Interfacial Forces in Dispersion Science and Technology

George Kaptay
BAY-NANO Research Institute and University of Miskolc, Miskolc, Hungary

Interfacial forces determine many phenomena in dispersion science and technology. Eight types of interfacial forces are classified in this article. A general equation for all of them is derived here, with particular equation for each of them (being valid for simplified geometries, such as spheres, cylinders, etc.). As a new element, an interfacial anti-stretching force is introduced in this article, being equivalent to the definition of the interfacial energy in terms of tension as understood by Young. The differences and similarities between the interfacial gradient force and the interfacial spreading force (the Marangoni force) are shown. The well-known case of the liquid bridge induced interfacial force is supplemented by its less known version of a gaseous bridge induced interfacial force.

Keywords Capillary forces, disjoining pressure, infiltration, interfacial forces, meniscus

1. INTRODUCTION

The behavior of different dispersed phases (solid particles, liquid droplets, gaseous bubbles) in composites, foams and emulsions at or near interfaces is mostly determined by interfacial forces. The basics of the subject of this article were founded in the works of Young[1] and Laplace[2] more than 200 years ago. The majority of forces considered here have been described in previous reviews.[3–6] However, a general approach like this has not been found elsewhere before. By definition, interfacial forces are those which become zero when all interfacial energies (or all interfacial areas) in the system are zero. Interfacial forces have been classified in[7] according to the number of phases involved and to the direction of the force relative to the major interface in the system. This system is slightly corrected in this article (Table 1). The goal of the present article is to derive equations connecting all eight forces with interfacial energies (tensions) and geometrical parameters of the system.

In this article, the terms surface tension, interfacial tension, surface energy, interfacial energy, etc. will all be called as “interfacial energy” and denoted as $\sigma_{\Phi\Psi}$, with a unit of J/m$^2$. Double subscripts are used for phases surrounding interfaces: $v$ = vapor, $g$ = gas, $l$ (or $L$) = liquid, $s$ = solid, more generally: $\alpha$, $\beta$, $\gamma$, $\delta$ or $\Phi$, and $\Psi$. The interfacial energy in this article will be defined in a thermodynamic way as an excess interfacial Gibbs energy of the surface/interface per unit area[9,10]

$$\sigma_{\Phi\Psi} = \frac{\Delta G_{\Phi\Psi}}{\omega_{\Phi\Psi}}, \quad [1]$$

where $\Delta G_{\Phi\Psi}$ is the change of the Gibbs energy accompanying the transfer of one mole of material from both of the bulk phases $\Phi$ and $\Psi$ to the common interface $\Phi/\Psi$ (J/mol), $\omega_{\Phi\Psi}$ is the molar interfacial area (m$^2$/mol) of the $\Phi/\Psi$ interface.

2. GENERAL EQUATION FOR INTERFACIAL FORCES

Now, let us consider a general scheme of deriving the magnitude and direction of an interfacial force acting on a phase (see Figure 1). Let us select direction $x$ and phase $\alpha$ to be studied. Both selections are made in an arbitrary way. If the present procedure is repeated in three perpendicular directions ($x$, $y$, $z$), the resulting force components $F_{x,x}$, $F_{x,y}$, and $F_{x,z}$ can be summed as vectors and in this way the actual magnitude and direction of the interfacial force acting on the selected phase $\alpha$ is obtained. The same procedure can be applied to derive the interfacial force acting on other phases in the system. Now, let us write the total interfacial energy of the system as function of $x$, that is, while phase $\alpha$ moves along direction $x$ in Figure 1:

$$G_{x}(x) = \sum_{\Phi,\Psi} A_{\Phi\Psi}(x) \cdot \sigma_{\Phi\Psi}(x) \quad [2]$$
where $G_r$ is the total interfacial energy of the system (J), $A_{\Phi\Psi}$ is the interfacial area of the $\Phi/\Psi$ interface ($m^2$), $\sigma_{\Phi\Psi}$ is defined by Equation (1). According to Newton and Gibbs, the force acting on phase $a$ along direction $x$ is defined as:

$$F_{a,x} \equiv -\frac{dG_r(x)}{dx} \quad [3]$$

The negative sign in Equation (3) indicates that the transfer of phase $a$ along path $x$ (Figure 1) is spontaneous, that is, takes place towards more negative values of the total interfacial Gibbs energy. In other words, Equation (3) describes the inner driving force of the system, arising as the system is in a macroscopic non-equilibrium state, while local equilibrium is supposed at a molecular level along all interfaces. Thus, the driving force described by Equation (3) drives the system towards its macroscopic equilibrium state. In Equations (2)–(3) it was supposed that the transfer of phase $a$ along path $x$ (Figure 1) is not connected with any change of the bulk Gibbs energies of any of the phases. It is also supposed that the transfer of phase $a$ along path $x$ takes place infinitely slowly, that is, through equilibrium steps. Now, let us substitute Equation (2) into Equation (3) to obtain the final, general equation for the interfacial force:

$$F_{a,x} = -\sum_{\Phi,\Psi} A_{\Phi\Psi}(x) \frac{d\sigma_{\Phi\Psi}(x)}{dx} - \sum_{\Phi,\Psi} \sigma_{\Phi\Psi}(x) \frac{dA_{\Phi\Psi}(x)}{dx} \quad [4]$$

