the solution film does not exist. It will be shown that the existence of the limiting sizes is responsible for the specific behavior of the droplet thermodynamic characteristics and the work of droplet formation at deliquescence transition from the droplet state with a partly dissolved nucleus to the state of complete dissolution of the nucleus and provides a thermodynamic reason for the two-dimensional nucleation theory of the deliquescence stage.

## II. WORK OF DROPLET FORMATION ON A PARTIALLY DISSOLVING CONDENSATION NUCLEUS

Let us consider a closed system in its initial state with a solid spherical condensation nucleus of nonvolatile one-component matter and the vapor of another component within a given volume  $V$  at an absolute temperature  $T$ . The vapor can condense on the nucleus surface to form an enveloping liquid film where the matter of the nucleus is soluble. We also consider the final state of the system (at the same values of  $V$  and  $T$ ) with a droplet consisting of a solution film around the partially dissolved nucleus residue in the atmosphere of the solvent vapor. Our first goal is finding an expression for the minimal work required for heterogeneous formation of such a droplet.

In the case under consideration, the formation work  $W$  is determined through the difference between the free energies  $\Phi_2$  and  $\Phi_1$  of the whole system in its final and initial states as follows:

$$W \equiv \Phi_2 - \Phi_1. \quad (1)$$

The free energy  $\Phi_1$  can be written as

$$\Phi_1 = \mu^\beta N + \mu_n \nu_n + \Omega_1, \quad (2)$$

where  $\mu^\beta$  is the vapor chemical potential of solvent molecules,  $N$  is the total number of the solvent molecules,  $\mu_n$  is the chemical potential of molecules of the matter inside the solid nucleus in its initial state when the number of these molecules equals  $\nu_n$ , and  $\Omega_1$  is the grand thermodynamic potential of the whole system in its initial state. The system free energy  $\Phi_2$  in the final stage can be written in a similar way,

$$\Phi_2 = \mu^\beta(N - \nu) + \mu_\nu \nu + \mu'_n \nu'_n + \mu_n^\alpha(\nu_n - \nu'_n) + \Omega_2, \quad (3)$$

where  $\nu$  is the number of solvent molecules condensed in the droplet out of the vapor,  $\mu_\nu$  and  $\mu_n^\alpha$  are the chemical potentials of the solvent and solute molecules in the liquid solution film, respectively,  $\mu'_n$  and  $\nu'_n$  are the solute chemical potential and the number of solute molecules inside the solid nucleus residue, respectively, and  $\Omega_2$  is the grand thermodynamic potential of the whole system at its final state. It is admitted in Eq. (3) that the droplet formation affects negligibly the solvent vapor chemical potential  $\mu^\beta$ . This fulfills for a sufficiently large system.

Assuming the shapes of a condensation nucleus and its residue to be spherical and using Gibbs' approach to interfaces, we can represent the grand potentials  $\Omega_1$  and  $\Omega_2$  of the system in its initial and final states as

$$\Omega_1 = f^\gamma V_1^\gamma - p^\beta(V - V_1^\gamma) + 4\pi R_n^2 \sigma^{\gamma\beta} - \mu_n \nu_n, \quad (4)$$

$$\Omega_2 = f^\gamma V_2^\gamma - p^\beta(V - V_R) - p^\alpha(V_R - V_2^\gamma) - \mu'_n \nu'_n + 4\pi R_n'^2 \sigma^{\alpha\gamma} + 4\pi R^2 \sigma^{\alpha\beta} + \Omega_{II}, \quad (5)$$

where  $f^\gamma$  is the density of the free energy of the solute in the solid state (this quantity does not vary at dissolving a rigid solid),  $V_1^\gamma$  and  $V_2^\gamma$  are the volumes of the initial solid nucleus and its residue in the droplet, respectively,  $V_R = V_2^\gamma + V^\alpha$  is the total volume of the droplet, and  $V^\alpha$  is the volume of the liquid solution film. The superscripts  $\alpha$ ,  $\beta$ , and  $\gamma$  refer to the liquid, gas, and solid phases, respectively, whereas the double superscripts  $\gamma\beta$ ,  $\gamma\alpha$ , and  $\alpha\beta$  refer to the interfaces between corresponding phases. We consider the solvent vapor pressure  $p^\beta$  (as well as the chemical potential  $\mu^\beta$ ) be the same in the initial and final states of the system. The quantities  $\sigma^{\gamma\beta}$ ,  $\sigma^{\gamma\alpha}$ , and  $\sigma^{\alpha\beta}$  in Eqs. (4) and (5) are the surface tensions at the corresponding interfaces;  $4\pi R_n^2$ ,  $4\pi R_n'^2$ , and  $4\pi R^2$  are the surface areas of the spherical surfaces with the radii  $R_n \equiv R^{\beta\gamma}$ ,  $R_n' \equiv R^{\alpha\gamma}$ , and  $R \equiv R^{\alpha\beta}$ , respectively, and  $p^\alpha$  is the pressure in the bulk liquid solution at the same values of the chemical potentials  $\mu_\nu$  and  $\mu_n^\alpha$  as in the solution film around the nucleus residue. The pressure  $p^\alpha$  does not coincide with the pressure in the film if the film is thin and the opposite surface layers overlap.<sup>17–20</sup> The effect of surface layers overlapping is also taken into account by the last term  $\Omega_{II}$  in Eq. (5). An explicit form of the term will be revealed below.

Let us introduce the quantity

$$x = \frac{\nu_n - \nu'_n}{\nu}. \quad (6)$$

With neglecting adsorption on the opposite film sides, the quantity  $x$  coincides with the relative concentration in the bulk solution at the same values of the chemical potentials  $\mu_\nu$  and  $\mu_n^\alpha$  of the solvent and solute as in the film around the nucleus residue. Neglecting adsorption also means the independence of surface tensions  $\sigma^{\gamma\alpha}$  and  $\sigma^{\alpha\beta}$  from the solution concentration.

