Mechanics of Nanoparticle Adhesion – a Continuum Approach

Jürgen Tomas
Mechanical Process Engineering, Department of Process Engineering and Systems Engineering, Otto-von-Guericke-University, Universitätsplatz 2, D - 39106 Magdeburg, Germany

Abstract
The fundamentals of particle-particle adhesion are presented by continuum mechanics approaches. The models for elastic (Hertz, Huber, Cattaneo, Mindlin and Deresiewicz), elastic-adhesion (Derjagin, Bradley, Johnson), plastic-adhesion (Krupp, Molerus, Johnson, Maugis and Pollock) contact deformation response of a single, normal or tangential loaded, isotropic, smooth contact of two spheres are discussed. The force-displacement behavior of elastic-plastic (Schubert, Thornton), elastic-dissipative (Sadd), plastic-dissipative (Walton) and viscoplastic-adhesion (Rumpf) contacts is also shown. Based on these theories, a general approach for the time and deformation rate dependent and combined viscoelastic, plastic, viscoplastic, adhesion and dissipative behaviors of a spherical particle contact is derived and explained. The decreasing contact stiffness with decreasing particle diameter is the major reason for adhesion effects at nanoscale. Using the model “stiff particles with soft contacts”, the combined influence of elastic-plastic and viscoplastic repulsions in a characteristic (averaged) particle contact is shown. The attractive particle adhesion term is described by a sphere-sphere model for van der Waals forces without any contact deformation and a plate-plate model for this micro-contact flattening is presented. Various contact deformation paths for loading, unloading, reloading and contact detachment are discussed. Thus, the varying adhesion forces between particles depend directly on this “frozen” irreversible deformation, the so-called contact pre-consolidation history. Finally, for colliding particles the correlation between particle impact velocity and contact deformation response is obtained using energy balance. This constitutive model approach is generally applicable for solid micro- or nanocontacts but has been shown here for dry titania nanoparticles.

Keywords: Powder, particle mechanics, contact behavior, constitutive models, adhesion force, nanoparticles

1 Phone: ++49 391 67 18783, Fax: ++49 391 67 11160, e-mail: juergen.tomas@vst.uni-magdeburg.de
1. Introduction

In terms of particle processing and product handling, the well-known flow problems of cohesive powders in storage and transportation containers, conveyors or process apparatuses include bridging, channeling and oscillating mass flow rates. In addition, flow problems are related to particle characteristics associated with feeding and dosing, as well as undesired effects such as widely spread residence time distribution, time consolidation or caking, chemical conversions and deterioration of bioparticles. Finally, insufficient apparatus and system reliability of powder processing plants are also related to these flow problems. The rapid increasing production of cohesive to very cohesive nanopowders, e.g. very adhering pigment particles, micro-carriers in biotechnology or medicine, auxiliary materials in catalysis, chromatography or silicon wafer polishing, make these problems much serious. Taking into account this list of technical problems and hazards, it is essential to deal with the fundamentals of particle adhesion, powder consolidation and flow, i.e. to develop a reasonable combination of particle and continuum mechanics.

The well-known failure hypotheses of Tresca, Coulomb-Mohr, Drucker-Prager (in [1, 2]), the yield locus concept of Jenike [3, 4] and Schwedes [5] and the Warren-Spring equations [6 - 9], Tüzün [12] etc. were supplemented by Molerus [14 - 16] to describe the cohesive, steady-state flow criterion. Nedderman [17, 18], Jenkins [19] and others discussed the rapid and collisional flow of non-adhering particles as well as Tardos [20] discussed the frictional flow for compressible powders without any cohesion from the fluid mechanics point of view. Additionally, the simulation of particle dynamics of free flowing granular media is increasingly used, see e.g. Cundall [21], Campbell [22], Walton [23, 24], Herrmann [25] and Thornton [26]. Additionally, particle adhesion effects are related to undesired powder blocking at conveyor transfer chutes or in pneumatic pipe bends [27] in powder handling and transportation, to desired particle cake formation on filter media [28, 29], to wear effects of adhering solid surfaces [30, 31], fouling in membrane filtration, fine particle deposition in lungs, formulation of particulate products [32 - 35] or to surface cleaning of silicon wafers [36 - 40, 126], etc.

The force-displacement behaviors of elastic, elastic-adhesion, plastic-adhesion, elastic-plastic, elastic-dissipative, plastic-dissipative and viscoplastic-adhesion contacts are shown. Based on these single theories, a general approach for the time and deformation rate dependent and combined viscoelastic, plastic, viscoplastic, adhesion and dissipative behaviors of a spherical particle contact is derived and explained.

2. Particle contact constitutive models

In terms of particle technology, powder processing and handling, Molerus [13, 14] explained the consolidation and non-rapid flow of dry, fine and cohesive powders (particle diameter d <
10 µm) in terms of the adhesion forces at particle contacts. In principle, there are four essential mechanical deformation effects in particle-surface contacts and their force-response (stress-strain) behavior can be explained as follows, Table 1:

(1) *elastic* contact deformation (Hertz [41], Huber [42], Derjaguin [43], Bradley [44], Cattaneo [45], Mindlin [46], Sperling [47], Krupp [48], Johnson [49], Dahneke [50], Thornton [51, 52], Sadd [53]) which is reversible, independent of deformation rate and consolidation time effects and valid for all particulate solids;

(2) *plastic* contact deformation with adhesion (Derjaguin [43], Krupp [54], Schubert [55], Molerus [13, 14], Maugis [56], Walton [57] and Thornton [58]) which is irreversible, deformation rate and consolidation time independent, e.g. mineral powders;

(3) *viscoelastic* contact deformation (Yang [59], Krupp [48], Rumpf [60] and Sadd [53]) which is reversible and dependent on deformation rate and consolidation time, e.g. bioparticles;

(4) *viscoplastic* contact deformation (Rumpf [60]) which is irreversible and dependent on deformation rate and consolidation time, e.g. nanoparticles fusion.

This paper is intended to focus on a characteristic, *soft* contact of two isotropic, *stiff*, linear elastic, smooth, mono-disperse spherical particles. Thus, this soft or compliant contact displacement is assumed to be small \( h_K/d \ll 1 \) compared to the diameter of the stiff particle. The contact area consists of a representative number of molecules. Hence, continuum approaches are only used here to describe the force-displacement behavior in terms of nanomechanics. The microscopic particle shape remains invariant during the dynamic stressing and contact deformation at this nanoscale. In powder processing, these particles are manufactured from uniform material in the bulk phase. These prerequisites are assumed to be suitable for the mechanics of dry nanoparticle contacts in many cases of industrial practice.

### 2.1 Elastic, plastic and viscoplastic contact deformations

#### 2.1.1 Elastic contact displacement

For a single elastic contact of two spheres 1 and 2 with a maximum contact circle radius \( r_{K,el} \) but small compared with the particle diameter \( d_1 \) or \( d_2 \), an elliptic pressure distribution \( p_{el}(r_K) \) is assumed, Hertz [41]:

\[
\left( \frac{p_{el}}{p_{max}} \right)^2 = 1 - \left( \frac{r_K}{r_{K,el}} \right)^2
\]  

(1)

With the maximum pressure \( p(r_K = 0) = p_{max} \) in the center of contact circle at depth \( z = 0 \),

\[
p_{max} = \frac{3 \cdot F_N}{2 \cdot \pi \cdot r_{K,el}^2}
\]  

(2)

and the median particle radius \( r_{1,2} \) (characteristic radius of contact surface curvature), Fig. 1,
\[ r_{1,2} = \left( \frac{1}{r_1} + \frac{1}{r_2} \right)^{-1} \]  

and the average material stiffness (E modulus of elasticity, \( \nu \) Poisson ratio)

\[ E^* = 2 \left( \frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2} \right)^{-1} \]  

one can calculate the correlation between normal force \( F_N \) and maximum contact radius \( r_{K,el} \):

\[ r_{K,el}^3 = \frac{3 \cdot r_{1,2} \cdot F_N}{2 \cdot E^*} \]  

Considering surface displacement out of the contact zone, details in Huber [42], the so-called particle center approach or height of overlap of both particles \( h_K \) is [41]:

\[ h_K = \frac{r_k}{r_{1,2}} \]  

Substitution of Eq. (6) in Eq. (5), results in a non-linear relation between elastic contact force and deformation [41], Fig. 1:

\[ F_N = \frac{2}{3} \cdot E^* \cdot \sqrt{r_{1,2} \cdot h_K^3} \]  

Eq. (7) is shown as the dashed curve marked Hertz. The maximum pressure \( p_{\text{max}} \), Eq. (2), is 1.5 times the average pressure \( F_N / (\pi \cdot r_{K,el}^2) \) on the contact area and lies below the micro-yield strength \( p_t \). Because of surface bending and, consequently, the opportunity for unconfined yield at the surface perimeter outside of the contact circle \( r_k \geq r_{K,el} \), Fig. 1b), a maximum tensile stress is found [42] \( \sigma_{t,\text{max}} \approx -0.15 \cdot p_{\text{max}} \) (here negative because of positive pressures in powder mechanics):

\[ \left. \frac{\sigma_t}{p_{\text{max}}} \right|_{r_k \geq r_{K,el}} = -\frac{1 - 2 \cdot \nu}{3} \cdot \frac{r_k^2}{r_{K,el}^2} \]  

This critical stress for cracking of a brittle particle material with low tensile strength is smaller than the maximum shear stress \( \tau_{\text{max}} \approx 0.31 \cdot p_{\text{max}} \) according to Eq. (11) which is found at the top of a virtual stressing cone below the contact area on the principal axis \( \tau_K = x^2 + y^2 = 0 \) in the depth of \( z \approx r_{K,el}/2 \). Combining the major principal stress distribution, Eq. (9), \( \sigma_1 = \sigma_t(z) \) at contact radius \( r_k = 0 \)

\[ \left. \frac{\sigma_t(z)}{p_{\text{max}}} \right|_{r_k = 0} = \frac{r_{K,el}^2}{r_{K,el}^2 + z^2}, \]  

and the minor principal stress, Eq. (10), \( \sigma_2 = \sigma_y = \sigma_t(z) [42] \)

\[ \left. \frac{\sigma_t(z)}{p_{\text{max}}} \right|_{r_k \leq r_{K,el}} = -\frac{1}{2} \cdot \frac{r_{K,el}^2}{r_{K,el}^2 + z^2} + (1 + \nu) \left[ 1 - \frac{z}{r_{K,el}} \cdot \arctan \frac{r_{K,el}}{z} \right]. \]
the maximum shear stress inside a particle contact \( r_K \leq r_{K,el} \) is obtained using the Tresca hypothesis for plastic failure \( \tau_{\text{max}} = (\sigma_1 - \sigma_2) / 2 \) \[1\]:

\[
\frac{\tau(z)}{p_{\text{max}}} \bigg|_{r_K \leq r_{K,el}} = \frac{3}{4} \frac{r_{K,el}^2}{r_{K,el}^2 + z^2} - \frac{1 + \nu}{2} \left[ 1 - \frac{z}{r_{K,el}} \cdot \arctan \frac{r_{K,el}}{z} \right]
\]

This internal shear stress distribution becomes more and more critical for ductile or soft solids with a small transition to yield point, and consequently, plastic contact deformation like nanoparticles with very low stiffness, see section 2.3.

