Effect of Contact Deformations on the Adhesion of Particles

B. V. DERJAGUIN, V. M. MULLER, AND YU. P. TOPOROV

Department of Surface Phenomena, Institute of Physical Chemistry, Academy of Sciences, Moscow, U.S.S.R.

Received October 10, 1974; accepted April 30, 1975

A strict theory of reciprocal influence of the contact deformation and molecular attraction of a ball and a plane has been developed. It has been shown that despite the van der Waals' forces being capable of increasing the elastic contact area between the ball and the plane, the force that is required to overcome the molecular forces arising when the contact is broken does not increase thereby. In fact, it remains equal to the attraction force value that is determined when considering the point contact of a nondeformed ball with a plane.

In the absence of the electrostatic component, the adhesion force is equivalent to the first power of the ball radius and to the amount of work per unit area as required for effecting the equilibrium tearing-off of a flat surface of the same nature.

Determination of the force of adhesion of small particles to one another or to a solid surface is essential to solving many applied and scientific problems. However, most calculations of the adhesion force of small particles carried out up to now (1) do not take into account the effect of contact deformation that inevitably arises upon contact of particles with a solid surface.

As long ago as 1934, one of the authors of the present paper was first to pose a problem on the effect of contact deformations on the adhesion of particles and vice versa (3). At that time an approach also was suggested to solving this problem by using the virtual displacement (thermodynamic) method taking into account the adhesion energy in combination with the Hertz theory. This enabled one to calculate the surplus contact deformation due to the adhesion energy and to assume that the contact deformations do not increase the adhesion force that is needed to interrupt the contact.

But this assumption could not unambiguously substantiated because we disregarded the energy of the noncontact adhesion forces acting within the ring-shaped zone surrounding the contact area.

The same thermodynamic method referred to as an approximate theory was used in a recent paper (2) [the authors probably were unaware of the earlier work (3)].

The object of the present work is to clarify this matter. For this purpose, the calculation takes into account the energy of molecular attraction in the ring-shaped zone of noncontact adhesion.

Recently, an attempt has been made (4) to take into account the effect of contact deformation on the adhesion force. However, in that work the contact deformations were accounted for incorrectly, leading to an erroneous conclusion that taking into account the contact deformation on the basis of Hertz's theory should have resulted not only in an increase in the adhesion force of particles, but also in a variation (or modification) of the type of its dependence on the size of particles. Now, Ref. (3) allows us to draw the opposite conclusion.

The earlier paper (3) considered the general case of a contact between any convex surfaces,
which resulted in deriving rather cumbersome formulas. In view of this, now we shall limit ourselves to the simplest case of contact between a spherical particle of radius $R$ and a plane solid surface. The more general case of two spheres of radii $R_1$, $R_2$ may be included in our analysis by replacing $R$ by $R_1 R_2 / (R_1 + R_2)$.

For this purpose, let us first of all establish how the shape of the surface of a spherical particle near the contact area will be changed under the effect of contact deformations; that is, let us define the law of variation of distance between the opposite points of a sphere and a plane, depending upon their remoteness from the contact area.

I. DETERMINATION OF THE SHAPE OF THE SURFACE OF AN ELASTIC SPHERICAL PARTICLE NEAR TO THE ZONE OF ITS CONTACT WITH A FLAT RIGID SURFACE

Let us consider the case of elastic interaction of an elastic ball with an absolute hard surface, that is, the case where $E_{ball} / E_{surf} \ll 1$. Yet the modulus of elasticity of the ball should not be too small, so that the molecular attraction forces would not be able to change the ball form appreciably outside the contact area, as compared with that defined by the Hertz. Ref. (2) considered the opposite case of a very small value of the elastic modulus. The authors, however, motivated their limiting to that case only by practical considerations, without referring to other reasons. These considerations (e.g., the difficulty of eliminating the influence of substrates roughness or of dust particles) prove to be unconvincing when there is a contact between very smooth particles of small radius, for which the present analysis is exactly intended. Note that in the case of a very high elastic modulus the form of a gap between the surfaces has nothing in common with that considered in (2). Let us also point out that in that case (2) the deformation field close to the boundaries of the contact area will exhibit the continuity breakups, which is likely to interfere with the making of a strict calculation even to the first approximation. Nonetheless, the calculations and their comparison with the experiment, as given by the authors (2), present a great interest.

In accordance with the Hertz theory (5), the distribution of the normal pressure all over the contact area, which is circular in the case under consideration, with normal load $F$ applied thereto, will be described by

$$P_z(\rho) = \frac{3F}{2\pi a^2} \left(1 - \frac{\rho^2}{a^2}\right),$$

where $\rho$ is a distance from the center of a contact circle to the point considered, $a$ is the radius of the contact circle (see Fig. 1), and $\alpha$ is the shift of the center of the ball having radius $R$ toward the plane under the effect of force $F$.