**TABLE 1**

Classification of interfacial forces, according to the number of involved phases and according to the orientation of the force in respect to the major interface in the system

<table>
<thead>
<tr>
<th>Orientation number of phases</th>
<th>Parallel to the main interface</th>
<th>Perpendicular to the main interface</th>
<th>Independent of the main interface</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Interfacial anti-stretching force</td>
<td>Curvature induced interfacial force</td>
<td>Interfacial gradient force</td>
</tr>
<tr>
<td>3</td>
<td>Interfacial spreading force</td>
<td>Interfacial capillary force</td>
<td>Interfacial adhesion force</td>
</tr>
<tr>
<td>4</td>
<td>Interfacial meniscus force</td>
<td>Fluid bridge induced interfacial force</td>
<td></td>
</tr>
</tbody>
</table>

**FIG. 1.** To the definition of interfacial forces: Phase $a$ moves within phase $\beta$ along vector (path) $x$ in a 4-phase ($a$, $\beta$, $\gamma$, $\delta$) system.
From Equation (4) one can conclude that an interfacial force acting on phase $a$ along path $x$ will appear, if any of the interfacial energies $\sigma_{\phi_{W}}$ or any of the interfacial areas $A_{\phi_{W}}$ of the system changes when phase $a$ moves along path $x$. If none of them change during this process, the interfacial force is zero. Calculating $F_{a,x}$ by Equation (4), both positive and negative values can be obtained. If the calculated value is positive, the direction of the force coincides with the direction of the arbitrary chosen direction $x$, and vice versa.

3. THE INTERFACIAL ANTI-STRETCHING FORCE

Let us consider a liquid film of width $w$ stretched on a perfectly wetted frame along direction $x$ (see Figure 2). To stretch the frame with a constant and infinitely slow rate, a force is needed to compensate the effect of an interfacial force. This force is called here the “interfacial anti-stretching force” ($F_{a,\text{str}}$). For the derivation let us neglect the thickness ($\delta$) of the liquid film and the diameter of the frame. Thus, the problem becomes a two-phase problem (liquid and vapor). Also, surface tension $\sigma_{lv}$ is taken as a constant, and so only the second term of Equation (4) applies, without summation. The total interfacial area of the liquid film from Figure 2: $A_{lv}(x) = P \cdot x$, where $P$ is the perimeter (m) around the liquid film, perpendicular to direction $x$. Substituting this equation into Equation (4), the following equation is obtained:

$$F_{a,\text{str}} = -P \cdot \sigma_{lv}$$

The interfacial anti-stretching force has not been considered as a special class of interfacial forces.$^{[3–7]}$ Instead, the experiment in Figure 2 is used to define the surface tension of liquids.$^{[4]}$ Indeed, surface tension (N/m) has an identical numerical value with that of the interfacial anti-stretching force (N) if $w = 0.5$ m and $P = 1$ m. In this article surface tension is defined on thermodynamic grounds by Equation (1) and, thus, Equation (5) is free to define the interfacial anti-stretching force. This force can be used to derive the equilibrium shapes of phases (ie., the Young equation$^{[5]}$) and equilibrium size of bubbles detaching from orifices.$^{[11,12]}$

4. THE CURVATURE INDUCED INTERFACIAL FORCE

The force, arising due to the curvature of an interface is called the “curvature induced interfacial force” ($F_{cur}$), being zero for a flat interface. This force acts perpendicular to the interface. If this force is divided by the surface area it is converted into the “curvature induced interfacial pressure” ($p_{cur}$). Let us consider a small spherical bubble of radius $x$ in a liquid (Figure 3). As the system contains two phases (liquid and gas) and the surface tension of the liquid is considered as constant, only one term remains in Equation (4). The interfacial area equals: $A_{lv}(x) = 4 \cdot \pi \cdot x^2$. Substituting this equation into Equation (4), the following equation is obtained:

$$F_{cur} = -8 \cdot \pi \cdot x \cdot \sigma_{lv}$$

Dividing this equation by the equation for the surface area of the bubble, the equation for the curvature induced interfacial pressure is obtained:

$$p_{cur} = -\frac{2 \cdot \sigma_{lv}}{x}$$

As follows from the negative sign of Equation (6), $p_{cur}$ acts to shrink the smaller phase (the bubble in Figure 3). Equation (6) is a particular case of a more general Laplace equation$^{[2]}$:

$$|p_{cur}| = \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \cdot \sigma_{lv}$$

FIG. 2. A liquid film stretched using a frame (to the derivation of the interfacial anti-stretching force, $F_{a,\text{str}}$). $F_{a,\text{str}}$ acts along the $lv$ interface, against stretching the liquid film.

