

# Generalization of the Gibbs–Kelvin–Köhler and Ostwald–Freundlich equations for a liquid film on a soluble nanoparticle

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A derivation of chemical equilibrium equations for a spherical thin film of solution around a soluble solid nanoparticle is presented. The equations obtained generalize the Gibbs–Kelvin–Köhler and Ostwald–Freundlich equations for a soluble particle immersed in the bulk phase. The generalized equations describe the dependence of the chemical potentials of a condensate and dissolved nanoparticle matter in the thin solution film, the condensate saturated pressure, and the solubility of the nanoparticle matter on the film thickness, and the nanoparticle size with account of the disjoining pressure of the liquid film. © 2008 American Institute of Physics.

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## I. INTRODUCTION

Gibbs' relationship<sup>1</sup>

$$\mu_1 = \mu_{1,\infty} + \frac{2\sigma^{\alpha\beta}v_1^\alpha}{R} \quad (1)$$

is basic for the thermodynamics of homogeneous and heterogeneous nucleations. Equation (1) determines how the condensate chemical potential  $\mu_1$  in a spherical embryo of phase  $\alpha$ , surrounded by metastable phase  $\beta$ , depends on radius  $R$  of the embryo surface at a fixed temperature  $T$ . Here  $\mu_{1,\infty}$  is the condensate chemical potential at the equilibrium of phases  $\alpha$  and  $\beta$  with a flat interface,  $v_1^\alpha$  is the volume per condensate molecule in phase  $\alpha$  under the assumption that the phase is incompressible, and  $\sigma^{\alpha\beta}$  is the surface tension related to the embryo surface of tension; all the quantities are taken at the same temperature  $T$ . If phase  $\beta$  is an ideal gas and phase  $\alpha$  is a liquid (correspondingly, the embryo is a droplet), Eq. (1) can be rewritten in the form of the Gibbs–Kelvin equation,<sup>2</sup>

$$k_B T \ln \frac{p_{1,R}^\beta}{p_{1,\infty}^\beta} = \frac{2\sigma^{\alpha\beta}v_1^\alpha}{R} \quad (2)$$

for the equilibrium partial pressure  $p_{1,R}^\beta$  of the condensate vapor ( $p_{1,\infty}^\beta$  is a value of  $p_{1,R}^\beta$  for a flat interface between phases  $\alpha$  and  $\beta$  and  $k_B$  is the Boltzmann constant). If the droplet includes, in addition to the condensate (component 1) playing the role of a solvent, also a solute (component 2) with a relative bulk concentration  $x \equiv c_2^\alpha/c_1^\alpha$  [ $c_i$  is the number of molecules of component  $i$  ( $i=1,2$ ) per unit volume; the variable  $x$  coincides with the molar fraction for dilute solutions], then the Gibbs–Kelvin equation transforms into the Gibbs–Kelvin–Köhler equation,<sup>3</sup>

$$k_B T \ln \frac{p_{1,R}^\beta}{p_{1,\infty}^\beta} = \frac{2\sigma^{\alpha\beta}v_1^\alpha}{R} - k_B T x. \quad (3)$$

A relationship for the solubility  $x_R$  of a small solid particle (phase  $\gamma$ ) of radius  $R$  in the ideal bulk solution (phase  $\alpha$ ) is

analogous to the Gibbs–Kelvin equation and is called the Ostwald–Freundlich equation,<sup>4,5</sup>

$$k_B T \ln \frac{x_R}{x_\infty} = \frac{2\sigma^{\alpha\gamma}v_2^\gamma}{R}. \quad (4)$$

Here  $x_\infty$  is the relative concentration of solute in phase  $\alpha$  at the equilibrium of phases  $\alpha$  and  $\gamma$  with a flat interface,  $v_2^\gamma$  is the volume per molecule in the solid particle, and  $\sigma^{\alpha\gamma}$  is the surface tension of the solid particle at its boundary with phase  $\alpha$ ; all the quantities being taken at the same temperature  $T$ .

