



How Carbon-Based Nanosheets Protect: Mechanistic Models

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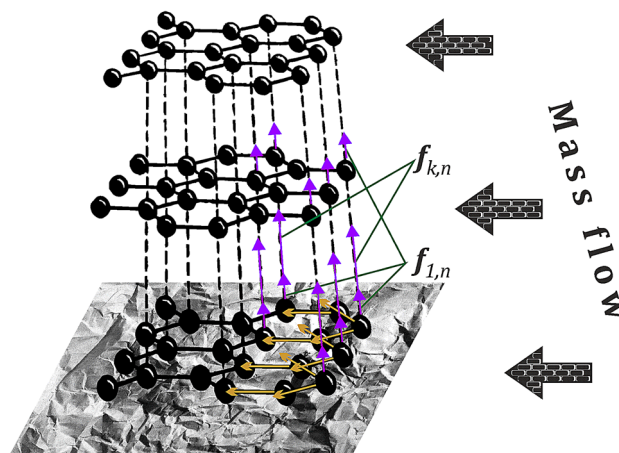
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Abstract

Graphite- and graphene-based surface protective films are shown to undergo different tangent impacts in working units and mechanisms. The thicker the graphite film is, the more it is subjected to deterioration because tangential components of acting forces turn into normal ones because of distortion of the graphite lattice and elasticity of the interlayer van der Waals bonds. Critical pressure of sliding friction force on the film has been estimated according to real conditions in a combustion engine. The amplification effect has been evaluated and shown to be roughly proportional to a number of layers in the film. The function-amplifier has been constructed, its asymptotical behaviour at small and big number of layers has been analysed. An expression in quadrature representing the working surface wear on the basis of deteriorated film area and working pressure with its fluctuations has been proposed. Its structure is related to a mutual correction of factors related to how (i) intensively and (ii) extensively the surface fragments are affected through the wear.

Graphic Abstract

Graphene- vs. graphite-based greases: surface protective films



Keywords Nanosheets · Protective films · Friction · Nano-grease · Graphene · Graphite

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1 Introduction

A nearly magic prefix «nano-» created a virtually immense field for advancements in various branches of science as well as in technological and industrial solutions. As a typical representative of those can serve improvement of tribo- and rheological characteristics of multi-component consistent lubricants (greases) [1–3] aimed in the issue to resist wear. This is to be substantially achieved by means of (i) reduction of friction, (ii) redistribution of load, (iii) heat transfer enhancement, and (iv) in situ recovery of contact surfaces. This appears again to be an issue to distinguish between or to optimise both “form and content”. Whereas the form of nano-particles the grease has been enriched with is able to contribute to reduction of an impact mechanically (e.g. nano-tubes, -onions or -horns [4] to replace sliding with rolling), material properties are expected to alleviate operating of the contact surfaces mediate (e.g. through improvement of thermal conductivity with carbon-based [5] and viscosity with alumina-based additives [6], electrostatic repulsion of contact surfaces through metallic nano-particles in grease due to their “electronic tails” beyond the lattice [7], repair of surfaces in contact through chemical bond formation [8] or even polishing [9]).

Out of different types of additives distinguished through their composition (e.g. inorganic, incl. metallic, and steric, or capped nano-particles), carbon-based nano-particles are typically considered as an independent group with its own sub-groups which differ allotropically or structurally [1,3]. This is probably because of conventional long-term usage and abundance of carbon-based greases along with their heat transfer properties and well-tested fabrication technologies. Extended with discovery of graphene and fullerene, members of the carbon-related group appeared to be subject to intensive comparison with one another [3,10,11]. Diversity of characteristics and variety of factors and circumstances resulted sometimes in the polar evaluation of carbon-based additives. Thus, adherence of protective films with graphene-based nano-particles was characterised as doubtful because of chemical inertness and hardness in [4] and by reason of the van der Waals forces weakness in [11], whereas a good adsorption of multi-layer graphene on rubbing surfaces was uncovered in [12]. A particular problem is related to nano-particles agglomeration to occur [13], should their concentration be spontaneously increased while attempting to reach better protection [4]. This phenomenon is related to surface energy increase at dispersing the substance [14,15]. One of particular means to resist could be thermodynamic stabilisation of the metallic nano-ensemble, developed in [16,17] and related to substance ultra-dispersing (particle size ≤ 10 nm in the nano-ensemble).

Hereinafter, we focus on the sub-group of sheet-shaped carbon-based additives. Such a form appears to be most naturally (although not exclusively) associated with a film-based protection of rubbing surfaces with the aim to reduce wear in the contact area. A number of studies were devoted to this issue, related to various allotropic modifications of carbon and considering such aspects as fabrication of film-forming additives and experimental investigation of both properties and anti-wear effect of greases as a whole [12,18–21]. The goal of this paper is to introduce transparent mechanistic models of graphene- and graphite-based greases, to evaluate on this basis the most important characteristics of protective films and run-time environment (pressure, tension) and to propose an approach to the calculation of macroscopic characteristics of wear in quadrature.

