Influence of adsorption on the formation of embryo lunules

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ABSTRACT

This paper discusses from a theoretical standpoint the influence of the adsorption of capillarly active substances on the formation of liquid embryo lunules[1] on the surface of imperfectly wetted spheric nuclei. By considering the thermodynamic potential of the system "nucleus–water vapour" before and after the formation of an embryo on the nucleus and, by using the method developed by Kaischew & Mutaftschiew, an expression is derived for the work of formation of an embryo lunule in the presence of adsorption. By taking into account the relation between the contact angle, changed by the decrease in specific surface energy due to adsorption, a general expression is given. This relation is expressed in terms of supersaturation, initial contact angle between the pure nucleus and the liquid, variation in specific surface energy caused by adsorption and between the radius of the nucleus and the radius of the embryo when no adsorption is involved. This formula is most general and under corresponding boundary conditions changes to all known expressions for the work of formation of embryos in homogeneous water vapour on a plane substratum and perfectly and imperfectly wetted condensation nuclei, respectively to those given by Gibbs, Volmer, Krastanov and Fletcher, as well as to the work of formation of embryos in homogeneous water vapour and plane substratum in the presence of adsorption, derived by Kaischew & Mutafschiew. In addition, this formula enables us to discuss embryo formation on condensation nuclei many times larger than the embryo formed at a corresponding supersaturation.

KRASTANOV (1941, 1947–1948, 1957) derived the kinetics and the thermodynamics of the formation of liquid embryos on imperfectly and perfectly wetted condensation nuclei.

The work of formation of an embryo of radius r_k on an imperfectly wetted condensation nucleus of radius r_0 and contact angle φ is given by the expression (KRASTANOV, 1947–1948)

$$A_k^* = \frac{4}{3}\pi r_k^2 \sigma - \frac{4}{3}\pi r_0^2 \sigma \left(3 \cos \varphi - 2\frac{r_o}{r_k}\right). \quad (1)$$

This expression is derived on the assumption that, despite imperfect wetting, the condensation nucleus attaches water molecules on its entire surface, considered homogeneous with respect to its surface properties, with the only difference that the more imperfectly wetted the nucleus is, so much the harder are water molecules adsorbed on its surface. As will be discussed later, this concept is most acceptable for small condensation nuclei.

It is readily shown that when the nucleus is imperfectly wetted layer lunules are formed instead of continuous spheric liquid layers. This holds for the cases when $r_0 \gtrless r_k$.

Then the work of formation of an embryo will be

$$A_k^* = \frac{2}{3}\pi r_k^2 \sigma \left\{1 + \left(\frac{1+xm}{g}\right)^3 + 3x^2 m\left(\frac{x-m}{g} - 1\right) + x^3\left[2 - 3\left(\frac{x-m}{g}\right) + \left(\frac{x-m}{g}\right)^3\right]\right\}, \quad (2)$$

where

$$x = r_o/r_k, \quad m = \cos \varphi, \quad g = \sqrt{1 + x^2 - 2xm}$$

derived by FLETCHER (1958) by means of the difference between the thermodynamic potentials of the system before and after the formation of the embryo. The same expression is

[1] The embryo formed on a portion of the convex surface of the nucleus will be referred to in this paper as lunule.

obtained by means of the Volmer-Krastanov method, derived and generalised in KRASTANOV and MILOSHEV (1963).

Relation (2) is a most general expression for the formation of embryos, since it covers all existing cases. In fact, for $x = 0$, (2) changes to the formula for the work of formation of embryos in homogeneous water vapour given by GIBBS (1892), while for $m = 1$ it transforms into Krastanov's expression for perfectly wetted condensation nuclei, and for $x \to \infty$, when $r_0 \to \infty$ it transforms into VOLMER's (1939) expression for the work of formation of embryos on a plane substratum.

If we compare expression (1) for incompletely wetted condensation nuclei with (2) we can easily show (KRASTANOV and MILOSHEV, 1963) that the more perfectly wetted and the smaller condensation nuclei are, so much closer is the value of $\hat{A}_k^*$ to that of A_k^*. Only for imperfect wetting and for large condensation nuclei is the difference between the two formulas substantial, $\hat{A}_k^*$ remaining smaller than A_k^* for any size of the condensation nuclei. For small condensation nuclei and for contact angles close to complete wetting (1) is reasonably accurate.