The normally applied, concentrated load $P_{el}\delta \omega$ results in setting up a deformation of the ball surface whose normal component is equal to (6)

$$d\omega(R') = \frac{1 - \sigma^2 P_{el}\delta \omega}{\pi R'}$$

where $R'$ is the distance from the load application point to the point at which the de-
formation is considered, $E$ is the modulus of elasticity of the ball material; $\sigma$ is its Poisson coefficient, and $d\omega$ is an element of the contact area. It is quite natural that in the case considered, the total normal deformation may be found from expression [2] by substituting $P_s$ from formula [1] therein, and by integrating with respect to the entire contact area.

Now, if we take a point found at the surface of a ball having coordinates $r, z$, then the normal component of deformation will be

$$ w(R') = \frac{1 - \sigma^2}{\pi E} \int_0^\alpha \int_0^{2\pi} \frac{P_s(\rho)}{R'} \rho d\rho d\varphi. \quad [3] $$

Here

$$ R' = (r^2 - \rho^2)^{1/2}. \quad [4] $$

Let us show first of all that when calculating the deformation of points found at the surface of a ball near to the perimeter of the contact area, in all cases the value of $z$ may be neglected in expression [4]. As will become apparent from Fig. 1, the relative influence of $z$ on the value of $\rho$ increases with the distance from the pressure area, for that influence is proportional to $\cos \gamma$. Yet at $r \gg a$

$$ R' = (r^2 + z^2)^{1/4}. $$

As at a nondeformed surface (with $r \gg a$)

$$ z = r^2/2R $$

while the ball deformation is likely to decrease $z$,

$$ R' = (r^2 + z^2)^{1/4} \leq r(1 + r^2/4R^4)^{1/4}. $$

The value $[r/(2R)]^2$ may be neglected compared with unity. The entire theory of Hertz was developed in that approximation.

Consequently, in all the cases where the deformation of a surface is substantial

$$ w(R') \approx \frac{3\theta F}{2\pi a^5} \int_0^\alpha \int_0^{2\pi} \frac{(1 - \rho^2/2a^2)^{1/2} \rho d\rho d\varphi = \frac{\theta F}{r}} \quad [5] $$

where $\theta = (1 - \sigma^2)/(\pi E)$, i.e., in all cases the deformation of the surface of a ball may be calculated by assuming $z=0$.

On having taken in expression [4], $z=0$, we obtain

$$ w(r) = \frac{3\theta F}{\pi a^3} T_1 \quad [5] $$

where

$$ T_1 = \int_0^\alpha \int_0^{2\pi} \frac{(a^2 - \rho^2)^{1/2} \rho d\rho d\varphi}{(\rho^2 + r^2 - 2\rho r \cos \varphi)^{1/2}}. $$

It will be easy to show that at $\rho \leq r$

$$ \int_0^{2\pi} \frac{d\varphi}{(\rho^2 + r^2 - 2\rho r \cos \varphi)^{1/2}} = \frac{2K'(\rho)}{\rho} \quad [6] $$

where $K$ is the complete elliptic integral of the first kind having modulus $K = \rho/r$. Consequently, in expression [5] the value of $T_1$ is, equal to

$$ T_1 = \frac{1}{r} \int_0^\alpha 2K(\frac{\rho}{r})(a^2 - \rho^2)^{1/2} \rho d\rho $$

$$ = \frac{a^3}{r} \int_0^\alpha K[(xy)^{1/2}](1 - y)^{1/2}dy = \frac{a^3}{r} T_2 \quad [7] $$

where

$$ x = a^2/r^2 \leq 1, \quad y = \rho^2/a^2. $$

However, according to (7),

$$ K[(xy)^{1/2}] = \frac{\pi}{2} \sum_{n=0}^\infty C_n^2 x^n y^n \quad [8] $$

where

$$ C_n = \frac{(2n - 1)!!}{2^n n!}. \quad [9] $$

Substituting the value of $K(xy)^{1/2}$ from expression [8] into formula [7], we find the value of $T_2$

$$ T_2 = \int_0^1 K(xy)^{1/2}(1 - y)^{1/2}dy = \frac{\pi}{2} \sum_{n=0}^\infty C_n^2 x^n $$

$$ \times \int_0^1 y^n(1 - y)^{1/2}dy = \frac{\pi}{2} \sum_{n=0}^\infty C_n^2 a_x x^n \quad [10] $$

where

$$ a_n = \int_0^1 y^n(1 - y)^{1/2}dy = B(n + 1, \frac{1}{2}) $$

$$ = \frac{\Gamma(n + 1)\Gamma(\frac{1}{2})}{\Gamma(n + \frac{3}{2})} = \frac{2^{n+1}n!}{(2n + 3)!!}. \quad [11] $$
where $\Gamma$ and $B$ are the corresponding Eulerian functions. From expressions [9] and [11], it follows that

