Adhesion at friction and wear

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Received: 30 July 2021 / Revised: 29 August 2021 / Accepted: 14 October 2021
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Abstract: Our understanding of the surrounding world, from friction to the origin of life, depends on how we imagine the contact interaction of condensed bodies. What are the forces acting in contact with solids? Do they attract (adhesive) or repel (dehesive)? Theory and research at the atomic–molecular level have shown that the forces are adhesive, but everyday experiences cast doubt on this conclusion. This article addresses this issue by considering the mistakes made in experimental and theoretical tribology and surface physics. Taking into account the theories of hybridization and dehybridization of electron orbitals and valence bonds, the views on the structure of the surfaces of condensed bodies and the force arising during contact interaction are revised. The influence of van der Waals, hydrogen, covalent, metallic, and ionic bonds on the properties of lubricants is evaluated. The contours of the dehesive–deformation theory of friction and wear are also outlined.

Keywords: atomic and molecular interactions; adhesion; cohesion; dehesion; friction; wear

1 Introduction

Our understanding of the world around us, from friction to the origin of life, depends on how we imagine the contact interaction between condensed bodies. The question for billions is: What are the forces acting in contact with solids? Do they attract (adhesive) or repel (dehesive)? We see that the bodies around us repel, but the theory says otherwise.

The theory of friction and wear, since the time of Desaguliers and Coulomb to the present day, developed under the sign of adhesion. The maxim “The Sticky Universe”, which Kendall [1] chose as the subtitle of his book Molecular Adhesion and Its Applications, can be taken as the device of all modern physics of contact interaction and the area of tribology concerned with external friction. However, the physical picture of our world is more in line with Newton’s aphorism that Kendall used as an epigraph in Ref. [1], expressed by the maxim “The coherent and repelling universe”. In the world around us, adhesion is an extremely rare phenomenon that manifests itself mainly through the wetting of solid bodies by liquids. Fortunately, a handshake does not end with people sticking to each other like in a Grimm fairy tale. The purpose of this article is to demonstrate that friction in our world exists because solids repel instead of sticking to each other. Adhesion, contrary to popular belief, does not create friction but fights it by providing a lubricating effect.

Dozens of chemical elements used in technology create a variety of substances, the contact interaction of which is accompanied by a wide range of effects. Despite this diversity, only two basic laws govern all types of friction in all substances: Coulomb’s law of solid friction (Eq. (1)) and Newton’s law of liquid and gas friction (Eq. (2)). The intensity of all types of wear (I) (excluding elastomers) obeys the Archard dependence (Eq. (3)):

\[ F = F_0 + Nf \]  
\[ F = \eta Ag \]  
\[ I = kN/HV \]
where $F$ is the friction force; $F_0$ is the adhesive component of the friction force; $\eta$ is the viscosity; $A$ is the contact area; $g = \frac{du}{dy}$, is the flow velocity gradient; $f$ is the coefficient of friction; $N$ is the normal force; $HV$ is the Vickers hardness; and $k$ is the numerical coefficient.

The universality of the laws of friction and wear at the macro level is ensured by the universal laws of the interaction of atoms and molecules, which are common to all types of interatomic bonds in all substances and processes of friction. In 1929, Tomlinson [2] wrote, “It is now generally agreed that friction is a consequence of the forces which molecules exert on one another when sufficiently close together.” He also postulated that friction was “a molecular mechanism by which work may become transformed into heat”, and attempted to prove that such a mechanism was the formation and rupture of adhesive bonds. He essentially proved the non-involvement of adhesive bonds in the friction of solids.

The hypothesis of adhesive bonds of solids is the basis of the generally accepted adhesive–deformation theory (ADT) of friction and wear. At first glance, this hypothesis is consistent with modern quantum-mechanical ideas on the structure of atoms and the formation of bonds between them during the formation of individual molecules, liquids, and solids; this has also been confirmed by studies at the atomic-molecular scale [3–5]. The adhesion hypothesis is supported by experiments on the adhesion of certain metals in vacuum and air. Contrary to the adhesion hypothesis, there is a single but weighty argument: Adhesive forces are not detected in contacts between the vast majority of solids (adhesion is observed only between indium and some metals and between fresh lead surfaces). Thus, followers of the adhesion hypothesis are compelled to search for counterarguments. McFarlane and Tabor [6] attributed this to the experimental difficulty of avoiding a “peeling” action when measuring adhesion and the effect of released elastic stresses. However, how come no strong bonds are formed between solids even after plastic deformation that removes most elastic stresses, and after friction at low speeds? It is obvious that there is a large gap between the continuum and atomic–molecular theories of contact interaction [7–10].

Perhaps there are no experimental difficulties. Perhaps the physics of surface and contact interaction still represents “dark territory”. Is it worth looking for adhesion where there is none? According to Wolfgang Pauli [11], “God made the bulk; surfaces were invented by the devil”.

The theory of the adhesion of solids can be ranked among the greatest scientific misconceptions, such as Ptolemy’s celestial mechanics and the theory of phlogiston. Oddly enough, progress in the study of the construction of the atom and the laws of atomic-molecular interaction has reinforced this misconception. The more deeply science penetrates the world of atoms, the less it is understood about what happens in the world of real bodies. Having fallen victim to this misconception, tribology has been developed mainly as a phenomenological science.

This study considers the pro et contra of ADT. Section 2 is devoted to the analysis of errors made in theoretical and experimental tribology. Section 3 focuses on surface physics. Taking into account the theories of hybridization and dehybridization of electron orbitals and valence bonds, the force interaction of various substances at the atomic level is considered, and the viability of an alternative dehesive–deformation theory (DDT) of friction and wear based on the hypothesis of repulsion (dehesion) of solids is evaluated. The DDT explains all the features of friction and wear that are inexplicable from the perspective of ADT.

2 Proof of the fallacy of the adhesive theory of friction and wear

2.1 Modern concepts of atomic–molecular interaction at friction

Atomic–molecular forces are usually divided into attractive (i.e., adhesive and cohesive) and repulsive forces, which have yet to be named. The term “adhesive” refers to intermolecular forces and forces acting between bodies. The term “cohesive” refers to interatomic forces and forces acting inside bodies. According to modern concepts, friction between solids occurs owing to the mechanical engagement between protrusions of microroughness and their adhesive bonds. It is believed that the nature of
adhesive forces can be covalent, metallic, or van der Waals bonds [3]. The forces of attraction at very small distances are balanced by repulsive exchange interactions. It is argued that both adhesive and cohesive forces have the same nature as the attraction of electric charges [12]. Hydrogen creates exchange bonds both within and between molecules that are weaker than covalent and metallic bonds (binding energy > 0.1 eV/atom). Acid-hydrogen bonds explain the adhesive properties of rubbers [13]. The division of atomic bonds into types is conditional. In most cases, they are of a mixed nature. Therefore, metals are often carried out by localized electrons and are covalent. Electron in localized d-orbital, which is characterized by a rigid orientation in space, plays an important role. For compounds such as $A_2B_6$ or $A_3B_5$, an ionic bond forms along with the covalent bond owing to the exchange of charges between different types of atoms [14, 15]. Strong covalent and metallic bonds with energies of up to 8 eV/atom dominate at short distances of a fraction of angstroms at the tips of microroughness. The avalanche-like growth of metal bonds on microcontacts is attributed to the “seizure” phenomenon observed during friction in pure metals [12]. Long-range van der Waals forces, including the “orientation” Kiesom interaction between rotating permanent dipoles, the “Debye induction”, and the “dispersion” force including dipole–dipole interactions between nonpolar molecules, produce compounds with strengths of tens of MPa (binding energy < 0.1 eV/atom) at distances up to tens of nanometers [16, 17].