FIG. 3. To the derivation of the curvature induced interfacial force ($F_{cur}$). $F_{cur}$ acts to shrink the smaller phase, perpendicular to the curved liquid/gas interface.
where $R_1$ and $R_2$ are the two principal radii of the interface in the given point. The equivalency of Equations (6)–(7) is shown here to demonstrate that the Laplace equation is one of the particular cases of the general Equation (4).

5. THE INTERFACIAL GRADIENT FORCE

When a particle (droplet, bubble, etc.) is placed in a matrix phase with an interfacial energy gradient, it will be driven by the so-called “interfacial gradient force” ($F_{\text{grad}}^{\text{lv}}$) towards places of lower interfacial energy. This gradient is created by the gradient of any physical quantity on which it depends, such as composition, temperature, and electric potential:

$$\frac{d\sigma_{\text{lv}}}{dx} = \frac{d\sigma_{\text{lv}}}{dT} \frac{dT}{dx} + \sum_c \frac{d\sigma_{\text{lv}}}{dx_c} \frac{dx_c}{dx} + \frac{d\sigma_{\text{lv}}}{dE} \frac{dE}{dx} \quad [8a]$$

where $T$ is absolute temperature (K), $x_c$ is the mole fraction of the $c$-th component in the matrix phase, and $E$ is the electric potential (V) at the metal/ionic interface if such is present.

For simplicity let consider a vapor phase of a constant shape and area of $A_{\text{lv}}$, dispersed in a liquid, moving along vector $x$. As there are only two phases (liquid and vapor), only one term of Equation (4) remains to determine the equation for the interfacial gradient force:

$$F_{\text{grad}}^{\text{lv}} = -k \cdot A_{\text{lv}} \cdot \frac{d\sigma_{\text{lv}}(x)}{dx} \quad [8b]$$

where $k$ is the numerical factor, taking into account the influence of the moving phase on the temperature, concentration, or electric potential gradients inside the matrix phase. As follows from Equation (8b), the direction of this force will coincide with the direction of the decrease of the interfacial energy. As surface tension of liquids usually decreases with increased temperature and with the increase of concentration of a surface active component $c$, bubbles in liquids are usually driven by the interfacial gradient force towards regions with a higher temperature and/or a higher concentration of surface active components.

Similarly to $F_{\text{grad}}^{\text{lv}}$, other forces can be defined along other types of interfaces, such as $F_{\text{grad}}^{\text{sl}}$. For this case Equation (8b) is still valid if the subscripts $lv$ are replaced by subscripts $sl$, respectively. However, for interfaces with at least one solid phase involved, the interfacial gradient force might cancel by the well-known “no-slip” hydrodynamic boundary condition at the solid interface, being valid for macroscopic fluid particles. Around microscopic or nanosized particles surface diffusion along the particle/fluid interface might provide the necessary mechanism to ensure that the interfacial gradient force is active even at the solid/fluid interfaces. This is supported by comparison with some experimental results. Finally, it should be mentioned that migration of phases due to the “interfacial gradient force” is sometimes called “thermocapillary convection,” “Marangoni migration,” or “Marangoni-induced motion” in the literature. This question is discussed below.

6. THE INTERFACIAL SPREADING FORCE

As was documented since the nineteenth century, an oil film rapidly spreads over water. The force spreading liquids over surfaces of another, immiscible liquid surfaces is called the “interfacial spreading force” ($F_{\text{spr}}^{\text{lv}}$). As shown in Figure 4a, two immiscible liquids ($L$, $l$) and the vapor ($v$) phase participate in creating the interfacial spreading force. The driving force for spreading is the difference in interfacial energies: $\Delta \sigma_{\text{spr}} \equiv \sigma_{LV} - \sigma_{LV} - \sigma_{Ll}$. As follows from the Young equation, the condition of perfect wettability of the lower phase $L$ by the upper phase $l$ in $v$ is $\Delta \sigma_{\text{spr}} \geq 1$. The same is the condition of the positive driving force of spreading.

Let us take all interfacial energies and thus $\Delta \sigma_{\text{spr}}$ as constants. Then, Equation (4) will have 3 terms. The corresponding interfacial areas are written from Figure 4a (the thickness of the liquid film $l$ is neglected): $A_{\text{lv}} = A_{\text{lv}} = w \cdot x$, $A_{\text{lv}} = w \cdot (a - x)$. Substituting these into Equation (4) and taking into account $\Delta \sigma_{\text{spr}} = \sigma_{LV} - \sigma_{LV} - \sigma_{Ll}$, the following