$$ a_n C_n^2 = \frac{2^{n+1} n! [(2n - 1)!!]}{(2n + 3)!! 2^{2n} n!} $$

From expressions [-9] and [11], it follows that

$$ a_n C_n^2 = \frac{2C_n}{(2n + 3)(2n + 1)} $$

On having substituted this value of $a_n C_n^2$ into formula [10], we obtain

$$ T_2 = \pi \sum_{n=0}^{\infty} \frac{C_n x^n}{(2n + 3)(2n + 1)} \cdot \frac{2C_n}{(2n + 3)(2n + 1)} $$

It will be easy to show (8) that for values $C_n$ that can be expressed by formula [9]

$$ \sum_{n=0}^{\infty} C_n x^n = (1 - x)^{-1}. \quad \text{[13]} $$

Multiplying the left and right parts of expression [13] by $\frac{1}{x^2}$, and integrating twice from 0 to $x$, we find:

$$ \sum_{n=0}^{\infty} \frac{C_n x^{n+1}}{(2n + 3)(2n + 1)} $$

$$ = \frac{x^2}{8} \{2[x(1-x)]^4 - (1-2x) \arccos (1-2x)\} $$

or, by dividing by $x^4$, we find $T_2$

$$ T_2 = \pi - \frac{1}{8} \{2[x(1-x)]^4 - (1-2x) \arccos (1-2x)\}. \quad \text{[14]} $$

Using expressions [14], [7], and [5], we obtain

$$ w(r) = \frac{3\theta F}{8a^3} \left\{2a(r^2 - a^2)^\frac{1}{2} + (2a^2 - r^2) \arccos \left(1 - \frac{a^2}{r^2}\right) \right\}. \quad \text{[15]} $$

Formula [15] describes the deformation in the direction of axis $z$ only outside the contact area, that is, at $r \geq a$. At $r = a$

$$ w(r = a) = w(a) = \frac{3\pi \theta F}{8a}. \quad \text{[16]} $$

The deformation at the origin of coordinates, i.e., at $r = z = 0$, may be found directly from expression [3]. It will be equal to

$$ w(r = 0) = \frac{3\pi \theta F}{4a} = 2w(a). \quad \text{[17]} $$

For any point of the deformed surface, there will be a valid and obvious relationship

$$ z = z_0 + w - \alpha \quad \text{[18]} $$

where $z_0$ is the coordinate of a point at the ball surface prior to its deformation. In the case under consideration

$$ z_0 = r^2/(2R). \quad \text{[19]} $$

It appears that at the origin of coordinates $z = z_0 = 0$ and $w(0) = \alpha$, i.e.,

$$ \alpha = \frac{3\pi \theta F}{4a}, \quad \text{[20]} $$

while along the contact area perimeter

$$ r = a, \quad z = 0, \quad z_0 = a^2/(2R). $$

Taking into account that according to Eq. [17] $w(a) = a/2$, we find from expression [18] the well-known relationship (9),

$$ \frac{a^2}{2R} + \frac{\alpha}{2} - \alpha = 0; \quad \alpha = \frac{a^2}{2R}. \quad \text{[21]} $$

Comparing expressions [20] and [21], we obtain

$$ \frac{3\theta F}{4a^3} = \frac{1}{\pi R}, $$

which, after substituting into expression [15], gives

$$ w(r) = \frac{1}{2\pi R} \left\{2a(r^2 - a^2)^\frac{1}{2} + (2a^2 - r^2) \arccos \left(1 - \frac{2a^2}{r^2}\right) \right\}. \quad \text{[22]} $$
Selected Works – 3

Substituting into formula [18] the values of \( z_n, w, \alpha \) from expressions [19], [21], and [22], and carrying out simple conversions, we find

\[
z = \frac{1}{\pi R} \int a(r^2 - a^2)^{\frac{3}{2}} - (2a^2 - r^2)
\times \arctan \left( \frac{r}{a^2} - 1 \right) \right] + \epsilon. \quad [23]
\]

In combination with expressions [20] and [21], formula [23] defines the shape of the surface of a deformed ball depending upon the value of approaching \( \alpha \) (or upon the value of an elastic force).

This formula determines the distance between the opposite points of the ball and plane, depending upon their respective spacing from the contact area. Now, at the very contact area the distance between such points is not equal to zero, but to a certain value \( \epsilon \) (of the order of magnitude of 3 to 4 Å); therefore, \( \epsilon \) should be added to the value \( z \) determinable by formula [23]. Thus, the final dependence \( z(1, \cdot) \) will become:

\[
z = \frac{1}{\pi R} \int a(r^2 - a^2)^{\frac{3}{2}} - (2a^2 - r^2)
\times \arctan \left( \frac{r}{a^2} - 1 \right) \right] + \epsilon. \quad [23a]
\]

Using this expression, one may calculate the component of the molecular interaction force acting between a plane and the surface of a deformed ball situated outside the contact area.