Due to the parabolic curvature \( F_N(h_K) \), the particle contact becomes stiffer with increasing diameter \( r_{1,2} \), contact radius \( r_K \) or displacement \( h_K \) (\( k_N \) is the contact stiffness in normal direction):

\[
k_N = \frac{dF_N}{dh_K} = E^* \sqrt{r_{1,2} \cdot h_K} = E^*r_K
\]

The influence of a tangential force in a normal loaded spherical contact was considered by Cattaneo \[45\] and Mindlin \[46, 61\]. About this and complementary theories as well as loading, unloading and reloading hysteresis effects, one can find a detailed discussion by Thornton \[51\]. He has expressed this tangential contact force as \[51, 52\]:

\[
F_t = 4 \cdot \psi \cdot G^* \sqrt{r_{1,2} \cdot h_K} \cdot \Delta \delta \mp \left( 1 - \psi \right) \cdot \tan \varphi_i \cdot \Delta F_N
\]

Here \( \Delta \delta \) is the tangential contact displacement, \( \psi \) the loading parameter dependent on loading, unloading and reloading, \( \varphi_i \) the angle of internal friction, \( G = E/2(1 + \nu) \) the shear modulus, and the averaged shear modulus is given as:

\[
G^* = 2 \left( \frac{2 - \nu_1}{G_1} + \frac{2 - \nu_2}{G_2} \right)^{-1}
\]

Thus, with \( \psi = 1 \) the ratio of the initial tangential stiffness

\[
k_T = \frac{dF_T}{d\delta} = 4 \cdot G^* \cdot r_K
\]

to the initial normal stiffness according to Eq. (12) is:

\[
\frac{k_T}{k_N} = \frac{2 \cdot (1 - \nu)}{2 - \nu}
\]

Hence this ratio ranges from unity, for \( \nu = 0 \), to 2/3, for \( \nu = 0.5 \) \[61\], which is different from the common linear elastic behavior of a cylindrical rod.

2.1.2 Elastic displacement of an adhesion contact

The adhesion in the normal loaded contact of spheres with elastic displacement will be additionally shown. For fine and stiff particles, the Derjagin, Muller and Toporov DMT model
[43, 63, 64] predicts that half of the interaction force $F_{H,DMT}/2$ occurs outside in the annular area which is located at the perimeter closed by the contact, Eq. (17). This is in contrast to the Johnson, Kendall and Roberts JKR model [65] which assumes that all the interactions occur within the contact radius of the particles. The median adhesion force $F_{H,DMT}$ (index H,DMT) of a direct spherical contact can be expressed in terms of the work of adhesion $W_A$, conventional surface energy $\gamma_A$ or surface tension $\sigma_{sls} W_A = 2 \cdot \gamma_A = 2 \cdot \sigma_{sls}$. The index sls means particle surface - adsorption layers (with liquid equivalent mechanical behavior) – particle surface interaction. If only molecular interactions with separations near the contact contribute to the adhesion force the so-called Derjaguin approximation [43] is valid:

$$F_{H,DMT} = 4 \cdot \pi \cdot \sigma_{sls} \cdot r_{1,2}$$  \hspace{1cm} (17)

This surface tension $\sigma_{sls}$ equals half the energy needed to separate two flat surfaces from an equilibrium contact distance $a_{F=0}$ to infinity [71]:

$$\sigma_{sls} = -\frac{1}{2} \cdot \int_{p_{vuw}(a)}^{\infty} \frac{C_{H,sls}}{24 \cdot \pi \cdot a_{F=0}^2} \, da$$  \hspace{1cm} (18)

Using this and for comparison of the adhesion or bond strength, a dimensionless ratio of adhesion force $\sigma_{sls} \cdot r_{1,2}$ to elastic repulsion force $E^* \cdot \sqrt{r_{1,2}^3 \cdot h_{r_{1,2}}^3}$ as response of mean asperity height displacement $h_{r_{1,2}}$ can be defined as the “adhesion parameter” $\Phi_T$ first introduced by Tabor [30, 70]:

$$\Phi_T = \left( \frac{4 \cdot r_{1,2} \cdot \sigma_{sls}^2}{E^* \cdot h_{r_{1,2}}^3} \right)^{1/2}$$  \hspace{1cm} (19)

The DMT model works for small and stiff particles $\Phi_T < 0.1$ [76]. For separating a stiff, non-deformed spherical point contact, the DMT theory [63] predicts a necessary pull-off force $F_{N,Z}$ equivalent to the adhesion reaction force expressed by Eq. (17).

Compared with the stronger covalent, ionic, metallic or hydrogen bonds, these particle interactions are comparatively weak. From Eq. (18) the surface tension is about $\sigma_{sls} = 0.25 – 50$ mJ/m$^2$ or the Hamaker constant according to Lifshitz continuum theory amounts to $C_{H,sls} = (0.2 – 40) \cdot 10^{-20}$ J [69, 71]. Notice here, the particle interactions depend greatly on the applied load, which is experimentally confirmed by atomic force microscopy [73, 74, 92].

A balance of stored elastic energy, mechanical potential energy and surface energy delivers the contact radius [49], expressed here with a constant adhesion force $F_{H,JKR}$ due to Eq. (22):

$$r_k^3 = \frac{3 \cdot r_{1,2}^2}{2 \cdot E^*} \left( F_N + F_{H,JKR} + \sqrt{2 \cdot F_{H,JKR}^2 + F_N^2} \right)$$  \hspace{1cm} (20)

Eq. (20) indicates a contact radius enhancement with increasing work of adhesion. The contact force-displacement relation is obtained from Eqs. (6) and (20) and can be compared with the Hertz relation Eq. (7) by the curves in Fig. 2 marked with Hertz and JKR:
\[
F_N = \frac{2 \cdot E^*}{3} \cdot r_{i,2} \cdot h_k^3 - \sqrt{\frac{4 \cdot E^* \cdot F_{H,JKR}}{3}} \cdot r_{i,2} \cdot h_k^3
\]

(21)

For small contact deformation the so-called JKR limit [49] is half of constant adhesion force \(F_{H,JKR}\). This JKR model can be applied for bond strength \(\Phi_T > 5\) [70, 76, 77, 78]. It is valid for comparatively larger and softer particles than the DMT model predicts [109]:

\[
\left| F_{N,Z,JKR} \right| = \frac{F_{H,JKR}}{2} = 3 \cdot \pi \cdot \sigma_{sls} \cdot r_{i,2}
\]

(22)

Thus the contact radius for zero load \(F_N = 0\),

\[
r_{k,0} = \sqrt{\frac{3 \cdot r_{i,2} \cdot F_{H,JKR}}{E^*}}
\]

(23)

is reduced to the pull-off contact radius, i.e.,

\[
r_{k,\text{pull-off}} = r_{k,0} / \sqrt{4}.
\]

(24)

Additionally, with applying an increasing tangential force \(F_T\), the contact radius \(r_k\) is reduced by the last term within the square root:

\[
r_k^3 = \frac{3 \cdot r_{i,2}}{2 \cdot E^*} \left( F_N + F_{H,JKR} + \sqrt{2 \cdot F_{H,JKR} \cdot F_N + F_{H,JKR}^2 - \frac{F_T^2 \cdot E^*}{4 \cdot G^*}} \right),
\]

(25)

When the square root in Eq. (25) disappears to zero, a critical value \(F_{T,\text{crit}}\) is obtained, the so-called “peeling” of contact surfaces [62, 82]:

\[
F_{T,\text{crit}} = 2 \sqrt{\left(2 \cdot F_{H,JKR} \cdot F_N + F_{H,JKR}^2 \right) \cdot G^*}
\]

(26)

An effective or net normal force \((F_N + F_{H,JKR})\) remains in the contact [52]. Considering \(F_T > F_{T,\text{crit}}, i.e., contact failure by sliding, see Mindlin [61], the tangential force limit is expressed as \(F_T = \tan \phi_i \cdot (F_N + F_{H0})\). The adhesion force \(F_{H0}\) (index H0) is constant during contact failure and the coefficient (or angle) of internal friction \(\mu_i = \tan \phi_i\) is also assumed to be constant for a multi-asperity contact [76]. This constant friction was often confirmed for rough surfaces in both elastic and plastic regime, e.g. [75, 78], but not for a single-asperity contact with nonlinear dependence of friction force on normal load [76, 78].

Rearranging Eq. (25), the extended contact force-displacement relation shows a reduction of the Hertz (first square-root) and JKR contributions to normal load \(F_N\) which is needed to obtain a given displacement \(h_K\):

\[
F_N = \frac{2 \cdot E^*}{3} \cdot r_{i,2} \cdot h_k^3 - \sqrt{\frac{4 \cdot E^* \cdot F_{H,JKR}}{3}} \cdot r_{i,2} \cdot h_k^3 - \frac{F_T^2 \cdot E^*}{4 \cdot G^*}
\]

(27)

However, the increase of contact area with elastic deformation does not lead to a significant increase of attractive adhesion forces because of a practically too small magnitude of van der
Waals energy of adhesion, Eq. (18). The reversible elastic repulsion restitutes always the initial contact configuration. Consequently, the increase of adhesion by compression, e.g. forming a snow ball, the well-known cohesive consolidation of a powder or the particle interaction and remaining strength after tabletting must be influenced by irreversible contact deformations, which are shown for a small stress level in a powder bulk in Fig. 2 and Fig. 3.

If the maximum pressure $p_{\text{max}} = p_f$ in the center of the contact circle reaches the micro-yield strength, the contact starts with irreversible plastic yielding (index $f$). From Eqs. (2) and (5) the transition radius $r_{K,f}$ and from Eq. (6) the center approach $h_{K,f}$ are calculated as:

$$r_{K,f} = \frac{\pi \cdot r_{1,2} \cdot p_f}{E^*}$$  \hspace{1cm} (28)

$$h_{K,f} = \frac{\pi^2 \cdot r_{1,2} \cdot p_f^2}{E^*^2}$$  \hspace{1cm} (29)

Fig. 2 demonstrates the dominant irreversible deformation over a wide range of contact forces. This transition point $Y$ for plastic yielding is essentially shifted towards smaller normal stresses because of particle adhesion influence.

Rumpf et al. [60] and Molerus [13, 14] introduced this philosophy in powder mechanics and the JKR theory was the basis of adhesion mechanics [56, 65, 79, 80, 84].

### 2.1.3 Perfect plastic and viscoplastic contact displacement

Actually, assuming perfect contact plasticity one can neglect the surface deformation outside of the contact zone and obtain with the following geometrical relation of a sphere

$$r_{K}^2 = r_{i}^2 - (r_i - h_{K,1})^2 = 2 \cdot r_i \cdot h_{K,1} - h_{K,1}^2 \approx d_i \cdot h_{K,1}$$  \hspace{1cm} (30)

the total particle center approach of both spheres:

$$h_k = h_{K,1} + h_{K,2} = \frac{r_{K}^2}{d_1} + \frac{r_{K}^2}{d_2} = \frac{r_{K}^2}{2 \cdot r_{1,2}}$$  \hspace{1cm} (31)

Because of this, a linear force-displacement relation is found for small spherical particle contacts. The repulsive force as a resistance against plastic deformation is given as:

$$F_{N,pl} = p_f \cdot A_k = \pi \cdot d_{1,2} \cdot p_f \cdot h_k$$  \hspace{1cm} (32)

Thus, the contact stiffness is constant for perfect plastic yielding behavior, but decreases with smaller particle diameter $d_{1,2}$ especially for cohesive fine powders and nanoparticles:

$$k_{N,pl} = \frac{dF_{N}}{dh_k} = \pi \cdot d_{1,2} \cdot p_f$$  \hspace{1cm} (33)
Additionally, the rate dependent, perfect viscoplastic deformation (at the point of yielding) expressed by contact viscosity $\eta_K$ times indentation rate $\dot{h}_K$ is assumed to be equivalent to yield strength $p_f$ multiplied by indentation height increment $h_K$

$$p_f \cdot h_K = \eta_K \cdot \dot{h}_K$$

and one obtains again a linear model regarding strain rate:

$$F_{N,vis} = \eta_K \cdot \dot{A}_K = \pi \cdot d_{1,2} \cdot \eta_K \cdot \dot{h}_K$$

Consequently, the material parameters: contact micro-yield strength $p_f$ and viscosity $\eta_K$ are measures of irreversible particle contact stiffness or softness. Both plastic and viscous contact yield effects were intensified by mobile adsorption layers on the surfaces. The sum of deformation increments results in the energy dissipation. For larger particle contact areas $A_K$, the conventional linear elastic and constant plastic behavior is expected.