The partial molecular volumes  $\nu^\alpha$  and  $\nu_n^\alpha$  of the solvent and solute in the solution are determined by the following relations:

$$\left(\frac{\partial \mu_\nu}{\partial p^\alpha}\right) = v^\alpha, \quad \left(\frac{\partial \mu_n^\alpha}{\partial p^\alpha}\right) = v_n^\alpha. \quad (7)$$

Assuming the liquid phase to be incompressible, we may neglect the dependence of the partial volumes  $v^\alpha$  and  $v_n^\alpha$  on concentration  $x$  and pressure  $p^\alpha$ . For a nonvolatile solute with a negligible adsorption at the film boundaries, the number  $\nu$  of solvent molecules in a droplet with a partially dissolved condensation nucleus can be related to the droplet volume  $V_R$ , the volume  $V_2^\gamma$  of the nucleus residue, the partial volumes  $v^\alpha$  and  $v_n^\alpha$ , the numbers  $\nu_n$  and  $\nu_n'$  of the solute molecules in the nucleus and its residue as

$$\nu = [V_R - V_2^\gamma - v_n^\alpha(\nu_n - \nu_n')]/v^\alpha. \quad (8)$$

With the spherical form of a droplet, a nucleus and its residue, we have

$$V_R = \frac{4\pi}{3}R^3, \quad V_1^\gamma = \frac{4\pi}{3}R_n^3, \quad V_2^\gamma = \frac{4\pi}{3}R_n'^3, \quad (9)$$

$$\nu_n = \frac{4\pi R_n^3}{3v_n}, \quad \nu_n' = \frac{4\pi R_n'^3}{3v_n}. \quad (10)$$

Using Eqs. (9) and (10) together with Eqs. (8) and (6) determines a relation between  $\nu$ ,  $\nu_n$ ,  $\nu_n'$ , and  $x$  and radii  $R$ ,  $R_n$ ,  $R_n'$ .

For weakly compressible solutions, the solvent and solute chemical potentials  $\mu_\nu$  and  $\mu_n^\alpha$  can be represented as functions of pressure  $p^\alpha$  and concentration  $x$  by the following relations:<sup>21</sup>

$$\mu_\nu(p^\alpha, x) = \mu_\infty - k_B T x + v^\alpha(p^\alpha - p_\infty), \quad (11)$$

$$\mu_n^\alpha(p^\alpha, x) = \mu_{n^\infty}^\alpha + k_B T \ln \frac{x}{x_\infty} + v_n^\alpha(p^\alpha - p_\infty), \quad (12)$$

where  $\mu_\infty$  and  $p_\infty$  are the values of the solvent chemical potential and the saturated vapor pressure over a flat surface of a pure solvent, respectively,  $\mu_{n^\infty}^\alpha$  and  $x_\infty$  are the values of the solute chemical potential and concentration, respectively, in the solution saturated over a flat surface of the solid phase of a pure solute at the same pressure  $p_\infty$ , and  $k_B$  is the Boltzmann constant. The value  $\mu_{n^\infty}^\alpha$  equals the value  $\mu_{n^\infty}$  of the solute chemical potential in the solid phase<sup>15,16</sup> and is related to the solid free energy density  $f^\gamma$  as

$$\mu_{n^\infty}^\alpha = \mu_{n^\infty} = v_n(f^\gamma + p_\infty). \quad (13)$$

Substituting Eqs. (11)–(13) into Eqs. (2)–(5) and recognizing Eqs. (1), (9), and (10), lead to the following expression for the work of droplet formation around a partly dissolved condensation nucleus:

$$\begin{aligned} W = & -\nu(\mu^\beta - \mu_\infty) - k_B T \nu x + k_B T (\nu_n - \nu_n') \ln \frac{x}{x_\infty} \\ & + 4\pi R_n'^2 \sigma^{\gamma\alpha} + 4\pi R^2 \sigma^{\alpha\beta} - 4\pi R_n^2 \sigma^{\gamma\beta} + \Omega_{\text{II}} \\ & + (V_R - V_{R_n})(P^\beta - P_\infty). \end{aligned} \quad (14)$$

The term  $\Omega_{\text{II}}$  in Eq. (14) stands for the contribution of the disjoining pressure of a thin liquid film with overlapping surface layers.<sup>18</sup> The disjoining pressure  $\Pi$  may be defined

for a spherical liquid film with the inner and outer radii  $R_n'$  and  $R$  as<sup>20</sup>

$$\Pi \equiv p_N(R_n', h) - p^\alpha, \quad (15)$$

where  $p_N$  is the normal component of the film pressure tensor, and  $h \equiv R - R_n'$  is the thickness of the film. Using an analogy with the case of a spherical one-component film on a wettable substrate and neglecting the dependence of the disjoining pressure on the concentration of the weak solution, the term  $\Omega_{\text{II}}$  can be written in the following form:<sup>22,23</sup>

$$\Omega_{\text{II}} = 4\pi R_n'^2 \int_{R-R_n'}^{\infty} \Pi dh. \quad (16)$$

It is recognized in Eq. (16) that the substrate and droplet surfaces are the concentric spheres with radii  $R_n'$  and  $R$ .