The dependences of interatomic and intermolecular forces on distance are based on the simplified models of electromagnetic interaction [14, 15, 18, 19] and the results of experiments on gas and liquid molecules. The dependence $\Phi(r)$, known as the Lennard–Jones dependence or the pair potential of the intermolecular interaction “12–6”, is the most frequently used in tribology [20, 21]:

$$\Phi(r) = 4\varepsilon[(e/r)^{12} - (e/r)^{6}]$$

(4)

where $r$ is the distance between particles, $e$ is the distance at which $\Phi(r) = 0$, and $\varepsilon$ is a constant. Figure 1(a) shows the typical dependence of the potential on the distance between atoms in the molecule [18]. Figure 1(b) shows the potential between molecules and the corresponding force dependence.

We introduce the following definitions of the forces arising between two atoms or molecules when they approach each other: adhesive-increasing attractive forces, cohesive-decreasing attractive forces, and dehesive-increasing repulsive forces. Accordingly, the entire interparticle distance is divided into four ranges (Fig. 1(b)): I—Dehesive, II—Cohesive, III—Adhesive, and IV—No forces.

The Lennard–Jones relationship was derived from a study of gas and liquid properties. The Deryagin–Muller–Toporov, Johnson–Kendall–Roberts, and other contact interaction models based on the Lennard–Jones relationship [22–25] were tested on polymers, rubbers, and colloids, between which van der Waals and hydrogen bonds act. However, is it possible to extend it to the contact of solids with covalent and metal bonds [1, 26, 27]?

From the assumption that the potential of Eq. (5) determines both the internal and surface energies of solids, the specific force of attraction acting between the surfaces of friction pairs $\overline{p}$, is calculated as [28]:

$$\overline{p} = c(z_0/z)^2 [(z_0/z)^6 - 1]$$

(5)

where $z$ is the distance between the surfaces and $c$ is a constant.

Thus, the idea of the adhesive coupling of bodies under friction is the basis of modern tribology. However,
based on the hypothesis of adhesive interaction, the attempts to determine the atomic–molecular mechanisms of mechanical energy dissipation (friction mechanisms) and the wear mechanisms of solids must deal with inexplicable paradoxes and unsolvable problems. Let us consider the problems arising from the development of friction and wear mechanisms based on the adhesion hypothesis.

2.2 Critical analysis of atomic–molecular mechanisms of friction and wear

Two mechanisms of friction are proposed to explain how the work of external forces is converted into thermal energy at the atomic and molecular levels: the Tomlinson mechanism and Prandtl–Deryagin mechanism. All other atomic–molecular mechanisms [27, 29–34] including the Kontorova–Frenkel 3D model of deformation of crystal bodies [35] have either limited applications or make minor contributions to the basic principles of converting mechanical energy into heat. In ADT the wear process is also explained by two main mechanisms: mechanical engagement with deformation of microasperities and adhesive transfer of materials.

2.2.1 Tomlinson friction mechanism (formation and breakage of adhesive bonds)

Tomlinson [2] attempted to build an atomic–molecular theory of friction based on the dependence of forces between solids, which does not differ fundamentally from that shown in Fig. 1(b). His theory contains ideas that allow us to get closer to the mechanisms of energy dissipation during friction. However, this theory is unrealistic, as it does not consider the features of the atomic structure of amorphous or crystal solids.

Tomlinson [2] stated that with the relative movement of bodies pressed together, molecular vibrations and energy dissipation (i.e., friction) occur in two cases (a graphical interpretation of Tomlinson’s ideas is shown in Fig. 2).

1) Molecules jump over the force barrier at point B (Fig. 1(b)). In this case, there are sharp damped oscillations, as shown in the curve 1 of Fig. 2. The energy of oscillations and friction depend on the height of the barrier, not on the speed. This is a characteristic of solid-state friction.

2) Molecules move in variable and barrier-free fields of adhesive-attractive forces at the distances greater than distance OB (Fig. 1(b)). Smooth oscillations occurred in this case (the curve 2 in Fig. 2). The frequency and energy of the oscillations and the friction depend on the velocity. The dependence of friction on velocity (Newton’s law) is a characteristic of liquid friction.

The actual contact area of solids is much smaller than the nominal one. A small fraction of molecules at the top of the microasperities falls within the dehesive range and withstands the external load and attractive forces from other molecules. Tomlinson [2] believed that the range of adhesive forces was much greater than that of repulsive forces. Therefore, the bulk of molecules must be within the range of long-range adhesive forces, and “the coefficient of friction of actual bodies would be reduced continuously as the velocity was reduced. This is quite contrary to experience.” The independence of the friction of solids from the velocity is the direct proof of the absence of adhesive forces between the solids. With his reasoning, Tomlinson [2] proved that there were no adhesive bonds between solids. Nevertheless, he preferred to explain the independence of the velocity from the friction of solids by the smoothing effect of the thermal vibrations of atoms at a frequency of $\sim 10^{13}$ Hz. In other words, with a high-frequency background, the energy releases when atoms approach becomes equal.

Fig. 2 Graphical interpretation of Tomlinson’s ideas on the character of molecule oscillations that occur when one body moves relative to another. Curve 1—Sharp oscillations generated when the molecules approach at the distances less than OB (Fig. 1); curve 2—Smooth oscillations generated when the molecules move at the distances above OB.
to that absorbed when they move away, making the friction forces conservative.

However, thermal vibrations do not make the friction forces conservative. They can weaken and even destroy the cohesive bond between the atoms or molecules of a solid body, leading to the replacement of solid-state friction by liquid or gas friction, thereby decreasing the friction.

2.2.2 Prandtl–Deryagin friction mechanism (the jump of atoms through the barriers of atomic–molecular roughness)

Prandtl [36] proposed the first theory of friction by overcoming the potential barriers formed by atoms in a crystal lattice. Figure 3 shows the simplified scheme of his model. Prandtl [36] did not consider the nature of forces, but believed that this principle of mechanical energy dissipation applied to both internal and external friction. Prandtl [36] stated that the nature of atomic motion was dependent on the ratio of normal and tangential forces $P/F$ (see. Fig. 3), i.e., on the relative height of the force barrier. If the barrier formed by the lower layer of atoms is low, then the atoms in the upper layer move without jumps, and the friction force changes smoothly (Fig. 4(a)). If the barrier is high, then the atoms move in a jump, causing reciprocating oscillations (Fig. 4(b)). Physically, the barrier height is dependent on the amplitude of the thermal oscillations of atoms. If the thermal oscillation amplitude is low and the atoms are mainly in range I of dehesive forces (Fig. 1(b)), then they move abruptly. If the atoms under the action of thermal oscillation are displaced by cohesive forces in range II (Fig. 1(b)), their movement becomes smooth. The smooth change in force $F$ (Fig. 4(a)) can be interpreted as the fluid flow that obeys Newton's law, and the jump-like change (Fig. 4(b)) as the friction of solids that obeys Coulomb's law. As in Tomlinson's theory [2], solid-state friction is replaced by liquid friction owing to the displacement of the average instantaneous position of atoms during their thermal motion from dehesive forces in range I to cohesive forces in range II (Fig. 1(b)).