FIG. 4. To the derivation of the interfacial spreading force. (a) A liquid $l$, spreading on the surface of another liquid $L$, in direction $x$ (the width perpendicular to the article is $w$). (b) A liquid $l$ with a constant $T$-gradient causing a surface tension gradient, leading to the surface liquid flow due to the interfacial spreading force.
The interfacial spreading force makes liquid $l$ to spread over the surface of liquid $L$ if $\Delta \sigma_{spr} \geq 1$. The interfacial spreading force was first described by Marangoni and, thus, it is called the Marangoni force. A similar phenomenon can be observed in a two-phase ($l/v$) system as well, with an interfacial energy gradient along the $l/v$ surface (see [28–30]). In Figure 4b, a liquid with a horizontal $T$-gradient is shown along direction $x$ by heating the left-hand side and cooling the right-hand side of a container with liquid $l$. This $T$-gradient causes a surface tension gradient along direction $x$. Similarly to the case shown in Figure 4a, an interfacial spreading force appears in Figure 4b along the surface in direction $x$, which causes a similar surface flow in Figures 4a and 4b. The equation for the interfacial spreading force can be obtained by multiplying and dividing Equation (9a) by the length of the container, $a$. Physically, the ratio $\Delta \sigma_{spr}/a$ is the specific driving force for liquid flow in case of Figure 4a. For Figure 4b, the specific driving force is the surface tension gradient along direction $x$: $d\sigma_{rv}(x)/dx$. Substituting these equations into Equation (4), the most general equation for the interfacial capillary force is obtained as:

$$F_{cap}^{spr} = \frac{d\sigma_{rv}(x)}{dx}$$  \hspace{1cm} [9b]

Equation (9b) is also called the “Marangoni force.” Now it is time to compare Equation (9b) with Equation (8b). One can see that the two forces are indeed equal in values (if $k = 1$ in Equation (8b)), but are opposite in directions: $F_{cap}^{spr} = -F_{grad}^{spr}$. Thus, only one of these forces can be called a “Marangoni force.” Historically it should be Equation (9b), the interfacial spreading force. The interfacial gradient force can be called a “Marangoni force induced interfacial gradient force” (see Figure 5 and [17]).

7. THE INTERFACIAL CAPILLARY FORCE

Let us consider a three-phase system, with one of the phases ($x$) situated at the interface of the two other phases $\beta$ and $\gamma$ (see Figure 6). An interfacial force will be acting along the three-phase line in this system, perpendicular to the $\beta/\gamma$ interface. As historically this situation was first described for solid capillaries at liquid/vapor interfaces,[12] this force will be called here the “interfacial capillary force” ($F_{cap}^{x/\beta\gamma}$). As three phases have three interfaces and the interfacial energies are taken as constant values, Equation (4) for this case will have 3 terms due to $A_{x\beta}(x)$, $A_{x\gamma}(x)$ and $A_{\beta\gamma}(x)$. Let us consider phase $x$ being rigid, with constant interfacial area $A_x$. Then, interfacial areas $A_{x\beta}(x)$ and $A_{x\gamma}(x)$ are interconnected: $A_{x\beta}(x) = A_x - A_{x\gamma}(x)$. As follows from Figure 6, phase $x$ covers a $\Delta A_{\beta\gamma}(x)$ part of the initial $\beta/\gamma$ interface ($A_{\beta\gamma}^{0}$) and thus: $A_{\beta\gamma}(x) = A_{\beta\gamma}^{0} - \Delta A_{\beta\gamma}(x)$. Substituting these equations into Equation (4), the most general equation for the interfacial capillary force is obtained as:

$$F_{cap}^{x/\beta\gamma} = \sigma_{\beta\gamma} \cdot \frac{d\Delta A_{\beta\gamma}(x)}{dx} + \left(\sigma_{x\beta} - \sigma_{x\gamma}\right) \cdot \frac{dA_{x\beta}(x)}{dx}$$  \hspace{1cm} [10a]

Now let us apply Equation (10a) for the case of $x = s$, $\beta = l$, $\gamma = v$, that is, for the solid particle at a liquid/vapor interface, by taking into account the Young equation:

$$F_{cap}^{s/lv} = \sigma_{lv} \cdot \frac{d\Delta A_{\beta\gamma}(x)}{dx} + \frac{dA_{x\beta}(x)}{dx} \cdot \cos \Theta$$  \hspace{1cm} [10b]

FIG. 5. The comparison of the interfacial gradient force and the interfacial spreading force in a system containing both a free liquid surface and a bubble in the liquid. The interfacial spreading force driving the liquid layer around the bubble towards the lower $T$ region can be considered as the driving force for the interfacial spreading force, driving the bubble towards the higher $T$ region.

FIG. 6. To the derivation of the interfacial capillary force. The interfacial capillary force acts on phase $x$ situated at the interface of a large, flat interface $\beta/\gamma$, perpendicular to this interface $\beta/\gamma$ (the meniscus is neglected here as the role of gravity is neglected).
Equation (10b) was used to derive equations for penetration/infiltration of liquids into porous solids of different morphologies: solids with capillaries of different shapes \cite{81–83} solids made of closely packed equal spheres \cite{34,33} solids made of cylindrical fibers \cite{136–138} solids with irregular porous structure \cite{139–142} being the extension of the Carman equation \cite{143,44–52}. Now, let us apply Equation (10b) to the classical problem of capillary rise. If phase $x$ in Figure 6 is fixed, solid capillary of inner radius $R$, partly immersed into the liquid phase $l$, the interfacial capillary force will act along the $s$-$l$-$v$ three-phase line. As the capillary is fixed, this force will move the liquid up or down in the capillary. The two geometrical parameters $A_s(x)$ and $\Delta A_s(x)$ are described as function of $x$ (with its vector directed upwards) by the equations: $A_s(x) = 2 \cdot R \cdot \pi \cdot x \cdot \Delta A_s(x) = \text{const.}$. Substituting these equations into Equation (10b), the interfacial capillary force raising the liquid up within the capillary is obtained as:

$$F_{s/l}^{cap} = 2 \cdot R \cdot \pi \cdot \sigma_{lv} \cdot \cos \Theta$$  \hspace{1cm} [10c]

This equation is the Young-Laplace equation for capillary rise. \cite{6} It is shown here to demonstrate that the Young-Laplace equation is also the consequence of the general Equation (4).

