Classification and general derivation of interfacial forces, acting on phases, situated in the bulk, or at the interface of other phases

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In the present paper the general equation and algorithm to derive interfacial forces, acting on phases, situated in the bulk, or at the interface of other phases are given. Based on that, interfacial forces are classified into the following six major types: (i) the "curvature induced interfacial force" (due to Laplace), (ii) the "interfacial gradient force", acting on particles in inhomogeneous fluid phases, due to composition-, temperature- and electrical potential gradient (known as Marangoni force, or thermocapillary force), (iii) the "interfacial capillary force", acting on a phase at an interface of two large phases, including the behaviour of solid particles at the liquid/gas, fluid/fluid and solid/solid interfaces (known as the capillary force, and as the Zener pinning force), (iv) the "interfacial meniscus force," acting between two, solid phases, situated at a curved fluid/fluid or solid/solid interface, the curvature being due to the gravitational or electric fields (known also as the lateral capillary force, or electrodipping force), (v) the "liquid bridge induced interfacial force," acting between two, solid particles, due to the liquid bridge of small volume between them, and (vi) the "interfacial adhesion force," acting between two particles in a homogeneous fluid phase (with the phenomenological Derjaguin- and Hamaker constants, re-visited).
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1. Introduction

Interfacial phenomena play an increasing role in materials science and technology, as materials production is shifting from the requirement to control phenomena at the mm- and μm-level, towards the requirement to control the phenomena at the nm-level.

The majority of interfacial phenomena are connected with the individual movement of small solid particles, liquid droplets or gaseous bubbles in the bulk of a larger phase, or along, and/or across the interface between two other phases. In order to understand and control such phenomena, the interfacial forces, acting on these phases should be known, and coupled with other forces, such as gravity, buoyancy, drag, etc. The goal of this paper is to present a general algorithm to derive all possible kinds of interfacial forces, acting on separate phases. In addition to a general equation on interfacial forces, six major types of different specific interfacial forces will be classified, being different due to different situations of the phase, at which those forces act. Some of the simplified equations of this paper will be given for spherical, rigid particles, allowing some mathematical simplifications. However, the six types of forces will act on any phase, regardless of its state (solid, liquid, gas) and shape. It should be mentioned, however, that non-rigid phases might change their shapes under the influence of the interfacial (or other) force, what, on the other hand, will alter the magnitude of the interfacial force.

2. The general equation to derive interfacial forces

Imagine a system, consisting of any number of phases. Let us consider the interfacial force, acting at an arbitrary chosen phase in an arbitrary chosen direction, x. The equation for the interfacial force can be obtained in the following way. First, the total interfacial energy of the system should be described as function of parameter x:

$$G_\sigma = \sum_{i,j} A_{i/j} \cdot \sigma_{i/j} \tag{1}$$

where i and j are numbers, denoting different phases, $\sigma_{i/j}$ is the interfacial energy between them (J/m^2), $A_{i/j}$ is the interfacial area between them (m^2) and G_σ is the total interfacial energy of the system (J).

Then, following Newton and Gibbs, the interfacial force, acting on the chosen phase in direction x can be obtained as a derivative of G_σ by x, taken with a negative sign:

$$F_{\sigma,x} = -\frac{dG_\sigma}{dx} \tag{2}$$

The negative sign follows from the sign convention of thermodynamics, saying that spontaneous processes take place along paths with some negative change of the Gibbs energy. When the interfacial force appears to be positive from Equation 2, its direction (as a vector) is the same as that of vector x, and vice versa.

Substituting Equation 1 into Equation 2, the following general equation can be obtained:

$$F_{\sigma,x} = -\sum_{i,j} \sigma_{i/j} \cdot \frac{dA_{i/j}}{dx} - \sum_{i,j} A_{i/j} \cdot \frac{d\sigma_{i/j}}{dx} \quad (3)$$

As follows from Equation 3, the interfacial force might appear for two reasons: due to the change of any interfacial energy, or of any interfacial area in the system, while the studied phase moves along the path x. If none of these quantities change along the path of the studied phase, the interfacial force, acting on this phase equals zero. Equation 3 is applicable only, if along the considered path x the interfacial Gibbs energy of the system is a continuous function of x, i.e. if there is no break on the $G_\sigma(x)$ curve.