Deryagin [37, 38] attempted to take into account the adhesive forces by supplementing Prandtl's theory with the following concept of atomic–molecular roughness: Atomic–molecular roughness is formed by the atomic–molecular structure of bodies, and is characterized by the height of geometric barriers $\Delta z$ (Fig. 5). Assuming that the forces of attraction have a large radius of effective action (compared with the force of repulsion), their tangential components can be assumed to be zero in the first approximation, and the resulting normal components can be considered constant and do not change with shear. That is, by their tribological action, the forces of attraction are equivalent to the external pressure, and cannot create resistance to the lateral movement of the atom by

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Fig. 3  Prandtl model of the occurrence of friction forces when the atom of the upper layer is shifted relative to the lower one (the lower layer is represented by a force barrier formed by cohesive–dehesive forces).

Fig. 4  Character of the change in the friction forces depending on the relative height of the force barrier formed by the lower layer of atoms according to Prandtl: (a) smooth oscillations that occur when jumping over a low barrier; (b) abrupt reciprocating oscillations that occur when jumping over a high barrier.

Fig. 5  Scheme of the forces that arises when the atoms of the upper layer overcome the barriers of the atomic–molecular roughness formed by the atoms of the lower layer (according to Deryagin [37, 38]).
themselves. The static friction force is expressed as

$$F_s = fP = \tan\alpha (P_{\text{adh}} + P_{\text{ext}})$$

(6)

where $P_{\text{ext}}$ and $P_{\text{adh}}$ are the external and adhesive forces, respectively, $P$ is their sum, $N$ is the normal component, $F$ is the friction force, $f$ is the coefficient of friction, $\Delta z$ is the height of the geometric barrier characterizing the atomic–molecular roughness, and $\alpha$ is the angle between the forces of $N$ and $P$.

The energy $W_p$ required to overcome the geometric barrier $\Delta z$ is determined by the work of an adhesive forces $P_{\text{adh}}$ and the work of an external force $P_{\text{ext}}$.

$$W_p = \Delta z (P_{\text{adh}} + P_{\text{ext}})$$

(7)

During the jump, this potential energy turns into kinetic energy $W_k$, dissipates, and transforms into the thermal vibration energy of particles $Q$ in accordance with the thermal equivalent of the Joule.

$$W_p \rightarrow W_k = \frac{mv^2}{2} \rightarrow Q$$

(8)

where $m$ and $v$ are the mass and velocity of the atom, respectively.

In the initial state, the atoms of solids occupy positions with the maximum potential energy; however, when the shift begins, they do not have time to occupy such positions. This is one of the reasons why the static friction is always greater than the sliding friction.

The Prandtl–Deryagin model assumes that the forces of attraction significantly affect both the external and internal friction of solids. However, experience has shown that the external friction of solids and the adhesive component $P_{\text{adh}}$ are negligible, and the yield strength of crystalline solids (internal static friction) is weakly dependent on the pressure. That is, the laws of the external and internal friction of solids can be written as $F = \tan\alpha P_{\text{ext}}$ and $F = \tan\alpha P_{\text{coh}} = \Lambda \tau_i$ respectively, where $P_{\text{coh}}$ is the cohesive force attracting the layers of atoms, $\tau_i$ is the shear stress, and $\Lambda$ is the real contact area.

The analysis of the Prandtl–Deryagin model shows as the following.

1) Internal friction occurs in solids as a result of the atoms jump from range I to range II (Fig. 1(b)) and their overcoming of barriers of the atomic–molecular roughness. In other words, the solid-state friction is dependent on the barrier height and not the deformation rate.

2) In liquids, the barriers of atomic–molecular roughness are destroyed by thermal motion. Liquid friction occurs owing to the movement of particles in an alternating field of cohesive forces in range II (Fig. 1(b)). The frequency of particle vibrations and, accordingly, the energy and friction force, are dependent on the gradient of the flow velocity.

3) If the thermal motion breaks the attractive forces of the molecules, then gas friction is realized (range IV (Fig. 1(b))). As in liquids, the friction force in gases is dependent on the velocity gradient; however, this dependence is caused by the frequency of molecular collisions instead of the oscillation of cohesive forces.

The results of the analysis of the Tomlinson and Prandtl–Deryagin friction mechanisms can be summarized as follows. Both mechanisms assume that adhesive forces have a significant influence on the external friction of solids. According to Tomlinson [2], the movement of molecules in the field of adhesive forces leads to the strong dependence of friction on the sliding speed. According to the Prandtl–Deryagin theory, adhesive forces will produce an essential adhesive component to Coulomb’s law of friction. In the following sections, we will prove that at low speeds and pressures, only repulsive forces act between solids; however, if the speeds and pressures exceed the critical values, then cohesive coupling occurs. Adhesive forces (i.e., increasing attractive forces) act only during the contact of solids with liquids and gases.

2.3 Critical analysis of wear mechanisms

Many substances in the liquid state form adhesive bonds with solids. However, the same substances in the solid state do not exhibit a tendency to adhere (e.g., water–steel and ice–steel). Strong connections between solids are formed by means of strong metallic and covalent bonds if the local friction energy released is comparable to the melting energy. The cleaner the surface and the lower the melting point, the less energy is required to bond the surfaces. Indium can easily bond with some metals [6]. For freshly cut lead surfaces to stick together, they must not only be
pressed but also slightly twisted [38]. The connection between a tungsten indenter and nickel crystal in an ultra-high vacuum is formed at a pressure of over 600 MPa. To break this bond, a tensile stress of \(-6.3\) GPa must be applied, as shown in Fig. 6 [30, 39], while the yield strength of nickel is only 120 MPa. An increase of over ten-fold in the strength of the “adhesion” zone indicates significant structural changes (Section 3.2 will show that this is the zone of cohesive forces).

The “adhesive” transfer of most metals is observed only in high-energy friction modes (e.g., the “adhesion” of steel to a tungsten carbide cutter at a high speed and temperature). Each pair of materials has a critical friction regime in which a transition occurs from a low-energy to a high-energy wear mode, and from the mechanical to cohesive interaction between surfaces.

