

Nucleation Theory and Applications

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12 Thermodynamics and Kinetics of Deliquescence of Small Soluble Particles

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**All truth passes through three stages.
First, it is ridiculed.
Second, it is violently opposed.
Third, it is accepted as being self-evident.**

Arthur Schopenhauer

Abstract

The thermodynamic theory of deliquescence of small soluble solid particles in an under-saturated vapor is presented. The work of droplet formation as a function of droplet size and size of the solid residue of the particle in the droplet is analyzed. Two-dimensional and one-dimensional approaches are considered. The first refers to the case when droplet size and size of the soluble solid core are considered as independent. The second assumes that the soluble solid core is in chemical equilibrium with the solution in the droplet, and its size depends on droplet size. The chemical potential of the condensing matter serving as a solvent and the chemical potential of a dissolved particle matter within the solution in the droplet are derived. The limits of chemical equilibrium of the residue of the particle with a solution in the droplet, as well as the limits of one-dimensional thermodynamic approach and its relation to the two-dimensional approach are considered. The quasi-equilibrium distributions of droplets with partially and completely dissolved solid cores and kinetics of establishing the final aggregative equilibrium between these droplets in

undersaturated vapor are described within the one-dimensional approach. The specific kinetic times of establishing these distributions are found.

12.1 Introduction

The stage of nucleation by soluble particles in the atmosphere of solvent vapor, when arising droplets consist of a liquid solution film around incompletely dissolved particles, is called the deliquescence stage. In a supersaturated vapor, this stage is the initial one in the whole condensation process, and the particles inside the droplets will completely dissolve in the growing droplets with time. In an undersaturated vapor, this stage finishes by establishing the aggregative equilibrium between droplets of different sizes, with residues of the particles (solid cores within the droplets) varying in size down to complete dissolution. Experimenters are able now to monitor the equilibrium droplet size as a function of the undersaturated vapor concentration [1-3]. By increasing the vapor concentration, they observe thickening of a liquid film around the soluble nucleus with gradual dissolution of the nucleus until it completely disappears. Subsequent decreasing the vapor concentration leads to evaporation of the droplet until the solid nucleus crystallizes inside the droplet. The experiment clearly demonstrates a hysteresis effect at increasing and decreasing vapor concentration, and locations of the corners in the hysteresis loop can provide us with important information on solubility and effective surface tension of small particles serving as nuclei of condensation and the parameters of the solution films around the particles.

A thermodynamic theory of the deliquescence has been considered within two approaches: the one-dimensional approach [4-6] and the two-dimensional approach [7-11]. The one-dimensional approach assumes that the chemical equilibrium between the soluble solid core and the liquid film establishes fast at every droplet size. As a result, the solution concentration within a droplet equals the solubility of the core matter at the core size. Thus the droplet size can be considered as the only independent variable of the droplet state. The two-dimensional approach is more sophisticated and assumes that the internal chemical equilibrium in the droplet between the residue of the particle and the solution may not be achieved. Thus two independent variables are considered, for instance, the solution concentration and the number of condensate molecules in the droplet, or the sizes of the soluble core and the droplet. Which physical situation is realized in experiment depends upon the relations between the parameters of the problem. In fact, as

will be shown in this paper, in many cases these relations allow us to use the one-dimensional approach.

To understand some peculiarities of the deliquescence and its experimental observation, the thermodynamics of deliquescence should be supplemented with kinetics. Activation energy for transition between the metastable droplet with partially dissolved solid core and the critical droplet, which corresponds to unstable equilibrium with the vapor, determines the deliquescence barrier for transformation into metastable droplet with completely dissolved core at the same vapor chemical potential. Intensive fluctuating overcoming of the deliquescence barrier by growing droplets starts at vapor concentrations below the maximum in the curve of the undersaturated vapor concentration as a function of the droplet size. This maximum realizes for condensation nuclei, with not small solubility in the condensing solvent, in the region of undersaturated vapor concentrations. Thus the kinetics of the transitions between states with incompletely and completely dissolved particles can be observable in an undersaturated vapor [1-3].

The quasi-steady kinetic solution of the problem has been recently given within the framework of the two-dimensional approach by Djikaev [9]. Nevertheless, the one-dimensional kinetics of deliquescence may be of interest in many cases, and can provide us with rather simple theoretical and numerical estimates. Therefore we will consider the one-dimensional approach to the kinetics of deliquescence in this paper. Even though our approach will have here a phenomenological form, by contrast to the classical approach it takes into account the effects of overlapping of the surface layers from the solid and the vapor sides of a liquid film around the residue of the particle. In this way, the theory considered here will be able to give both a qualitative and quantitative thermodynamic and kinetic description of the deliquescence of small soluble particles.

12.2 The Work of Droplet Formation on Partially or Completely Dissolved Nuclei of Condensation

Let us denote by W the work of droplet formation. We suppose that, in the initial state, the system under consideration consists of a solid nucleus and vapor within a fixed volume V at absolute temperature T . In the final state, the system includes a droplet, with partially or completely dissolved condensation nucleus, and vapor. If volume V , temperature T and numbers of molecules of every component stay fixed in both states of the system, then the work W can be

determined as a difference of the free energies Φ_2 and Φ_1 in the final and initial states, correspondingly. Thus we have

$$W \equiv \Phi_2 - \Phi_1 . \quad (12.1)$$

The free energy Φ_1 can be written as

$$\Phi_1 = \mu^\beta N + \mu_n \nu_n + \Omega_1 , \quad (12.2)$$

where μ^β is the vapor chemical potential, N is the number of vapor molecules, μ_n is the chemical potential of the solid particle matter in the initial state when the number of molecules within the particle equals ν_n and there is no droplet, Ω_1 is the grand potential of the system in the initial state. Analogously, the free energy Φ_2 of the system in the final state has the form

$$\Phi_2 = \mu^\beta (N - \nu) + \mu_\nu \nu + \mu'_n \nu'_n + \mu_n^\alpha (\nu_n - \nu'_n) + \Omega_2 , \quad (12.3)$$

where ν is the number of molecules condensed in the droplet from vapor (number of solvent molecules), μ_ν is the chemical potential of solvent molecules in the droplet, μ'_n and ν'_n are the chemical potential and the number of molecules of the soluble particle matter within the residue of the particle in the droplet in the final state of the system, μ_n^α is the chemical potential of solute in the droplet coming into solution film from the particle, Ω_2 is the grand potential of the system in the final state. Though the matter of soluble condensation nucleus is typically an electrolyte and dissociates into ions under dissolution in a polar condensate, we will consider below a simpler situation of the solid particle matter with molecular dissolution in the condensing solvent without dissociation.

The grand potentials Ω_1 and Ω_2 of the system in the initial and final states, can be represented under assumption that the particle and its residue have a spherical form as

$$\Omega_1 = -P_1^\gamma (\mu_n) V_{R_n} - P^\beta (\mu^\beta) (V - V_{R_n}) + 4\pi R_n^2 \sigma^{\gamma\beta} , \quad (12.4)$$

$$\begin{aligned} \Omega_2 = & -P_2^\gamma (\mu'_n) V_{R'_n} - P^\beta (\mu^\beta) (V - V_R) - P^\alpha (\mu_\nu, \mu_n^\alpha) (V_R - V_{R'_n}) \\ & + 4\pi R_n'^2 \sigma^{\alpha\gamma} + 4\pi R^2 \sigma^{\alpha\beta} + \Omega_D , \end{aligned} \quad (12.5)$$

where V_{R_n} , $V_{R'_n}$, and V_R are the volumes of the initial particle, the residue of the particle and the droplet, respectively. Indices α , β , γ mark the quantities referred to the liquid film, vapor and solid particle, correspondingly, while the double indices $\gamma\beta$, $\gamma\alpha$, and $\alpha\beta$ mark the quantities referred to the interfaces between the solid particle and vapor, solid particle and liquid film, the film and the vapor, respectively.