2 The Mechanistic Model of a Graphite Film Detachment

We consider first the mechanistic analogy with how the graphite-based additives act. Our description pretends to be neither of phenomenological equivalence nor derived *ab initio*. Nevertheless, as the pendulum model helps demonstrate and better understand, e.g. a number of electromagnetic or even quantum mechanical phenomena, our simple mechanistic models can serve similar to those and enable one to apply the outcomes to estimate and/or to compare particular systems.

2.1 General Characteristics

While added to a consistent or other lubricant, graphite particles fill in and smooth out microroughnesses of the rubbing surfaces during running-in a pair “metal–metal”, through a surface film formation. Depending on a bond type between the surface and the film, this leads in a greater or lesser extent to the enhancement of bearing capacity, anti-friction and anti-static properties, water resistance, etc. The use of graphite-based greases is mainly restricted to low-speed and non-high-precision units and mechanisms. This is polarised graphite which is eventually employed instead of the usual one to increase the grease adhesion to metallic surfaces. The adhesion is sure to be conditioned by the van der Waals forces since there is neither chemical reactions nor embedding into the substrate lattice.

The graphite lattice is hexagonal and consists of coplanar layers formed by regular hexagons with C-atoms in vertices. In the most usual graphite allotropic modification, C-atoms of each layer are located facing the centres of hexagons of the neighbouring (lower and upper) layers, i.e. each layer turns out to be orderly shifted relative to the other, and all the odd layers are positioned equivalently as well as all the

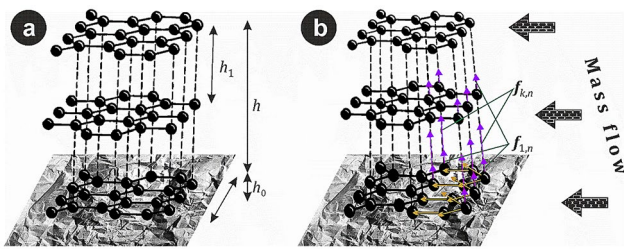


Fig. 1 Graphite film on a metal substrate (three layers are shown). **a** in the absence of external forces; **b** in the presence of external forces due to mass flow inside an operating unit/mechanism. Solid bonds: covalent; dashed bonds—van der Waals's. The vectors (yellow) directed along the substrate: expansion of the tangential component of the force along the basis of covalent bonds; directed along the vertical axes (crimson colour) vectors: $f_{1,n}$ is the external force normal component at each node of each layer (except for the uppermost layer) because of an overlying layer shear (shown for the first two layers), $f_{k,n}$ is the superposition of normal components of forces originated from each overlying layer, applied to each node of the lowest layer

even layers are. Every C-atom within its layer has covalent bonds with three neighbouring atoms. The interlayer bonds are usually considered as due to van der Waals forces what is, generally speaking, typical for minerals with a hexagon lattice within one layer [22], although there are debatable ideas that such bonds can differ in their nature [23]. The latter, however, does not matter for our following consideration since the interlayer bond energy is ca. 1/10 of the hexagonal bond energy anyway. Therefore, graphite possesses sharply anisotropic properties. Thus, ultimate stress limit is the highest at squeeze and equal to 70.0–100.0 MN/m², whereas it constitutes 20.0–38.0 MN/m² at slow bend and 12.5–20.0 MN/m² at stretching [24].

2.2 Lattice Deformation Model at Rubbing

Figure 1a represents, with a certain degree of conventionality, the structure of a graphite film on a metal substrate. The first (lower) layer, due to adhesion, holds the entire film on the metal substrate.

Figure 1b represents the same system under the load due to mass flow. External forces F are acting on each layer. Initially applied to the foremost nodes, they are being transmitted in the form of tangential components F_t along covalent bonds through the entire lattice. Since (i) they are the covalent bonds which are the strongest among all the bonds in the lattice, and (ii) this is squeeze which is the lattice's most resisting deformation, the tangential components' impact on the lattice has the form of a layer shear only, whereas deformation of the hexagonal cells turns out to be negligible. The normal (with respect to the substrate's "in average"—horizontal surface) components F_n of external forces appear to be applied to the nodes along the van der Waals