2.3.1 Wear mechanisms below critical values of speeds and pressures

The principles of energy dissipation caused by irregularities at the atomic–molecular level (on the atomic–molecular roughness) based on the ideas of Tomlinson [2], Prandtl [36], and Deryagin [37, 38] can explain the mechanics of solid deformation and liquid flow, i.e., internal wear-free friction. However, to explain the mechanisms of external friction and wear of solids, it is necessary to use the geometric parameters of the surface: height and sharpness of protrusions at the nano- and micro-levels.

The surface topography at the macro- and micro-levels affects the friction and wear only if the height, steepness, and hardnass of protrusions and the relative velocity of surfaces are sufficient to cut into the softer surface and deform it. This was confirmed by the following experiments: 1) The coefficients of sliding friction of metal bars with the same surface contamination and different roughness (e.g., planed in different directions, ground, polished, etc.) were indistinguishable within the error of the experiment; 2) the mirror blade of the katana remained motionless and clean after being hit by a lead bullet. In contrast, the less polished blade vibrated after cutting the bullet, and traces of lead from the bullet remained on the blade. The latest experiment showed that lead, unlike indium, was not transferred to the steel even at very high sliding speeds.

Although hard protrusions and abrasive particles deform and destroy (cut, scratch) the surface, they also wear out. Following the wear, blunting, and smoothing of protrusions or solid particles, the intensity of abrasive wear decreases but does not stop completely. The ADT explains this by the action of adhesive forces. Archard [40, 41] considered a model of adhesive wear based on the adhesive coupling and cutting of microprotrusions, as shown in Fig. 7. Kragelsky [42] noted that the adhesive mechanism cannot explain all the features of wear: “If forces of adhesion are sufficient to separate a part of the material of one body and transfer it to another, then there is no reason for the separation of this material from the second body. In the end, the entire surface of the second body must be covered with a film of the material of the first body, which is equivalent to the friction of homogeneous materials.

![Fig. 6](image_url)  
Dependence of apparent contact pressure on load between a clean tungsten tip with a radius of \(R = 1 \) μm and a clean nickel single crystal in ultrahigh vacuum. Reproduced with permission from Ref. [30], © Kluwer Academic Publishers 1992.

![Fig. 7](image_url)  
Archard’s scheme of the cut of adhesive-bonded micro-protrusions and the transfer of material. A–B is the contact line of the protrusions and C–D is the cut-off line.
If this were the case, the wear would not depend on the nature of the counter body and would be the same for all counter bodies.” The ADT cannot explain why a solid metal transfers to soft paper, and why the sliding friction of most solids has a magnitude close to the static friction and is not dependent on speed.

The sharp increase in friction and the transition to catastrophic types of wear on very smooth and clean metal [29] and glass [43] surfaces are attributed to adhesive bonding. However, experiments have shown that at sliding speeds below the welding threshold, neither metal transfer nor adhesive bonding of glass fragments are observed. Scoring occurs on metals with similar hardness and hardening tendencies. Scoring is a process by which pressure is redistributed and two mechanically coupled teeth are formed (Fig. 8).

Both teeth were pressed into the counter surfaces, alternately plowing them and raking the metal in front of them, leaving deep expanding furrows on both surfaces [44–46]. One of the teeth after leaving the friction zone was cut off but remained mechanically linked to the counter body. The cut-off teeth were assumed to be fragments of adhesive transfer [47, 48], but this was refuted by the fact that the teeth were easily separated by a small force, as shown in Fig. 9.

A closer inspection shows that the transfer from a soft metal (except indium) to a hard metal at low sliding speeds is unrelated to adhesion. The transfer occurs as a result of the mechanical embedding of the soft material into the hollows on the surface of the hard material. Figure 10 shows the embedding of copper in the irregularities on steel surfaces. The greater the number of interaction cycles and the higher the roughness of the steel surface, the greater the amount copper transferred. Various methods of cleaning and washing surfaces, including in an autoclave in acetone vapor, do not change the nature of the transfer. It is possible to transfer copper to mirror surfaces only at pressures close to the yield point after a large number of repeated cycles and damage to the surfaces by scratches, in which the copper particles were embedded.

2.3.2 Wear mechanisms at speeds and pressures exceeding critical values

There are boundary sliding speeds at which the low-energy mechanisms of catastrophic wear are replaced by high-energy ones [40–42]. For metallic materials, this change is accompanied by a transition from crystalline to amorphous deformation mechanisms (in steels, the low-energy mechanism is called scoring, and the high-energy mechanism is called galling). After being transferred to a colder surface, the amorphous layer cools rapidly, retaining its amorphous structure (called a morphite). The higher the cooling rate, the higher the hardness is, as shown in Fig. 11. During repeated contact, the white layer acts as a cutter.

A deeper and more biased consideration of the arguments for and against the adhesive interaction of solids shows that sticking and transfer do indeed occur, but only when a certain energy threshold is exceeded (Section 3.2 will show that in this case, cohesive rather than adhesive forces act). In Section 3, the dehesive repulsion of solids at low speeds and pressures and their strong coupling when stresses
Friction and speeds exceed critical values are explained based on the modern theory of the periodic filling of electron levels (shells) and according to the changes in the properties of chemical elements, Polling’s doctrine on the hybridization of electron orbitals, and the conception of the necessity of a nucleus (cluster) of critical size for metal bond formation.

3 Interaction of atomic–molecular structures

3.1 Structure of surface bonds

The application of computational methods of physical chemistry to solve problems related to surface phenomena is difficult because of the absence of translational invariance [8]. Moreover, it is impossible to apply them to the chaos of frictional interactions; hence, other methods should be used to solve such problems [49]. As noted in Section 1, the universality of the laws of friction and wear implies their connection to fundamental physical laws, i.e., the laws of thermodynamics.

It is assumed that when a crystal splits, a certain number of localized bonds between particles are broken, forming a new surface with broken or dangling bonds. The energy of the body increases proportionally with the surface area \( A \):

\[
E = TS - P_v V + \mu n + \gamma A \tag{9}
\]

where \( T \) is the body temperature, \( S \) is the entropy, \( P_v \) is the pressure, \( V \) is the body volume, \( n \) is the number of particles, \( \mu \) is the chemical potential, and \( \gamma \) is the specific surface energy.

The coefficient \( \gamma \) is often called the “surface tension” because its dimension, J/m², coincides with that of the force \( F_s \) acting tangentially to the surface along a segment of the unit length, N/m [50]. This coincidence leads to the identification of the specific surface energy \( \gamma \) and the surface tension force \( F_s \), and to a distorted view of surface phenomena. Simplified thermodynamic analysis of a two-phase system without considering plastic deformation [51], as well as Gibbs’ replacement of the transition layer between phases with a zero-thickness boundary [15, 52], contributed to the substitution of these concepts. Such assumptions lead to the erroneous conclusion that if the system can freely rearrange itself as a liquid or deformable solid [52, 53], then the specific surface energy \( \gamma \) (taken as the surface tension force \( F_s \)) does not change with the deformation and coincides with the surface stress. In other words, the surfaces of the liquids and/or deformable solids adhere to each other.