The problem of description of chemical equilibrium of a droplet condensing out the vapor-gas environment around partially dissolving solid nanoparticle (the so-called deliquescence problem) recently roused a considerable interest in view of new experimental technique for studying ultrafine aerosols.<sup>6,7</sup> Such a droplet consists of a spherical liquid film of saturated solution of the particle matter and the solid core (the remainder of the particle). It was experimentally proven<sup>6,7</sup> that, in the case of high solubility of the solid matter, the droplet with a soluble solid core can be stable in an undersaturated vapor. It is theoretically expected<sup>8</sup> that, in the case of low solubility, the droplet can be stable also in slightly supersaturated vapor. As a rule, the liquid film in a stable droplet is thin, with thickness much smaller than the radius of a solid core.

As was first shown theoretically,<sup>8</sup> the existence of thin stable films on partially dissolved cores can be explained using the concept of the film disjoining pressure. The disjoining pressure takes into account the difference of the normal component of the pressure tensor in a thin liquid film from the pressure in the bulk liquid phase of the same nature and at same values of temperature and chemical potentials of components as in the film.<sup>9</sup> The disjoining pressure is produced by overlapping of the surface layers related to the boundaries with the core and the vapor-gas medium. This overlapping is a result of long-ranged electrostatic and molecular forces (the electrostatic and molecular contributions

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to the disjoining pressure) and near-to-wall ordering (the structural contribution to the disjoining pressure).<sup>9</sup>

Earlier, the applications and extensions of the Gibbs–Kelvin–Köhler equation for the condensate chemical potential in the film on soluble solid core and the Ostwald–Freundlich equation for the solubility of solid matter in the film with account of disjoining pressure were considered in Refs. 8, 10, and 11. The relationships found in Ref. 8 referred to the quasiflat films of a dilute solution around partially soluble macroscopic condensation nuclei, with the surface tensions at the film boundaries taken the same as for a film of pure condensate. The Ostwald–Freundlich equation was taken in the form expressed in Eq. (4), and the difference between the partial molecular volumes of condensate and solute was neglected. An account of this difference and an extension of the Ostwald–Freundlich equation for a film of ideal solution on a nanoscaled condensation nucleus were presented in more recent papers.<sup>10,11</sup>

Expanding recently the definition of the disjoining pressure to the case of thin liquid films on small solid particles, we showed the condition of mechanical equilibrium in a spherical film with overlapping surface layers to be written as [Ref. 12, Eq. (80)]

$$p^\alpha - p^\beta = \frac{2\sigma^{\alpha\beta}}{R} - (p_N - p^\alpha) \frac{R_n^2}{R^2}, \quad (5)$$

where  $p^\alpha$  and  $p^\beta$  are the total pressures in the mother bulk phase of the film and the vapor phase at equilibrium with the film,  $R$  is the outer film radius,  $p_N$  is the normal component of the pressure tensor in the film at the boundary with the particle, and  $R_n$  is the particle radius. This refinement is important in the case of nanoscaled condensation nuclei, but it was earlier not recognized in the analysis of Gibbs–Kelvin–Köhler and Ostwald–Freundlich equations for thin films. Besides, when considering the conditions of equilibrium of a solid particle, one should take into account the difference between the thermodynamically and mechanically defined surface tensions of the particle and the fact that the chemical potential of the particle matter cannot be the same in solid particle and solution even at true equilibrium.<sup>1,13,14</sup> In addition, the surface tensions at the film boundaries depend, for thin films, on the film thickness and are related to the disjoining pressure.<sup>12,15,16</sup> Finally, because a thin film is inhomogeneous and the bulk density cannot be achieved anywhere within the film, the question arises what one should understand as a solute concentration entering Gibbs–Kelvin–Köhler and Ostwald–Freundlich equations for a thin film.