3. The "curvature induced interfacial force" (the Laplace equation)

Let us consider a spherical phase 1 of radius x in an infinitely large, homogeneous fluid phase 2. Let the radius of the sphere increase infinitely slowly, without changing the bulk energy of the system. Then, the only 1/2 interface of the system will have a constant interfacial energy, but a variable interfacial area. Therefore, Equation 3 will have only one of the first terms. Substituting $A_{1/2} = 4 \cdot \pi \cdot x^2$ for a sphere, performing the derivation and dividing the resulting interfacial force by the same expression for $A_{1/2}$, the following equation for the "curvature induced interfacial pressure" is obtained:

$$P_{\sigma,x}^{curv} \equiv \frac{F_{\sigma,x}^{curv}}{A_{1/2}} = -\frac{2 \cdot \sigma_{1/2}}{x} \quad (4)$$

Equation 4 is the classical, 200-years old equation of Young and Laplace for a sphere [1–2] (see also [3]). The minus sign indicates that the interfacial pressure acts from outside towards the centre of the sphere, along its interface. This "curvature induced interfacial force" acts only due to the existence of the curved interface, and non-zero interfacial energy. Equation 4 is derived here for two reasons. First, to demonstrate that the well-known Laplace equation follows from the general Equation 3. Second, to show that the Laplace equation is not the basis for all other interfacial forces, it is just one of the consequences of a most general Equation 3. It should be mentioned that the force considered here is a general force acting on the interface to ensure both mechanical and chemical equilibrium of the system.

4. The "interfacial gradient force"

Let us consider phase 1 of a constant size and shape, moving inside of an infinitely large, inhomogeneous phase 2. The temperature-, composition- and electric potential inhomogeneities in phase 2 might cause the variation of the interfacial energy along path x:

$$\frac{d\sigma_{1/2}}{dx} = \frac{d\sigma_{1/2}}{dT} \cdot \frac{dT}{dx} + \sum_i \frac{d\sigma_{1/2}}{dx_i} \cdot \frac{dx_i}{dx} + \frac{d\sigma_{1/2}}{dE} \cdot \frac{dE}{dT}$$

$$(5)$$

where T is temperature, x_i is mole fraction of component i in phase 2, E is electric potential. As along the path of phase 1 its interfacial area $A_{1/2}$ remains constant, only the second term of Equation 3 will be effective in this case. Then, the "interfacial gradient force" will equal:

$$F_{\sigma,x}^{grad} = -A_{1/2} \cdot \frac{d\sigma_{1/2}}{dx} \quad (6)$$

The 'minus' sign in Equation 6 indicates that the force is pointed towards the region of phase 2 with lower interfacial energy (usually of higher temperature and with higher concentration of interface active components).

Generally the temperature- and composition gradient in phase 2 (in absence of phase 1) is different from that along the interface of phases 1 and 2 (in presence of phase 1). Thus, for a spherical particle of radius r Equation 6 becomes:

$$F_{\sigma,x}^{grad} = -k \cdot \pi \cdot r^2 \cdot \frac{d\sigma_{1/2}}{dx} \quad (6a)$$

where in ideal case $k = 4$, but generally k is a function of other physical parameters and hydrodynamic conditions around (and inside for a fluid) phase 1. Particularly, eddies might form behind a moving solid spherical particle, what might mix phase 2, and thus the composition gradient will be active only along the front surface of the sphere, and so $k = 2$ is applicable for this case. Parameter k will be a function of the ratio of heat conductivity of phases 1 and 2, when the interfacial energy gradient is caused by a temperature gradient.

The interfacial gradient force was introduced into the metallurgical literature by Mukai and Lin [4] with $k = 8/3$, who also performed very precise experimental measurements [5]. Parameter k was later modified to $k = 4$ for an ideal case [6] and to $k = 2$ for the particular case [7]. An equation with $k = 2$ was derived in an implicit form much earlier for bubbles in a temperature gradient field [8, 9] (see also experimental verification [10,11]).