Now, let us consider Figure 6 with phase $x$ being a spherical solid particle of radius $R$, situated at a liquid/vapor interface, immersed into the liquid at a depth of $x \leq 2R$ (see \cite{43–53}). Let us neglect the effect of gravity and the effect of curved menisci. As the particle is not fixed, the interfacial capillary force will move it up or down, perpendicular to a large liquid/gas interface. From the geometry of a sphere and Figure 6: $A_s(x) = 2 \cdot R \cdot \pi \cdot x - \pi \cdot x^2$, $A_g(x) = 2 \cdot R \cdot \pi \cdot x$. Substituting these equations into Equation (10b), the interfacial capillary force, acting on a solid sphere at the $l$/$v$ interface is obtained as:

$$F_{s/l}^{cap} = 2 \cdot R \cdot \pi \cdot \sigma_{lv} \cdot (1 + \cos \Theta - \frac{x}{R})$$  \hspace{1cm} [10d]

For a small particle with gravity neglected, the particle will gain its equilibrium when $F_{s/l}^{cap} = 0$. Substituting this condition into Equation (10d), the equilibrium depth of immersion $x_{eq,\Theta}$ of the solid particle with radius $R$ at a liquid/vapor interface is obtained as:

$$x_{eq,\Theta} = R \cdot (1 + \cos \Theta)$$  \hspace{1cm} [10e]

As follows from Equation (10e), a small solid spherical particle will be fully ($x \geq 2R$) immersed into a liquid only if $\Theta = 0^\circ$. Expressing $1 + \cos \Theta$ from Equation (10e) and substituting it back into Equation (10d), the interfacial capillary force is obtained in a more simple form:

$$F_{s/l}^{cap} = 2 \cdot \pi \cdot \sigma_{lv} \cdot (x_{eq,\Theta} - x)$$  \hspace{1cm} [10f]

As follows from Equation (10f), if $x \neq x_{eq,\Theta}$ the interfacial capillary force will always push the particle back to its equilibrium position. Thus, the interfacial capillary force will behave like a spring. This special property of the interfacial capillary force makes it suitable to ensure stabilization of foams and emulsions by solid particles \cite{56–80}

8. THE INTERFACIAL MENISCUS FORCE

As known, the meniscus around particles is usually curved \cite{81}. First, let us derive the conditions when the meniscus remains flat around a floating spherical particle. If only the gravity and the buoyancy forces act on a solid spherical particle of radius $R$ at a flat liquid/gas interface, the condition of mechanical equilibrium of the particle is expressed as:

$$\rho^* = \frac{x_{eq,g}^2 \cdot (3 \cdot R - x_{eq,g})}{4 \cdot R^3}$$  \hspace{1cm} [11a]

where $x_{eq,g}$ is the equilibrium depth of immersion of the particle due to gravity only. $\rho^*$ is the dimensionless density defined as: $\rho^* = (\rho_g - \rho_e)/(\rho_l - \rho_e)$. On the other hand, the equilibrium depth of immersion of the particle due to the interfacial capillary force $(x_{eq,\Theta})$ is written by Equation (10e). There is a special combination of densities and contact angle when $x_{eq, g} = x_{eq, \Theta}$. This condition can be found by substituting $x_{eq, \Theta}$ for $x_{eq, g}$ from Equation (10e) into Equation (11a):

$$\rho^*_{flat} = \frac{(1 + \cos \Theta)^2 \cdot (2 - \cos \Theta)}{4}$$  \hspace{1cm} [11b]

where $\rho^*_{flat}$ is the special value of $\rho^*$ with a property that at $\rho^* = \rho^*_{flat}$ the meniscus around the spherical particle is flat. The equilibrium depth of immersion of the particle will be in the interval between $x_{eq,g}$ and $x_{eq,\Theta}$. When $\rho^* > \rho^*_{flat}$, then $x_{eq, g} > x_{eq} > x_{eq,\Theta}$, that is, the gravity force pushes the particle lower than the interfacial force and vice versa (see Figure 7).