We assume here, that the vapor pressure $P^\beta(\mu^\beta)$ remains the same in the initial and final states of the system; $P_1^\gamma(\mu_n)$ and $P_2^\gamma(\mu'_n)$ are the scalar pressures in the initial particle and in its residue (for simplicity, we consider a solid particle as a structureless body characterized by a scalar pressure); $\sigma^{\gamma\beta}$, $\sigma^{\gamma\alpha}$, and $\sigma^{\alpha\beta}$ are the surface tensions referred to indicated interfaces; $4\pi R_n^2$, $4\pi R'_n{}^2$, and $4\pi R^2$ are the corresponding spherical surface areas with radii R_n , R'_n , and R . $P^\alpha(\mu_\nu, \mu_n^\alpha)$ is the pressure in the bulk liquid solution with the same chemical potentials μ_ν and μ_n^α of the solvent and solute as they are in the solution film around the residue of the particle [12]. It does not coincide with a pressure in that film if the film is thin and the surface layers from opposite film sides overlap [12-14]. The effect of interface overlapping is described by the last term in Eq. (12.5).

Let

$$x = (\nu_n - \nu'_n)/\nu \quad (12.6)$$

be the relative solute concentration in the film. The partial molar volumes v^α and v_n^α for solvent and solute, respectively, can be defined as

$$(\partial\mu_\nu/\partial P^\alpha) \equiv v^\alpha, \quad (\partial\mu_n^\alpha/\partial P^\alpha) \equiv v_n^\alpha. \quad (12.7)$$

Assuming the solution concentration x to be not large, we will neglect the dependencies of v^α and v_n^α on x . The number of condensate molecules in the droplet with partially dissolved nucleus may be related to the droplet volume V_R and the nucleus residue volume $V_{R'_n}$ by the relation

$$\nu = [V_R - V_{R'_n} - v_n^\alpha(\nu_n - \nu'_n)]/v^\alpha. \quad (12.8)$$

We ignore in Eq. (12.8) the contributions to ν from adsorptions on the opposite sides of the liquid film and assume that the surface tensions $\sigma^{\gamma\alpha}$ and $\sigma^{\alpha\beta}$ are independent of solution concentration. Because of the spherical shape of the droplet, the soluble particle and its residue, we have

$$V_R = \frac{4\pi}{3}R^3, \quad V_{R_n} = \frac{4\pi}{3}R_n^3, \quad V_{R'_n} = \frac{4\pi}{3}R'_n{}^3, \quad (12.9)$$

$$\nu_n = 4\pi R_n^3 / 3v_n, \quad \nu'_n = 4\pi R'_n{}^3 / 3v_n. \quad (12.10)$$

Thus Eqs. (12.6)-(12.10) determine the relations between x , ν , ν_n , and ν'_n and the radii R , R_n , and R'_n .

Below we will consider for simplicity the case of diluted solutions. For diluted solutions, the chemical potentials μ_ν and μ_n^α of solvent and solute in the liquid film can be represented as functions of pressure P^α and concentration x in the form [15]

$$\mu_\nu(P^\alpha, x) = \mu_\infty - k_B T x + v^\alpha (P^\alpha - P_\infty), \quad (12.11)$$

$$\mu_n^\alpha(P^\alpha, x) = \mu_{n\infty} + k_B T \ln \frac{x}{x_\infty} + v_n^\alpha (P^\alpha - P_\infty), \quad (12.12)$$

where $\mu_{n\infty}$ and x_∞ are the chemical potential and the solubility of the nucleus matter at equilibrium with a flat interface between solid phase of the nucleus substance and the solution, k_B is the Boltzmann constant. Analogously, the chemical potentials μ_n and μ'_n of the substance in the condensation nucleus may be represented as functions of pressure in the phase γ

$$\mu_n = \mu_{n\infty} + v_n (P_1^\gamma - P_\infty), \quad \mu'_n = \mu_{n\infty} + v_n (P_2^\gamma - P_\infty). \quad (12.13)$$

All Eqs. (12.11)-(12.13) assume incompressibility of phases α and γ .

A substitution of Eqs. (12.11)-(12.13) into Eqs. (12.2)-(12.5) yields, taking into consideration Eqs. (12.1), (12.9), and (12.10), the following expression for the work of droplet formation on partially dissolved condensation nucleus

$$\begin{aligned} W = & 4\pi R_n'^2 \sigma^{\alpha\gamma} + 4\pi R^2 \sigma^{\alpha\beta} - 4\pi R_n^2 \sigma^{\gamma\beta} - (\mu^\beta - \mu_\infty) \nu \\ & - k_B T \nu x + k_B T (\nu_n - \nu'_n) \ln \frac{x}{x_\infty} + \Omega_D + (P^\beta - P_\infty) (V_R - V_{R_n}). \end{aligned} \quad (12.14)$$

The term Ω_D in Eq. (12.14) can be determined with the help of the disjoining pressure of a thin liquid film. In accordance with Refs. 12 and 16, we define the disjoining pressure Π_D as

$$\Pi_D \equiv P_N(R'_n, h) - P^\alpha, \quad (12.15)$$

where P_N is the normal component of the pressure tensor inside the spherical liquid film with thickness $h \equiv R - R'_n$, taken at the surface of the spherical

solid residue of the nucleus. By analogy with the case of a pure solvent film on a wettable substrate [13], the term Ω_D has the form

$$\Omega_D = 4\pi R_n'^2 \int_{R-R_n'}^{\infty} \Pi_D dh, \quad (12.16)$$

where we have taken into account that the surface of the substrate is spherical with a radius R_n' and the outer surface of the film is also spherical with a radius R . Using Eq. (12.16) in Eq. (12.14) and neglecting the difference $P^\beta - P_\infty$ gives

$$\begin{aligned} W = & 4\pi R_n'^2 \sigma^{\alpha\gamma} + 4\pi R^2 \sigma^{\alpha\beta} - 4\pi R_n'^2 \sigma^{\gamma\beta} - (\mu^\beta - \mu_\infty) \nu \\ & - k_B T \nu x + k_B T (\nu_n - \nu_n') \ln \frac{x}{x_\infty} + 4\pi R_n'^2 \int_{R-R_n'}^{\infty} \Pi_D dh. \end{aligned} \quad (12.17)$$

In the case of a completely dissolved nucleus we have $R_n' = 0$, $\nu_n' = 0$ and, in view of Eq. (12.16), $\Omega_D = 0$. Neglecting the term $(P^\beta - P_\infty) V_R$, one can reduce Eq. (12.14) in this case to the form

$$\begin{aligned} W = & 4\pi R^2 \sigma^{\alpha\beta} - 4\pi R_n'^2 \sigma^{\gamma\beta} - (\mu^\beta - \mu_\infty) \nu - k_B T \nu x \\ & + k_B T \nu_n \ln \left(\frac{x}{x_\infty} \right). \end{aligned} \quad (12.18)$$

Another limiting situation realizes in the case of an insoluble nucleus with $\nu_n' = \nu_n$, $R_n' = R_n$ and, in view of Eq. (12.6), with $x = 0$. As follows from Eqs. (12.17), we have in this case [13, 14]

$$\begin{aligned} W = & 4\pi R^2 \sigma^{\alpha\beta} + 4\pi R_n'^2 (\sigma^{\alpha\gamma} - \sigma^{\gamma\beta}) - (\mu^\beta - \mu_\infty) \nu \\ & + 4\pi R_n'^2 \int_{R-R_n}^{\infty} \Pi_D(h) dh. \end{aligned} \quad (12.19)$$

12.3 The Generating Properties of the Work of Droplet Formation

According to the definition of the work of droplet formation, the partial derivatives of the work W with respect to the number ν of solvent molecules and to the number ν'_n of molecules in the residue of the condensation nucleus determines the chemical potentials μ_ν and μ_n^α

$$\frac{\partial W}{\partial \nu} = \mu_\nu - \mu^\beta, \quad \frac{\partial W}{\partial \nu'_n} = \mu'_n - \mu_n^\alpha. \quad (12.20)$$

Before we start to analyze Eq. (12.20), let us simplify the problem. As was said in Section 12.2, surface tensions $\sigma^{\alpha\gamma}$ and $\sigma^{\alpha\beta}$ are considered to be independent of the solution concentration. Moreover, the dependence of the disjoining pressure Π_D on concentration x can be also omitted, since the solution concentration in thin films is almost constant and equals approximately the solubility x_∞ .