Having recourse to an energetic approach and to the virtual displacement method, let us discuss the effect of this component of molecular interaction on adhesion of the ball to the plane.

II. MACROSCOPIC CALCULATION OF A STICKING FORCE WHILE TAKING INTO ACCOUNT THE CONTACT DEFORMATIONS OF A BALL

Let us calculate the energy of interaction of an elastic ball and a rigid plane, depending upon the amount \( \alpha \) the center of the ball has approached the plane under the effect of an external force \( P \) and under that of surface and elastic forces. This energy is a sum of two parts; namely, the volume energy of elastic deformations \( W_\varepsilon \) and the surface energy \( W_s \) (energy of molecular forces). It is generally supposed that the surface forces rapidly decrease as the distance diminishes, and that they are of a reversible equilibrium nature.

The elastic energy is obviously equal to

\[
W_\varepsilon = \int_0^a F_\varepsilon(\alpha)d\alpha \quad [24]
\]

where \( F_\varepsilon \) is the elastic force.

Using the known method (3), the surface energy may be represented as

\[
W_s = \int_0^L \varphi(H)2\pi r dr. \quad [25]
\]

Here, \( \varphi(H) \) is the interaction energy per unit area of a flat surface (an analog of surface tension). The energy \( \varphi(H) \) rapidly decreases as \( H \) increases; therefore, within the region \( H \ll R \), which is of interest to us, the precise knowledge of the upper limit of integrating \( L \) in expression [25] is inessential; it may simply be assumed to be equal to infinity. Moreover, in expression [25] the distance \( H \) is the known function of \( \alpha \) and \( r \), i.e., \( H = H(r, \alpha) \). As at the contact surface, i.e., at \( 0 \leq r \leq a \), \( H = \epsilon = \text{const.} \), then the corresponding part of free energy is equal to

\[
W_s' = \int_0^a \varphi(\epsilon)2\pi r dr = \pi \alpha^2 \varphi(\epsilon) \quad [26]
\]

where \( \epsilon \) is the least possible spacing between the surfaces of the ball and the plane. Since, as has been shown earlier,

\[
a^2 = \alpha R, \quad [27]
\]

then

\[
W_s' = \pi \alpha R \varphi(\epsilon). \quad [28]
\]
At \( r \geq a \), as has been shown above,

\[
H(r, \alpha) = \frac{1}{\pi R} \left[ a (r^2 - a^2) + (r^2 - 2a^2) \times \arctan \frac{r^2 - a^2}{a} \right] + \epsilon \tag{29}
\]

and hence, the noncontact part of the free surface energy is equal to

\[
W''(\alpha) = 2\pi \int_0^\infty \varphi[H(r, \alpha)] r \, dr \tag{30}
\]

Substituting (into expression \(30\)) \( r^2 - a^2 = x^2 \), we obtain an integral depending upon parameter \( \alpha \), but having constant limits (which is essential to the following):

\[
W''(\alpha) = 2\pi \int_0^\infty \varphi[H(x, \alpha)] x \, dx \tag{31}
\]

and

\[
H(x, \alpha) = \frac{1}{\pi R} \left[ ax + (x^2 - a^2) \arctan \frac{x}{a} \right] + \epsilon. \tag{32}
\]

Since \( a \) is correlated with \( \alpha \) in relationship \(27\), then assuming some particular form of function \( \varphi(H) \) and using expressions \(28\), \(31\), and \(32\), it will be possible to find the dependence of surface energy \( W_s \) upon \( \alpha \).

Now, let us calculate the generalized force

\[
F_s = \frac{dW_s}{d\alpha} = \frac{dW_s'}{d\alpha} + \frac{dW_s''}{d\alpha} = \pi R \varphi(\epsilon)
\]

and hence, from expression \(38\), we obtain

\[
x \, dx = RdH. \tag{39}
\]

Substituting expressions \(37\)-\(39\) into formula \(34\), we obtain

\[
F_s''(\alpha = 0) = 2\pi \int_0^\infty \varphi[H(H)(-\frac{1}{2})RdH
\]

\[
= -\pi R \varphi(\epsilon) \bigg|_0^{\infty} = \pi R \varphi(\epsilon) \tag{40}
\]

because \( \varphi(\infty) = 0 \). Finally, from expressions \(40\) and \(33\) it will follow that

\[
F_s(\alpha = 0) = \frac{dW_s}{d\alpha} = \pi R \varphi(\epsilon) + \pi R \varphi(\epsilon)
\]

\[
= 2\pi R \varphi(\epsilon) \tag{41}
\]
and in this case the sign of value \( F_*(\alpha = 0) \) coincides with that of potential \( \varphi \).