Any system of material particles, including those on the surface of condensed bodies, tends to move...
toward a state with minimal free energy and maximum entropy. The real surfaces of solid bodies are unlike the ideal crystal planes created in laboratories and computer simulations, which are used to justify the adhesive attraction.

Landau [54] first considered the dependence of the energy of the crystal plane (the “surface tension”) on the orientation of the crystal face. Each step on the crystal surface (Fig. 12) should produce additional surface energy $\beta$. Since the steps do not merge with each other nor flow out of the face $[1n]$, they must repel each other and form the ends of the crystal face. Otherwise, all the crystals would spontaneously have perfect facets. Since there are $1/na$ steps in a unit of length, the repulsive energy $\lambda$ on the face located at the angle $\theta$ is equal to

$$\lambda(\theta) = \lambda(0) + \beta(1/na) \approx \lambda(0) + (\beta/a)\theta$$

(10)

Here, it is considered that for a large $n$, $\theta = \arctan(1/n) \approx 1/n$. Figure 13 shows the dependence of $\lambda(\theta)$ on angle $\theta$ in the direction from $[110]$ face to $[100]$ face of the Pb crystal [55]. The surface energy is determined by the uniformity of the electron distribution on the surface by the strength of the planes for shear, chipping, separation, etc. [56].

The $[111]$ plane has the weakest coupling and the most uniform electron distribution; hence, it is concluded that its surface energy is minimal. In reality, a close-packed face $[111]$ has the minimum value of $\lambda$ and the greatest adhesive ability, characterized by the specific energy $\gamma$. The greater the deviation of the crystal plane from the ideal close-packed one, the larger the number of steps on it; the greater the energy $\lambda$, which characterizes the repulsive ability; and the lower the energy $\gamma$, which characterizes the attraction ability of the surface.

Nature does not tolerate uncompensated forces and the associated free energy. If we assume that the two binding electrons that fall on each orbital in the volume are divided between the two halves of the crystal when splitting, then each of the broken orbitals is half-filled. In this case, a partial weakening of hybridization, i.e., dehybridization, may occur on the surface. Pauling [57] suggested that in complex molecules and condensed matter, one of the valence electrons moves from the lower to the upper sublevel (e.g., from the $s$ orbital to the unfilled $p$ orbital) and then pairs with the unpaired electron of another atom to form a hybrid pair. He called this phenomenon the hybridization of electron orbitals. The energy of the electrons on the broken bonds increases. Thus, it is advantageous to rearrange the connections on the surface area such that the number of broken connections decreases. In the simplest case, neighboring atoms of the surface layer are combined into pairs called dimers. The atoms of each dimer approach each other while simultaneously moving away from neighboring atoms on the surface that have entered other dimers. Here, the period of the crystal lattice changes on the surface. Figure 14 shows the reconstruction of a surface with an index of $2\times1$. The

![Fig. 12](image12) Model of a stepped surface with the height of a step $a$ and the length of the terraces $na$, oriented at an angle $\theta$ to the close-packed atomic face. Reproduced with permission from Ref. [15], © LLC “Publishing House LAN” 2016.

![Fig. 13](image13) Dependence $\lambda(\theta)/\lambda(0)$ of the face-centered Pb crystal at $T = 323$ K. Reproduced with permission from Ref. [15], © LLC “Publishing House LAN” 2016.

![Fig. 14](image14) An example of the reconstruction of the surface layer of atoms with the formation of dimers (rearrangement – $2\times1$) Reproduced with permission from Ref. [58], © Journal Nauka i Zhizn 1986.
period along one direction doubled but remained the same along another [58].

There are as many ways to rearrange surfaces as there are atomic–molecular structures. A few are listed below [15].

1) Reduction in the number of free bonds by increasing the bond multiplicity between neighboring atoms [59]. An increase in the multiplicity of the bond increases its energy and decreases its length, contributing to the appearance of tangential forces of surface tension. In the case of carbon, the length of a single bond (C–C), double bond (C=C), and triple bond (C≡C) is 1.54, 1.34, and 1.20 Å, respectively. Pauling [57] proposed an empirical relation for estimating the bond length:

\[ d(\xi) = d(1) - 0.6 \log(\xi) \]  \hspace{1cm} (11)

where \( \xi \) is the multiplicity of a bond.

2) Redistribution of the electron density and increase in the density of the binding orbitals are at the expense of the dangling ones.

3) Electron tunneling underneath the barrier on the surface decreases their concentration in the surface region and changes the lattice parameters.

4) Changes in the connection type of the surface layer. There are practically no crystals that can be completely attributed to one of the five types of bonds: molecular (van der Waals), covalent, ionic, metallic, and hydrogen. In most cases, this indexing is conditional, and the bond between atoms is of a mixed nature. On the metal surface, bonds have a partially covalent character. Bulk germanium or silicon bonds have a covalent character, and an increase in the proportion of metal and ionic bonds on the surface is possible.

5) The formation of surface defects, the number of which, \( N_{\text{def}} \), follows from the requirements of the thermal equilibrium of the system and obeys the Frenkel equation:

\[ N_{\text{def}} = C \exp \left( - \frac{E_{\text{def}}}{kT} \right) \]  \hspace{1cm} (12)

where \( C \) is a constant and \( E_{\text{def}} \) is the energy of formation of the corresponding defect.

6) Modification of the electronic structure and/or change in the filling of surface states during the occurrence of compensating charges.

7) Changes in the stoichiometric composition of the surface area. For example, on face [111] of NiO, the surface layer contains 3/4 of the Ni atoms and 1/4 of the O atoms.

8) Reconstruction (e.g., relaxation owing to the formation of steps) and/or faceting (changes in the crystallographic orientation, i.e., phase transition). Relaxation leads to a change in the hybridization of surface atoms.

Thus, in systems that allow the rearrangement of the atomic structure by melting or deformation, the free surface bonds are switched to neighboring particles and the real physical forces of surface tension arise. In liquids, these forces can be measured instrumentally. As a result, the free energy of the broken bond \( \gamma A \) is converted into the internal energy of the surface layer \( \mu_{S}N_{S} \). There is no reason why in the crystallizing liquid, the internal energy of the surface layer \( \mu_{S}N_{S} \) would again transfer to the free surface energy \( \gamma A \).

The surface structure of real solids undergoes restructuring during the process of creation. The restructuring occurs along the direction of relaxation of dangling bonds, including relaxation due to the adsorption of environmental atoms, especially on friction surfaces.

### 3.2 Force interaction of condensed matter surfaces

The simplified interaction between atomic–molecular substances can be described as follows.

The electron levels (shells) of atoms are built up by period. Each period ends with an inert gas with a completely built-up shell. When atoms of inert gases collide with atoms of all other atoms, quantum mechanical repulsive forces (dehesive forces) arise. Atoms with unfinished shells combine into molecules, complementing their shells to the structure of inert gases with valence bonds. During high-velocity collisions (\( T > \) boiling point), the molecules jump off each other like atoms of inert gases. At \( T < \) boiling point, the molecules combine in the liquid via weaker hybrid bonds. Hybridization allows each atom to combine with a larger number of neighboring atoms. In liquids, unstable hybrid bonds constantly switch between atoms or molecules, preventing them from flying out. In the outer layer of liquids, valence bonds...
partially remain (dehybridization process). As a result, surface tension forces arise between neighboring atoms of the surface layer, while repulsive forces arise between adjacent surfaces. This allows pond skaters to run on water as they do on dry land without getting their feet wet.