Now, what are the consequences of small contact flattening with respect to a varying, i.e., load or pre-history dependent adhesion?

2.2 Particle contact consolidation by varying adhesion force

Krupp [48] and Sperling [47, 54] developed a model for the increase of adhesion force $F_H$ (index $H$) which is called here as “consolidation” of the contact. This considerable effect is expressed as the sum of adhesion force $F_{H0}$ according to Eq. (17) plus an attractive/repulsive force contribution due to irreversible plastic flattening of the spheres ($p_f$ is the repulsive “microhardness” or micro-yield strength of the softer contact material of both particles, $\sigma_{ss}/a_0$ is the attractive contact pressure, index $ss$ represents solid-vacuum-solid interaction):

$$F_H = 4 \cdot \pi \cdot r_{1,2} \cdot \sigma_{ss} \cdot \left(1 + \frac{2 \cdot \sigma_{ss}}{a_0 \cdot p_f}\right)$$

Dahneke [50] modified this adhesion model by the van der Waals force without any contact deformation $F_{H0}$ plus an attractive van der Waals pressure (force per unit surface) $p_{VdW}$ contribution due to partially increasing flattening of the spheres which form a circular contact area $A_K$ ($C_H$ is the Hamaker constant based on interacting molecule pair additivity [68, 71]):

$$F_H = F_{H0} + A_K \cdot p_{VdW} = \frac{C_H \cdot r_{1,2}}{6 \cdot a_0^2} \cdot \left(1 + \frac{2 \cdot h_K}{a_0}\right)$$

The distance $a_0$ denotes a characteristic adhesion separation. If stiff molecular interactions provided (no compression of electron sheath), this separation $a_0$ was assumed to be constant during contact loading. By addition the elastic repulsion of the solid material according to Hertz, Eq. (7), to this attraction force, Eq. (37), and by deriving the total force $F_{tot}$ with respect to $h_K$, the maximum adhesion force was obtained as absolute value

$$F_{H,\text{max}} = \frac{C_H \cdot r_{1,2}}{6 \cdot a_0^2} \cdot \left(1 + \frac{2 \cdot C_H^2 \cdot r_{1,2}}{27 \cdot E^* \cdot a_0^3}\right)$$
which occurs at the center approach of the spheres [50]:

$$h_{k,\text{max}} = \frac{C_H^2 \cdot r_{1,2}}{9 \cdot E \cdot \pi^2 \cdot a_0^4}$$  \hspace{1cm} (39)

But as mentioned before, this increase of contact area with elastic deformation does not lead to a significant increase of attractive adhesion force. The reversible elastic repulsion restores always the initial contact configuration. The practical experience with the mechanical behavior of fine powders shows that an increase of adhesion force has to be influenced by an irreversible or “frozen” contact flattening which depends on the external force $F_N$ [55]. Generally, if this external compressive normal force $F_N$ is acting at a single soft contact of two isotropic, stiff, smooth, mono-disperse spheres the previous contact point is deformed to a contact area, Fig. 1a) to Fig. 2c), and the adhesion force between these two partners increases, see in Fig. 3 the so-called “adhesion boundary” for incipient contact detachment. During this surface stressing the rigid particle is not so much deformed that it undergoes a certain change of the particle shape. In contrast, soft particle matter such as biological cells or macromolecular organic material do not behave so.

For soft contacts Rumppf et al. [60] have developed a constitutive model approach to describe the linear increase of adhesion force $F_H$, mainly for plastic contact deformation:

$$F_H = \left( 1 + \frac{p_{\text{VdW}}}{p_f} \right) \cdot F_{H0} + \frac{p_{\text{VdW}}}{p_f} \cdot F_N = (1 + \kappa_p) \cdot F_{H0} + \kappa_p \cdot F_N$$  \hspace{1cm} (40)

With analogous prerequisites and derivation, Molerus [14] obtained an equivalent expression:

$$F_H = F_{H0} + \frac{p_{\text{VdW}}}{p_f} \cdot F_N = F_{H0} + \kappa_p \cdot F_N$$  \hspace{1cm} (41)

The adhesion force $F_{H0}$ without additional consolidation ($F_N = 0$) can be approached as a single rigid sphere-sphere contact, Fig. 1a). But, if this particle contact is soft enough the contact is flattened by an external normal force $F_N$ to a plate-plate contact, Fig. 2c). The coefficient $\kappa_p$ describes a dimensionless ratio of attractive van der Waals pressure $p_{\text{VdW}}$ for a plate-plate model to repulsive particle micro-hardness $p_f$ which is temperature sensitive:

$$\kappa_p = \frac{p_{\text{VdW}}}{p_f} = \frac{C_{H,\text{sls}}}{6 \cdot \pi \cdot a_{F=0} \cdot p_f}$$  \hspace{1cm} (42)

This is referred to here as a plastic repulsion coefficient. The Hamaker constant $C_{H,\text{sls}}$ for solid-liquid-solid interaction (index sls) according to Lifshitz theory [69] is related to continuous media which depends on their permittivities (dielectric constants) and refractive indices [71]. The characteristic adhesion separation for a direct contact is of a molecular scale (atomic center-to-center distance) and can be estimated for a molecular force equilibrium ($a = a_{F=0}$) or interaction potential minimum [71, 85]. Its magnitude is about $a_{F=0} \approx 0.3 - 0.4$ nm. This separation depends mainly on the properties of liquid-equivalent packed adsorbed water layers. This particle contact behavior is influenced by mobile adsorption layers due to molecular rearrangement. The minimum separation $a_{F=0}$ is assumed to be constant during
molecular rearrangement. The minimum separation $a_{F=0}$ is assumed to be constant during loading and unloading for technologically relevant powder pressures $\sigma < 100$ kPa, Fig. 2c).

For a very hard contact this plastic repulsion coefficient is infinitely small, i.e. $\kappa_p \approx 0$ and for a soft contact $\kappa_p \rightarrow 1$.

If the contact circle radius $r_K$ is small compared to the particle diameter $d$, the elastic and plastic contact displacements can be combined and expressed with the annular elastic $A_{el}$ and circular plastic $A_{pl}$ contact area ratio [55]:

$$F_H = F_{H0} + \frac{p_{\text{vaw}}}{p_f \left(1 + \frac{2}{3} \frac{A_{el}}{A_{pl}}\right)} F_N$$

(43)

For a perfect plastic contact displacement $A_{el} \rightarrow 0$ and one obtains again Eq. (41):

$$F_H \approx F_{H0} + \kappa_p \cdot F_N$$

(44)

This linear enhancement of adhesion force $F_H$ with increasing pre-consolidation force $F_N$, Eqs. (40), (41) and (44), was experimentally confirmed for micrometer sized particles, e.g. by Schütz [88, 89] ($\kappa_p = 0.3$ for limestone) and Newton [90] ($\kappa_p = 0.333$ for poly(ethylenglycol), $\kappa_p = 0.076$ for starch, $\kappa_p = 0.017$ for lactose, $\kappa_p = 0.016$ for CaCO$_3$) with centrifuge tests [86] as well as by Singh et al. [91] ($\kappa_p = 0.12$ for poly(methylnethacrylate), $\kappa_p \approx 0$ for very hard sapphire, $\alpha$-Al$_2$O$_3$) with an Atomic Force Microscope (AFM). The two methods are compared with rigid and rough glass spheres ($d = 0.1$ to $10 \, \mu m$), without any contact deformation, by Hoffmann et al. [92]. Additionally, using the isostatic tensile strength $\sigma_0$ determined by powder shear tests [85, 116, 141, 143], this adhesion level is of the same order of magnitude as the average of centrifuge tests, see Spindler et al. [93].

The enhancement of adhesion force $F_H$ due to pre-consolidation was confirmed by Tabor [30], Maugis [79, 80] and Visser [104]. Also Maugis and Pollock [56] found that separation was always brittle (index br) with a small initial slope of pull-off force, $dF_{N,Z,br}/dF_N$ ($F_{N,Z,br} \approx - F_H$), for a comparatively small surface energy $\sigma_{ss}$ of the rigid sphere-gold plate contact (index ss). In contrast, a pull-off force $F_{N,Z,br}$ proportional to $\sqrt{F_N}$ was obtained from the JKR theory [56] for the full plastic range of high loading and brittle separation of the contact, Table 1:

$$F_{N,Z,br} = -\sigma_{ss} \cdot E^* \cdot \frac{F_N}{\pi \cdot p_f^3}$$

(45)

Additionally, a load dependent adhesion force was also experimentally confirmed in wet environment of the particle contact by Butt et al. [73, 74] and Higashitani et al. [81] with AFM measurements.

The dominant plastic contact deformation of surface asperities during the chemical-mechanical polishing process of silicon wafers was also recognized, e.g., by Rimai and Busnaina [105] and Ahmadi and Xia [135]. These particle-surface contacts and, consequently, asperity stressing by simultaneous normal pressure and shearing, contact deformation, micro-
crack initiation and propagation, and microfracture of brittle silicon asperity peaks affect directly the polishing performance. Thus the Coulomb friction becomes dominant also in wet environment.

2.3 Variation in adhesion due to non-elastic contact consolidation

2.3.1 Elastic-plastic force-displacement model

All interparticle forces can be expressed in terms of a single potential function \( F_i = \pm \partial U_i(h_i)/\partial h_i \) and thus are superposed. This is valid only for a conservative system in which the work done by the force \( F_i \) versus distance \( h_i \) is not dissipated as heat, but remains in the form of mechanical energy, simply in terms of irreversible deformation, e.g. initiation of nanoscale distortions, dislocations or lattice stacking faults. The overall potential function may be written as the sum of the potential energies of a single contact \( i \) and all particle pairs \( j \). Minimizing this potential function \( \sum_i \sum_j \partial U_{ij}/\partial h_j = 0 \) one obtains the potential force balance.

Thus, the elastic-plastic force-displacement models introduced by Schubert et al. [55], Eq. (43), and Thornton [58] Eq. (46)

\[
F_N = \pi \cdot p_F \cdot r_{i,2} \cdot (h_K - h_{K,f} / 3)
\]  

(46)

should be supplemented here with a complete attractive force contribution of contact flattening described before. Taking into account Eqs. (40), (41) and (43), the particle contact force equilibrium between attraction (−) and elastic plus, simultaneously, plastic repulsion (+) is given by (\( r_K^* \) represents the coordinate of annular elastic contact area):

\[
\sum F = -F_{h_0} - p_{vdw} \cdot \pi \cdot r_K^2 - F_N + p_f \cdot \pi \cdot r_{K,pl}^2 + 2 \cdot \pi \cdot \int_{r_{K,pl}}^{r_K^*} p_{el}(r_K^*) \cdot r_K^* \cdot dr_K^*
\]  

(47)

\[
F_N + F_{h_0} + p_{vdw} \cdot \pi \cdot r_K^2 = p_f \cdot \pi \cdot r_{K,pl}^2 + 2 \cdot \pi \cdot p_{max} \cdot r_K^2 / 3 \cdot \left[ 1 - \left( \frac{r_{K,pl}}{r_K} \right)^2 \right]^{3/2}
\]  

(48)

At the yield point \( r_K = r_{K,pl} \) the maximum contact pressure reaches the yield strength \( p_{el} = p_f \).

\[
F_N + F_{h_0} + p_{vdw} \cdot \pi \cdot r_K^2 = p_f \cdot \pi \cdot r_{K,pl}^2 + 2 \cdot \pi \cdot p_{max} \cdot r_K^2 / 3 \cdot \left[ 1 - \left( \frac{r_{K,pl}}{r_K} \right)^2 \right]
\]  

(49)

Because of plastic yielding, a pressure higher than \( p_f \) is absolutely not possible and thus, the fictitious contact pressure \( p_{max} \) is eliminated by Eq. (1):

\[
F_N + F_{h_0} + p_{vdw} \cdot \pi \cdot r_K^2 = p_f \cdot \pi \cdot r_{K,pl}^2 + 2 \cdot \pi \cdot r_K^2 / 3 \cdot \left[ 1 - \left( \frac{r_{K,pl}}{r_K} \right)^2 \right]
\]  