The "interfacial gradient force", discussed in this chapter was called also "Marangoni force" [10, 12, 13]. Indeed, the Marangoni convection is also driven by a gradient in the interfacial energy. However, the Marangoni convection starts along the fluid/fluid interface, and is directed towards places with higher interfacial energy along the interface. In our case the particle (droplet, bubble) is situated in the bulk of a fluid phase, and it is moved towards places with lower interfacial energy. That is why the difference between the

Marangoni force and the "interfacial gradient force" is essential. The "interfacial gradient force" was also called "thermocapillary force" for the case when it is induced by temperature gradient [14]. In this specific case the present author suggests to use the term "temperature gradient induced interfacial gradient force". Alternatively, the terms "concentration gradient induced interfacial gradient force" and "electric potential gradient induced interfacial gradient force" are suggested. The temperature gradient induced interfacial gradient force was recently exploited to produce egg-type [12] and core-type [13] composite microstructures in monotectic alloys.

5. The "interfacial capillary force"

Let us consider a rigid phase 3, situated at the interface of two fluid phases 1 and 2 (at depth of immersion x in phase 1), and transferring with an infinitely small velocity from phase 2 into phase 1 (see Fig. 1). During this process the three interfaces will gradually change, hence Equation 1 will include the following three terms:

$$
\begin{aligned}
G_\sigma &= A_{1/2} \cdot \sigma_{1/2} + A_{1/3} \cdot \sigma_{1/3} + A_{2/3} \cdot \sigma_{2/3} \\
&= A_{1/2}(x) \cdot \sigma_{1/2} + A_3^{\mathrm{o}} \cdot \sigma_{2/3} \\
&\quad + A_{1/3}(x) \cdot (\sigma_{1/3} - \sigma_{2/3})
\end{aligned} \tag{7}
$$

where $A_{1/2}(x)$ is the x-dependent fluid/fluid interface area, A_3^{o} is the total surface area of phase 3 and $A_{1/3}(x)$ is the x-dependent interfacial area between phases 1 and 3.

Substituting Equation 7 into Equation 2 and performing the derivation, the general equation can be derived for the "interfacial capillary force", acting on phase 3, in a perpendicular direction to the fluid/fluid interface of phases 1 and 2:

$$
F_{\sigma,\mathrm{x}}^{\mathrm{cap}} = (\sigma_{2/3} - \sigma_{1/3}) \cdot \frac{\mathrm{d} A_{1/3}(x)}{\mathrm{d}x} - \sigma_{1/2} \cdot \frac{\mathrm{d} A_{1/2}(x)}{\mathrm{d}x} \tag{8a}
$$

In the particular case, when 1 = liquid, 2 = gas, 3 = solid, Equation 8a can be re-written applying the Young

Figure 1 A rigid particle 3 (solid), situated at the interface of phases 1 (liquid) and 2 (gas).

equation, as:

$$
F_{\sigma,\mathrm{x}}^{\mathrm{cap}} = \sigma_{1/\mathrm{g}} \cdot \left[\frac{\mathrm{d} A_{\mathrm{s/l}}}{\mathrm{d}x} \cdot \cos\Theta - \frac{\mathrm{d} A_{1/\mathrm{g}}}{\mathrm{d}x} \right] \tag{8b}
$$

where Θ—the contact angle of the liquid on the solid in the gas environment.

Equation 8a–b can be applied to particles, droplets and bubbles of any shape. When the particle is fixed, the same Equation 8b can be applied for the force, pulling the liquid on the surface of the particle. When the solid phase 3 is taken as a cylindrical capillary, Equation 8b transforms into the well-known Laplace equation of the capillary pressure (see [15]). The same equation can be used to reproduce and improve further the Carman-equation [15,16] of penetration.