bonds. Let the whole number of layers be equal to $k + 1$ where $k = 0$ corresponds to the lowest layer. The normal component of the force applied to each node of the lowest layer can be thought of as a superposition¹ of the two forces which are $f_{1,n}$ due to that part of the second-layer shear invoked by an external force acting exactly on the second layer tangentially, and $f_{k-1,n}$ representing the sum of forces applied to the nodes of $(k - 1)$ uppermost overlying layers, with which the corresponding node of the lowest layer is bonded by van der Waals forces along the entire film in a vertical direction. Notated as $F_{1,n} = \sum f_{1,n}$ where the summation is being carried out over all nodes within the lowest layer, and $F_{(k-1),n} = \sum f_{(k-1),n}$ (over all nodes of $k - 1$ uppermost layers), we can decompose external forces into tangential and normal components within the crystal lattice:

$$F = F_t + F_n \quad (1)$$

where $F_n = F_{1,n} + F_{(k-1),n}$ is applied to the lowest layer with respect to which we will consider further Eq. (1). We introduce the function-amplifier $A(k)$ defined for integer $k \geq 2$, as

$$F_{(k-1),n} = A(k)F_{1,n} \quad (2)$$

Inequality $A(k) < k - 1$ is valid beginning already with $k = 2$ and means that the superposition of forces incoming from the uppermost $(k - 1)$ layers is smaller than $(k - 1)$ -fold $F_{1,n}$, since the transfer of some constituent of forces in the tangential direction inevitably takes place on account of an imperfect orthogonality of the tangential and normal basis directions due to the lattice distortion under the influence of an external force. As a result, the tangential component of the forces turns out to be small, because the elasticity of normal bonds invokes a conversion of the tangential impact into a normal one. Taking into account Eq. (2), for the normal component of the force acting on the lowest layer, we obtain the equation

$$F_n = [1 + A(k)]F_{1,n} \quad (3)$$

Equation (3) explains the reason why graphite-based lubricants have not found application in high-speed mechanisms and high-precision technologies, in which, because of small tolerances, significant forces are not being extinguished by secondary factors. Because of the large number of layers k , the monotonously increasing function $A(k)$ significantly amplifies the normal impact onto the lowest layer, transforming the tangential impact into normal through the van der Waals bonds. Should the

¹ This is related to some error because the action of the force's normal component can be transmitted with some retardation and weakening along the lattice in the tangential direction. However, on account of a big number of layers in the film (about 200 for the film thickness 60 nm as an example) this effect is negligible.

external force be strong enough to overcome the adhesion forces, the lower layer is being detached from the metal substrate. This detachment begins from that edge of one of the substrate's numerous linear defects (dislocations), which is located on the external force side. In terms of our mechanistic analogy, the graphite film detachment is going on in the manner of tearing off a climbing ladder gradually along its entire length (in the case of a film, until the next dislocation, where the film most probably breaks).

2.3 Critical Pressure of Sliding Friction Force on the Film

Let us determine a critical value of pressure produced by the sliding friction force, at which tearing off the graphite film's fragment takes place. The film's side area subjected to an external force is equal to $S = hw = (kh_1 + h_0)w$ (Fig. 1a), where $h_1 = 0.3354$ nm is an interlayer spacing in the graphite lattice, h_0 is the distance from the lowest layer to the substrate's "averaged" surface. At the critical pressure P_c resulting in film detachment, the following equality is valid:

$$E_{ad} = l(kh_1 + h_0)wP_c \quad (4)$$

where l is the linear size of the graphite film fragment being detached. Because of uniformity of directions, one can consider $l \sim w$ and further, instead of their product, approximately use the square of a dislocation linear size w^2 averaged out over the substrate surface. Adhesive bond energy E_{ad} for the film's fragment being detached is equal to

$$E_{ad} = (N/N_A)E_{ad}^{(1)}$$

where N is the number of nodes in the film's fragment being detached, N_A is the Avogadro number, $E_{ad}^{(1)}$ is the adhesive bond energy for 1 mol of C-atoms in the film. Graphite elementary 2D cell encompasses 2 atoms, its lattice constant is equal to $a_0 = 0.246$ nm. Therefore, the number of nodes in the film fragment being detached is equal to $N = 2w^2/a_0^2$. With all the above in mind, we transform Eq. (4) to the form:

$$P_c = 2 \frac{E_{ad}^{(1)}}{N_A a_0^2} \frac{1}{kh_1 + h_0} \quad (5)$$

We cannot exactly calculate $E_{ad}^{(1)}$ because it depends on a huge variety of parameters characterising the substrate surface. Nevertheless, we can make an upper estimate for this. $E_{ad}^{(1)} < E_{ilb}$, where E_{ilb} is graphite interlayer bond energy, otherwise the film would rather interstitially break than detach from the substrate surface. According to [25], graphite interlayer bond energy $E_{ilb} \sim 0.37$ J/m² = 6.7×10^3 J/mole. Upon substituting all known parameters into Eq. (5), we obtain

$$P_c < \frac{0.368}{kh_1 + h_0} \times 10^9 \text{ Pa,}$$

where the film thickness $kh_1 \approx (kh_1 + h_0)$ in the denominator is expressed in nanometres. Just as an estimate, for film thickness 15 nm [18] one would obtain $P_c < 24.5$ MPa, or ~ 250 atm.