(50)

Finally, the contact force equilibrium
Introducing the particle center approach of two particles \( \kappa_A \approx \text{const.} \) in (54), a very useful linear force-displacement model approach is obtained again for \( \kappa_A \approx \text{const.} \):  

\[
F_N + F_{H0} = \pi \cdot r_{\text{r},2} \cdot p_f \cdot (\kappa_A - \kappa_p) \cdot h_K
\]  

(57)

Checking this model, Eq. (55), with pure elastic contact deformation, i.e., \( \kappa_p \rightarrow 0 \) and \( \kappa_A = 2/3 \) the elastic transition radius \( r_{K,f} \), Eq. (28), is also obtained. For example, nanodisperse titania particles (\( d_{50,3} = 610 \) nm is the median diameter on mass basis (index 3), \( E = 50 \) kN/mm\(^2\) modulus of elasticity, \( \nu = 0.28 \) Poisson ratio, \( p_f = 400 \) N/mm\(^2\) micro-yield strength, \( \kappa_A \approx 5/6 \) contact area ratio, \( \kappa_p = 0.44 \) plastic repulsion coefficient) a contact radius of \( r_{K,f,\text{el-pl}} = 2.1 \) nm and, from Eq. (56), a homeopathic center approach of only \( h_{K,f,\text{el-pl}} = 0.03 \) nm are obtained. This is a very small indentation calculated, in principle, by means of a continuum approach. The contact deformation is equivalent to a microscopic force \( F_N = 2.1 \) nN or to a small macroscopic pressure level of about \( \sigma = 1.4 \) kPa (porosity \( \varepsilon = 0.8 \)) in powder handling and processing.

Introducing the particle center approach of two particles Eq. (6) in (54), a very useful linear force-displacement model approach is obtained again for \( \kappa_A \approx \text{const.} \):  

\[
F_N + F_{H0} = \pi \cdot r_{l,2} \cdot p_f \cdot (\kappa_A - \kappa_p) \cdot h_K
\]  

(57)
But if one considers the contact area ratio of Eq. (63), a slightly nonlinear (progressively increasing) curve is obtained. Using the elastic-plastic contact consolidation coefficient $\kappa$ due to definition Eq. (69) one can write:

$$F_N + F_{h0} = \frac{\pi \cdot r_{1,2} \cdot p_f \cdot K_A \cdot h_K}{1 + \kappa}$$  \hspace{1cm} (58)

The curve of this model is shown in Fig. 2 for titania powder which was recalculated from material data and shear test data [141, 143]. The slope of this plastic curve is a measure of irreversible particle contact stiffness or softness, Eq. (33). Because of particle adhesion impact the transition point for plastic yielding is shifted to the left compared with the rough calculation of Eq. (28).

The previous contact model may be supplemented by viscoplastic stress-strain behavior, i.e. strain rate dependency on initial yield stress. One obtains for elastic-viscoplastic contact deformation with Eqs. (35) and (57) ($\kappa_A \approx \text{const.}$):

$$F_N + F_{h0} = \pi \cdot r_{1,2} \cdot p_f \cdot (\kappa_A - \kappa_{p,t}) \cdot h_K$$  \hspace{1cm} (59)

A dimensionless viscoplastic contact repulsion coefficient $\kappa_{p,t}$ is introduced as the ratio of the van der Waals attraction to viscoplastic repulsion effects which are additionally acting in the contact after attaining the maximum pressure for yielding.

$$\kappa_{p,t} = \frac{p_{\text{vW}}}{\eta_k \cdot h_k}$$  \hspace{1cm} (60)

The consequences for the variation in adhesion force are discussed in section 2.3.3 [141].

2.3.2 Unloading and reloading hysteresis

If one replaces $F_N$ in Eq. (70) by the normal force-displacement relation, Eq. (57), one obtains additionally a plausible adhesion force-displacement relation which shows the increased pull-off force level after contact flattening, $h_K = h_{K,A}$ compared with Eq. (37) and point A in the diagram of Fig. 4:

$$F_{h0} = F_{h0} + \pi \cdot r_{1,2} \cdot p_{\text{vW}} \cdot h_{K,A}$$  \hspace{1cm} (61)

At this so-called adhesion (failure) boundary the contact microplates fail and detach with the increasing distance $a = a_{F=0} + h_{K,A} - h_K$. The actual particle separation $a$ can be used by a long-range hyperbolic adhesion force curve $F_{N,a} \propto a^{-3}$ with the van der Waals pressure as given in Eq. (42).

Consequently, the unloading and reloading hysteresis for an adhesion contact takes place between the two characteristic straight-lines for compression, the elastic-plastic yield boundary Eq. (57), and for tension, the remaining adhesion (pull-off) boundary Eq. (61) and Fig. 3.
Between the points U – E the contact recovers elastically along an extended Hertzian parabolic curve, Eq. (7), down to the perfect plastic displacement, $h_{K,E}$, obtained in combination with Eq. (57):

$$h_{K,E} = h_{K,U} - \frac{1}{3} h_{K,f} \cdot h_{K,U}^2$$  \hspace{1cm} (62)

Thus, the contact area ratio $\kappa_A$ is expressed more in detail with Eqs. (6) and (53) for elastic $\kappa_A = 2/3$ and perfect plastic contact deformation, $\kappa_A = 1$ if $h_{K,U} \to \infty$:

$$\kappa_A = \frac{2}{3} + \frac{h_{K,E}}{3 \cdot h_{K,U}} = 1 - \frac{1}{3} \sqrt[3]{\frac{h_{K,f}}{h_{K,U}}}$$ \hspace{1cm} (63)

Beyond point E to point A the same curve runs down to the intersection with the adhesion boundary, Eq. (61), to the displacement $h_{K,A}$:

$$F_{N,unload} = \frac{2}{3} \cdot E^* \cdot r_{1,2} \cdot (h_K - h_{K,A})^3 - F_{H,A}$$ \hspace{1cm} (64)

Consequently, the reloading runs along the symmetric curve

$$F_{N,reload} = -\frac{2}{3} \cdot E^* \cdot r_{1,2} \cdot (h_{K,U} - h_K)^3 + F_{N,U}$$ \hspace{1cm} (65)

from point A to point U to the displacement $h_{K,U}$ as well, Fig. 3. The displacement $h_{K,A}$ at point A of contact detachment is calculated from Eqs. (56), (57), (61) and (64) as an implied function (index (0) for the beginning of iterations) of the displacement history point $h_{K,U}$:

$$h_{K,A,(t)} = h_{K,U} - \frac{1}{3} h_{K,f,pl} \cdot (h_{K,U} + \kappa \cdot h_{K,A,(0)})^2$$ \hspace{1cm} (66)

These generalized functions in Fig. 3 for the combination of elastic-plastic, adhesion and dissipative force-displacement behavior of a spherical particle contact were derived on the basis of the theories of Krupp [48], Molerus [13], Maugis [56], Sadd [53] and, especially, Thornton [51, 58]. The complete survey of loading, unloading, reloading, dissipation and detachment behaviors of titania is shown in Fig. 5 as a combination of Fig. 1a) to Fig. 4e). This approach may be expressed here in terms of engineering mechanics of macroscopic continua [1, 2] as the history dependent contact behavior.

2.3.3 Viscoplastic contact behavior and time dependent consolidation

An elastic-plastic contact may be additionally deformed during the indentation time, e.g., by viscoplastic flow, section 2.1.3. Thus, the adhesion force increases with interaction time [32, 48, 72, 122]. This time dependent consolidation behavior (index t) of particle contacts in a powder bulk was previously described by a parallel series (summation) of adhesion forces, see Table 1, last line marked with Tomas [116 to 119, 140 to 143]. This previous method refers more to incipient sintering or contact fusion of a thermally sensitive particle material [60].
without interstitial adsorption layers. This micro-process is very temperature sensitive [116, 118, 119, 140]. Additionally, the increasing adhesion may be considered in terms of a sequence of rheological models as the sum of resistances due to plastic and viscoplastic repulsion \( \kappa_p + \kappa_{p,t} \), 5th line in Table 2. Hence the repulsion effect of “cold” viscous flow of comparatively strongly bonded adsorption layers on the particle surface is taken into consideration. This rheological model is only valid for a short term indentation of \( t < \eta_K / (\kappa \cdot p_t) \), e.g. \( t < 5 \) d for the titania used as a very cohesive powder (specific surface area \( A_{s,m} = 12 \) m\(^2\)/g, with a certain water adsorption capacity). All the material parameters are collected in Table 2.

A viscoelastic relaxation in the particle contact may be added as a time dependent function of the average modulus of elasticity \( E^* \), Yang [59] and Krupp [48] (\( t_{relax} \) is the characteristic relaxation time):

\[
\frac{1}{E^*} = \frac{1}{E_0'(t \to \infty)} + \left( \frac{1}{E_0'(t = 0)} - \frac{1}{E_0'} \right) \cdot \exp \left( -\frac{t}{t_{relax}} \right)
\]

(67)

The slopes of the elastic-plastic, viscoelastic-viscoplastic yield and adhesion boundaries as well as the unloading and reloading curves, which include a certain relaxation effect, are influenced by the increasing softness or compliance of the spherical particle contact with loading time, Fig. 6. This model system includes all the essential constitutive functions of the authors named before [41, 53, 55, 58, 59]. A survey of the essential contact force-displacement models is given in Fig. 7 and Table 1.

Obviously, contact deformation and adhesion forces are stochastically distributed material functions. Usually one may focus here only on the characteristic or averaged values of these constitutive functions.

### 2.3.4 Adhesion force model

Starting with all these force-displacement functions one turns to an adhesion and normal force correlation to find out the physical basis of strength-stress relations in continuum mechanics [13, 14, 116, 143]. Replacing the contact area in Eq. (37), the following force-force relation is directly obtained:

\[
F_H = F_{H0} + p_{vdw} \cdot A_K = F_{H0} + \frac{p_{vdw}}{\frac{2}{3} + \frac{1}{3} \cdot \frac{A_{pl}}{A_K} - \frac{p_{vdw}}{p_t}} \cdot \frac{F_{H0} + F_N}{p_t}
\]

(68)

Therefore, with a so-called elastic-plastic contact consolidation coefficient \( \kappa \),

\[
\frac{\kappa}{\kappa_A - \kappa_p}
\]

(69)

a linear model for the adhesion force \( F_H \) as function of normal force \( F_N \) is obtained, Fig. 8:
The dimensionless strain characteristic $\kappa$ is given by the slope of adhesion force $F_H$ which is influenced by predominant plastic contact failure. It is a measure of irreversible particle contact stiffness or softness. A shallow slope designates low adhesion level $F_H \approx F_{H0}$ because of stiff particle contacts, but a large slope means soft contacts, or consequently, a cohesive powder flow behavior [85, 141, 143]. The contact flattening may be additionally dependent on time or displacement rate, section 2.1.3. Thus the contact reacts softer and, consequently, the adhesion level is higher than before. This new adhesion force slope $\kappa_{vis}$ is modified by the viscoplastic contact repulsion coefficient $\kappa_{p,t}$, which includes certain viscoplastic microflow at the contact, Table 2 and Fig. 8,

$$F_{H,\text{tot}} = \frac{\kappa_{A,t}}{\kappa_{A,t} - \kappa_p - \kappa_{p,t}} \cdot F_{H0} + \frac{\kappa_p + \kappa_{p,t}}{\kappa_{A,t} - \kappa_p - \kappa_{p,t}} \cdot F_N = \left(1 + \kappa_{vis}\right) \cdot F_{H0} + \kappa_{vis} \cdot F_N$$  \hspace{1cm} (71)

with the so-called total viscoplastic contact consolidation coefficient $\kappa_{vis}$ that includes the elastic-plastic $\kappa_p$ and the viscoplastic contributions $\kappa_{p,t}$ of contact flattening,

$$\kappa_{vis} = \frac{\kappa_p + \kappa_{p,t}}{\kappa_{A,t} - \kappa_p - \kappa_{p,t}}$$  \hspace{1cm} (72)