In the process of solidification, temporary random bonds are replaced by permanent structured bonds of the crystal lattice or by the chaotic amorphous bonds of an internally stressed framework. The strength of the lattice or framework is provided by the bonds of each atom with a certain coordination number of the nearest atoms. When the liquids solidify, the strength of the internal hybrid bonds and surface valence bonds increases. The processes described in Section 3.1 result in the creation of inert electron structures on solid surfaces and the replacement of attractive forces between surfaces with repulsive forces. The inverse dependence of the attraction and repulsion forces on the distance is a consequence of the law of periodic filling electron shells. The complete absence of cohesive forces is equivalent to the action of dehesive forces.

In accordance with modern concepts, metals cannot create inert electronic structures on the surface. The bonds between single metal atoms are unstable. Another quantitative principle works in this case. There is a minimum number of neighboring atoms (nucleus or cluster of crystals) that stabilizes the crystal structure. In accordance with this principle, the steps on the crystal faces were repelled. In the contact between commensurate crystal faces, there are sufficient cells capable of forming a single metal crystal when approaching in a vacuum. However, contact along any plane, even in a vacuum, requires pressures several times higher than the yield strength to rearrange and combine individual bonds into a crystalline lattice or an amorphous framework (Fig. 6). The avalanche-like build-up of metal bonds on microcontacts of pure metals is one of many tribological myths. A metallic, covalent, or ionic compound can only be formed if the external energy determined by the pressure, shear rate, and temperature exceeds the critical value.

Atmospheric gases and vapors, which are adsorbed and joined in chemical reactions, complete the dehybridization process of surface bonds. In air, the surface of solid bodies is instantly covered by a layer of molecules of adsorbed gases and vapors. For example, nitrogen covers 99.9% of the metal surface in $10^{-8}$ s [60]. To overcome the forces of dehesion and create a strong cohesive connection of solids in air, a large amount of external energy is required, i.e., the activation energy. This eliminates the possibility of cohesive bonds between the friction surfaces of solids at low speeds, temperatures, and pressures. The dependence of forces that arises between atoms when condensed bodies come together (Fig. 15) is fundamentally different from the dependence between atoms and molecules shown in Fig. 1 because of the absence of the range of adhesive forces. The dehesive forces before point A (range I, Fig. 15) and beyond point B (range V, Fig. 15) are different in nature. Before point A, the electrostatic repulsion of the atomic nuclei and the quantum mechanical repulsion of internal fully filled shells can be referred to as dehesion–nuclear repulsion (although the pure nuclear repulsion of atoms can only occur in H$_2$ molecules). Dehesion–nuclear repulsion can increase almost infinitely. Beyond point B, dehesive forces arise due to the repulsion of the outer and complete to inert electronic shells. Dehesion-shell forces increase until the shells merge and form a single solid. At point B, the forces are inverted. Upon reaching the critical pressure $F_K$, the orbitals of surface layer atoms are instantly rearranged, and dehesion is replaced by cohesion. For example, under pressure, solid monoliths are formed from snowflakes or marble chips. The higher the temperature, the lower the $F_K$. During friction, the kinetic energy of the atoms increases; although for most substances in technical
Friction pairs, the critical pressure \( F_k \) is much higher than the limit of plasticity or strength. Therefore, high velocities, pressures, and temperatures are necessary for dehesion–cohesion inversion and surface grip to occur.

In catastrophic modes of friction, the critical levels of activation energy are exceeded. The dehesive–cohesive inversion of forces occurs, and dehesive repulsion is replaced by cohesive attraction. The harder the body, the greater its activation energy is. For instance, mercury droplets merged with a simple contact. Among crystalline metals, indium has the lowest activation energy and hence, the greatest gripping tendency [6]. Two fresh lead surfaces must be pressed and scrolled to stick together [38]. The cohesive connection of steel surfaces in air can only be achieved at high pressures, sliding speeds, and temperatures (friction welding).

### 3.3 Role of adhesive forces at lubricating friction

Section 3.2 shows that when most solids approach, dehesive-shell repulsive forces first arise. Then, when the contact energy parameters reach critical values, they are instantly replaced by cohesive forces. The contact between solids has no adhesive component: Friction and wear at low pressures and speeds occurs because of the interaction at various levels of roughness and the galling at high pressures and speeds (Remark: Thermodynamically, only crystals are true solids). For example, nucleic acids in the crystalline state lose their adhesive properties and the ability to replicate life. Liquids that maintain an amorphous state during cooling lose their fluidity and adhesive properties gradually and at different rates. During solidification, polymers can retain their adhesive properties for a long period of time.

To reduce friction and wear, solids can only be separated by a layer with low shear resistance, i.e., lubrication. For a lubricant to have a lubricating effect, it must be pulled in and held in the contact area. Both molecular forces and roughness protrusions can pull the lubricant into the contact zone and hold it there.

In microelastohydrodynamics, the “lambda ratio” \( \Lambda = h_{\text{min}}/(R_1^2 + R_2^2)^{1/2} \) is used to assess the effect of asperities on the flow of the lubricant layer [61], where \( h_{\text{min}} \) is the minimum film thickness, \( R_1 \) and \( R_2 \) are the roughnesses of solid surfaces. However, the capacity of asperities to pull liquids into the friction zone is limited: Higher asperities capture more liquid but are also quickly destroyed. Even smooth hydrophobic surfaces can draw liquids into the friction zone by pushing through the surface film of the liquid with nanoroughness protrusions; however, the friction of hydrophobic surfaces of any roughness remains an order of magnitude higher than that of hydrophilic surfaces [62]. The effectiveness of the relief designed to hold the lubricant (oil-retaining relief) is also low because it reduces the actual contact area and bearing capacity of the friction unit. It is not surprising that modern tribotechnics is moving toward the direction of increasing the smoothness of friction surfaces by increasing their adhesive–cohesive interaction with lubricants.

Liquids behave differently during rolling and sliding owing to differences in their resistance to normal and tangential stresses and differences in the strength of adhesive–cohesive bonds at separation and shear. When the sliding and rolling ratio changes, the character of dependence of the coefficient of friction on the product of the sliding speed and the viscosity of the lubricant changes (character of Stribeck curves [63] or, taking into account the pressure, the Hersi–Stribeck curves). The functions of lubricants and their adhesive–cohesive abilities also change with slippage changes.