The problems noted indicate that some corrections to the derivation of Gibbs–Kelvin–Köhler and Ostwald–Freundlich equations are required in the case of thin spherical solution films on soluble solid nanoparticles, and we elaborate such corrections in this work. Resulting generalized equations will allow us to find the dependence on the film thickness and the nanoparticle size for the chemical potentials of all species, the saturated pressure of condensate vapor, and the solubility of the nanoparticle.

## II. RELATIONSHIPS FOR THE CHEMICAL POTENTIALS OF CONDENSATE AND DISSOLVED CORE MATTER IN A CURVED THIN FILM

Let us consider a droplet in the form of a liquid film around a spherical nonvolatile one-component solid core, the drop being in equilibrium with a surrounding vapor-gas medium. The solid matter is soluble in the film, so that the evaporation-condensation process between the drop and its surroundings can be accompanied by the dissolution-deposition process between the solid core and the film. We mark quantities referred to liquid, gas, and solid phases with superscripts  $\alpha$ ,  $\beta$ , and  $\gamma$ , respectively. It should be noted at once that the state of a bulk phase can be unattainable inside the core and the enveloping film in view of their small dimensions. It does not matter for the core because only surface monolayer plays the determinative role for solids,<sup>17</sup> although we may use also quantities referred to the solid reference bulk phase. The properties of liquid bulk phase  $\alpha$  can differ from those for the thin film. However, phase  $\alpha$  is a mother phase for the film and, when taken at the same values of temperature and chemical potentials, is of fundamental importance for description of the film.

We mark the condensing component by subscript 1 and the dissolving component by subscript 2. Let the outer radius of a droplet with a core be  $R$  and the core radius  $R_n$ . Our first task will be finding an isothermal dependence of the condensate and solute chemical potentials in the film on radii  $R$  and  $R_n$ .

Let us start with the condensate chemical potential  $\mu_1^\alpha$  in the phase  $\alpha$  being a uniform solution of the core matter in the condensate with relative concentration  $x$  at pressure  $p^\alpha$  and temperature  $T$ . As is known, the dissolution of foreign matter always decreases the chemical potential of a solvent, the effect being the stronger, the higher the solute concentration. This effect can be described in terms of the osmotic pressure  $\pi(x)$  under the assumption of incompressibility of phase  $\alpha$  as

$$\mu_1^\alpha(p^\alpha, x) = \mu_{1,0}^\alpha(p^\alpha) - v_1^\alpha \pi(x), \quad (6)$$

where  $\mu_{1,0}^\alpha$  is the molecular chemical potential in a pure condensate at the same pressure and temperature, and  $v_1^\alpha$  is the partial molecular volume of the condensate in the solution.

Let  $\Delta p \equiv p^\alpha - p^\beta$  be the total pressure difference for the liquid and gas phases. Then Eq. (6) with the same accuracy can be rewritten in the form

$$\mu_1^\alpha(p^\beta + \Delta p, x) = \mu_{1,0}^\alpha(p^\beta) + v_1^\alpha [\Delta p - \pi(x)]. \quad (7)$$

If the solution film around the core is thin, then overlapping the surface layers produces the disjoining pressure  $\Pi$  in the film. We define  $\Pi$  as<sup>12</sup>

$$\Pi \equiv p_N - p^\alpha, \quad (8)$$

where  $p^\alpha$  is pressure in the mother phase of the film at the same temperature and chemical potentials as in the film and  $p_N$  is the normal component of the pressure tensor in the film at its inner boundary with the core. Thus, when phase  $\alpha$  is at equilibrium with the spherical thin film, the chemical potentials of condensate and solvent in the phase  $\alpha$  and the film coincide, but in view of Eqs. (5) and (8) pressure  $p^\alpha$  in phase  $\alpha$  differs from the external pressure  $p^\beta$  by the quantity

$$\Delta p \equiv p^\alpha - p^\beta = \frac{2\sigma^{\alpha\beta}}{R} - \frac{R_n^2}{R^2}\Pi, \quad (9)$$

where  $\sigma^{\alpha\beta}$  is the surface tension at the boundary between the film and the gas phase. Disjoining pressure  $\Pi$  equals zero for a thick film, and Eq. (9) reduces to the Laplace equation in this case. In the general case, pressure  $\Pi$  is evident to depend on concentration  $x$  of the solute in the bulk solution kept in equilibrium with the film. In its turn, concentration  $x$  is determined by the values of chemical potentials in phase  $\alpha$ .