Substituting Eq. (16) into Eq. (14), taking into account Eq. (6), and neglecting term  $(V_R - V_1^\gamma)(p^\beta - p_\infty)$  as relatively small with respect to other contributions in Eq. (14), we obtain the final expression for the formation work  $W$ ,

$$\begin{aligned} W = & -\nu(\mu^\beta - \mu_\infty) + k_B T (\nu_n - \nu_n') \left( \ln \frac{x}{x_\infty} - 1 \right) \\ & + 4\pi R_n'^2 \sigma^{\gamma\alpha} + 4\pi R^2 \sigma^{\alpha\beta} - 4\pi R_n^2 \sigma^{\gamma\beta} \\ & + 4\pi R_n'^2 \int_{R-R_n'}^{\infty} \Pi dh. \end{aligned} \quad (17)$$

Evidently, we have  $R_n' = 0$  and  $\nu_n' = 0$  in the case of complete dissolution of the condensation nucleus in the droplet. As follows from Eq. (16),  $\Omega_{\text{II}} = 0$  in this case and we can rewrite Eq. (17) in the following form:

$$\begin{aligned} W = & -\nu(\mu^\beta - \mu_\infty) + k_B T \nu_n \left( \ln \frac{x}{x_\infty} - 1 \right) + 4\pi R^2 \sigma^{\alpha\beta} \\ & - 4\pi R_n^2 \sigma^{\gamma\beta}, \end{aligned} \quad (18)$$

which is known in the theory on nucleation on completely soluble nuclei.

Another limiting situation is realized in the case of an insoluble condensation nucleus. Setting  $\nu_n' = \nu_n$  and  $R_n' = R_n$ , we have  $x = 0$  in accordance with Eq. (6). Then Eq. (17) reduces, in the case of an insoluble condensation nucleus, to the following form:<sup>22,23</sup>

$$\begin{aligned} W = & -\nu(\mu^\beta - \mu_\infty) + 4\pi R^2 \sigma^{\alpha\beta} + 4\pi R_n^2 (\sigma^{\alpha\gamma} - \sigma^{\gamma\beta}) \\ & + 4\pi R_n^2 \int_{R-R_n}^{\infty} \Pi(h) dh. \end{aligned} \quad (19)$$

### III. GENERATING PROPERTIES OF THE FORMATION WORK: THE GENERALIZED GIBBS–KELVIN–KÖHLER AND OSTWALD–FREUNDLICH EQUATIONS

The work of the droplet formation possesses generating properties in the thermodynamics of nucleation because the work is expressed via the difference of thermodynamic potentials for the initial and final states of a system. For example, the partial derivatives of work  $W$  with respect to the solvent molecular number  $\nu$  (at a fixed number  $\nu_n'$  of mol-

ecules in the nucleus residue) and with respect to  $\nu'_n$  (at a fixed  $\nu$ ) equal the chemical potential differences  $\mu_\nu - \mu^\beta$  and  $\mu'_n - \mu_n^\alpha$ ,

$$\left. \frac{\partial W}{\partial \nu} \right|_{\nu'_n} = \mu_\nu - \mu^\beta, \quad \left. \frac{\partial W}{\partial \nu'_n} \right|_{\nu} = \mu'_n - \mu_n^\alpha. \quad (20)$$

Let us use Eq. (17) in the first of Eqs. (20). As was already mentioned in the preceding section, we assume partial volumes  $v^\alpha$  and  $v_n^\alpha$ , surface tensions  $\sigma^{\alpha\gamma}$  and  $\sigma^{\alpha\beta}$ , and the disjoining pressure  $\Pi$  to be independent of the solution relative concentration  $x$ . We also neglect the dependence of  $\sigma^{\alpha\gamma}$  on the nucleus residue radius and the dependence of  $\sigma^{\alpha\beta}$  on the droplet radius. By differentiating work  $W$  with respect to  $\nu$  and taking account of Eqs. (6) and (8)–(10), we obtain from Eq. (20)

$$\mu_\nu = \mu_\infty - k_B T x + \frac{2\sigma^{\alpha\beta} v^\alpha}{R} - \frac{R_n'^2}{R^2} \Pi v^\alpha. \quad (21)$$

As it should be expected, the right-hand side of Eq. (21) coincides with the expression for the solvent chemical potential in the droplet [Eq. (22) in Ref. 17]. One can also derive Eq. (21) from Eq. (11) by neglecting the relatively small term  $v^\alpha(P^\alpha - P_\infty)$  and accounting for the condition of mechanical equilibrium for a spherical film with the inner radius  $R_n'$  and the outer radius  $R$  as<sup>20</sup>

$$p^\alpha = p^\beta + \frac{2\sigma^{\alpha\beta}}{R} - \frac{R_n'^2}{R^2} \Pi. \quad (22)$$

Similarly, using Eq. (17) in the second of Eqs. (20), differentiating work  $W$  with respect to  $\nu'_n$ , and taking account of Eqs. (6) and (8)–(10), we have

$$\begin{aligned} \mu'_n - \mu_n^\alpha &= \frac{2\sigma^{\gamma\alpha} v_n}{R_n'} + \frac{2\sigma^{\alpha\beta}(v_n - v_n^\alpha)}{R} - k_B T \ln \frac{x}{x_\infty} \\ &+ \frac{2v_n}{R_n'} \int_{R-R_n'}^{\infty} \Pi dh + \Pi \left[ v_n - \frac{R_n'^2}{R^2} (v_n - v_n^\alpha) \right]. \end{aligned} \quad (23)$$