3 The Mechanistic Model of Graphene Film Detachment

Monolayer graphene is basically an allotropic 2D modification of carbon. To model it, one is to let $k = 0$ in the considerations in Sect. 2, *i.e.* the lowest layer only remains. With the approximations introduced there, the tangential forces in the film, because of their insignificance, are not to be considered among those affecting detachment. Equation (5) for the critical pressure with film detachment has the form

$$P_c = \frac{2E_{ad}^{(1)}}{N_A a_0^2} \frac{1}{h_0} \quad (6)$$

in the case of graphene what results in the estimate for P_c in the case of a one-layer graphene film as

$$P_c < \frac{0.368}{h_0} \times 10^9 \text{ Pa} \sim 1000 \text{ MPa}$$

For the multi-layer (with 4 layers) graphene similar to that considered in [12], we obtain correspondingly $P_c < \sim 200$ MPa.

4 Discussion

One can easily understand by considering Eqs. (5) and (6), why graphene sheets in the adsorbed state on a substrate surface appear to be much more stable under a tangent impact than the graphite film. The following relationship is a direct consequence of these equations:

$$p_c^{\text{graphene}} / p_c^{\text{graphite}} = 1 + k(h_1/h_0) \quad (7)$$

Taking into account that for a thick graphite film the inequality $k(h_1/h_0) \gg 1$ takes place, the critical pressure at which the graphene film detaches is $\sim k$ times as much as the critical pressure for the graphite film. That there is a working pressure p inside the unit or mechanism pressing and therefore stabilising the film, does not affect Eq. (7) much, because $P_c \gg p \sim 10$ atm takes place inside, *e.g.*, the combustion engine:

$$p_c^{\text{graphene}} / p_c^{\text{graphite}} \approx k$$

provided $h_1 \approx h_0$.

It is worth making here also a general note, that in a real practise this is a question of the balance “strength vs. tangential force susceptibility” of the film, which can be answered in different ways. For example, the authors of work [12] where fabrication of a multi-layer graphene film was presented might have found that a four-layer film represents an optimum in this sense under particular conditions.

Let us (i) discuss now a possible form of function $A(k)$ in Eqs. (2) and (3) and construct it as well as (ii) obtain solution in quadrature for a unit or mechanism wear depending on pressure and its deviations.

4.1 Function-Amplifier A(k)

The energy of the adhesive bond, in addition to the above equations, is also equal to the work of the force on displacement of the lowest layer (in the case of graphene, the only one) by a distance Δx , at which detachment occurs:

$$E_{ad} = \sqrt{F_t^2 + F_n^2} \Delta x \tag{8}$$

From Eqs. (4) and (8), we obtain an equation for the normal component of the force acting on the lowest layer provided the film would tangentially experience some pressure $P < P_c$:

$$F_n = \sqrt{\left[\frac{P(kh_1 + h_0)\bar{w}^2}{\Delta x} \right]^2 - F_t^2} \tag{9}$$

Let us consider in terms of Eq. (3) the ratio of the normal and tangential components for the forces applied in one case to a graphite film, and in another case to a graphene film, for which $k = 0$:

$$\frac{F_n^{\text{graphene}}}{F_n^{\text{graphite}}} = [1 + A(k)]^{-1} \tag{10}$$

On the other hand, the same force ratio, according to Eq. (9), is equal to

$$\frac{F_n^{\text{graphene}}}{F_n^{\text{graphite}}} = \frac{\sqrt{(Ph_0\bar{w}^2/\Delta x)^2 - [F_t(k=0)]^2}}{\sqrt{(P(kh_1 + h_0)\bar{w}^2/\Delta x)^2 - [F_t(k)]^2}} \tag{11}$$

Here, we have to take into account, that the tangential component of the external force, when applied to the film layers, depends, generally speaking, on k . We obtain then from Eqs. (10) and (11)

$$A(k) = \frac{\sqrt{(P(kh_1 + h_0)\bar{w}^2/\Delta x)^2 - [F_t(k)]^2}}{\sqrt{(Ph_0\bar{w}^2/\Delta x)^2 - [F_t(k=0)]^2}} - 1 \tag{12}$$