Taking into account the condition of equality of the condensate chemical potentials in phase  $\alpha$  and the film, we find, using Eqs. (7) and (9), the following relationship for the condensate chemical potential  $\mu_1$  in the film:

$$\begin{aligned} \mu_1 &= \mu_1^\alpha(p^\beta + \Delta p, x) \\ &= \mu_{1,0}^\alpha(p^\beta) + \frac{2\sigma^{\alpha\beta}v_1^\alpha}{R} - v_1^\alpha \left[ \frac{R_n^2}{R^2}\Pi + \pi(x) \right]. \end{aligned} \quad (10)$$

In view of the approximate equality  $\mu_{1,0}^\alpha(p^\beta) \approx \mu_{1,\infty}$  [the difference  $p^\beta - p_{1,\infty}^\beta$  is assumed to be much smaller than  $\Delta p$  or  $\pi(x)$  for nanosized droplets], Eq. (10) generalizes the Gibbs equation (1) to the case of thin spherical solution film on a solid core.

It is not hard to obtain, in a similar way, an expression for the solute chemical potential  $\mu_2$ . Using the condition of equality of the solute chemical potentials in phase  $\alpha$  and the film, we find, with the help of Eq. (9), the following relationship:

$$\mu_2 = \mu_2^\alpha(p^\beta + \Delta p, x) = \mu_2^\alpha(p^\beta, x) + \frac{2\sigma^{\alpha\beta}v_2^\alpha}{R} - v_2^\alpha \frac{R_n^2}{R^2}\Pi, \quad (11)$$

where  $\mu_2^\alpha$  is the solute chemical potential and  $v_2^\alpha$  is the solute partial molecular volume in phase  $\alpha$ . On the other hand, the chemical potential  $\mu_2$  should be equal to the chemical potential of the core matter at the core surface.<sup>17</sup> As is known,<sup>1,13,14</sup> the equality of the chemical potentials of the core matter inside the spherical solid particle and in the solution breaks. Nevertheless, if we know the value of the solute chemical potential in the solution, we know the value of the chemical potential of the solid at the core surface. Using Eq. (21) from Ref. 13 and assuming the core incompressible, one may write the following expression for the chemical potential  $\mu_2^\gamma(p^\beta)$  of the core matter at the surface of the core under external pressure  $p^\beta$ :

$$\mu_2^\gamma(p^\beta) = \mu_{2,\infty}^\gamma + v_2^\gamma \frac{2\sigma_{R_n}^{\alpha\gamma}}{R_n} + v_2^\gamma \frac{d\sigma_{R_n}^{\alpha\gamma}}{dR_n}, \quad (12)$$

where  $\mu_{2,\infty}^\gamma$  is the chemical potential of the solid matter at the flat interface between the solid substrate and the bulk solution with pressure  $p^\beta$  and concentration  $x_\infty$  and  $\sigma_{R_n}^{\alpha\gamma}$  is the thermodynamic surface tension at the core-solution boundary. Note that chemical potential  $\mu_{2,\infty}^\gamma$  can be represented<sup>1,13</sup> as

$$\mu_{2,\infty}^\gamma = v_2^\gamma(f + p_{N,\infty}) = \mu_{2,\infty}^\alpha, \quad (13)$$

where  $f$  is the free energy density in the solid phase,

$$p_{N,\infty} = p^\beta \quad (14)$$

is the normal component of the pressure tensor in the film at the boundary with the flat substrate, and