If a diffusion equilibrium is attained for a solute within the liquid film and at the solid surface of a nucleus residue and for a solvent in the droplet and in the vapor, one has  $\mu'_n = \mu_n^\alpha$  and  $\mu_\nu = \mu^\beta$ . In accordance with Eq. (20), the extreme work conditions

$$\frac{\partial W}{\partial \nu} = 0, \quad \frac{\partial W}{\partial \nu'_n} = 0 \quad (24)$$

are the diffusion equilibrium conditions in terms of the variables  $\nu$  and  $\nu'_n$ . In view of Eq. (24), following from Eqs. (21) and (23) equations

$$-\mu^\beta + \mu_\infty - k_B T x + \frac{2\sigma^{\alpha\beta} v^\alpha}{R} - \frac{R_n'^2}{R^2} \Pi v^\alpha = 0, \quad (25)$$

$$\begin{aligned} \frac{2v_n}{R_n'} \left( \sigma^{\gamma\alpha} + \int_{R-R_n'}^{\infty} \Pi dh \right) - \frac{2\sigma^{\alpha\beta}(v_n - v_n^\alpha)}{R} - k_B T \ln \frac{x}{x_\infty} \\ + \Pi \left[ v_n - \frac{R_n'^2}{R^2} (v_n - v_n^\alpha) \right] = 0 \end{aligned} \quad (26)$$

determine, with the help of Eqs. (6) and (8)–(10), couples of values of  $\nu$  and  $\nu'_n$  corresponding to minima and the saddle point for the work  $W$  of the droplet formation at a given value  $\mu^\beta$  of the solvent vapor chemical potential and a given initial amount  $\nu_n$  of the nucleus matter (at a given initial radius  $R_n$  of the nucleus). The analysis of numerical solutions of these equations will be given in Sec. V.

With the equality,

$$\mu^\beta - \mu_\infty = k_B T \ln \frac{p^\beta}{p_\infty}, \quad (27)$$

Eq. (25) can be transformed into the generalized Gibbs–Kelvin–Köhler equation of the theory of nucleation on soluble particles [Eq. (32) in Ref. 17]. Equation (26) is a generalization of the Ostwald–Freundlich equation of the theory of solutions [Eq. (30) in Ref. 17] and yields the dependence of the solubility of the nucleus residue on its size and the droplet size. With account of Eq. (6) for concentration  $x$  as a function of  $\nu$  and  $\nu'_n$ , Eq. (26) establishes a relation between  $\nu$  and  $\nu'_n$  (or between  $R$  and  $R_n'$ ) at the diffusion equilibrium between the nucleus matter in the droplet and the nucleus residue surface. The fact that Eqs. (24) yield correct equations of diffusion equilibrium with respect both to a solute and a solvent gives a confirmation of results obtained in Ref. 17 and exhibits the thermodynamic consistency of Eq. (17) for the work of formation of a droplet on a soluble nucleus.

#### IV. DROPLET FORMATION WORK AT EXPONENTIAL APPROXIMATION OF DISJOINING PRESSURE

As an analytical representation of the disjoining pressure  $\Pi$  as a function of the film thickness  $h \equiv R - R_n'$ , we will use an exponential approximation<sup>19,22–24</sup> for the structural component of the disjoining pressure,

$$\Pi = K \exp\left(-\frac{R - R_n'}{l}\right). \quad (28)$$

Here  $l$  is a parameter called the correlation length in the solution film around the nucleus residue. The pre-exponential multiplier  $K$  is related to the surface tensions  $\sigma^{\gamma\beta}$ ,  $\sigma^{\alpha\gamma}$ , and  $\sigma^{\alpha\beta}$  and to the correlation length  $l$  as<sup>24</sup>

$$K = \frac{\sigma^{\gamma\beta} - \sigma^{\alpha\gamma} - \sigma^{\alpha\beta}}{l}. \quad (29)$$

Since, as was mentioned above, we consider the case when dependence of the disjoining pressure on the solution concentration is negligible, we assume parameters  $l$  and  $K$  to be independent of the solution concentration.

Using Eq. (28), we rewrite the droplet formation work [Eq. (17)] as



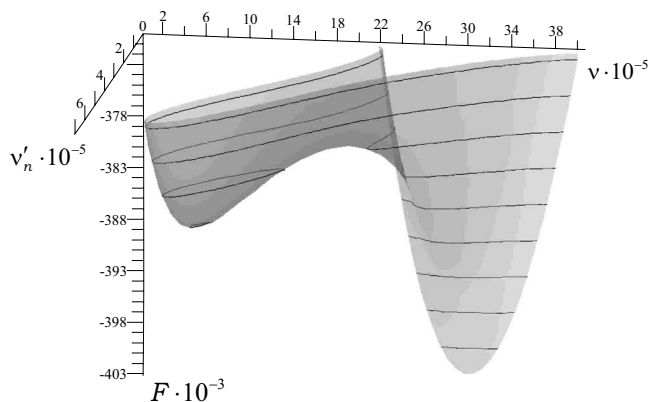


FIG. 1. The two-dimensional work  $F$  of the droplet formation on a soluble nucleus in an undersaturated vapor at the vapor chemical potential  $b = -0.2$ .

$$\begin{aligned}
 W = & -\nu(\mu^\beta - \mu_\infty) + k_B T(\nu_n - \nu'_n) \left( \ln \frac{x}{x_\infty} - 1 \right) \\
 & + 4\pi R_n'^2 \sigma^{\gamma\alpha} + 4\pi R^2 \sigma^{\alpha\beta} - 4\pi R_n^2 \sigma^{\gamma\beta} \\
 & + 4\pi R_n'^2 l K \exp\left(-\frac{R - R_n'}{l}\right). \quad (30)
 \end{aligned}$$

Herein after, it is convenient to deal with the dimensionless droplet formation work,

$$F \equiv W/k_B T, \quad (31)$$

the dimensionless vapor chemical potential,

$$b \equiv (\mu^\beta - \mu_\infty)/k_B T, \quad (32)$$

and the dimensionless condensate chemical potential,

$$b_\nu \equiv (\mu_\nu - \mu_\infty)/k_B T. \quad (33)$$

To perform calculations, we determine the numerical values of the parameters in Eq. (30) as

$$\begin{aligned}
 R_n = 15 \text{ nm}, \quad \nu_n = 0.02 \text{ nm}^3, \quad \nu^\alpha = 0.03 \text{ nm}^3, \\
 \nu_n^\alpha = 0.022 \text{ nm}^3, \quad T = 298 \text{ K}, \\
 \sigma^{\alpha\gamma} = 200 \text{ mJ m}^{-2}, \quad \sigma^{\alpha\beta} = 72 \text{ mJ m}^{-2}, \quad x_\infty = 0.2, \quad (34)
 \end{aligned}$$

$$l = 2 \text{ nm}, \quad K = 3 \times 10^8 \text{ Pa}.$$

These values are taken for a realistic solid condensation nucleus and water as a condensate.