It is interesting to discuss the work of formation of embryos on perfectly wetted and imperfectly wetted condensation nuclei, under conditions involving adsorption of foreign substances on the substratum and on the surface of the condensing liquid. IZMAILOVA, PROHOROV and DERIAGIN (1957) demonstrated experimentally that it was possible to modify the activity of the condensation nuclei and the embryo formation in the presence of foreign substances. The variation in the specific surface energy of the liquid due to adsorption is expressed in terms of the coefficient of filling with adsorbed molecules by the well-known equation suggested by Shishkovski

$$\sigma - \sigma_a = \Delta\sigma = kTL_\infty \ln(1 - \theta), \tag{3}$$

where L_∞ is the greatest number of molecules which can be adsorbed per square centimeter. This variation in the specific surface energy is taken into account in the expressions for the work of formation of the embryos.

In a previous paper (KRASTANOV and MILOSHEV, 1961) we derived an expression for the formation of embryos on imperfectly wetted condensation nuclei in the presence of adsorption and under the assumptions made in the derivation of (1)

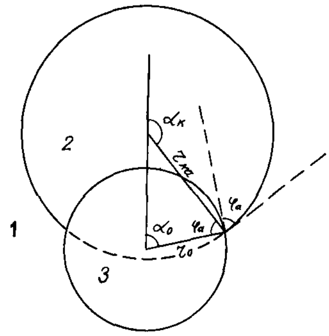

Fig. 1.

$$A_{ka}^* = \frac{4}{3}\pi r_k^2 \sigma \left(1 - \frac{\Delta\sigma}{\sigma}\right)^3 - \frac{4}{3}\pi r_0^2 \sigma \times \left[3\left(\cos\varphi - \frac{\Delta\sigma_0}{\sigma}\right) - 2\frac{r_0}{r_k}\right]. \tag{4}$$

However, it should be pointed out that eq. (4) as well as (1) are reasonably accurate only for small condensation nuclei and for contact angles close to complete wetting.

It becomes therefore indispensable to derive (2) under conditions involving adsorption of foreign substances. This formula will thus become quite general and will cover all cases of embryo formation under natural conditions and in the presence of adsorption of foreign substances. In addition, this formula will enable us to discuss the formation of embryos on condensation nuclei several times bigger than the embryo formed at a corresponding supersaturation.

To this effect we shall use once more the method of derivation developed elsewhere (KRASTANOV and MILOSHEV, 1961) and based upon the work of KAISCHEW and MUTAFTSCHIEW (1959).

In the presence of adsorption of foreign substances the embryo on a spherical substratum of radius r_0 and contact angle φ_a will be a liquid lunule of radius r_{ka} modified with respect to the radius in the absence of adsorption. We shall form out of the gaseous phase and on the substratum of radius r_0 a lunule of the same size r_{ka} and contact angle φ_a as in the case when no adsorption is involved. The work of formation of this lunule is given by the difference between the thermodynamic potentials of the system before and after its formation. If we have the condensation nucleus r_0 (Fig. 1) and if the fraction of its surface which takes part in the process has a surface energy, $2\pi r_0^2(1-\cos\alpha_0)\sigma_{1,3}$, is placed in vapour with thermodynamic potential μ, then the thermodynamic potential of the system "nucleus–water vapour" will be

$$G_1 = N\mu + 2\pi r_0^2(1-\cos\alpha_0)\sigma_{1,3},$$

where N denotes the number of molecules in the gaseous phase. After formation on the nucleus of a portion of a sphere of volume

$$V = \frac{4}{3}\frac{\pi}{V_f} r_{ka}^3\left(\frac{1}{2}-\frac{3}{4}\cos\alpha_k+\frac{1}{4}\cos^3\alpha_k\right) - \frac{4}{3}\frac{\pi}{V_f} r_0^3\left(\frac{1}{2}-\frac{3}{4}\cos\alpha_0+\frac{1}{4}\cos^3\alpha_0\right),$$

where V_f is the volume per molecule, part of the free surface of the nucleus vanishes, giving rise to the interface liquid–nucleus with specific interface energy $\sigma_{2,3}$. The thermodynamic potential after the formation of the lunule is expressed by