$$\mu_{2,\infty}^\alpha \equiv \mu_2^\alpha(p^\beta, x_\infty). \quad (15)$$

Changing the normal component of the pressure tensor at the substrate-solution boundary by quantity  $\Delta p_N \equiv p_N - p^\beta$ , where  $p_N$  corresponds, as before, to the value at the inner boundary of the spherical film around the solid core, we obtain from Eqs. (12)–(15) the following useful relationship:

$$\begin{aligned} \mu_2 &= \mu_2^\gamma(p^\beta + \Delta p_N) \\ &= \mu_2^\alpha(p^\beta, x_\infty) + v_2^\gamma \left( \Delta p_N + \frac{2\sigma^{\alpha\gamma}}{R_n} + \left. \frac{\partial \sigma^{\alpha\gamma}}{\partial R_n} \right|_{h=R-R_n} \right), \end{aligned} \quad (16)$$

which is hard to get for free by another approach. In this procedure surface tension  $\sigma_{R_n}^{\alpha\gamma}$  turns in Eq. (16) into surface tension  $\sigma^{\alpha\gamma}$  at the inner boundary of the film, the derivative  $d\sigma_{R_n}^{\alpha\gamma}/dR_n$  at a fixed state of the bulk solution into derivative  $(\partial \sigma^{\alpha\gamma}/\partial R_n)|_{h=R-R_n}$  at a fixed film thickness  $h=R-R_n$ . Therewith, the quantity  $\Delta p_N \equiv p_N - p^\beta$  has a sense of the difference of normal components of the pressure tensor at the inner and outer film boundaries. Note that the state of a curved thin film depends not only on the film thickness but also on the curvatures of each of the film boundaries as well because the curvatures can be varied independently. The fact that we fix only the film thickness means that the solid core is assumed to be large in comparison with the molecular size. Thus, the condition of a fixed film thickness which is strictly valid for a flat film serves here as an approximation.

Using the equality

$$\Delta p_N \equiv p_N - p^\beta = \Pi + \frac{2\sigma^{\alpha\beta}}{R} - \frac{R_n^2}{R^2}\Pi, \quad (17)$$

which follows from Eqs. (8) and (9), we find from Eq. (16)

$$\begin{aligned} \mu_2 &= \mu_2^\alpha(p^\beta, x_\infty) + v_2^\gamma \left( \Pi + \frac{2\sigma^{\alpha\beta}}{R} - \frac{R_n^2}{R^2}\Pi \right. \\ &\quad \left. + \frac{2\sigma^{\alpha\gamma}}{R_n} + \left. \frac{\partial \sigma^{\alpha\gamma}}{\partial R_n} \right|_{h=R-R_n} \right). \end{aligned} \quad (18)$$

This expression for the solute chemical potential allows us to derive an equation for the core activity and solubility.

### III. THE CORE SOLUBILITY AND THE SATURATED VAPOR PRESSURE OF THE CONDENSATE AS FUNCTIONS OF THE FILM AND CORE RADII

The standard expression for the chemical potential  $\mu_2^\alpha(p^\beta, x)$  in phase  $\alpha$ , which is the bulk solution of the solid core matter in the condensate with relative concentration  $x$  and activity  $a(x)$  at pressure  $p^\beta$  and temperature  $T$ , has a form

$$\mu_2^\alpha(p^\beta, x) = \mu_2^*(p^\beta) + k_B T \ln a(x), \quad (19)$$

where  $\mu_2^*$  is the standard part of the solute chemical potential (as  $x \rightarrow 0$ ). The analogous expression for  $\mu_{2,\infty}^\alpha$  can be written as

$$\mu_{2,\infty}^\alpha = \mu_2^*(p^\beta) + k_B T \ln a_\infty, \quad (20)$$

with  $a_\infty \equiv a(x_\infty)$ . Substituting Eq. (19) into Eq. (11) and, correspondingly, Eq. (20) into Eq. (18) and equating the right-hand sides of Eqs. (11) and (18), we obtain an equation for the solute activity as a function of radii  $R_N$  and  $R$ ,

$$k_B T \ln \frac{a(x)}{a_\infty} = v_2^\gamma \left( \Pi + \frac{2\sigma^{\alpha\gamma}}{R_n} + \left. \frac{\partial \sigma^{\alpha\gamma}}{\partial R_n} \right|_{h=R-R_n} \right) + (v_2^\gamma - v_2^\alpha) \left( \frac{2\sigma^{\alpha\beta}}{R} - \frac{R_n^2}{R^2} \Pi \right). \quad (21)$$