Let us show that with the calculation method given, in the absence of a contact and with the ball approaching the plane, the resultant force of molecular attraction continuously passes over into a "generalized" force of contact sticking, \( F_* \). (This problem was first considered in Ref. (3); however, when passing over from the point contact to the surface one, neglecting a noncontact component of force \( F_*'' \) in formula \([33]\) produced a result two times smaller than the true one.) Indeed, in the absence of a direct contact (see Fig. 2), that is, in the absence of a deformation, at \( r \ll R \)

\[
H \approx \frac{r^2}{2R} + H_0, \quad rdr = RdH. \tag{42}
\]

Substituting Eq. \([42]\) into Eq. \([25]\), we find

\[
W_*(H_0) = 2\pi R \int_{H_0}^{\infty} \varphi(H) dH. \tag{43}
\]

Now, with a point contact the sticking force is equal to

\[
F_*(\epsilon) = -\left. \frac{dW_*}{dH_0} \right|_{H_0=\epsilon} = 2\pi R \varphi(\epsilon), \tag{44}
\]

which exactly corresponds to the value of \( F_* \) that is obtained by the use of Eq. \([41]\).

That the opposite signs were put before energy derivatives with respect to coordinates \( \alpha \) in Eq. \([33]\), and with respect to \( H_0 \) in Eq. \([44]\), was conditioned by the following consideration: in both cases, the generalized sticking force should be determined by differentiating energy with respect to coordinate \( x \) of the gravity center of a particle, but for a deformed ball

\[
x' = R + \epsilon - \alpha
\]

\((R \text{ and } \epsilon \text{ are constants}), \text{ while for a non-deformed ball } x'' = H_0 + R, \text{ i.e.,}

\[
-\frac{dW_*}{dx'} = +\frac{dW_*}{d\alpha} \quad \text{and} \quad -\frac{dW_*}{dx''} = -\frac{dW_*}{dH_0}.
\]

Let us further show that force \( F_*'' \), and hence, the total force \( F_* \) decreases as \( \alpha \) increases (as to its absolute value). To this effect, let us differentiate equality \([34]\)

\[
\frac{dF_*''}{d\alpha} = 2\pi \int_{0}^{\infty} \varphi''(H) \varphi(H) \left( \frac{dH}{d\alpha} \right)^2
\]

\[
+ \varphi''(H) \varphi(H) \left( \frac{d^2H}{d\alpha^2} \right) dH \tag{45}
\]

and make \( \alpha \to 0 \). In this case, \( \varphi'' \) and \( \varphi'''' \) always remain finite, because \( H \gg \epsilon \), while from expressions \([35]\) and \([36]\) at \( \alpha \to 0 \) it follows that

\[
\left( \frac{dH}{d\alpha} \right)^2 \to \frac{1}{4}, \quad \frac{dH}{d\alpha} \sim \frac{1}{\pi \sqrt{\alpha}} \quad \text{as } H \to \infty \tag{46}
\]

and as the sign of \( \varphi'' \) is opposite to that of \( \varphi \) (it has been stipulated that the potential rapidly tends to zero with the growth of \( H \)), then in Eq. \([45]\) at \( \alpha \to 0 \)

\[
\frac{dF_*''}{d\alpha} \sim \frac{b}{\alpha^4} \to \infty \tag{47}
\]

(here \( b \) is a positive constant), while the sign of the derivative is opposite to that of \( \varphi \), and hence, \( F_* \).

---

**Fig. 2.** Schematic diagram showing the interaction of a ball with a rigid plane.
Thus, at a small value of $\alpha$, independently of the specific form of potential $\varphi(H)$,

$$F_* = \frac{dW}{d\alpha} = F_0[1 - 2b(\alpha)^4 + \cdots] \quad [48]$$

where $F_0 = 2\pi R \varphi(\epsilon)$. It is apparent that as $\alpha$ grows the character of the dependence of force $F_*$ upon distance varies, and at great values of $\alpha$, $F_*$ tends to a constant value

$$F_*' = \pi R \varphi(\epsilon) = F_0/2.$$

If $F_*'$ is the molecular attraction force, and $F_*$ is the elastic repelling (repulsive) force, while in accordance with the Hertz theory (5),

$$F_* = \frac{4(R)^4F_0}{3(1 - \sigma^2)} \alpha^4 = k\alpha^4, \quad [49]$$

then it will become apparent that the tearing-off force, i.e., an external force that is equal to a difference in the absolute values between the molecular and elastic forces, has its maximum value, which may be regarded as measure of sticking at $\alpha = 0$, that is, with the point contact, as has already been pointed out above (3).