When phase 3 is a solid, spherical particle of radius r, the following equations are valid: $A_{1/2} = A_{1/2}^{\mathrm{o}} - 2 \cdot r \cdot \pi \cdot x + \pi \cdot x^2$ ($A_{1/2}^{\mathrm{o}}$ is the total 1/2 interface area), $A_{1/3} = 2 \cdot r \cdot \pi \cdot x$. Substituting these equations into Equation 8a, the following general equation is obtained:

$$
F_{\sigma,\mathrm{x}}^{\mathrm{cap}} = 2 \cdot r \cdot \pi \cdot \sigma_{1/2} \cdot \left[1 + \frac{\sigma_{2/3} - \sigma_{1/3}}{\sigma_{1/2}} - \frac{x}{r} \right] \tag{9a}
$$

For the particular case when a solid particle 3 is situated at a liquid/gas interface, Equation 9a can be re-written, as:

$$
F_{\sigma,\mathrm{x}}^{\mathrm{cap}} = 2 \cdot r \cdot \pi \cdot \sigma_{1/\mathrm{g}} \cdot \left(1 + \cos\Theta - \frac{x}{r} \right) \tag{9b}
$$

An equation, similar to Equation 9b was derived by different authors independently several times [17–20]. It should be mentioned that during the last decades there were also papers in the literature with different and incorrect equations, published for the same situation.

In the absence of other forces, the particle reaches its equilibrium at the liquid/gas interface when the interfacial capillary force equals zero. Substituting this condition into Equation 9b, the equilibrium depth of immersion of the particle equals:

$$
x_{\mathrm{eq}} = r \cdot (1 + \cos\Theta) \tag{10a}
$$

As follows from Equations 9b–10a, the interfacial capillary force always tends to return the spherical particle into its equilibrium position, if its actual position is different from that. Moreover, the interfacial force increases with the deviation of the actual position of the particle from its equilibrium position. In other words, the interfacial capillary force acts as an "elastic stabilizer", or as a "spring". This unique property of this force is what is behind the ability of small solid particles to stabilize liquid foams [21–24] and emulsions [25]. The same force will stabilize small solid particles at the liquid/gas interface even if the density of the particles is larger than that of the liquid. The critical size of the particles to detach from the liquid/gas interface was calculated and compared with experiments in [20, 26–27].
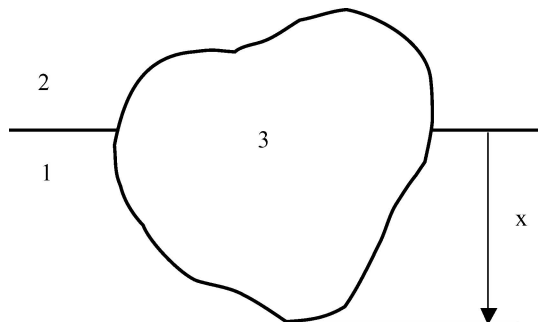
When phase 3 is a solid, spherical particle of radius r, situated at the grain boundary of solid grains 1 and 2, Equation 9a is applicable. When the two neighbouring grains 1 and 2 are identical (both in composition and orientation), $\sigma_{2/3} = \sigma_{1/3}$, the maximum interfacial capillary force at $x = 2r$ is found as: $F_{\sigma,x}^{\text{cap}} = -2 \cdot r \cdot \pi \cdot \sigma_{1/2}$. This force is known as the "Zener pinning force" in the literature. It should be noted that coefficient 2 is missing from the original equation of Zener (see [28]), corrected later by Ashby *et al.* [29] (see also review [30]).

6. The "interfacial meniscus force"

The equations derived above are based on the assumption that the horizontal liquid/gas interface is not disturbed by the solid particle. In reality, however, it is usually not the case, and a curved meniscus is formed around the particle. Although the curved meniscus has no significant influence on the value of the interfacial capillary force, it will create the "interfacial meniscus force" between two particles at the same fluid/fluid interface. The curvature of the meniscus can be caused by the particle weight in the gravitational field [31–41], or by the electric field around a charged particle [42, 43]. Only the gravity induced interfacial meniscus force will be considered here in details.

First, let us analyse the condition that a horizontal meniscus is formed around a spherical particle in the gravitational field, in absence of an electric charge on the surface of the particles. Considering only the balance of the gravity and buoyancy forces, the following equality will hold at the equilibrium position of the particle:

$$\rho^* \equiv \frac{\rho_s - \rho_g}{\rho_l - \rho_g} = \frac{x_{\text{eq}}^2 \cdot (3 \cdot r - x_{\text{eq}})}{4 \cdot r^3} \qquad (10b)$$

where ρ is the density of solid (*s*), liquid (*l*) and gas (*g*) phases.