The surface of the work  $F$  constructed, according to Eqs. (30), (31), and (8)–(10) and the data from Eq. (34), in variables  $\nu$  and  $\nu'_n$  is presented in Figs. 1 and 2 at  $\nu_n = 7.068 \times 10^5$  for two values of the vapor chemical potential:  $b = -0.2$  and  $b = -0.25$ . The relief depicted in Figs. 1 and 2 shows a trajectory of transition of a growing droplet from the state of equilibrium between the liquid film, the vapor, and the surface of a partly dissolved nucleus to the state of equilibrium of the droplet with its vapor at complete dissolution of the nucleus. Two points of minima and the saddle point of the droplet formation work are visible in Figs. 1 and 2. The point of the first minimum of the work  $F$  at a small  $\nu$  corresponds to a droplet with a partly dissolved nucleus being in a stable equilibrium with respect to a solute in the solution

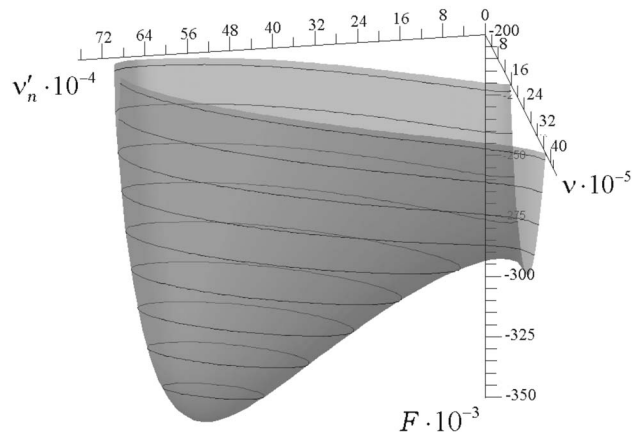
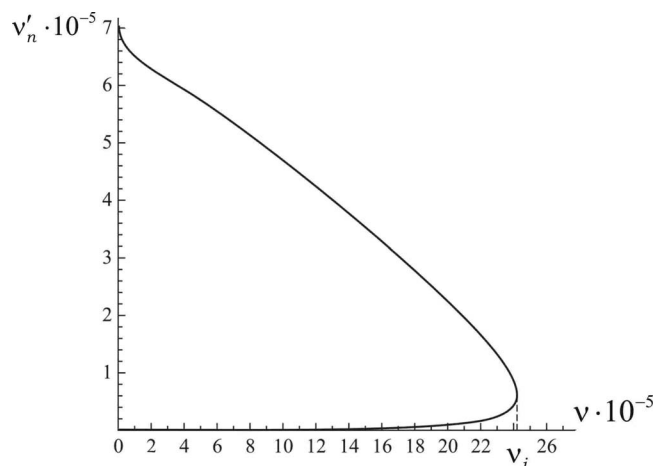


FIG. 2. The two-dimensional work  $F$  of the droplet formation on a soluble nucleus in an undersaturated vapor at the vapor chemical potential  $b = -0.25$ .

film. Along with that, the droplet is in a stable equilibrium with respect to a solvent with the surrounding vapor. The first minimum of the work  $F$  is provided by the overlap of the surface layers within a thin liquid film. If we ignore the disjoining pressure of the film, the first minimum does not exist. The point of the second minimum at  $\nu'_n = 0$  corresponds to a droplet with a completely dissolved nucleus at a stable equilibrium with the vapor with respect to a solvent. The second minimum of the work  $F$  exists due to the effect of decreasing the solvent chemical potential by the presence of a solute. The saddle point of the work  $F$  in Fig. 1 corresponds to a critical droplet with a partly dissolved nucleus in the state of unstable equilibrium with a solvent vapor and stable equilibrium with respect to a solute within the droplet. The saddle point of the work  $F$  in Fig. 2 corresponds to a critical droplet with a partly dissolved nucleus in the state of unstable equilibrium with respect to a solute within the droplet and stable equilibrium with a solvent vapor. Both the figures display the existence of activation barriers for the direct and reverse transitions between the droplet states with a partly and completely dissolved nucleus at the above values of the vapor chemical potential  $b$  and the initial nucleus size  $\nu_n$ . Figure 1 illustrates the situation when the direct transition (the deliquescence transition) occurs with a higher probability and the droplet state with a completely dissolved nucleus is more stable than the state with a partly dissolved nucleus. The opposite situation is shown in Fig. 2 when the reverse transition (the efflorescence transition) is of a higher probability since the state of a droplet with a partly dissolved nucleus is more stable.