Figure 3 represents the character of the dependence of the tearing-off force $F_d$ upon $\alpha$. At first glance, it may become unclear why the force $F_*$ first decreases and then remains constant with flattening, i.e., it depends only slightly, and contrary to what is expected, upon the contact area $S$. However, this may be clarified if one takes into consideration that the Hertz equations already account for the molecular attraction forces acting between the elements of contacting surfaces, with these forces actually participating in the elastic reaction of the surfaces. Yet the correction that we have introduced takes into account only the molecular attraction forces that are acting within the zone surrounding the contact area, and the width of this zone in the radial direction decreases as the flattening proceeds.

Let us now present the specific form of the potential. Let us avail ourselves of the form of the potential of molecular forces that is well known both from the macroscopic theory (10, 11) and from experiments:

$$\varphi(H) = \frac{1}{12\pi H^2} \quad [50]$$

($\lambda$ is the Hamaker constant). In this case,

$$F_0 = 2\pi R \varphi(\epsilon) = \frac{AK}{6\epsilon^2} \quad [51]$$

and according to Eq. (50) and Eqs. [33]–[35],

$$\frac{F_*(\alpha)}{F_0} = \frac{1}{2} \int_0^\alpha \frac{1}{\pi} \left[ \arctan(\xi/\alpha^4) - \frac{\xi}{\alpha^4} (\alpha + \xi^4) \right] d\xi, \quad [52]$$

Here

$$\hat{\alpha} = \frac{\alpha}{\epsilon}, \quad \hat{\xi} = \frac{\xi}{(R\epsilon)^4}. \quad [53]$$

Expanding expression [52] in a series with respect to powers of small value $(\alpha/\epsilon)^4$ (at $\alpha \ll \epsilon$), we obtain

$$\frac{F_*(\alpha)}{F_0} = 1 - \frac{3}{4} \left( \frac{\alpha}{\epsilon} \right)^4 + \frac{1}{4} + \frac{\alpha}{\epsilon} + \cdots \quad [54]$$

which corroborates the correctness of expansi-
TABLE I

DEPENDENCE OF THE TOTAL FORCE UPON DEFORMATION

<table>
<thead>
<tr>
<th>(\alpha/\varepsilon)</th>
<th>(F/F_0 [52])</th>
<th>(F/F_0 [54])</th>
<th>(F/F_0 [59])</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00001</td>
<td>0.9967</td>
<td>0.9966</td>
<td></td>
</tr>
<tr>
<td>0.0001</td>
<td>0.9896</td>
<td>0.9894</td>
<td></td>
</tr>
<tr>
<td>0.001</td>
<td>0.9683</td>
<td>0.9667</td>
<td></td>
</tr>
<tr>
<td>0.01</td>
<td>0.9107</td>
<td>0.8964</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>0.6902</td>
<td>0.6896</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>0.6387</td>
<td>0.7379</td>
<td></td>
</tr>
<tr>
<td>10.00</td>
<td>0.3435</td>
<td>0.5513</td>
<td></td>
</tr>
<tr>
<td>100.00</td>
<td>0.5106</td>
<td>0.5110</td>
<td></td>
</tr>
<tr>
<td>1000.00</td>
<td>0.5022</td>
<td>0.5024</td>
<td></td>
</tr>
<tr>
<td>10000.00</td>
<td>0.5004</td>
<td>0.5005</td>
<td></td>
</tr>
</tbody>
</table>

\(\frac{F_*(\alpha)}{F_0} = \frac{1}{2} \left[ \frac{3\pi^2}{\alpha} \right]^{1/3} \left[ \frac{4\pi^2}{\alpha} \right]^{1/3} + \cdots \) \[59\]

Hence, at \(\alpha > \varepsilon\), it follows that \(F_*(\alpha) \to F_0/2\). This also corroborates the correctness of the general conclusions drawn above.

Table I presents the machine-calculated values of \(F_*/F_0\) depending upon the \(\alpha/\varepsilon\) value.

As an example, Table II presents the results of calculating the contact area \(S\) of polystyrene particles on steel. In the calculation, it has been assumed that \(\varepsilon = 3 \times 10^{-8}\) cm, \(\sigma = 0.33\), \(E = 3 \times 10^{10}\) dyne/cm², \(A = 10^{-12}\) erg.