The meniscus around the particle will be horizontal, if the equilibrium position of the particle due to the interfacial capillary force (Equation 10a) from the one hand, and due to the balance of the gravity and buoyancy forces (Equation 10b) from the other hand, will equal. This condition is equivalent to the equality of the dimensionless density (ρ^*) to its special value ρ_{flat}^*. The expression for ρ_{flat}^* can be found by substituting Equation 10a into Equation 10b, as:

$$\rho_{\text{flat}}^* = \frac{1}{4} \cdot (1 + \cos \Theta)^2 \cdot (2 - \cos \Theta) \qquad (10c)$$

Now, let us consider two spherical particles 3 and 4, separated by a distance of x (x is measured between their interfaces), at the interface of two fluid phases 1 and 2 (see Fig. 2). When the condition $\rho^* = \rho_{\text{flat}}^*$ is fulfilled for two, identical particles (see Fig. 2b), the menisci around both the particles are flat, and therefore the interfacial energy G_σ of the system will not change as function of their distance. Thus, as follows from Equation 2, there is no interfacial meniscus force between them. However, for the majority of particle/liquid com-
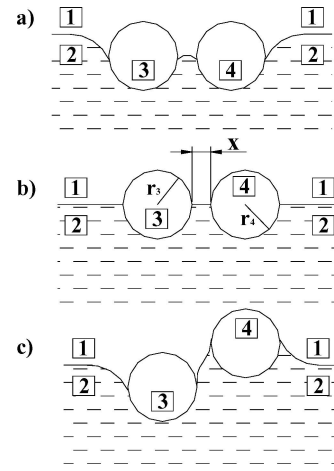

Figure 2 Two, spherical particles 3 and 4 at the interface of two fluid phases 1 and 2 with identical particles (a), with identical neutral particles (b) and with different particles (c).

binations the condition $\rho^* = \rho_{\text{flat}}^*$ is not fulfilled, and therefore the meniscus around the particles is not flat (see Figs 2a and c). Therefore, the shape of the meniscus between two neighbouring particles will be a function of their separation, i.e. the total interfacial energy G_σ of the system will be also the function of x. As a consequence, in all cases when $\rho^* \neq \rho_{\text{flat}}^*$ the "interfacial meniscus force" will arise, being responsible for the coagulation of identical particles on liquid surfaces. From Equation 3 the following equation can be written:

$$F_{\sigma,x}^{\text{menis}} = F_{\sigma,x}^{\text{bridge}} = \sigma_{1/2} \cdot \left(\frac{\mathrm{d}A_{2/3}}{\mathrm{d}x} \cdot \cos \Theta_{3/2/1} + \frac{\mathrm{d}A_{2/4}}{\mathrm{d}x} \right.$$
$$\left. \cdot \cos \Theta_{4/2/1} - \frac{\mathrm{d}A_{12}}{\mathrm{d}x} \right) \qquad (11)$$

where $\Theta_{i/2/1}$ is the contact angle of phase 2 on phase *i* ($i = 3$ or 4) in the environment of phase 1.

In order to apply Equation 11, first the interfacial areas $A_{2/3}$, $A_{2/4}$ and $A_{1/2}$ should be derived as function of x. The interfacial meniscus force was calculated numerically for the gravitational field [31–33] and for the electrical field [43]. The analytical solution exists only when certain approximations are used. The approximated equation for the gravity induced interfacial meniscus force between particle 3 with mass m_3 and particle 4 with mass m_4 can be written in a simplified way as [34]:

$$F_{\sigma,x}^{\text{menis}} \cong -\frac{81 \cdot g^2}{32 \cdot \pi} \cdot \frac{m_3 \cdot m_4}{x \cdot \sigma_{1/2}} \cdot (\rho_3^* - \rho_{3,\text{flat}}^*)$$
$$\cdot (\rho_4^* - \rho_{4,\text{flat}}^*) \qquad (12)$$

where g—the gravitational constant (9.81 m/s² on the Earth).