Using Eq. (12.17) in the first equation from Eqs. (12.20) yields

$$\mu_\nu - \mu^\beta = \mu_\infty - \mu^\beta - k_B T x + \frac{2\sigma^{\alpha\beta} v^\alpha}{R} - \frac{R_n'^2}{R^2} \Pi_D v^\alpha, \quad (12.21)$$

where we took into account Eqs. (12.6), (12.8)-(12.10). Eq. (12.21) represents indeed the expression for the chemical potential of the solvent in the droplet. It can also be derived from Eq. (12.11) if one neglects the difference $P^\beta - P_\infty$ and recognizes that the condition of mechanical equilibrium of the spherical liquid film with inner radius R_n' and outer radius R has the form [16]

$$P^\alpha = P^\beta + \frac{2\sigma^{\alpha\beta}}{R} - \frac{R_n'^2}{R^2} \Pi_D. \quad (12.22)$$

Using Eq. (12.17) in the second equation from Eq. (12.20) yields

$$\begin{aligned} \mu'_n - \mu_n^\alpha = & \frac{2\sigma^{\gamma\alpha} v_n}{R_n'} - \frac{2\sigma^{\alpha\beta} (v_n^\alpha - v_n)}{R} - k_B T \ln \frac{x}{x_\infty} \\ & + \frac{2v_n}{R_n'} \int_{R-R_n'}^{\infty} \Pi_D dh + \Pi_D \left[v_n - \frac{R_n'^2}{R^2} (v_n - v_n^\alpha) \right], \end{aligned} \quad (12.23)$$

where we took into account Eqs. (12.6), (12.8)-(12.10). In order to prove that Eq. (12.23) represents indeed the expression for the difference in the chemical potential of molecules in the condensation nucleus and the chemical potential of solute in the droplet, one can use Eqs. (12.12) and (12.13). It follows from Eqs. (12.12) and (12.13) that

$$\mu'_n - \mu_n^\alpha = -k_B T \ln \frac{x}{x_\infty} + v_n (P_2^\gamma - P_\infty) - v_n^\alpha (P^\alpha - P_\infty) . \quad (12.24)$$

The condition of mechanical equilibrium for a spherical residue of the condensation nucleus within the droplet can be written as

$$P_2^\gamma = P_N (R'_n) + \frac{2\tilde{\sigma}^{\gamma\alpha}}{R'_n} , \quad (12.25)$$

where $\tilde{\sigma}^{\alpha\gamma}$ is the surface tension of the inner side of the thin film that does not generally coincide with the macroscopic value $\sigma^{\alpha\gamma}$. Thermodynamics of thin flat films [17] provides us with the relationship

$$\frac{\partial(\tilde{\sigma}^{\alpha\beta} + \tilde{\sigma}^{\alpha\gamma})}{\partial h} = -\Pi_D \quad (12.26)$$

with $\tilde{\sigma}^{\alpha\beta}$ being the surface tension of the outer side of the thin film. According to the definitions Eqs. (12.15) and (12.16) (i.e., according to the fact that the disjoining pressure is defined by the normal component of the pressure at the surface of the nucleus residue, and Ω_D is proportional to the residue area), we can replace $\tilde{\sigma}^{\alpha\beta}$ for a spherical film by the macroscopic value $\sigma^{\alpha\beta}$ and reduce Eq. (12.26) to the form

$$\frac{\partial\tilde{\sigma}^{\alpha\gamma}}{\partial h} = -\Pi_D . \quad (12.27)$$

Integrating Eq. (12.27) and substituting the result, as well as Eqs. (12.15) and (12.22), into Eq. (12.25) yields

$$P_2^\gamma = P^\beta + \frac{2\sigma^{\alpha\beta}}{R} - \frac{R_n'^2}{R^2} \Pi_D + \Pi_D + \frac{2}{R'_n} \left(\sigma^{\gamma\alpha} + \int_{R-R'_n}^{\infty} \Pi_D dh \right) . \quad (12.28)$$

In the limit of a flat film as $R'_n \rightarrow \infty$ and $R \rightarrow \infty$, $P_2^\gamma = P^\beta$. Substituting Eqs. (12.28) and (12.22) into Eq. (12.24) and neglecting the difference $P^\beta - P_\infty$ leads to Eq. (12.23).

If the chemical equilibrium with respect to both components in the droplet, the soluble component in the nucleus residue, and the condensing component in vapor is reached, then $\mu_\nu = \mu^\beta$ and $\mu'_n = \mu_n^\alpha$. In view of Eq. (12.20), we have at complete equilibrium

$$\frac{\partial W}{\partial \nu} = 0, \quad \frac{\partial W}{\partial \nu'_n} = 0. \quad (12.29)$$

As follows from Eqs. (12.21), (12.23), (12.6), (12.8)-(12.10), equations

$$\mu_\infty - \mu^\beta - k_B T x + \frac{2\sigma^{\alpha\beta} v^\alpha}{R} - \frac{R_n'^2}{R^2} \Pi_D v^\alpha = 0, \quad (12.30)$$

$$\begin{aligned} \frac{2v_n}{R'_n} \left(\sigma^{\gamma\alpha} + \int_{R-R'_n}^{\infty} \Pi_D dh \right) - \frac{2\sigma^{\alpha\beta} (v_n^\alpha - v_n)}{R} \\ - k_B T \ln \frac{x}{x_\infty} + \Pi_D \left[v_n - \frac{R_n'^2}{R^2} (v_n - v_n^\alpha) \right] = 0 \end{aligned} \quad (12.31)$$

determine the values ν and ν'_n corresponding to the minimum and the saddle points of the work W which are important for barrier kinetics.

Eq. (12.30) is a generalization of the Gibbs-Kelvin-Köhler equation of the theory of nucleation on soluble particles. Eq. (12.31) is a generalization of the Ostwald-Freundlich equation of the theory of solutions. It gives the dependence of nucleus residue solubility on the residue size and size of the droplet. In view of Eq. (12.6) for the concentration x as a function of ν and ν'_n , Eq. (12.31) can be regarded as a relation between ν and ν'_n (or between R and R'_n) at the chemical equilibrium in droplet between the solute component and the nucleus residue.

12.4 Two- and One-Dimensional Theories of Deliquescence

Let us now consider the relation between two- and one-dimensional theories of deliquescence stage of nucleation on soluble particles in undersaturated vapor. The two-dimensional theory starts with the investigation of the two-dimensional plot of the work of droplet formation as a function of the number ν of condensate molecules in the droplet and number ν'_n of molecules in the solid nucleus residue. To deal with undersaturated vapor, we will consider the vapor chemical potential μ^β fixed somewhere below μ_∞ , $\mu^\beta - \mu_\infty < 0$. As a good approximation for the disjoining pressure Π_D , we will employ the approximation [12-14]

$$\Pi_D = K \exp\left(-\frac{R - R'_n}{l}\right) \quad (12.32)$$

with l being the correlation length for the condensation film around the nucleus and the factor K being related to surface tensions $\sigma^{\beta\gamma}$, $\sigma^{\alpha\gamma}$, $\sigma^{\alpha\beta}$ and length l by the formula [13, 14]

$$K = \left(\sigma^{\beta\gamma} - \sigma^{\alpha\gamma} - \sigma^{\alpha\beta}\right) / l . \quad (12.33)$$

As we noted in Section 12.3, we do not consider the dependence of the quantities l and K on the solution concentration and take them at a concentration x_∞ .