Since, even for small polystyrene particles found at the steel surface, the value of \(\alpha/\varepsilon > 1\), then for the analytical assessment of the dependence of the contact area upon the radius of the particles, one may use (in accordance with Table I and formula [59]) an approximate relationship:

\(F_m = \frac{AR}{2 \varepsilon^2}\)

TABLE 2

THE CONTACT AREA OF POLYSTYRENE PARTICLES AT THE STEEL SURFACE

<table>
<thead>
<tr>
<th>(R (\mu m))</th>
<th>(\alpha/\varepsilon)</th>
<th>(S (cm^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03</td>
<td>2.1</td>
<td>(7 \times 10^{-13})</td>
</tr>
<tr>
<td>0.3</td>
<td>4.5</td>
<td>(1.5 \times 10^{-11})</td>
</tr>
<tr>
<td>3.0</td>
<td>10.0</td>
<td>(3.2 \times 10^{-10})</td>
</tr>
<tr>
<td>30.0</td>
<td>21.0</td>
<td>(7.0 \times 10^{-8})</td>
</tr>
</tbody>
</table>
Then the equilibrium value of $\alpha$ (at $F_m = F_e$) will be determined from condition

$$\frac{AR}{12\epsilon^3} = \frac{4(R)E}{3(1 - \sigma^2)}$$

Hence

$$\alpha = \frac{2\epsilon R\pi(1 - \sigma^2)^\frac{1}{3}}{8\epsilon F_e^\frac{1}{3}}$$

which, after substituting into Eq. [60], will give

$$S = \frac{2\epsilon R\pi(1 - \sigma^2)^\frac{1}{3}}{8}\epsilon F_e^\frac{1}{3}$$

From the calculation thus carried out, it follows that though the effect of molecular attraction forces leads to the formation of some contact area where the forces of molecular attraction are active, the sticking force which has to be applied to break up the contact does not increase thereby. Its magnitude remains equal to that calculated on the basis of assuming the presence of the point contact and the absence of any contact deformation.

Thus, at the very moment the point contact has been established, the tearing-off force should reach its maximum (peak), balancing the resultant force of molecular attraction. That force is proportional to both the radius of a particle and the surface energy.

In Ref. (4), there is an incorrect discussion of the same problem of the effect of the molecular attraction forces on the contact deformation, and vice versa, that of the contact deformation on the sticking force; this resulted in drawing an erroneous conclusion that taking into account the elastic deformation on the basis of the Hertz theory should have resulted, not only in an abrupt increase in the sticking force, but also in the appearance of its quadratic dependence upon the radius of a particle.

The main decisive error of Dahneke consists in his joint using of mutually completely incompatible formulas [9] and [10] of Ref. (4)

$$F_{\text{att}} = -\left[\frac{A\epsilon d}{(12\epsilon^3)}\right](1 + 2h/z_0)$$  [9]

$$F_{\text{rep}} = \left[\frac{2(2\epsilon d)^\frac{1}{3}}{3k}\right]h.$$  [10]

Here, $A$ is the constant of the Hamaker molecular interaction; $d$ is the diameter of a particle; $z_0$ is the least distance between the surfaces of a sphere and a plane, which in Ref. (4) is equal to 4 Å; and $h$ is the amount the ball center has approached the plane. The value of $K$, which is characteristic of the mechanical properties of the materials contacting bodies are made of, is equal to

$$K = K_1 + K_2,$$

where

$$K_i = \left(1 - \sigma_i^2\right)/E_i$$

($E$ and $\sigma$ are the corresponding values of the modulus of elasticity and Poisson's coefficient, respectively).

In the Dahneke formula [9] (under the condition, $h \gg z_0$), the first chief term expresses in its sense the resultant of the molecular attraction forces acting over the contact area $S$, found according to the diagram of Fig. 1 of Ref. (4), and therefore, proportional to value $h$. (Note that this diagram has nothing in common with the form of contact deformation according to the Hertz theory. Therefore, the value of $S$ found in Ref. (4) is two times greater than the true one). The value of $F_{\text{rep}}$ is the resultant of normal elastic stresses acting over the area of the Hertz contact deformation. It is an obvious truth that passing over from the macroscopic picture of elastic stresses and pressures to their molecular interpretation, we should make $F_{\text{rep}}$ equal to the resultant of all the molecular interactions; and if we want to take into account separately the close-range repelling (repulsive) forces and far-range attraction forces, $F_{\text{rep}}$ should have been made equal to a difference between the former and the latter. Limiting ourselves only to the former when interpreting the contact interaction [as was done in (4)], implies making a gross error which is of the same magnitude as the main component of term $F_{\text{att}}$ that was
taken into account by Dahneke in calculating
the total sticking force.

Therefore, if we correct this discrepancy,
then instead of expression [11] that was
derived by Dahneke for force $F$, we obtain

$$F = -\frac{Ad}{12z_0^3} + \frac{[2(2d)^{1/3}k]h^4}{12z_0^3}.$$ 

This expression is likely to monotonically
diminish in its absolute value with the growth
of parameter $h$ employed in the Hertz theory.