Let us discuss Eq. (12). With an increase of k , the conversion of the tangential component of the force into the normal one on average decreases, because, on account of elasticity of van der Waals bonds, the elastic shear of the upper layers increases under the action of an external force. On the other hand, the larger the layer’s number, the smaller its contribution to $F_{k,l}$ in Eq. (2) due to a certain reduction factor (noted above) which the amplifying function $A = A(k)$ converts the tangential stresses to normal stresses with. Therefore, Eq. (12) characterises the true function $A(k)$ for bounded k . This is logical to extent the definition of $A(k)$ at $k = 1$ as $A(k = 1) = 0$ what means that had the film just two layers (0th and 1st), there were no further layer able to add some force component to that of the uppermost (1st) layer. Such an extension enables us to obtain some hint concerning a dependence of F_t on k :

$$F_t(k = 1) = \sqrt{[F_t(k = 0)]^2 + [P(h_1 + h_0)\bar{w}^2/\Delta x]^2 - [Ph_0\bar{w}^2/\Delta x]^2} \tag{13}$$

At bigger k , a dependence $F_t = F_t(k)$ meets the following expectations: for $k > k_{eff}$ the dependence of A on k weakens till negligibility because of processes related to bond ruptures and dissipation, whereas for $k \ll k_{eff}$ it represents a sublinear law. On the basis of general considerations and while referring to the graphite film, one could expect that k_{eff} is a constant of several tens of units in magnitude. Dependence of $F_t(k)$ on k can be generally represented in the form

$$F_t(k) = F_{1,t}g(k) \tag{14}$$

where $F_{1,t}$ is the tangential component of an external force applied to one layer, $g(k)$ is some function whose properties are to be commented below. Besides that, this follows from the earlier said that $F_{1,t}$ is sufficiently small, so that the inequality

$$Ph_1\bar{w}^2/\Delta x \gg F_{1,t} \tag{15}$$

takes place and justifies a transition from Eq. (12) to Eq. (13). By substituting Eq. (14) into Eq. (12), we complete the construction of the function $A(k)$:

$$A(k) = \frac{\sqrt{(P(kh_1 + h_0)\bar{w}^2/\Delta x)^2 - F_{1,t}^2g^2(k)}}{\sqrt{(Ph_0\bar{w}^2/\Delta x)^2 - F_{1,t}^2}} - 1 \tag{16}$$

Since it is pressure P that creates the tangential force F_t , whose asymptotical growth at big k is governed by function $g(k)$ according to Eq. (14), in the mathematically correct,

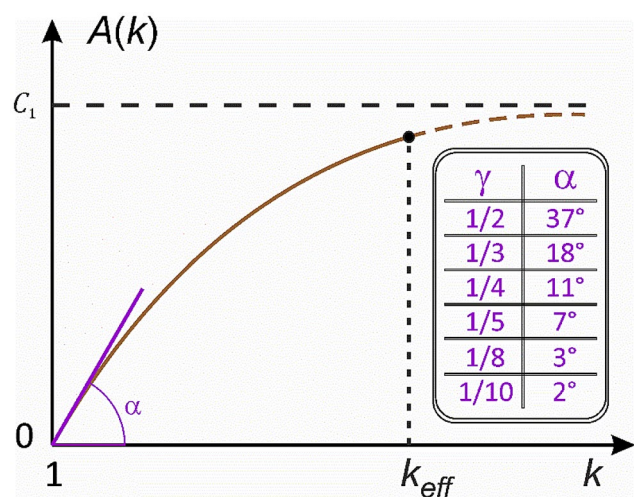


Fig. 2 Dependence of function-amplifier A on the number of layers k in a graphite film

although physically unreachable limit, the following expression under the square root sign in Eq. (16) has to be limited

$$2 \frac{P^2 h_0 h_1 \bar{w}^2}{(\Delta x)^2 F_{1,t}^2} k + \left(\frac{P h_1 \bar{w}^2}{\Delta x} \right)^2 \frac{1}{F_{1,t}^2} k^2 - g^2(k) = \tilde{g}(k) < +\infty$$

so that A(k) has the following asymptotical behaviour at k → ∞, taking into account inequality (15):

$$A(k) \sim C_1 - \frac{C_2}{k} + O\left(\frac{1}{k^2}\right) \tag{17}$$

where it is considered $\tilde{g}(k) = \frac{1}{2\mu^2} \left(\tilde{C}_1 - \frac{\tilde{C}_2}{k} \right) = C_1 - \frac{C_2}{k}$

order to meet the physically reasonable requirement above imposed on behaviour of A(k) at big k, and $\mu = \frac{P \bar{w}^2}{F_{1,t} \Delta x} h_0 \sim \frac{P \bar{w}^2}{F_{1,t} \Delta x} h_1 > 1$ can be considered as a film stress factor when the external force is applied, C₁, C₂, \tilde{C}_1 and \tilde{C}_2 are some positive constants determined by the properties of van der Waals forces acting between the graphite layers. μ includes pressure P associated with the total force applied to the graphite film, the tangential component F_{1,t} of this force, the spacing between the substrate and the graphite film, and the average square of the linear size of the film fragment being torn off, \bar{w}^2 . The general form of function A(k), which satisfies the asymptotic behaviour for small and big k according to Eqs. (13) and (17), is qualitatively presented in Fig. 2. Angle α can be estimated if one formally considers all k-dependent functions as continuous rather than discrete and substitutes then the Taylor expansion of F_t in the vicinity of k = 1 as F_t(k) ≈ F_t(k = 1) + β(k - 1), where the first term is determined in Eq. (13) and β = dF_t(k = 1)/dk, into Eq. (12):

$$\alpha \approx \arctan \left\{ \frac{\beta F_t(k = 1)}{[P h_0 \bar{w}^2 / \Delta x]^2 - [F_t(k = 0)]^2} \right\} \tag{18}$$