Using Eq. (12.32), we can rewrite the work W given by Eq. (12.17) in the form

$$\begin{aligned} W = & 4\pi R_n'^2 \sigma^{\alpha\gamma} + 4\pi R^2 \sigma^{\alpha\beta} - 4\pi R_n'^2 \sigma^{\gamma\beta} - \left(\mu^\beta - \mu_\infty\right) \nu \\ & - k_B T \nu x + k_B T (\nu_n - \nu'_n) \ln \frac{x}{x_\infty} - 4\pi R_n'^2 l K \exp\left(-\frac{R - R'_n}{l}\right) . \end{aligned} \quad (12.34)$$

We define the numerical values for the parameters entering Eq. (12.34) as

$$\begin{aligned} R_n &= 15 \cdot 10^{-7} \text{ cm} , & \nu_n &= 2 \cdot 10^{-23} \text{ cm}^3 , \\ \nu^\alpha &= 3 \cdot 10^{-23} \text{ cm}^3 , & \nu_n^\alpha &= 2.2 \cdot 10^{-23} \text{ cm}^3 , \\ T &= 298 \text{ K} , & \sigma^{\alpha\gamma} &= 200 \text{ dyn/cm} , & \sigma^{\alpha\beta} &= 72 \text{ dyn/cm} , \\ x_\infty &= 0.2 , & l &= 2 \cdot 10^{-7} \text{ cm} , & K &= 3 \cdot 10^9 \text{ dyn/cm}^2 . \end{aligned} \quad (12.35)$$

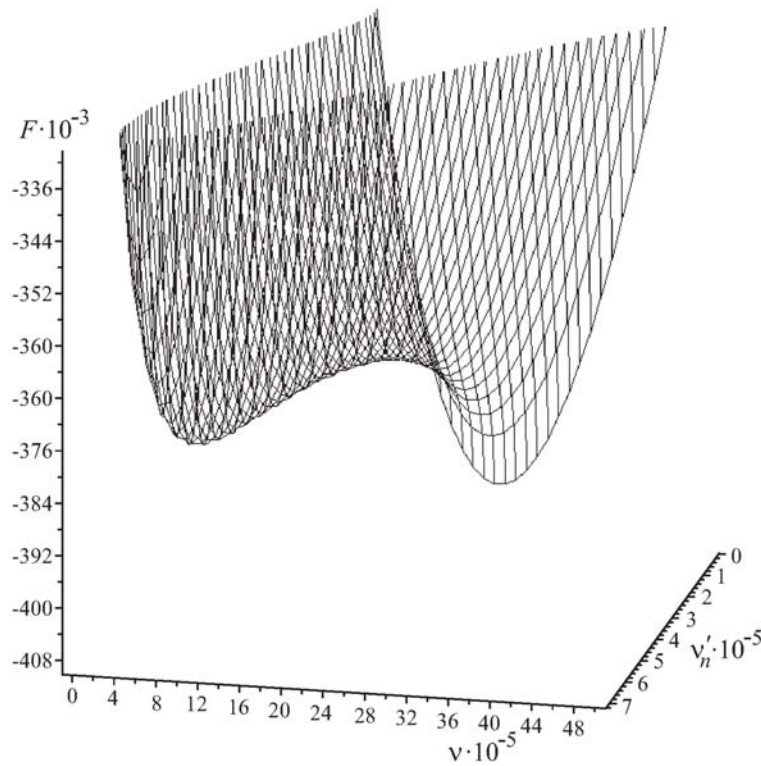


Fig. 12.1 The two-dimensional work F of droplet formation on a soluble nucleus in undersaturated vapor at the vapor chemical potential $b = -0.2$

These values of the parameters are close to those for real condensation nuclei and water as a condensate.

It is convenient to deal with dimensionless work of droplet formation, $F \equiv W/k_B T$, dimensionless chemical potentials of vapor, $b \equiv (\mu^\beta - \mu_\infty)/k_B T$, and solvent, $b_\nu \equiv (\mu_\nu - \mu_\infty)/k_B T$, all of them expressed in terms of thermal units $k_B T$. The plot of F as a function of ν and ν'_n is shown in Figs. 12.1 and 12.2 for two values of the vapor chemical potential: $b = -0.2$ and $b = -0.25$. The relief of the "waterfall path" in Figs. 12.1 and 12.2 shows the trajectory for a droplet transition from the state with partially dissolved condensation nucleus to the state with completely dissolved nucleus. Both considered cases demonstrate the existence of the activation barrier for such a transition, at this Fig. 12.1 illustrates the situation when such a transition occurs with a high probability, and

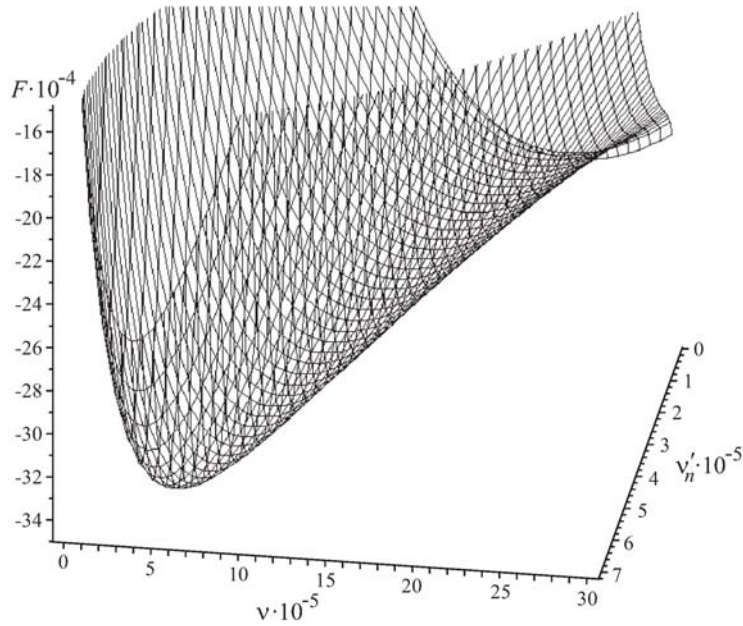


Fig. 12.2 The two-dimensional work F of droplet formation on soluble nucleus in undersaturated vapor at vapor chemical potential $b = -0.25$

the state with completely dissolved nucleus is more stable than the state with partially dissolved nucleus. Fig. 12.2 refers to the opposite case when a droplet state with partially dissolved nucleus is more stable.