Consequently, if we eliminate the chief
error from the reasoning of the author of
reference (4), no conclusion can be drawn
about the influence of elastic deformation
on the adhesion of spherical particles. A plurality
of other shortcomings (drawbacks) of the
Dahneke work also will have to be noted.
Instead of the modern theory of molecular
attraction by Lifshits and his co-workers (10),
Dahneke uses calculations that are based on
an assumption of the additivity of the paired
interactions of molecules, an assumption that
is known to be incorrect. In his final formulas,
he uses such a value for the maximum approach
of surfaces $z_0$ to one another, which has not
been accurately preset.

The authors of the present paper have
employed such an essentially thermodynamic
approach, which enables one to obtain the
parameter mentioned above.

Trying to substantiate his conclusions by
the published experimental data, Dahneke has
ignored a number of works wherein the molecu-
lar sticking force was found to be proportional
to the first, but not to the second power of the
radius of particles (12, 13). As for Ref. (14),
it covers investigating the sticking by the use
of a dynamic method, wherein the tearing off
was preceded by the pressing-on through an
inertial force whose magnitude was equal to
the tearing-off force set up in the second step
of the process and was intended to overcome
the sticking force.

That the force required to overcome the
sticking force obeyed the quadratic dependence
upon the radius of particles was explained by
the effect of a double electric layer forming
during the pressing-on stage within the zone
of the contact area.

This explanation was corroborated quanti-
tatively by the direct measurement of charges
that were carried off by the particles after their
tearing off the substrate (15). Further, it is
unclear why Dahneke, in criticizing that
explanation, has described as semi-empirical
the notion of a double electric layer at the
boundary between two solids, which was first
introduced by Helmholtz, as well as the assertion
that the corresponding electrostatic attraction
is proportional to the contact area.

Dahneke contends that the difference in
potentials between the plates of the double
electric layer rarely reaches the value of
0.5 V. However, we have already presented
data proving the contrary (16, 17). Independ-
ently, we have presented in Ref. (15) the
measurements of the charge of a particle being
torn off, which show the charge density is
sufficient for explaining the measured values
of the sticking force.

Dahneke has referred to a paper by Krupp
(18), trying to substantiate that the van der
Waals’ sticking force component prevails over
the electrostatic one. This reference is quite
inadequate to support the above contention.
The point is that the Krupp paper assumes
that the contact deformation is, as a rule,
plastic, which, by the way, cannot be con-
ceded at all, as has already been pointed out
above (16). Dahneke himself considers it to
be elastic, obeying the Hertz formulas based
on the Hook’s linear elasticity. In this case, the
tearing-off process will occur in a reversible
manner (in the absence of electrostatic attrac-
tion), and hence, during the tearing-off process
the contact area will decrease gradually under
the effect of an elastic reaction as the tearing-
off force increases, thus tending to zero.
Therefore, the tearing-off force should over-
come the total molecular attraction force
applied to the starting contact area, not at
once as Krupp believed, but step by step.

The molecular attraction forces of surfaces
tend to decrease rapidly as the surfaces are
drawn apart. On the contrary, the electrostatic attraction of the plates of a double layer, which is separated as the contact has been broken up, does not diminish until a discharge and the neutralization of opposite charges occurs. This is the cause of the contact deformation within the elasticity range giving rise to an electric component of the sticking force, which is proportional to the maximum contact area. That is exactly what is able to give preponderance to the electrostatic component of the sticking force over the molecular one.

GENERAL CONCLUSIONS

We have developed here a strict theory of the mutual influence of the contact deformation and the molecular attraction of a ball to a plane. The van der Waals' forces are capable of increasing the area of elastic contact of the ball with the plane, yet it has been shown that the force, as required for overcoming the van der Waals' forces and breaking up the contact, does not increase thereby and may be calculated, if one considers the point contact of a nondeformed ball with a plane.

The sticking force (in the absence of the electrostatic component) is proportional to the first power of the ball radius and to the work as required for effecting the equilibrium tearing off the flat surfaces of the same nature per unit area.

The calculations done by Dahneke, which have resulted in the quadratic dependence of the sticking force upon the ball area, are grossly erroneous. The main error consists in considering the molecular repulsive forces equal to the normal elastic stress at the contact area, without taking into account the attraction forces.

In (14, 15) there the proportionality of the sticking force to the square of the radius of balls was established. This is explained by the effect of electric attraction forces between the plates of a double electric layer. In accordance with the conditions of the aforementioned experiments, that double electric layer is likely to form under the effect of a pressing-on pulse all over the pressing-on area.

When tearing off under the effect of inertia forces, the attraction forces between the plates of the double electric layer to be drawn apart considerably exceed the molecular sticking and ensure the proportionality between the sticking force and the square of the ball radius. This conclusion has been confirmed by the quantitative measurement of the density of a charge carried away when tearing off particles.

REFERENCES

3. Derjaguin, B. V., Koll. Z. 69, N2, 155 (1934).


18. **Krupp, H.**, *Advances in Colloid Interface Sci.* 1, 111 (1967).