$$G_2 = (N-V)\mu + V\mu_f + 2\pi r_0^2(1-\cos\alpha_0)\sigma_{2,3} + 2\pi r_{ka}^2(1-\cos\alpha_k)\sigma_{1,2},$$

where μ_f is the thermodynamic potential of an infinitely large liquid, and $\sigma_{1,2}$—its specific surface energy. The work of formation of the lunule will be

$$\begin{aligned} A_1 = G_2 - G_1 &= 2\pi r_{ka}^2(1-\cos\alpha_k)\sigma_{1,2} - 2\pi r_0^2(1-\cos\alpha_0)\sigma_{1,2}\cos\alpha_a \\ &- \left[\frac{4}{3}\frac{\pi}{V_f} r_{ka}^3\left(\frac{1}{2}-\frac{3}{4}\cos\alpha_k+\frac{1}{4}\cos^3\alpha_k\right) - \frac{4}{3}\frac{\pi}{V_f} r_0^3\left(\frac{1}{2}-\frac{3}{4}\cos\alpha_0+\frac{1}{4}\cos^3\alpha_0\right)\right](\mu-\mu_f). \end{aligned} \quad (5)$$

The difference between the thermodynamic potentials of the gaseous phase and the infinitely large liquid is given by the equation of Thomson-Gibbs

$$\mu-\mu_f = \mu_{r_k}-\mu_\infty = RT\ln\frac{p_{r_k}}{p_\infty} = \frac{2\sigma_{1,2}V_f}{r_k}. \quad (6)$$

Let us separate the lunule formed in this way from its substratum and transfer it on another one, containing the substance to be adsorbed and placed in vapour with the same pressure. In order to separate the lunule from the substratum the following work will be necessary

$$A_2 = 2\pi r_0^2(1-\cos\alpha_0)(\sigma_{1,2}-\sigma_{1,3}-\sigma_{2,3}), \quad (7)$$

where $S = 2\pi r_0^2(1-\cos\alpha_0)$ denotes the surface at the interface embryo-substratum. The deposition of the lunule on the substratum containing the adsorbed substance will require the work

$$A_3 = 2\pi r_{ka}^2(1-\cos\alpha_k)(\sigma_{1,2}^a-\sigma_{1,2}) + 2\pi r_0^2(1-\cos\alpha_0)(\sigma_{2,3}'-\sigma_{1,3}^a-\sigma_{1,2}), \quad (8)$$

where $\sigma_{1,2}^a\ \sigma_{1,3}^a$ are the corresponding specific surface energies in the presence of adsorption, whereas $\sigma_{2,3}'$ is the specific interface energy between the liquid and the substratum with the adsorbed substance. $S^* = 2\pi r_{ka}^2(1-\cos\alpha_k)$ is the interface between the lunule and the gaseous phase. The first term in (8) denotes the work required for the reversible adsorption of foreign molecules on the surface S^*, while the second one refers to the work required for the deposition of the lunule on the new substratum.

The work of formation of an embryo upon adsorption of foreign substances on the substratum and on the condensing liquid is equal to the sum of the works A_1, A_2, and A_3.

$$\begin{aligned} A_{ka}^* &= 2\pi r_{ka}^2(1-\cos\alpha_k)\sigma_{1,2} - 2\pi r_0^2(1-\cos\alpha_0)\sigma_{1,2}\cos\varphi_a \\ &- \left[\frac{4}{3}\frac{\pi}{V_f} r_{ka}^3\left(\frac{1}{2}-\frac{3}{4}\cos\alpha_k+\frac{1}{4}\cos^3\alpha_k\right) - \frac{4}{3}\frac{\pi}{V_f} r_0^3\left(\frac{1}{2}-\frac{3}{4}\cos\alpha_0+\frac{1}{4}\cos^3\alpha_0\right)\right]\frac{2\sigma_{1,2}V_f}{r_k} \\ &+ 2\pi r_0^2(1-\cos\alpha_0)(\sigma_{1,2}+\sigma_{1,3}-\sigma_{2,3}) \\ &+ 2\pi r_{ka}^2(1-\cos\alpha_k)(\sigma_{1,2}^a-\sigma_{1,2}) \\ &+ 2\pi r_0^2(1-\cos\alpha_0)(\sigma_{2,3}'-\sigma_{1,3}^a-\sigma_{1,2}). \end{aligned} \quad (9)$$