Eqs. (70) and (71) consider also the flattening response of soft particle contacts at normal force $F_N = 0$ caused by the adhesion force $\kappa \cdot F_{H0}$ (Krupp [54]) and $\kappa_{vis} \cdot F_{H0}$. Hence, the adhesion force $F_{H0}$ represents the sphere-sphere contact without any contact deformation at minimum particle-surface separation $a_{F=0}$. This initial adhesion force $F_{H0}$ may also include a characteristic nanometer sized height or radius of a rigid spherical asperity $a_{F=0} < h_{r1,2} << r_{1,2}$ with its center located at an average radius of the spherical particle, Krupp [48], Rumpf et al. [33] and Schubert et al. [34]:

$$F_{H0} = \frac{C_{H,\text{als}} \cdot h_{r1,2}}{6 \cdot a_{F=0}^2} \left[1 + \frac{r_{1,2} / h_{r1,2}}{(1 + 2 \cdot h_{r1,2} / a_{F=0})^2} \right] \approx \frac{C_{H,\text{als}} \cdot h_{r1,2}}{6 \cdot a_{F=0}^2}$$  \hspace{1cm} (73)

This rigid adhesion force contribution $F_{H0}$, see also the fundamentals [67, 68] and supplements [32, 48, 54, 65, 92 to 106], is valid only for perfect stiff contacts. Additionally, for mono-sized spheres $d = 4 \cdot r_{1,2}$ an averaged asperity height $h_r = 2 \cdot h_{r1,2}$ can be used with $h_{r1,2} = \left(1 / h_{r1} + 1 / h_{r2}\right)^{-1}$. When the asperity height is not too far from the averaged sphere radius $h_{r1,2} < r_{1,2}$, then the adhesion force can be calculated as, see Hoffmann (index Ho) [92]:

$$F_{H0,\text{Ho}} = \frac{C_{H,\text{als}} \cdot h_{r1,2}}{6 \cdot a_{F=0}^2} \left[1 + \frac{r_{1,2} / h_{r1,2}}{(1 + 2 \cdot h_{r1,2} / a_{F=0})^2} \right] \approx \frac{C_{H,\text{als}} \cdot h_{r1,2}}{6 \cdot a_{F=0}^2} \left(1 + h_{r1,2} / r_{1,2}\right)$$  \hspace{1cm} (74)
If the radius of the roughness exceeds the minimum separation of the sphere-plate system in order of magnitudes \( (h_r \gg a_{F=0}) \), the contribution of the plate, second term in Eq. (74), can be neglected and the adhesion force may be described as the sphere-sphere contact [92].

Rabinovich et al. [107, 108, 109] have used the root mean square of roughness (RMS) from AFM measurements and the average peak to peak distance between these asperities \( \lambda_r \) to calculate the interaction between a smooth sphere and a surface with nanoscale roughness profile (index Ra):

\[
F_{H0,Ra} = \frac{C_{H,sls} \cdot r_{1,2}}{6 \cdot a_{F=0}^2} \left[ \frac{1}{1 + 58.14 \cdot r_{1,2} \cdot \text{RMS} / \lambda_r^2 + \frac{1}{(1 + 1.817 \cdot \text{RMS} / a_{F=0})^2} \right] 
\]

(75)

The first term in brackets represents the contact interaction of the particle with an asperity and the second term accounts for the non-contact interaction of the particle with an average surface plane. This approach describes stiff nanoscale roughness as caps of asperities with their centers located far below the surface. For example, roughness of only 1 or 2 nm RMS is significant enough to reduce the theoretical adhesion force \( F_{H0} \) by an order of magnitude or more [109]. Johnson [65] described the elastic and plastic deformations of random surface asperities of contacts by the standard deviation of roughness and mean pressure.

The intersection of function (70) with abscissa \( (F_H = 0) \) in the negative of consolidation force \( F_N \), Fig. 8, is surprisingly independent of the Hamaker constant \( C_{H,sls} \):

\[
F_{N,Z} = -\pi \cdot a_{F=0} \cdot h_{r_{1,2}} \cdot p_r \cdot \kappa_A \left[ 1 + \frac{r_{1,2} / h_{r_{1,2}}}{(1 + 2 \cdot h_{r_{1,2}} / a_{F=0})^2} \right] \approx -\pi \cdot a_{F=0} \cdot h_{r_{1,2}} \cdot p_r 
\]

(76)

This minimum normal (tensile or pull-off) force limit \( F_{N,Z} \) for nearly brittle contact failure combines the influences of the particle contact hardness \( p_r \approx (3 - 15) \sigma_f \) (\( \sigma_f \) yield strength in tension, details in Ghadiri [111]) for a confined plastic micro-stress field in indentation [110] and the particle separation distribution, which is characterized here by the mean particle roughness height \( h_{r_{1,2}} \), and the molecular center separation distance \( a_{F=0} \). Obviously, this value characterizes also the contact softness with respect to a small asperity height \( h_r \) as well, see Eq. (33).

This elastic-plastic model Eq. (70) can be interpreted as a general linear constitutive contact model concerning loading pre-history dependent particle adhesion, i.e. linear in forces and stresses, but non-linear regarding material characteristics.

But if one eliminates the center approach \( h_K \) of the loading and unloading functions, Eqs. (57) and (64), an implied non-linear function between the contact pull-off force \( F_{H,A} \) at the detachment point A is obtained for the normal force at the unloading point \( F_N = F_{N,U} \):

\[
F_{H,A(t)} = F_{H0} + \kappa \cdot (F_N + F_{H0}) - \pi \cdot r_{1,2}^2 \cdot \kappa_p \cdot p_r \cdot \left[ \frac{3}{2} \cdot \frac{F_N + F_{H0}}{r_{1,2}^2 \cdot F_N + F_{H0}} \right]^{2/3} 
\]

(77)

This unloading point U is stored in the memory of the contact as pre-consolidation history. This general non-linear adhesion model, dashed curve in Fig. 8, implies the dimensionless,
elastic-plastic contact consolidation coefficient $\kappa$ and, additionally, the influence of adhesion, stiffness, average particle radius $r_{1,2}$, average modulus of elasticity $E^*$ in the last term of the equation. The slope of the adhesion force is reduced with increasing radius of surface curvature $r_{1,2}$. Generally, the linearised adhesion force equation (70) is used first to demonstrate comfortably the correlation between the adhesion forces of microscopic particles and the macroscopic stresses in powders [85, 140, 141]. Additionally, one can obtain a direct correlation between the micromechanical elastic-plastic particle contact consolidation and the macro-mechanical powder flowability expressed by the semi-empirical flow function $f_f$ according to Jenike [4].

It should be pointed out here that the adhesion force level in Fig. 8 is approximately $10^5$ - $10^6$ times the particle weight for fine and very cohesive particles. This means, in other words, that one has to apply these large values as acceleration ratios $a/g$ with respect to gravity to separate these pre-consolidated contacts or to remove mechanically such adhered particles from surfaces.

For a moist particle packing, the liquid bridge bonding forces caused by capillary pressure of interstitial pores and surface tension contribution of the free liquid surface additionally determine the strength [112 - 116]. Attraction by capillary pressure and increasing van der Waals forces by contact flattening due to normal load (application of an external pressure) are also acting in particle contacts of compressed water-saturated filter cakes or wet-mass powders [85, 138, 139, 144].

### 2.4 Energy absorption in a contact with dissipative behavior

If one assumes a single elastic-plastic particle contact as a conservative mechanical system without heat dissipation, the energy absorption equals the lens-shaped area between the unloading and reloading curves from point U to A as shown in Fig. 3:

$$W_{\text{diss}} = \int_{h_{K,U}}^{h_{K,A}} F_{N,\text{reload}}(h_K) \, dh_K - \int_{h_{K,A}}^{h_{K,U}} F_{N,\text{unload}}(h_K) \, dh_K$$

(78)

from Eqs. (64), (61) for $F_{H,A}$ and (65), (57) for $F_{N,U}$ one obtains finally:

$$W_{\text{diss}} = \frac{8 \cdot E^*}{15} \sqrt{r_{1,2}} \cdot (h_{K,U} - h_{K,A})^5 - \pi \cdot r_{1,2} \cdot p_f \cdot \left[\kappa_A \cdot h_{K,U} - \kappa_P \cdot (h_{K,U} - h_{K,A})\right] \cdot (h_{K,U} - h_{K,A})$$

(79)

Additionally, the specific or mass related energy absorption includes the average particle mass $m_p = 4/3 \cdot \pi r_{1,2}^3 \rho_s$ a characteristic contact number in the bulk powder (coordination number $k \approx \pi/\varepsilon$ [13]) and the dissipative work $W_{m,\text{diss}} = k \cdot W_{\text{diss}} / m_p$.

$$W_{m,\text{diss}} = \frac{-E^*}{20 \cdot \varepsilon \cdot \rho_s} \left(\frac{h_{K,U} - h_{K,A}}{r_{1,2}}\right)^{5/2} + \frac{3 \cdot \pi \cdot p_f \cdot (h_{K,U} - h_{K,A})}{32 \cdot r_{1,2}^2 \cdot \varepsilon \cdot \rho_s} \left[\kappa_A \cdot h_{K,U} - \kappa_P \cdot (h_{K,U} - h_{K,A})\right]$$

(80)
A specific energy absorption of 3 to 85 µJ/g was dissipated during a single unloading-reloading cycle in the titania bulk powder with an average pressure of only \( \sigma_{M,\text{st}} = 2 \) to 18 kPa (or major principal stress \( \sigma_1 = 4 \) to 33 kPa) \([141, 143]\).

3. Particle impact and contact displacement response

In a shear zone, when two particles (particle 2 is assumed to be fixed) come into contact and collide, the velocity of particle 1 is reduced gradually. Part of the initial kinetic energy is radiated into both particles as elastic waves. Now the contact force reaches a maximum value (maximum de-acceleration) and the particle velocity is reduced to zero.

\[
W_{el} = \frac{2}{3} \cdot E^* \int_0^{h_k} \sqrt{r_{l,2} \cdot h_k} \, dh_k = \frac{4}{15} \cdot E^* \sqrt{r_{l,2} \cdot h_k^5}
\]

(81)

With the particle mass \( m_{1,2} = \rho_s \cdot \frac{4}{3} \cdot \pi \cdot r_{l,2}^3 \), the correlation between particle velocity \( v_1 \) and center approach \( h_k \) is obtained:

\[
v_1^2 = \frac{E^*}{3 \cdot \pi \cdot \rho_s} \left( \frac{h_k}{r_{l,2}} \right)^{5/2}
\]

(82)

In the recovery stage the stored elastic energy is released and converted into kinetic energy and the particle moves with the rebound velocity \( v_{1,R} \) into the opposite direction. The so-called impact number or coefficient of restitution \( e = \hat{F}_{1,R} / \hat{F}_1 \) indicates the impact force ratio of the contact decompression phase after impact and the contact compression phase during impact, \( e = 0 \) for perfect plastic, \( 0 < e < 1 \) for elastic-plastic, \( e = 1 \) for perfect elastic behavior, see examples in \([29, 120, 124, 127]\). Thus \( e^2 < 1 \) characterizes the energy dissipation (\( W_{\text{diss}} \) is the inelastic deformation work of particle contact, \( E_{\text{kin},1} = m_p \cdot v_1^2 / 2 \) is the kinetic energy of particle 1 before impact):

\[
e^2 = \frac{E_{\text{kin},1} - W_{\text{diss}}}{E_{\text{kin},1}}
\]

(83)

In terms of a certain probability of particle adhesion inside of the contact zone a critical velocity (index H) as the stick/bounce criterion was derived by Thornton (index Th) \([58]\) who used the JKR model:

\[
v_{1,H,\text{Th}} = \frac{1.871 \cdot F_{H,\text{JKR}}}{m_p} \left( \frac{3 \cdot F_{H,\text{JKR}}^2}{d \cdot E^*} \right)^{1/3}
\]

(84)

For an impact velocity \( v_1 > v_{1,H} \) particle bounce occurs and the coefficient of restitution is obtained as \([58]\):
\[ e = \sqrt{\frac{v_{1,R}^2}{v_1^2}} = \sqrt{1 - \frac{v_{1,H}^2}{v_1^2}} \] 

(85)

Even if the impact velocity \( v_1 \) is ten times higher than the critical sticking velocity \( v_{1,H,th} \), the coefficient of restitution is 0.995 [58].