The equilibrium concentration  $x$  entering Eq. (21) refers not to the film itself, but to the film mother phase. It would coincide with the solubility  $x_{R_n}$  of the nanoparticle of radius  $R_n$  if the nanoparticle was immersed in the bulk phase  $\alpha$ . The real solubility  $x^f$  of the nanoparticle matter in the film is different from  $x$  and  $x_{R_n}$  because the distribution of the solute in the film is inhomogeneous. Evidently, the real distribution of the solute in the film can be represented as the bulk concentration in phase  $\alpha$  and adsorptions at the film boundaries. The adsorbed matter at the core surface is indistinguishable from the core itself and can easily be taken into account by the choice of radius  $R_n$ . As far as the adsorption at the film boundary with the gas phase is concerned, this adsorption is negligible in the typical case of surface inactive matter of the core (for instance, NaCl) that usually constitutes soluble condensation nuclei. Thus, the average solute concentration in the film and the bulk concentration in phase  $\alpha$  can be considered to be almost equal at the same temperature and chemical potentials, and we may call the equilibrium concentration  $x$  the solubility of the solid core in the film.

Evidently, Eq. (21) represents a more general form of the Ostwald–Freundlich equation (4) for the problem considered. Let us introduce some simplifications into the problem. Below we will consider only dilute ideal solutions and neglect the dependence of surface tensions  $\sigma^{\alpha\beta}$  and  $\sigma^{\alpha\gamma}$ , partial volumes  $v_1^\alpha$ ,  $v_2^\alpha$ , and the disjoining pressure  $\Pi$  on solute concentration. Equations (10) and (21) can therewith be rewritten as

$$\mu_1 - \mu_{1,0}^\alpha(p^\beta) = \frac{2\sigma^{\alpha\beta}v_1^\alpha}{R} - v_1^\alpha \frac{R_n^2}{R^2} \Pi - k_B T x, \quad (22)$$

$$k_B T \ln \frac{x}{x_\infty} = \frac{2\sigma^{\alpha\beta}(v_2^\gamma - v_2^\alpha)}{R} + \left( \frac{2\sigma^{\alpha\gamma}}{R_n} + \left. \frac{\partial \sigma^{\alpha\gamma}}{\partial R_n} \right|_{h=R-R_n} \right) v_2^\gamma - (v_2^\gamma - v_2^\alpha) \frac{R_n^2}{R^2} \Pi + v_2^\gamma \Pi. \quad (23)$$

In the particular case of a flat film, it follows from Eqs. (22) and (23), as  $R_n \rightarrow \infty$  and  $R \rightarrow \infty$ ,

$$\mu_1 - \mu_{1,\infty}^\alpha = -v_1^\alpha \Pi(h) - k_B T x, \quad (24)$$

$$k_B T \ln \frac{x}{x_\infty} = v_2^\alpha \Pi(h), \quad (25)$$

where  $h$  is the flat film thickness.

The surface tensions  $\sigma^{\alpha\gamma}$  and  $\sigma^{\alpha\beta}$  at the boundaries of the film are related to the disjoining pressure  $\Pi$ . This cannot be neglected for a thin film in the general case. The thermodynamics of flat thin films<sup>12,15</sup> gives the following relation:

$$\frac{\partial(\sigma^{\alpha\beta} + \sigma^{\alpha\gamma})}{\partial h} = -\Pi(h). \quad (26)$$