For cases involving adsorption of foreign substances BLIZNAKOV (1952) first pointed out the necessity of modifying the Thomson-Gibbs equation

$$RT \ln \frac{p_{r_k}}{p_\infty} = \frac{2\sigma_a V_f}{r_{ka}}, \tag{10}$$

where r_{ka} is the radius of the droplet in equilibrium with supersaturated vapour in the presence of adsorption. Taking the ratio of equations (6) and (10) in presence and absence of adsorption we obtain the relationship (KAISCHEW and MUTAFTSCHIEW, 1959)

$$\frac{r_{ka}}{r_k} = \frac{\sigma_a}{\sigma} = 1 - \frac{\Delta\sigma}{\sigma}. \tag{11}$$

By taking into account (11) as well as the relationships

$$\sigma_{1,3} = \sigma_{2,3} + \sigma_{1,2}\cos\varphi_a,$$

$$\sigma^a_{1,3} = \sigma'_{2,3} + \sigma^a_{1,2}\cos\varphi_a,$$

from which we have

$$(\sigma'_{2,3} - \sigma_{2,3}) - (\sigma^a_{1,3} - \sigma_{1,3}) = (\sigma_{1,2} - \sigma^a_{1,2})\cos\varphi_a \tag{12}$$

and by substituting them in the expression for the work of formation of an embryo around an imperfectly wetted condensation nucleus upon adsorption of foreign substances on the substratum and on the condensing liquid, we obtain, after some rearrangements

$$\hat{A}^*_{ka} = \frac{2}{3}\pi r^2_{ka}\sigma_a\left\{1 + \left(\frac{1 - x_a m_a}{g_a}\right)^3 + 3x_a^2 m_a\left(\frac{x_a - m_a}{g_a} - 1\right) + x_a^3\left[2 - 3\left(\frac{x_a - m_a}{g_a}\right) + \left(\frac{x_a - m_a}{g_a}\right)^3\right]\right\}, \tag{13}$$

where

$$x_a = r_0/r_{ka}, \quad m_a = \cos\varphi_a, \quad g_a = \sqrt{1 + x_a^2 - 2x_a m_a}.$$

The value of the contact angle in the presence of adsorption can be derived from the relationships

$$\sigma_{1,3} = \sigma_{2,3} + \sigma_{1,2}\cos\varphi, \quad \sigma^a_{1,3} = \sigma_{2,3} + \sigma^a_{1,2}\cos\varphi_a$$

from which we have, for $\cos\varphi_a$ (KAISCHEW and MUTAFTSCHIEW, 1959),

$$\cos\varphi_a = \frac{\cos\varphi - \dfrac{\Delta\sigma_0}{\sigma}}{1 - \dfrac{\Delta\sigma}{\sigma}} \tag{14}$$

where $\Delta\sigma_0 = \sigma_{1,3} - \sigma^a_{1,3}$ denotes the change in the specific surface energy of the substratum due to adsorption, while $\Delta\sigma = \sigma_{1,2} - \sigma^a_{1,2}$ is the corresponding change in the surface energy of the liquid. Substituting $\cos\varphi_a$ from (14) and the values for r_{ka} and σ_a from (11) in (13) we obtain for $\hat{A}^*_{ka}$

$$\hat{A}^*_{ka} = \frac{2}{3}\pi r_k^2\sigma\left(1 - \frac{\Delta\sigma}{\sigma}\right)^3$$

$$\times\left\{1 + \left[\frac{1 - \dfrac{r_0}{r_k}\dfrac{\left(\cos\varphi - \dfrac{\Delta\sigma_0}{\sigma}\right)}{\left(1 - \dfrac{\Delta\sigma}{\sigma}\right)^2}}{\left(1 + \dfrac{r_0^2}{r_k^2}\dfrac{1}{\left(1 - \dfrac{\Delta\sigma}{\sigma}\right)^2} - 2\dfrac{r_0}{r_k}\dfrac{\left(\cos\varphi - \dfrac{\Delta\sigma_0}{\sigma}\right)}{\left(1 - \dfrac{\Delta\sigma}{\sigma}\right)^2}\right)^{\frac{1}{2}}}\right]^3\right.$$

$$+ 3\frac{r_0^2}{r_k^2}\frac{\left(\cos\varphi - \dfrac{\Delta\sigma_0}{\sigma}\right)}{\left(1 - \dfrac{\Delta\sigma}{\sigma}\right)^3}$$