If two floating solid particles appear close to each other at the same liquid/vapor interface, the menisci around them will overlap, leading to the appearance of the so-called “interfacial meniscus force” ($F_{s/l}^{cap}$). This force acts parallel to the macroscopic liquid/vapor interface between the two neighboring particles. \cite{82–84}. The “interfacial meniscus force” was called also as “lateral capillary force”.\cite{84}

There are four phases involved in this situation: two solid particles ($s1$ and $s2$), the liquid ($l$) phase and the vapor ($v$) phase. As all interfacial energies are taken as constant values, Equation (4) will have five terms, due to $A_{s1}(x)$, $A_{s2}(x)$, $A_{s1}(x)$, $A_{s2}(x)$ and $A_{s2}(x)$. The following two obvious relationships exist between them: $A_{s1}(x) = \cdots$
The shapes of the liquid/vapor menisci around three different particles with the meniscus curved down (particle s1), with the flat meniscus (particle s2) and with the meniscus curved up (particle s3). The width of the meniscus is shown by \( w_{\text{men}} \).

\[ \rho^* > \rho^*_{\text{flat}} \]
\[ \rho^* = \rho^*_{\text{flat}} \]
\[ \rho^* < \rho^*_{\text{flat}} \]

FIG. 7. The shapes of the liquid/vapor menisci around three different particles with the meniscus curved down (particle s1), with the flat meniscus (particle s2) and with the meniscus curved up (particle s3). The width of the meniscus is shown by \( w_{\text{men}} \).

\( A_{s1} - A_{s1}(x) \) and \( A_{s2}(x) = A_{s2} - A_{s2}(x) \). Substituting these equations into Equation (4) and taking into account the Young equation, the general equation for the interfacial meniscus force is obtained as:

\[
F_{s1/s2}^{\text{men}} = -\sigma_l \left( \frac{dA_{s1}(x)}{dx} - \frac{dA_{s1}(x)}{dx} \cdot \cos \Theta_1 \right) - \frac{dA_{s2}(x)}{dx} \cdot \cos \Theta_2 \tag{12a}
\]

where \( \Theta_{s1} \) and \( \Theta_{s2} \) are the contact angles of the liquid on solid particles s1 and s2, respectively. Equation (12a) can be solved only if the equations for the shapes of all interfaces are found by solving the Laplace equation coupled with the effect of gravity. The analytical solution of this complex problem is not known.

The following approximated equation exists for the interaction of two floating particles with radii \( R_1 \) and \( R_2 \):

\[
F_{s1/s2}^{\text{men, float}} \approx -\frac{8 \cdot \pi \cdot R_1^3 \cdot R_2^2 \cdot g^2 \cdot (\rho_1 - \rho_2)^2}{9 \cdot \theta_c \cdot (x + R_1 + R_2)} \cdot \Delta \rho_1^* \cdot \Delta \rho_2^* \tag{12b}
\]

where \( g = 9.81 \text{ m/s}^2 \) (the acceleration due to gravity), \( \Delta \rho_i^* \) is defined as: \( \Delta \rho_i^* = \rho_i^* - \rho_{i, \text{flat}}^* \). The force is attracting when its sign is negative and vice versa. This force is inversely proportional to the distance between the centres of the spheres (similarly to forces due to gravity, electro-magnetic fields, etc.). This force is proportional to \( R_1^3 \cdot R_2^2 \cdot (\rho_1 - \rho_2)^2 \cdot g^2 / \theta_c \), expression showing that the force is due to the compensation of the curved \( l/v \) surface area of the meniscus between the particles while they approach each other. This is the only interfacial force being inversely (and not linearly) proportional to the interfacial energy. This is because a larger interfacial energy allows smaller curvature of the meniscus at the same gravity force being proportional to \( R_1^3 \cdot R_2^2 \cdot g^2 \). It also follows that for particles between two immiscible liquids with same densities (\( \rho_1 - \rho_2 = 0 \)) the interfacial meniscus force will be zero, as there will be no curvature around the floating particles due gravity (the same is true in microgravity environment, \( g = 0 \)). The force described by Equation (12b) is proportional to \( -\Delta \rho_1^* \cdot \Delta \rho_2^* \). It means that the force is attracting between two similar particles with menisci of the same sign around them (both curved down or both curved up). The force is repulsing when two particles with dissimilar menisci meet, and the force becomes zero if the meniscus around at least one of the particles is flat. Finally it should be reminded that the approximated Equation (12b) is not valid at \( \sigma_{lv} = 0 \).

The horizontal extension of a curved meniscus around a spherical particle \( (w_{\text{men}}) \) equals \( \frac{\pi}{2} \) (Figure 7):

\[
w_{\text{men}} \approx \sqrt{\frac{\sigma_{lv}}{(\rho_1 - \rho_2) \cdot g}}.
\]

It is identical to the so-called “capillary length,” being independent of the radius of the particle. When the distance between the particles is larger than \( 2w_{\text{men}} \), the interfacial meniscus force becomes negligible.