#### 3.3.1 Rolling

In experiments in Refs. [46, 64], the coefficient of friction of a ball bearing with a diameter of 40 mm (free rolling, sliding speed \( v_{\text{sl}} = 0 \)) without lubrication was approximately 0.0001 and was not affected by the speed. After lubrication with diesel oil (viscosity index 90, kinematic viscosity at 100 °C, 14–15 mm²/s) at a load of 2,000 N (maximum Hertz pressure per ball ~600 MPa), the coefficient of friction gradually increased from 0.0007 to 0.001 as the rolling speed increased from 0 to 1,000 r/min (\( v_{\text{rol}} \approx 2 \) m/s). The increase in rolling speed was accompanied by a decrease in the intensity of metal contact, as determined by the electronic monitoring method. At a speed of 1,000 r/min, a hydrodynamic lubrication mode occurred, and the shot of the electrocircuit stopped.
When rolling, the lubricant at low speeds prevents fretting and smoothes the peak pressure; at high speeds, it produces a hydrodynamic lubrication mode.

In friction pairs (e.g., wheel–rail), lubrication reduces the coefficient of sliding friction and prevents the traction of the wheel with the rail. The entry of liquids accelerates crack development (Rehbinder effect). Therefore, the entry of liquids into rails reduces the performance of wheel–rail friction pairs or makes it totally impossible.

3.3.2 Rolling–sliding

An increase in the proportion of sliding during rolling–sliding initially causes the rapid increase in the coefficient of friction (creep zone), which then becomes constant (steady-state friction zone), as shown in Fig. 16 [46]. Slippage (slide-to-roll ratio) is defined as the ratio of the difference between the rotational speeds of the rollers and that of the faster rotating roller \( S = (n_1 - n_2)/n_1 \). Starting from \( S \approx 2\%-3\% \), the coefficient of friction reached a constant level and did not change until 100% slippage, both with dry (curve 2) and liquid friction (curves 3 and 4) in Fig. 16. In Refs. [46, 65], it was shown that the coefficient of friction of plastic solids increased in the range of \( 0 < S < 3\% \) owing to the plastic deformation of the surface layer (plastic creep). According to Derjaguin [38, 66], the properties of the boundary layer of the lubricant are similar to those of the liquid crystal phases of mesogenic substances: Under friction, the boundary layer of the lubricant behaves as a surface layer of a solid. The similarity between the creep curves for dry friction and friction with grease confirms this assumption.

During friction of brittle loose materials such as sand, plastic deformation is excluded; therefore, the slope of curve 1 in Fig. 16 in the creep zone (\( 0 < S < 0.5\% \)) is steeper and approaches the elastic solution of Carter [67]. The slope of the initial section of the creep curve of elastic bodies, such as rubber or polydimethylsiloxane, is determined by the elastic creep and can be very flat. The slope of the creep curve at high rolling speeds and/or low temperatures may change in accordance with changes in the elastic and plastic properties of the surface layer or boundary layer owing to changes in the speed and temperature.

One of the main consequences of increased slippage is the increase in the friction power and heating rate of surfaces. For this reason, the operating range of pressures and speeds of sliding friction units are much lower than those of rolling-friction units.

It is noted that a section of the Stribeck curve with a constant coefficient of friction at near zero speed is often designated as the boundary lubrication zone. However, if the adhesion between the bodies and lubricant is low and the lubricant is completely squeezed out of the friction zone, then solid-state friction is realized in this zone (e.g., Ref. [62]). If the adhesion is high and the lubricant is not completely squeezed out, the boundary lubrication friction is realized. Owing to the similarity in tribological characteristics, these are often confused; however, this is not just a matter of terminology. With poor aerodynamics, increased slippage increases the range of solid-state friction and boundary lubrication. However, with solid-state friction, the unit will fail; with boundary lubrication, it will continue to operate.

3.3.3 Sliding

Bowden and Tabor [68] established a binomial law of friction under boundary lubrication as in Eq. (13):

\[
F = A[\alpha \tau_m + (1 - \alpha) \tau_b]
\]  

where \( \tau_m \) is the shear resistance of the irregularities and \( \tau_b \) is the shear resistance of the lubricating layer. The similarity between the solid-state and boundary modes led to the erroneous idea that the liquid film completely separates the surfaces and supports the
load only in the hydrodynamic lubrication mode [69]. Is it possible to refer to the absence of metal contacts as hydrodynamic lubrication? In the boundary lubrication mode, the run-in surfaces are also completely separated by the liquid. The increased coefficient of friction in the boundary mode is not due to metal contact but to a change in the structure of the boundary layer [4, 70, 71]. This was confirmed by our studies on the running-in process of diesel sliding bearing models [46, 64]. At the final stage of running-in, when the coefficient of friction and temperature have stabilized, rare metal contacts may still occur, but they no longer affect the coefficient of friction. This was used to determine the effects of sliding speed, pressure, and temperature on the thickness of the lubricant layer. Figure 17 shows the dependence of the frequency of metal contact on an actually run-in model of a diesel locomotive bearing assembly [46, 64]. Immobile surfaces are electrically closed. When sliding begins, the short circuit frequency per 1 mm of sliding distance decreased rapidly; at a speed of 0.006 m/s, it reached an almost constant level with a very slow decrease. The thickness of the lubricant layer changed in the same manner. The coefficient of friction, as on fully worked-in pads, was 0.008, proportional to the load, and independent of the sliding speed, i.e., the friction obeyed Coulomb’s law of friction (Eq. (1)). The model, similar to the real friction units of diesel engines, had poor aerodynamics and operated almost continuously in the boundary lubrication mode. In completely run-in models with a fully formed boundary layer, no metal contact occurred. When the oil temperature rose above the critical level, the boundary layer was destroyed. The heating rate of the oil bath was determined by the value of the coefficient of friction. The coefficients of friction of the completely running-in pads made of tin–lead bronze and Al–Sn–Pb alloys were 0.021 and 0.008–0.009, respectively. The Al₈₀Sn₁₀Pb₁₀ alloy allowed high-speed wear-in under extreme conditions. Steel pads cannot be wear-in even with the mildest running-in modes. This confirms the fact that the operating capacity of friction pairs in the boundary mode is determined by the physicochemical properties of both lubricants and solids.

In the boundary lubrication mode, the surface roughness should be minimized. The separation of surfaces and thickness differentiation of the properties of the lubricating layer should be ensured by the adhesive–cohesive characteristics. Only adhesive forces can effectively pull the lubricant into the friction zone, and only cohesive forces can hold it and differentially distribute the flow velocity and compressive strength over the thickness of the film. To some extent, this corresponds to modern concepts in which adhesive forces (Fig. 1(b)) are interpreted as physical bonds and cohesive forces (Fig. 15) as chemical bonds [69]. Various oils with different additives can form layers with different viscosities on friction surfaces to prevent metal contact and reduce the coefficient of friction in the boundary lubrication mode to almost the hydrodynamic level [69, 71–73]. Polar molecules of base oil form organometallic compounds (adhesive → cohesive transition). Antiwear additives, such as zinc dialkyldithiophosphate, form an inorganic phosphate glassy structure (dehesive → cohesive transition). The former provides an easily sliding protective layer, whereas the latter provides the load-carrying capacity. The resultant boundary film is stronger and durable [69]. Under the condition of uniform pressure, liquids exhibit the properties of solids while solids flow like liquids, thus ensuring their joint lubricating effect.