But in terms of combined elastic-plastic deformation the kinetic energy is mainly dissipated. If one uses the center approach \( h_{K,f} \) of Eq. (29) the critical impact velocity \( v_{1,f} \) for incipient plastic yield (index \( f \)) is calculated from Eq. (82) as [125, 126, 127]:

\[ v_{1,f} = \left( \frac{\pi \cdot p_f}{E_*} \right)^2 \cdot \frac{p_f}{3 \cdot p_s} \] 

(86)

The critical velocity \( v_{1,H} \) to stick or to adhere the particles with a plastic contact deformation was derived by Hiller (Index HL) [120]:

\[ v_{1,H,HL} = \left( \frac{1 - e^2}{e^2} \right)^{1/2} \cdot \frac{1}{d} \cdot \frac{C_{H,sl}}{\pi \cdot a_{F=0}^2 \cdot \sqrt{6 \cdot p_s \cdot p_f}} \] 

(87)

This can be rearranged if one uses the dimensionless plastic repulsion coefficient \( \kappa_p \) according to Eq. (42) to obtain the following simple expression:

\[ v_{1,H,HL} = \left( \frac{1 - e^2}{e^2} \right)^{1/2} \cdot \frac{a_{F=0}}{d} \cdot \kappa_p \cdot \frac{6 \cdot p_f}{p_s} \] 

(88)

Unfortunately, Eq. (88) does not include the increase of “soft” contact flattening response \( h_K \) by increasing particle impact velocity \( v_1 \). Now this dominant energy absorption \( W_{diss} \) during particle impact stressing, beginning at any unloading point \( U \), is considered approximately as a trapezium shaped area between elastic-plastic yield boundary and adhesion boundary for the contact of particles 1 and 2 in the force-displacement diagram of Fig. 9. With the contribution of the work of adhesion \( W_A \) to separate this contact from equilibrium separation \( a_{F=0} \) to infinity, the energy balance gives (\( A_K \) is the contact area):

\[ \frac{m_{1,2}}{2} \left( v_1^2 - v_{1,R}^2 \right) = \int_{h_{K,f}}^{h_{K,U}} F_N(h_K) \, dh_K + \int_{h_{K,f}}^{h_{K,U}} - F_{N,z}(h_K) \, dh_K + A_K \cdot \int_{a_{F=0}} x p_{vqw}(a) \, da \] 

(89)

\[ v_1^2 - v_{1,R}^2 = \frac{3 \cdot p_f}{4 \cdot p_s \cdot \tau_{t,2}^2} \left[ \kappa_A \cdot (h_{K,U}^2 - h_{K,f}^2) + \kappa_p \cdot h_{K,U} \cdot a_{F=0} \right] \] 

(90)

The difference in characteristic impact velocities results directly in a center approach, \( h_{K,U} \), expressed by the unloading point \( U \). The response of this contact displacement \( h_{K,U} \) is a consolidation force, \( F_{N,U} \). Additionally, a certain pre-consolidation level, \( F_{N,U} \), in a shear zone may affect the sticking/bounce probability. If the rebound velocity \( v_{1,R} = 0 \) the two particles will adhere. Consequently, the critical sticking velocity \( v_{1,H} \) is obtained without any additional losses, e.g. due to elastic wave propagation:
\[
\nu_{1,H} = \sqrt{\frac{3 \cdot p_f}{4 \cdot p_s \cdot \sigma_{R,2}}} \left[ \kappa_A \left( h_{k,u}^2 - h_{k,f}^2 \right) + \kappa_p \cdot h_{K,u} \cdot a_{F=0} \right]
\] 

(91)

For example using data from [141, 143], this critical sticking velocity lies between 0.2 and 1 m/s for titania, curve in the sticking velocity-displacement diagram of Fig. 9, which is equivalent to an average pressure level \(\sigma_{M,st} = 2 \text{ to } 18 \text{ kPa} \) (or major principal stress \(\sigma_1 = 4 \text{ to } 33 \text{ kPa}\)) [145]. These calculation results of particle adhesion are in agreement with the practical experiences in powder handling and transportation, e.g. undesired powder blocking at conveyor transfer chutes. In terms of powder flow the behavior after multiple stressing of soft deforming contacts in the nanoscale of center approach \(h_K\), may be described as “healing contacts”.

To demonstrate this enormous adhesion potential, 1 \(\mu\)m silica particles were completely removed from a 100 mesh woven metal screen (147 \(\mu\)m wide) with 40 m/s air velocity [121] and 32 \(\mu\)m glass beads from glass surface with more than 117 m/s [123]. Air velocities of 10 to 20 m/s were necessary to blow off about 50% of quartz particles (d = 5 to 15 \(\mu\)m) which had adhered to filter media after impact velocities of about 0.28 to 0.84 m/s [28, 29].

These fundamentals of particle adhesion dynamics may also be important to chemically clean silicon wafers [36, 128 to 135] or mechanical tool surfaces by jet pressures up to 2 MPa and \(\text{CO}_2\)-ice particle velocities up to 280 m/s [129].

4. Conclusions

The models for elastic (Hertz, Huber, Cattaneo, Mindlin and Deresiewicz), elastic-adhesion (Derjaguin, Johnson), plastic-adhesion (Derjaguin, Krupp, Molerus, Johnson, Maugis and Pollock) contact deformation response of a single, normal or tangential loaded, isotropic, smooth contact of two spheres were discussed. The force-displacement behaviors of elastic-plastic (Schubert, Thornton), elastic-dissipative (Sadd), plastic-dissipative (Walton) and viscoplastic-adhesion (Rumpf) contacts were also shown. With respect to these theories, a general approach for the time and deformation rate dependent and combined viscoelastic, plastic, viscoplastic, adhesion and dissipative behaviors of a spherical particle contact was derived and explained.

As the main result, the adhesion force \(F_{H}\) is found to be a function of the force contribution \(F_{H0}\) without any deformation plus a pre-consolidation or load-history dependent term with the normal force \(F_N\). These linear and non-linear approaches can be interpreted as general constitutive models of the adhesion force. It should be pointed out here that the adhesion force level discussed in this paper is approximately \(10^5 - 10^6\) times the particle weight of nanoparticles. This means, in other words, that one has to apply this large values as acceleration ratio \(a/g\) with respect to gravity to separate these pre-consolidated contacts or to remove mechanically such adhered particles from solid surfaces.

For colliding particles a correlation between particle impact velocity and contact displacement response is obtained using energy balance. These constitutive model approaches are generally
applicable for micro- and nanocontacts of particulate solids [85, 142, 143]. Hence, these contact models are intended to be applied for modern data evaluation of product quality characteristics such as powder flow properties, i.e., yield loci, consolidation and compression functions or design of characteristic processing apparatus dimensions [116, 136 to 145].

5. Acknowledgements

The author would like to acknowledge his coworkers Dr. S. Aman, Dr. T. Gröger, Dr. W. Hintz, Dr. Th. Kollmann and Dr. B. Reichmann for providing relevant information and theoretical tips. The advices from Prof. H.-J. Butt and Prof. S. Luding with respect to the fundamentals of particle and powder mechanics were especially appreciated during the collaboration of the project “shear dynamics of cohesive, fine-disperse particle systems” of the joint research program “Behavior of Granular Media” of German Research Association (DFG).

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>nm</td>
<td>contact separation</td>
</tr>
<tr>
<td>A</td>
<td>nm²</td>
<td>particle contact area</td>
</tr>
<tr>
<td>C_H</td>
<td>J</td>
<td>Hamaker constant</td>
</tr>
<tr>
<td>d</td>
<td>µm</td>
<td>particle diameter</td>
</tr>
<tr>
<td>E</td>
<td>kN/mm²</td>
<td>modulus of elasticity</td>
</tr>
<tr>
<td>F</td>
<td>N</td>
<td>force</td>
</tr>
<tr>
<td>F_H</td>
<td>nN</td>
<td>adhesion force</td>
</tr>
<tr>
<td>F_H0</td>
<td>nN</td>
<td>adhesion force of a rigid contact without any deformation</td>
</tr>
<tr>
<td>F_N</td>
<td>nN</td>
<td>normal force</td>
</tr>
<tr>
<td>F_T</td>
<td>nN</td>
<td>tangential force</td>
</tr>
<tr>
<td>G</td>
<td>kN/mm²</td>
<td>shear modulus</td>
</tr>
<tr>
<td>h</td>
<td>mm</td>
<td>zone height</td>
</tr>
<tr>
<td>h_K</td>
<td>nm</td>
<td>height of overlap, indentation or center approach</td>
</tr>
<tr>
<td>k</td>
<td>-</td>
<td>coordination number</td>
</tr>
<tr>
<td>k_N</td>
<td>N/mm</td>
<td>contact stiffness in normal direction</td>
</tr>
<tr>
<td>k_T</td>
<td>N/mm</td>
<td>contact stiffness in tangential direction</td>
</tr>
<tr>
<td>m</td>
<td>kg</td>
<td>mass</td>
</tr>
<tr>
<td>p</td>
<td>kPa</td>
<td>contact pressure</td>
</tr>
<tr>
<td>p_f</td>
<td>MPa</td>
<td>plastic micro-yield strength of particle contact</td>
</tr>
<tr>
<td>r</td>
<td>µm</td>
<td>particle radius</td>
</tr>
<tr>
<td>r_K</td>
<td>nm</td>
<td>contact radius</td>
</tr>
<tr>
<td>t</td>
<td>h</td>
<td>time</td>
</tr>
<tr>
<td>v</td>
<td>m/s</td>
<td>particle velocity</td>
</tr>
<tr>
<td>v_H</td>
<td>m/s</td>
<td>critical sticking velocity</td>
</tr>
<tr>
<td>v_R</td>
<td>m/s</td>
<td>bounce velocity</td>
</tr>
<tr>
<td>W</td>
<td>J</td>
<td>deformation work</td>
</tr>
<tr>
<td>W_m</td>
<td>J/g</td>
<td>mass related specific energy absorption by deformation</td>
</tr>
<tr>
<td>δ</td>
<td>nm</td>
<td>tangential contact displacement</td>
</tr>
<tr>
<td>ε</td>
<td>-</td>
<td>porosity</td>
</tr>
<tr>
<td>η_K</td>
<td>Pa·s</td>
<td>particle contact viscosity</td>
</tr>
<tr>
<td>κ</td>
<td>-</td>
<td>elastic-plastic contact consolidation coefficient, see Eq. (69)</td>
</tr>
<tr>
<td>κ_p</td>
<td>-</td>
<td>plastic repulsion coefficient, see Eq. (42)</td>
</tr>
</tbody>
</table>
$\kappa_{p,t}$ - viscoplastic repulsion coefficient, see Eq. (60)
$\kappa_{\text{vis}}$ - total viscoplastic contact consolidation coefficient, see Eq. (72)
$\mu_i$ - coefficient of internal friction, i.e. Coulomb friction
$\nu$ - Poisson ratio
$\varphi_i$ deg - angle of internal friction between particles
$\rho$ kg/m$^3$ - density
$\sigma$ kPa - normal stress
$\sigma_{\text{M}}$ kPa - center stress of Mohr circle [1, 143]
$\sigma_{\text{R}}$ kPa - radius stress of Mohr circle [1, 143]
$\sigma_{\text{sls}}$ mJ/m$^2$ - surface tension of solid-liquid-solid interaction
$\sigma_i$ kPa - tensile stress
$\sigma_0$ kPa - isostatic tensile strength of the unconsolidated powder
$\sigma_1$ kPa - major principal stress
$\sigma_2$ kPa - minor principal stress
$\tau$ kPa - shear stress
$\Phi_T$ - dimensionless bond strength according to Tabor [70]
$\psi$ - loading parameter according to Thornton [51]