Let us now try to describe the situation, illustrated in Figs. 12.1 and 12.2, by using a one-dimensional approach. This approach assumes that chemical equilibrium between solute and the soluble core establishes rather quickly, and Eq. (12.31) holds for every value of the number ν of solvent molecules in a droplet. It is convenient to rewrite Eq. (12.31) in view of Eqs. (12.6) and (12.32) in the form

$$k_B T \ln \left(\frac{\nu_n - \nu'_n(\nu)}{\nu} \right) = \frac{2\nu_n}{R'_n(\nu)} \left[\sigma^{\gamma\alpha} + lK \exp \left(-\frac{R - R'_n}{l} \right) \right] - \frac{2\sigma^{\alpha\beta} (\nu_n^\alpha - \nu_n)}{R} \\ + K \exp \left(-\frac{R - R'_n}{l} \right) \left[\nu_n - \frac{R_n'^2(\nu)}{R^2} (\nu_n - \nu_n^\alpha) \right]. \quad (12.36)$$

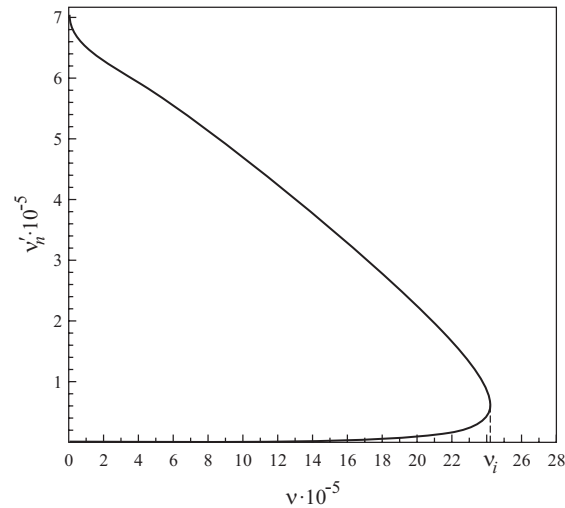


Fig. 12.3 Plot of ν'_n as a function of ν according to Eq. (12.36)

The number of molecules $\nu'_n(\nu)$ in the equilibrium residue of the condensation nucleus, found as a function of the number of solvent molecules ν by solving Eq. (12.36) with account of Eqs. (12.35), (12.8)-(12.10), is shown in Fig. 12.3. The plot demonstrates that there is no equilibrium solution for ν'_n above a certain value $\nu = \nu_i$ ($\nu_i \simeq 2.414 \cdot 10^6$ in Fig. 12.3). This means that rather small soluble solid cores ($\nu'_n < 62300$ in Fig. 12.3) become unstable and inevitably dissolve if the limiting value $\nu = \nu_i$ is reached.

The whole picture becomes clearer if one considers the one-dimensional work $\tilde{F} = F(\nu'_n = \nu'_n(\nu))$ with ν'_n being determined as a function of ν in accordance with Eq. (12.36) and the curve depicted in Fig. 12.3. The plots of \tilde{F} are presented in Figs. 12.4 and 12.5 for two values of the vapor chemical potential: $b = -0.2$ and $b = -0.25$. Both plots have two branches corresponding to the regions of partial and complete dissolution of condensation nucleus along the ν -axis. In Fig. 12.4, the branch for the partial dissolution of the nucleus has minimum and maximum points located before the turning point $\nu = \nu_i$ to solution instability ($\nu_i \simeq 2.414 \cdot 10^6$, the same as in Fig. 12.3) and the point of intersection with the branch for complete dissolution. This means that the one-dimensional theory is applicable in the situation in Fig. 12.4 for the kinetic analysis of droplet transition between states with partial and complete dissolution of the nucleus.

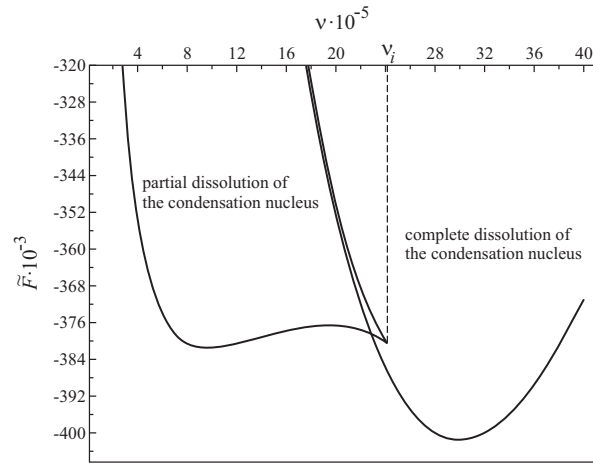


Fig. 12.4 Plot of the one-dimensional work \tilde{F} of droplet formation at vapor chemical potential $b = -0.2$

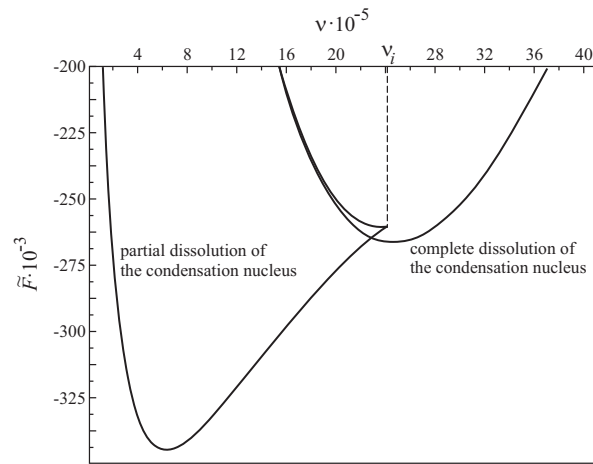


Fig. 12.5 Plot of one-dimensional work \tilde{F} of droplet formation at vapor chemical potential $b = -0.25$

Another situation is shown in Fig. 12.5. Here the maximum point appears somewhere beyond the turning point and a direct application of the one-dimensional theory is questionable. But we will see in Sections 12.5 and 12.6 that the situation shown in Fig. 12.5 is not interesting from the point of view of the kinetics.

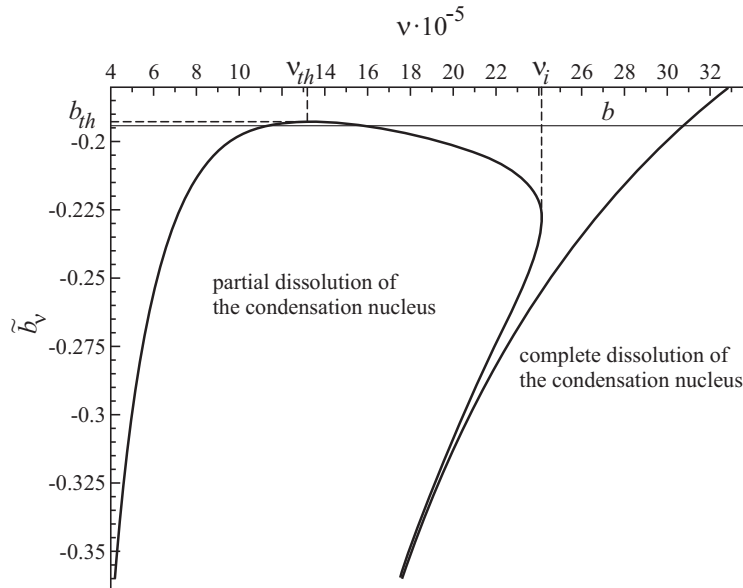


Fig. 12.6 Plot of one-dimensional chemical potential \tilde{b}_ν of the solvent in the droplet

The relation between the two- and one-dimensional approaches can be finally clarified with the help of Eq. (12.21). Substituting Eqs. (12.6) and (12.32) into Eq. (12.21), we obtain

$$b_\nu = -\frac{\nu_n - \nu'_n}{\nu} + \frac{2\sigma^{\alpha\beta}v^\alpha}{Rk_B T} - \frac{R'_n{}^2 v^\alpha}{R^2 k_B T} K \exp\left(-\frac{R - R'_n}{l}\right). \quad (12.37)$$

Using Eqs. (12.35), (12.8) - (12.10) and the dependence $\nu'_n(\nu)$ given by Eq. (12.36) (as shown in Fig. 12.3) to calculate the one-dimensional chemical potential of the solvent $\tilde{b}_\nu \equiv b_\nu(\nu'_n = \nu'_n(\nu))$ as a function of ν leads to the plot presented in Fig. 12.6. As well as the plots in Figs. 12.4 and 12.5, the plot of \tilde{b}_ν has also two branches corresponding to the regions of partial and complete dissolution of condensation nucleus along the ν -axis.