Equation (12b) refers to floating particles. However, particles can be larger than the thickness of the liquid layer. When the particles are supported against gravity by the flat fixed solid surface with some liquid around them, they are called “immersed” particles. Immersed particles also experience the effect of interfacial meniscus force, when they appear close enough to each other. The approximated solution of Equation (12a) for two vertically immersed cylindrical particles of radii \( R_1 \) and \( R_2 \) is written as:

\[
F_{\text{men, imm}}^{s1/s2} \approx -\pi \cdot \sigma_l \cdot \frac{R_1 \cdot R_2}{(x + R_1 + R_2)} \cdot \cos \Theta_1 \cdot \cos \Theta_2 \tag{12c}
\]

Equations (12b) and (12c) are similar in that both are inversely proportional to the distance between the centres of the particles. However, the curvature of the meniscus in the case of immersed particles has nothing to do with gravity. It is rather determined by the contact angles around the two particles. The two immersed particles will be attracting each other, if they are similarly wetted or non-wetted and vice versa. If the contact angle around any of the particles is \( 90^\circ \), the interfacial meniscus force is zero. This force has been used to interpret the self-arrangement of nanotube arrays.

9. THE FLUID BRIDGE INDUCED INTERFACIAL FORCE

Two solid particles connected by a small liquid bridge in a vapor environment are shown in Figure 8a. The “liquid bridge induced interfacial force” \( (F_{\text{br}}^{s1/s2}) \) will attract or repulse the two particles. This force is called also “normal capillary force” for making a difference from the “lateral capillary force.” As in this case also two
FIG. 8. To the derivation of the fluid bridge induced interfacial force. (a) Two solid particles connected by a liquid bridge in a vapor. (b) Two solid particles connected by a gaseous bridge in a liquid.

particles appear at the liquid/vapor interface, the general Equation (12a) will remain valid. An analytical solution exists only in the limit of negligible liquid volume and zero separation \( x \) between two spherical particles of radii \( R_1 \) and \( R_2 \) wetted by the liquid with contact angles of \( \Theta_1 \) and \( \Theta_2 \):[86,87]

\[
\lim_{x \to 0} F_{1-\text{hr}}^{p} = -2 \cdot \pi \cdot \frac{R_1 \cdot R_2}{R_1 + R_2} \cdot \sigma_{lv} \cdot (\cos \Theta_1 + \cos \Theta_2) \quad [13]
\]

For more realistic cases of \( x > 0 \) and higher liquid volumes the force will have a lower absolute value than that calculated by Equation (13) and will be gradually approaching zero by increasing the volume of the liquid and/or \( x \) (see[87]). This force is attracting when its sign is negative and vice versa. Thus, the liquid bridge induced interfacial force will attract the two solid particles if the particles are wetted by the liquid \((\cos \Theta_1 + \cos \Theta_2 > 0)\) or at equal contact angles: \( \Theta_1 = \Theta_2 < 90^\circ \) and vice versa.

Two solid particles connected by a gaseous bridge in a liquid environment are shown in Figure 8b. From the similarity of Figures 8a and 8b it is clear that the gaseous bridge induced interfacial force is opposite of the liquid bridge induced interfacial force:

\[
F_{g-\text{hr}}^{s} = -F_{1-\text{hr}}^{p} \quad [14]
\]

This force is attracting when its sign is negative and vice versa. Thus, the gaseous bridge induced interfacial force will attract the two solid particles if the particles are not wetted by the liquid \((\cos \Theta_1 + \cos \Theta_2 < 0)\), or at equal contact angles: \( \Theta_1 = \Theta_2 > 90^\circ \) and vice versa.

10. THE INTERFACIAL ADHESION FORCE

Let us consider two phases \( x \) and \( \beta \) in a larger phase \( \gamma \), the particles being far from the outer interface of phase \( \gamma \). If the particles are also far from each other, the interfacial force acting on both of them will be zero. However, if the particles are close enough to each other (yet not touching each other) the molecules/atoms in their interfaces will generate some change in the energetic states of each other. In other words, the \( x\gamma \) and \( \beta\gamma \) interfacial energies will become functions of particle separation \( x \) and, therefore, an interfacial force will arise.[5,6,88,89] As for like particles this force leads to strong adhesion between them, this force is called here the “interfacial adhesion force.” The same force might also be repulsing between unlike particles, as follows from the term “disjoining pressure.”[5] The interfacial adhesion force is responsible for re-distribution of particles during solidification of composites.[90–104]

There are three phases involved in this situation: \( x \), \( \beta \), and \( \gamma \). Vector \( x \) is chosen as the separation (distance between closest interfaces) of phases \( x \) and \( \beta \). Phases \( x \) and \( \beta \) are considered rigid, that is, their interfacial areas are kept constant. Thus Equation (4) will have only two terms, due to the \( x \)-dependent interfacial energies. To simplify the geometrical situation, two equal cubic solid particles are considered, turned to each other by their equal parallel sides. In this configuration the following simplified equalities are valid: \( A_{x\gamma} = A_{\beta\gamma} \equiv A \). Substituting these equations into Equation (4) the interfacial adhesion force is written as:

\[
F_{x\beta}^{\text{adh}} = -A \cdot \left( \frac{d\sigma_{x\gamma}}{dx} + \frac{d\sigma_{\beta\gamma}}{dx} \right) \quad [15a]
\]