**Indices**
- A: detachment or contact area related
- at: attraction
- b: bulk
- br: brittle
- c: compressive
- crit: critical
- diss: dissipation
- e: effective
- el: elastic
- f: flow or yield
- F=0: potential force minimum
- H: adhesion
- i: internal
- iso: isostatic
- K: particle contact
- l: liquid
- m: mass related
- M: center
- min: minimum
- N: normal
- p: pressure related
- pl: plastic
- r: micro-roughness
- R: radius
- rep: repulsion
- s: solid
- S: surface, shear
- sls: solid-liquid-solid interaction between particles
- ss: solid-vacuum-solid interaction between particles
- st: stationary
References

[27] H. Rumpf, Chemie Ingenieur Technik 6, 317-327 (1953)
[34] H. Schubert, Chemie Ingenieur Technik 51, 266-277 (1979)
[38] A. Saito, and K. Ota, in [36] pp. 105-114
[40] H. Inaba, in [36] pp. 137-152
[43] B.V. Derjagin, Kolloid Zeitsehr. 69, 155-164 (1934)
[64] V.M. Muller, V.S. Yuschenko, and B.V. Derjaguin, J. Colloid Interface Sci. 77, 91-
K.L. Johnson, Contact Mechanics, Cambridge University Press (1985)
R.S. Bradley, Phil. Mag. 13 853-862 (1932)
H.C. Hamaker, Physica 4 1058-1072 (1937)
D. Tabor, J. Colloid Interface Sci. 58 2-12 (1977)
S. Ecke and H.J. Butt, J. Colloid Interface Sci. 244, 432-435 (2001)
A.R. Savkoor, in [83] pp. 25-45
J. Visser, Powder Technol. 58, 1-10 (1989)
<table>
<thead>
<tr>
<th>authors</th>
<th>assumptions</th>
<th>characteristic force-displacement or adhesion force models</th>
<th>contact area and characteristic diagrams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hertz [41]</td>
<td>elastic behavior, normal force $F_N$</td>
<td></td>
<td><img src="image1.png" alt="Diagram" /></td>
</tr>
<tr>
<td>1882</td>
<td>$\left( \frac{P_{el}}{P_{max}} \right)^2 = 1 - \left( \frac{F_N}{F_{el,K}} \right)^2$</td>
<td>$F_N = \frac{2}{3} \cdot E \cdot r_{K,el} \cdot \sqrt{1 \cdot h_{K}^3}$</td>
<td></td>
</tr>
<tr>
<td>Huber [42]</td>
<td>elastic behavior, principal stresses</td>
<td></td>
<td><img src="image2.png" alt="Diagram" /></td>
</tr>
<tr>
<td>1904</td>
<td>$\sigma_y (r_K) = \frac{1}{p_{max}} \cdot \frac{2}{3} \cdot \nu \cdot \frac{r_{K,el}^2}{r_K^2} \left[ 1 - \left( 1 - \frac{r_K^2}{r_{K,el}^2} \right)^{3/2} \right] - \sqrt{1 - \frac{r_K^2}{r_{K,el}^2}}$ for $r_K \leq r_{K,el}$</td>
<td>$\sigma_y (r_K) = \frac{1}{p_{max}} \cdot \frac{2}{3} \cdot \nu \cdot \frac{r_{K,el}^2}{r_K^2}$ for $r_{K,el} \leq r_K$</td>
<td></td>
</tr>
<tr>
<td>Cattaneo [45]</td>
<td>elastic behavior, tangential force $F_T$</td>
<td></td>
<td><img src="image3.png" alt="Diagram" /></td>
</tr>
<tr>
<td>1938</td>
<td>$r_{K,slip}^2 = r_{K,el}^2 \cdot \left( 1 - \frac{F_T}{\mu \cdot F_N} \right)$</td>
<td>$\tau = \frac{3 \cdot \mu \cdot F_N}{2 \cdot \pi \cdot r_{K,el}^3} \left( \sqrt{r_{K,el}^2 - r_K^2} - \sqrt{r_{K,slip}^2 - r_K^2} \right)$ for $0 \leq r_K \leq r_{K,slip}$</td>
<td></td>
</tr>
<tr>
<td>Mindlin [46]</td>
<td>elastic behavior, tangential slip, slide force and shear stress $\tau$</td>
<td></td>
<td><img src="image4.png" alt="Diagram" /></td>
</tr>
<tr>
<td>1949</td>
<td>$\tau = \frac{3 \cdot \mu \cdot F_N}{2 \cdot \pi \cdot r_{K,el}^3} \left( \sqrt{r_{K,el}^2 - r_K^2} \right)$ for $r_{K,slip} \leq r_K \leq r_{K,el}$</td>
<td>$\tau = \frac{3 \cdot \mu \cdot F_N}{2 \cdot \pi \cdot r_{K,el}^3} \left( \sqrt{r_{K,el}^2 - r_K^2} \right)$ for $r_{K,slip} \leq r_K \leq r_{K,el}$</td>
<td></td>
</tr>
<tr>
<td>Author</td>
<td>Year</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>--------------------------------</td>
<td>------</td>
<td>-----------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Mindlin and Deresiewicz</td>
<td>1953</td>
<td>elastic behavior, tangential unloading hysteresis</td>
<td></td>
</tr>
<tr>
<td>Yang</td>
<td>1966</td>
<td>viscoelastic relaxation, normal force</td>
<td></td>
</tr>
<tr>
<td>Johnson, Kendall and Roberts</td>
<td>1971</td>
<td>elastic behavior, normal force, constant adhesion</td>
<td></td>
</tr>
<tr>
<td>Dahneke</td>
<td>1972</td>
<td>elastic behavior, normal force, varying adhesion</td>
<td></td>
</tr>
</tbody>
</table>

\[
\delta = \frac{3(2-\nu)\mu_i F_N}{16G r_{K,el}} \left[ 2\left(1 - \frac{F_T^* - F_T}{2\mu_i F_N}\right)^{2/3} - \left(1 - \frac{F_T^*}{\mu_i F_N}\right)^{2/3} - 1 \right]
\]

\[
r_k^2 = \frac{3r_{1,2} F_N}{2E^*} \left[ \frac{E_0^*}{E_0^*(t \to \infty)} + \left(1 - \frac{E_0^*}{E_0^*}\right) \cdot \exp\left(-t/t_{relax}\right) \right]
\]

\[
r_k^2 = \frac{3r_{1,2}}{2E^*} \left( F_N + F_{H,JKR} + \sqrt{2F_{H,JKR} \cdot F_N + F_{H,JKR}^2} \right)
\]

\[
F_H = F_{H0} + A_K \cdot p_{vdw} = \frac{C_H \cdot r_{1,2}}{6a_0^2} \cdot \left(1 + \frac{2h_K}{a_0}\right)
\]

\[
F_{H,max} = \frac{C_H \cdot r_{1,2}}{6a_0^2} \cdot \left(1 + \frac{2 \cdot C_H^2 \cdot r_{1,2}}{27E^* a_0^2}\right)
\]
<table>
<thead>
<tr>
<th>Author(s) [References]</th>
<th>Behavior</th>
<th>Conditions</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Derjaguin [43], 1934, Muller and Toporov [63], 1975</td>
<td>elastic behavior, normal force, constant adhesion $F_{H0}$</td>
<td>$F_{H0} = 4 \cdot \pi \cdot r_{i,2} \cdot \left(\sigma_{sg} - \frac{\sigma_{ss}}{2}\right)$</td>
<td><img src="image1.png" alt="Graph" /></td>
</tr>
<tr>
<td>Molerus [13, 14], 1975/78</td>
<td>perfect plastic behavior, varying adhesion, shearing</td>
<td>$F_{H} = F_{H0} + \frac{P_{VdW}}{p_{f}} \cdot F_{N} = F_{H0} + \kappa_{p} \cdot F_{N}$</td>
<td><img src="image2.png" alt="Graph" /></td>
</tr>
<tr>
<td>Schubert et al. [55], 1976</td>
<td>elastic-plastic behavior, varying adhesion force $F_{H}$</td>
<td>$F_{H} = F_{H0} + \frac{P_{VdW}}{p_{f} \cdot (1 + 2 \cdot A_{cl}/(3 \cdot A_{pl})}) \cdot F_{N}$</td>
<td><img src="image3.png" alt="Graph" /></td>
</tr>
<tr>
<td>Rumpf et al. [60], 1976</td>
<td>viscoelastic behavior, normal force</td>
<td>$r_{k}^{2} = \frac{3 \cdot r_{i,2} \cdot F_{N}}{2} \left[1 + \frac{t}{E_{0}(t = 0) + \eta_{k}}\right]$</td>
<td><img src="image4.png" alt="Graph" /></td>
</tr>
<tr>
<td>Rumpf et al. [60], 1976</td>
<td>viscoplastic flow, normal force, sintering</td>
<td>$r_{k}^{2} = \frac{2 \cdot t}{5 \cdot \eta_{k}} \left[\frac{2 \cdot \sigma_{ss}}{d} + \frac{1}{\pi} \cdot \frac{F_{N}}{d^{2}}\right]$</td>
<td><img src="image5.png" alt="Graph" /></td>
</tr>
<tr>
<td>Savkoor and Briggs [62], 1977</td>
<td>elastic behavior, constant adhesion, tangential force</td>
<td>$r_{k}^{2} = \frac{3 \cdot r_{i,2}}{2 \cdot E^{<em>}} \left(F_{N} + 2 \cdot F_{HJKR} \cdot \sqrt{2 \cdot F_{HJKR} \cdot F_{N} + F_{HJKR}^{2}} - \frac{F_{N}^{2} \cdot E^{</em>}}{4 \cdot G^{*}}\right)$</td>
<td><img src="image6.png" alt="Graph" /></td>
</tr>
</tbody>
</table>
Maugis and Pollock [56] 1984
elastic-plastic behavior, normal force, varying adhesion, load, unload
\[ F_{N,Z,\text{brittle}} = \sigma_{ss} \cdot E \cdot \sqrt{\frac{F_N}{\pi \cdot p^3}} \]
\[ F_{N,Z,\text{ductile}} = \pi \cdot r_{K,cl}^2 \cdot \sigma_f \]

Walton and Braun [57] 1986
plastic behavior, normal, tangential force, load, unload
\[ F_{N,\text{load}} = k_{N,1} \cdot h_K \]
\[ k_T = k_{T,0} \cdot \left(1 - \frac{\pm F_T + F_T^*}{\mu_i \cdot F_N + F_T^*}\right)^{1/3} \]
\[ F_{N,\text{unload}} = k_{N,2} \cdot (h_K - h_{K,E}) \]

Thornton and Yin [51] 1991
elastic behavior, constant adhesion, tangential force; load, unload, reload hysteresis
\[ F_T = 4 \cdot \psi \cdot G \cdot \sqrt{\frac{r_{i,2} \cdot h_K \cdot \Delta \delta}{F_N}} \]
\[ \psi^3_{\text{load}} = 1 - \frac{F_T + \mu_i \cdot \Delta F_N}{\mu_i \cdot F_N} \]
\[ \psi^3_{\text{unload}} = 1 - \frac{F_T^* - F_T + 2 \cdot \mu_i \cdot \Delta F_N}{2 \cdot \mu_i \cdot F_N} \]
\[ \psi^3_{\text{unload}} = 1 - \frac{F_T - F_T^* + 2 \cdot \mu_i \cdot \Delta F_N}{2 \cdot \mu_i \cdot F_N} \]