From a thermodynamic point of view, the phenomenon of deliquescence is connected with the existence of the maximum in the branch of the chemical potential of the solvent in the region of partial dissolution of the nucleus. This maximum is clearly seen in Fig. 12.6 at $\nu = \nu_{th}$. The stage of deliquescence is long-living when the value of the vapor chemical potential b appears to be below from that maximum (as shown in Fig. 12.6). A prompt transition from a droplet state with partially dissolved nucleus to a state with complete dissolution of the nucleus occurs if the vapor chemical potential reaches the close vicinity of the maximum from below or exceeds the maximum. In this sense, the maximal value $b_{th} = \tilde{b}_\nu \Big|_{\nu=\nu_{th}}$ of the solvent chemical potential determines the deliquescence threshold, i.e. a certain value of the vapor chemical potential, above which all the droplets barrierlessly transform into a state with completely dissolved condensation nuclei. Below the threshold, the transition between the states requires an activation energy which may be called the deliquescence barrier. As follows from Eq. (12.37),

$$b_{th} = -\frac{\nu_n - \nu'_n(\nu_{th})}{\nu_{th}} \quad (12.38)$$

$$+ \frac{v^\alpha}{k_B T} \left[\frac{2\sigma^{\alpha\beta}}{R_{th}} - K \left(\frac{R'_n(\nu_{th})}{R_{th}} \right)^2 \exp \left(-\frac{R_{th} - R'_n(\nu_{th})}{l} \right) \right],$$

where ν_{th} is the root of the equation

$$\frac{d\tilde{b}_\nu}{d\nu} \Big|_{\nu=\nu_{th}} = \left[\frac{\partial b_\nu}{\partial \nu} + \frac{\partial b_\nu}{\partial \nu'_n} \frac{d\nu'_n(\nu)}{d\nu} \right] \Big|_{\nu=\nu_{th}, \nu'_n=\nu'_n(\nu_{th})} = 0 \quad (12.39)$$

with $\nu'_n(\nu)$ and $d\nu'_n(\nu)/d\nu$ found from Eq. (12.36), $R_{th} \equiv R|_{\nu=\nu_{th}, \nu'_n=\nu'_n(\nu_{th})}$ and $R'_n(\nu_{th}) \equiv R'_n|_{\nu'_n=\nu'_n(\nu_{th})}$ determined with the help of Eqs. (12.6), (12.8)-(12.10).

As can be seen from Fig. 12.6, if the vapor chemical potential is close enough to the deliquescence threshold from below, the one-dimensional approach is applicable as far as the vapor chemical potential will be above the value $b_i \equiv \tilde{b}_\nu \Big|_{\nu=\nu_i}$ of the chemical potential of the solvent at the turning point corresponding to the beginning of the instability (the same turning point $\nu = \nu_i$ as in Figs. 12.3-12.5). It is the case for the situation shown in Fig. 12.1. It is not the case for the situation shown in Fig. 12.2. The part of the \tilde{b}_ν -curve, located in Fig. 12.6 beyond the turning point on the branch with partial dissolution of a nucleus, has no physical meaning.

12.5 Kinetics of Droplet Growth over the Deliquescence Barrier

Let us consider, now, the kinetics of droplet growth over the deliquescence barrier in the situation when the one-dimensional approach is applicable, i.e. in the situation illustrated by Fig. 12.4. We denote by $\nu_s^{(1)}$, ν_c , and $\nu_s^{(2)}$ the positions of the extrema of the one-dimensional work of droplet formation. They are roots of the equation

$$b = \tilde{b}_\nu \Big|_{\nu=\nu_s^{(1)}, \nu=\nu_c, \nu=\nu_s^{(2)}} \quad (12.40)$$

and correspond to the intersection points of the b -line with the \tilde{b}_ν -curve in Fig. 12.6 (note that the vapor is undersaturated in the situations illustrated by Figs. 12.4 and 12.6). The root $\nu = \nu_s^{(1)}$ corresponds to the stable equilibrium droplet with $\nu'_n > 0$ (partly dissolved nucleus) at the bottom of the first potential well of the one-dimensional work \tilde{F} in the undersaturated vapor at a given vapor chemical potential b . The root $\nu = \nu_c$ corresponds to the critical droplet with $\nu'_n > 0$ (the residue of the nucleus still present in the droplet), which is in unstable equilibrium with the vapor at the same b . This root determines the location of the maximum in the curve of the one-dimensional work \tilde{F} of droplet formation. The root $\nu = \nu_s^{(2)}$ refers to the droplet with completely dissolved nucleus, which is in a stable equilibrium with the vapor at the same b at the bottom of the second potential well of the one-dimensional work \tilde{F} .

Introducing $F_s^{(1)} \equiv \tilde{F} \Big|_{\nu=\nu_s^{(1)}}$, $F_c \equiv \tilde{F} \Big|_{\nu=\nu_c}$, and $F_s^{(2)} \equiv F(\nu'_n = 0) \Big|_{\nu=\nu_s^{(2)}}$, let us define the activation barriers

$$\Delta F^{(1)} \equiv F_c - F_s^{(1)} \quad , \quad \Delta F^{(2)} \equiv F_c - F_s^{(2)} \quad (12.41)$$

for the direct (denoted with index (1)) and reversal (denoted with index (2)) transitions of droplets over the deliquescence barrier. As follows from general formulas of heterogeneous nucleation ([14], Eq. (2.11)) and can be seen from Figs. 12.4 and 12.5, the following chain of inequalities,

$$\frac{\partial F_s^{(2)}}{\partial b} < \frac{\partial F_c}{\partial b} < \frac{\partial F_s^{(1)}}{\partial b} < 0 \quad , \quad (12.42)$$

holds for the derivatives of $F_s^{(1)}$, F_c , and $F_s^{(2)}$ with respect to vapor chemical potential b . As a result, the direct barrier $\Delta F^{(1)}$ decreases with increasing the vapor chemical potential, while the reversal barrier $\Delta F^{(2)}$ increases.

Let η_n be the number of nuclei with an initial radius R_n (and with a corresponding number ν_n of molecules of soluble substance) per unit of the system volume. Denoting by $\eta^{(1)}(t)$ and $\eta^{(2)}(t)$ the total numbers of droplets at the bottoms of the first and second potential wells of the work of droplet formation at a given vapor chemical potential b , we have

$$\eta_n = \eta^{(1)}(t) + \eta^{(2)}(t) . \quad (12.43)$$

We will be interested in finding the numbers $\eta^{(1)}(t)$ and $\eta^{(2)}(t)$ as functions of time t and the barriers $\Delta F^{(1)}$ and $\Delta F^{(2)}$ at a given vapor chemical potential b .

The droplets under consideration, belonging to the first and the second potential wells of work \tilde{F} , are in distinct aggregative quasi-equilibrium states. They are separated by the region of the maximum of the work \tilde{F} where droplets obey the quasi-steady state. Mutual aggregative equilibrium state of droplets is achieved as a result of kinetic processes. Two distinct quasi-equilibrium distributions in droplet sizes at the bottoms of the potential wells of the work \tilde{F} can be written as [16]

$$c_n^{(1)} = \frac{\eta^{(1)}(t)}{\pi^{1/2} \Delta \nu_s^{(1)}} \exp \left[- \left(\tilde{F} - F_s^{(1)} \right) \right] , \quad (12.44)$$

$$c_n^{(2)} = \frac{\eta^{(2)}(t)}{\pi^{1/2} \Delta \nu_s^{(2)}} \exp \left[- \left(F(\nu'_n = 0) - F_s^{(2)} \right) \right] ,$$

where

$$\Delta \nu_s^{(1)} \equiv \left[\frac{2}{d^2 \tilde{F} / d\nu^2} \right]_{\nu=\nu_s^{(1)}}^{1/2} = \left[\frac{2}{d\tilde{b}_\nu / d\nu} \right]_{\nu=\nu_s^{(1)}}^{1/2} , \quad (12.45)$$

$$\Delta \nu_s^{(2)} \equiv \left[\frac{2}{d^2 F(\nu'_n = 0) / d\nu^2} \right]_{\nu=\nu_s^{(2)}}^{1/2} = \left[\frac{2}{db_\nu(\nu'_n = 0) / d\nu} \right]_{\nu=\nu_s^{(2)}}^{1/2} \quad (12.46)$$

are correspondingly the half-widths of the left and right wells in the curve of the work \tilde{F} of droplet formation along the ν -axis. To write the second right-hand parts in Eqs. (12.45) and (12.46), we took into account Eq. (12.20) and the definitions $F \equiv W/k_B T$, $b_\nu \equiv (\mu_\nu - \mu_\infty)/k_B T$.