To make Equation (15a) explicit, one has to express the interfacial energies as function of \( x \). To find this relationship, let us first define the boundary conditions:

i. at infinite separation \((x \to \infty)\) the interfacial energies have their standard, \( x \)-independent values:

\[
\sigma_{x\gamma}(\infty) = \sigma_{x\gamma}, \quad \sigma_{\beta\gamma}(\infty) = \sigma_{\beta\gamma},
\]

ii. at zero separation \((x = 0)\) the two particles touch each other and so the sum of their interfacial energies becomes the interfacial energy of the \( x\beta \) interface:

\[
\sigma_{x\gamma}(0) + \sigma_{\beta\gamma}(0) = \sigma_{x\beta}. \quad \text{Formally this can be divided into two parts as:} \quad \sigma_{x\gamma}(0) = p \cdot \sigma_{x\beta} \quad \text{and} \quad \sigma_{\beta\gamma}(0) = (1 - p) \cdot \sigma_{x\beta}
\]

with parameter \( 0 < p < 1 \) (later parameter \( p \) will fall out).

The interaction energies are assumed to change inversely proportional to square of \( x \). Then, one can write the following approximated equations for the separation dependent interfacial energies, in accordance with the
above boundary conditions:

\[
\sigma_{x'y'}(x) = \sigma_{x'y'} + (p \cdot \sigma_{x'y'} - \sigma_{x'y'}) \cdot \left( \frac{d}{d + x} \right)^2 \tag{15b}
\]

\[
\sigma_{\beta\gamma}(x) = \sigma_{\beta\gamma} + [(1 - p) \cdot \sigma_{\beta\gamma} - \sigma_{\beta\gamma}] \cdot \left( \frac{d}{d + x} \right)^2 \tag{15c}
\]

where \(d\) is the diameter of a molecule (atom) in phase \(x\).

Substituting Equations (15b) and (15c) into Equation (15a), the following final equation is obtained:

\[
F_{\gamma \beta} = 2 \cdot A \cdot \Delta \sigma_{x'y'} \cdot \frac{d^2}{(d + x)^3} \tag{15d}
\]

Equation (15d) is valid for two, parallel slabs. For other geometries see other works.[5,6,88,89] The key parameter in Equation (15) is \(\Delta \sigma_{x'y'}\). Its definition follows from the above derivation:

\[
\Delta \sigma_{x'y'} \equiv \sigma_{x'y'} - \sigma_{x'y'} - \sigma_{\beta\gamma} \tag{15e}
\]

Since Equation (15e) was introduced by Derjaguin[88] and later by Hamaker,[89] two incorrect equations have been published to replace it. One of them is \(\Delta \sigma_{x'y'} \equiv \sigma_{x'y'} - \sigma_{x'y'}\),[90] the other one was introduced by this author[7,96] \(\Delta \sigma_{x'y'} \equiv 2 \cdot \sigma_{x'y'} - \sigma_{x'y'} - \sigma_{\beta\gamma}\). Both of these equations should be disregarded.1

From Equation (15e) it is obvious that \(\Delta \sigma_{x'y'} \equiv \Delta \sigma_{x'y'}\). The interfacial adhesion force is attractive when its value is negative and vice versa. The following cases are worth to discuss:

1. For two equal phases \(x = \beta\): \(\sigma_{x'y'} = 0\) and \(\sigma_{x'y'} = \sigma_{x'y'}\), that is, \(\Delta \sigma_{x'y'} = -2 \cdot \sigma_{x'y'} < 0\). Thus, the interfacial adhesion force between identical phases is always attractive.
2. When phase \(y\) is a vacuum, \(\sigma_{x'y'} < \sigma_{x'y'} + \sigma_{\beta\gamma}\), as there is always some adhesion energy between \(x\) and \(\beta\) missing at an interface with a vacuum. Thus, \(\Delta \sigma_{x'y'} < 0\) and, thus, the interfacial adhesion force trough a vacuum is also always attractive.
3. When phase \(y\) is a vapor, or especially if it is a liquid or solid, \(\Delta \sigma_{x'y'}\), and the interfacial adhesion force can have any sign, that is, it can be attractive or repulsive.

### 11. CONCLUSIONS

In this article, all known interfacial forces being essential for dispersion science and technology have been reviewed. The interfacial forces are classified and are divided into eight different classes, depending on the number and geometrical arrangement of the phases and on the direction of the given interfacial force (Table 1). Equations to calculate the interfacial forces for all these 8 cases are derived from the same general equation (4) being the consequence of ideas of Newton and Gibbs. All known interfacial forces and pressures are shown to be particular cases of this general Equation (4). As a new element, an interfacial anti-stretching force is introduced in this article, being equivalent to the definition of the interfacial energy in terms of tension as understood by Young. Also, the differences and similarities between the interfacial gradient force and the interfacial spreading force (the Marangoni force) are shown. Further, the well-known case of the liquid bridge induced interfacial force is supplemented by its less known version of a gaseous bridge induced interfacial force. It is expected that further possible interfacial forces would also follow from the same general equation (4) in complex situations arising during analyzing scientific and technological challenges in dispersion science and technology.

**REFERENCES**