## V. BARRIER AND BARRIERLESS FORMATION OF A DROPLET

Let us investigate the behavior of thermodynamic characteristics of stable and unstable equilibrium droplets satisfying the conditions expressed in Eqs. (24), as depending on the solvent vapor chemical potential. Taking into account Eqs. (6) and (28), it is convenient to rewrite the generalized Ostwald-Freundlich equation [Eq. (26)] as

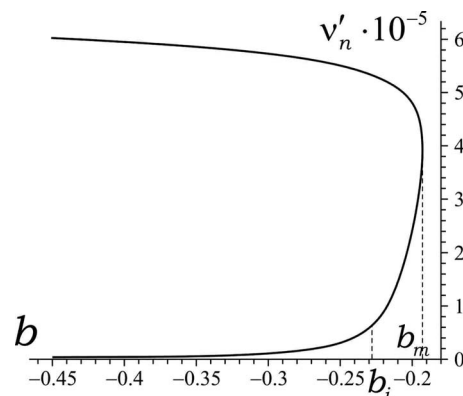
FIG. 3. The equilibrium value of  $\nu'_n$  as a function of  $\nu$ .

$$k_B T \ln \left( \frac{\nu_n - \nu'_n}{\nu x_\infty} \right) = \frac{2\nu_n}{R'_n} \left[ \sigma^{\alpha\gamma} + lK \exp \left( -\frac{R - R'_n}{l} \right) \right] - \frac{2\sigma^{\alpha\beta}(\nu_n^\alpha - \nu_n)}{R} + K \exp \left( -\frac{R - R'_n}{l} \right) \times \left[ \nu_n - \frac{R_n'^2}{R^2} (\nu_n - \nu_n^\alpha) \right]. \quad (35)$$

Note that a parametric dependence on  $\nu_n$  is also present in Eq. (35). A numerical solution of Eq. (35) with the help of Eqs. (8)–(10) and data from Eq. (34) permits the determination of  $\nu'_n(\nu)$  as a function of  $\nu$  at an equilibrium in a droplet between the nucleus residue and the solution film with respect to a solute. The resulting function at  $\nu_n = 7.068 \times 10^5$  is depicted in Fig. 3. It is two-valued and has a reverse point  $\nu = \nu_i$  [ $\nu_i = 2.414 \times 10^6$  and  $\nu'_n(\nu_i) = 62\,289$  in Fig. 3], whereas the inverse function  $\nu(\nu'_n)$  is single-valued and ranged within  $0 < \nu(\nu'_n) < \nu_i$  at any value of the variable  $\nu'_n$  from 0 to  $\nu_n$ . The value  $\nu_i$  grows with increasing  $\nu_n$ . The existence of the reverse point and the two-valuedness of the function  $\nu'_n(\nu)$  mean that, at a fixed  $\nu_n$ , the solution film cannot be in stable or unstable equilibrium with the nucleus residue in the droplet at  $\nu > \nu_i$ .

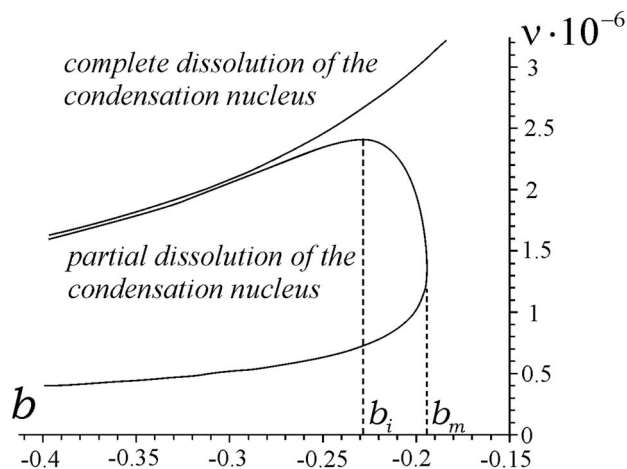
If a value of  $\nu$  is not arbitrary but corresponds to a root of Eq. (25) at a given value of the solvent vapor chemical potential [value of  $b$  in view of Eq. (32)], then different values of  $b$  correspond to different pairs  $\nu'_n$  and  $\nu$  in the curve depicted in Fig. 3. The dependencies of equilibrium values of  $\nu'_n$  and  $\nu$  on  $b$  are shown in Figs. 4 and 5 as obtained from the joint solution of Eqs. (25) and (35) with account of Eqs. (6), (8)–(10), (28), and (34). Note that the dependence  $\nu(b)$  is plotted in Fig. 5 in the region of both partial and complete dissolution of a nucleus in a droplet. Although the curves  $\nu(b)$  in the regions of partial and complete dissolution of a nucleus in a droplet come very close to each other and seem to merge in Fig. 5 at smaller values of the vapor chemical potential  $b$ , they do not intersect in fact.

Another reverse point  $b = b_m$  is seen in Figs. 4 and 5 [ $b_m = -0.19275$ ,  $\nu'_n(b_m) = 3.969 \times 10^5$ ,  $\nu(b_m) = 1.318 \times 10^6$ ], so that there are no stable equilibrium values of  $\nu'_n$  and  $\nu$  at  $b > b_m$  in the region of the partial dissolution of a nucleus, but

FIG. 4. The dependence of the equilibrium value of  $\nu'_n$  on the dimensionless vapor chemical potential  $b$ .

there are stable values of  $\nu$  in the region of the complete dissolution of a nucleus. The quantity  $b_m$  has the meaning of a threshold value<sup>5,7,18</sup> of the chemical potential of an undersaturated vapor for the transition from droplets with a partially dissolved nucleus to droplets with a completely dissolved nucleus, so that the transition is realized barrierlessly at  $b \geq b_m$ . Note that the maximum point in the curve  $\nu(b)$  in the region of a partial dissolution of a nucleus corresponds to the values  $b = b_i$  [ $b_i = -0.228\,92$ ,  $\nu(b_i) = 2.414 \times 10^6$ , and  $\nu'_n(b_i) = 62\,289$ ] indicated in Figs. 4 and 5, whereas the values  $\nu(b_i)$  and  $\nu'_n(b_i)$  themselves coincide with the coordinates  $\nu_i$  and  $\nu'_n(\nu_i)$  of the reverse point in Fig. 3.