If achievement of the quasi-equilibrium states at the bottoms of potential wells and the quasi-steady state at the top of the potential hump of the work of droplet formation requires much less time than is needed for establishing the total equilibrium, one can use the following equation for transition kinetics over the deliquescence barrier,

$$\frac{d\eta^{(1)}(t)}{dt} = - \left(J^{(1)}(t) + J^{(2)}(t) \right). \quad (12.47)$$

Direct nucleation rate $J^{(1)}(t)$ and reversal nucleation rate $J^{(2)}(t)$ can be determined here as

$$J^{(1)}(t) = \frac{\eta^{(1)}(t)}{\pi \Delta\nu_c \Delta\nu_s^{(1)}} W_c^+ \exp \left[-\Delta F^{(1)} \right], \quad (12.48)$$

$$J^{(2)}(t) = -\frac{\eta^{(2)}(t)}{\pi \Delta\nu_c \Delta\nu_s^{(2)}} W_c^+ \exp \left[-\Delta F^{(2)} \right],$$

where

$$\Delta\nu_c \equiv \left[\frac{2}{\left| d^2 \tilde{F} / d\nu^2 \right|} \right]_{\nu=\nu_c}^{1/2} = \left[\frac{2}{\left| d\tilde{b}_\nu / d\nu \right|} \right]_{\nu=\nu_c}^{1/2} \quad (12.49)$$

is the half-width of the maximum of the work of droplet formation at $\nu = \nu_c$ (we again took into account Eq. (12.20) and the definitions $F \equiv W/k_B T$, $b_\nu \equiv (\mu_\nu - \mu_\infty)/k_B T$),

$$W_c^+ = \pi \alpha_C v_T n_\infty^\beta e^b R_c^2 \quad (12.50)$$

is the rate of attachment of vapor molecules to the droplet with radius $R_c \equiv R|_{\nu=\nu_c, \nu'_n=\nu'_n(\nu_c)}$ at the maximum of the work of droplet formation, α_C is the condensation coefficient, v_T is the mean thermal velocity of the vapor molecules, n_∞^β is the concentration of vapor at equilibrium with a flat interface between the vapor and its condensate. A substantiation of Eq. (12.48) can be given in the

usual way in nucleation theory. For instance, it was done in Ref. 16 for the case of micellization in surfactant solutions.

Solving Eq. (12.47) with the initial conditions,

$$\eta^{(1)}(0) = \eta_n, \quad \eta^{(2)}(0) = 0, \quad (12.51)$$

yields

$$\eta^{(1)}(t) = \frac{\eta_n}{1+A} \left\{ A + \exp \left[-\frac{J^{(1)}(0)}{\eta_n} (1+A)t \right] \right\}, \quad (12.52)$$

$$\eta^{(2)}(t) = \frac{\eta_n}{1+A} \left\{ 1 - \exp \left[-\frac{J^{(1)}(0)}{\eta_n} (1+A)t \right] \right\}, \quad (12.53)$$

where

$$A \equiv \frac{\Delta\nu_s^{(2)}}{\Delta\nu_s^{(1)}} \exp \left(\Delta F^{(1)} - \Delta F^{(2)} \right). \quad (12.54)$$

As follows from Eqs. (12.52) and (12.53), a characteristic time t_d of the deliquescence transition, i.e. of establishing the mutual aggregative equilibrium between droplets with partially and completely dissolved condensation nuclei, is determined as

$$t_d = \frac{\eta_n}{J^{(1)}(0)(1+A)}. \quad (12.55)$$

According to the considerations given above in the commentary to Eq. (12.42), the smaller direct barrier $\Delta F^{(1)}$ the larger is the reversal barrier $\Delta F^{(2)}$. If $\Delta F^{(1)} \ll \Delta F^{(2)}$ then Eqs. (12.54), (12.51), (12.48) and (12.55) give $A \rightarrow 0$, and

$$t_d \rightarrow \frac{\pi \Delta\nu_c \Delta\nu_s^{(1)}}{W_c^+} \exp \left(\Delta F^{(1)} \right) \quad (12.56)$$

is fulfilled in this case. Evidently, the time t_d can be considered, in view of the right-hand side of Eq. (12.56), as a mean expectation time for droplet transition in the volume $1/\eta_n$. The time-lag of reaching the quasi-equilibrium states at the bottoms of the potential wells, $t_s^{(1)}$ and $t_s^{(2)}$, and the time-lag of establishing

the quasi-steady state at the top of the potential hump of the work of droplet formation, t_c , can be estimated [14] as

$$t_s^{(1)} = \frac{(\Delta\nu_s^{(1)})^2}{2W_s^{(1)}}, \quad t_c = \frac{(\Delta\nu_c)^2}{2W_c^+}, \quad t_s^{(2)} = \frac{(\Delta\nu_s^{(2)})^2}{2W_s^{(2)}}, \quad (12.57)$$

where $W_s^{(1)}$ and $W_s^{(2)}$ are determined by Eq. (12.50) with replacing R_c^2 by $(R_s^{(1)})^2$ and $(R_s^{(2)})^2$ correspondingly, where

$$R_s^{(1)} \equiv R|_{\nu=\nu_s^{(1)}, \nu'_n=\nu'_n(\nu_s^{(1)})}, \quad R_s^{(2)} \equiv R|_{\nu=\nu_s^{(2)}, \nu'_n=0}. \quad (12.58)$$

The following hierarchy of kinetic times,

$$t_1 \ll t_s^{(1)} \sim t_c \sim t_s^{(2)} \ll t_d, \quad (12.59)$$

should exist if $\Delta\nu_s^{(1)} \approx \Delta\nu_c \approx \Delta\nu_s^{(2)}$. The time t_1 is here a specific time of establishing the internal chemical equilibrium in the droplet with solid dissolving core which was calculated in Ref. 5 by considering kinetics of dissolution, diffusion and adsorption of the core substance in the droplet. As follows from Eqs. (12.56)-(12.59), the validity of the approach in this section is controlled by the strong inequality

$$\exp(\Delta F^{(1)}) \gg 1. \quad (12.60)$$

The larger $\Delta F^{(1)}$ (and the smaller $\Delta F^{(2)}$) the larger is the parameter A and the slower is the transition.