That the denominator is non-zero is obvious because F_t(k = 0) is near to be infinitesimal what was pointed out to above. Although β remains unknown, we can make a rough estimate of angle α. Considering F_t(k = 0) negligible, we take h₁ ~ h₀ ≈ 4Δx, i.e. should displacement Δx constitute γ = 1/4 of h₀, the film detachment would occur (seems to be an overabundant assumption), β ~ δF_t(k = 1)/δk ≈ F_t(k = 1) since δk = k = 1. We obtain then the following upper estimate for angle α, dependent on γ only:

$$\alpha \approx \arctan \left\{ \gamma^2 \frac{[F_t(k = 1)]^2}{k P^2 (\bar{w}^2)^2} \right\} \approx \arctan(3\gamma^2) \approx 11^\circ$$

For function g(k) in Eq. (14), we correspondingly obtain in the limit of big k:

$$g(k \rightarrow \infty) = \sqrt{\mu^2 \frac{h_1}{h_0} k \left(1 + \frac{h_1}{h_0} k \right) - C_1 + \frac{C_2}{k}}$$

As noted earlier, the asymptotic value at k → ∞ is a mathematical idealisation and is certainly not achieved due to the effective “cut-off” of conversion of the tangential component to the normal one upon reaching a certain value k = k_{eff}.

4.2 Natural Distortions of Films

The presentation above could not be complete without a brief discussion of which effects one has (or does not have) to expect, should the film experience distortions possibly having been arisen due to a whole variety of natural reasons. Real films can possess (and do) surface corrugations incl. ripples and wrinkles, crumples [26], exhibit swelling [27] and be subjected to intercalation (especially graphite) [28].

Crumples, wrinkles and ripples typically associated with graphene as a 2D material, do not seem to crucially affect the phenomena considered here. All these effects have the fluctuational nature to compensate basic thermodynamic instability of 2D crystals [16,17]. In particular, C–C-bonds appear to be modulated because of thermal vibrations, interatomic interactions, different thermal expansion coefficients of carbon films and the metal substrate and relaxation processes in the films. While all these factors are basically related to the behaviour of van der Waals bonds, taking them into account would seem to lead just to some small corrections.

Swelling of carbon materials is typically associated with medium (air-)-related contamination resulting in loss of intrinsically hydrophilic properties what was earlier erroneously interpreted as basic hydrophobic feature. Contamination edge effect is potentially capable of increasing the effective surface area subjected to tangential forces. As this effect is normally associated with graphite, its magnitude is not expected to be considerable because of a naturally big (macroscopic) number of graphite layers. Graphene contamination would effectively increase its susceptibility to the tangential forces because of a bigger relative distortion of the crystal compared to graphite. There exist estimates of difference in surface energies of clean and “dirty” graphite/graphene (up to 25% decrease in the case of “dirty” carbon materials). For a multi-layer graphene, it could be damped through the layers and finally result in an effect of possibly $\sim 5\%$ (see Eqs. (5) and (6) for reference purposes).

Intercalation is normally associated with compounds related for example (but not restricted) to intercalating ions of alkali metals. Detailed consideration of this effect goes beyond the scope of this study as that appears to be highly dependent on the nature of the alien affecting the crystal bond energy.

Limitations of the model considered originate mainly from its mechanistic nature. The model does not consider quantum–mechanical nature of bonds as, *e.g.* related exchange and correlation effects in the crystals. Therefore, it is illustrative and can serve to make estimates.

4.3 Wear of Units and Mechanisms

A general equation characterising the total area σ of film fragments detached over the entire surface Ξ of the machine element, taking into account pressure working p in the unit or mechanism and the stochastic nature of this phenomenon, is expressed by the following integral:

$$\sigma = \Phi(t) \int_{\Xi} w^2 \varphi(w) dw \quad (19)$$

where $\varphi(w)$ is a distribution function of film fragments whose detachment occurs, on their linear size, normalised to unity

$$\int_{\Xi} \varphi(w) dw = 1$$

and the time stochastic factor $\Phi(t)$ reads

$$\Phi(t) = \int_0^t \frac{\delta p(\tau)}{p(\tau)} \psi(\tau) d\tau \quad (20)$$

where $\delta p(t)$ denotes pressure fluctuations in the unit or mechanism, $\psi(t)$ is the time-dependent fluctuation distribution function normalised to unity as well:

$$\int_0^{\infty} \psi(\tau) d\tau = 1$$

Let us discuss Eq. (20). When a new unit or mechanism is in operation, pressure fluctuations are minimal due to minimal wear and optimum component tolerances. As wear increases, fluctuations $\delta p(t)$ also increase so that in the limit $t \rightarrow \infty$, the pressure and its oscillations are commensurable $\delta p(t)/p(t) \rightarrow 1$ what would mean a destruction of the unit or mechanism.