Sadd, Tai and Shukla [53] 1993
elastic behavior, normal load, hysteresis for unload, reload, unload
\[ F_{N,\text{load}} = \alpha_{\text{load}} \cdot h_K^p \]
\[ F_{N,\text{unload}} = \alpha_{\text{unload}} \cdot h_K^{p+q} \]
\[ q = (k_{N,\text{unload}} \cdot h_{K,max})^2 \]
\[ F_{N,\text{reload}} = \beta_{\text{rel}} \cdot F_{N,\text{load}} + (1 - \beta_{\text{rel}}) \cdot F_{N,\text{unload}} \]
\[ \beta_{\text{rel}} = \frac{h_K - h_{K,\text{min}}}{h_{K,max} - h_{K,\text{min}}} \]

\[ F_{N} \]
\[ F_{T} \]
\[ F_T = \mu_i F_N \]
\[ \delta \]
<table>
<thead>
<tr>
<th>Year</th>
<th>Authors</th>
<th>Behavior</th>
<th>Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1998</td>
<td>Thornton and Ning [58]</td>
<td>Elastic-plastic behavior, normal force, varying adhesion, unload</td>
<td>[ F_{N,\text{load}} = \frac{2}{3} \cdot E^* \cdot \sqrt{r_{i,2} \cdot h_{K,f}^3} + \pi \cdot p_f \cdot r_{i,2} \cdot \left( h_K - h_{K,f} \right) ] [ F_{N,\text{unload}} = \frac{2}{3} \cdot E^* \cdot \sqrt{r_{i,2} \cdot (h_K - h_{K,U})^3} ]</td>
</tr>
<tr>
<td>1999</td>
<td>Tomas [140]</td>
<td>Elastic-plastic and viscoplastic behaviors, varying adhesion, normal and shear force</td>
<td>[ F_H = F_{H0} + \left( \frac{p_{VdW}/p_f}{2/3 + A_p/(3 \cdot A_K)} - p_{VdW}/p_f + \frac{p_{VdW}}{\eta_K / \tau} \right) \cdot (F_{H0} + F_N) ] [ F_k \cdot \left[ (1 + (\kappa + \kappa_t) \cdot F_{H0} / F_R) \cdot \tan \varphi_n \cdot \cos 2\alpha \right] / (1 + (\kappa + \kappa_t) \cdot F_{H0} + F_M + (\kappa + \kappa_t) \cdot F_{HM}) \leq \tan \varphi_n ]</td>
</tr>
</tbody>
</table>
Table 2: Material parameters for characteristic adhesion force functions $F_{H}(F_N)$ in Fig. 8

<table>
<thead>
<tr>
<th>Constitutive model of contact deformation</th>
<th>Instantaneous contact consolidation</th>
<th>Time dependent consolidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Repulsion coefficient</td>
<td>$\kappa_p = \frac{p_{VdW}}{p_f} = \frac{C_{H,sls}}{6 \cdot \pi \cdot a_{F=0}^3 \cdot p_f}$</td>
<td>$\kappa_{p,t} = \frac{p_{VdW}}{\eta_K} \cdot t$</td>
</tr>
<tr>
<td>Constitutive models of combined contact deformation</td>
<td>elastic-plastic</td>
<td>elastic-plastic and viscoplastic</td>
</tr>
<tr>
<td>Contact area ratio</td>
<td>$\kappa_A = \frac{2}{3} + \frac{A_{pl}}{3 \cdot (A_{pl} + A_{el})}$</td>
<td>$\kappa_{A,t} = \frac{2}{3} + \frac{A_{pl} + A_{vis}}{3 \cdot (A_{pl} + A_{vis} + A_{el})}$</td>
</tr>
<tr>
<td>Contact consolidation coefficient</td>
<td>$\kappa = \frac{\kappa_p}{\kappa_A - \kappa_p}$</td>
<td>$\kappa_{vis} = \frac{\kappa_p + \kappa_{p,t}}{\kappa_{A,t} - \kappa_p - \kappa_{p,t}}$</td>
</tr>
<tr>
<td>Intersection with $F_{N,Z}$ axis (abscissa)</td>
<td>$F_{N,Z} \approx -\pi \cdot a_{F=0} \cdot h_{rl,2} \cdot p_f \neq f(C_{H,sls})$</td>
<td>$F_{N,Z, tot} \approx \frac{\pi \cdot a_{F=0} \cdot h_{rl,2} \cdot p_f}{1 + p_f \cdot t / \eta_K} \neq f(C_{H,sls})$</td>
</tr>
</tbody>
</table>
Fig. 1: Characteristic spherical particle contact deformation – a) approach and b) elastic contact deformation (titania, primary particles \( d = 20 - 300 \) nm, surface diameter \( d_s = 200 \) nm, median particle diameter \( d_{50,3} = 610 \) nm, specific surface area \( A_{S,m} = 12 \) m\(^2\)/g, solid density \( \rho_s = 3870 \) kg/m\(^3\), surface moisture \( X_W = 0.4 \% \), temperature \( \theta = 20^\circ\text{C} \)) [142]. Pressure and compression are defined as positive but tension and extension are negative. The origin of this diagram \( h_K = 0 \) is equivalent to the characteristic adhesion separation for direct contact (atomic center to center distance), and can be estimated for a molecular force equilibrium \( a = a_0 = a_{F=0} \). After approaching from an infinite distance \(-\infty\) to this minimum separation \( a_{F=0} \) the sphere-sphere-contact without any contact deformation is formed by the attractive adhesion force \( F_{H0} \) (the so-called “jump in”). Then the contact may be loaded \( F_{H0} - Y \) and, as a response, is elastically deformed with an approximate circular contact area due to the curve marked with Hertz, Fig. 1b). The tensile contribution of principal stresses according to Huber [42] at the perimeter of contact circle is neglected for the elliptic pressure distribution, drawn below Figure b).
c) elastic-plastic contact deformation of a partial plate-plate contact, with circular plastic center and annular elastic zone

Fig. 2: Characteristic particle contact deformation – c) elastic-plastic compression [142]. The dominant linear elastic-plastic deformation range between pressure levels of powder mechanics [4] is demonstrated here. If the maximum pressure in the contact center reaches the micro-yield strength \( p_{\text{max}} = p_f \) at the yield point \( Y \) then the contact starts with plastic yielding which is intensified by mobile adsorption layers. Next, the combined elastic-plastic yield boundary of the partial plate-plate contact is achieved as given in Eq. (57). This displacement is expressed with the annular elastic \( A_{el} \) (thickness \( r_{K,el} \)) and circular plastic \( A_{pi} \) (radius \( r_{K,pi} \)) contact area, shown below Figure c).
Fig. 3: Characteristic particle contact deformation – d) elastic unloading and reloading with dissipation (titania) [142]. After unloading U – E the contact recovers elastically in the compression mode and remains with a perfect plastic displacement $h_{K,E}$. Below point E on the axis the tension mode begins. Between the points U – E – A the contact recovers elastically according to Eq. (64) to a displacement $h_{K,A}$. The reloading curve runs from point A to U to the displacement $h_{K,U}$, Eq. (65).
Fig. 4: Characteristic particle contact deformation – e) contact detachment [142]. Again, if one applies a certain pull-off force $F_{N,Z} = - F_{H,A}$ as given in Eq. (61) but here negative, the adhesion boundary line at failure point A is reached and the contact plates fail and detach with the increasing distance $a = a_{F=0} + h_{K,A} - h_K$. This actual particle separation is considered for the calculation by a hyperbolic adhesion force curve $F_{N,Z} = - F_{H,A} \propto a^{-3}$ of the plate-plate model Eq. (42).
Fig. 5: Characteristic particle contact deformation – a) to e) the complete survey of loading, unloading, reloading, dissipation and detachment behaviors of titania [142]. This hysteresis behavior could be shifted along the elastic-plastic boundary and depends on the pre-loading, or in other words, pre-consolidation level. Thus, the variation in adhesion forces between particles depend directly on this frozen irreversible deformation, the so-called contact pre-consolidation history.
Fig. 6: Characteristic elastic-plastic, viscoelastic-viscoplastic particle contact deformations – (titania, primary particles d = 20 – 300 nm, surface diameter d_s = 200 nm, median particle diameter d_{50,3} = 610 nm, specific surface area A_{s,m} = 12 m^2/g, solid density ρ_s = 3870 kg/m^3, surface moisture X_W = 0.4 %, temperature θ = 20°C, loading time t = 24 h). The material data, modulus of elasticity E = 50 kN/mm^2, modulus of relaxation E_∞ = 25 kN/mm^2, relaxation time t_{relax} = 24 h, plastic micro-yield strength p_f = 400 N/mm^2, contact viscosity η_K = 1.8 \times 10^{14} \text{ Pa s}, Poisson ratio ν = 0.28, Hamaker constant C_{H,sls} = 12.6 \times 10^{-20} \text{ J}, equilibrium separation for dipole interaction a_{F=0} = 0.336 nm, contact area ratio κ_A = 5/6 are assumed as appropriate for the characteristic contact properties. The plastic repulsion coefficient κ_p = 0.44 and viscoplastic repulsion coefficient κ_{p,t} = 0.09 are recalculated from shear test data in a powder continuum [141, 143].
Fig. 7: Constitutive models of contact deformation of smooth spherical particles in normal direction without (only compression +) and with adhesion (tension -). The basic models for elastic behavior were derived by Hertz [41], for viscoelasticity by Yang [59], for constant adhesion by Johnson et al. [49] and for plastic behavior by Thornton and Ning [58] and Walton and Braun [57] and for plasticity with variation in adhesion by Molerus [13] and Schubert et al. [55]. This has been expanded stepwise to include nonlinear plastic contact hardening and softening equivalent to shear-thickening and shear-thinning in suspension rheo-
rheology [85]. Energy dissipation was considered by Sadd et al. [53] and time dependent viscoelasticity by Rumpf et al. [60]. Considering all these theories, one obtains a general contact model for time and rate dependent viscoelastic, plastic, viscoplastic, adhesion and dissipative behaviors, Tomas [85, 140, 141, 142, 145].
Fig. 8: Particle contact forces for titania powder (median particle diameter $d_{50,3} = 610$ nm, specific surface area $A_{S,m} = 12$ m$^2$/g, surface moisture $X_W = 0.4$ %, temperature = 20 °C) according to the linear model Eq. (70), non-linear model Eq. (77) for instantaneous consolidation $t = 0$ and the linear model for time consolidation $t = 24$ h Eq. (71). The powder surface moisture $X_W = 0.4$ % is accurately analyzed with Karl-Fischer titration. This is equivalent to an idealized mono-molecular adsorption layer being in equilibrium with ambient air temperature of 20°C and 50% humidity.
Fig. 9: Recalculated plastic contact deformation and sticking/bounce at central impact stressing using data from Fig. 6. Two particles approach with velocities $v_1$ and $v_2$, impact and the contact is elastic-plastically deformed, upper Figure. The inelastic deformation energy is dissipated into the contact. This is equivalent to the areas (gray tones) between elastic-plastic boundary and adhesion boundary of the force-displacement lines which are obtained by integration, Eq. (89). If the kinetic energy of these particles would be large enough, these particles can detach with the rebound velocities $v_{1R}$ and $v_{2R}$. The critical impact velocity for incipient yield of the contact is shown, Eq. (86). Above this value, the two particles adhere or stick in practice, i.e. $v_{1R} = 0$. From this, the critical impact velocity $v_{1,H}$ follows and is shown in the Figure below versus particle center approach or displacement $h_{K,U}$. The model of Hiller/Löffler predicts a constant velocity, Eq. (88). But the practical experience shows us that the faster the particles move and impact, the larger is the contact displacement, and as the consequence, the higher is the tendency to stick. This is demonstrated by the curve of Eq. (91) in the Figure below versus displacement $h_{K,U}$.