12.6 Some Approximate Formulas and Conclusions

The application of the one-dimensional theory allows us to obtain rather simple approximate formulas for distributions of droplets Eq. (12.44) and the specific times Eq. (12.57). As was previously said, the values of the vapor chemical potential b , at which an intensive kinetic overcoming of the activation barrier of deliquescence does occur, should be rather close to the threshold value b_{th} . This fact permits one to use a parabolic approximation for the solvent chemical potential b_ν in the vicinity of its maximum b_{th} [14]. In this case, the direct barrier

$\Delta F^{(1)}$, the locations $\nu_s^{(1)}$, ν_c and the half-widths $\Delta\nu_s^{(1)}$, $\Delta\nu_c$ of the first potential well and potential hump of the one-dimensional work \tilde{F} of droplet formation along the ν -axis can be expressed at $b < b_{th}$ as [13, 14]

$$\Delta F^{(1)} = \frac{4}{3} (b_{th} - b)^{3/2} \left[\frac{2}{|d^2\tilde{b}_\nu/d\nu^2|} \right]_{\nu=\nu_{th}}^{1/2}, \quad (12.61)$$

$$\nu_s^{(1)} = \nu_{th} - \left[\frac{2(b_{th} - b)}{|d^2\tilde{b}_\nu/d\nu^2|_{\nu=\nu_{th}}} \right]^{1/2}, \quad (12.62)$$

$$\nu_c^{(1)} = \nu_{th} + \left[\frac{2(b_{th} - b)}{|d^2\tilde{b}_\nu/d\nu^2|_{\nu=\nu_{th}}} \right]^{1/2},$$

$$\Delta\nu_s^{(1)} = \Delta\nu_c = \left[\frac{2}{(b_{th} - b) |d^2\tilde{b}_\nu/d\nu^2|_{\nu=\nu_{th}}} \right]^{1/4}. \quad (12.63)$$

In view of Eq. (12.39), the second derivative of the dimensionless condensate chemical potential \tilde{b}_ν with respect to the number of condensate molecules ν in the droplet can be written at $\nu = \nu_{th}$ in the form

$$\begin{aligned} \frac{d^2\tilde{b}_\nu}{d\nu^2} \Big|_{\nu=\nu_{th}} &= \left[\frac{\partial^2 b_\nu}{\partial\nu^2} + 2 \frac{\partial^2 b_\nu}{\partial\nu \partial\nu'_n} \frac{d\nu'_n(\nu)}{d\nu} + \frac{\partial^2 b_\nu}{\partial\nu'^2_n} \left(\frac{d\nu'_n(\nu)}{d\nu} \right)^2 \right. \\ &\quad \left. + \frac{\partial b_\nu}{\partial\nu'_n} \left[\frac{\partial}{\partial\nu} \left(\frac{d\nu'_n(\nu)}{d\nu} \right) + \frac{d\nu'_n(\nu)}{d\nu} \frac{\partial}{\partial\nu'_n} \left(\frac{d\nu'_n(\nu)}{d\nu} \right) \right] \right]_{\nu=\nu_{th}, \nu'_n=\nu'_n(\nu_{th})} \end{aligned} \quad (12.64)$$

with $\nu'_n(\nu)$, $d\nu'_n(\nu)/d\nu$, $\partial(d\nu'_n(\nu)/d\nu)/\partial\nu$ and $\partial(d\nu'_n(\nu)/d\nu)/\partial\nu'_n$ determined with the help of Eq. (12.36).

Now we have all necessary formulas to estimate the characteristic times and values of thermodynamic quantities at the deliquescence threshold and below it. Substituting Eqs. (12.36) and (12.37) into Eq. (12.39) and solving Eq. (12.39)

with respect to ν_{th} with the help of Eqs. (12.8)-(12.10) and the set of parameters determined by Eq. (12.35), we obtain

$$\begin{aligned}\nu_{th} &\simeq 1.319 \cdot 10^6, & R_{th} &= 2.3495 \cdot 10^{-6} \text{ cm}, \\ \nu'_n(\nu_{th}) &\simeq 3.9671 \cdot 10^5, & R'_n(R_{th}) &= 1.2373 \cdot 10^{-6} \text{ cm}.\end{aligned}\quad (12.65)$$

As follows from Eqs. (12.38), (12.64) and (12.65) with the help of Eqs. (12.36), (12.37), (12.8)-(12.10) and (12.35), the one-dimensional vapor chemical potential and its second derivative with respect to the number of solvent molecules are equal at the deliquescence threshold

$$b_{th} = -0.19275, \quad \left. \frac{d^2 \tilde{b}_\nu}{d\nu^2} \right|_{\nu=\nu_{th}} = -6.2874 \cdot 10^{-14}. \quad (12.66)$$

The negative sign of b_{th} in Eq. (12.66) means that the deliquescence threshold does realize in the undersaturated vapor.

Making estimations for the barrier transition from a deliquescence state to a state with completely dissolved nucleus, let us choose a not too high value for the direct activation barrier $\Delta F^{(1)}$. For instance, taking $\Delta F^{(1)} = 10$, we assume that the transition occurs intensively. It follows from Eqs. (12.61) and (12.66) at $\Delta F^{(1)} = 10$ that the value of the vapor chemical potential b , corresponding to such barrier, is

$$b = -0.19287. \quad (12.67)$$

Substituting Eqs. (12.65)-(12.67) into Eqs. (12.62) and (12.63) yields the following values of the quantities $\nu_s^{(1)}$, ν_c and $\Delta\nu_s^{(1)}$, $\Delta\nu_c$ at $\Delta F^{(1)} = 10$

$$\nu_s^{(1)} = 1.2570 \cdot 10^6, \quad \nu_c = 1.3811 \cdot 10^6, \quad \Delta\nu_s^{(1)} = \Delta\nu_c = 2.2647 \cdot 10^4. \quad (12.68)$$

It is easy now to check the accuracy of the formulas (12.61)-(12.63). Direct solving of Eq. (12.40) with the help of Eqs. (12.35)-(12.37) for a value of b given by Eq. (12.67) yields

$$\begin{aligned}\nu_s^{(1)} &= 1.2594 \cdot 10^6, & \nu_c &= 1.3835 \cdot 10^6, & \nu_s^{(2)} &= 3.0950 \cdot 10^6, \\ \nu'_n(\nu_s^{(1)}) &= 4.1079 \cdot 10^5, & \nu'_n(\nu_c) &= 3.8135 \cdot 10^5.\end{aligned}\quad (12.69)$$

As follows from Eqs. (12.45), (12.46) and (12.49) in view of Eqs. (12.35)-(12.37) and (12.69),

$$\Delta\nu_s^{(1)} = 2.1788 \cdot 10^4, \quad \Delta\nu_c = 2.3528 \cdot 10^4, \quad \Delta\nu_s^{(2)} = 5.326 \cdot 10^3. \quad (12.70)$$

Substituting Eqs. (12.35), (12.67) and (12.69) into Eqs. (12.34) with the help of Eqs. (12.6), (12.8)-(12.10) and (12.41) results in

$$\Delta F^{(1)} = 10.004, \quad \Delta F^{(2)} = 34152. \quad (12.71)$$

Comparing Eqs. (12.68) with Eqs. (12.69)-(12.71), one can conclude that the accuracy of Eqs. (12.61)-(12.63) is appropriate.

Now we are able to estimate the characteristic kinetic times t_d , $t_s^{(1)}$ and t_c . As follows from Eq. (12.71), $\Delta F^{(1)} \ll \Delta F^{(2)}$ in the considered case, and we can use Eq. (12.56) to find t_d . Assuming $\alpha_C = 1$, $v_T = 10^4$ cm/s, $n_\infty^\beta = 10^{17}$ cm⁻³ and using Eq. (12.35) in Eq. (12.50), substituting the result together with Eq. (12.68) into Eqs. (12.56) and (12.57), we find at $\Delta F^{(1)} = 10$

$$\begin{aligned} t_d &= 2.4 \cdot 10^3 \text{ s}, & t_s^{(1)} &= 1.7 \cdot 10^{-2} \text{ s}, \\ t_c &= 1.9 \cdot 10^{-2} \text{ s}, & t_s^{(2)} &= 6 \cdot 10^{-4} \text{ s}. \end{aligned} \quad (12.72)$$

The estimates in Eq. (12.72) show that the hierarchy of specific kinetic times expressed by Eq. (12.59) is fulfilled for the data chosen to illustrate the results of the one-dimensional theory of deliquescence.

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