Thus, according to Eqs. (19) and (20), the total area of wear of a unit or mechanism is to be expressed by the product of two independent integrals. The first of them is to be calculated over time and characterises the degree of how *intensively* local surface fragments are affected, whereas the second is to be taken over the surface of a machine element or its fragment undergoing a critical impact, and represents how *extensively* the surface is encroached. Either of the integrals serves as a refining factor for another one.

5 Conclusion

In this paper, the mechanistic models of behaviour of graphite and graphene films adsorbed on the metal substrate have been proposed. One of the models' consequences is that the graphite film appears to undergo the tangent impact *ca. k* $\approx h/0.3354$ times (*h*, nm, is the graphite film thickness incl. spacing between the film and substrate surface) as much as the graphene film does. The reason is a conversion of the tangential components of forces into normal with respect to the surface due to elasticity of graphite interlayer bonds and distortion of the lattice. Since many layers of the graphite film contribute, there occurs an amplifying effect represented in the model through the function-amplifier *A(k)* which has been constructed and has the form presented in Fig. 2. Film deterioration leads to the substrate surface damage what appears to be the origin of the unit or mechanism wear to be expressed in quadrature as the product of two integrals. One of them is to be taken over the surface with a film deterioration distribution function and another one should be calculated over time and takes into account working pressure fluctuations. Such an approach to wear calculation is advantageous compared to the calculation of either of the integrals because it takes into account both interrelated factors (film deterioration and pressure fluctuations tending to more significant deviations) and a latent retardation of the surface damage upon the surface film deterioration.