Equation 12 is approximately valid only for small particles (with radii smaller than 1 mm) [33]. From Equation 12 one can see that the sign of the interfacial meniscus force depends on the signs of the two last terms. If the particles are identical, or similar in a sense that for both of them ($\rho^* - \rho_{\text{flat}}^*$) has the same sign (see

Fig. 2a), the force will be negative, i.e. attractive. For dissimilar particles, for which $(\rho^* - \rho^*_{\text{flat}})$ have different signs (see Fig. 2c), the force will be positive, i.e. repulsive.

It is interesting to note that among all the interfacial forces, the interfacial meniscus force is the only one, which is inversely proportional to the interfacial energy. The reason is that interfaces with lower interfacial energies appear to be more curved under the influence of particles of the same mass, and thus the interfacial meniscus force, arising due to the compensation of these curved menisci, will be also higher. It is also important to note that the gravity induced interfacial meniscus force (Equation 12) is the only interfacial force, disappearing in absence of gravity.

The approximated validity of Equation 12 was proven experimentally on the surface of ordinary liquids [35–38]. The agglomeration of particles was observed directly on the surface of liquid metals [39, 40] and even at the liquid metal/slag interface [41]. From the recorded velocity of the particles the interfacial meniscus force was estimated and the results have been found to be in good agreement with the above theory.

The "interfacial meniscus force" was called also as "lateral capillary force" [33, 38]. To the opinion of the present author it is important to underline in the name of this force that it arises only due to the existence of curved menisci around the particles. If one wants to specify this force further, the names "gravity induced interfacial meniscus force", or "electric field induced interfacial meniscus force" are suggested in this paper. The later was also called recently as "electrodipping force" [43].

Kainuma et al. [44] recently observed that liquid droplets coalesce with unexpectedly high velocity at grain boundaries. It is possible that the reason of this fast coalescence is the interfacial meniscus force, acting on liquid droplets along the curved grain boundaries.

7. The liquid bridge induced interfacial force

In Fig. 2 small solid particles are situated on the surface of a large liquid phase. When the volume of the liquid phase is much smaller than that of the solid particles, this liquid will form a liquid bridge between the particles. Although Equation 11 remains valid also for this case, the particular solutions will be very much different. That is why it has a sense to define this force by a different name: the "liquid bridge induced interfacial force".

The solution of Equation 11 is possible only numerically, obtained for equal spheres by [45, 46] and for unequal-sized spheres by [47, 48]. An approximated solution exists only for equal spheres of radii r, in the limit of $V_{\text{liquid}} \to 0$ and $x \to 0$ [45]:

$$F_{\sigma,x}^{\text{bridge}} \cong -2 \cdot \pi \cdot r \cdot \sigma_{\text{l/g}} \cdot \cos \Theta \qquad (13)$$

From Equation 13 one can see that the liquid bridge induced interfacial force at the limit $V_{\text{liquid}} \to 0$ and $x \to 0$ will be negative, i.e. it will attract the parti-

cles only, if the particles are wetted by the liquid with a contact angle below 90°. The liquid bridge induced interfacial force will be weaker, and the critical contact angle at which the force changes from being attractive to repulsive will be also lower when the volume of the liquid bridge and the distance between the particles increase.

The liquid bridge induced interfacial force, measured experimentally in liquid metallic systems [45, 49, 50] was found to be in good agreement with theory [45]. Also, the relative shrinkage of the sintered sample was found to be approximately proportional to the theoretically calculated force [46], confirming the validity of the theoretical equations.

8. The interfacial adhesion force

Let us consider two, solid particles 2 and 3, with a smallest distance x between their interfaces, within a homogeneous fluid phase 1. The two particles will attract or repulse each other due to the so called "interfacial adhesion force". This force is mainly responsible for agglomeration (clustering) of solid particles in liquids. In this case the total interfacial energy G_σ contains two terms, corresponding to the fluid 1/solid 2 and to the fluid 1/solid 3 interfaces. If the interfacial energies are treated as constants, and the particles are considered rigid, G_σ will not be a function of x, and thus the interfacial adhesion force will be zero (see Equation 3). However, when the two particles appear close to each other, they will influence the energy of the surface atoms of each other, i.e. $\sigma_{1/2}$ and $\sigma_{1/3}$ become functions of x, and thus the interfacial adhesion force will appear. In this case, the effective surface areas of the two particles ($A^*_{1/2}$ and $A^*_{1/3}$), influenced by each other will always equal, i.e. $A = A^*_{1/2} = A^*_{1/3}$. Then, from the second term of Equation 3:

$$F_{\sigma,x}^{\text{adh}} = -A \cdot \left(\frac{\mathrm{d}\sigma_{1/2}(x)}{\mathrm{d}x} + \frac{\mathrm{d}\sigma_{1/3}(x)}{\mathrm{d}x} \right) \qquad (14)$$