Recognizing that the disjoining pressure is determined by the normal component of the pressure tensor at the internal boundary of the film and assuming the main contribution to Eq. (26) to be given by the surface tension  $\sigma^{\alpha\gamma}$  at the same boundary, we can approximately replace the surface tension  $\sigma^{\alpha\beta}$  at the external boundary of the film by its macroscopic value  $\sigma_\infty^{\alpha\beta}$ . It allows us to rewrite Eq. (26) in the form

$$\frac{\partial \sigma^{\alpha\gamma}}{\partial h} \approx -\Pi(h). \quad (27)$$

Integrating Eq. (27) over thickness  $h$  at a fixed radius  $R_n$ , we find

$$\sigma^{\alpha\gamma} \approx \sigma_{R_n}^{\alpha\gamma} + \int_{R-R_n}^{\infty} \Pi(h) dh, \quad (28)$$

where the surface tension  $\sigma_{R_n}^{\alpha\gamma}$  corresponds, as before, to the solid core boundary with bulk phase  $\alpha$ . Using Eq. (28) and equality  $\sigma^{\alpha\beta} = \sigma_\infty^{\alpha\beta}$  in Eqs. (22) and (23) gives

$$\mu_1 - \mu_{1,0}^\alpha(p^\beta) = \frac{2\sigma_\infty^{\alpha\beta}v_1^\alpha}{R} - v_1^\alpha \frac{R_n^2}{R^2} \Pi - k_B T x, \quad (29)$$

$$k_B T \ln \frac{x}{x_\infty} = \frac{2(v_2^\gamma - v_2^\alpha)\sigma_\infty^{\alpha\beta}}{R} + \frac{2v_2^\gamma\sigma_{R_n}^{\alpha\gamma}}{R_n} + v_2^\gamma \frac{d\sigma_{R_n}^{\alpha\gamma}}{dR_n} - (v_2^\gamma - v_2^\alpha) \frac{R_n^2}{R^2} \Pi + v_2^\gamma \Pi + \frac{2v_2^\gamma}{R_n} \int_{R-R_n}^{\infty} \Pi(h) dh. \quad (30)$$

It follows from the condition of equilibrium of the film with the gas phase that  $\mu_1 = \mu_1^\beta$  at  $p_1^\beta = p_{1,R}^\beta$ . We have already noted that  $\mu_{1,0}^\alpha(p^\beta) \approx \mu_{1,\infty}^\alpha$  and  $\mu_{1,\infty}^\alpha = \mu_1^\beta(p_{1,\infty}^\beta)$ , where  $p_{1,\infty}^\beta$  is the saturated partial pressure of condensate vapor at a flat interface between pure liquid condensate and vapor. Thus, in the approximation of ideality of phase  $\beta$ , the difference  $\mu_1 - \mu_{1,0}^\alpha(p^\beta)$  can be expressed as

$$\mu_1 - \mu_{1,0}^\alpha(p^\beta) \approx k_B T \ln \frac{p_{1,R}^\beta}{p_{1,\infty}^\beta}. \quad (31)$$

Substituting Eq. (31) in the left-hand side of Eq. (29) gives

$$k_B T \ln \frac{p_{1,R}^\beta}{p_{1,\infty}^\beta} = \frac{2\sigma_\infty^{\alpha\beta}v_1^\alpha}{R} - v_1^\alpha \frac{R_n^2}{R^2} \Pi - k_B T x. \quad (32)$$

Jointly with Eq. (30), Eq. (32) determines the dependence of the pressure of the condensate vapor saturated over the spherical film of solution, on radii  $R_n$  and  $R$  of internal and

external boundaries of the film. Thus, Eq. (32) is a generalization of the Gibbs–Kelvin–Köhler equation for the condensate vapor pressure saturated over a droplet with a spherical solid core partially dissolved in the droplet. With the choice of radii  $R_n$  and  $R$  of the internal and external film boundaries as independent variables of the film state, with specified isotherm of the disjoining pressure as a function of the film thickness and a known dependence of  $\sigma_{R_n}^{\alpha\gamma}$  on  $R_n$ , Eq. (30) first allows one to find the core solubility  $x$ , and then, with the aid of Eqs. (29) and (32), also to determine the chemical potential of the condensate in the film and the pressure of the condensate vapor saturated over the film. Doing in this way solves the problem posed in Introduction.