The dependence  $\nu(b)$  shown in Fig. 5 may be easily transformed with the help of Eqs. (27) and (8)–(10) into the dependence of the droplet radius on the solvent vapor pressure saturated over the droplet with a given initial radius of the condensation nucleus. Such dependence can be plotted directly from experimental data.<sup>1–4</sup> Figure 6 demonstrate the dependence of the so-called growth factor  $R/R_n$  on the relative humidity (RH)  $\equiv p^\beta/p_\infty^\beta$  of the solvent vapor obtained by the mentioned transformation of Fig. 5. As in Fig. 5, the curves  $R/R_n$  in the regions of partial and complete dissolutions of a nucleus in a droplet come very close to each other and seem to merge in Fig. 6 at smaller values of the RH, but they do not intersect.

FIG. 5. The dependence of the equilibrium value of  $\nu$  on the dimensionless vapor chemical potential  $b$ .

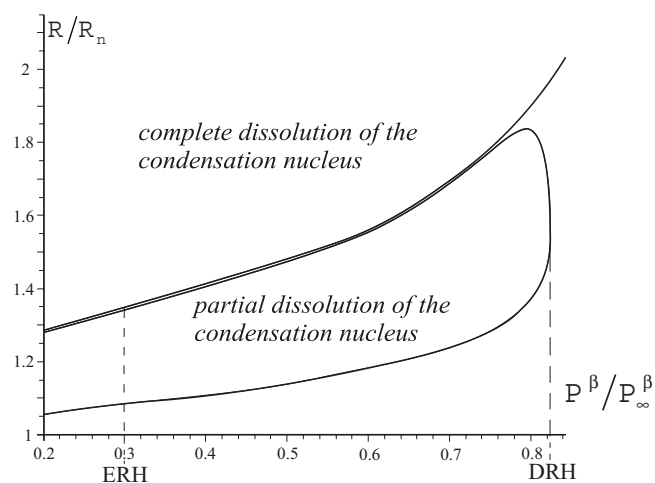


FIG. 6. The growth factor  $R/R_n$  as a function of the relative humidity  $RH \equiv P^\beta/P_\infty^\beta$ .

Let us now comment how the behavior of growth factor versus relative humidity shown in Fig. 6 corresponds to the hysteresis effect found in experiment.<sup>1-4</sup> The hysteresis effect manifests itself in the difference between the humidities at which deliquescence and efflorescence set in. As shown in Fig. 6, the deliquescence relative humidity (DRH) corresponds to the threshold value  $b_m$ . The efflorescence relative humidity (ERH) cannot be obtained from the pure thermodynamic approach presented here. It requires a kinetic consideration of spontaneous crystallization in a droplet which is out of the scope of this paper. As a result of kinetic mechanism, the ERH point lies in Fig. 6 considerably below the value of RH at  $b_i$  (we can set it approximately at  $RH=0.3$ ). Evidently, only the parts of the plot in Fig. 6, which correspond to a stable equilibrium of the droplet with vapor, can be observed in experiment. The branch of the curve  $R/R_n$  vs RH in the region of incomplete nucleus dissolution, which lies below the DRH point, and the branch in the region of complete dissolution, which lies above the ERH point, are such parts.

The values  $b_m$  and  $b_i$  for the vapor chemical potential are important for the description of the barrierless and barrier

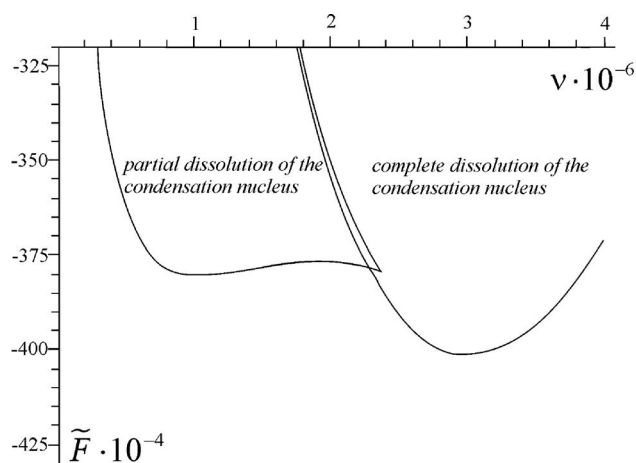


FIG. 7. The plot of the one-dimensional work of droplet formation  $\tilde{F}$  vs  $\nu$  at the vapor chemical potential  $b=-0.2$ .

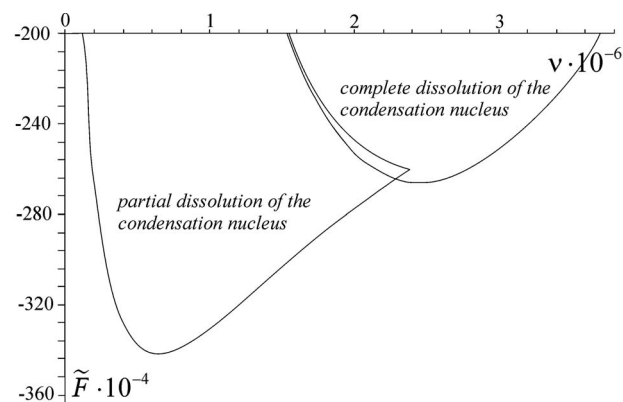


FIG. 8. The plot of the one-dimensional work of droplet formation  $\tilde{F}$  vs  $\nu$  at the vapor chemical potential  $b=-0.25$ .

transitions of droplets between the states with a partially and completely dissolved nucleus. Let us consider the one-dimensional work of formation of a droplet  $\tilde{F} \equiv F[\nu, \nu'_n = \nu'_n(\nu)]$  with molecular number  $\nu'_n$  in the nucleus residue determined as a function of  $\nu$  in accordance with Eq. (35) [i.e., in accordance with the curve  $\nu'_n(\nu)$  plotted in Fig. 3]. At  $\nu'_n \neq 0$   $\tilde{F}$  corresponds to the projection of the “weir line” on the plane  $(F, \nu)$  in Figs. 1 and 2. The  $\tilde{F}$  vs  $\nu$  plots are depicted in Figs. 7-9 for three values of the vapor chemical potential:  $b_m b > b_i$  ( $b=-0.2$ ),  $b < b_i$  ( $b=-0.25$ ), and  $b > b_m$  ( $b=-0.18$ ). In all the cases, the dependence of  $\tilde{F}$  on  $\nu$  consists of two branches corresponding to the regions with partially and completely dissolved condensation nuclei.