In summary, adhesion is the main weapon against all types of friction. Both adhesive bonds and asperities can pull the lubricant into the friction zone, but adhesive bonds are much more effective in wear.

Fig. 17 Dependence of the frequency of electrical contact on the sliding speed. The tested scheme is shaft-pad. The nominal contact pressure is 1 MPa (curve 2) and 20 MPa (curve 1). Shaft material is steel 45% C with diameter of 45 mm; pad material aluminum alloy is with 20% Sn and 1% Pb; contact area is 300 mm².
reduction. Therefore, the surfaces of lubricated friction pairs should be as smooth as possible with the highest adhesion ability to the lubricant. Adhesive bonds provide the working capacity of not only liquid but also solid lubricants (graphite and MoS₂ do not work well without adhesive components). With increasing slippage, the strength of cohesive bonds that form the boundary layer should increase. If the bodies are hydrophobic and do not form adhesive bonds with the lubricant, then a solid-state friction mode exists at low speeds and high pressures, which is mistakenly identified as the boundary lubrication mode. Therefore, wear is not an exceptional sign of dry friction. Moreover, the absence of wear is not an exceptional sign of hydrodynamic friction.

4 Contours of DDT

The existence of a critical energy, beyond which the dehesive repulsion of surfaces is replaced by cohesive bonds, turns all the ideas on friction and wear on their heads, forcing us rethink the huge amounts of accumulated data, relationship patterns, and theories. The critical temperatures, velocities, and pressures that separate low-energy from high-energy wear types have become the most important characteristics of friction pairs. For the internal friction of solids, exceeding the critical parameters leads to a transition from crystallographic to amorphous deformation (this is the topic of a separate article); for external friction, this leads to the replacement of the mechanical engagement of asperities by cohesive bonds.

The dehesive repulsion of surfaces in the low-energy friction range eliminates all mechanisms of external friction and wear, except for the mechanical engagement of protrusions of different sizes, from macro- (e.g., file teeth) to nano-protrusions of mirror surfaces. As clarified above, the surface geometry at the macro- and micro-levels can affect friction and wear only if the height, steepness, hardness, and relative velocity of the roughness protrusions are sufficient to press them onto a softer surface to deform and destroy it. Such a wear mechanism is a type of mechanical processing, i.e., abrasive grinding or microcutting. In this case, friction is created by the deformation (i.e., internal friction) of the surface of the softer body. As
the friction and wear process. The shear strength of conglomerates under all-round compression conditions can exceed the strength of the bodies. They can also plow through friction surfaces, leaving scratches that correspond to their size.

If the hardness of one body is similar to that of another, the sliding speed is low, then a low-speed type of catastrophic wear (i.e., scoring) occurs at the critical pressure, as shown in Fig. 8. If the sliding velocity exceeds the critical velocity, then the transition from crystallographic to amorphous deformation occurs [44, 74], and a high-energy type of catastrophic wear (i.e., galling) occurs, as shown in Fig. 11.

The only method to reduce friction and eliminate wear during the external friction of solids is lubrication. The DDT enables the systematization of an infinite variety of compositions, structures, and properties of solids, lubricating layers, and the external environment. It provides new opportunities for the scientifically based development of new friction materials and lubricants, and the design and optimization of the operating modes of friction units.

5 Conclusions

Interatomic and intermolecular forces are divided according to the direction and sign of the gradient: adhesive – increasing attractive forces; cohesive – decreasing attractive forces; and dehesive – increasing repulsive forces, subdivided into “nuclear” and “shell”.

All material objects, from molecules to celestial bodies, tend to minimize the free energy created by surface forces. The most stable configurations are the completely filled shells of inert gases formed at the end of each period. Nuclear dehesive–repulsive forces act between atoms with completely filled inert electron shells. Adhesive–attractive forces act between all other atoms; when approaching, these first turn into cohesive forces and then into nuclear dehesive forces, forming molecules. At high temperatures, the molecules exist as gases, constantly colliding and bouncing off each other under the action of dehesive shell forces. When the temperature decreases, the molecules combine by the hybridization of internal valence bonds, forming liquids followed by solids. On the surface, dangling bonds dehybridize and form stable valence bonds. Strong valence bonds on the surface of bodies lead to the emergence of shell dehesive–repulsive forces that prevent surfaces from sticking together. The stronger the valence bonds, the greater the shell dehesive–repulsive forces. The inverse dependence of the attraction and repulsion forces on the distance is a consequence of the law of periodic filling of electron shells. There are critical values of the pressure, temperature, and velocity at which the dehesive forces between solids instantly transform into cohesive forces. Metals do not form valence bonds. A strong metal bond occurs only when a sufficient number of atoms combine to form a nucleus of the crystal lattice, which also requires a critical activation energy. Commensurate surfaces can combine and create a single body, while incommensurable surfaces were repelled. Atmospheric gases and vapors, which are adsorbed and undergo chemical reactions, complete the dehybridization and deactivation of surface bonds.

For liquids, under the influence of thermal motion, the hybrid and valence bonds of atoms are constantly broken and new ones are created. Internal friction forces in liquids are created as a result of the energy consumption for vibrations that occur when atoms move in the variable barrier-free field of cohesive forces (Newton’s liquid friction). When the liquid solidifies, the permanent structured bonds of the crystal lattice or chaotic amorphous bonds in the internal stressed framework replace temporary random bonds. The internal friction of solids occurs when the atoms overcome the potential barriers of atomic–molecular roughness.

The external friction of solids, owing to their dehesive repulsion, is realized because of the mechanical engagement and deformation of asperities of different sizes and shapes, from the macro- to the nano-level. The number and size of engaged asperities are proportional to the load; up to a certain limit, these are not dependent on the speed (Coulomb friction). There is a maximum speed of solid friction at which crystallographic deformation is replaced by amorphous deformation. Exceeding the critical speed of external friction leads to a change in the mechanical engagement of protrusions by their cohesive coupling and the
occurrence of a high-energy type of catastrophic wear (i.e., galling).

The only method to reduce friction and eliminate wear during the contact between solids is lubrication. Wetting is required to prevent the lubricant from being squeezed out of the contact area and to separate the surfaces. Adhesion is the main weapon against all types of friction. Both adhesive bonds and asperities can pull the lubricant into the friction zone, but adhesive bonds are much more effective at reducing wear. Therefore, the surfaces of lubricated friction pairs should be as smooth as possible with the highest ability to adhere to the lubricant. Only adhesive forces can effectively pull the lubricant into the friction zone, and only cohesive forces can hold it and differentially distribute the flow velocity and compressive strength over the thickness of the film.

Acknowledgements

I remember the English tribologist with warm feelings, Doctor of technical Sciences, Prof. David Arthur Kelly, University of Leicester, UK, and our joint work on the theory of catastrophic wear, which was the first step toward DDT. I am deeply grateful to the winner of the Gold Medal of the International Council of Tribology, Doctor of Technical Sciences, Prof. Nikolai Alexandrovich Busher for supporting my experimental and theoretical efforts to undermine the foundations of orthodox theory of friction and wear.

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