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Declarations

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References

1. Deepika, S.: Nanotechnology implications for high performance lubricants. *SN Appl. Sci.* **2**, 1128 (2020). <https://doi.org/10.1007/s42452-020-2916-8>
2. Jazaa, Y.: Effect of Nanoparticle Additives on the Tribological Behavior of Oil Under Boundary Lubrication. Iowa State University Ames, Iowa (2018)
3. Anand, G., Saxena, P.: A review on graphite and hybrid nanomaterials as lubricant additives. *IOP Conf. Series* **149**, 012201 (2016). <https://doi.org/10.1088/1757-899X/149/1/012201>
4. Zin, V., Barison, S., Agresti, F., Colla, L., Pagura, C., Fabrizio, M.: Improved tribological and thermal properties of lubricants by graphene based nano-additives. *RSC Adv.* **6**, 59477 (2016). <https://doi.org/10.1039/c6ra12029f>
5. Mohamed, A., Ali, S., Osman, T.A., Kamel, B.M.: Development and manufacturing an automated lubrication machine test for nano grease. *J. Mater. Res. Technol.* **9**(2054), 2062 (2020). <https://doi.org/10.1016/j.jmrt.2019.12.038>
6. Prasher, R., Song, D., Wang, J., Phelan, P.: Measurements of nanofluid viscosity and its implications for thermal applications. *Appl. Phys. Lett.* **89**, 133108 (2006). <https://doi.org/10.1063/1.2356113>
7. Di Lecce, S., Kornyshev, A.A., Urbakh, M., Bresme, F.: Lateral ordering in nanoscale ionic liquid films between charged surfaces enhances lubricity. *ACS Nano* **14**(13256), 13267 (2020). <https://doi.org/10.1021/acsnano.0c05043>
8. Niste, V.B., Ratoi, M.: Tungsten dichalcogenide lubricant nanoadditives for demanding applications. *Mater. Today Commun.* **8**(1), 11 (2016). <https://doi.org/10.1016/j.mtcomm.2016.04.015>
9. Wu, Y.Y., Tsui, W.C., Liu, T.C.: Experimental analysis of tribological properties of lubricating oils with nanoparticle additives. *Wear* **262**(819), 825 (2007). <https://doi.org/10.1016/j.wear.2006.08.021>
10. Cheng, Z.-L., Qin, X.-X.: Study on friction performance of graphene-based semi-solid grease *Chin. Chem. Lett.* **25**(1305), 1307 (2014). <https://doi.org/10.1016/j.ccllet.2014.03.010>
11. Younes, H., Christensen, G., Groven, L., Hong, H., Smith, P.: Three dimensional (3D) percolation network structure: key to form stable carbon nano grease. *Rev Mex. Trastor Aliment* **14**(375), 382 (2016). <https://doi.org/10.1016/j.jart.2016.09.002>
12. Fan, X., Xia, Y., Wang, L., Li, W.: Multilayer graphene as a lubricating additive in bentone grease. *Tribol. Lett.* **55**(455), 464 (2014). <https://doi.org/10.1007/s11249-014-0369-1>
13. Bakunin, V.N., Suslov, A.Y.Y., Kuzmina, G.N., Parenago, O.P., Topchiev, V.: Synthesis and application of inorganic nanoparticles as lubricant components: a review. *J. Nanopart. Res.* **6**(273), 284 (2004)
14. MacWan, D.P., Dave, P.N., Chaturvedi, S.: A review on nano-TiO₂ sol-gel type syntheses and its applications. *J. Mater. Sci.* **46**(3669), 3686 (2011)
15. Lidorenko, N.S., Chizhik, S.P., Gladkikh, N.T., Grigorjeva, L.K., Kuklin, R.N.: O roli razmernogo faktora v sdvige khimicheskogo ravnovesiya [About the role of dimensional factor in a chemical equilibrium shear]. *Doklady AN SSSR* **257**(1114), 1118 (1981)
16. Vigdorowitsch, M., Tsygankova, L.E., Vigdorovich, V.I., Knyazeva, L.G.: To the thermodynamic properties of nano-ensembles. *Mater. Sci. Eng. B* **263C**, 114897 (2021). <https://doi.org/10.1016/j.mseb.2020.114897>
17. Vigdorowitsch, M.: Thermodynamics and stability of metallic nanoensembles. In: Gluzman, S. (ed.) *Physics and Mechanics of Structured Media*. Elsevier, Amsterdam (2021)
18. Huang, H.D., Tu, J.P., Gan, L.P., Li, C.Z.: An investigation on tribological properties of graphite nanosheets as oil additive. *Wear* **261**(140), 144 (2006). <https://doi.org/10.1016/j.wear.2005.09.010>
19. Kamel, B.M., Mohamed, A., El Sherbiny, M., Abed, K.A., Abd-Rabou, M.: Tribological properties of graphene nanosheets as an additive in calcium grease. *J. Dispersion Sci. Technol.* **38**, 1495–1500 (2017). <https://doi.org/10.1080/01932691.2016.1257390>
20. Kamel, B.M., Mohamed, A., El-Sherbiny, M., Abed, K.A., Abd-Rabou, M.: Rheological characteristics of modified calcium grease with graphene nanosheets. *Fullerenes Nanotubes Carbon Nanostruct.* **25**(429), 434 (2017). <https://doi.org/10.1080/1536383X.2017.1330265>
21. Stoller, M.D., Park, S., Zhu, Y., An, J., Ruoff, R.S.: Graphene-based ultracapacitors. *Nano Lett* **8**(3498), 3502 (2008). <https://doi.org/10.1021/nl802558y>
22. Ordin, S.V., Sharupin, B.N., Fedorov, M.I.: Normal lattice vibrations and the crystal structure of anisotropic modifications of boron nitride. *Semiconductors* **32**(924), 932 (1998). <https://doi.org/10.1134/1.1187516>
23. Bordag, M., Klimchitskaya, G.L., Mohideen, U., Mostepanenko, V.M.: *Advances in the Casimir Effect*. Oxford University Press, Oxford (2015)
24. Klinov, I.Ya.: Corrosion of chemical equipment and corrosion-resistant materials [Korroziya khimicheskoy apparatury i korrozionno-stojkie materialy]. *Mashinostroenie*, Moscow (1967)
25. Wang, W., Dai, S., Li, X., Yang, J., Srolovitz, D.J., Zheng, Q.: Measurement of the cleavage energy of graphite. *Nat. Commun.* **6**, 7853 (2015). <https://doi.org/10.1038/ncomms8853>
26. Deng, S., Berry, V.: Wrinkled, rippled and crumpled graphene: an overview of formation mechanism, electronic properties, and applications. *Mater. Today* **19**, 197 (2016). <https://doi.org/10.1016/j.mattod.2015.10.002>
27. Liu, H., Li, L.: Graphitic materials: intrinsic hydrophilicity and its implications. *Extreme Mech. Lett.* **14**, 44 (2017). <https://doi.org/10.1016/j.eml.2017.01.010>
28. Li, Y., Lu, Y., Adelhelm, P., Titirici, M.-M., Hu, Y.-S.: Intercalation chemistry of graphite: alkali metal ions and beyond. *Chem. Soc. Rev.* **48**, 4655 (2019). <https://doi.org/10.1039/C9CS00162J>

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