Note now that radii  $R_n$  and  $R$  at the internal and external film boundaries may be determined as functions of the number  $N_1^\alpha$  of condensate molecules and the number  $N_2^\alpha$  of dissolved core molecules in the solution film (one can use the total number  $N_2$  of molecules of the core component instead of  $N_2^\alpha$ ). As it follows from the conditions of material balance and incompressibility in the core and the solution film, we have

$$\frac{4}{3}\pi R_n^3 = v_2^\gamma(N_2 - N_2^\alpha), \quad (33)$$

$$\frac{4}{3}\pi R^3 = (N_2 - N_2^\alpha)v_2^\gamma + N_1^\alpha v_1^\alpha + N_2^\alpha v_2^\alpha. \quad (34)$$

Substituting Eqs. (33) and (34) in Eq. (30) transforms Eq. (30) (with account of equality  $x \equiv N_2^\alpha/N_1^\alpha$ ) into a transcendental equation for  $N_1^\alpha$  and  $N_2^\alpha$ . Considering number  $N_2$  as a parameter, this equation can be solved at constant surface tensions and the assumption that  $N_1^\alpha = N_1$ , where  $N_1$  is the total number of condensate molecules in the film. The function  $N_2^\alpha(N_1)$  obtained in this way allows one to determine  $R_n$  and  $R$  with the use of Eqs. (33) and (34), i.e., to find the function  $R_n(R)$  at a specified  $N_2$ . Substituting this function in Eq. (32) establishes a relation between the pressure of condensate vapor saturated above the liquid film on a partially dissolved solid core and the external radius of the film at a specified initial (i.e., before the film formation) size of the core. Such a relation can be observed in direct experiment with soluble solid nanoparticles in the undersaturated solvent gas environment.<sup>6,7</sup>

#### IV. DISCUSSION

As has been mentioned in Introduction, the extensions of the Gibbs relation for the condensate chemical potential in the film on a soluble solid core, the corresponding Gibbs–Kelvin equation for the saturated vapor pressure of condensate, and the Ostwald–Freundlich equation for solubility of the core matter were earlier considered with account of the

disjoining pressure in our paper<sup>8</sup> and papers by Djikaev *et al.*<sup>10,11</sup> The equations obtained in Refs. 8, 10, and 11 have, however, some distinctions from Eqs. (29), (30), and (32) representing the main result of this paper. In particular, the relations from Ref. 8 referred to films on macroscopic condensation nuclei at  $R - R_n \ll R_n$ , where surface tensions  $\sigma^{\alpha\beta}$  and  $\sigma^{\alpha\gamma}$  at the film boundaries were assumed to be equal to their tabular values for a film of pure condensate and the difference in molecular volumes  $v_2^\gamma$  and  $v_2^\alpha$  was neglected. As a result, Eq. (30) was reduced in Ref. 8 to the form of classical equation (4). In its turn, the approach in Refs. 10 and 11 neglected the difference in  $\Delta p_N^\alpha$  and  $\Delta p$ , which leads, as can be seen from Eq. (30), to the loss of important term  $v_2^\gamma \Pi$  in the Ostwald–Freundlich equation. Besides, both in Ref. 8 and Refs. 10 and 11, the factor  $R_n^2/R^2$  before the disjoining pressure in the condition of mechanical equilibrium of a film (provided by spherical geometry of the film<sup>12</sup>) was replaced by unity and the relation between  $\sigma^{\alpha\gamma}$  and  $\Pi$  [which gives rise to the term  $(2v_2^\gamma/R_n) \int_{R-R_n}^\infty \Pi(h)dh$  in Eq. (30)] was not taken into account. Thus, we can say an estimable progress has been achieved in the present work.

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