The distance-dependence of the interfacial energies can be described as [51, 52]:

$$\sigma_{1/2}(x) = \sigma_{1/2} + (\sigma_{2/3} - \sigma_{1/2}) \cdot \left(\frac{d}{d+x} \right)^2 \qquad (15a)$$

$$\sigma_{1/3}(x) = \sigma_{1/3} + (\sigma_{2/3} - \sigma_{1/3}) \cdot \left(\frac{d}{d+x} \right)^2 \qquad (15b)$$

where d—is the diameter of the atom or molecule in the liquid.

Now, for simplicity, let us apply Equation 14 for two, flat particles with parallel areas of A, facing each other. Then, after substituting Equations 15a–b into Equation 14 and performing the derivation, the following equation is obtained:

$$F_{\sigma,x}^{\text{adh}} = 2 \cdot A \cdot \Delta\sigma \cdot \frac{d^2}{(d+x)^3} \qquad (16a)$$

TABLE I Geometrical parameters of Equation 16b for some simple cases

Phase 2	Phase 3	Position	k	n	Ref
Plane of area A	Plane of area A	Parallel	$2 \cdot A$	3	[56]
Plane of ∞ area	Sphere of radius r	–	$2 \cdot r \cdot \pi$	2	[54]
Sphere of radius r_2	Sphere of radius r_3	–	$2 \cdot \pi \cdot \frac{r_2 \cdot r_3}{r_2 \pm r_3}$	2	[54]
Cylinder of radius r_2	Cylinder of radius r_3	Crossing under α*	$2 \cdot \pi \cdot \frac{\sqrt{r_2 \cdot r_3}}{\sin \alpha}$	2	[55]

*α—is the angle between the axes of the two cylinders.

with

$$\Delta\sigma = 2 \cdot \sigma_{2/3} - \sigma_{1/2} - \sigma_{1/3} \qquad (17a)$$

Equation 16a is a specific form of a more general equation [3, 53]:

$$F_{\sigma,x}^{adh} = k \cdot \Delta\sigma \cdot \frac{d^2}{(d+x)^n} \qquad (16b)$$

with the geometrical parameters k and n listed in Table I.

Comparing Equations 16a–b and the first line of Table I, one can see that these two equations are identical. The only deviation between our present results from the classical results is the definition of parameter $\Delta\sigma$. In opposite to what is derived in Equation 17a [51, 52] the classical result of Derjaguin [55] and Hamaker [57] is written as (see also [53, 58]):

$$\Delta\sigma = \sigma_{2/3} - \sigma_{1/2} - \sigma_{1/3} \qquad (17b)$$

Although the difference between Equations 17a–b is only in a coefficient 2, these two equations often lead to different signs of the interfacial adhesion force. Equation 17b is inadequate, as the simplified method of $\Delta G_\sigma/\Delta x$ was applied during its derivation [55, 57, 58], instead of the dG_σ/dx, according to Equation 2. The validity of Equation17a is confirmed by the results of pushing/engulfment experiments (see [52] and references thereof).

It is interesting to note that the generally contradicting Equations 17a and b simplify to the same equation for the interaction of two, chemically identical particles (phase 2 = phase 3, i.e. $\sigma_{2/3} = 0$, $\sigma_{1/2} = \sigma_{1/3}$):

$$\Delta\sigma = -2 \cdot \sigma_{1/2} \qquad (17c)$$

As follows from Equation 17c, identical particles will always attract each other. For dissimilar particles it is not always the case.

9. Conclusions
A general algorithm to derive equations for the interfacial forces has been suggested. Equations for six different types of interfacial forces have been derived for rigid particles, appearing in different situations. The classification of different interfacial forces is suggested.

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