$$\times\left[\frac{\dfrac{r_0}{r_k}\dfrac{1}{\left(1 - \dfrac{\Delta\sigma}{\sigma}\right)} - \dfrac{\left(\cos\varphi - \dfrac{\Delta\sigma_0}{\sigma}\right)}{\left(1 - \dfrac{\Delta\sigma}{\sigma}\right)}}{\left(1 + \dfrac{r_0^2}{r_k^2}\dfrac{1}{\left(1 - \dfrac{\Delta\sigma}{\sigma}\right)^2} - 2\dfrac{r_0}{r_k}\dfrac{\left(\cos\varphi - \dfrac{\Delta\sigma_0}{\sigma}\right)}{\left(1 - \dfrac{\Delta\sigma}{\sigma}\right)^2}\right)^{\frac{1}{2}}} - 1\right]$$

$$+ \frac{r_0^3}{r_k^3}\frac{1}{\left(1 - \dfrac{\Delta\sigma}{\sigma}\right)^3}$$

$$\times\left[2 - 3\left\{\frac{\dfrac{r_0}{r_k}\dfrac{1}{\left(1 - \dfrac{\Delta\sigma}{\sigma}\right)} - \dfrac{\left(\cos\varphi - \dfrac{\Delta\sigma_0}{\sigma}\right)}{\left(1 - \dfrac{\Delta\sigma}{\sigma}\right)}}{\left(1 + \dfrac{r_0^2}{r_k^2}\dfrac{1}{\left(1 - \dfrac{\Delta\sigma}{\sigma}\right)^2} - 2\dfrac{r_0}{r_k}\dfrac{\left(\cos\varphi - \dfrac{\Delta\sigma_0}{\sigma}\right)}{\left(1 - \dfrac{\Delta\sigma}{\sigma}\right)^2}\right)^{\frac{1}{2}}}\right\}\right.$$

$$
+\left[\frac{\dfrac{r_0}{r_k}\dfrac{1}{\left(1-\dfrac{\Delta\sigma}{\sigma}\right)}-\dfrac{\left(\cos\varphi-\dfrac{\Delta\sigma_0}{\sigma}\right)}{\left(1-\dfrac{\Delta\sigma}{\sigma}\right)}}{\left(1+\dfrac{r_0^2}{r_k^2}\dfrac{1}{\left(1-\dfrac{\Delta\sigma}{\sigma}\right)^2}-2\dfrac{r_0}{r_k}\dfrac{\left(\cos\varphi-\dfrac{\Delta\sigma_0}{\sigma}\right)}{\left(1-\dfrac{\Delta\sigma}{\sigma}\right)^2}\right)^{\frac{1}{2}}}\right]^3\Bigg]\Bigg\}. \tag{15}
$$

For $r_0=0$ expression (15) transforms into the expression for the work of formation of embryos in homogeneous water vapour in the presence of adsorption

$$
A^0_{ka}=\frac{4}{3}\pi r_k^2\sigma\left(1-\frac{\Delta\sigma}{\sigma}\right)^3, \tag{16}
$$

while for $r_0\to\infty$ it becomes identical with the expression for the work of formation of embryos on a plane substratum upon adsorption

$$
\bar{A}^*_{ka}=\frac{4}{3}\pi r_k^2\sigma\left(1-\frac{\Delta\sigma}{\sigma}\right)^3\left[\frac{1}{2}-\frac{3}{4}\left(\frac{\cos\varphi-\dfrac{\Delta\sigma_0}{\sigma}}{1-\dfrac{\Delta\sigma}{\sigma}}\right)+\frac{1}{4}\left(\frac{\cos\varphi-\dfrac{\Delta\sigma_0}{\sigma}}{1-\dfrac{\Delta\sigma}{\sigma}}\right)^3\right] \tag{17}
$$

derived by Kaischew and Mutaftschiew (1959).