At  $b_m > b > b_i$ , the branch corresponding to a partially dissolved nucleus in Fig. 7 has the minimum and maximum points located before the reverse point  $\nu = \nu_i$  ( $\nu_i = 2.414 \times 10^6$ , as also in Fig. 3). As follows from the comparison of Figs. 1 and 7, the part of this branch corresponding to  $\nu'_n < \nu'_n(\nu_i)$  and  $\nu < \nu_i$  has no physical meaning within the frames of the one-dimensional approach. The apparent intersection of the branches for the partial and complete dissolutions of a nucleus in a droplet has also no physical sense. The points of a minimum of the function  $\tilde{F} = F(\nu, \nu'_n = \nu'_n(\nu))$  are obvious to correspond to minima of the full two-dimensional function  $F$ , and the points of a maximum of  $\tilde{F} = F[\nu, \nu'_n$

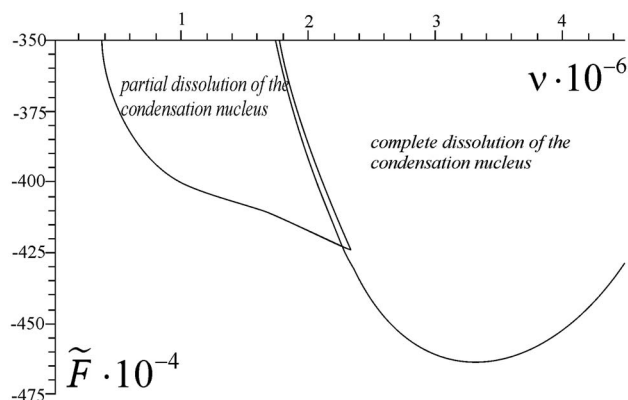


FIG. 9. The plot of the one-dimensional work of droplet formation  $\tilde{F}$  vs  $\nu$  at the vapor chemical potential  $b=-0.18$ .

$=\nu'_n(\nu)$ ], if any, correspond to saddle points (see Fig. 1). The activation barrier for the transition of a droplet from the state with a partially dissolved nucleus to the state with a completely dissolved nucleus is determined by the difference of values of work  $F$  in its saddle point and the point of the first minimum and can be estimated as the difference between a maximum and a minimum of the quasi-one-dimensional function  $\tilde{F}$  in the case under consideration. This means that the one-dimensional theory can be used for the kinetic analysis of transition of a droplet from the state with a partially dissolved nucleus to the state with a completely dissolved nucleus in the situation at  $b_m > b > b_i$  shown in Fig. 7.

At  $b < b_i$  in Fig. 8, the branch corresponding to a partially dissolved condensation nucleus has a minimum but no maximum at  $\nu < \nu_i$ . This does not mean the absence of a saddle point for the total work  $F$  and, correspondingly, the absence of an activation barrier for the transition of a droplet from the state with a partially dissolved nucleus to the state with a completely dissolved nucleus. However, this means that one cannot calculate the activation barrier within the one-dimensional theory at  $b < b_i$ .

A particular case is presented in Fig. 9. Extremes of the droplet formation work are absent at all in the region of a partially dissolved nucleus at  $b > b_m$ , and the work curve itself monotonically falls with the growth of  $\nu$ . Thus, the transition of a droplet from the state with a partially dissolved nucleus to the state with a completely dissolved nucleus becomes barrierless in this case.

## VI. DISCUSSION

Let us now summarize the important facts that have been revealed by the analysis presented of the numerical solution of the generalized Gibbs–Kelvin–Köhler and Ostwald–Freundlich equations and by the issuing computation of thermodynamic characteristics of a droplet nucleating on a soluble condensation nuclei in the atmosphere of an undersaturated solvent vapor. In agreement with the previous results<sup>5,7–9,23</sup> (but with more details presented here), it has been shown that the existence of stable droplets with a slightly dissolved nucleus and a thin solution film can be explained by overlapping surface layers within the film. The effect is described by the terms with the disjoining pressure in Eqs. (25) and (26) and provides a minimum for the work of droplet formation with a partial dissolution of a condensation nucleus, given by Eqs. (17) and (30).

A new behavior of the thermodynamic parameters of critical droplets with small nucleus residues and thick solution films has been established by investigating the link between the equilibrium sizes of the droplet and the soluble nucleus residue at various values of the chemical potential of a solvent vapor saturated over the droplet. The appearance of limiting values  $\nu_i$  and  $b_i$  demonstrates a gradual exchange of the roles of variables  $\nu$  and  $\nu'_n$  in description of a critical

droplet with decreasing the solvent vapor chemical potential below the threshold value for the deliquescence transition. While the critical droplet is stable with respect to the solute equilibrium with the nucleus residue (stable with respect to  $\nu'_n$ ) and unstable with respect to the solvent equilibrium with the vapor (unstable with respect to  $\nu$ ) at the values of the vapor chemical potential slightly below the deliquescence threshold ( $b_m > b > b_i$ ), the situation becomes opposite with considerably decreasing the vapor chemical potential ( $b_i > b$ ) to the efflorescence threshold. As was shown in Sec. V, this fact imposes a limitation on using the one-dimensional approach in the theory of deliquescence transition.

## ACKNOWLEDGMENTS

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