In addition, when there is no adsorption (i.e. $\Delta\sigma/\sigma=\Delta\sigma_0/\sigma=0$) (15) changes to the work of formation of a lunule under natural conditions (2). The latter, in turn, transforms for $r_0=0$ into the work of formation of embryos in homogeneous water vapour, given by Gibbs (1892)

$$
A^0_k=\frac{4}{3}\pi r_k^2\sigma. \tag{18}
$$

When $m=\cos\varphi=1$ we obtain Krastanov's expression for perfectly wetted nuclei (1947–1948)

$$
A_k=\frac{4}{3}\pi r_k^2\sigma-\frac{4}{3}\pi r_0^2\sigma\left(3-2\frac{r_0}{r_k}\right). \tag{19}
$$

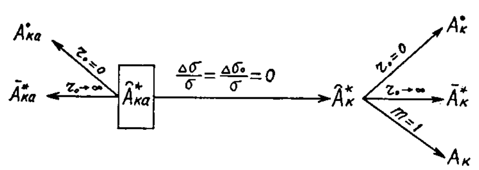

Fig. 2.

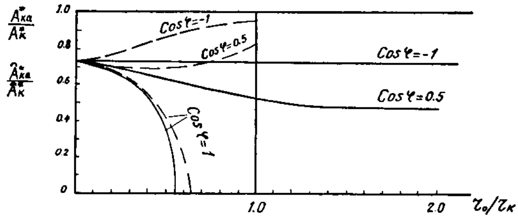

Fig. 3.

For $x\to\infty$ when $r_0\to\infty$ we have the work of formation of embryos on a plane substratum Volmer (1939)

$$
\bar{A}^*_k=\frac{4}{3}\pi r_k^2\sigma\left(\frac{1}{2}-\frac{3}{4}\cos\varphi+\frac{1}{4}\cos^3\varphi\right). \tag{20}
$$

These relationships are to be seen best in Fig. 2.

In order to illustrate the influence of adsorption on the process of embryo formation let us consider the ratio

$$
\frac{\hat{A}^*_{ka}}{\hat{A}^*_k}=\frac{\left(1-\dfrac{\Delta\sigma}{\sigma}\right)^3\left\{1+\left(\dfrac{1-x_am_a}{g_a}\right)^3+3x_a^2m_a\left(\dfrac{x_a-m_a}{g_a}-1\right)+x_a^3\left[2-3\left(\dfrac{x_a-m_a}{g_a}\right)+\left(\dfrac{x_a-m_a}{g_a}\right)^3\right]\right\}}{\left\{1+\left(\dfrac{1-xm}{g}\right)^3+3x^2m\left(\dfrac{x-m}{g}-1\right)+x^3\left[2-3\left(\dfrac{x-m}{g}\right)+\left(\dfrac{x-m}{g}\right)^3\right]\right\}}. \tag{21}
$$

In the presence of adsorption of foreign substances on the condensing liquid only, that is, for $\Delta\sigma/\sigma=0.1$ and $\Delta\sigma_0/\sigma=0$ and for determined contact angles $\cos\varphi=1, 0.5, \sigma, -1$ we plot ratio (21) against different values of r_0/r_k in Fig. 3 (full line).

It can be easily seen that for all contact angles in the interval $0°\leqslant\varphi\leqslant180°$, the ratio

$\bar{A}^*_{ka}/A^*_k$ is smaller than unity, i.e., the work upon adsorption is smaller than the work when there is no adsorption for all values of the ratio r_0/r_k. Let us compare now in Fig. 2 Eq. (21) with the ratio A^*_{ka}/A^*_k, given on the same figure with dashed lines

$$\frac{A^*_{ka}}{A^*_k} = \frac{\left(1-\frac{\Delta\sigma}{\sigma}\right)^3 - 3\left(\frac{r_0}{r_k}\right)^2\left(\cos\varphi - \frac{\Delta\sigma_0}{\sigma}\right) + 2\left(\frac{r_0}{r_k}\right)^3}{1-3\left(\frac{r_0}{r_k}\right)^2\cos\varphi + 2\left(\frac{r_0}{r_k}\right)^3}. \quad (22)$$

It is evident that for small condensation nuclei and for contact angles close to full wetting, ratio (22) is close to ratio (21). Only for imperfect wetting and for large values of r_0/r_k is the discrepancy substantial. Therefore, for small condensation nuclei and for contact angles close to 0°, expressions (1) and (4) can be used with a reasonable claim to accuracy. The more accurate expressions (2) and (13) have the advantage of enabling us to discuss the influence of adsorption also for values of the ratio $r_0/r_k > 1$.

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